

**GŁÓWNY INSTYTUT GÓRNICTWA –
PAŃSTWOWY INSTYTUT BADAWCZY
W KATOWICACH**



ROZPRAWA DOKTORSKA

**MODEL PROCESU OCZYSZCZANIA ŚCIEKÓW
Z WYKORZYSTANIEM ZWIĄZKÓW CERU
POCHODZĄCYCH Z ODPADÓW
PRZEMYSŁOWYCH**

mgr inż. Paweł Lejwoda

Promotor:

prof. dr hab. inż. Barbara Białecka

Promotor pomocniczy:

dr inż. Maciej Thomas

Katowice, listopad 2025 r.

Podziękowania

Serdecznie dziękuję Pani prof. dr hab. inż. Barbarze Białeckiej oraz Panu dr. inż. Maciejowi Thomasowi za cenne rady, sugestie, pomoc i poświęcony czas.

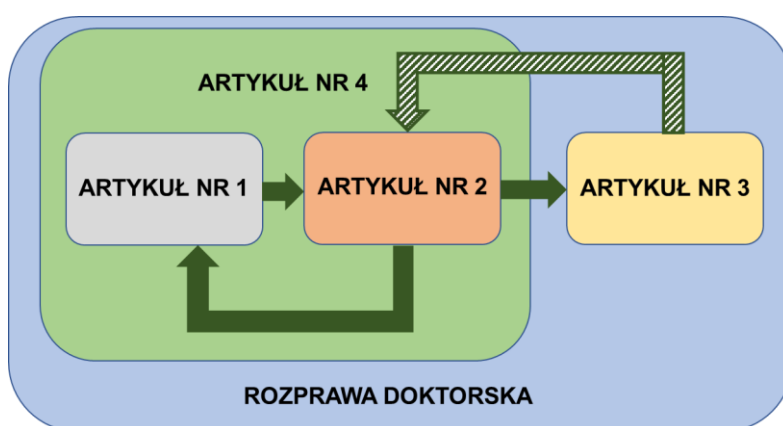
Spis treści

1. Wykaz publikacji będących podstawą rozprawy doktorskiej wraz z oświadczeniami współautorów	4
2. Wykaz ważniejszych skrótów	10
3. Streszczenie.....	11
4. Abstract.....	13
5. Wprowadzenie	15
6. Cele i teza pracy	20
7. Metodyka prowadzenia badań	22
8. Metody badań	25
8.1. Metody analityczne	25
8.2. Metody optymalizacyjne	27
8.3. Materiały badawcze i metodyka	28
8.3.1 Wybór odpadu przemysłowego.....	28
8.3.2 Usuwanie fosforanów(V) z zastosowaniem koagulantu cerowego	28
8.3.3 Odzysk ceru z osadów ściekowych.....	30
8.3.4 Utlenianie toksycznych zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego przy użyciu siarczanu(VI) ceru(IV).....	31
8.3.5 Ocena ekologiczna i ekonomiczna procesu	32
9. Omówienie wyników badań	34
9.1. Wybór materiału badawczego	34
9.2. Usuwanie fosforanów(V) ze ścieków browarniczych za pomocą chlorku ceru(III) pochodzącego ze zużytego środka polerskiego: badania odzysku i optymalizacji.....	34
9.3. Odzysk soli ceru z osadów ściekowych powstałych w wyniku koagulacji ścieków browarniczych za pomocą odzyskanego koagulantu cerowego	38
9.4. Ocena możliwości wykorzystania siarczanu(VI) ceru(IV) oraz procesu Fentona i procesu podobnego do procesu Fentona do utleniania zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego	43
9.5. Ekologiczna i ekonomiczna ocena procesu oczyszczania ścieków z odzyskiem koagulantu cerowego.....	49
10. Weryfikacja tez rozprawy doktorskiej	52
11. Wnioski i perspektywy dalszych prac badawczych	53
12. Literatura.....	56
13. Spis tabel i rysunków	61
14. Spis załączników	62
15. Wykaz innych publikacji naukowych	63
16. Udział w konferencjach	64

1. Wykaz publikacji będących podstawą rozprawy doktorskiej wraz z oświadczeniami współautorów

Na rozprawę doktorską składa się cykl czterech powiązanych ze sobą tematycznie publikacji naukowych, zgodnie ze schematem przedstawionym na rysunku 1:

1. **Lejwoda, P.**, Białecka, B., & Thomas, M. (2023). *Removal of phosphate from brewery wastewater by cerium(III) chloride originating from spent polishing agent: Recovery and optimization studies*. *Science of The Total Environment*. <https://doi.org/10.1016/j.scitotenv.2023.162643>, (IF = 9,8, 200 pkt MNiSW)
2. **Lejwoda, P.**, Białecka, B., Barbusiński, K., & Thomas, M. (2024). *Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant*. *Materials*, 17(4), 938. <https://doi.org/10.3390/ma17040938>, (IF = 3,4, 140 pkt MNiSW)
3. **Lejwoda, P.**, Białecka, B., & Thomas, M. (2024). *Holistic insight into the viability of employing cerium(IV) sulphate to oxidise toxic contaminants in effluent from the coal gasification process: Optimisation studies*. *Journal of Water Process Engineering*, 67, 106243. <https://doi.org/10.1016/j.jwpe.2024.106243>, (IF = 6,3, 100 pkt MNiSW)
4. **Lejwoda, P.**, Białecka, B., Śliwińska, A., Krawczyk, P., & Thomas, M. (2025). *Innovative Integrated Model of Industrial Wastewater Treatment with the Circular Use of Cerium Compounds as Multifunctional Coagulants: Comprehensive Assessment of the Process and Environmental and Economic Aspects*. *Molecules*, 30(16), 3428. <https://doi.org/10.3390/molecules30163428>, (IF = 4,6, 140 pkt MNiSW)



Rysunek 1. Schemat powiązań zagadnień badawczych zrealizowanych i przedstawionych w poszczególnych artykułach składających się na niniejszą rozprawę doktorską
Źródło: Opracowanie własne

Praca została sfinansowana ze środków Ministerstwa Nauki i Szkolnictwa Wyższego przeznaczonych na badania statutowe w Głównym Instytucie Górnictwa – Państwowym Instytucie Badawczym:

- 11331012-332 (2022) pn. *„Analiza możliwości zastosowania pierwiastków ziem rzadkich uzyskanych z odpadów do oczyszczania ścieków”*
- 11331013-324 (2023) pn. *„Analiza możliwości odzysku pierwiastków ziem rzadkich z osadów ściekowych - optymalizacja parametrów procesowych”*

Katowice, 23.09.2025

Oświadczenie o procentowym udziale autorów w publikacji naukowej:

"Removal of phosphate from brewery wastewater by cerium(III) chloride originating from spent polishing agent: Recovery and optimization studies"

Data publikacji: 06.03.2023 r.

Udział procentowy poszczególnych autorów publikacji:

Lp.	Imię i nazwisko współautora	Udział procentowy	Zakres merytoryczny
1	mgr inż. Paweł Lejwoda	80%	Opracowanie koncepcji eksperymentu, wybór metodologii, przygotowanie materiału badawczego, przeprowadzenie badań, analiza wyników, przygotowanie pierwszej wersji manuskryptu, korekta manuskryptu, wykonanie analiz ICP-OES, ICP-MS, OWO, RWO, N _{og.} , jonów amonu, pełnienie roli autora korespondencyjnego, korespondencja z redakcją, przygotowanie odpowiedzi na pytania recenzentów, przygotowanie ostatniej wersji manuskryptu.
2	prof. dr hab. inż. Barbara Białecka	10%	Współdział w opracowaniu koncepcji eksperymentu, pomoc w doborze metodologii, pomoc w przygotowaniu pierwszej wersji manuskryptu, współdział w korekcie manuskryptu.
3	dr inż. Maciej Thomas	10%	Współdział w opracowaniu koncepcji eksperymentu, pomoc w doborze metodologii, pomoc w przygotowaniu pierwszej wersji manuskryptu, współdział w korekcie manuskryptu.

Potwierdzam poprawność danych:



PODPIS ZAUFANY

PAWEŁ
LEJWODA
23.09.2025 19:11:44 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym



PODPIS ZAUFANY

MACIEJ
THOMAS
23.09.2025 19:37:03 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym

Strona 6 z 64

mgr inż. Paweł Lejwoda
Rozprawa doktorska

Model procesu oczyszczania ścieków z wykorzystaniem
związków ceru pochodzących z odpadów przemysłowych

Katowice, 23.09.2025

Oświadczenie o procentowym udziale autorów w publikacji naukowej:

*"Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of
Brewery Wastewater with Recycled Cerium Coagulant"*

Data publikacji: 17.02.2024 r.

Udział procentowy poszczególnych autorów publikacji:

Lp.	Imię i nazwisko współautora	Udział procentowy	Zakres merytoryczny
1	mgr inż. Paweł Lejwoda	70%	Opracowanie koncepcji eksperymentu, wybór metodologii, przygotowanie materiału badawczego, przeprowadzenie badań, analiza wyników, przygotowanie pierwszej wersji manuskryptu, korekta manuskryptu, analiza ICP-OES, ICP-MS, pełnienie roli autora korespondencyjnego, korespondencja z redakcją, przygotowanie odpowiedzi na pytania recenzentów, przygotowanie ostatniej wersji manuskryptu.
2	prof. dr hab. inż. Barbara Białecka	10%	Współudział w opracowaniu koncepcji eksperymentu, opieka merytoryczna, współudział w korekcie manuskryptu.
3	prof. dr hab. inż. Krzysztof Barbusiński	10%	Współudział w opracowaniu koncepcji eksperymentu, opieka merytoryczna, współudział w korekcie manuskryptu.
4	dr inż. Maciej Thomas	10%	Współudział w opracowaniu koncepcji eksperymentu, analiza wyników, metodologia, opieka merytoryczna, przygotowanie pierwszej wersji manuskryptu, współudział w korekcie manuskryptu.

Potwierdzam poprawność danych:



PODPIS ZAUFANY

PAWEŁ
LEJWODA

23.09.2025 19:15:37 [GMT+2]

Dokument podpisany elektronicznie
podpisem zaufanym



PODPIS ZAUFANY

MACIEJ
THOMAS

23.09.2025 19:39:20 [GMT+2]

Dokument podpisany elektronicznie
podpisem zaufanym



Signed by /
Podpisano przez:

Krzysztof
Barbusiński
Politechnika
Śląska

Date / Data:
2025-09-24 17:45

Strona 7 z 64

mgr inż. Paweł Lejwoda
Rozprawa doktorska

Model procesu oczyszczania ścieków z wykorzystaniem
wiązków ceru pochodzących z odpadów przemysłowych

Katowice, 23.09.2025

Oświadczenie o procentowym udziale autorów w publikacji naukowej:

"Holistic insight into the viability of employing cerium(IV) sulphate to oxidise toxic contaminants in effluent from the coal gasification process: Optimisation studies"

Data publikacji: 27.09.2024 r.

Udział procentowy poszczególnych autorów publikacji:

Lp.	Imię i nazwisko współautora	Udział procentowy	Zakres merytoryczny
1	mgr inż. Paweł Lejwoda	80%	Opracowanie koncepcji eksperymentu, wybór metodologii, przygotowanie materiału badawczego, przeprowadzenie badań, analiza wyników, przygotowanie pierwszej wersji manuskryptu, korekta manuskryptu, wykonanie analiz ICP-OES, ICP-MS, RWO, cyjanków całkowitych, indeksu fenolowego, pełnienie roli autora korespondencyjnego, korespondencja z redakcją, przygotowanie odpowiedzi na pytania recenzentów, przygotowanie ostatniej wersji manuskryptu.
2	prof. dr hab. inż. Barbara Białecka	10%	Współdział w opracowaniu koncepcji eksperymentu, opieka merytoryczna, przygotowanie pierwszej wersji manuskryptu, współdział w korekcie manuskryptu.
3	dr inż. Maciej Thomas	10%	Współdział w opracowaniu koncepcji eksperymentu, analiza wyników, opieka merytoryczna, przygotowanie pierwszej wersji manuskryptu, współdział w korekcie manuskryptu.

Potwierdzam poprawność danych:



PODPIS ZAUFANY
PAWEŁ
LEJWODA
23.09.2025 19:16:24 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym



PODPIS ZAUFANY
MACIEJ
THOMAS
23.09.2025 19:40:59 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym

Strona 8 z 64

mgr inż. Paweł Lejwoda
Rozprawa doktorska

Model procesu oczyszczania ścieków z wykorzystaniem
związków ceru pochodzących z odpadów przemysłowych

Katowice, 23.09.2025

Oświadczenie o procentowym udziale autorów w publikacji naukowej:

"Innovative Integrated Model of Industrial Wastewater Treatment with the Circular Use of Cerium Compounds as Multifunctional Coagulants: Comprehensive Assessment of the Process and Environmental and Economic Aspects"

Data publikacji: 20.08.2025 r.

Udział procentowy poszczególnych autorów publikacji:

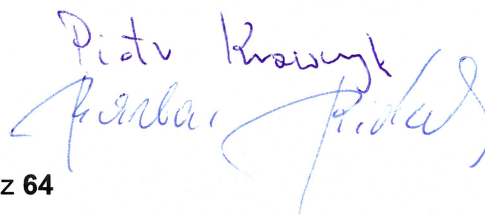
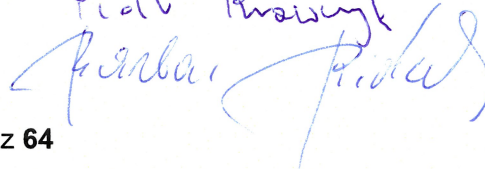
Lp.	Imię i nazwisko współautora	Udział procentowy	Zakres merytoryczny
1	mgr inż. Paweł Lejwoda	60%	Główny udział w opracowaniu koncepcji oczyszczania ścieków, analiza wyników, metodologia, przygotowanie pierwszej wersji manuskryptu, korekta manuskryptu, pełnienie roli autora korespondencyjnego, korespondencja z redakcją, przygotowanie odpowiedzi na pytania recenzentów, przygotowanie ostatniej wersji manuskryptu.
2	prof. dr hab. inż. Barbara Białecka	10%	Współudział w opracowaniu koncepcji oczyszczania ścieków, przygotowanie pierwszej wersji manuskryptu, opieka merytoryczna, współudział w korekcie manuskryptu
3	dr Anna Śliwińska	10%	Ocena ekologiczna procesu, metodologia, współudział w korekcie manuskryptu
4	dr Piotr Krawczyk	10%	Ocena ekonomiczna procesu, metodologia, współudział w korekcie manuskryptu
5	dr inż. Maciej Thomas	10%	Współudział w opracowaniu koncepcji oczyszczania ścieków, analiza wyników, opieka merytoryczna, współudział w korekcie manuskryptu.

Potwierdzam poprawność danych:

 **PODPIS ZAUFANY**
PAWEŁ LEJWODA
23.09.2025 19:14:07 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym

 **PODPIS ZAUFANY**
MACIEJ THOMAS
23.09.2025 19:42:42 [GMT+2]
Dokument podpisany elektronicznie
podpisem zaufanym

 **PODPIS ZAUFANY**
ANNA ŚLIWIŃSKA
26.09.2025 07:28:44 GMT+0200
Dokument podpisany elektronicznie
podpisem zaufanym

Strona 9 z 64

mgr inż. Paweł Lejwoda
Rozprawa doktorska

Model procesu oczyszczania ścieków z wykorzystaniem
wiązków ceru pochodzących z odpadów przemysłowych

2. Wykaz ważniejszych skrótów

AOPs – Advanced Oxidation Processes/Zaawansowane procesy utleniania

aqua regia – Woda królewska

cz.d.a. – Czysty do analizy

CCD – Central Composite Design/Plan centralny kompozycyjny

ChZT_(Cr) – Chemiczne zapotrzebowanie tlenu

DGC – Dynamic Generation Cost/Dynamiczny koszt jednostkowy

IC – Ion Chromatography/Chromatografia jonowa

ICP-OES – Inductively Coupled Plasma - Optical Emission Spectroscopy/Optyczna spektrometria emisyjna z indukcyjnie sprzężoną plazmą

ICP-MS – Inductively Coupled Plasma – Mass Spectrometry/Spektrometria mas z indukcyjnie sprzężoną plazmą

LCA – Life Cycle Assessment/Ocena cyklu życia

LCI – Life Cycle Inventory/Inwentaryzacja cyklu życia

LCIA – Life Cycle Impact Assessment/Ocena wpływu cyklu życia

N_{og.} – Azot ogólny

•OH – Rodnik hydroksylowy

OWO – Ogólny węgiel organiczny

PAHs – Polycyclic aromatic hydrocarbons

P_{og.} – Fosfor ogólny

PTFE – Politetrafluoroetylen

R² – współczynnik determinacji

R²_{adj} – dopasowany współczynnik determinacji

RDF – Refuse Derived Fuel/Paliwo alternatywne

REE – Rare Earth Elements/Pierwiastki ziem rzadkich

RSM – Response Surface Methodology/Metoda powierzchni odpowiedzi

RWO – Rozpuszczony węgiel organiczny

sp. cz. – Spektralnie czysty

UCG – Underground coal gasification/Podziemne zgazowanie węgla

WWA – Wielopierścieniowe węglowodory aromatyczne

3. Streszczenie

Zwiększająca się liczba ludności, rosnąca konsumpcja, niekorzystne zmiany klimatyczne, wzrastająca ilość wytwarzanych odpadów oraz kurczące się zasoby wody zdatnej do spożycia, stanowią cywilizacyjne wyzwania XXI wieku. Powszechnie stosowanym rozwiązaniem problemu zanieczyszczonych wód i ścieków jest kierowanie ich do oczyszczalni ścieków (np.: podczyszczalni (oczyszczalni) zakładowych, przemysłowych, komunalnych), w celu usunięcia szkodliwych substancji i bezpiecznego odprowadzenia odpowiednio oczyszczonych ścieków do środowiska. Wymóg osiągania coraz niższych stężeń zanieczyszczeń w ściekach oczyszczonych, skłania do opracowywania i wdrażania nowych oraz udoskonalania obecnie stosowanych technologii oczyszczania ścieków, co w konsekwencji ma prowadzić do zmniejszenia oddziaływania pierwiastków biogennych, takich jak azot i fosfor oraz pozostałych zanieczyszczeń na środowisko. W przypadku niekontrolowanego uwolnienia zanieczyszczeń do gleb, rzek i jezior, dochodzi do zanieczyszczenia m.in.: metalami ciężkimi, cyjankami, fenolami, związkami azotowymi, fosforowymi oraz organizmami chorobotwórczymi, takimi jak m.in. wirusy i bakterie. Obecność tych niepożądanych substancji i organizmów w wodach powierzchniowych może skutkować m.in.: zjawiskiem eutrofizacji, wymieraniem organizmów wodnych oraz istotnym pogarszaniem się jakości wód.

Celem niniejszej pracy było (i) opracowanie modelu oczyszczania ścieków z zastosowaniem związków ceru pochodzących z odpadów, (ii) zastosowanie soli ceru do oczyszczania wybranych ścieków przemysłowych, (iii) ponowny odzysk związków ceru z wytworzonych osadów ściekowych oraz (iv) ocena ekologiczna i ekonomiczna zaproponowanego procesu. Na przykładzie ścieków browarniczych, użycie siedmiowodnego chlorku ceru(III) ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) w najkorzystniejszych warunkach umożliwiło efektywne obniżenie m.in. stężenia fosforanów(V) (PO_4^{3-}) o 99,86%, przy czym użyty cer (Ce) został w 99,94% związany w osadzie. Osad zawierający Ce 101,5 g/kg oraz fosfor (P) 22,2 g/kg poddano ekstrakcji kwasem chlorowodorowym (HCl), w wyniku której do roztworu uwolniono 99,6% ceru oraz 97,5% fosforu. Następnie, cer wytrącono w postaci uwodnionego szczawianu ceru(III) ($\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, gdzie $n = 9-10$), który poddano termicznemu rozkładowi w temperaturze $350 \pm 5^\circ\text{C}$ do tlenku ceru(IV) (CeO_2). Uzyskany tlenek rozpuszczono w kwasie chlorowodorowym (HCl) i nadtlenu wodoru (H_2O_2), co pozwoliło otrzymać siedmiowodny chlorek ceru(III) ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) z wydajnością odzysku 97,0% o czystości 98,6%.

Ponadto, uzyskano sole w postaci siarczanu(VI) ceru(III) ($\text{Ce}_2(\text{SO}_4)_3$) z wydajnością 97,4% i o czystości 95,9% oraz siarczan(VI) ceru(IV), ($\text{Ce}(\text{SO}_4)_2$), (wydajność 98,3%, czystość 97,5%), który charakteryzował się właściwościami utleniającymi, co było przyczynkiem do zbadania możliwości zastosowania siarczanu(VI) ceru(IV) $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ do obniżenia

stężeń zanieczyszczeń takich jak cyjanki, fenole, wielopierścieniowe węglowodory aromatyczne (WWA) oraz rozpuszczony węgiel organiczny (RWO) obecnych w kwaśnych ściekach pochodzących z symulacji procesu podziemnego zgazowania węgla kamiennego (UCG).

W ramach przedstawionej do oceny rozprawy doktorskiej zweryfikowano efektywność zastosowania samej soli $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ oraz w modyfikacji z H_2O_2 co odniesiono do efektywności klasycznego odczynnika Fentona. W rezultacie, skutecznie obniżono stężenia WWA, fenoli, cyjanków oraz RWO w pierwszym przypadku odpowiednio o 99,40%, 99,97%, 97,67% i 65,34%, a w drugim o 99,91%, 99,66%, 98,14% i 76,35%. Po zakończeniu utleniania w układzie $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$ i alkalizacji ścieków, zaobserwowano związanie 99,996% zastosowanego ceru w osadzie, co jest zjawiskiem wysoce pożądanym.

Obiecujące wyniki poszczególnych etapów obiegu ceru w procesie oczyszczania ścieków oraz jego recyklingu pozwoliły na opracowanie koncepcji cyrkularnego obiegu ceru, gdzie dodatkowo w celu zmniejszenia oddziaływania na środowisko oraz zmniejszenia zapotrzebowania na kwas solny (HCl) założono odzysk chloru i wodoru ze strumieni gazowych powstałych w poszczególnych etapach procesu. Ocena cyklu życia (LCA) wykazała korzyści środowiskowe związane z redukcją eutrofizacji, przy jednoczesnym obciążeniu środowiska wynikającym z użycia reagentów takich jak HCl i kwasu szczawiowego ($\text{H}_2\text{C}_2\text{O}_4$). Choć metoda ta jest droższa niż konwencjonalne strącanie chemiczne wykorzystujące związki żelaza i glinu, może znaleźć zastosowanie w dużych oczyszczalniach ścieków, szczególnie w przypadkach wymagających wysokiej skuteczności usuwania fosforu, konieczności ograniczenia ilości osadów ściekowych oraz spełnienia wymagań zgodności z założeniami gospodarki o obiegu zamkniętym.

4. Abstract

The growing global population, increasing consumption, adverse climate change, rising amounts of generated waste, and diminishing resources of potable water constitute the major civilisational challenges of the 21st century. A commonly applied solution to the problem of polluted water and wastewater is directing them to treatment plants (e.g. on-site, industrial, or municipal treatment facilities), in order to remove harmful substances and ensure the safe discharge of adequately treated effluents into the environment. The requirement of achieving increasingly lower concentrations of pollutants in treated wastewater prompts the development and implementation of new technologies, as well as the improvement of currently applied methods, which in turn aims to reduce the environmental impact of biogenic elements such as nitrogen and phosphorus, along with other contaminants. In the case of uncontrolled release of pollutants into soils, rivers, and lakes, contamination may occur with, among others, heavy metals, cyanides, phenols, nitrogen- and phosphorus-based compounds, as well as pathogenic organisms such as viruses and bacteria. The presence of these undesirable substances and organisms in surface waters may result, inter alia, in eutrophication, the extinction of aquatic organisms, and a significant deterioration in water quality.

The objectives of this study were: (i) to develop a wastewater treatment model using cerium compounds recovered from waste, (ii) to apply cerium salts for the treatment of selected industrial wastewater, (iii) to recover cerium compounds from the resulting sewage sludge, and (iv) to carry out an ecological and economic assessment of the proposed process. Using brewery wastewater as a case study, the application of cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) under optimal conditions enabled highly efficient reduction of, inter alia, phosphate(V) (PO_4^{3-}) concentration by 99.86%, while 99.94% of the applied cerium (Ce) was immobilised in the sludge. The sludge, containing Ce at 101.5 g/kg and phosphorus (P) at 22.2 g/kg, was subjected to hydrochloric acid (HCl) extraction, releasing 99.6% of cerium and 97.5% of phosphorus into solution. Subsequently, cerium was precipitated as hydrated cerium(III) oxalate ($\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$, where $n = 9\text{--}10$), which was thermally decomposed at $350 \pm 5^\circ\text{C}$ to cerium(IV) oxide (CeO_2). The obtained oxide was dissolved in hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2), allowing the recovery of cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) with a yield of 97.0% and a purity of 98.6%.

In addition, salts such as cerium(III) sulphate(VI) ($\text{Ce}_2(\text{SO}_4)_3$) with a yield of 97.4% and a purity of 95.9%, and cerium(IV) sulphate(VI) ($\text{Ce}(\text{SO}_4)_2$) with a yield of 98.3% and a purity of 97.5% were obtained. The latter, exhibiting oxidising properties, motivated further investigation into the possibility of using cerium(IV) sulphate(VI) ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) for the reduction of contaminants such as cyanides, phenols, polycyclic aromatic hydrocarbons

(PAHs), and dissolved organic carbon (DOC) in acidic wastewater generated during the simulation of underground coal gasification (UCG).

Within this doctoral dissertation, the efficiency of using $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ alone, as well as in combination with H_2O_2 , was assessed and compared with the performance of the classical Fenton reagent. As a result, in the first case, PAHs, phenols, cyanides, and DOC concentrations were successfully reduced by 99.40%, 99.97%, 97.67%, and 65.34%, respectively, and in the second case by 99.91%, 99.66%, 98.14%, and 76.35%. Following oxidation with the $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$ system and subsequent wastewater alkalisation, 99.996% of the applied cerium was bound in the sludge, which is a highly desirable phenomenon.

The promising results of individual stages of cerium cycling in wastewater treatment and its recycling enabled the development of a concept of circular cerium utilisation. Additionally, in order to reduce environmental impacts and minimise hydrochloric acid (HCl) consumption, the recovery of chlorine and hydrogen from gaseous streams generated at different process stages was envisaged. Life cycle assessment (LCA) demonstrated environmental benefits related to eutrophication reduction, while also highlighting environmental burdens associated with the use of reagents such as HCl and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). Although this method is more expensive than conventional chemical precipitation with iron and aluminium compounds, it may find application in large-scale wastewater treatment plants, particularly in cases requiring high phosphorus removal efficiency, reduced sewage sludge generation, and compliance with the principles of the circular economy.

5. Wprowadzenie

Woda, substancja niezbędna do życia ludzi, pokrywa 71% powierzchni Ziemi, a jej całkowite zasoby szacowane są na 1,385 miliarda km³. Z tej objętości, 97,5% stanowi woda słona, która nie nadaje się do spożycia. Woda słodka stanowi jedynie 2,5% całkowitych zasobów wodnych, z czego 69% zgromadzone jest w lodowcach i pokrywie śnieżnej. Wody podziemne stanowią 30,1% zasobów słodkiej wody, natomiast jeziora 0,26%, gleba 0,05%, atmosfera 0,04%, mokradła 0,03%, rzeki 0,006%, a woda biologiczna jedynie 0,003% [1]. Ciągły przyrost populacji [2], wzrastająca konsumpcja [3] oraz postępujące zanieczyszczenie środowiska spowodowane m.in. intensyfikacją produkcji przemysłowej, przyczyniają się do pogarszania jakości zasobów wodnych [4–6]. Dodatkowo, nieefektywna gospodarka odpadami w krajach o niskim poziomie rozwoju zwiększa obciążenie systemów oczyszczania wody [7]. Niezbędne jest zatem podjęcie działań na rzecz ochrony środowiska, w tym efektywniejsze oczyszczanie ścieków, tak aby po odpowiednim oczyszczeniu mogły one zostać bezpiecznie odprowadzone do środowiska lub odzyskały właściwości wody zdatnej do użycia i spożycia [8]. Zgodnie z danymi Głównego Urzędu Statystycznego, w 2023 roku, w Polsce 1296,0 hm³ wody przeznaczono na potrzeby ludności, co przyczyniło się do powstania 1394,8 hm³ ścieków bytowych, z czego 99,71% zostało poddane oczyszczaniu. W przemyśle zużycie wody wynosiło 5414,0 hm³ (głównie na cele ciepłownicze) z czego 730,0 hm³ ścieków przemysłowych wymagało oczyszczenia, a zaledwie 81,90% zostało poddanych temu procesowi.

Zanieczyszczenie wód jest problemem wieloaspektowym, ze względu na źródła zanieczyszczeń jak i ich różnorodność. Ścieki bytowe, nierozdzielnie związane z egzystencją człowieka składają się głównie z substancji zawierających pierwiastki biogenne, takie jak węgiel, azot i fosfor, oraz z zanieczyszczeń biologicznych, takich jak wirusy, bakterie i inne patogeny [9]. Rozwój cywilizacji przyczynił się również do skomplikowania składu ścieków poprzez wzrost stężeń wielu substancji, takich jak farmaceutyki i ich metabolity [10], środki powierzchniowo-czynne [11], mikroplastik [12] oraz metale ciężkie [13]. Kolejnym źródłem zanieczyszczeń wód jest działalność rolnicza [14]. W przypadku zbyt intensywnego nawożenia pól oraz intensywnych opadów deszczu może dochodzić do wypłukiwania nawozów z gleby, co skutkuje przedostaniem się spływów powierzchniowych o podwyższonej zawartości związków fosforowych i azotowych do okolicznych cieków wodnych, a następnie do większych rzek oraz do Morza Bałtyckiego. Według danych Głównego Urzędu Statystycznego za rok 2022, rzekami do Morza Bałtyckiego w ciągu roku przedostało się 108,3 tysiąca ton związków azotowych (jako azot ogólny) oraz 3,9 tysiąca ton związków fosforowych (jako fosfor ogólny) [15].

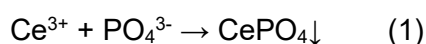
Innym istotnym źródłem zanieczyszczeń są również ścieki przemysłowe, które charakteryzują się dużą zmiennością składu chemicznego, w zależności od typu działalności przedsiębiorstwa. Ścieki z przemysłu spożywczego, np. z browarów, pod względem składu chemicznego są podobne do ścieków komunalnych, lecz zawierają zanieczyszczenia w wyższych stężeniach [16–18], co w przypadku dużego udziału w dopływie ścieków do oczyszczalni, może zakłócić jej prawidłowe funkcjonowanie. W odróżnieniu od nich, ścieki np. z przemysłu koksowniczego lub procesów zgazowania węgla [19], charakteryzują się wysokimi stężeniami cyjanków, fenoli oraz wielopierścieniowych węglowodorów aromatycznych (WWA) [20–22], które oprócz wysokiej toksyczności wobec (mikro)organizmów żywych mogą spowodować poważne komplikacje w biologicznych procesach oczyszczania ścieków, łącznie z całkowitym zahamowaniem aktywności osadu czynnego. Sektor przemysłu chemicznego związany z procesami wytwarzania powłok metalicznych (galwanizernie oraz inne zakłady powierzchniowej obróbki metali) generuje, w zależności od rodzaju stosowanej technologii, ścieki zawierające podwyższone stężenia metali ciężkich, takich jak np. Cu, Ni, Cr oraz Cd [23–25]. Nieskuteczne oczyszczanie tego typu ścieków może skutkować wprowadzaniem do środowiska wodnego pierwiastków toksycznych, które wykazują zdolność do akumulacji i bioakumulacji, co stanowi zagrożenie dla organizmów wodnych i może prowadzić do długofalowych konsekwencji ekologicznych. Niedostateczne usuwanie metali ciężkich oraz innych substancji toksycznych powoduje nie tylko ograniczenie dostępności wody bezpiecznej dla ludzi i zwierząt, lecz także wywołuje długotrwałe, często nieodwracalne zmiany środowiskowe i zdrowotne.

Dodatkowo, niewystarczające oczyszczanie ścieków komunalnych i przemysłowych z pierwiastków biogennych, w połączeniu ze spływami rolniczymi, prowadzi do eutrofizacji – procesu nadmiernego wzbogacenia wód powierzchniowych w związki azotu i fosforu. Skutkiem tego jest intensywny rozwój glonów, wzrost mętności wody oraz deficyt tlenu, co w istotny sposób zagraża stabilności ekosystemów wodnych. Zjawiskom tym towarzyszy również pogorszenie jakości wody pod względem zapachu i smaku [26,27]. Usuwanie nadmiaru azotu i fosforu w konwencjonalnych oczyszczalniach ścieków stanowi poważne wyzwanie technologiczne, wymagające zastosowania zaawansowanych procesów biologicznych, takich jak denitryfikacja (usuwanie związków azotu) [28], oraz procesów chemicznych, takich jak koagulacja (usuwanie związków fosforu) [29].

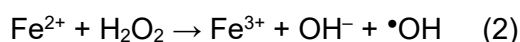
Koagulacja umożliwia usuwanie zanieczyszczeń odpowiedzialnych za mętność i barwę wody, a także obniżenie stężenia związków fosforu, poprzez zastosowanie koagulantów w postaci roztworów m.in. soli żelaza lub glinu. Mechanizm działania głównie polega na wytrąceniu wodorotlenków metali w odpowiednim zakresie pH, na powierzchni których zachodzi adsorpcja zanieczyszczeń. Utworzone kłaczkii sedymentują, co prowadzi

do oddzielenia osadu od oczyszczanej wody lub ścieków [30,31]. Skuteczność koagulantów jest silnie zależna od wartości pH oczyszczanych ścieków. W przypadku soli żelaza(III) optymalne pH wynosi 5,5–7,0 [32], a dla soli glinu 5,7–6,0 [33]. Dla soli żelaza(III) skuteczność usuwania fosforanów(V) może osiągać 98%, natomiast dla soli glinu wynosi zazwyczaj ok. 83%. Główną wadą tych koagulantów jest powstawanie znacznych ilości uwodnionego osadu, który wymaga dalszego zagospodarowania. Oczyszczone ścieki są następnie odprowadzane do wód powierzchniowych.

W obliczu narastającego zanieczyszczenia wód konieczne jest wdrażanie skutecznych strategii ograniczania emisji azotu i fosforu zarówno w rolnictwie, jak i w obszarach miejskich, aby zapobiegać dalszej degradacji jakości zasobów wodnych [34,35]. W porównaniu z konwencjonalnymi koagulantami, skuteczniejsze usuwanie zanieczyszczeń ze ścieków można osiągnąć przy użyciu innowacyjnych koagulantów zawierających cyrkon [36–38], tytan [39,40] lub cer [16,41,42]. W przypadku związków fosforu szczególnie obiecujące są koagulanty cerowe. Najnowsze badania wskazują, że zastosowanie chlorku ceru(III) do usuwania fosforanów(V) z odcieków powstających podczas odwadniania osadów ściekowych jest wysoce efektywne [42]. Koagulanty żelazowe i glinowe wiążą fosforany(V) w zależności od pH ścieków, zarówno na drodze sorpcji na kłaczkach strąconych wodorotlenków, jak i poprzez bezpośrednie wytrącanie trudno rozpuszczalnych osadów takich jak fosforan(V) żelaza(III) lub fosforan(V) glinu. W przeciwieństwie do nich, roztwór ceru dodany do ścieków wiąże fosforany(V) w wyniku bezpośredniej reakcji prowadząc do powstania trudno rozpuszczalnego osadu fosforanu(V) ceru(III), zgodnie z reakcją (1).



Związki ceru(III) okazały się skuteczne w usuwaniu fosforanów(V), a fakt istnienia ceru(IV), który jest wykorzystywany w chemii analitycznej jako utleniacz stwarza potencjał do wykorzystania w procesach jednoczesnego utleniania zanieczyszczeń obecnych w ściekach przemysłowych, np. w ściekach z koksowni lub z procesu zgazowania węgla, gdzie siarczan(VI) ceru(IV) ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) można zastosować do utleniania m.in. WWA, cyjanków i fenoli [43]. Z kolei zaawansowane procesy utleniania (AOPs) to metody wykorzystujące rodniki hydroksylowe ($\cdot\text{OH}$) o wysokim potencjale utleniającym do oczyszczania ścieków. Przykładem takiego procesu z udziałem rodników hydroksylowych stosowanego w oczyszczaniu ścieków jest proces Fentona, przebiegający zgodnie z reakcją (2).



Modyfikacje oryginalnej metody określane są jako procesy podobne do procesu Fentona [44] i obejmują m.in. zastosowanie soli żelaza(III) jak również katalizatorów

heterogenicznych, takich jak: tlenek żelaza(II,III) (Fe_3O_4), tlenek ceru(IV) (CeO_2), srebro metaliczne (Ag), tlenek manganu(IV) (MnO_2), tlenek manganu(II,III) (Mn_3O_4) oraz miedź metaliczna (Cu). Powstawanie rodników hydroksylowych, oprócz procesu opartego na reakcji Fentona i jej modyfikacjach (procesy podobne do procesu Fentona), zachodzi również w szeregu procesów fizycznych, a także kombinacjach procesów chemicznych i fizycznych, takich jak zastosowanie: światła z zakresu UV/VIS (foto-Fenton), promieniowania jonizującego (promieniowanie gamma), procesów elektrochemicznych (elektro-Fenton), kombinacji układów utleniających, np. $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, a nawet ultradźwięków [45,46].

Stosowanie związków ceru w oczyszczaniu ścieków jest obiecujące, jednak produkcja metali ziem rzadkich (REE) jest ograniczona do kilku krajów na świecie (m.in. Chiny, USA, Birma), co w przypadku niekorzystnych zmian geopolitycznych niesie ryzyko zaburzeń w łańcuchach dostaw. W Unii Europejskiej (UE) niemal całość zużywanych REE pochodzi z importu, podczas gdy recykling obejmuje jedynie ok. 1% tych pierwiastków [47], co podkreśla konieczność intensyfikacji działań na rzecz ich odzysku. Biorąc również pod uwagę wyższą cenę koagulantów cerowych w porównaniu z powszechnie stosowanymi solami żelaza i glinu, istotne jest poszukiwanie możliwości ich recyklingu np. z odpadów przemysłowych (proszki polerskie, katalizatory, ceramika, szkło, czerwony szlam z produkcji tlenku glinu). Zarówno stosowany cer, jak i usuwany fosfor są surowcami krytycznymi dla gospodarki UE. Fosfor, pozyskiwany z minerałów takich jak fluoroapatyt ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), chloroapatyt ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) i hydroksyapatyt ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), jest kluczowym składnikiem nawozów mineralnych, niezbędnych dla wydajnej produkcji rolnej [48]. Podobnie jak w przypadku REE, złoża fosforu są skoncentrowane w kilku krajach na świecie (m.in. w Maroku i Chinach), co generuje istotne ryzyko przerwania dostaw i wymusza poszukiwanie alternatywnych źródeł, tego pierwiastka. Ze względu na niemal całkowite uzależnienie UE od importu tych surowców, wdrażanie technologii pozwalających na zamknięcie obiegu ceru i fosforu poprzez ich odzysk z osadów ściekowych ma szczególne znaczenie dla gospodarki. Integracja takich rozwiązań w systemach oczyszczania ścieków wspiera nie tylko gospodarkę o obiegu zamkniętym, lecz także zwiększa niezależność surowcową UE [47].

W niniejszej pracy przedstawiono badania nad usuwaniem związków fosforu ze ścieków browarniczych [16], recyklingiem ceru z osadów ściekowych [49], oraz utleniania zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego [22].

Przeprowadzone badania i eksperymenty w skali laboratoryjnej i półtechnicznej pozwoliły zaproponować komplementarny proces odzysku i ponownego wykorzystania związków ceru do usuwania fosforu ze ścieków przemysłowych. Praca doktorska

podsumowuje cykl badań, które wykazały przydatność koagulantów cerowych i ich recyklingu, umożliwiając zamknięcie obiegu ceru w oczyszczaniu ścieków [16,22,49,50].

Proponowany nowy proces odzysku i wykorzystania związków ceru został poddany kompleksowej ocenie procesowej, środowiskowej i ekonomicznej. Przegląd literatury wykazał, że dotychczas nie przeprowadzono takiej oceny, ani nie opracowano takiego procesu. W pracy [50] przedstawiono wyniki badań wraz z oceną procesu przy założeniu przeskalowania ze skali laboratoryjnej do przemysłowej. Opracowanie obejmuje projekt 10-etapowego procesu, bilans masowy, ocenę cyklu życia (LCA, *Life Cycle Assessment*,) oraz analizę kosztów metodą DGC (*Dynamic Generation Cost*), wypełniając tym samym zidentyfikowaną lukę badawczą. Praca ta może być istotnym krokiem w kierunku projektowania, rozwoju, oceny i dyskusji nad zaawansowanymi procesami strącania, koagulacji i odzysku związków ceru z odpadów, służących lepszej ochronie środowiska, zgodnymi z ideami gospodarki cyrkularnej, zielonej chemii oraz zrównoważonego rozwoju.

6. Cele i teza pracy

Przyjęto, że **głównym celem pracy** jest opracowanie metodyki odzysku i zastosowania soli ceru jako innowacyjnych reagentów do oczyszczania rzeczywistych ścieków przemysłowych pochodzących z różnych źródeł. Zakres pracy obejmował opracowanie metodyki odzysku soli ceru z odpadu i osadów ściekowych, zastosowanie do usuwania fosforanów(V) oraz utleniania zanieczyszczeń wraz z optymalizacją i weryfikacją tych procesów w skali laboratoryjnej oraz oceną aspektów ekologicznych i ekonomicznych zaprojektowanych procesów.

W związku z przyjętym głównym celem pracy doktorskiej, określono następujące **cele prowadzenia badań naukowych**:

- charakterystyka i opracowanie metodyki odzysku soli ceru(III) z proszku polerskiego,
- obniżenie stężenia fosforanów(V) w ściekach browarniczych,
- charakterystyka i opracowanie metodyki odzysku soli ceru z osadu ściekowego wraz z ich oczyszczeniem,
- obniżenie stężenia zanieczyszczeń takich jak WWA, fenole, cyjanki w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego przez zastosowanie soli ceru(IV) jako utleniacza,
- wykorzystanie metody powierzchni odpowiedzi do modelowania i optymalizacji procesu usuwania fosforanów(V) ze ścieków browarniczych z jednoczesną minimalizacją pozostałości koagulantu po procesie oczyszczania,
- wykorzystanie metody powierzchni odpowiedzi do ustalenia optymalnych warunków ekstrakcji ceru oraz fosforu z osadów ściekowych,
- wykorzystanie metody powierzchni odpowiedzi do modelowania i optymalizacji procesu utleniania zanieczyszczeń z zastosowaniem soli ceru(IV),
- ocena aspektów ekologicznych i ekonomicznych zaproponowanych procesów.

Dla sformułowanego głównego celu pracy, przyjęto następujące **cele użytkowe**:

- określenie optymalnych warunków procesowych usuwania fosforanów(V) z zastosowaniem koagulantu cerowego,
- określenie optymalnych warunków procesowych ekstrakcji ceru z osadu ściekowego z zastosowaniem kwasu chlorowodorowego,
- określenie optymalnych warunków procesowych utleniania zanieczyszczeń z symulacji procesu podziemnego zgazowania węgla kamiennego,
- Weryfikacja aspektów ekologicznych i ekonomicznych opracowanych rozwiązań.

Sformułowano następujące **tezy pracy doktorskiej**:

(1) istnieje możliwość odzysku związków ceru z odpadów i ich zastosowania do oczyszczania wybranych ścieków przemysłowych oraz ponownego odzysku z wytworzonych osadów ściekowych

oraz

(2) istnieje możliwość ekonomicznego i ekologicznego odzysku oraz wykorzystania związków ceru do oczyszczania ścieków przemysłowych.

7. Metodyka prowadzenia badań

W ramach realizacji pracy doktorskiej prowadzono badania obejmujące syntezę soli ceru z odpadu przemysłowego, jej zastosowanie jako koagulantu w oczyszczaniu ścieków browarniczych oraz ocenę efektywności procesu w usuwaniu fosforanów(V). Dodatkowo przeprowadzono badania nad możliwością odzysku ceru z osadu powstającego po koagulacji. Rozwiązanie to wpisuje się w założenia gospodarki o obiegu zamkniętym, umożliwiając zarówno znaczne obniżenie zanieczyszczeń, jak i ponowne wykorzystanie cennych surowców.

Przeprowadzona analiza literaturowa pozwoliła na ocenę dotychczas stosowanych metod chemicznego usuwania związków fosforu ze ścieków, opartych głównie na solach żelaza i glinu, oraz na wskazanie ich ograniczeń, związanych m.in. z niską efektywnością i powstawaniem znacznych ilości osadów. Przeanalizowano mechanizmy działania związków ceru oraz oceniono możliwości odzysku i ponownego wykorzystania. Dokonano charakterystyki wybranych odpadów w kontekście odzysku soli ceru jako potencjalnego alternatywnego koagulantu. W oparciu o literaturę zidentyfikowano także kluczowe problemy badawcze, takie jak: dobór odpowiednich warunków koagulacji, określenie parametrów procesu ekstrakcji soli ceru z osadów, możliwość zastosowania soli ceru(IV) do utleniania toksycznych zanieczyszczeń, ocena wpływu procesów na środowisko oraz ocena ekonomiczna cyrkularnego stosowania soli ceru w procesie oczyszczania ścieków.

Pierwsza faza badań laboratoryjnych obejmowała odzysk soli ceru(III) z odpadowego proszku polerskiego, następnie przygotowanie koagulantu cerowego oraz optymalizację procesu usuwania fosforanów(V) ze ścieków browarniczych, prowadzoną z zastosowaniem narzędzi statystycznych tj.: plan centralny kompozycyjny (CCD, *Central Composite Design*) i metoda powierzchni odpowiedzi (RSM, *Response Surface Methodology*). Analizowano wpływ czasu reakcji, stosunku molowego $Ce^{3+}:PO_4^{3-}$ oraz wartości pH na efektywność procesu. Na tej podstawie opracowano modele matematyczne umożliwiające prognozowanie efektywności usuwania fosforu i minimalizowania pozostałości koagulantu cerowego w zależności od przyjętych parametrów operacyjnych.

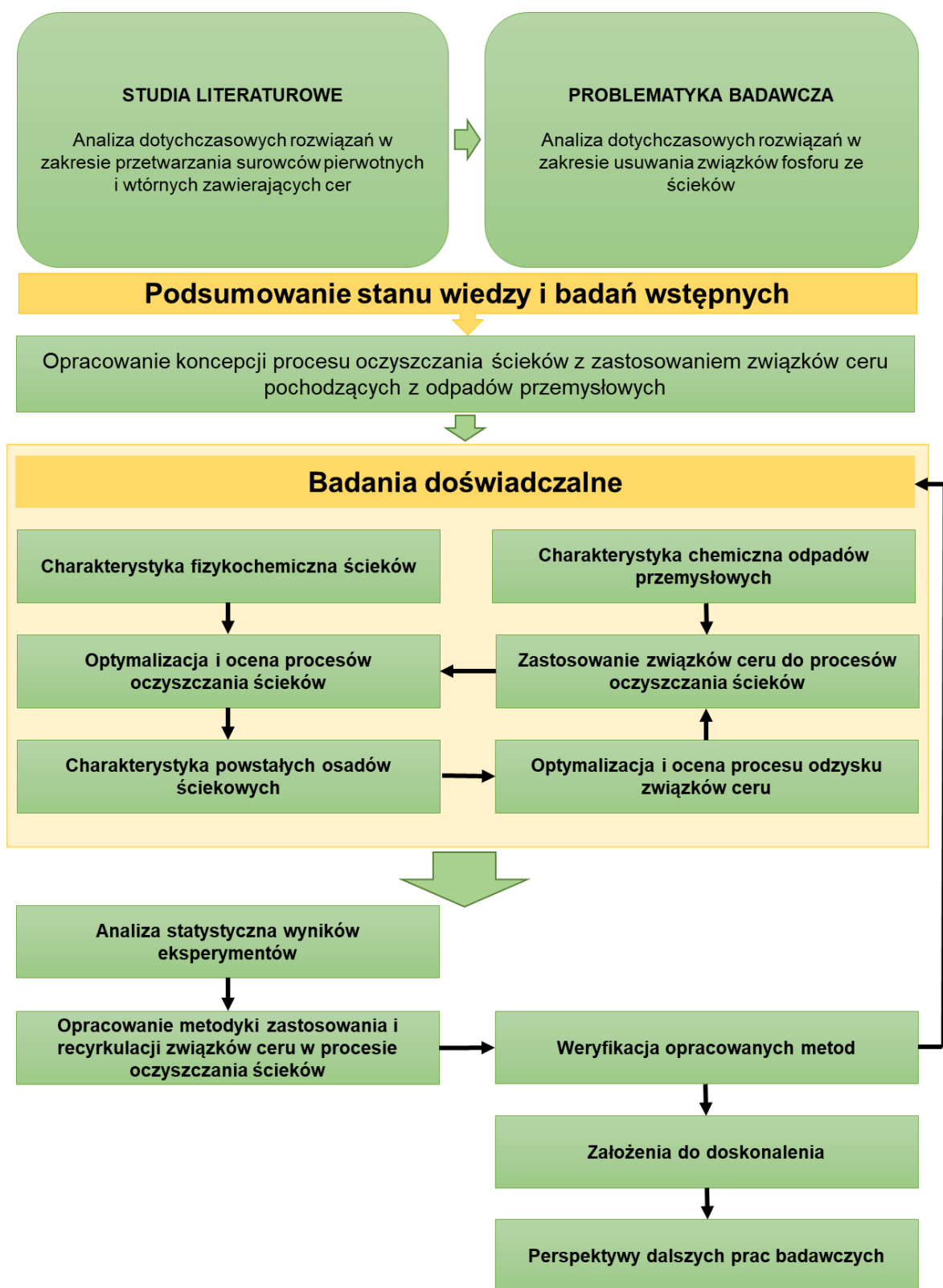
W kolejnym etapie przeprowadzono badania nad odzyskiem soli ceru i fosforu z osadów powstających po koagulacji. Stosując narzędzia statystyczne jak CCD oraz RSM opracowano proces ekstrakcji z zastosowaniem kwasu chlorowodorowego, gdzie analizowanymi parametrami były stosunek objętościowo-masowy ekstrahenta do osadu ściekowego, czas ekstrakcji oraz ilość użytego HCl. Z otrzymanego ekstraktu po przeprowadzeniu szeregu procesów fizykochemicznych uzyskano sole cerowe o wysokiej czystości. Dla wyznaczonych modeli matematycznych wykonano eksperymenty weryfikacyjne, które potwierdziły skuteczność przyjętych założeń.

Odzyskane sole ceru(III) mogą zostać użyte m.in. jako koagulanty, natomiast otrzymany siarczan(VI) ceru(IV) ze względu na właściwości utleniające został zbadany pod kątem zastosowania jako środek do utleniania toksycznych zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego. Stosując metody statystyczne CCD oraz RSM określono optymalne warunki dla procesu utleniania uwzględniając parametry takie jak czas reakcji, stosunek molowy Ce^{4+} :RWO, pH, temperatura. Przeanalizowano także skuteczność zmodyfikowanego układu utleniającego z dodatkiem nadtlenu wodoru (H_2O_2) oraz porównano z klasycznym procesem Fentona.

Dla procesów koagulacji oraz odzysku ceru z osadów ściekowych opracowano model procesu oczyszczania z przeskalowaniem rezultatów laboratoryjnych na skalę przemysłową i poddano ocenie ekologicznej z zastosowaniem metody LCA (*Life Cycle Assessment*) oraz ocenę ekonomiczną z wykorzystaniem metody DGC (*Dynamic Generation Cost*). Analizy pozwoliły na ocenę zalet i wad proponowanego rozwiązania w ujęciu środowiskowym oraz w jakiej skali i przy jakich wymaganiach efektywności oczyszczania proces będzie ekonomicznie uzasadniony.

W końcowej części pracy dokonano krytycznej analizy uzyskanych rezultatów w odniesieniu do dostępnych danych literaturowych. Na tej podstawie sformułowano wnioski, kierunki doskonalenia oraz wytyczne do dalszych badań.

Schemat metodyki prowadzonych badań nad wykorzystaniem soli ceru do usuwania fosforanów(V) i odzysku pierwiastków z osadów przedstawiono na rysunku 2.



Rysunek 2. Metodyka prowadzenia badań
Źródło: Opracowanie własne

8. Metody badań

8.1. Metody analityczne

Oznaczenie stężeń pierwiastków w roztworach wodnych wykonano metodą optycznej emisyjnej spektroskopii atomowej z plazmą wzbudzoną indukcyjnie (ICP-OES), (Optima 5300DV, Perkin-Elmer, USA), zgodnie z normą EN ISO 11885:2009. Do oznaczenia niskich stężeń ceru ($< 500 \mu\text{g/l}$) zastosowano metodę spektrometrii mas z plazmą wzbudzoną indukcyjnie (ICP-MS), (NexION 300S, Perkin-Elmer, USA), zgodnie z normą EN ISO 17294-2:2006. Oznaczenia stężeń metali i niemetalii powyższymi metodami było obarczone niepewnością pomiarową 10%, 15%, 20% lub 25% w zależności od pierwiastka i jego stężenia w analizowanym roztworze.

Oznaczenie stężenia fosforanów(V) wykonano techniką spektrofotometryczną UV-VIS (Pharo 300, Merck KGaA, Niemcy) zgodnie z normą PN-EN ISO 6878:2006 + Ap1, Ap2:2010, rozdz. 4; niepewność pomiarowa 10%.

Przewodność elektryczna właściwa oraz pH roztworów zostały określone miernikiem wieloparametrowym (inoLab, WTW, Polska) zgodnie z normami EN 27888:1999 oraz EN ISO 10523:2012; niepewność pomiarowa dla przewodności elektrycznej właściwej 5% oraz 0,1 jednostki dla pH.

Potencjał redoks oznaczono metodą potencjometryczną zgodnie z procedurą SC-1.2.2.PB.07.66 ed. 1.3 z dn. 28.08.23; niepewność pomiarowa $\pm 30 \text{ mV}$.

Oznaczenie chemicznego zapotrzebowania tlenu ($\text{ChZT}_{(\text{Cr})}$) wykonano metodą dichromianową z pomiarem spektrofotometrycznym UV-VIS (Pharo 300, Merck KGaA, Niemcy), zgodnie z normą PN-ISO 15705:2005; niepewność pomiarowa 15%.

Analizy stężeń ogólnego węgla organicznego (OWO) oraz rozpuszczonego węgla organicznego (RWO), zostały wykonane metodą wysokotemperaturowego rozkładu z detekcją w podczerwieni (TOC-L CPH, Shimadzu, Japonia) zgodnie z normą EN 1484:1999; niepewność pomiarowa 15%.

Stężenie azotu ogólnego określono metodą wysokotemperaturowego rozkładu z detekcją chemiluminescencyjną (TNM-L, Shimadzu, Japonia) zgodnie z normą EN 12260:2004; niepewność pomiarowa 15%.

Stężenie anionów chlorkowych, azotanowych(V) oraz siarczanowych(VI) (Cl^- , NO_3^- , SO_4^{2-}) określono metodą chromatografii jonowej (IC), (DIONEX ICS 5000, Thermo Fisher Scientific, USA) zgodnie z normą EN ISO 10304-1:2009; niepewność pomiarowa 10%, 15% lub 20%, w zależności od stężenia analitu w próbce.

Stężenie azotanów(III), (NO_2^-), zostało określone metodą spektrofotometryczną UV-VIS (Pharo 300, Merck KGaA, Niemcy) zgodnie z normą PN-EN 26777:1999; niepewność pomiarowa 10%.

Zawartość jonów amonu (NH_4^+) została określona metodą spektrofotometryczną, techniką wstrzykowej analizy przepływowej – FIA (ang. Flow Injection Analysis), (FIAModula, MLE GmbH, Niemcy), zgodnie z normą EN ISO 11732:2007; niepewność pomiarowa 10%.

Analiza zawartości cyjanków (CN^-) została przeprowadzona metodą ciągłej analizy przepływowej z detekcją spektrofotometryczną – CFA (*Continuous Flow Analysis*) zgodnie z normą PN-EN ISO 14403-2:2012; niepewność pomiarowa 10%.

Oznaczenie indeksu fenolowego wykonano metodą ciągłej analizy przepływowej z detekcją spektrofotometryczną – CFA (*Continuous Flow Analysis*) zgodnie z normą PN-EN ISO 14402:2004 pkt 4; niepewność pomiarowa 8%, 15%, 30%, w zależności od stężenia analitu w próbce.

Stężenie wielopierścieniowych węglowodorów aromatycznych (WWA) zostało oznaczone metodą wysokosprawnej chromatografii cieczowej z detekcją fluorescencyjną (HPLC-FID) (EN ISO 17993:2003; Agilent 1200, Agilent Technologies, Inc., USA); niepewność pomiarowa 25%.

Zawiesiny ogólne oznaczono metodą wagową zgodnie z normą EN 872:2007; niepewność pomiarowa 10% lub 15% w zależności od stężenia w roztworze.

Mętność została oznaczona metodą nefelometryczną zgodnie z normą EN ISO 7027-1:2016–09; niepewność pomiarowa 10%.

Barwę oznaczono metodą spektrofotometryczną zgodnie z normą EN ISO 7887:2012 (metoda C) ; niepewność pomiarowa 20%.

Mineralizację osadów po procesach koagulacji oraz po procesach utleniania został przeprowadzony zgodnie z normą ISO 15587-1:2002.

Identyfikacja faz została przeprowadzona metodą dyfrakcji rentgenowskiej (XRD) proszkowej (DSH) w geometrii Bragga-Brentano przy użyciu dyfraktometru Bruker D8 DISCOVER, (USA), promieniowania $\text{CuK}\alpha$, filtra niklowego oraz detektora LYNXEYE XE. Skład mineralny został określony i obliczony na podstawie standardów licencjonowanych w bazach danych PDF-4+2022 RDB ICDD (International Centre for Diffraction Data), ICSD (Inorganic Crystal Structure Database) oraz NIST (National Institute of Standards and Technology). Do rejestracji i analizy wykorzystano oprogramowanie DIFFRAC v.4.2, TOPAS v.4.2 oraz Bruker AXS. Ilościowe obliczenia faz krystalicznych i substancji amorficznej przeprowadzono metodą Rietvela. Niepewność pomiarowa 0,5-1%.

Morfologia powierzchni ziaren oraz skład chemiczny w mikroobszarach zostały przeanalizowane za pomocą skaningowej mikroskopii elektronowej (SEM) i spektroskopii

dyspersji energii promieniowania rentgenowskiego (EDS) przy użyciu mikroskopu SU3500 SEM (Hitachi, Japonia) w połączeniu z detektorem UltraDry EDS (Thermo Fisher Scientific, USA) w następujących warunkach: napięcie przyspieszające – 15 keV, detektor – BSE, czas skanowania – 40 s, powiększenie x1000 – x3000. Obrazy wykonano po napyleniu próbki złotem.

8.2. Metody optymalizacyjne

Klasyczne podejście do optymalizacji zakładające użycie metody jednoczynnikowej (OFAT, *One Factor At Time*) wymaga przeprowadzenia dużej liczby doświadczeń, co wydłuża czas oraz zwiększa koszt całego procesu, nie zawsze zapewniając miarodajne wyniki [51]. Aby zmniejszyć liczbę eksperymentów dla każdego z etapów badań zastosowano plan centralny kompozycyjny (CCD, *Central Composite Design*) wraz z metodą powierzchni odpowiedzi (RSM, *Response Surface Methodology*). CCD jest jedną z najczęściej stosowanych metod projektowania eksperymentów, ponieważ umożliwia efektywne badanie wpływu wielu czynników jednocześnie przy ograniczonej liczbie prób. Natomiast RSM pozwala na modelowanie zależności między zmiennymi oraz optymalizację odpowiedzi w sposób nieliniowy, co czyni ją skutecznym narzędziem w optymalizacji procesów technologicznych. Każdy z planów eksperymentalnych przygotowano za pomocą oprogramowania Statistica 13 (TIBCO Software Inc., USA), gdzie założono wykonanie pomiarów różnych kombinacji wartości parametrów wejściowych (zmiennych niezależnych). Plan w przestrzeni trójwymiarowej, obejmuje pomiar punktów stanowiących naroża planu (*square points*, *cube points*), punkty gwiazdne (*axial points*) oraz punkt centralny, którego pomiar wykonywany jest w kilku powtórzeniach, co pozwala na ocenę błędu modelu. Liczba eksperymentów koniecznych do wykonania jest zależna od liczby testowanych parametrów wejściowych (zmiennych niezależnych) oraz liczby powtórzeń w centrum planu i wyrażona jest wzorem (3) [52].

$$N = 2^f + 2f + n_c \quad (3)$$

N – ilość eksperymentów w planie,

f – ilość parametrów wejściowych (zmiennych niezależnych),

n_c – ilość punktów w centrum planu.

Realizacja założeń eksperymentalnych planu centralnego kompozycyjnego pozwala na otrzymanie modelu matematycznego drugiego stopnia, co z kolei umożliwia uzyskanie odpowiedniego dopasowania powierzchni odpowiedzi do wyników eksperymentalnych, zgodnie ze wzorem ogólnym (4).

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_1^2 + \beta_3 x_2 + \beta_4 x_2^2 + \beta_5 x_3 + \beta_6 x_3^2 + \beta_7 x_1 x_2 + \beta_8 x_1 x_3 + \beta_9 x_2 x_3 + \varepsilon \quad (4)$$

Y – zmienna zależna,

β – współczynnik regresji,

x_1, x_2, x_3 – zmienne niezależne,

ε – błąd modelu.

Dopasowanie modelu oraz jego istotność statystyczną oceniano przy użyciu analizy wariancji (ANOVA) oraz skorygowanego współczynnika determinacji R^2_{adj} , co pozwoliło określić jakość uzyskanego modelu. W przeciwieństwie do R^2 , który może wskazywać na pozornie wysokie dopasowanie przy zwiększaniu liczby zmiennych, R^2_{adj} kompensuje wzrost współczynnika determinacji spowodowany dodawaniem kolejnych zmiennych objaśniających. Wartość R^2_{adj} rośnie w przypadku dodania do modelu zmiennych zwiększających zdolności predykcyjne modelu, w przeciwnym przypadku maleje. W celu potwierdzenia poprawności przyjętych warunków optymalnych wykonywano eksperymenty weryfikacyjne. Gdy wyniki eksperymentów były zgodne z prognozowanymi przez model, przyjmowano, że opracowany model jest poprawny. Skuteczność CCD i RSM zależy od jakości dobranych punktów eksperymentalnych oraz zakresu badanych parametrów. W niektórych przypadkach, zwłaszcza gdy układ eksperymentalny jest silnie nieliniowy, może być konieczne zastosowanie bardziej złożonych modeli jak np. modele stopnia trzeciego.

8.3. Materiały badawcze i metodyka

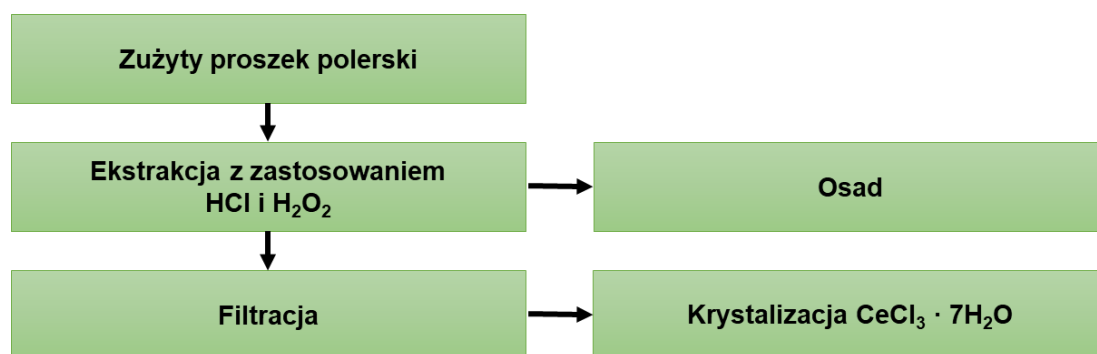
8.3.1 Wybór odpadu przemysłowego

Do selekcji materiałów bogatych w cer wytypowano cztery odpady przemysłowe potencjalnie zawierające pierwiastki ziem rzadkich (REE): muł węglowy (niskiej jakości paliwo z uwagi na wysoką zawartość popiołu, lecz potencjalnie zasobne w REE), popiół ze współspalania węgla kamiennego z RDF (w którym, na skutek redukcji masy podczas spalania, wzrasta stężenie REE), odpadowy materiał skalny z hałdy przy KWK (pochodzący z procesów przeróbki węgla kamiennego, powszechnie występujący w aglomeracji górnośląskiej) oraz zużyty proszek polerski (z CeO_2 jako głównym składnikiem). Analizę składu chemicznego badanych materiałów wykonano metodami opisanymi w podrozdziale 8.1.

8.3.2 Usuwanie fosforanów(V) z zastosowaniem koagulantu cerowego

W eksperymentach użyto ścieki browarnicze pobrane z końcowej studzienki kanalizacyjnej znajdującej się na terenie browaru. Materiał pobrany w ilości ok. 80 l przetransportowano do laboratorium i przechowywano w temperaturze 4 ± 1 °C. Każdorazowo przed użyciem ścieki dokładnie mieszano w celu zapewnienia jednorodności próbek jednostkowych.

Odpadem przemysłowym użytym w badaniach był zużyty proszek polerski, którego główny składnik stanowił tlenek ceru(IV) (CeO_2). Był to podstawowy surowiec do syntezy $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, do której użyto również 30%, sp. cz. kwas chlorowodorowy (HCl) oraz 30%, cz.d.a. nadtlenu wodoru (H_2O_2). Odzysk ceru ze zużytego proszku polerskiego przeprowadzono w kilku etapach według schematu przedstawionego na rysunku 3, który jest modyfikacją metody opisanej w literaturze [53,54].



Rysunek 3. Schemat odzysku soli ceru(III) ze zużytego proszku polerskiego
Źródło: [16]

Pierwszy etap polegał na odważeniu 10,00 g wysuszonego w $105 \pm 1^\circ\text{C}$ do stałej masy proszku polerskiego, umieszczeniu go w kolbie trój szyjnej i dodaniu 30% roztworu HCl w nadmiarze 200% i 30% roztworu H_2O_2 w nadmiarze 100% (w obu przypadkach przeliczone na 100% m/m reagenta) w stosunku do stechiometrycznej ilości CeO_2 w próbce odpadów. Następnie do kolby dołączono chłodnicę zwrotną i ogrzewano do temperatury $80 \pm 1^\circ\text{C}$ przez 4 h przy ciągłym mieszaniu. Po upływie tego czasu uzyskany roztwór o odczynie silnie kwasowym schłodzono do temperatury ok. 25°C , przefiltrowano przez filtr strzykawkowy ($0,45\ \mu\text{m}$, hydrofilowy PTFE), poddano zagęszczeniu poprzez odparowanie roztworu w temperaturze $105 \pm 1^\circ\text{C}$ do uzyskania gęstej, syropowatej cieczy i pozostawiono do wykrystalizowania. Z otrzymanych kryształów przygotowano roztwór CeCl_3 o stężeniu $0,05\ \text{mol/l}$. Badania optymalizacyjne usuwania fosforanów(V) ze ścieków browarniczych prowadzono poprzez odmierzenie $250 \pm 1\ \text{ml}$ ścieków do zlewek o pojemności 400 ml. Następnie mieszano z prędkością $250 \pm 10\ \text{obr/min}$, korygowano pH za pomocą 15% roztworu HCl lub 15% roztworu NaOH , dodawano ustaloną objętość koagulatu cerowego i kontrolowano czas procesu zgodnie z przyjętym planem eksperymentalnym. Po zakończeniu procesu oczyszczania, każdorazowo, wstępnie oczyszczone ścieki pozostawiano na ok. 5 min celem sedimentacji powstałych osadów. Następnie pobierano ciecz znad osadu, filtrowano przez filtr strzykawkowy ($0,45\ \mu\text{m}$, hydrofilowy PTFE) i poddawano analizie wybranymi metodami opisanymi w podrozdziale 8.1.

8.3.3 Odzysk ceru z osadów ściekowych

Materiał do badań recyklingu koagulantu cerowego stanowił osad ściekowy uzyskany w procesie oczyszczania ścieków browarniczych. Przed badaniami odzysku osad wysuszono w temperaturze otoczenia (20 ± 1 °C) do stałej masy. Skład chemiczny określono po rozтворzeniu próbki osadu ściekowego w wodzie królewskiej *aqua regia* (HCl:HNO₃, 3:1, V/V). W badaniach wykorzystano sp.cz. kwas azotowy (60%) (Merck, Niemcy), sp.cz. kwas solny (30%) (Merck, Niemcy), cz.d.a. kwas siarkowy (96%) (Chempur, Polska), cz.d.a. nadtlenuk wodoru (30%) (Chempur, Polska), cz.d.a. wodorotlenek sodu (Chempur, Polska), cz.d.a. kwas szczawiovy (Warchem, Polska) oraz wodę dejonizowaną o przewodności elektrycznej właściwej poniżej 0,05 µS/cm.

Optymalizację procesu ekstrakcji przeprowadzono według przyjętego planu eksperymentalnego obejmującego wykonanie 20 doświadczeń. Parametrami wejściowymi (zmiennymi niezależnymi) były: stosunek objętościowo-masowy cieczy ekstrakcyjnej do masy osadu ściekowego, masa dodanego HCl oraz czas reakcji, natomiast parametrami wyjściowymi (zmiennymi zależnymi) były stężenia masowe ceru oraz fosforu. Ekstrakty uzyskane podczas eksperymentów przesączono przez filtr strzykawkowy (0,45 µm, hydrofilowy PTFE) i poddano analizie. Do kwaśnego ekstraktu o pH 0,3, uzyskanego w optymalnych warunkach, dodano stale mieszając roztwór kwasu szczawioowego (H₂C₂O₄) w nadmiarze 5% względem ilości wynikającej ze stechiometrii reakcji i następnie roztwór NaOH w celu zwiększenia pH do 1,8, co pozwoliło na efektywne wytrącenie szczawianu ceru(III), Ce₂(C₂O₄)₃·10H₂O [55]. Roztwór mieszano z prędkością 250 ± 10 obr/min przez 30 min i pozostawiano na 12 h w celu uzyskania grubokrystalicznego osadu [56]. Otrzymany Ce₂(C₂O₄)₃·10H₂O filtrowano przez sącdek membranowy (hydrofilowy PTFE) o wielkości porów 0,45 µm i przemyto wodą w celu usunięcia pozostałości roztworu zawierającego niepożądane jony. Materiał suszono w temperaturze 105 ± 1 °C do uzyskania stałej masy, zważono i następnie poddano termicznemu rozkładowi w piecu muflowym w temperaturze 350 ± 5 °C [57].

W pierwszym procesie wytwarzania soli cerowej otrzymany tlenek ceru(IV) (CeO₂) zważono i poddano reakcji z HCl (30%) oraz H₂O₂ (30%) odpowiednio w nadmiarze 200% i 100% względem ilości wynikającej ze stechiometrii jak podczas otrzymywania chlorku ceru(III) z proszku polerskiego. W kolejnym etapie reagenty mieszano i ogrzewano do temperatury ok. 90 °C przez 4 h [54]. Następnie, roztwór przesączono przez sącdek membranowy (0,45 µm, hydrofilowy PTFE), odparowano, krystalizowano oraz suszono w temperaturze 70 ± 1 °C.

Drugi proces polegał na reakcji tlenku ceru(IV) (CeO_2) z nadmiarem H_2SO_4 (96% m/m) względem stechiometrycznej ilości kwasu, w celu uzyskania $\text{Ce}_2(\text{SO}_4)_3$. Substraty mieszano i ogrzewano w temperaturze $100 \pm 1^\circ\text{C}$ przez 1 h. Po zakończeniu ogrzewania rozcieńczano wodą dejonizowaną i redukowano Ce(IV) do Ce(III) za pomocą H_2O_2 (30% m/m). Otrzymaną mieszaninę filtrowano przez filtr membranowy (hydrofilowy PTFE) o wielkości porów $0,45\ \mu\text{m}$, odparowywano, krystalizowano i suszono w temperaturze $300 \pm 5^\circ\text{C}$.

Trzeci proces polegał na reakcji tlenku ceru(IV) (CeO_2) z nadmiarem H_2SO_4 (96% m/m) w celu uzyskania siarczanu(VI) ceru(IV) ($\text{Ce}(\text{SO}_4)_2$). Reagenty mieszano i ogrzewano w temperaturze $100 \pm 1^\circ\text{C}$ przez 1 h, po czym ogrzewano w piecu mufowym w temperaturze $300 \pm 5^\circ\text{C}$ przez 1 h w celu usunięcia nadmiaru H_2SO_4 . Każdą z otrzymanych soli poddano analizie składu chemicznego z zastosowaniem technik ICP-OES, ICP-MS, IC oraz SEM-EDS.

8.3.4 Utlenianie toksycznych zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego przy użyciu siarczanu(VI) ceru(IV)

Materiałem badawczym w procesach utleniania zanieczyszczeń z zastosowaniem siarczanu(VI) ceru(IV) były ścieki pochodzące z symulacji procesu podziemnego zgazowania węgla kamiennego przeprowadzonego z użyciem powietrza wzbogaconego tlenem, pod ciśnieniem atmosferycznym. W eksperymentach stosowano mieszaniny utleniające przygotowane z siarczanu(VI) ceru(IV) ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), cz.d.a. nadtlenu wodoru (H_2O_2), 30%) (Chempur, Polska), cz.d.a. siarczanu(VI) żelaza(II) ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Chempur, Polska). Korektę pH przeprowadzano za pomocą roztworów kwasu solnego sporządzonych z 30% HCl, (Suprapur®, Merck, Niemcy) oraz roztworu wodorotlenku sodu (NaOH), cz.d.a. (Chempur, Polska). Do rozcieńczeń używano wody dejonizowanej ($< 0,05\ \mu\text{S/cm}$).

Utlenianie zanieczyszczeń z zastosowaniem siarczanu(VI) ceru(IV) przeprowadzano poprzez odmierzenie porcji ścieków do zlewek o pojemności 200 ml, wyposażonych w mieszadło magnetyczne. Następnie regulowano pH, ogrzewano zlewki oraz dodawano stały siarczan(VI) ceru(IV) ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) w ilości określonej w planie eksperymentalnym. Ścieki mieszano z prędkością $250 \pm 10\ \text{obr./min}$. Ogrzewanie ścieków miało na celu odzwierciedlenie warunków temperaturowych po opuszczeniu skrubera, gdzie w analizowanym przypadku temperatura maksymalna osiągała ok. 90°C . Ponadto założono, że wykorzystanie ciepła odpadowego może poprawić efektywność procesu utleniania zanieczyszczeń. Optymalizacja warunków procesu metodą powierzchni odpowiedzi (RSM) została przeprowadzona poprzez wykonanie 29 eksperymentów zgodnie z założeniami planu centralnego kompozycyjnego (CCD), w którym uwzględniono cztery parametry wejściowe (zmiennie niezależne) tj. czas z przedziału 5–65 min, stosunek molowy Ce^{4+} do rozpuszczonego węgla organicznego (RWO) wynoszący 2–10, temperaturę 10–90 °C oraz

pH 0,5–4,5 [58,59]. Po zakończeniu procesu utleniania, ścieki alkalizowano do pH 8,2, w celu wytrącenia użytego utleniacza w postaci m.in. $\text{Ce}(\text{OH})_3$ i/lub $\text{Ce}(\text{OH})_4$.

Proces utleniania w układzie $\text{Ce}^{4+} + \text{H}_2\text{O}_2$ przeprowadzono w 9 eksperymentach stosując 9 różnych molowych stosunków $\text{RWO}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$, wybranych na podstawie badań dotyczących zastosowania procesu Fentona opisanych w literaturze [60,61]. Stosunek molowy Ce^{4+} do RWO mieścił się w przedziale 1–3, a stosunek molowy H_2O_2 do RWO w przedziale 5–15. W celu oznaczenia zawartości ceru (Ce) w osadzie ściekowym przeprowadzono jego mineralizację w wodzie królewskiej (*aqua regia*), zgodnie z normą podaną w podrozdziale 8.1.

8.3.5 Ocena ekologiczna i ekonomiczna procesu

Analizę procesu przeprowadzono jako wstępną ocenę wykonalności technologicznej proponowanej metody oczyszczania ścieków z koagulantem cerowym i jego recyklingiem. Przyjęto warunki eksploatacyjne, skalując wyniki badań laboratoryjnych i pilotowych do oczyszczalni ścieków o przepustowości 5000 m³/dobę. Pełny cykl obiegu ceru w procesie podzielono na 10 etapów zestawionych w tabeli 1.

Tabela 1. Etapy procesu oczyszczania ścieków z zastosowaniem związku ceru wraz z recyklingiem reagentów

Numer etapu	Etap
I	Strącenie fosforanów(V)
II	Filtracja
III	Ekstrakcja osadu
IV	Filtracja
V	Strącenie szczawianu ceru(III)
VI	Filtracja, zagospodarowanie odcieków
VII	Rozkład termiczny
VIII	Synteza chlorku ceru(III)
IX	Krystalizacja
X	Odzysk HCl

Źródło: [50]

W koncepcji uwzględniono przebieg reakcji chemicznych, przyjęto parametry technologiczne, konfigurację aparatury (m.in. reaktory, prasy filtracyjne, zbiorniki buforowe), bilans masowy reagentów i produktów. Zidentyfikowano także produkty uboczne (osady, odcieki, gazy reakcyjne) i ich potencjalny wpływ środowiskowy. Przyjęto założenia minimalizacji emisji poprzez odzysk HCl, wykorzystanie pozostałych osadów jako źródła energii oraz odzysk soli z wód poreakcyjnych. Celem było wskazanie potencjalnych punktów krytycznych procesu i przygotowanie podstaw do dalszej oceny środowiskowej (LCA) i ekonomicznej (DGC).

Oceny ekologicznej dokonano metodą LCA (*Life Cycle Assessment*), zgodnie z normami ISO 14040 i ISO 14044. Proces obejmował 4 fazy, a mianowicie zdefiniowanie celu i zakresu, analizę inwentarzową (LCI, *Life Cycle Inventory*), ocenę wpływu (LCIA, *Life Cycle Impact Assessment*) oraz interpretację wyników.

Ponieważ analizowana technologia stanowi uzupełnienie procesu oczyszczania ścieków, nie jest możliwe wydzielenie osobnej taryfy za jej stosowanie. W związku z tym, zastosowano metodę DGC (*Dynamic Generation Cost*) wyrażoną wzorem (5).

$$DGC = \frac{\sum_{t=0}^n \frac{KI_t + KE_t}{(1+i)^t}}{\sum_{t=0}^n \frac{P_t}{(1+i)^t}} \quad (5)$$

gdzie:

KI_t - koszty inwestycyjne poniesione w danym roku,

KE_t - koszty operacyjne poniesione w danym roku,

P_t - objętość oczyszczonych ścieków w danym roku,

i - stopa dyskontowa,

t - rok, w zakresie od 0 do n , gdzie 0 oznacza rok poniesienia pierwszych kosztów, a n – rok zakończenia eksploatacji oczyszczalni ścieków.

Nakłady inwestycyjne oszacowano na podstawie koncepcji instalacji i dostępnych cenników urządzeń (poziom cen Q1 2025) na kwotę 2 405 060 USD. Dla analizy DGC przyjęto stopę dyskontową 4% oraz okres 22 lat (2025–2046), obejmujący 2 lata inwestycji i 20 lat eksploatacji. Dokładność szacunków kosztowych odpowiada klasie AACE Class 4 (błąd -15% do -30% po stronie niedoszacowania, +20% do +50% po stronie przeszacowania).

9. Omówienie wyników badań

9.1. Wybór materiału badawczego

W celu wyboru odpowiedniego materiału badawczego o dużej zawartości ceru przeprowadzono szereg analiz mających na celu określenie zawartości tego pierwiastka (Ce). Wyniki analiz zestawiono w tabeli 2.

Tabela 2. Zawartość ceru w analizowanych odpadach

Odpad	Ce, mg/kg
Muł węglowy	$19,6 \pm 3,9$
Popiół po współspaleniu węgla kamiennego z RDF	$122,8 \pm 24,6$
Materiał skalny z hałdy przy KWK	$22,8 \pm 4,6$
Zużyty proszek polerski	$667\,540 \pm 6\,675$

Źródło: Opracowanie własne

Przeprowadzone analizy technikami ICP-OES, ICP-MS oraz XRD jednoznacznie wykazały, że najbardziej perspektywicznym materiałem do dalszych badań był zużyty proszek polerski zawierający 66,75% Ce. W przypadku pozostałych materiałów zawartość ceru jest niska, co przekłada się na konieczność wykonania wielu operacji fizykochemicznych w celu zatężenia odzyskiwanego pierwiastka i uzyskania soli o odpowiedniej czystości, co wielokrotnie zwiększy koszt odzysku względem wartości rynkowej.

9.2. Usuwanie fosforanów(V) ze ścieków browarniczych za pomocą chlorku ceru(III) pochodzącego ze zużytego środka polerskiego: badania odzysku i optymalizacji

Pierwszym celem badań opisanych w **artykule nr 1** było pozyskanie chlorku ceru(III) z materiału odpadowego, którym był zużyty proszek polerski. Wyniki analizy składu fazowego, uzyskane techniką XRD i przedstawione w tabeli 3, wskazują, że badany odpad zawierał 82,0% tlenku ceru(IV) oraz substancję amorficzną, którą najprawdopodobniej był tlenek krzemu(IV) pochodzący z procesu polerowania powierzchni szklanych. Poddanie materiału procesowi ekstrakcji z zastosowaniem kwasu chlorowodorowego oraz nadtlenu wodoru skutkowało uzyskaniem chlorku ceru(III) z wydajnością 77,8% i czystością 98,3%. Niepełna ekstrakcja mogła być spowodowana otrzymaniem tlenku ceru(IV) w temperaturze powyżej 620°C, typowej dla przeróbki surowców zawierających pierwiastki ziem rzadkich. Związek ten otrzymany w procesie wysokotemperaturowym charakteryzuje się podwyższoną odpornością na działanie czynników chemicznych, co w konsekwencji wpływa negatywnie na skuteczność ekstrakcji [57,62]. W omawianym przypadku otrzymana sól cerowa posłużyła do przygotowania koagulantu o stężeniu jonów ceru(III) 0,05 mol/l.

Tabela 3. Skład fazowy zużytego proszku polerskiego określony metodą XRD

Parametr	Jednostka	Wartość ± niepewność pomiarowa
Tlenek ceru(IV) (CeO ₂)	%	82,0 ± 1,0
Nierozpoznany minerał	%	2,0 ± 1,0
Substancja amorficzna	%	14,5 ± 0,5

Źródło: [16]

Drugim materiałem wykorzystanym w badaniach były ścieki browarnicze. Przed eksperymentami oczyszczania zostały one poddane analizie fizykochemicznej technikami opisanymi w podrozdziale 8.1. Wyniki analizy przedstawione w tabeli 4 wykazały m.in. podwyższone stężenie fosforanów(V) w porównaniu ze ściekami bytowymi [63], co potwierdziło przydatność materiału do zastosowania w dalszych badaniach.

Tabela 4. Skład fizykochemiczny ścieków browarniczych

Parametr	Jednostka	Wartość ± niepewność pomiarowa
pH	-	7,5 ± 0,1
Przewodność elektryczna właściwa	μS/cm	2200 ± 110
Sód (Na)	mg/l	578 ± 58
Potas (K)	mg/l	21,1 ± 2,1
Magnez (Mg)	mg/l	13,8 ± 1,4
Wapń (Ca)	mg/l	61,1 ± 6,1
Żelazo (Fe)	mg/l	2,00 ± 0,20
Mangan (Mn)	mg/l	0,35 ± 0,04
Glin (Al)	mg/l	0,60 ± 0,09
Cynk (Zn)	mg/l	0,15 ± 0,02
Siarka ogólna, (S _{og.})	mg/l	65,3 ± 9,8
Azot ogólny, (N _{og.})	mg/l	46,0 ± 6,9
Azotany(V), NO ₃ ⁻	mg/l	0,68 ± 0,07
Azotany(III), NO ₂ ⁻	mg/l	< 0,006 ± 0,001
Jony amonu, NH ₄ ⁺	mg/l	39,1 ± 3,9
Fosfor ogólny, (P _{og.})	mg/l	19,8 ± 2,0
Fosforany(V), PO ₄ ³⁻	mg/l	43,0 ± 4,3
Zawiesina, TSS	mg/l	630 ± 63
ChZT _(Cr)	mg O ₂ /l	827 ± 124
Ogólny węgiel organiczny, OWO	mg/l	130 ± 20
Rozpuszczony węgiel organiczny, RWO	mg/l	71,0 ± 10,7
Mętność	NTU	390 ± 39
Barwa	mg Pt/l	170 ± 34
Cer (Ce)	μg/l	< 0,25 ± 0,04

Źródło: [16]

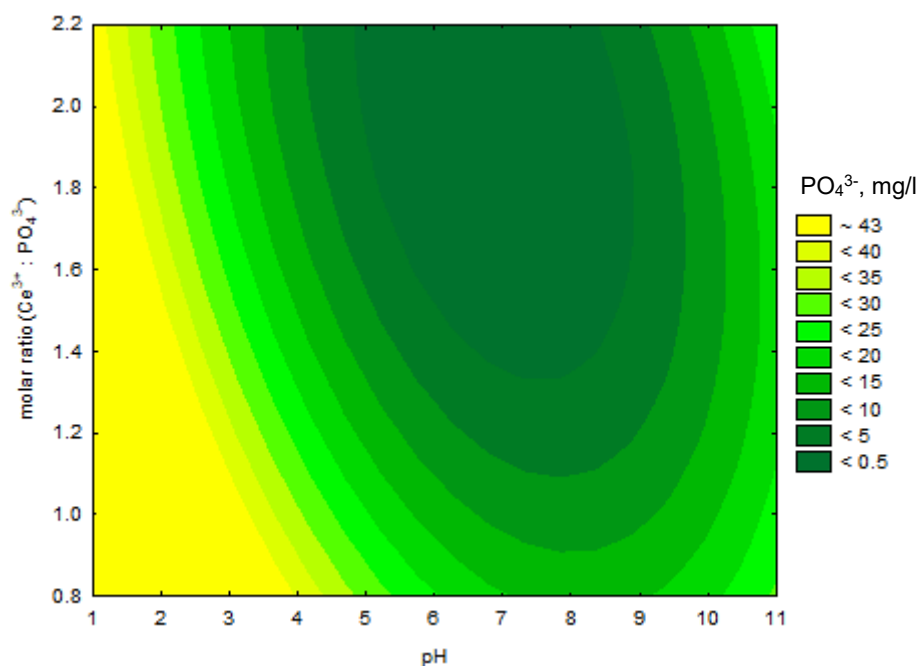
Eksperymenty optymalizacji parametrów procesowych usuwania fosforanów(V) z zastosowaniem koagulantu cerowego przeprowadzono zgodnie z założeniami planu centralnego kompozycyjnego (CCD). Plan obejmował wykonanie 16 eksperymentów dla trzech parametrów wejściowych (zmiennych niezależnych) w zakresach: czas 8,56–21,4 min, stosunek molowy Ce³⁺ do PO₄³⁻ 0,856–2,144:1, pH 2,14–9,86. Wartości poszczególnych parametrów eksperymentalnych oraz wyniki przedstawiono w tabeli 5.

Tabela 5. Warunki eksperymentalne dla CCD/RSM oraz wyniki (Ce^{3+} i PO_4^{3-}) dla ścieków browarniczych (pH 2,14–9,86, stosunek molowy $\text{Ce}^{3+}:\text{PO}_4^{3-}$ (0,856–2,144:1), czas 8,56–21,4 min); *- centrum planu

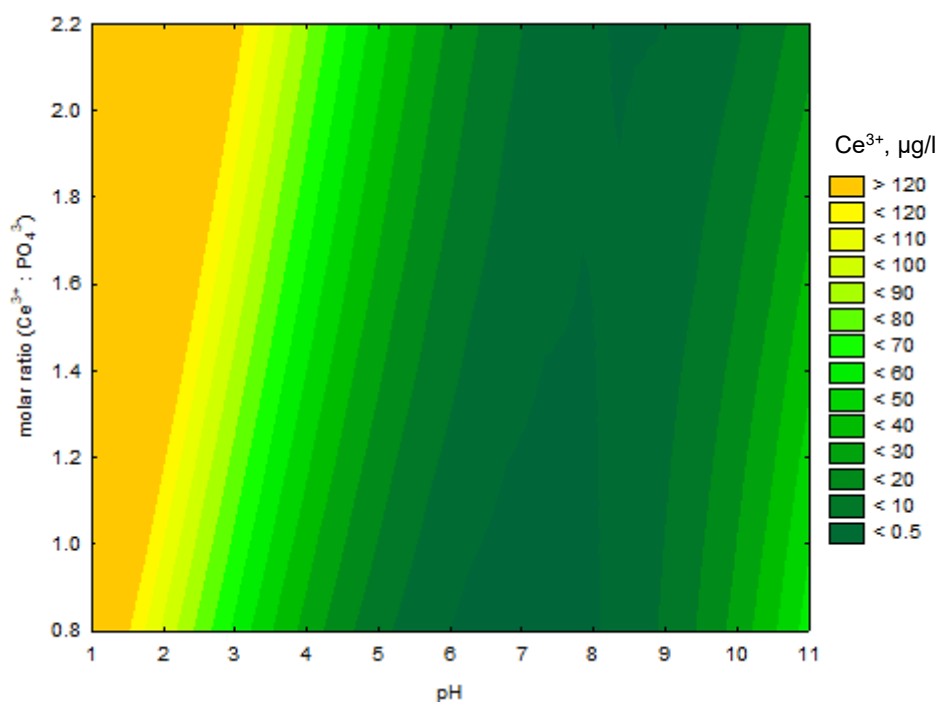
Test	Warunki eksperymentów			Wyniki eksperymentów	
	pH, x_1	Czas (min), x_2	Stosunek molowy $\text{Ce}^{3+}:\text{PO}_4^{3-}$, x_3	PO_4^{3-} , mg/l	Ce^{3+} , mg/l
1	3,00	10,0	1,000	$43,5 \pm 4,4$	$73,8 \pm 11,1$
2	3,00	10,0	2,000	$13,8 \pm 1,4$	133 ± 20
3	3,00	20,0	1,000	$42,2 \pm 4,2$	$69,9 \pm 10,5$
4	3,00	20,0	2,000	$12,0 \pm 1,2$	126 ± 19
5	9,00	10,0	1,000	$9,57 \pm 0,96$	$0,015 \pm 0,002$
6	9,00	10,0	2,000	$2,93 \pm 0,29$	$0,171 \pm 0,026$
7	9,00	20,0	1,000	$15,0 \pm 1,5$	$0,070 \pm 0,011$
8	9,00	20,0	2,000	$1,48 \pm 0,15$	$0,158 \pm 0,024$
9	2,14	15,0	1,500	$46,7 \pm 4,7$	109 ± 16
10	9,86	15,0	1,500	$0,570 \pm 0,060$	$0,124 \pm 0,019$
11	6,00	8,56	1,500	$0,059 \pm 0,006$	$0,194 \pm 0,029$
12	6,00	21,4	1,500	$0,045 \pm 0,005$	$0,145 \pm 0,022$
13	6,00	15,0	0,856	$15,0 \pm 1,5$	$1,02 \pm 0,15$
14	6,00	15,0	2,144	$< 0,010 \pm 0,001$	$0,719 \pm 0,108$
15*	6,00	15,0	1,500	$0,043 \pm 0,004$	$0,147 \pm 0,022$
16*	6,00	15,0	1,500	$0,039 \pm 0,004$	$0,184 \pm 0,028$

Źródło: [16]

Analiza statystyczna uzyskanych wyników pozwoliła na określenie istotności poszczególnych parametrów wejściowych, co w następnym etapie umożliwiło wyznaczenie powierzchni odpowiedzi (rysunek 4 i 5) i ustalenie optymalnych warunków procesowych dla minimalizacji stężenia fosforanów(V) oraz pozostałych po koagulacji jonów ceru(III) w oczyszczonych ściekach. Uzyskane modele matematyczne charakteryzowały się skorygowanym współczynnikiem determinacji $R_{adj}^2 = 0,929$ dla usuwania fosforanów(V), oraz $R_{adj}^2 = 0,945$ dla minimalizacji stężenia jonów ceru(III) po koagulacji, co oznacza wyjaśnienie odpowiednio 92,9% i 94,5% wyników eksperymentalnych względem wyników przewidywanych przez modele. Ustalono, że minimalizację obu analizowanych parametrów można osiągnąć podczas prowadzenia procesu przy pH z przedziału 7,0–8,5, stosunku molowym Ce^{3+} do PO_4^{3-} 1,5–2,0:1 i czasie 15 min.



Rysunek 4. Powierzchnia odpowiedzi wpływu stosunku molowego $\text{Ce}^{3+}:\text{PO}_4^{3-}$ i wartości pH, na stężenie jonów PO_4^{3-} w oczyszczanych ściekach browarniczych, czas = 15 min
Źródło: [16]



Rysunek 5. Powierzchnia odpowiedzi wpływu stosunku molowego $\text{Ce}^{3+}:\text{PO}_4^{3-}$ i wartości pH, na stężenie jonów Ce^{3+} w oczyszczanych ściekach browarniczych, czas = 15 min
Źródło: [16]

Przyjęte założenia zweryfikowano przez wykonanie eksperymentu przy pH ścieków 7,5, stosunku molowym Ce^{3+} do PO_4^{3-} 1,5:1 i czasie 15 min. Prowadzenie procesu w tych warunkach pozwoliło na obniżenie stężenia fosforanów(V) (PO_4^{3-}) o 99,86%, fosforu ogólnego

o 99,56%, ChZT_(Cr) o 81,86%, zawiesiny o 96,67%, OWO o 60,38%, azotu ogólnego o 19,24%, mętność o 98,18%, barwy 70,59%. Stężenie jonów ceru(III) wynosiło 0,058 mg/l, co stanowiło 0,06% wartości początkowej wynikającej z ilości dodanej do oczyszczania ścieków. Otrzymane bardzo dobre wyniki pozytywnie zweryfikowały założone parametry prowadzenia procesu. Skuteczne związanie ceru i fosforu w osadzie wskazuje, że może on stanowić potencjalne źródło tych pierwiastków, co stało się podstawą do podjęcia badań nad ich odzyskiem w kolejnej pracy. Szczegółowe wyniki eksperymentu weryfikacyjnego przedstawiono w tabeli 6.

Tabela 6. Wybrane parametry fizykochemiczne ścieków browarniczych przed i po procesie oczyszczania z zastosowaniem roztworu chlorku ceru(III) o stężeniu 0,05 mol/l

Parametr	Jednostka	Ścieki surowe	Ścieki browarnicze po oczyszczaniu ^a	
			Wartość zmierzona	Procent usunięcia ^b , %
pH	-	7,5 ± 0,1	7,5 ± 0,1	-
Mętność	NTU	390 ± 39	7,1 ± 0,7	98,18
Barwa	mg Pt/l	170 ± 34	50 ± 10	70,59
PO ₄ ³⁻	mg/l	43,0 ± 4,3	0,062 ± 0,006	99,86
P _{og.}	mg/l	19,8 ± 2,0	0,085 ± 0,017	99,56
N _{og.}	mg/l	46,0 ± 6,9	37,1 ± 5,6	19,24
Zawiesina	mg/l	630 ± 63	21,0 ± 2,1	96,67
OWO	mg/l	130 ± 19	51,5 ± 7,7	60,38
ChZT _(Cr)	mg O ₂ /l	827 ± 124	150 ± 22	81,86
Ce ³⁺	mg/l	95,2 ^c ± 14,3	0,058 ± 0,009	99,94

^a W warunkach optymalnych, t.j., pH = 7,5, Ce³⁺ = 0,095 g/l (stosunek molowy Ce³⁺:PO₄³⁻, 1,5:1), i czas = 15 min

^b Skuteczność oczyszczania ścieków = (C₁ - C₂)/C₁ × 100%, gdzie C₁ to stężenie substancji w surowych ściekach browarniczych, a C₂ to stężenie substancji w ściekach oczyszczonych

^c Obliczone stężenie jonów Ce³⁺ po dodaniu do surowych ścieków browarniczych (zawartość jonów Ce³⁺ w surowych ściekach browarniczych < 0,25 µg/l)

Źródło: [16]

9.3. Odzysk soli ceru z osadów ściekowych powstałych w wyniku koagulacji ścieków browarniczych za pomocą odzyskanego koagulantu cerowego

W artykule nr 2 przedstawiono metodę odzysku ceru z osadu ściekowego wraz z optymalizacją procesu. Badany materiał pochodził z procesu oczyszczania ścieków browarniczych, gdzie został zastosowany koagulant cerowy. Skład chemiczny osadu przedstawiono w tabeli 7. Materiał zmineralizowano w *aqua regia*, przesączono, rozcieńczono i poddano analizie technikami ICP-OES oraz ICP-MS. Wyniki analiz wskazują na wysoką zawartość ceru (10,15%) przez co materiał jest przydatnym surowcem do odzysku tego pierwiastka, zwłaszcza w kontekście znikomych zasobów naturalnych tego pierwiastka w Polsce [64].

Tabela 7. Skład chemiczny osadu ściekowego po koagulacji chlorkiem ceru(III)

Parametr	Jednostka	Wartość $\pm$ niepewność pomiarowa
Cer (Ce)	g/kg	101,5 $\pm$ 10,2
Fosfor ogólny (P)	g/kg	22,2 $\pm$ 2,2
Sód (Na)	g/kg	3,65 $\pm$ 0,37
Mangan (Mg)	g/kg	1,05 $\pm$ 0,11
Wapń (Ca)	g/kg	21,3 $\pm$ 2,1
Żelazo (Fe)	g/kg	3,46 $\pm$ 0,35
Mangan (Mn)	g/kg	0,10 $\pm$ 0,02
Glin (Al)	g/kg	1,23 $\pm$ 0,12
Bar (Ba)	g/kg	0,185 $\pm$ 0,037
Stront (Sr)	g/kg	0,084 $\pm$ 0,021
Cynk (Zn)	g/kg	0,417 $\pm$ 0,083

Źródło: [49]

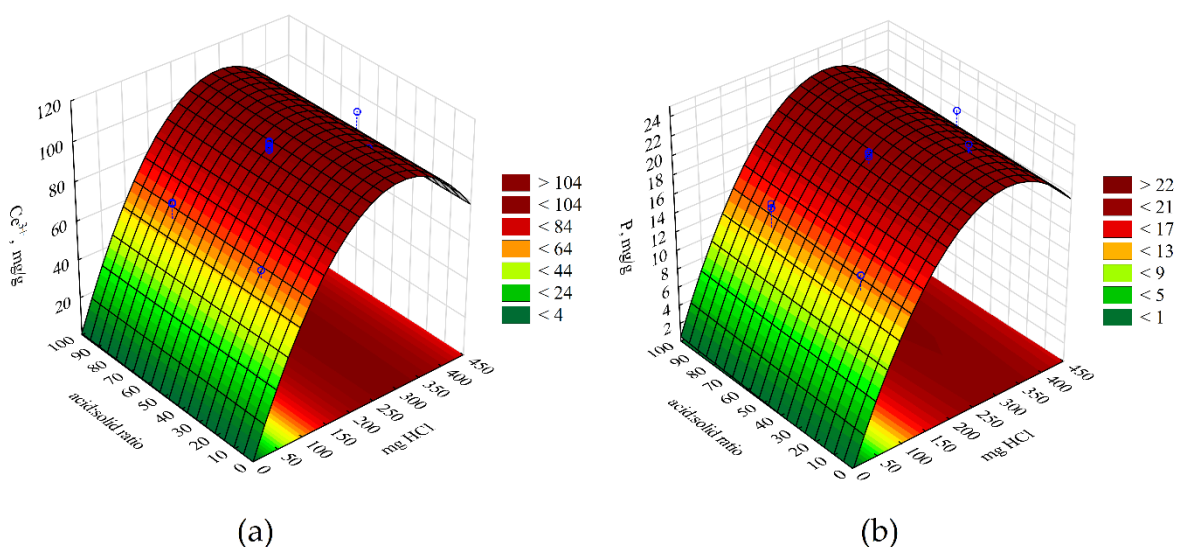
Do badań nad efektywną ekstrakcją ceru i fosforu z osadu ściekowego zastosowano roztwór kwasu chlorowodorowego (HCl). Optymalizację ekstrakcji przeprowadzono zgodnie z założeniami planu centralnego kompozycyjnego (CCD), co pozwoliło na wyznaczenie powierzchni odpowiedzi (RSM) i ustalenie optymalnych warunków ekstrakcji. Przeprowadzono 20 eksperymentów, gdzie zmiennymi niezależnymi były: masa dodanego HCl, czas reakcji oraz stosunek objętościowo-masowy cieczy ekstrakcyjnej do masy osadu ściekowego odpowiednio w zakresach 35,0–405,0 mg/g, 6,36–73,6 min, 7,96–92,0:1 ml/g. Na podstawie wyników eksperymentów przedstawionych w tabeli 8. przeprowadzono analizę statystyczną badanych parametrów wejściowych (zmiennych niezależnych).

Tabela 8. Warunki eksperymentalne dla CCD/RSM oraz wyniki stężeń P i Ce po ekstrakcji z osadów ściekowych (HCl 35,0–405,0 mg, stosunek masy ciecz:ciało stałe (7,96–92,0:1), czas 6,36–73,6 min); * – centrum planu

Warunki eksperymentu				Wyniki	
Test	Stosunek (m/V) ciecz:osad, x_1	Czas (min), x_2	HCl, mg, x_3	P, mg/g	Ce ³⁺ , mg/g
1	25,0	20,0	110	14,24 ± 2,14	67,95 ± 10,19
2	25,0	20,0	330	22,73 ± 3,41	104,5 ± 15,68
3	25,0	60,0	110	14,27 ± 2,14	67,86 ± 10,18
4	25,0	60,0	330	21,80 ± 3,27	101,6 ± 15,24
5	75,0	20,0	110	15,09 ± 2,26	71,73 ± 10,76
6	75,0	20,0	330	20,48 ± 3,07	98,54 ± 14,78
7	75,0	60,0	110	15,54 ± 2,33	72,23 ± 10,84
8	75,0	60,0	330	21,76 ± 3,26	102,6 ± 15,39
9	7,96	40,0	220	18,23 ± 2,73	91,89 ± 13,78
10	92,0	40,0	220	19,91 ± 2,99	91,44 ± 13,72
11	50,0	6,36	220	18,99 ± 2,85	93,18 ± 13,98
12	50,0	73,6	220	19,58 ± 2,94	93,35 ± 14,00
13	50,0	40,0	35	1,014 ± 0,152	11,17 ± 1,68
14	50,0	40,0	405	21,84 ± 3,28	101,4 ± 15,22
15*	50,0	40,0	220	19,67 ± 2,95	97,03 ± 14,55
16*	50,0	40,0	220	20,96 ± 3,14	101,1 ± 15,16
17*	50,0	40,0	220	21,23 ± 3,18	103,2 ± 15,47
18*	50,0	40,0	220	21,42 ± 3,21	105,3 ± 15,80
19*	50,0	40,0	220	19,45 ± 2,92	104,8 ± 15,72
20*	50,0	40,0	220	18,93 ± 2,84	102,2 ± 15,33

Źródło: [49]

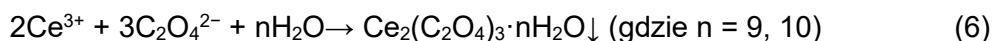
Analiza statystyczna (ANOVA) pozwoliła na eliminację parametrów nieistotnych statystycznie w opracowanym modelu, co w efekcie poprawiło jego dopasowanie do danych eksperymentalnych. Skorygowane współczynniki determinacji modelu dla ceru oraz fosforu wynosiły odpowiednio $R_{adj}^2 = 0,902$ oraz $R_{adj}^2 = 0,868$, co oznacza, że opracowany model objaśnia 90,2% (bardzo dobre dopasowanie) oraz 86,8% (dobre dopasowanie) danych eksperymentalnych. Najprawdopodobniej zastosowanie modelu bardziej złożonego (np. trzeciego stopnia) pozwoliłoby na jeszcze lepsze dopasowanie. Na podstawie wyznaczonych powierzchni odpowiedzi (rysunek 6), ustalono, że optymalnymi warunkami prowadzenia procesu są czas 40 min, stosunek objętości ekstrahenta do masy osadu wynoszący 25 ml/g, oraz masa HCl przypadająca na 1 g osadu w ilości 350 mg co jest zabiegiem kompromisowym pozwalającym na skuteczną ekstrakcję obu pierwiastków.



Rysunek 6. Powierzchnie odpowiedzi przedstawiające uzysk Ce (a) oraz P (b) w zależności od ilości zastosowanego HCl oraz stosunku objętości kwasu do objętości osadu
Źródło: [49]

W wyniku ekstrakcji przeprowadzonej w optymalnych warunkach otrzymano ciemnobrązowy ekstrakt zawierający 99,6% masy ceru i 97,5% masy fosforu pierwotnie obecnych w osadzie ściekowym.

W kolejnym etapie procesu odzysku ceru ekstrakt przesączono, celem oddzielenia roztworu od materii nierozpuszczalnej. Następnie w celu wytrącenia trudno rozpuszczalnego osadu szczawianu ceru(III) do roztworu o pH 0,3 dodano roztwór kwasu szczawowego i podniesiono pH do 1,8 [55], po czym nastąpiło wytrącenie trudno rozpuszczalnego osadu szczawianu ceru(III) z wydajnością 99,97%, zgodnie z reakcją (6).



Rozkład termiczny osadu w piecu mufowym, w temperaturze $350 \pm 5 \text{ }^\circ\text{C}$ skutkowało otrzymaniem tlenku ceru(IV) z wydajnością 99,5%. Temperatura rozkładu została dobrana w taki sposób, aby wytworzyć drobnokrystaliczny materiał, który jest bardziej podatny na działanie czynników chemicznych niż tlenek otrzymany w warunkach wysokotemperaturowych [57]. Materiał ten był substratem w trzech różnych procesach otrzymywania soli cerowych.

Pierwszy proces miał na celu uzyskanie $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ poprzez zmieszanie CeO_2 z 200% nadmiarem HCl (30%) oraz 100% nadmiarem H_2O_2 (30%) względem stechiometrii reakcji [16,54], ogrzewanie mieszaniny reakcyjnej do temperatury $90 \pm 1 \text{ }^\circ\text{C}$ przez 4 h, filtrację przez filtr membranowy ($0,45 \text{ }\mu\text{m}$, hydrofilowy PTFE) i odparowanie roztworu do momentu uzyskania gęstej, syropowatej cieczy. Po ochłodzeniu następowała krystalizacja uwodnionego chlorku ceru(III). W opisanych warunkach proces przebiegł z wydajnością

97,0%. Próbkę otrzymanej substancji poddano analizie chemicznej, która wykazała, że cer stanowił 98,6% spośród 30 analizowanych kationów.

Drugi proces prowadził do otrzymania $\text{Ce}_2(\text{SO}_4)_3$ poprzez dodanie nadmiaru stężonego H_2SO_4 (96%, m/m) do CeO_2 , wymieszanie i ogrzewanie do temperatury $100 \pm 1^\circ\text{C}$ przez 60 ± 1 min, a następnie rozcieńczenie wodą dejonizowaną oraz redukcję Ce(IV) do Ce(III) przy użyciu H_2O_2 (30%, m/m). Otrzymaną mieszaninę przesączono przez filtr membranowy ($0,45\ \mu\text{m}$, hydrofilowy PTFE), odparowano, poddano krystalizacji i wysuszono w temperaturze $300 \pm 5^\circ\text{C}$. W tym przypadku, $\text{Ce}_2(\text{SO}_4)_3$ uzyskano z wydajnością 97,4%, a analiza chemiczna potwierdziła, że cer stanowił 95,9% spośród 30 analizowanych kationów.

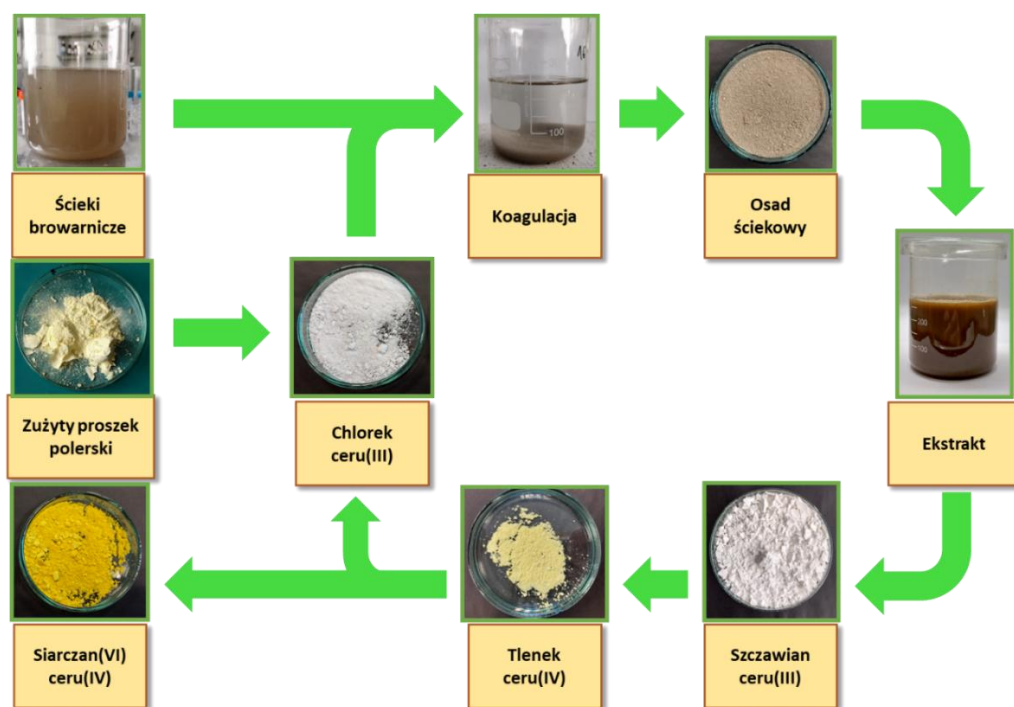
Z kolei, trzeci z procesów prowadził do otrzymania $\text{Ce}(\text{SO}_4)_2$ poprzez reakcję uzyskanego CeO_2 z nadmiarem stężonego H_2SO_4 (96%, m/m) względem wymaganej ilości stechiometrycznej, a następnie ogrzewanie do temperatury $100 \pm 1^\circ\text{C}$ przez 60 ± 1 min oraz dalsze ogrzewanie w piecu muflowym w temperaturze $300 \pm 5^\circ\text{C}$, do momentu zakończenia wydzielania się białych dymów z rozkładu kwasu siarkowego(VI). Wydajność otrzymywania $\text{Ce}(\text{SO}_4)_2$ w tym procesie wyniosła 98,3%. Przeprowadzona analiza chemiczna uzyskanego związku wykazała, że cer stanowił 97,5% spośród wszystkich 30 analizowanych kationów.

Na rysunku 7 przedstawiono wysuszony w temperaturze otoczenia osad ściekowy (A) będący materiałem wejściowym do eksperymentów odzysku ceru oraz produkty końcowe recyklingu koagulantu cerowego – siedmiowodny chlorek ceru(III) (B) oraz siarczan(VI) ceru(IV) (C).



Rysunek 7. Osad wysuszony w temperaturze otoczenia (A), uzyskany chlorek ceru(III) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (B), uzyskany siarczan(VI) ceru(IV) $\text{Ce}(\text{SO}_4)_2$ (C)
Źródło: [49]

Rezultaty przeprowadzonych badań pozwoliły na zamknięcie obiegu ceru w procesie oczyszczania ścieków zgodnie ze schematem przedstawionym na rysunku 8.

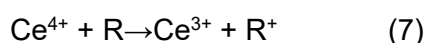


Rysunek 8. Schemat obiegu ceru w procesie oczyszczania ścieków
Źródło: Opracowanie własne

9.4. Ocena możliwości wykorzystania siarczanu(VI) ceru(IV) oraz procesu Fentona i procesu podobnego do procesu Fentona do utleniania zanieczyszczeń w ściekach z symulacji procesu podziemnego zgazowania węgla kamiennego

Badania przedstawione w **artykule nr 3** miały na celu określenie optymalnych warunków prowadzenia procesu utleniania zanieczyszczeń, w którym czynnikiem utleniającym był siarczan(VI) ceru(IV).

Odzysk ceru z osadu ściekowego może prowadzić do otrzymania soli ceru(III) lub ceru(IV). W przypadku odzysku soli ceru(III) można go ponownie wykorzystać do sporządzenia roztworu, który będzie koagulantem w oczyszczaniu ścieków. Natomiast, gdy produktem jest cer(IV) będący silnym utleniaczem, może on zostać zastosowany jako czynnik zmniejszający stężenie zanieczyszczeń podatnych na utlenianie jak ma to miejsce w przypadku ścieków z symulacji procesu podziemnego zgazowania węgla kamiennego, zgodnie z ogólną reakcją (7).



Skład fizykochemiczny otrzymanych ścieków przedstawiono w Tabeli 9.

Tabela 9. Skład fizykochemiczny ścieków z symulacji procesu podziemnego zgazowania węgla kamiennego

Parametr	Jednostka	Wartość ± niepewność pomiarowa
pH	-	1,8 ± 0,1
Potencjał redoks	mV	480
RWO	mg/l	148,0 ± 22,2
Cer (Ce)	µg/l	< 0,10 ± 0,15
Żelazo (Fe)	mg/l	11,537 ± 1,154
Mangan (Mn)	mg/l	0,197 ± 0,039
Kadm (Cd)	mg/l	< 0,005 ± 0,001
Chrom (Cr)	mg/l	2,441 ± 0,244
Miedź (Cu)	mg/l	< 0,020 ± 0,005
Nikiel (Ni)	mg/l	1,088 ± 0,109
Ołów (Pb)	mg/l	1,603 ± 0,160
Cynk (Zn)	mg/l	2,544 ± 0,254
Cyjanki całkowite	µg/l	21000 ± 2100
Indeks fenolowy	µg/l	61950 ± 4956
Naftalen	µg/l	153,78 ± 38,45
Acenaften	µg/l	284,56 ± 71,14
Fluoren	µg/l	107,39 ± 26,85
Fenantren	µg/l	263,23 ± 65,81
Antracen	µg/l	93,81 ± 23,45
Fluoranten	µg/l	133,79 ± 33,45
Piren	µg/l	322,10 ± 80,53
Benzo(a)antracen	µg/l	291,30 ± 72,83
Chryzen	µg/l	143,09 ± 35,77
Benzo(b)fluoranten	µg/l	151,23 ± 37,81
Benzo(k)fluoranten	µg/l	85,26 ± 21,32
Benzo(a)piren	µg/l	231,81 ± 57,95
Dibenzo(a,h)antracen	µg/l	51,53 ± 12,88
Benzo(g,h,i)perylene	µg/l	47,85 ± 11,96
Indeno(1,2,3-cd)piren	µg/l	95,40 ± 23,85
Σ WWA	µg/l	2459,11 ± 614,78

Źródło [22]

W tabeli 10 przedstawiono wartości zmiennych wejściowych dla 29 eksperymentów wraz z wynikami. Analiza statystyczna uzyskanych wyników przy zadanych wartościach parametrów wejściowych (zmiennych niezależnych tj., czas reakcji, stosunek molowy Ce^{4+} :RWO, pH, temperatura) pozwoliła na określenie ich istotności. Następnie po eliminacji najmniej istotnych efektów liniowych, kombinacji efektów liniowych oraz efektów kwadratowych wyznaczono powierzchnie odpowiedzi (rysunek 9) i ustalono optymalne warunki procesowe. Wartość skorygowanego współczynnika determinacji $R^2_{adj} = 0,850$ oznacza, że model jest dobrze dopasowany do danych eksperymentalnych wyjaśniając 85% uzyskanych wyników.

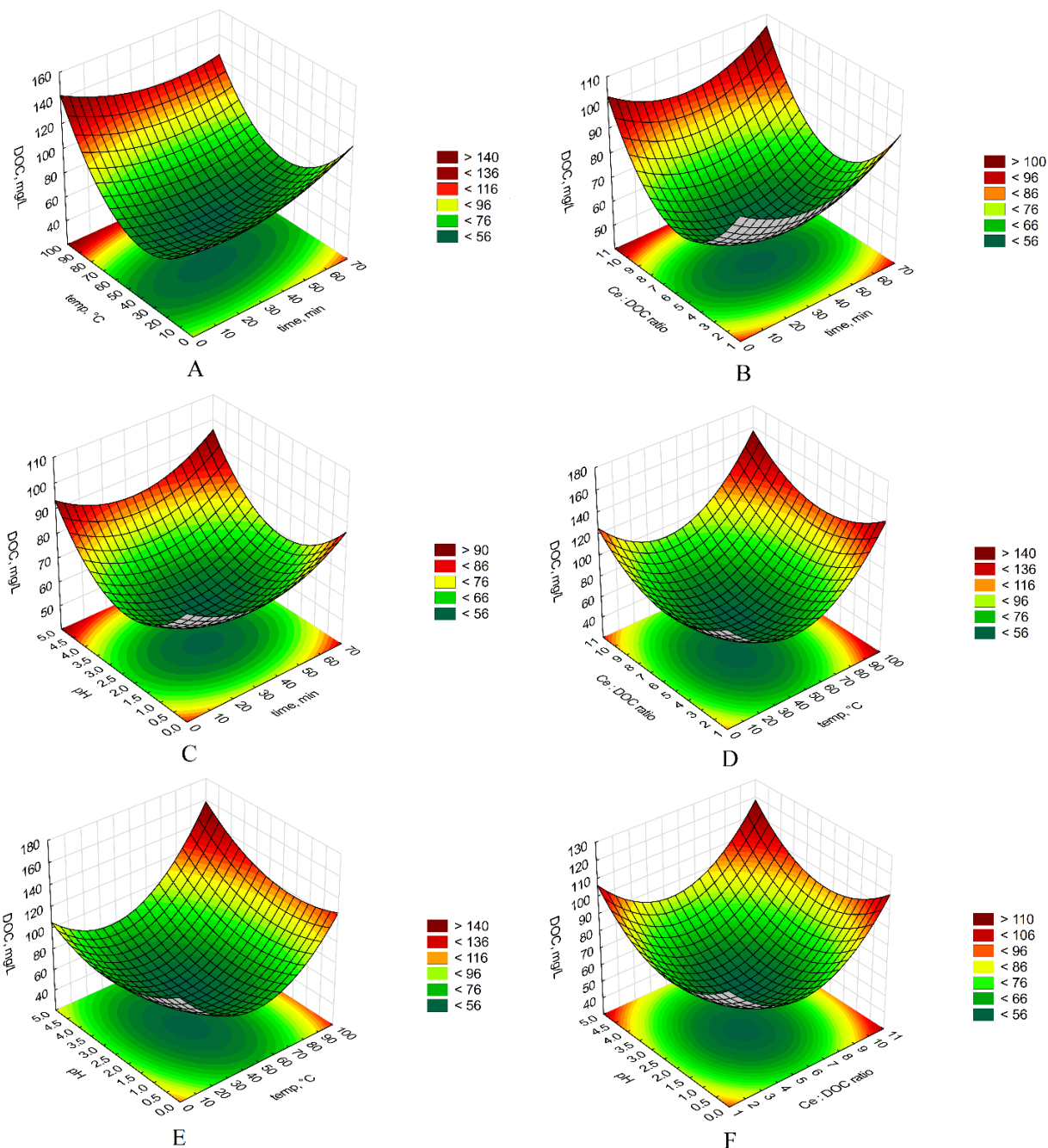
Tabela 10. Warunki eksperymentalne dla CCD/RSM oraz wyniki (RWO) po utlenianiu zanieczyszczeń (czas 5–65 min, stosunek molowy Ce^{4+} :RWO 2–10, pH 0,5–4,5, temperatura 10–90 °C);
* – centrum planu

Test	Warunki eksperymentu				Wyniki eksperymentów
	czas (min), x_1	Stosunek molowy Ce^{4+} :RWO, x_2	pH, x_3	Temperatura °C, x_4	RWO, mg/l
1	20	4	1,5	30	63,0 ± 9,5
2	20	4	3,5	30	64,8 ± 9,7
3	20	8	1,5	30	67,6 ± 10,1
4	20	8	3,5	30	68,1 ± 10,2
5	20	4	1,5	70	73,1 ± 11,0
6	20	4	3,5	70	78,5 ± 11,8
7	20	8	1,5	70	81,4 ± 12,2
8	20	8	3,5	70	81,8 ± 12,3
9	50	4	1,5	30	69,9 ± 10,5
10	50	4	3,5	30	70,5 ± 10,6
11	50	8	1,5	30	78,8 ± 11,8
12	50	8	3,5	30	70,3 ± 10,5
13	50	4	1,5	70	72,0 ± 10,8
14	50	4	3,5	70	81,1 ± 12,2
15	50	8	1,5	70	75,5 ± 11,3
16	50	8	3,5	70	83,1 ± 12,5
17	5	6	2,5	50	67,2 ± 10,1
18	65	6	2,5	50	62,9 ± 9,4
19	35	6	2,5	10	68,1 ± 10,2
20	35	6	2,5	90	107,0 ± 16,1
21	35	2	2,5	50	68,9 ± 10,3
22	35	10	2,5	50	81,4 ± 12,2
23	35	6	0,5	50	62,8 ± 9,4
24	35	6	4,5	50	77,3 ± 11,6
25*	35	6	2,5	50	56,7 ± 8,5
26*	35	6	2,5	50	52,7 ± 7,9
27*	35	6	2,5	50	51,7 ± 7,8
28*	35	6	2,5	50	54,5 ± 8,2
29*	35	6	2,5	50	62,2 ± 9,3

Źródło: [22]

W warunkach optymalnych, określonych na podstawie wyznaczonego modelu, przedstawionego na rysunku 9 tj. przy czasie reakcji 20–40 min, stosunku molowym Ce^{4+} :C 4–6:1, pH 2,0–2,5 oraz temperaturze w zakresie 30–50 °C, stwierdzono największe obniżenie stężenia RWO. Eksperyment weryfikacyjny przeprowadzono przy czasie reakcji 35 min, stosunku molowym Ce^{4+} :C 5:1, pH 2,5 oraz temperaturze 40 °C, potwierdzając skuteczne obniżenie stężeń cyjanków, fenoli, WWA, RWO odpowiednio o 97,67%, 99,97%, 99,40% i 65,34%. Po alkalizacji ścieków do pH 8,2, które miało na celu związanie pozostałych w roztworze jonów ceru w postaci osadu wodorotlenków, zaobserwowano obniżanie pH

w czasie 60 ± 1 min do wartości 5,9. Stwierdzono, że zmniejszenie wartości pH powodowało uwolnienie jonów ceru, co skutkowało wtórnym zanieczyszczeniem ścieków oczyszczonych i mimo skutecznego obniżenia stężeń WWA, cyjanków, fenoli i RWO jest to ograniczenie przedstawionej metody.



Rysunek 9. Powierzchnie odpowiedzi przedstawiające stężenie RWO w funkcji poszczególnych zestawów zmiennych niezależnych, (A) temperatura i czas, (B) stosunek molowy Ce^{4+} :RWO i czas, (C) pH i czas, (D) stosunek molowy Ce^{4+} :RWO i temperatura, (E) pH i temperatura, (F) pH i stosunek molowy Ce^{4+} :RWO

Źródło: [22]

W alternatywnym procesie utlenianie zanieczyszczeń z zastosowaniem jonów ceru(IV) zostało zmodyfikowane o dodatek 30% (m/m) roztworu nadtlenu wodoru. Proces ten według danych literaturowych należy do grupy procesów podobnych do procesu Fentona (*Fenton-like processes*). Założono w nim, że produktem reakcji między jonami ceru(IV), a nadtlaniem wodoru jest rodnik hydroksylowy, który jest jednym z najsilniejszych utleniaczy (tabela 11).

Tabela 11. Potencjały redoks wybranych utleniaczy

Utleniacz	Eh, V
•OH	2.80
O	2.42
O ₃ (warunki kwasowe)	2.07
H ₂ O ₂ (warunki kwasowe)	1.78
HO ₂ •	1.70
Ce ⁴⁺ w 1M HClO ₄	1.70
Ce ⁴⁺ w 1M H ₂ SO ₄	1.44
Ce ⁴⁺ w 1M HCl	1.28
O ₂ (warunki kwasowe)	1.23

Źródło: [22]

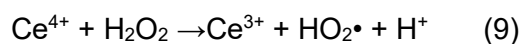
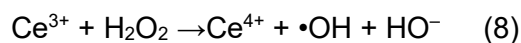
W tabeli 12, przedstawiono wyniki stężeń rozpuszczonego węgla organicznego (RWO) po 9 procesach utleniania, z zastosowaniem różnych proporcji molowych pomiędzy węglem (C) pochodzącym z zanieczyszczeń, jonami ceru(IV) oraz nadtlaniem wodoru (H₂O₂).

Tabela 12. Stężenie RWO w zależności od ilości dodanego siarczanu(VI) ceru(IV) (Ce(SO₄)₂·4H₂O) i nadtlenu wodoru (H₂O₂); pH ścieków = 2,5, czas = 35 min, temperatura = 40 °C

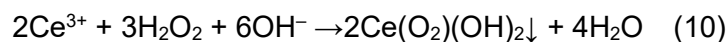
Stosunek molowy C:Ce ⁴⁺ :H ₂ O ₂	RWO, mg/l
1:1:5	38,7 ± 5,8
1:1:15	37,9 ± 5,7
1:2:2	41,8 ± 6,3
1:2:5	42,4 ± 6,4
1:2:10	37,1 ± 5,6
1:2:15	39,0 ± 5,9
1:3:5	36,7 ± 5,5
1:3:10	41,8 ± 6,3
1:3:15	39,0 ± 5,9

Źródło: [22]

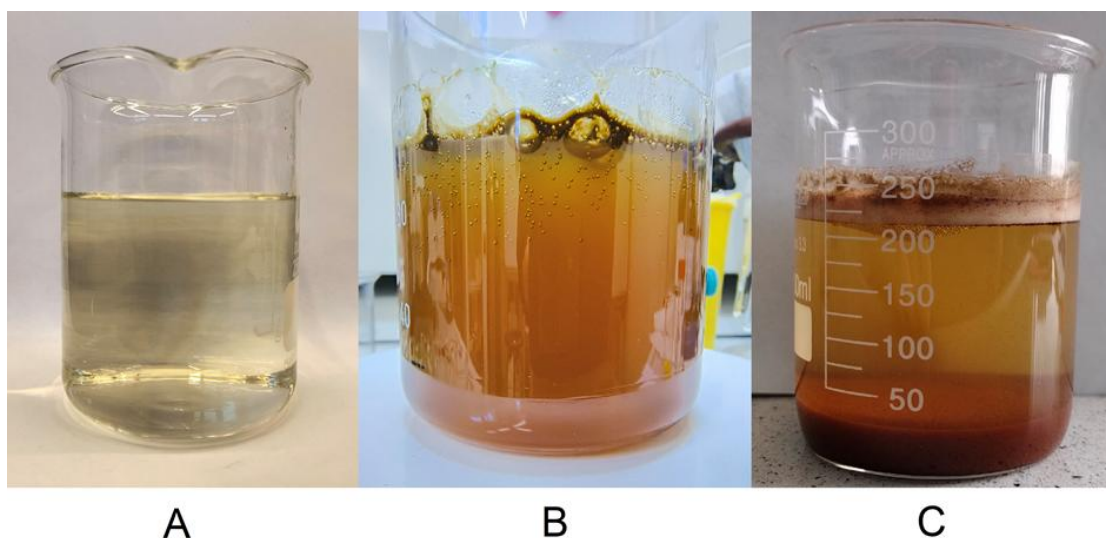
Ze względu na podobieństwo otrzymanych rezultatów, arbitralnie wybrano wartość bliską środkowej dla analizowanych proporcji poszczególnych reagentów mieszanej utleniającej tj. stosunek C:Ce⁴⁺:H₂O₂ 1:2:10. Rysunek 10 przedstawia przefiltrowane ścieki przed oczyszczaniem (A), w trakcie utleniania (B) oraz po alkalizacji do pH 8,2 kończącej utlenianie i po sedymentacji osadu (C). Z punktu widzenia prowadzenia procesu utleniania niezwykle istotne jest, aby odczyn ścieków był kwasowy, ponieważ tylko w takich warunkach możliwe jest zachodzenie reakcji bezpośredniego utleniania jonami Ce⁴⁺ (7), oraz reakcji z wytworzeniem rodników (8) i (9) umożliwiających skuteczne utlenianie zanieczyszczeń.



W środowisku zasadowym, zdolności oksydacyjne zostają zablokowane przez utworzenie stabilnego związku, który wiąże jony ceru w stabilnym osadzie według reakcji (10).



Po zakończeniu utleniania spowodowanym alkalizacją ścieków do pH 8,2 i po upływie 60 ± 1 min zaobserwowano niewielkie zwiększenie pH do 8,7 mogące świadczyć o częściowym rozkładzie osadu otrzymanego w reakcji (10). Analiza składu chemicznego ścieków oczyszczonych wykazała, że 99,996% ceru zostało związane w stabilnym osadzie, co przekładało się na stężenie jonów ceru na poziomie $3,7 \mu\text{g/l}$. W tym przypadku, osiągnięto obniżenie stężenia cyjanków, fenoli, WWA oraz RWO odpowiednio o 98,14%, 99,66%, 99,91% i 76,35%.



Rysunek 10. Przefiltrowane ścieki z symulacji procesu podziemnego zgazowania węgla kamiennego (A), roztwór podczas utleniania zanieczyszczeń w optymalnych warunkach, przy stosunku molowym RWO: Ce^{4+} : H_2O_2 1:2:10, pH = 2,5, czas reakcji = 35 min, temperatura = 40°C (B), roztwór po zakończonym utlenianiu zanieczyszczeń i sedymentacji osadu przy pH 8,2 (C)
Źródło: [22]

Celem porównania opisanych powyżej metod utleniania z dobrze znanym i szeroko opisanym w literaturze procesem Fentona bazującym na zastosowaniu soli żelaza(II) i nadtlenu wodoru przeprowadzono dodatkowy proces oczyszczania. Eksperyment porównawczy przeprowadzono z zastosowaniem identycznych proporcji reagentów jak w przypadku procesu z zastosowaniem ceru(IV) i nadtlenu wodoru (H_2O_2) tj. stosunek molowy RWO: Fe^{2+} : H_2O_2 1:2:10, czas reakcji 35 min, pH 2,5, temperatura 40°C . Przedstawione w tabeli 13. wyniki eksperymentów wykazały wysoką efektywność w obniżaniu stężeń

zanieczyszczeń w każdym z analizowanych układów utleniających, przy czym w przypadku RWO, będącym ogólnym wskaźnikiem zanieczyszczenia, najskuteczniejszym układem utleniającym był $Ce^{4+} + H_2O_2$. Istotną zaletą procesu podobnego do procesu Fentona w układzie $Ce^{4+} + H_2O_2$ względem zastosowania wyłącznie roztworu soli Ce^{4+} do utleniania zanieczyszczeń była znikoma zawartość jonów ceru(III) i ceru(IV), które zostały w 99,996% związane w osadzie, co w przypadku zastosowania wyłącznie ceru(IV) nie było tak skuteczne (związanie 91,72% jonów Ce) i powodowało wtórne zanieczyszczeniem ścieków oczyszczonych.

Tabela 13. Właściwości fizykochemiczne ścieków przed i po procesie oczyszczania

Parametr	Jednostka	Ścieki surowe	Utleniacze		
			Ce^{4+}	$Ce^{4+} + H_2O_2$	$Fe^{2+} + H_2O_2$
pH	-	$1,8 \pm 0,1$	$5,9^a \pm 0,1$	$8,7^a \pm 0,1$	$7,9^a \pm 0,1$
Potencjał redoks	mV	480	1153 ^b	585 ^b	559 ^b
RWO	mg/L	$148,0 \pm 22,2$	$51,3 \pm 7,7$	$35,0 \pm 5,3$	$64,4 \pm 9,7$
Cer (Ce)	µg/L	$< 0,10 \pm 0,15$	7655 ± 766	$3,7 \pm 0,6$	$< 0,10 \pm 0,15$
Żelazo (Fe)	mg/L	$11,537 \pm 1,154$	$0,003 \pm 0,001$	$0,002 \pm 0,001$	$0,003 \pm 0,001$
Mangan (Mn)	mg/L	$0,197 \pm 0,039$	$< 0,005 \pm 0,001$	$< 0,005 \pm 0,001$	$< 0,005 \pm 0,001$
Kadm (Cd)	mg/L	$< 0,005 \pm 0,001$	$< 0,005 \pm 0,001$	$< 0,005 \pm 0,001$	$< 0,005 \pm 0,001$
Chrom (Cr)	mg/L	$2,441 \pm 0,244$	$0,0010 \pm 0,0003$	$0,91 \pm 0,09$	$0,41 \pm 0,08$
Miedź (Cu)	mg/L	$< 0,020 \pm 0,005$	$< 0,020 \pm 0,005$	$< 0,020 \pm 0,005$	$< 0,020 \pm 0,005$
Nikiel (Ni)	mg/L	$1,088 \pm 0,109$	$0,766 \pm 0,153$	$0,514 \pm 0,103$	$0,409 \pm 0,082$
Ołów (Pb)	mg/L	$1,603 \pm 0,160$	$< 0,050 \pm 0,013$	$< 0,050 \pm 0,013$	$< 0,050 \pm 0,013$
Cynk (Zn)	mg/L	$2,544 \pm 0,254$	$< 0,050 \pm 0,013$	$< 0,050 \pm 0,013$	$< 0,050 \pm 0,013$
Cyjanki całkowite	µg/L	21000 ± 2100	489 ± 49	390 ± 39	1036 ± 104
Indeks fenolowy	µg/L	61950 ± 4956	$18,5 \pm 2,8$	$207,8 \pm 31,2$	$32,5 \pm 4,9$
Naftalen	µg/L	$153,78 \pm 38,45$	$4,64 \pm 1,16$	$0,14 \pm 0,04$	$< 0,050 \pm 0,013$
Acenaften	µg/L	$284,56 \pm 71,14$	$0,36 \pm 0,09$	$0,23 \pm 0,06$	$0,06 \pm 0,02$
Fluoren	µg/L	$107,39 \pm 26,85$	$0,25 \pm 0,06$	$0,78 \pm 0,20$	$< 0,050 \pm 0,013$
Fenantren	µg/L	$263,23 \pm 65,81$	$6,55 \pm 1,64$	$0,36 \pm 0,09$	$0,38 \pm 0,10$
Antracen	µg/L	$93,81 \pm 23,45$	$0,09 \pm 0,02$	$0,42 \pm 0,11$	$0,07 \pm 0,02$
Fluoranten	µg/L	$133,79 \pm 33,45$	$1,22 \pm 0,31$	$0,16 \pm 0,04$	$0,37 \pm 0,09$
Piren	µg/L	$322,10 \pm 80,53$	$0,45 \pm 0,11$	$0,10 \pm 0,03$	$0,45 \pm 0,11$
Benzo(a)antracen	µg/L	$291,30 \pm 72,83$	$0,08 \pm 0,02$	$< 0,050 \pm 0,013$	$0,10 \pm 0,03$
Chryzen	µg/L	$143,09 \pm 35,77$	$0,08 \pm 0,02$	$< 0,050 \pm 0,013$	$0,08 \pm 0,02$
Benzo(b)fluoranten	µg/L	$151,23 \pm 37,81$	$0,09 \pm 0,02$	$< 0,050 \pm 0,013$	$0,08 \pm 0,02$
Benzo(k)fluoranten	µg/L	$85,26 \pm 21,32$	$0,05 \pm 0,01$	$< 0,050 \pm 0,013$	$0,05 \pm 0,01$
Benzo(a)piren	µg/L	$231,81 \pm 57,95$	$0,11 \pm 0,03$	$< 0,050 \pm 0,013$	$0,12 \pm 0,03$
Dibenzo(a,h)antracen	µg/L	$51,53 \pm 12,88$	$0,03 \pm 0,01$	$< 0,050 \pm 0,013$	$0,05 \pm 0,01$
Benzo(g,h,i)perylen	µg/L	$47,85 \pm 11,96$	$0,45 \pm 0,11$	$0,31 \pm 0,08$	$0,36 \pm 0,09$
Indeno(1,2,3-cd)piren	µg/L	$95,40 \pm 23,85$	$0,17 \pm 0,04$	$< 0,050 \pm 0,013$	$0,16 \pm 0,04$
Σ WWA	µg/L	$2459,11 \pm 614,78$	$14,64 \pm 3,66$	$2,25 \pm 0,56$	$2,32 \pm 0,58$

^a – pH ścieków oczyszczonych po 1 h od zakończenia procesu i podniesienia pH do 8,2

^b – Potencjał redoks po dodaniu utleniacza do ścieków surowych

Źródło: [22]

9.5. Ekologiczna i ekonomiczna ocena procesu oczyszczania ścieków z odzyskiem koagulantu cerowego

Przeprowadzona analiza ekologiczna wykazała, że choć dziesięciokrotne obniżenie stężenia fosforanów(V) w porównaniu z koagulacją opartą na solach żelaza(II), żelaza(III)

i glinu jest efektem wysoce pożądanym, istnieje szereg aspektów wymagających dalszych badań. Analiza ekonomiczna procesu wskazała, że głównym kosztem proponowanej technologii jest zakup surowców chemicznych. Choć recykling koagulantu jest droższy niż import z Chin, w przypadku embarga staje się on opłacalny i zwiększa uniezależnienie od zewnętrznych dostaw. Istotnym kierunkiem rozwoju jest optymalizacja syntezy chlorku ceru(III), co pozwoli na ograniczenie zużycia kwasu solnego – głównego reagenta w całym procesie.

Proces oczyszczania ścieków z użyciem związków ceru(III) umożliwia obniżenie stężenia fosforanów(V) o ponad 99,8%, a ponadto zastosowany koagulant można odzyskiwać metodą ekstrakcji z HCl z skutecznością 97,0–98,3%, co pozwala na jego ponowne wykorzystanie przy minimalnym uzupełnianiu strat. Dodatkową zaletą zaproponowanego rozwiązania jest zmniejszenie ilości osadów ściekowych o 20–25% oraz możliwość zagospodarowania produktów ubocznych w procesach energetycznych i chemicznych. Zamknięty obieg reagentów sprawia, że proces wpisuje się w zasady gospodarki o obiegu zamkniętym oraz idee zrównoważonego rozwoju.

Ocena cyklu życia (LCA) przeprowadzona metodą ReCiPe 2016 wykazała, że technologia ta odgrywa istotną rolę w ochronie wód słodkich i morskich przed eutrofizacją. Z drugiej strony, spośród ocenianych 17 kategorii wpływu znaczące obciążenie środowiskowe związane jest z procesami produkcyjnymi zużywanych reagentów, przede wszystkim z zastosowaniem kwasu szczawiowego i solnego, które podczas produkcji odpowiadają m.in. za emisję gazów cieplarnianych, ekotoksyczność oraz zwiększają wskaźniki toksyczności rakotwórczej dla ludzi (w analizie LCA kategoria human carcinogenic toxicity). Duży udział w oddziaływaniu środowiskowym ma także zużycie energii elektrycznej, co wskazuje na potrzebę zwiększenia efektywności energetycznej oraz zwiększenia udziału energii pochodzącej ze źródeł odnawialnych. Dodatkowo, wyniki znormalizowane względem światowych obciążeń wykazały, że dominującymi kategoriami wpływu są toksyczność dla ludzi oraz ekotoksyczność wód, natomiast emisje gazów cieplarnianych i zużycie zasobów kopalnych miały mniejsze znaczenie.

Analiza ekonomiczna metodą DGC określiła koszt usuwania fosforanów(V) z wykorzystaniem chlorku ceru(III) na 1,37 USD/m³. Choć jest to więcej niż w przypadku aktualnie stosowanych metod wykorzystujących sole żelaza lub glinu, koagulacja chlorkiem ceru(III) zapewnia znacznie wyższą skuteczność usuwania fosforanów(V) i mniejszą produkcję osadów. Przegląd cen rynkowych i danych literaturowych [41,42] pokazuje, że ceny chlorku ceru(III) mogą być 2,5 do 14 razy wyższe niż ceny powszechnie stosowanych koagulantów na bazie żelaza lub glinu. Niemniej jednak, zastosowanie koagulantu cerowego zapewnia bardzo wysoką skuteczność usuwania fosforu, co może uzasadniać jego stosowanie w dużych

oczyszczalniach przy jednoczesnych wysokich wymaganiach odnośnie stężenia związków fosforu w ściekach oczyszczonych, minimalizacji powstających osadów, konieczności spełnienia zasad gospodarki cyrkularnej oraz działania w warunkach zasad zrównoważonego rozwoju. Dalsze prace powinny koncentrować się na zmniejszeniu oddziaływań środowiskowych, obniżeniu kosztów poszczególnych etapów proponowanego rozwiązania oraz lepszym wykorzystaniu produktów ubocznych, a także przeprowadzeniu badań porównawczych z wykorzystaniem innych innowacyjnych koagulantów na bazie cyrkonu czy tytanu oraz metodami tradycyjnymi.

10. Weryfikacja tez rozprawy doktorskiej

1. *Istnieje możliwość odzysku związków ceru z odpadów i ich zastosowania do oczyszczania wybranych ścieków przemysłowych oraz ponownego odzysku z wytworzonych osadów ściekowych.*

Teza została w całości potwierdzona, ponieważ w wyniku zaplanowanych i przeprowadzonych eksperymentów odzyskano chlorek ceru(III) z wybranego odpadu przemysłowego jakim był zużyty proszek polerski. W ustalonych (optymalnych) warunkach zastosowanie roztworu chlorku ceru(III) umożliwiło efektywne usunięcie fosforanów(V) ze ścieków browarniczych. Ponadto, przeprowadzone badania wykazały możliwość ekstrakcji ceru(III) z osadu ściekowego z zastosowaniem kwasu chlorowodorowego. W ustalonych (optymalnych) warunkach ekstrakcji i kolejnych etapach odzysku, takich jak strącanie szczawianu ceru(III), rozkład termiczny szczawianu ceru(III) do tlenku ceru(IV), uzyskano z wysoka wydajnością trzy sole ceru. tj.: chlorek ceru(III), siarczan(VI) ceru(III), siarczan(VI) ceru(IV), co niniejszym umożliwiło pozytywne zweryfikowanie sformułowanej tezy pracy.

2. *Istnieje możliwość ekonomicznego i ekologicznego odzysku oraz wykorzystania związków ceru do oczyszczania ścieków przemysłowych.*

Teza została potwierdzona częściowo, ponieważ przeprowadzona analiza ekonomiczna wykazała, że dla dużych oczyszczalni ścieków oraz w sytuacjach (instalacjach), w których wymagana jest wysoka efektywność usuwania związków fosforu, zaproponowany proces może być opłacalny, w porównaniu z dotychczas stosowanymi rozwiązaniami w zakresie usuwania związków fosforu z użyciem soli żelaza i glinu. Z kolei, wyniki analizy ekologicznej jednoznacznie wskazały, na korzyści wynikające z obniżenia eutrofizacji wód, jednakże zastosowanie procesów ekstrakcji związków ceru z odpadu oraz osadów będzie stanowiło obciążenie dla środowiska ze względu na konieczność zastosowania kwasu chlorowodorowego (HCl) oraz kwasu szczawowego ($H_2C_2O_4$).

11. Wnioski i perspektywy dalszych prac badawczych

Efektywność oczyszczania

Odpadowy proszek polerski zawierający 82,0% CeO_2 został wykorzystany do otrzymania $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ i następnie do przygotowania roztworu ceru(III) o stężeniu 0,05 mol/l. Roztwór ten został zastosowany w procesie usuwania fosforanów(V) ze ścieków browarniczych. Przeprowadzenie procesu w optymalnych warunkach (pH 7,5; stosunek molowy $\text{Ce}^{3+}:\text{PO}_4^{3-}$ 1,5:1; czas reakcji 15 min) umożliwiło obniżenie stężenia fosforanów(V) w ściekach oczyszczonych o 99,86% z jednoczesnym związaniem 99,94% jonów ceru(III) w osadzie, co uzasadniało recykling ceru z osadu ściekowego.

Zastosowanie $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ do utleniania zanieczyszczeń w ściekach o odczynie kwasowym pochodzących z symulacji procesu podziemnego zgazowania węgla kamiennego umożliwiło w optymalnych warunkach (tj. czasie reakcji 35 min, stosunku molowym $\text{Ce}^{4+}:\text{C}$ 5:1, pH 2,5 oraz temperaturze 40 °C) obniżenie stężeń zanieczyszczeń takich jak WWA, cyjanki, fenole, RWO odpowiednio o 99,40%, 97,67%, 99,97% i 65,34%. Przy czym po alkalizacji ścieków do pH 8,2, po czasie 60 min dochodziło do obniżenia pH do 5,9, co powodowało uwolnienie ceru z osadu i wtórne zanieczyszczenie ścieków oczyszczonych.

Zastosowanie $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ oraz H_2O_2 umożliwiło w ustalonych warunkach optymalnych (tj. stosunku molowym $\text{RWO}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$ 1:2:10, pH 2,5, czasie reakcji 35 min oraz temperaturze 40°C) obniżenie stężeń zanieczyszczeń takich jak WWA, cyjanki, fenole odpowiednio o 99,91%, 98,14%, 99,66% i 76,35%. Utworzony w wyniku alkalizacji ścieków do pH 8,2 stabilny osad związał 99,996% zastosowanego ceru(IV), co zapobiegło wtórnemu zanieczyszczeniu ścieków oczyszczonych oraz utracie cennego reagenta.

Odzysk surowców i recykling reagentów

Wykazano, że z powstałego osadu ściekowego, w optymalnych warunkach (czas reakcji 40 min, objętość użytego ekstrahenta 25 ml/g osadu, ilość dodanego HCl w stosunku do masy osadu 350 mg/g) możliwa jest efektywna ekstrakcja ceru – 99,6% (oraz fosforu – 97,5%), a następnie po strącaniu w środowisku kwasowym szczawianu ceru(III), rozkładzie termicznym do tlenku ceru(IV) oraz reakcjami z odpowiednimi reagentami możliwe jest odzyskanie soli ceru z wydajnością $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ – 97,0%, $\text{Ce}_2(\text{SO}_4)_3$ – 97,4%, $\text{Ce}(\text{SO}_4)_2$ – 98,3% oraz ponowne ich zastosowanie w procesach oczyszczania ścieków. Uzyskane związki ceru mogą być ponownie wykorzystane jako koagulanty (Ce^{3+}) lub utleniacz (Ce^{4+}), zamykając tym samym obieg reagentów w procesach. Otrzymane związki mogą również być wykorzystane jako surowce w przemyśle metalurgicznym (dodatek do stopów), w przemyśle szklarskim (jako dodatek do usuwania zabarwienia i stabilizacji szkła) do produkcji

katalizatorów (katalityczne konwertery układów wydechowych), jako dodatek do lakierów, mas ściernych (proszki polerskie) lub jako odczynniki chemiczne (cerometria).

Aspekty środowiskowe i gospodarka o obiegu zamkniętym

Opracowany proces wpisuje się w ideę gospodarki o obiegu zamkniętym, poprzez wykorzystanie odpadów przemysłowych, wytworzenie z nich użytecznych soli (w postaci koagulantów i utleniacza), recykling użytych w oczyszczaniu ścieków związków ceru, zagospodarowanie ubocznych produktów powstałych w trakcie recyklingu oraz odzysk surowców energetycznych. Analiza cyklu życia (LCA) wskazała na pozytywny wpływ technologii na ochronę wód słodkich i morskich w kontekście ich eutrofizacji.

Ograniczenia i kierunki rozwoju

Głównym ograniczeniem technologicznym jest konieczność zastosowania reagentów, takich jak kwas chlorowodorowy (HCl) i kwas szczawiowy ($\text{H}_2\text{C}_2\text{O}_4$), które (zgodnie z przeprowadzoną analizą LCA) podczas procesu ich wytwarzania mają istotny udział w kategoriach wpływu takich jak: zmiany klimatyczne, ekotoksyczność gleb, wyczerpywanie zasobów kopalnych, ekotoksyczność wód morskich. Kwas szczawiowy, kwas solny oraz nadtlenek wodoru są także głównymi czynnikami o znacznym udziale w kategorii wpływu – toksyczność rakotwórcza dla ludzi.

Dodatkowe badania powinny skupić się zatem na zmniejszeniu zużycia lub zastosowaniu alternatywnych reagentów, dalszemu obniżeniu kosztów procesu oraz poprawie efektywności uzysku wartościowych pod względem energetycznym i rynkowym produktów ubocznych.

Wnioski końcowe

Zaproponowana koncepcja technologiczna jest mniej korzystna ekonomicznie niż dotychczas stosowane metody strącania chemicznego, jej skuteczność i możliwości odzysku surowców czynią ją dobrą alternatywą dla dużych oczyszczalni ścieków w sytuacjach wymagających wysokiego stopnia oczyszczania ścieków, zmniejszenia ilości osadów ściekowych. Analiza opłacalności, wpływu na środowisko i skuteczności oczyszczania wskazuje, że warto kontynuować prace nad jej modyfikacjami, wdrażaniem i zastosowaniem alternatywnych rozwiązań mających na celu zmniejszenie zapotrzebowania na reagenty w poszczególnych etapach proponowanej koncepcji oczyszczania ścieków.

Perspektywy dalszych prac badawczych

Z punktu widzenia możliwości aplikacyjnych istotnym byłoby przeprowadzenie badań nad zastosowaniem związków ceru jako koagulantów lub utleniaczy do oczyszczania innych ścieków przemysłowych oraz identyfikację potencjalnych ograniczeń ich zastosowania.

Zbadanie przydatności osadów ściekowych po koagulacji związkami ceru do zastosowania jako materiał wsadowy w procesie hydrotermalnego upłynniania osadów ściekowych (HTL). Niemniej jednak, równie interesujące mogłyby być badania nad skutecznością utleniania zanieczyszczeń organicznych takich jak metabolity farmaceutyków, pestycydy oraz barwniki przemysłowe obecne w ściekach bytowych i przemysłowych z zastosowaniem siarczanu(VI) ceru(IV) wraz z modyfikacjami polegającymi m.in. na wspomaganiu promieniowaniem UV lub ultradźwiękami. Dotychczas przeprowadzona analiza literaturowa wykazała, że badanie takie nie zostały przeprowadzone. Dodatkowo, interesującym kierunkiem przyszłych badań byłaby optymalizacja procesu syntezy chlorku ceru(III) z tlenku ceru(IV) uzyskanego z osadów ściekowych, tak aby zmniejszyć zapotrzebowania na kwas chlorowodorowy (HCl).

12. Literatura

- [1] Kundzewicz ZW. Hydrosphere. Encyclopedia of Ecology, Elsevier; 2008, p. 1923–30. <https://doi.org/10.1016/B978-008045405-4.00740-0>.
- [2] O'Sullivan JN. Demographic Delusions: World Population Growth Is Exceeding Most Projections and Jeopardising Scenarios for Sustainable Futures. *World* 2023;4:545–68. <https://doi.org/10.3390/world4030034>.
- [3] Castano Garcia A, Ambrose A, Hawkins A, Parkes S. High consumption, an unsustainable habit that needs more attention. *Energy Res Soc Sci* 2021;80:102241. <https://doi.org/10.1016/j.erss.2021.102241>.
- [4] du Plessis A. Persistent degradation: Global water quality challenges and required actions. *One Earth* 2022;5:129–31. <https://doi.org/10.1016/j.oneear.2022.01.005>.
- [5] Jones ER, Bierkens MFP, van Puijenbroek PJTM, van Beek LPH, Wanders N, Sutanudjaja EH, et al. Sub-Saharan Africa will increasingly become the dominant hotspot of surface water pollution. *Nature Water* 2023;1:602–13. <https://doi.org/10.1038/s44221-023-00105-5>.
- [6] Rentschler J, Leonova N. Global air pollution exposure and poverty. *Nat Commun* 2023;14:4432. <https://doi.org/10.1038/s41467-023-39797-4>.
- [7] Zhang Z, Chen Z, Zhang J, Liu Y, Chen L, Yang M, et al. Municipal solid waste management challenges in developing regions: A comprehensive review and future perspectives for Asia and Africa. *Science of The Total Environment* 2024;930:172794. <https://doi.org/10.1016/j.scitotenv.2024.172794>.
- [8] Jeffrey P, Yang Z, Judd SJ. The status of potable water reuse implementation. *Water Res* 2022;214:118198. <https://doi.org/10.1016/j.watres.2022.118198>.
- [9] Grassly NC, Shaw AG, Owusu M. Global wastewater surveillance for pathogens with pandemic potential: opportunities and challenges. *Lancet Microbe* 2025;6:100939. <https://doi.org/10.1016/j.lanmic.2024.07.002>.
- [10] Thomas M, Nałęcz-Jawecki G, Giebułtowski J, Drzewicz P. Degradation of oxytetracycline by ferrate(VI): Treatment optimization, UHPLC-MS/MS and toxicological studies of the degradation products, and impact of urea and creatinine on the removal. *Chemical Engineering Journal* 2024;485:149802. <https://doi.org/10.1016/j.cej.2024.149802>.
- [11] Jena G, Dutta K, Daverey A. Surfactants in water and wastewater (greywater): Environmental toxicity and treatment options. *Chemosphere* 2023;341:140082. <https://doi.org/10.1016/j.chemosphere.2023.140082>.
- [12] Ahmed SF, Islam N, Tasannum N, Mehjabin A, Momtahin A, Chowdhury AA, et al. Microplastic removal and management strategies for wastewater treatment plants. *Chemosphere* 2024;347:140648. <https://doi.org/10.1016/j.chemosphere.2023.140648>.
- [13] Lejwoda P, Świnder H, Thomas M. Evaluation of the stability of heavy metal-containing sediments obtained in the wastewater treatment processes with the use of various precipitating agents. *Environ Monit Assess* 2023;195:442. <https://doi.org/10.1007/s10661-023-11036-9>.
- [14] Withers P, Neal C, Jarvie H, Doody D. Agriculture and Eutrophication: Where Do We Go from Here? *Sustainability* 2014;6:5853–75. <https://doi.org/10.3390/su6095853>.
- [15] Główny Urząd Statystyczny, Departament Rolnictwa i Środowiska. Ochrona środowiska 2023. Warszawa: 2023.

- [16] Lejwoda P, Białecka B, Thomas M. Removal of phosphate from brewery wastewater by cerium(III) chloride originating from spent polishing agent: Recovery and optimization studies. *Science of The Total Environment* 2023. <https://doi.org/10.1016/j.scitotenv.2023.162643>.
- [17] Hospido A, Moreira MT, Fernández-Couto M, Feijoo G. Environmental performance of a municipal wastewater treatment plant. *Int J Life Cycle Assess* 2004;9:261. <https://doi.org/10.1007/BF02978602>.
- [18] Verhuelsdonk M, Glas K, Parlar H. Economic evaluation of the reuse of brewery wastewater. *J Environ Manage* 2021;281:111804. <https://doi.org/10.1016/j.jenvman.2020.111804>.
- [19] Wiatowski M, Kapusta K, Strugała-Wilczek A, Stańczyk K, Castro-Muñiz A, Suárez-García F, et al. Large-Scale Experimental Simulations of In Situ Coal Gasification in Terms of Process Efficiency and Physicochemical Properties of Process By-Products. *Energies (Basel)* 2023;16:4455. <https://doi.org/10.3390/en16114455>.
- [20] Verma V, Chaudhari PK. Optimization of multiple parameters for treatment of coking wastewater using Fenton oxidation. *Arabian Journal of Chemistry* 2020;13:5084–95. <https://doi.org/10.1016/j.arabjc.2020.02.008>.
- [21] Zhang Q, Meng J, Su G, Liu Z, Shi B, Wang T. Source apportionment and risk assessment for polycyclic aromatic hydrocarbons in soils at a typical coking plant. *Ecotoxicol Environ Saf* 2021;222:112509. <https://doi.org/10.1016/j.ecoenv.2021.112509>.
- [22] Lejwoda P, Białecka B, Thomas M. Holistic insight into the viability of employing cerium(IV) sulphate to oxidise toxic contaminants in effluent from the coal gasification process: Optimisation studies. *Journal of Water Process Engineering* 2024;67:106243. <https://doi.org/10.1016/j.jwpe.2024.106243>.
- [23] Charazińska S, Lochyński P, Burszta-Adamiak E. Removal of heavy metal ions form acidic electrolyte for stainless steel electropolishing via adsorption using Polish peats. *Journal of Water Process Engineering* 2021;42:102169. <https://doi.org/10.1016/j.jwpe.2021.102169>.
- [24] Rao DP, Krishnasamy VD, Selvaraju M, Sundramurthy VP, Kandavalli SR, Chitra MS, et al. Adsorptive removal of cadmium from electroplating wastewater using hybrid composite of thiol-grafted seed gum of *Tamarindus indica* and Teff hay biocarbon. *Zeitschrift Für Physikalische Chemie* 2025;239:633–54. <https://doi.org/10.1515/zpch-2024-0715>.
- [25] Świnder H, Lejwoda P. Obtaining Nickel Concentrates from Sludge Produced in the Process of Electrochemical Metal Surface Treatment. *Water Air Soil Pollut* 2021;232:505. <https://doi.org/10.1007/s11270-021-05456-x>.
- [26] Akinawo SO. Eutrophication: Causes, consequences, physical, chemical and biological techniques for mitigation strategies. *Environmental Challenges* 2023;12:100733. <https://doi.org/10.1016/j.envc.2023.100733>.
- [27] Owodunni AA, Ismail S, Kurniawan SB, Ahmad A, Imron MF, Abdullah SRS. A review on revolutionary technique for phosphate removal in wastewater using green coagulant. *Journal of Water Process Engineering* 2023;52:103573. <https://doi.org/10.1016/j.jwpe.2023.103573>.
- [28] Huang S, Fu Y, Zhang H, Wang C, Zou C, Lu X. Research progress of novel bio-denitrification technology in deep wastewater treatment. *Front Microbiol* 2023;14. <https://doi.org/10.3389/fmicb.2023.1284369>.
- [29] Kim DW, Yu S II, Im K, Shin J, Shin SG. Responses of Coagulant Type, Dosage and Process Conditions to Phosphate Removal Efficiency from Anaerobic Sludge. *Int J Environ Res Public Health* 2022;19:1693. <https://doi.org/10.3390/ijerph19031693>.

- [30] Smith S, Takács I, Murthy S, Daigger GT, Szabó A. Phosphate Complexation Model and Its Implications for Chemical Phosphorus Removal. *Water Environment Research* 2008;80:428–38. <https://doi.org/10.1002/j.1554-7531.2008.tb00349.x>.
- [31] Mohammed SAM, Abbas Shanshool H. Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride. *Iraqi Journal of Chemical and Petroleum Engineering* 2009;10(2):47–52.
- [32] Szabó A, Takács I, Murthy S, Daigger GT, Licskó I, Smith S. Significance of Design and Operational Variables in Chemical Phosphorus Removal. *Water Environment Research* 2008;80:407–16. <https://doi.org/10.2175/106143008X268498>.
- [33] Wang J, Song J, Lu J, Zhao X. Comparison of Three Aluminum Coagulants for Phosphorus Removal. *J Water Resour Prot* 2014;06:902–8. <https://doi.org/10.4236/jwarp.2014.610085>.
- [34] Sengupta S, Nawaz T, Beaudry J. Nitrogen and Phosphorus Recovery from Wastewater. *Curr Pollut Rep* 2015;1:155–66. <https://doi.org/10.1007/s40726-015-0013-1>.
- [35] Zhou Q, Sun H, Jia L, Wu W, Wang J. Simultaneous biological removal of nitrogen and phosphorus from secondary effluent of wastewater treatment plants by advanced treatment: A review. *Chemosphere* 2022;296:134054. <https://doi.org/10.1016/j.chemosphere.2022.134054>.
- [36] Zhang Z, Wu C, Wu Y, Hu C. Comparison of coagulation performance and floc properties of a novel zirconium-glycine complex coagulant with traditional coagulants. *Environmental Science and Pollution Research* 2014;21:6632–9. <https://doi.org/10.1007/s11356-014-2575-7>.
- [37] Christensen E, Håkonsen T, Robertson LJ, Myrmet M. Zirconium and chitosan coagulants for drinking water treatment – a pilot study. *Journal of Water Supply: Research and Technology-Aqua* 2016;65:635–44. <https://doi.org/10.2166/aqua.2016.162>.
- [38] Aziz HA, Sahhari N, Amr SSA, Hussain S, Leeuwen J Van. Potential use of zirconium (IV) chloride as coagulant to treat semi-aerobic leachate treatment. *Int J Environ Waste Manag* 2016;18:205. <https://doi.org/10.1504/IJEWM.2016.080792>.
- [39] Thomas M, Bąk J, Królikowska J. Efficiency of titanium salts as alternative coagulants in water and wastewater treatment: short review. *Desalination Water Treat* 2020;208:261–72. <https://doi.org/10.5004/dwt.2020.26689>.
- [40] Gan Y, Li J, Zhang L, Wu B, Huang W, Li H, et al. Potential of titanium coagulants for water and wastewater treatment: Current status and future perspectives. *Chemical Engineering Journal* 2021;406:126837. <https://doi.org/10.1016/j.cej.2020.126837>.
- [41] Kajjumba GW, Marti EJ. A review of the application of cerium and lanthanum in phosphorus removal during wastewater treatment: Characteristics, mechanism, and recovery. *Chemosphere* 2022;309:136462. <https://doi.org/10.1016/j.chemosphere.2022.136462>.
- [42] Kajjumba GW, Fischer D, Risso LA, Koury D, Marti EJ. Application of cerium and lanthanum coagulants in wastewater treatment—A comparative assessment to magnesium, aluminum, and iron coagulants. *Chemical Engineering Journal* 2021;426. <https://doi.org/10.1016/j.cej.2021.131268>.
- [43] Minczewski J, Marczenko Z. *Chemia analityczna*. vol. 1. Warszawa: Wydawnictwo Naukowe PWN; 2022.
- [44] Hussain S, Aneggi E, Goi D. Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review. *Environ Chem Lett* 2021;19:2405–24. <https://doi.org/10.1007/s10311-021-01185-z>.

- [45] Mahbub P, Duke M. Scalability of advanced oxidation processes (AOPs) in industrial applications: A review. *J Environ Manage* 2023;345:118861. <https://doi.org/10.1016/j.jenvman.2023.118861>.
- [46] Nawrocki J. Uzdatnianie wody Procesy fizyczne, chemiczne i biologiczne Tom 1. vol. 1. Warszawa: Wydawnictwo Naukowe PWN ; 2010.
- [47] European Commission. Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 – Final report, Publications Office of the European Union, 2023, <https://data.europa.eu/doi/10.2873/725585> 2023.
- [48] Daneshgar S, Callegari A, Capodaglio A, Vaccari D. The Potential Phosphorus Crisis: Resource Conservation and Possible Escape Technologies: A Review. *Resources* 2018;7:37. <https://doi.org/10.3390/resources7020037>.
- [49] Lejwoda P, Białecka B, Barbusiński K, Thomas M. Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant. *Materials* 2024;17:938. <https://doi.org/10.3390/ma17040938>.
- [50] Lejwoda P, Białecka B, Śliwińska A, Krawczyk P, Thomas M. Innovative Integrated Model of Industrial Wastewater Treatment with the Circular Use of Cerium Compounds as Multifunctional Coagulants: Comprehensive Assessment of the Process and Environmental and Economic Aspects. *Molecules* 2025;30:3428. <https://doi.org/10.3390/molecules30163428>.
- [51] Thomas M, Drzewicz P, Więkol-Ryk A, Panneerselvam B. Effectiveness of potassium ferrate (VI) as a green agent in the treatment and disinfection of carwash wastewater. *Environmental Science and Pollution Research* 2022;29:8514–24. <https://doi.org/10.1007/s11356-021-16278-z>.
- [52] Myers RH, Montgomery DC, Anderson-Cook CM. Response surface methodology: process and product optimization using designed experiments. 3rd edition. John Wiley & Sons; 2009.
- [53] Borra C, Vlught T, Yang Y, Offerman S. Recovery of Cerium from Glass Polishing Waste: A Critical Review. *Metals (Basel)* 2018;8:801. <https://doi.org/10.3390/met8100801>.
- [54] Poscher A, Luidold S, Schnideritsch H, Antrekowitsch H. Extraction of Lanthanides from Spent Polishing Agent. *N Proceedings of the ERES2014-1st European Rare Earth Resources Conference* 2014:209–22.
- [55] Żelazny S, Świnder H, Białecka B, Jarosiński A. Odzysk pierwiastków ziem rzadkich z popiołów lotnych. Cz. II. Wytrącanie z roztworu. *PRZEMYSŁ CHEMICZNY* 2017;1:102–8. <https://doi.org/10.15199/62.2017.11.14>.
- [56] Chen F, Liu F, Wang L, Wang J. Comparison of the Preparation Process of Rare Earth Oxides from the Water Leaching Solution of Waste Nd-Fe-B Magnets' Sulfate Roasting Products. *Processes* 2022;10:2310. <https://doi.org/10.3390/pr10112310>.
- [57] Lopez HF, Mendoza H. Temperature Effects on the Crystallization and Coarsening of Nano-CeO₂ Powders. *ISRN Nanomater* 2013;2013:1–7. <https://doi.org/10.1155/2013/208614>.
- [58] Leili M, Shirmohammadi Khorram N, Godini K, Azarian G, Moussavi R, Peykoshian A. Application of central composite design (CCD) for optimization of cephalixin antibiotic removal using electro-oxidation process. *J Mol Liq* 2020;313:113556. <https://doi.org/10.1016/j.molliq.2020.113556>.
- [59] Saeed MO, Azizli K, Isa MH, Bashir MJK. Application of CCD in RSM to obtain optimize treatment of POME using Fenton oxidation process. *Journal of Water Process Engineering* 2015;8:e7–16. <https://doi.org/10.1016/j.jwpe.2014.11.001>.

- [60] Barbusiński K. Intensyfikacja procesu oczyszczania ścieków i stabilizacji osadów nadmiernych z wykorzystaniem odczynnika Fentona. vol. 1603. Gliwice: Zeszyty Naukowe Politechniki Śląskiej; 2004.
- [61] Çalik Ç, Çifçi Dİ. Comparison of kinetics and costs of Fenton and photo-Fenton processes used for the treatment of a textile industry wastewater. J Environ Manage 2022;304:114234. <https://doi.org/10.1016/j.jenvman.2021.114234>.
- [62] Gupta CK, Krishnamurthy N. Extractive metallurgy of rare earths. International Materials Reviews 1992;37:197–248. <https://doi.org/10.1179/imr.1992.37.1.197>.
- [63] Kaczor G. CHANGES IN CONCENTRATIONS AND LOADS OF TOTAL PHOSPHORUS IN DOMESTIC AND TREATED WASTEWATER OVER A 15-YEAR OBSERVATION PERIOD IN TERMS OF LIMITING NEGATIVE ANTHROPOPRESSURE ON THE QUALITY OF SURFACE WATER – CASE STUDY. Acta Scientiarum Polonorum Formatio Circumiectus 2020;19:3–14. <https://doi.org/10.15576/ASP.FC/2020.19.2.3>.
- [64] Szuflicki M, Malon A, Tymiąski M, red. BILANS ZASOBÓW ZŁÓŻ KOPALIN W POLSCE wg stanu na 31 XII 2024 r. Warszawa: Państwowy Instytut Geologiczny – Państwowy Instytut Badawczy; 2025.

13. Spis tabel i rysunków

Tabela 1. Etapy procesu oczyszczania ścieków z zastosowaniem związku ceru wraz z recyklingiem reagentów	32
Tabela 2. Zawartość ceru w analizowanych odpadach	34
Tabela 3. Skład fazowy zużytego proszku polerskiego określony metodą XRD	35
Tabela 4. Skład fizykochemiczny ścieków browarniczych	35
Tabela 5. Warunki eksperymentalne dla CCD/RSM oraz wyniki (Ce^{3+} i PO_4^{3-}) dla ścieków browarniczych (pH 2,14–9,86, stosunek molowy $Ce^{3+}:PO_4^{3-}$ (0,856–2,144:1), czas 8,56–21,4 min); * – centrum planu	36
Tabela 6. Wybrane parametry fizykochemiczne ścieków browarniczych przed i po procesie oczyszczania z zastosowaniem roztworu chlorku ceru(III) o stężeniu 0,05 mol/l	38
Tabela 7. Skład chemiczny osadu ściekowego po koagulacji chlorkiem ceru(III)	39
Tabela 8. Warunki eksperymentalne dla CCD/RSM oraz wyniki stężeń P i Ce po ekstrakcji z osadów ściekowych (HCl 35,0–405,0 mg, stosunek masy ciecz:ciało stałe (7,96–92,0:1), czas 6,36–73,6 min); * – centrum planu	40
Tabela 9. Skład fizykochemiczny ścieków z symulacji procesu podziemnego zgazowania węgla kamiennego	44
Tabela 10. Warunki eksperymentalne dla CCD/RSM oraz wyniki (RWO) po utlenianiu zanieczyszczeń (czas 5–65 min, stosunek molowy $Ce^{4+}:RWO$ 2–10, pH 0,5–4,5, temperatura 10–90 °C); * – centrum planu	45
Tabela 11. Potencjały redoks wybranych utleniaczy	47
Tabela 12. Stężenie RWO w zależności od ilości dodanego siarczanu(VI) ceru(IV) ($Ce(SO_4)_2 \cdot 4H_2O$) i nadtlenu wodoru (H_2O_2); pH ścieków = 2,5, czas = 35 min, temperatura = 40 °C	47
Tabela 13. Właściwości fizykochemiczne ścieków przed i po procesie oczyszczania	49
 Rysunek 1. Schemat powiązań zagadnień badawczych zrealizowanych i przedstawionych w poszczególnych artykułach składających się na niniejszą rozprawę doktorską	4
Rysunek 2. Metodyka prowadzenia badań	24
Rysunek 3. Schemat odzysku soli ceru(III) ze zużytego proszku polerskiego	29
Rysunek 4. Powierzchnia odpowiedzi wpływu stosunku molowego $Ce^{3+}:PO_4^{3-}$ i wartości pH, na stężenie jonów PO_4^{3-} w oczyszczanych ściekach browarniczych, czas = 15 min	37
Rysunek 5. Powierzchnia odpowiedzi wpływu stosunku molowego $Ce^{3+}:PO_4^{3-}$ i wartości pH, na stężenie jonów Ce^{3+} w oczyszczanych ściekach browarniczych, czas = 15 min	37
Rysunek 6. Powierzchnie odpowiedzi przedstawiające uzysk Ce (a) oraz P (b) w zależności od ilości zastosowanego HCl oraz stosunku objętości kwasu do objętości osadu	41
Rysunek 7. Osad wysuszony w temperaturze otoczenia (A), uzyskany chlorek ceru(III) $CeCl_3 \cdot 7H_2O$ (B), uzyskany siarczan(VI) ceru(IV) $Ce(SO_4)_2$ (C)	42
Rysunek 8. Schemat obiegu ceru w procesie oczyszczania ścieków	43
Rysunek 9. Powierzchnie odpowiedzi przedstawiające stężenie RWO w funkcji poszczególnych zestawów zmiennych niezależnych, (A) temperatura i czas, (B) stosunek molowy $Ce^{4+}:RWO$ i czas, (C) pH i czas, (D) stosunek molowy $Ce^{4+}:RWO$ i temperatura, (E) pH i temperatura, (F) pH i stosunek molowy $Ce^{4+}:RWO$	46
Rysunek 10. Przefiltrowane ścieki z symulacji procesu podziemnego zgazowania węgla kamiennego (A), roztwór podczas utleniania zanieczyszczeń w optymalnych warunkach, przy stosunku molowym $RWO:Ce^{4+}:H_2O_2$ 1:2:10, pH = 2,5, czas reakcji = 35 min, temperatura = 40 °C (B), roztwór po zakończonym utlenianiu zanieczyszczeń i sedymentacji osadu przy pH 8,2 (C)	48

14. Spis załączników

Załącznik nr 1 – Druk publikacji stanowiących rozprawę doktorską

15. Wykaz innych publikacji naukowych

1. Świnder, H., **Lejwoda, P.**, Krawczyk, P., Cempa, M., & Bauerek, A. (2024). *Potential for the Recovery of Selected Metals and Critical Raw Materials from Slags from Polymineral Zn–Pb Ore Metallurgy—Part II*, **Minerals** (2024) (IF = 2,2, 100 pkt MNiSW)
2. Cempa, M., **Lejwoda, P.**, Karabela, K., Pieprzyca, A., Świnder, H., & Bauerek, A. (2024). *Potential for the Recovery of Selected Metals and Critical Raw Materials from Slags from Polymineral Zn–Pb Ore Metallurgy—Part I*, **Minerals** (2024) (IF = 2,2, 100 pkt MNiSW)
3. **Lejwoda, P.**, Świnder, H., Thomas, M., *Evaluation of the mobility of heavy metals in the sediments originating from the post-galvanic wastewater treatment processes*, **Environmental Geochemistry and Health** (2023) (IF = 3,2, 100 pkt MNiSW)
4. **Lejwoda, P.**, Świnder, H., Thomas, M., *Evaluation of the stability of heavy metal-containing sediments obtained in the wastewater treatment processes with the use of various precipitating agents*, **Environmental Monitoring and Assessment** (2023) (IF = 2,9, 70 pkt MNiSW)
5. Molenda, T., Kostka, B., Malik, I., **Lejwoda, P.**, Radziejowski, W., Kidawa, J., *Polyhumous Dystrophic Pit Lakes: Hydrographic and Hydrochemical Characteristics on the Example of Reservoirs in the Włoszczowska Basin, Central Poland*, **Energies** (2022) (IF = 3,2, 140 pkt MNiSW)
6. Świnder, H., **Lejwoda, P.**, *Obtaining Nickel Concentrates from Sludge Produced in the Process of Electrochemical Metal Surface Treatment*, **Water, Air, & Soil Pollution** (2021) (IF = 2,984, 70 pkt MNiSW)
7. Diatta, J., Youssef, N., Tylman, O., Grzebisz, W., Markert, B., Drobek, L., Wünschmann, S., Bebek, M., Mitko, K., **Lejwoda, P.**, *Acid rain induced leakage of Ca, Mg, Zn, Fe from plant photosynthetic organs – Testing for deciduous and dicotyledons*, **Ecological Indicators** (2021) (IF = 6,263, 140 pkt MNiSW)
8. **Lejwoda, P.**, Pogoda, P., Radomski, P., Wzorek, Z., *Applicability of some mining wastes for construction purposes. Ocena przydatności niektórych odpadów górniczych do celów budowlanych*, **Przemysł Chemiczny** (2017) (IF = 0,399, 20 pkt MNiSW)

16. Udział w konferencjach

Lejwoda P., Białecka B., Thomas M. Zastosowanie $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ wytworzonego z odpadu do usuwania zanieczyszczeń ze ścieków browarniczych, XIII Konferencja Ochrona i Inżynieria Środowiska „Profesor Walery Goetel – prekursor zrównoważonego rozwoju, 19.09.2022 r. Kraków, Polska.

(prezentacja plakatowa)



Removal of phosphate from brewery wastewater by cerium(III) chloride originating from spent polishing agent: Recovery and optimization studies

Paweł Lejwoda^{a,*}, Barbara Białecka^a, Maciej Thomas^b

^a Central Mining Institute in Katowice, Department of Environmental Monitoring, Plac Gwarków 1, Katowice 40-166, Poland

^b Cracow University of Technology, Faculty of Environmental Engineering and Energy, Warszawska 24, Cracow 31-155, Poland

HIGHLIGHTS

- The brewery wastewater contains about 43 mg/L of phosphates.
- Ce^{3+} can reduce >99 % of PO_4^{3-} in brewery wastewater.
- >97 % of Ce and 89 % P can be recovered from brewery wastewater sludge.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Yifeng Zhang

Keywords:

Beer
Circular economy
Sediments
RSM
ICP-MS

ABSTRACT

This paper presents the possibility of using hydrated cerium(III) chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) recovered from a spent polishing agent containing cerium(IV) dioxide (CeO_2) to remove phosphate and other impurities from brewery wastewater (phosphate 43.0 mg/L, total P 19.8 mg/L, pH 7.5, $\text{COD}_{(\text{Cr})}$ 827 mg O_2 /L, TSS 630 mg/L, TOC 130 mg/L, total N 46 mg/L, turbidity 390 NTU, colour 170 mg Pt/L). CCD (Central Composite Design) and RSM (Response Surface Methodology) were applied to optimise the brewery wastewater treatment process. The removal efficiency (mainly of PO_4^{3-}) was the highest under optimal conditions (pH 7.0–8.5, $\text{Ce}^{3+}:\text{PO}_4^{3-}$ molar ratio of 1.5–2.0). Applying recovered CeCl_3 under optimal conditions yielded a treated effluent in which the concentration of PO_4^{3-} decreased by 99.86 %, total P by 99.56 %, $\text{COD}_{(\text{Cr})}$ by 81.86 %, TSS by 96.67 %, TOC by 60.38 %, total N by 19.24 %, turbidity by 98.18 %, and colour by 70.59 %. The Ce^{3+} ion concentration in the treated effluent was 0.058 mg/L. These findings suggest that $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ recovered from the spent polishing agent may constitute an optional reagent for phosphate removal from brewery wastewater. The sludge from wastewater treatment can be recycled for Ce and P recovery. The recovered cerium can be reused for wastewater treatment, creating a cyclic cerium cycle in the process, and the recovered phosphorus can be used, for example, for fertilization purposes. The optimised cerium recovery and application is in accordance with the ideas of circular economy.

1. Introduction

Beer is one of the most consumed beverages in the world (Verhuelsdonk et al., 2021). Globally, beer production in 2020 was 1.77 billion hL. Approximately 26.8 % of this production (475 million hL) was in Europe, and approximately 2.0 % (36.3 million hL) in the world's eleventh producer, Poland (Global Beer Consumption by Country in 2020). Beer production involves a number of processes consisting of mashing, mash

Abbreviations: BOD₅, biochemical oxygen demand; $\text{COD}_{(\text{Cr})}$, chemical oxygen demand; DOC, dissolved organic carbon; Total P, total phosphorus; Total N, total nitrogen; TOC, total organic carbon; TSS, total suspended solids.

* Corresponding author.

E-mail address: plejwoda@gig.eu (P. Lejwoda).

<http://dx.doi.org/10.1016/j.scitotenv.2023.162643>

Received 30 December 2022; Received in revised form 27 February 2023; Accepted 1 March 2023

Available online 6 March 2023

0048-9697/© 2023 Elsevier B.V. All rights reserved.

filtration, wort boiling (brewing), fermentation, beer maturation, filtration and bottling (Feng et al., 2009). In addition to the food product that is the low-alcohol beverage, the process also generates significant amounts of wastewater. The amount of wastewater generated depends on factors such as the type of beer produced, the production technology, the technical sophistication of the plant and others. However, it is estimated that for every litre of beer produced, 3–10 L of strongly contaminated wastewater are generated (Kanagachandran and Jayaratne, 2006), characterised by high values of COD_(Cr) (680–90,000 mg O₂/L), BOD₅ (1120–80,000 mg O₂/L), phosphate (8–124 mg/L), and TSS (100–8750 mg/L) (Alvarado-Lassman et al., 2008; Austermann-Haun et al., 1999; Ince et al., 2000; Parawira et al., 2005; Wen et al., 2010; Yu and Gu, 1996). Significant concentrations of pollutants can impose a heavy burden on on-site or municipal wastewater treatment plants and thus generate additional, increased wastewater treatment costs. In many cases, brewery wastewater is pre-treated in on-site wastewater treatment plants, allowing producers to avoid additional fees associated with discharging untreated or inadequately treated industrial wastewater into municipal sewers or the environment.

Phosphorus and its compounds are critical raw materials for the European Union economy (European Commission, 2010). Phosphorus compounds are used, inter alia, to produce mineral fertilisers applied in agriculture and to ensure more efficient agricultural production (Malhotra et al., 2018). These substances are derived from mined phosphate minerals such as fluorapatite (Ca₅(PO₄)₃F), chlorapatite (Ca₅(PO₄)₃Cl) and hydroxyapatite (Ca₅(PO₄)₃OH). The largest deposits of phosphate rock are located in Morocco and the Western Sahara, with the largest production in China. Global production is around 218 Mt./year. The total bulk of the world's deposits is estimated at over 300 billion tonnes, but the extraction of many of them is not economically or technologically feasible due to the low phosphorus content of the raw material (Daneshgar et al., 2018). For this reason, it is important to rationally manage phosphorus resources and compounds due to the limited availability of the deposits. This problem is related to the need to find alternative sources of phosphorus compounds, e.g. by using phosphorus-rich waste and controlling the circulation of phosphorus in the environment. Excessive phosphorus migrations to the environment are a result of natural phenomena, such as soil erosion, weathering and dissolution of phosphorus-containing rocks, as well as industrial, municipal and agricultural activities, which contribute to water eutrophication (Correll, 1998; Ngatia and Taylor, 2019). The consequences of this phenomenon include negative changes in water properties, such as the appearance of intense odour, colour and turbidity, lowered oxygen concentration, and anaerobic condition generation in the deeper layers of water bodies, resulting in a reduction in biodiversity and the death of flora and fauna. Thus, it becomes important to take measures to protect waters from pollution by biogenic substances. One method of removing phosphates from water and wastewater is e.g.: precipitation with Fe³⁺ (Caravelli et al., 2010), Al³⁺ (Wang et al., 2014), or Ce³⁺ ions in the form of hardly soluble compounds such as FePO₄, AlPO₄ and CePO₄ (Liu and Byrne, 1997). The formation of CePO₄ is based on the direct reaction of cerium ions with phosphate ions. Binding of PO₄^{3−} ions in the form of hardly soluble FePO₄ precipitates is favored at pH < 5. However, in the case of wastewater with a pH close to neutral (pH 6–8) the process of removing phosphates occurs mainly as a result of processes such as adsorption of ions on the surface of hydrous ferric oxide formed in the aqueous environment, precipitation of mixed cation phosphates and co-precipitation of phosphate (Smith et al., 2008). In the case of Al³⁺ ions, the optimal condition for the formation of AlPO₄ precipitate is pH in the range of 5.7–6.0. Below pH 5.5 AlPO₄ dissolves to form Al³⁺, and above pH 8 it dissolves to form Al(OH)₄[−] ions. In the reaction of Al³⁺ with water at a pH of about 7 an Al(OH)₃ precipitate may be formed, which can adsorb impurities on its surface (Mohammed and Abbas Shanshool, 2009).

Cerium is the most common element belonging to the rare earth element (REE) group, and it is present in the Earth's crust at an abundance of approximately 0.0046 % by mass. The cerium content in the Earth's crust is greater than that of antimony (Sb), tin (Sn), cadmium (Cd) and silver (Ag) (Haynes, 2014). The main sources of cerium are minerals such as monazite ((Ce,La,Y,Th)PO₄) and bastnasite ((Ce,La)(CO₃)F) (Meshram and Abhilash, 2020).

The processing of these raw materials to obtain the individual elements and their compounds is a complex process that involves a number of unit processes, such as physical enrichment and multi-step chemical processes (including alkaline digestion, acidic digestion, solvent extractions, ion exchange) (Gupta and Krishnamurthy, 1992). In addition to the many industrial applications of cerium compounds, including in metallurgy, in the production of automotive catalytic converters (Dey and Dhal, 2020), and in the production of polishing powders, they are currently used to a limited extent as coagulants in the treatment of wastewater containing substances such as phosphate (Kajjumba et al., 2021). Alternative sources of cerium can be found in waste materials, such as red mud (Abhilash et al., 2014), phosphogypsum waste (Hammas-Nasri et al., 2016), spent Ni-MH batteries (Fernandes et al., 2013), car catalytic converters (Zhao et al., 2020) and used polishing powders, which are the waste resulting from the consumption of approximately 16,000 t of polishing powder per year. Used polishing powders can be recycled (Kato et al., 2000) or processed into other useful products such as cerium(IV) sulphate (Ce(SO₄)₂) or cerium(III) chloride (CeCl₃) (Poscher et al., 2014), which can be applied as coagulants in wastewater treatment. Cerium, due to its electron configuration ([Xe] 4f¹ 5d¹ 6s²) can exist in two stable oxidation states in solutions, i.e.: +III, like all other lanthanides, but also on the +IV oxidation state as the only lanthanide. Ce³⁺ ions in aqueous solutions are colourless, and form poorly soluble compounds with substances such as phosphate, fluorides, hydroxides and carbonates (Ferri et al., 1983; Kajjumba et al., 2021; Kragten, 1978; Liu and Byrne, 1997; Menon et al., 1986). On the other hand, Ce⁴⁺ ions in aqueous solutions assume a yellow to orange colour (depending on the concentration). In acidic media, Ce⁴⁺ ions are strong oxidisers, and are therefore used in analytical chemistry (cerometry) (Kolthoff and Bhatia, 1960) and more recently in the treatment of industrial wastewater (ZHAO et al., 2010).

The aim of this study was to recover cerium in the form of CeCl₃·7H₂O from spent polishing agent waste by methods described in literature (Poscher et al., 2014), to use the obtained salt as a solution for the removal of phosphate from brewery effluent, and finally to recover cerium from the resulting sludge and to recycle it.

This paper presents the results of a study involving brewery wastewater treatment under optimal conditions determined using the response surface method (RSM) with a central composition design (CCD). One of the important aspects of the presented research was to evaluate and demonstrate the possibility of recovering cerium from the waste, using it to remove phosphate from brewery wastewater and then re-separating it from the resulting sludge in the form of a salt with a high cerium content, which would enable its reuse

Table 1
Selected physicochemical parameters of real brewery wastewater used in the study.

Parameter	Unit	Result ± measurement uncertainty
pH	–	7.5 ± 0.1
conductivity	µS/cm	2200 ± 110
Sodium (Na)	mg/L	578 ± 58
Potassium (K)	mg/L	21.1 ± 2.1
Magnesium (Mg)	mg/L	13.8 ± 1.4
Calcium (Ca)	mg/L	61.1 ± 6.1
Iron (Fe)	mg/L	2.00 ± 0.20
Manganese (Mn)	mg/L	0.35 ± 0.04
Aluminum (Al)	mg/L	0.60 ± 0.09
Zinc (Zn)	mg/L	0.15 ± 0.02
Total Sulphur, (S)	mg/L	65.3 ± 9.8
Total Nitrogen, (N)	mg/L	46.0 ± 6.9
Nitrate, NO ₃	mg/L	0.68 ± 0.07
Nitrite, NO ₂	mg/L	< 0.006 ± 0.001
Ammonia, NH ₄ ⁺	mg/L	39.1 ± 3.9
Total Phosphorus, (P)	mg/L	19.8 ± 2.0
Phosphate, PO ₄ ^{3−}	mg/L	43.0 ± 4.3
Total Suspended Solids, TSS	mg/L	630 ± 63
Chemical Oxygen Demand, COD _(Cr)	mg O ₂ /L	827 ± 124
Total Organic Carbon, TOC	mg/L	130 ± 20
Dissolved Organic Carbon, DOC	mg/L	71.0 ± 10.7
Turbidity	NTU	390 ± 39
Colour	mg Pt/L	170 ± 34
Cerium (Ce)	µg/L	< 0.25 ± 0.04

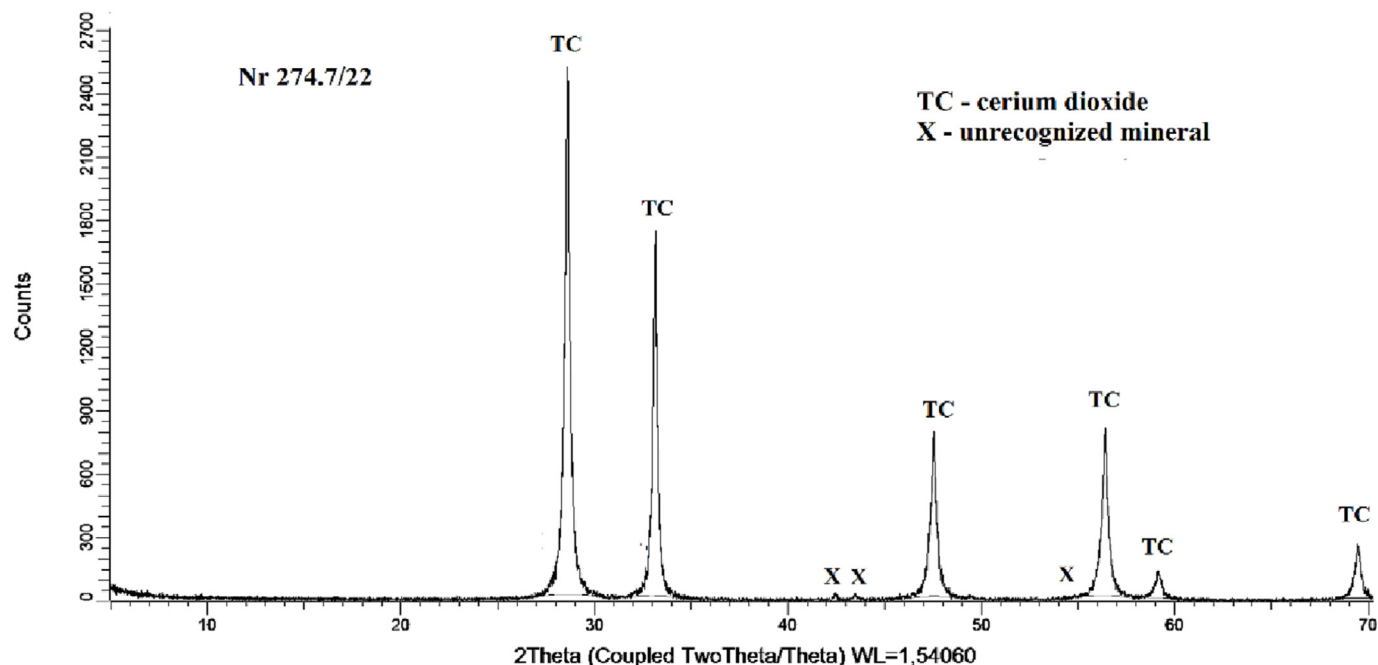


Fig. 1. Diffraction pattern of the spent polishing agent.

in the wastewater treatment process or for industrial purposes, e.g. for the production of cerium oxide and polishing powders. In addition, the cerium concentration in the treated wastewater was investigated in the context of its possible toxicity at higher concentrations (Aharchaou et al., 2020; González et al., 2015). The presented concept is in line with the assumptions of the circular economy through the rational use of waste (CeO_2) to produce a useful product ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), sludge precipitation (CePO_4) and sludge recycling with the re-creation of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ which is important in the context of decreasing mineral resources.

2. Materials and methods

2.1. Analytical methods

The determination of the selected element concentration (metals and non-metals) in wastewater was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) according to EN ISO 11885:2009 (Optima 5300DV, Perkin Elmer, USA). The content of rare earth elements in aqueous solutions was determined using inductively coupled plasma mass spectrometry (ICP-MS) according to EN ISO 17294:2016-2 (NexION 300S, Perkin Elmer, USA). The determination of metals and non-metals was performed with a level of uncertainty of 10 %, 15 %, 20 %, and 25 % depending on the element and its concentration in the tested solution, a coverage factor of 2 and a significance level of 95 %. The Inolab pH/ION/Cond 750 (WTW, Germany) was used to measure pH (EN ISO 10523:2012) and electrical conductivity (EN 27888:1999). The pH measurement was performed with an accuracy of ± 0.1 pH and conductivity was performed with uncertainty of 5 %. COD (Cr) was determined using a UV-VIS spectrophotometer (Pharo 300, Merck KGaA, Germany) according to PN-ISO 15705:2005 with an uncertainty of 15 %. The anion concentrations were determined by ion chromatography

(IC) according to EN ISO 10304-1:2009 (DIONEX ICS 5000, Thermo Fisher Scientific, USA), and phosphate content was determined using a UV-VIS spectrophotometer (Pharo 300, Merck KGaA, Germany) according to EN ISO 6878:2006 with an uncertainty of 10 %. Total suspended solids were determined by filtration (0.45 μm membrane) according to EN 872:2007, and turbidity was measured by a nephelometer according to EN ISO 7027-1:2016-09 with an uncertainty of 10 %. Colour was determined according to EN ISO 7887:2012 (method C) with an uncertainty of 20 %, TOC and DOC were determined using high-temperature combustion with infrared detection (TOC-L CPH, Shimadzu, Japan) according to EN 1484:1999 with an uncertainty of 15 %. The high-temperature combustion technique with chemiluminescence detection (TNM-L, Shimadzu, Japan) according to EN 12260:2004 with an uncertainty of 15 % was used for the determination of

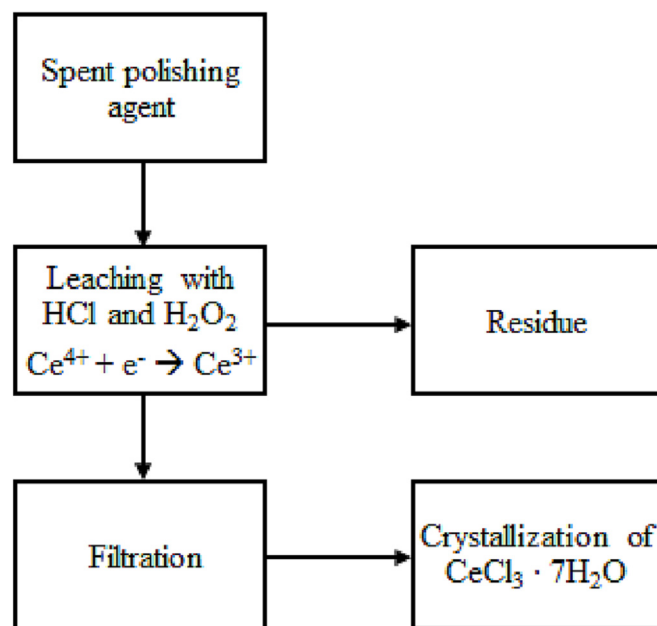


Fig. 2. Scheme for Ce recovery from a spent polishing powder and crystalline $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ preparation.

Table 2

Chemical composition of the spent polishing agent (XRD analysis).

Parameter	Unit	Result $\pm$ measurement uncertainty
Cerium dioxide (CeO_2)	%	82.0 $\pm$ 1.0
Unrecognized mineral	%	2.0 $\pm$ 1.0
Amorphous substance	%	14.5 $\pm$ 0.5

Table 3Chemical composition of the 0.05 mol/L CeCl_3 solution obtained from a spent polishing agent after leaching processes.

Parameter	Unit	Value	Parameter	Unit	Value
Cerium (Ce)	mg/L	6889 ± 689	Iron (Fe)	mg/L	0.79 ± 0.16
Lanthanum (La)	mg/L	< 0.20 ± 0.02	Manganese (Mn)	mg/L	< 0.20 ± 0.03
Praseodymium (Pr)	mg/L	< 0.20 ± 0.02	Boron (B)	mg/L	< 1.0 ± 0.3
Neodymium (Nd)	mg/L	< 0.20 ± 0.02	Aluminum (Al)	mg/L	< 1.0 ± 0.3
Samarium (Sm)	mg/L	< 0.20 ± 0.02	Cadmium (Cd)	mg/L	< 1.0 ± 0.3
Europium (Eu)	mg/L	< 0.20 ± 0.02	Chromium (Cr)	mg/L	< 1.0 ± 0.3
Gadolinium (Gd)	mg/L	27.3 ± 2.7	Copper (Cu)	mg/L	< 1.0 ± 0.3
Terbium (Tb)	mg/L	< 0.20 ± 0.02	Nickel (Ni)	mg/L	< 1.0 ± 0.3
Dysprosium (Dy)	mg/L	< 0.20 ± 0.02	Lead (Pb)	mg/L	< 1.0 ± 0.3
Holmium (Ho)	mg/L	< 0.20 ± 0.02	Antimony (Sb)	mg/L	< 1.0 ± 0.3
Erbium (Er)	mg/L	< 0.20 ± 0.02	Thallium (Tl)	mg/L	< 1.0 ± 0.3
Thulium (Tm)	mg/L	< 0.20 ± 0.02	Uranium (U)	mg/L	< 0.20 ± 0.02
Ytterbium (Yb)	mg/L	< 0.20 ± 0.02	Zinc (Zn)	mg/L	< 1.0 ± 0.3
Lutetium (Lu)	mg/L	< 0.20 ± 0.02	Arsenic (As)	mg/L	< 1.0 ± 0.3
Sodium (Na)	mg/L	75.8 ± 15.2	Calcium (Ca)	mg/L	18.2 ± 4.6

Total N content. The concentration of NH_4^+ was determined by FIA (FIAModula, MLE GmbH, Germany) according to EN ISO 11732:2007 with uncertainty of 10 %. A Phase identification was performed using powder X-ray diffraction (DSH) in Bragg-Brentano geometry, using a Bruker D8 DISCOVER diffractometer, $\text{CuK}\alpha$ radiation, Ni filter and LYNXEYE XE detector. Mineral composition was determined and calculated on the basis of standards licensed in PDF-4+2022 RDB ICDD (International Centre for Diffraction Data) and database ICSD (Inorganic Crystal Structure Database), and NIST (National Institute of Standard and Technology). DIFFRAC v.4.2 and TOPAS v.4.2, Bruker AXS programmes were applied for registration and diagnostics. Quantitative calculations of crystalline phases and the amorphous substance were performed using the Rietveld methodology.

2.2. Materials

Real brewery wastewater from a brewery located in Poland was used in the study (Fig. 3). Selected physicochemical parameters of the wastewater used in the study are presented in Table 1. A spent polishing powder containing CeO_2 was also used in the study. The diffractogram of the spent polishing powder obtained by XRD is presented in Fig. 1 and its physicochemical composition is provided Table 2.

Nitric acid (Suprapur®, Merck, Germany), hydrochloric acid (Suprapur®, Merck, Germany), 30 % hydrogen peroxide (Chempur, Poland), sodium hydroxide (Chempur, Poland), a certified multielement standard solution for ICP-MS with a concentration of each rare earth element of 50 mg/L (Sigma Aldrich, USA) and a certified multielement standard solution for ICP-OES with a metal concentration of 100 mg/L

(AccuStandards, USA) were also used in the study. Furthermore, a certified multielement anion standard solution for IC (AccuStandards, USA) and deionised water with an electrical conductivity of under 0.05 $\mu\text{S}/\text{cm}$ (Direct-Q3 UV, Millipore, USA) were used as well. A 0.05 mol/L solution of Ce^{3+} was prepared from $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ salt, which was obtained from the spent polishing powder according to the scheme depicted in Fig. 2. The chemical composition of the solution used is provided in Table 3.

2.3. Preparation of the precipitant

A spent polishing powder containing CeO_2 was used to prepare $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. Fig. 2. presents a scheme for the preparation of crystalline $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ using concentrated (30 %) HCl and concentrated (30 %) H_2O_2 .

The recovery of cerium from the spent polishing powder was carried out according to the scheme presented in Fig. 2. which is a modification of a method provided in literature (Borra et al., 2018; Poscher et al., 2014). The process was carried out by weighing an appropriate amount of the waste dried at 105 °C and averaged to a constant weight, inserting it into a three-neck flask, and adding concentrated HCl at 200 % and H_2O_2 at 100 % excess in relation to the mass of CeO_2 in the waste sample. Afterwards, a reflux condenser was applied and the resulting mixture was heated at 80° for 4 h with constant stirring. After this time, the resulting solution was cooled to 25 °C, filtered through a syringe filter (0.45 μm , hydrophilic PTFE) and crystallised. The crystals obtained were dried in an oven at 105 °C to a constant weight and used to prepare a 0.05 mol/L solution of CeCl_3 , the chemical composition of which is provided in Table 3. The Ce content in the salt obtained was 98.3 %.

Table 4

Empirical conditions for the CCD/RSM and results (COD, and PO_4^{3-}) for brewery wastewater (pH 2.14–9.86, molar ratio $\text{Ce}^{3+}:\text{PO}_4^{3-}$ (0.856–2.144: 1), Time 8.56–21.4 min); *- center of the plan.

Run	Experimental conditions			Experimental results	
	pH, x_1	Time (min), x_2	molar ratio $\text{Ce}^{3+}:\text{PO}_4^{3-}$, x_3	PO_4^{3-} mg/L,	Ce^{3+} , mg/L
1	3.00	10.0	1.000	43.5 ± 4.4	73.8 ± 11.1
2	3.00	10.0	2.000	13.8 ± 1.4	133 ± 20
3	3.00	20.0	1.000	42.2 ± 4.2	69.9 ± 10.5
4	3.00	20.0	2.000	12.0 ± 1.2	126 ± 19
5	9.00	10.0	1.000	9.57 ± 0.96	0.015 ± 0.002
6	9.00	10.0	2.000	2.93 ± 0.29	0.171 ± 0.026
7	9.00	20.0	1.000	15.0 ± 1.5	0.070 ± 0.011
8	9.00	20.0	2.000	1.48 ± 0.15	0.158 ± 0.024
9	2.14	15.0	1.500	46.7 ± 4.7	109 ± 16
10	9.86	15.0	1.500	0.570 ± 0.060	0.124 ± 0.019
11	6.00	8.56	1.500	0.059 ± 0.006	0.194 ± 0.029
12	6.00	21.4	1.500	0.045 ± 0.005	0.145 ± 0.022
13	6.00	15.0	0.856	15.0 ± 1.5	1.02 ± 0.15
14	6.00	15.0	2.144	< 0.010 ± 0.001	0.719 ± 0.108
15*	6.00	15.0	1.500	0.043 ± 0.004	0.147 ± 0.022
16*	6.00	15.0	1.500	0.039 ± 0.004	0.184 ± 0.028

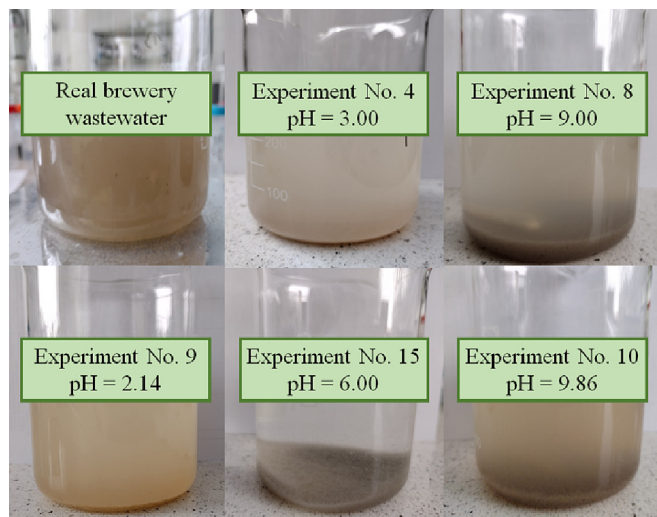


Fig. 3. Real brewery wastewater and experimental wastewater.

2.4. Wastewater treatment

Central Composite Design (CCD) and Response Surface Methodology (RSM) were used to determine the most favourable process conditions for phosphate removal from brewery wastewater (Khuri and Mukhopadhyay, 2010). Three input parameters were selected in the experimental plan, i.e.: pH, the molar ratio of Ce^{3+} added to PO_4^{3-} and the process time (min). It was assumed that these parameters would significantly influence the dependent parameter, i.e. the concentration of PO_4^{3-} (mg/L) in the treated effluent. Based on studies reported in literature (Thomas et al., 2022, 2021, 2020), the following independent input parameter values were adopted: pH from 3 to 9, molar ratio of Ce^{3+} added to PO_4^{3-} from 1:1 to 2:1 and process time from 10 to 20 min. The Design of Experiments (DOE) module of Statistica 13 (TIBCO Software Inc., USA) was used to develop a three-factor central composite design. The resulting experimental plan included the conduction of 16 experiments, whose input variable values are summarised in Table 4 (experimental conditions). All experiments were conducted at $20 \pm 2^\circ\text{C}$. The brewery wastewater treatment process was carried out by pouring 250 mL of wastewater into a 400 mL beaker. The effluent was stirred at 250 ± 10 rpm and its pH was adjusted with 15 % HCl or 15 % NaOH to the values specified in the experimental plan. An appropriate coagulant volume (0.05 mol/L CeCl_3) was then added, and the phosphate precipitation process was carried out for the time adopted in the experimental plan. After stirring stopped, the samples were left for 5 min to sediment the precipitated poorly soluble precipitates (Fig. 3). Samples for analysis were collected directly from the sediment, filtered through a syringe filter (0.45 μm , hydrophilic PTFE) and analysed chemically using the methods described in the Analytical Methods section. Table 4. (experimental results) shows the results obtained for 16 experiments according to the adopted plan, where the

dependent variable is the PO_4^{3-} (mg/L) concentration. In addition, for each of the wastewater samples treated according to the adopted plan, the concentration of cerium was determined after filtering the sample through a syringe filter (0.45 μm , hydrophilic PTFE).

2.5. Cerium recovery

After treatment, the effluent was percolated and the remaining sludge dried to an air-dry state. The averaged, weighed sludge was decomposed in *aqua regia* to determine the elemental composition provided in Table 10. The sludge was then leached with 5 %, 10 %, 15 % or 20 % HCl to determine the efficiency of cerium recovery from the sludge, after which the resulting solutions were analysed using the ICP-OES technique. The obtained extract compositions are displayed in Table 11. 15 % NaOH was added to the extract to increase the pH to about 1.8. In the next step, a solution of $\text{Na}_2\text{C}_2\text{O}_4$ was added to precipitate a poorly soluble $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ precipitate. The precipitate produced was filtered through a syringe filter (0.45 μm , hydrophilic PTFE), washed and dissolved in 30 % HCl. The resulting solution was filtered through a syringe filter (0.45 μm , hydrophilic PTFE), diluted and analysed by ICP-OES and ICP-MS techniques. The elemental composition of the solution obtained after sludge dilution is provided in Table 12.

3. Results and discussion

3.1. Brewery wastewater treatment

The brewery wastewater used in the study was characterised by high values of physicochemical parameters such as total P 19.8 ± 2.0 mg/L, phosphate 43.0 ± 4.3 mg/L, TSS 630 ± 63 mg/L, $\text{COD}_{(\text{Cr})}$ 827 ± 124 mg O_2 /L, TOC 130 ± 20 mg/L, turbidity 390 ± 39 NTU, and colour 170 ± 34 mg Pt/L. Compared to other brewery effluents reported in literature, some parameters were characterised by similar values, i.e. $\text{COD}_{(\text{Cr})}$ (680–90,000 mg O_2 /L), phosphate (8–124 mg/L), and TSS (100–8750 mg/L) (Alvarado-Lassman et al., 2008; Austermann-Haun et al., 1999; Ince et al., 2000; Parawira et al., 2005; Wen et al., 2010; Yu and Gu, 1996). The key dependent parameter subjected to optimisation was the concentration of PO_4^{3-} in the treated effluent. The substance used to treat phosphate-containing wastewater can include soluble cerium(III) compounds e.g. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. Cerium-containing waste, such as spent polishing agents, deserves special attention. This study involved a spent polishing agent containing 82.0 % CeO_2 . Literature data indicate that waste such as red mud (Sinha et al., 2016), spent FCC catalysts (YE et al., 2017) and NiMH batteries (Innocenzi and Vegliò, 2012) may contain only about 0.011 %, 1.57 %, 1.68 % cerium, which is a low content of this element compared to the spent polishing powder (Meshram and Abhilash, 2020).

Optimisation studies were carried out using RSM/CCD, which reduced the large number of optimisation experiments that would require conducting to analyse the effect of each individual independent factor on the initial PO_4^{3-} concentration. The results presented in Table 4. demonstrate that the lowest

Table 5

Analysis of the experiment with the central composite design using Statistica 13. Evaluation of the effects, PO_4^{3-} ; $R^2 = 0.956$; $R_{\text{adj}}^2 = 0.890$, MS = 30.448.

Parameter	Effect	Standard error	t(10)	p	CI (− 95 %)	CI (+ 95 %)	Factor	Standard error	CI (− 95 %)	CI (+ 95 %)
Intercept	0.540	3.198	0.169	0.871	− 7.284	8.365	0.540	3.198	− 7.284	8.365
(1) pH (L)	− 25.081	3.281	− 7.644	< 0.001	− 33.110	− 17.052	− 12.540	1.641	− 16.555	− 8.526
pH (Q)	27.432	4.711	5.823	0.001	15.906	38.959	13.716	2.355	7.953	19.480
(2) time, min (L)	0.145	3.281	0.044	0.966	− 7.884	8.173	0.072	1.641	− 3.942	4.086
time, min (Q)	− 1.042	4.710	− 0.221	0.832	− 12.567	10.483	− 0.521	2.355	− 6.283	5.241
(3) Ce^{3+} : PO_4^{3-} (L)*	− 17.558	3.280	− 5.353	0.002	− 25.585	− 9.531	− 8.779	1.640	− 12.793	− 4.766
Ce^{3+} : PO_4^{3-} (Q)*	7.942	4.706	1.687	0.142	− 3.574	19.458	3.971	2.353	− 1.787	9.729
1 L relative to 2 L	1.764	3.902	0.452	0.667	− 7.783	11.311	0.882	1.951	− 3.892	5.656
1 L relative to 3 L	9.953	3.902	2.551	0.043	0.406	19.500	4.977	1.951	0.203	9.750
2 L relative to 3 L	− 1.856	3.902	− 0.476	0.651	− 11.403	7.691	− 0.928	1.951	− 5.702	3.846

* - molar ratio, L - linear effects, Q - quadratic effects, statistically significant if $p < 0.05$.

Table 6

Results of the ANOVA test.

Parameter	SS	df	MS	F	p
(1) pH (L)	1779.085	1	1779.085	58.430	< 0.001
pH (Q)	1032.574	1	1032.574	33.913	0.001
(2) time, min (L)	0.059	1	0.059	0.002	0.966
time, min (Q)	1.490	1	1.490	0.049	0.832
(3) Ce^{3+} : PO_4^{3-} (L)*	872.311	1	872.311	28.649	0.002
Ce: PO_4^{3-} (Q)*	86.705	1	86.705	2.848	0.142
1 L relative to 2 L	6.223	1	6.223	0.204	0.667
1 L relative to 3 L	198.124	1	198.124	6.507	0.043
2 L relative to 3 L	6.889	1	6.889	0.226	0.651
Error	182.688	6	30.448		
Total sum of square	4166.841	15			

ANOVA model coefficients before excluding non-significant linear-linear interaction, linear time and quadratic time effects, statistically significant if $p < 0.05$, * - molar ratio, L - linear effects, Q - quadratic effects.

phosphate concentrations were obtained for the Ce^{3+} to PO_4^{3-} molar ratios of 1.5:1 and 2.144:1 at pH 6.00, and the highest for the molar ratio of 1:1 at pH 3.00 and the molar ratio of 1.5:1 at pH 2.14. The experiment results obtained at this stage indicate a significant correlation between pH and the molar ratio of Ce^{3+} to PO_4^{3-} . The coefficient of determination R^2 assumes values between 0 and 1, where a value of 0 indicates no relationship between the observations and the model, while a value of 1 indicates a perfect fit between the observed data and the model. According to literature, different divisions can be adopted to describe the strength of the relationship between the model and the data. One of the proposed divisions assumes that with R^2 from 0.9 to 1 the fit of the model is very good, from 0.8 to 0.9 the fit of the model is good, from 0.6 to 0.8 the fit of the model is satisfactory, from 0.5 to 0.6 the fit of the model is poor, from 0 to 0.5 the fit of the model is unsatisfactory (Kuc et al., 2022). Table 5 presents an evaluation of the effects for the individual independent parameters and their linear interactions. The calculated coefficient of determination R^2 was 0.956 and the adjusted R_{adj}^2 was 0.890, with a root mean square error (RMSE) of 30.448.

Table 6 presents the results of the ANOVA analysis for all the parameters comprising the model.

The statistical analysis carried out demonstrated that some of the parameters analysed were statistically insignificant ($p > 0.05$), therefore consequently, further analyses were carried out after excluding the most insignificant effects of linear/linear interactions 1 L relative to 2 L, 2 L relative to 3 L, and linear and quadratic effects for time. An assessment of effect significance after irrelevant parameter removal is presented in Table 7. In this case, the calculated coefficient of determination R^2 decreased slightly to 0.953, while the adjusted R_{adj}^2 increased to 0.929, indicating a very good fit of the model to the experimental data (Kuc et al., 2022), while the root mean square error (RMSE) decreased to 19.735, indicating a better fit of the model after removing some of the parameters.

Table 8 presents the results of the ANOVA analysis with an adopted significance level of $p < 0.05$. The analysis demonstrated the significance of four parameters, i.e. pH(L), pH(Q), Ce^{3+} : PO_4^{3-} (L) molar ratio and 1 L relative to 3 L.

Table 7Analysis of the experiment with the central composite design using Statistica 13. Evaluation of the effects, PO_4^{3-} ; $R^2 = 0.953$; $R_{adj}^2 = 0.929$, MS = 19.735.

Parameter	Effect	Standard error	t(10)	p	CI (− 95 %)	CI (+ 95 %)	Factor	Standard error	CI (− 95 %)	CI (+ 95 %)
Intercept	0.172	2.197	0.078	0.939	− 4.724	5.068	0.172	2.197	− 4.724	5.068
(1) pH (L)	− 25.081	2.642	− 9.495	< 0.001	− 30.967	− 19.195	− 12.541	1.321	− 15.483	− 9.598
pH (Q)	27.432	3.792	7.233	< 0.001	18.982	35.882	13.716	1.896	9.491	17.941
(3) Ce^{3+} : PO_4^{3-} (L)*	− 17.558	2.641	− 6.648	< 0.001	− 23.443	− 11.674	− 8.779	1.320	− 11.721	− 5.837
Ce^{3+} : PO_4^{3-} (Q)*	7.943	3.789	2.096	0.062	− 0.500	16.385	3.971	1.895	− 0.250	8.193
1 L relative to 3 L	9.953	3.141	3.168	0.010	2.954	16.952	4.977	1.571	1.477	8.476

ANOVA model coefficients after excluding non-significant linear-linear interaction, linear time and quadratic time effects, statistically significant if $p < 0.05$, * - molar ratio, L - linear effects, Q - quadratic effects.

Table 8

Results of the ANOVA test.

Parameter	SS	df	MS	F	p
(1) pH (L)	1779.091	1	1779.091	90.149	< 0.001
pH (Q)	1032.564	1	1032.564	52.322	< 0.001
(3) Ce^{3+} : PO_4^{3-} (L)*	872.311	1	872.311	44.201	< 0.001
Ce^{3+} : PO_4^{3-} (Q)*	86.717	1	86.717	4.394	0.062
1 L relative to 3 L	198.124	1	198.124	10.039	0.010
Error	197.350	10	19.735		
Total sum of square	4166.841	15			

* - molar ratio, L - linear effects, Q - quadratic effects, statistically significant if $p < 0.05$.

A graphical interpretation of the effect significance is displayed in the Pareto chart (Fig. 4.).

The graph shows the standardised The graph shows the standardised effect estimators grouped according to their absolute values. The red line in the graph indicates the significance threshold for a significance test of $p = 0.05$. The analysis performed enabled the ranking of the parameters tested according to their statistical significance, i.e.: linear effects of pH (most significant), quadratic effects of pH, linear effects of the Ce^{3+} to PO_4^{3-} molar ratio, interaction of linear effects of pH and the Ce^{3+} to PO_4^{3-} molar ratio, and quadratic effects of the Ce^{3+} to PO_4^{3-} molar ratio (least significant).

It is clear that the form in which the phosphates occur is determined by the pH of the effluent (eg. H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}) and that it also influences the concentration of the Ce^{3+} ions, because at pH above 7.1 Ce^{3+} ions in a 0.1 mol/L NO_3^- solution) precipitate as $Ce(OH)_3$ (Kragten, 1978). This suggests that reaction (1) cannot be ruled out:



as it can occur at a pH not much different from 7.1, which in turn depends on the composition of the solution, i.e. its concentration and the type of anions present. It is clear that the interaction between the independent variables, i.e. pH and the Ce^{3+} to PO_4^{3-} molar ratio, has an important influence on the process.

Based on the fitted model, a second-order Eq. (2) was determined to calculate the predicted PO_4^{3-} concentration in the treated effluent and to compare it with the results obtained from the experiments in Fig. 5.

$$\begin{aligned} \text{Concentration}(PO_4^{3-}) = & 172.0561 - 27.4448(\text{pH}) \\ & + 1.5240(\text{pH})^2 - 85.1205(\text{molar ratio}) \\ & + 15.8854(\text{molar ratio})^2 \\ & + 3.3176(\text{pH})(\text{molar ratio}) \end{aligned} \quad (2)$$

A graphical interpretation of the response surface is presented in the 2D contour plot in Fig. 6.

The optimisation carried out for the precipitation of PO_4^{3-} ions using Ce^{3+} ions from brewery wastewater using the response surface method indicates that the best process conditions occur at pH 7.0–8.5 and a molar concentration ratio of Ce^{3+} to PO_4^{3-} ions of 1.5–2.0 at a constant process time of 15 min. Fig. 7 presents a 2D contour plot highlighting the areas with the lowest Ce^{3+} content after the effluent treatment process, which

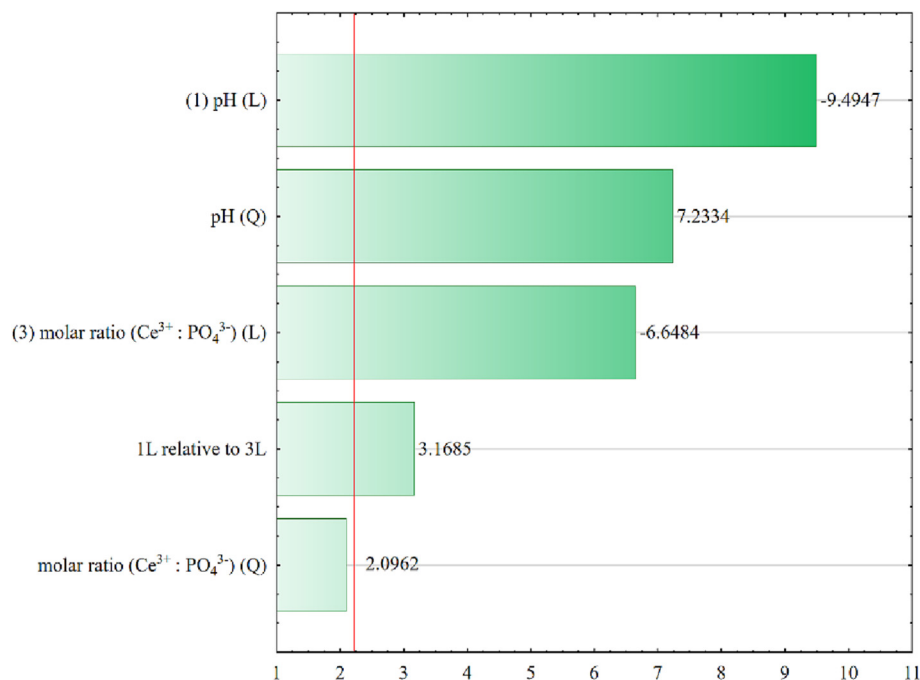


Fig. 4. Pareto chart - the absolute values of the standardised assessments of the effects (PO_4^{3-} (mg/L), 3 values, 1 block, 16 experiments, $\text{MS} = 19.735$).

was taken into account in the optimisation of the brewery effluent treatment parameters.

The reason for the high content of Ce^{3+} and PO_4^{3-} at low pH is the solubility of CePO_4 (Lin et al., 2021). In addition, the effect of complexation of Ce^{3+} ions by the components of the complex sewage matrix cannot be excluded, e.g. humic and fulvic acids, as well as formation of organometallic complexes. (Janhom et al., 2009; Zhang et al., 2015).

A treatment process to test the efficiency of phosphate removal from brewery effluent carried out under optimal conditions determined with CCD/RSM ($\text{pH} = 7.5$, molar ratio of Ce^{3+} to PO_4^{3-} of 1.5 and time = 15 min) confirmed the removal efficiency of phosphorus compounds (mainly phosphate), with a reduction of PO_4^{3-} by 99.86 %, total P by 99.56 %, COD_{Cr} by 81.86 %, total suspended solids by 96.67 %, TOC by 60.38 %, total N by 19.24 %, turbidity by 98.18 % and colour by 70.59 %, while Ce^{3+} ions content was 0.058 mg/L (Table 9).

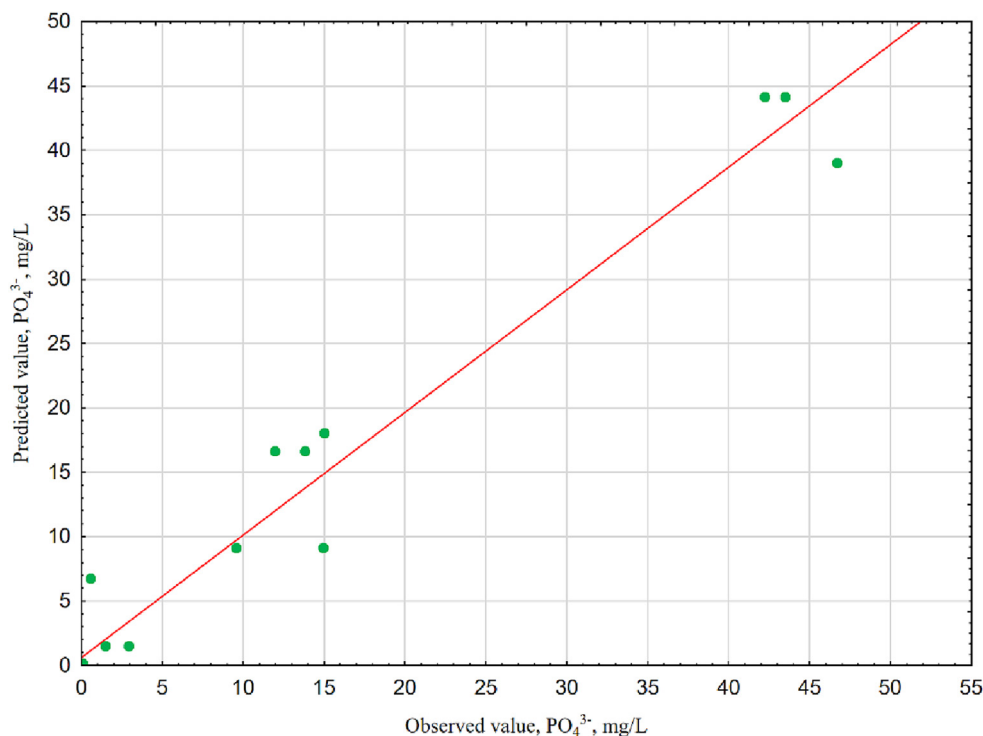


Fig. 5. Predicted vs. observed values for PO_4^{3-} (mg/L). The coefficient of determination R^2 is 0.953, adjusted R^2 is 0.929, $\text{MS} = 19.735$.

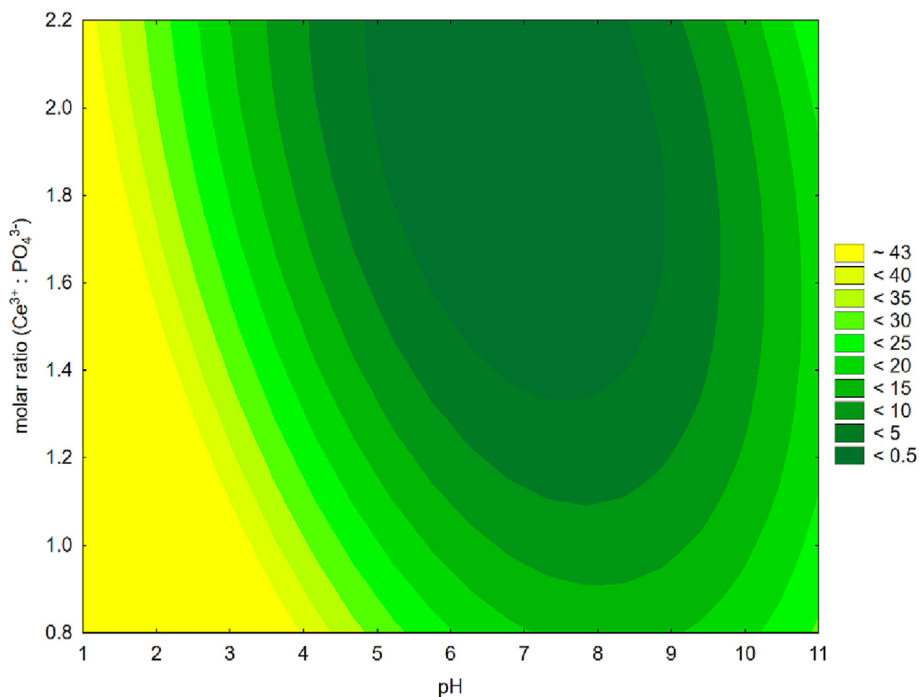


Fig. 6. Response surface of the influence of the molar ratio of $\text{Ce}^{3+} : \text{PO}_4^{3-}$ to the pH value on the content of PO_4^{3-} in brewery wastewater, time = 15 min. (MS = 19.735).

99.94 % of Ce^{3+} ions were bound in the precipitate mainly by reaction (3), which generated a poorly soluble precipitate of cerium(III) phosphate (Kajjumba et al., 2021; Liu and Byrne, 1997):



The non-stoichiometric, excess amount of Ce^{3+} added to the solution relative to the content of PO_4^{3-} may result from side reactions that bind

Ce^{3+} ions e.g. into carbonate precipitates (Ferri et al., 1983) and hydroxide precipitates (Kragten, 1978) in reactions (4) and (5) respectively:



The non-stoichiometric course of precipitate formation may also be caused by the co-precipitation of impurities with Ce^{3+} and PO_4^{3-} ions, and the

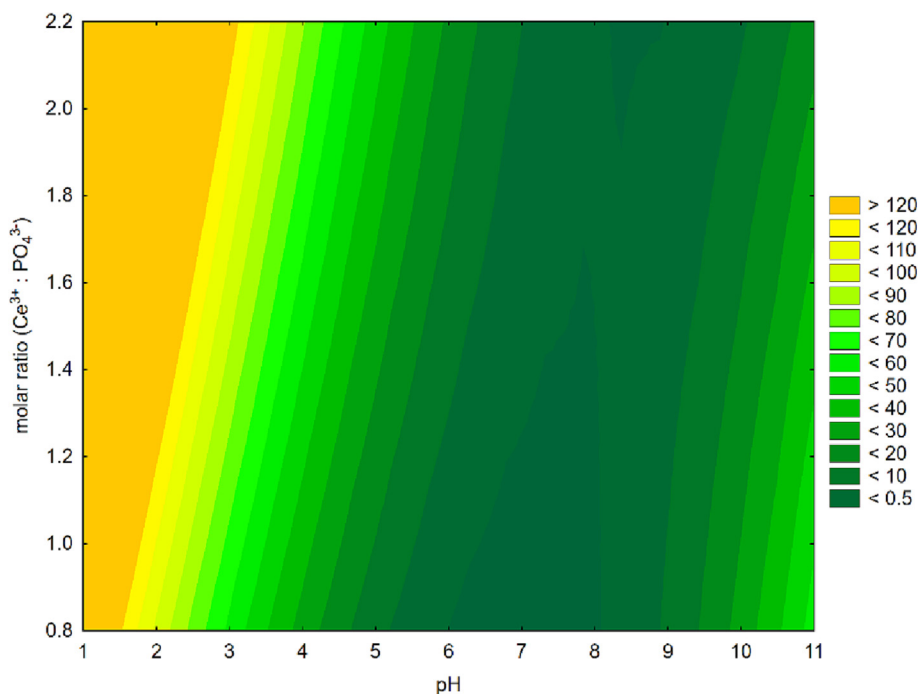


Fig. 7. Response surface of the influence of the molar ratio of $\text{Ce}^{3+} : \text{PO}_4^{3-}$ to pH value on the content of Ce^{3+} in brewery wastewater, time = 15 min. (MS = 142.9573).

Table 9

Selected physicochemical parameters of brewery wastewater before and after treatment using a 0.05 mol/L cerium(III) chloride (CeCl₃) solution.

Parameter	Unit	Brewery wastewater	Brewery wastewater after treatment ^a	
			Observed value	Removal ^b , %
pH	–	7.5 ± 0.1	7.5 ± 0.1	–
Turbidity	NTU	390 ± 39	7.1 ± 0.7	98.18
Colour	mg Pt/L	170 ± 34	50 ± 10	70.59
PO ₄ ^{3–}	mg/L	43.0 ± 4.3	0.062 ± 0.006	99.86
Total P	mg/L	19.8 ± 2.0	0.085 ± 0.017	99.56
Total N	mg/L	46.0 ± 6.9	37.1 ± 5.6	19.24
TSS	mg/L	630 ± 63	21.0 ± 2.1	96.67
TOC	mg/L	130 ± 19	51.5 ± 7.7	60.38
COD _{Cr}	mg O ₂ /L	827 ± 124	150 ± 22	81.86
Ce ³⁺	mg/L	95.2 ^c ± 14.3	0.058 ± 0.009	99.94

^a In optimal conditions, i.e., pH = 7.5, Ce³⁺ = 0.095 g/L (molar ratio 1.5:1, Ce³⁺: PO₄^{3–}), and time = 15 min.

^b Wastewater treatment efficiency = (C₁ – C₂)/C₁ × 100 %, where C₁ is the concentration of the substance in the brewery wastewater, C₂ is the concentration of the substance in the treated wastewater.

^c Calculated Ce³⁺ ion concentration after addition to the raw effluent (Ce³⁺ ion content in the raw effluent <0.25 µg/L).

Table 10

Chemical composition of the sludge.

Parameter	Unit	Value
Cerium (Ce)	g/kg	126.3 ± 12.6
Iron (Fe)	g/kg	3.37 ± 0.34
Manganese (Mn)	g/kg	0.180 ± 0.040
Cadmium (Cd)	g/kg	< 0.005 ± 0.001
Chromium (Cr)	g/kg	0.052 ± 0.013
Copper (Cu)	g/kg	< 0.05 ± 0.01
Nickel (Ni)	g/kg	< 0.05 ± 0.01
Lead (Pb)	g/kg	< 0.10 ± 0.03
Zinc (Zn)	g/kg	0.236 ± 0.059
Phosphorus (P)	g/kg	25.9 ± 2.6
Cobalt (Co)	g/kg	< 0.05 ± 0.01
Calcium (Ca)	g/kg	172.0 ± 17.0
Magnesium (Mg)	g/kg	10.6 ± 1.1
Sodium (Na)	g/kg	53.3 ± 5.3
Potassium (K)	g/kg	< 0.20 ± 0.05
Barium (Ba)	g/kg	1.46 ± 0.36
Strontium (Sr)	g/kg	0.84 ± 0.21

formation of CePO₄ precipitate with non-stoichiometric composition and hexagonal structure cannot be ruled out. (Vinothkumar et al., 2019).

The end result is an effluent with a low phosphorus content that will not promote the eutrophication process (Schindler et al., 2016). The total

nitrogen content was reduced by only 19.2 % (from 46.0 mg/L to 37.1 mg/L), however nitrogen compounds can be easily removed by denitrification (Tchobanoglous et al., 2003).

3.2. Sediment analysis

More than 99 % of the cerium used in the process and 99 % of the phosphate was bound in the sludge produced during wastewater treatment mainly as CePO₄ (Kajjumba et al., 2021). After draining, drying and averaging, the sludge was subjected to decomposition in aqua regia and then analysed by ICP-OES. The sludge composition is presented in Table 10. An analysis of the sludge demonstrated that it contained increased amounts of Ce and P, 126.3 ± 12.6 g/kg and 25.9 ± 2.6 g/kg respectively. The results obtained showed that the sludge is suitable for further processing involving the recovery of cerium compounds and their reuse.

3.3. Extraction of Ce and P

Therefore, in the next stage of the study, the sludge was leached using HCl at concentrations of 5 %, 10 %, 15 % and 20 % to determine the potential for cerium recovery. Table 11 presents the results of sludge leaching. The use of 10 %, 15 % and 20 % HCl exhibited comparably high cerium extraction efficiencies. In the following experiment, the solution obtained after leaching the precipitate with 10 % HCl was used, due to the lower consumption of acid needed to carry out the extraction and the lower consumption of NaOH needed to increase the pH of the solution in a further step of the experiment. This approach not only made it possible to reduce the amount of reactants, but also resulted in a reduction in the amount and concentration of post-process solutions. The extraction efficiency using 10 % HCl was 97.6 % for Ce and 89.6 % for P.

Portions of 15 % NaOH were added to the resulting extract to raise the pH to approximately 1.8 ± 0.1, which is the optimal value when precipitating lanthanide oxalates (Żelazny et al., 2017). The addition of a Na₂C₂O₄ solution resulted in the precipitation of a white, poorly soluble Ce₂(C₂O₄)₃ precipitate according to reaction (6).



The precipitate, after filtration and washing, was dissolved in 30 % HCl. Analysis of the resulting solution by ICP-OES and ICP-MS demonstrated that the component at the highest concentration was cerium, which accounted for 96.1 % of the cations determined (Table 12). The cerium recovery efficiency was 71.9 %. Waste types reported in literature, such as spent polishing powders, red mud, spent FCC catalysts and NiMH batteries, had similar cerium recovery values of 65–91 %, 74–99.99 %, 42–97 %, 32.54–99.9 %, respectively, while the extraction yield after separation was 95–99 %, 80–100 %, 74–98 %, 84–99 %, respectively, and was

Table 11

Chemical composition of the extracts after leaching by 5 %, 10 %, 15 % and 20 % HCl solution.

Parameter	Unit	HCl 5 %	HCl 10 %	HCl 15 %	HCl 20 %
Cerium (Ce)	g/kg	114.4 ± 11.4	123.3 ± 12.3	122.9 ± 12.3	129.4 ± 12.9
Iron (Fe)	g/kg	2.03 ± 0.20	2.51 ± 0.25	2.57 ± 0.26	2.65 ± 0.27
Manganese (Mn)	g/kg	0.161 ± 0.032	0.166 ± 0.033	0.162 ± 0.032	0.169 ± 0.034
Cadmium (Cd)	g/kg	< 0.005 ± 0.001	< 0.005 ± 0.001	< 0.005 ± 0.001	< 0.005 ± 0.001
Chromium (Cr)	g/kg	0.021 ± 0.005	0.032 ± 0.008	0.037 ± 0.009	0.042 ± 0.011
Copper (Cu)	g/kg	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01
Nickel (Ni)	g/kg	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01
Lead (Pb)	g/kg	< 0.10 ± 0.03	< 0.10 ± 0.03	< 0.10 ± 0.03	< 0.10 ± 0.03
Zinc (Zn)	g/kg	0.209 ± 0.042	0.213 ± 0.043	0.224 ± 0.045	0.234 ± 0.047
Phosphorus (P)	g/kg	22.0 ± 2.2	23.2 ± 2.3	23.5 ± 2.4	24.9 ± 2.5
Cobalt (Co)	g/kg	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01	< 0.05 ± 0.01
Calcium (Ca)	g/kg	152.6 ± 15.3	149.1 ± 14.9	151.1 ± 15.1	160.3 ± 16.0
Magnesium (Mg)	g/kg	9.16 ± 0.92	9.10 ± 0.91	9.01 ± 0.90	9.59 ± 0.96
Sodium (Na)	g/kg	46.0 ± 4.6	43.4 ± 4.3	43.2 ± 4.3	47.1 ± 4.7
Potassium (K)	g/kg	< 0.20 ± 0.05	< 0.20 ± 0.05	< 0.20 ± 0.05	< 0.20 ± 0.05
Barium (Ba)	g/kg	1.28 ± 0.26	1.22 ± 0.24	1.21 ± 0.24	1.28 ± 0.26
Strontium (Sr)	g/kg	0.81 ± 0.16	0.78 ± 0.15	0.77 ± 0.15	0.81 ± 0.16

Table 12
Chemical composition of the CeCl_3 solution obtained after $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ digestion.

Parameter	Unit	Value
Cerium (Ce)	mg/L	443.0 ± 44.3
Iron (Fe)	mg/L	$< 0.05 \pm 0.01$
Manganese (Mn)	mg/L	$< 0.05 \pm 0.01$
Cadmium (Cd)	mg/L	$< 0.05 \pm 0.01$
Chromium (Cr)	mg/L	$< 0.05 \pm 0.01$
Copper (Cu)	mg/L	$< 0.05 \pm 0.01$
Nickel (Ni)	mg/L	$< 0.05 \pm 0.01$
Lead (Pb)	mg/L	$< 0.05 \pm 0.01$
Zinc (Zn)	mg/L	0.480 ± 0.120
Phosphorus (P)	mg/L	1.52 ± 0.15
Cobalt (Co)	mg/L	$< 0.05 \pm 0.01$
Calcium (Ca)	mg/L	$< 0.5 \pm 0.1$
Magnesium (Mg)	mg/L	$< 0.3 \pm 0.1$
Sodium (Na)	mg/L	17.6 ± 2.6
Potassium (K)	mg/L	$< 2.0 \pm 0.5$
Barium (Ba)	mg/L	$< 0.05 \pm 0.01$
Strontium (Sr)	mg/L	$< 0.05 \pm 0.01$

similarly high to that obtained in the recovery of cerium from sludge (Meshram and Abhilash, 2020).

The performed tests involving the treatment of brewery effluent and the processing of sludge containing cerium compounds enable the development of a concept for the recovery and use of cerium compounds, as depicted in Fig. 8.

The concept involves the disposal of spent polishing powder waste by recovering cerium compounds through extraction, concentration and crystallization, and then using them as an alternative to iron and aluminum salts as a coagulant for precipitating phosphates from brewery wastewater. The resulting sludge after the wastewater treatment process can, in turn, be treated to recover cerium compounds and reuse them industrially. Phosphorus compounds can be recovered from the solution after extraction using methods widely described in the literature and used, for example, for fertilization purposes (Kato et al., 2006; Ye et al., 2014). In this way, the concept presented fits into the model of circular economy and sustainable use of resources in the form of cerium compounds.

4. Conclusions

A waste polishing powder containing 82.0 % CeO_2 was used to obtain $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, from which a 0.05 mol/L solution of Ce^{3+} was prepared. The solution had a high cerium content (99.1 %), which enabled its application in optimising the removal of phosphate (PO_4^{3-}) from brewery effluent using a response surface methodology with a central composite design. The results obtained demonstrated that the process has the highest efficiency under optimal process conditions (pH 7.0–8.5, molar concentration ratio of Ce^{3+} ions to PO_4^{3-} of 1.5–2.0, time 15 min.). This made it possible to reduce some of the pollutants by >96 % by binding them in the sludge. The sludge resulting from the application of an aqueous solution of Ce^{3+} ions bound >99 % of the cerium and phosphorus compounds, which could be a potential source for the recovery of not only cerium, but also potentially phosphorus.

The proposed method of wastewater treatment is an alternative to solutions based on the use of iron and aluminum compounds as conventional coagulants. The results obtained indicate not only the high efficiency of removal of individual pollutants from the wastewater, but also the possibility of further utilization of the sludge generated, which perfectly fits in with the ideas of a closed-cycle economy.

Funding

This work was supported by the Ministry of Science and Higher Education, Republic of Poland (Statutory Activity of the Central Mining Institute, Task no. 11131011-332).

CRediT authorship contribution statement

All authors contributed to the study conception and design. Material preparation, data collection, and formal analysis were performed by Paweł Lejwoda. The first draft of the manuscript was written by Paweł Lejwoda, Barbara Białecka, and Maciej Thomas, and all authors commented on previous versions of the manuscript. All authors read and approved the final version of the manuscript.

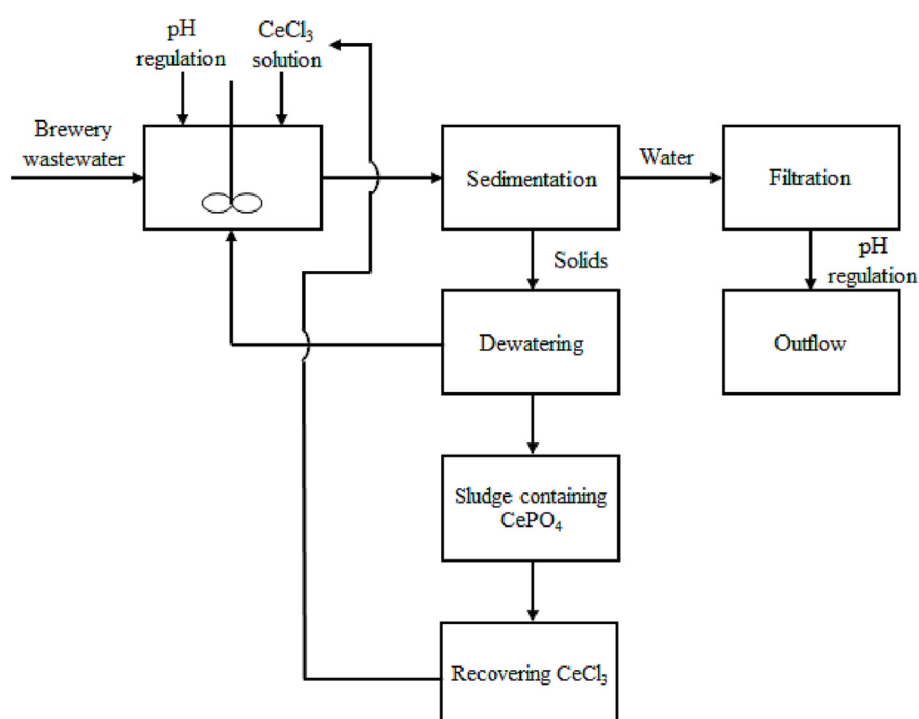


Fig. 8. Conception of removing phosphates from brewery wastewater with recovering $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$.

Ethics declarations

Ethics approval and consent to participate.
Not applicable.

Consent for publication

Not applicable.

Rights and permissions

Open Access This article is licensed under a Creative Commons Attribution 4.0 International Licence, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Abhilash, Sinha, S., Sinha, M.K., Pandey, B.D., 2014. Extraction of lanthanum and cerium from Indian red mud. *Int. J. Miner. Process.* 127, 70–73. <https://doi.org/10.1016/j.minpro.2013.12.009>.
- Aharchaoui, I., Beaubien, C., Campbell, P.G.C., Fortin, C., 2020. Lanthanum and cerium toxicity to the freshwater green alga *Chlorella fusca*: applicability of the biotic ligand model. *Environ. Toxicol. Chem.* 39, 996–1005. <https://doi.org/10.1002/etc.4707>.
- Alvarado-Lassman, A., Rustrián, E., García-Alvarado, M.A., Rodríguez-Jiménez, G.C., Houbroun, E., 2008. Brewery wastewater treatment using anaerobic inverse fluidized bed reactors. *Bioresour. Technol.* 99, 3009–3015. <https://doi.org/10.1016/j.biortech.2007.06.022>.
- Austermann-Haun, U., Meyer, H., Seyfried, C.F., Rosenwinkel, K.-H., 1999. Full scale experiences with anaerobic/aerobic treatment plants in the food and beverage industry. *Water Sci. Technol.* 40, 305–312. <https://doi.org/10.2166/wst.1999.0061>.
- Borra, C., Vlught, T., Yang, Y., Offerman, S., 2018. Recovery of cerium from glass polishing waste: a critical review. *Metals (Basel)* 8, 801. <https://doi.org/10.3390/met8100801>.
- Caravelli, A.H., Contreras, E.M., Zaritzky, N.E., 2010. Phosphorous removal in batch systems using ferric chloride in the presence of activated sludges. *J. Hazard. Mater.* 177, 199–208. <https://doi.org/10.1016/j.jhazmat.2009.12.018>.
- Correll, D.L., 1998. The role of phosphorus in the eutrophication of receiving waters: a review. *J. Environ. Qual.* 27, 261–266. <https://doi.org/10.2134/jeq1998.00472425002700020004x>.
- Daneshgar, S., Callegari, A., Capodaglio, A., Vaccari, D., 2018. The potential phosphorus crisis: resource conservation and possible escape technologies: a review. *Resources* 7, 37. <https://doi.org/10.3390/resources7020037>.
- Dey, S., Dhal, G.C., 2020. Cerium catalysts applications in carbon monoxide oxidations. *Mater. Sci. Energy Technol.* 3, 6–24. <https://doi.org/10.1016/j.mset.2019.09.003>.
- European Commission, 2010. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) Text with EEA relevance. <https://data.europa.eu/doi/10.2873/11619>.
- Feng, X., Huang, L., Zhang, X., Liu, Y., 2009. Water system integration of a brewhouse. *Energy Convers. Manag.* 50, 354–359. <https://doi.org/10.1016/j.enconman.2008.09.013>.
- Fernandes, A., Afonso, J.C., Dutra, A.J.B., 2013. Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation. *Hydrometallurgy* 133, 37–43. <https://doi.org/10.1016/j.hydromet.2012.11.017>.
- Ferri, D., Grenthe, I., Hietanen, S., Salvatore, F., Powell, D.L., Suchi, R., 1983. Studies on metal carbonate equilibria. 5. The Cerium(III) carbonate complexes in aqueous perchlorate media. *Acta Chem. Scand.* 37a, 359–365. <https://doi.org/10.3891/acta.chem.scand.37a-0359>.
- Global Beer Consumption by Country in 2020. https://www.kirinholdings.com/en/newsroom/release/2022/0127_04.html (accessed 25 July 22).
- González, V., Vignati, D.A.L., Pons, M.-N., Montarges-Pelletier, E., Bojic, C., Giamberini, L., 2015. Lanthanide ecotoxicity: first attempt to measure environmental risk for aquatic organisms. *Environ. Pollut.* 199, 139–147. <https://doi.org/10.1016/j.envpol.2015.01.020>.
- Gupta, C.K., Krishnamurthy, N., 1992. Extractive metallurgy of rare earths. *Int. Mater. Rev.* 37, 197–248. <https://doi.org/10.1179/imr.1992.37.1.197>.
- Hammas-Nasri, I., Horchani-Naifer, K., Férid, M., Barca, D., 2016. Rare earths concentration from phosphogypsum waste by two-step leaching method. *Int. J. Miner. Process.* 149, 78–83. <https://doi.org/10.1016/j.minpro.2016.02.011>.
- Haynes, W.M. (Ed.), 2014. CRC Handbook of Chemistry and Physics. CRC Press <https://doi.org/10.1201/b17118>.
- Ince, B.K., Ince, O., Sallis, P.J., Anderson, G.K., 2000. Inert COD production in a membrane anaerobic reactor treating brewery wastewater. *Water Res.* 34, 3943–3948. [https://doi.org/10.1016/S0043-1354\(00\)00170-6](https://doi.org/10.1016/S0043-1354(00)00170-6).
- Innocenzi, V., Vegliò, F., 2012. Recovery of rare earths and base metals from spent nickel-metal hydride batteries by sequential sulphuric acid leaching and selective precipitations. *J. Power Sources* 211, 184–191. <https://doi.org/10.1016/j.jpowsour.2012.03.064>.
- Janhom, T., Wattanachira, S., Pavasant, P., 2009. Characterization of brewery wastewater with spectrofluorometry analysis. *J. Environ. Manag.* 90, 1184–1190. <https://doi.org/10.1016/j.jenvman.2008.05.008>.
- Kajjumba, G.W., Fischer, D., Risso, L.A., Koury, D., Marti, E.J., 2021. Application of cerium and lanthanum coagulants in wastewater treatment—a comparative assessment to magnesium, aluminum, and iron coagulants. *Chem. Eng. J.* 426. <https://doi.org/10.1016/j.cej.2021.131268>.
- Kanagachandran, K., Jayaratne, R., 2006. Utilization potential of brewery waste water sludge as an organic fertilizer. *J. Inst. Brew.* 112, 92–96. <https://doi.org/10.1002/j.2050-0416.2006.tb00236.x>.
- Kato, K., Yoshioka, T., Okuwaki, A., 2000. Study for recycling of ceria-based glass polishing powder. *Ind. Eng. Chem. Res.* 39, 943–947. <https://doi.org/10.1021/ie990622x>.
- Kato, K., Murotani, N., Matsufuji, H., Saitoh, M., Tashiro, Y., 2006. Chemical removal and recovery of phosphorus from excess sludge in a sewage treatment plant. *Environ. Technol.* 27, 501–510. <https://doi.org/10.1080/09593332808618660>.
- Khuri, A.L., Mukhopadhyay, S., 2010. Response surface methodology. Wiley Interdiscip. Rev. Comput. Stat. 2, 128–149. <https://doi.org/10.1002/wics.73>.
- Kolthoff, I.M., Bhatia, B.B., 1960. Amperometric cerimetric titration of iron(II) with ferroin as indicator. *Microchem. J.* 4, 451–457. [https://doi.org/10.1016/0026-265X\(60\)90025-4](https://doi.org/10.1016/0026-265X(60)90025-4).
- Kragten, J., 1978. Hydroxide complexes of cerium(III). *Talanta* 25, 147–150. [https://doi.org/10.1016/0039-9140\(78\)80103-9](https://doi.org/10.1016/0039-9140(78)80103-9).
- Kuc, J., Thomas, M., Grochowalska, I., Kulczyk, R., Mikosz, G., Mrózek, F., Janik, D., Korta, J., Cwynar, K., 2022. Determination and removal of selected pharmaceuticals and total organic carbon from surface water by aluminum chlorohydrate coagulant. *Molecules* 27, 5740. <https://doi.org/10.3390/molecules27175740>.
- Lin, P., Yang, X., Werner, J.M., Honaker, R.Q., 2021. Application of Eh-pH diagrams on acid leaching systems for the recovery of REEs from bastnaesite, monazite and xenotime. *Metals (Basel)* 11, 734. <https://doi.org/10.3390/met11050734>.
- Liu, X., Byrne, R.H., 1997. Rare earth and yttrium phosphate solubilities in aqueous solution. *Geochim. Cosmochim. Acta* 61, 1625–1633. [https://doi.org/10.1016/S0016-7037\(97\)00037-9](https://doi.org/10.1016/S0016-7037(97)00037-9).
- Malhotra, H., Vandana, Sharma, S., Pandey, R., 2018. Phosphorus nutrition: plant growth in response to deficiency and excess. *Plant Nutrients and Abiotic Stress Tolerance*. Springer Singapore, Singapore, pp. 171–190. https://doi.org/10.1007/978-981-10-9044-8_7.
- Menon, M.P., James, J., Jackson, J.D., 1986. Complexation, solubilities and thermodynamic functions for cerium(III) fluoride-water system. *J. Radioanal. Nucl. Chem. Artic.* 102, 419–428. <https://doi.org/10.1007/BF02047916>.
- Meshram, P., Abhilash, 2020. Recovery and recycling of cerium from primary and secondary resources— a critical review. *Miner. Process. Extr. Metall. Rev.* 41, 279–310. <https://doi.org/10.1080/08827508.2019.1677647>.
- Mohammed, S.A.M., Abbas Shanshooh, H., 2009. Phosphorus removal from water and waste water by chemical precipitation using alum and calcium chloride. *Iraqi J. Chem. Pet. Eng.* 10 (2), 47–52.
- Ngatia, L., Taylor, R., 2019. Phosphorus eutrophication and mitigation strategies. *Phosphorus - Recovery and Recycling*. IntechOpen <https://doi.org/10.5772/intechopen.79173>.
- Parawira, W., Kudita, I., Nyandoroh, M.G., Zvauya, R., 2005. A study of industrial anaerobic treatment of opaque beer brewery wastewater in a tropical climate using a full-scale UASB reactor seeded with activated sludge. *Process Biochem.* 40, 593–599. <https://doi.org/10.1016/j.procbio.2004.01.036>.
- Poscher, A., Luidold, S., Schneideritsch, H., Antrekowitsch, H., 2014. Extraction of lanthanides from spent polishing agent. *Proceedings of the ERES2014-1st European Rare Earth Resources Conference*, pp. 209–222.
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb lake eutrophication is a success. *Environ. Sci. Technol.* 50, 8923–8929. <https://doi.org/10.1021/acs.est.6b02204>.
- Sinha, S., Abhilash, Meshram, P., Pandey, B.D., 2016. Metallurgical processes for the recovery and recycling of lanthanum from various resources—a review. *Hydrometallurgy* 160, 47–59. <https://doi.org/10.1016/j.hydromet.2015.12.004>.
- Smith, S., Takács, I., Murthy, S., Daigger, G.T., Szabó, A., 2008. Phosphate complexation model and its implications for chemical phosphorus removal. *Water Environ. Res.* 80, 428–438. <https://doi.org/10.1002/j.1554-7531.2008.tb00349.x>.
- Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2003. *Metcalf & Eddy, Inc. Wastewater Engineering: Treatment and Reuse*. McGraw-Hill, Boston.
- Thomas, M., Kozik, V., Barbusiński, K., Sochanik, A., Jampilek, J., Bąk, A., 2020. Potassium ferrate (VI) as the multifunctional agent in the treatment of landfill leachate. *Materials* 13, 5017. <https://doi.org/10.3390/ma13215017>.

- Thomas, M., Drzewicz, P., Więckol-Ryk, A., Panneerselvam, B., 2021. Influence of elevated temperature and pressure on treatment of landfill leachate by potassium Ferrate(VI). *Water Air Soil Pollut.* 232, 450. <https://doi.org/10.1007/s11270-021-05401-y>.
- Thomas, M., Drzewicz, P., Więckol-Ryk, A., Panneerselvam, B., 2022. Effectiveness of potassium ferrate (VI) as a green agent in the treatment and disinfection of carwash wastewater. *Environ. Sci. Pollut. Res.* 29, 8514–8524. <https://doi.org/10.1007/s11356-021-16278-z>.
- Verhuelsdonk, M., Glas, K., Parlar, H., 2021. Economic evaluation of the reuse of brewery wastewater. *J. Environ. Manag.* 281, 111804. <https://doi.org/10.1016/j.jenvman.2020.111804>.
- Vinothkumar, G., Lalitha, A.I., Suresh Babu, K., 2019. Cerium phosphate-cerium oxide heterogeneous composite nanozymes with enhanced peroxidase-like biomimetic activity for glucose and hydrogen peroxide sensing. *Inorg. Chem.* 58, 349–358. <https://doi.org/10.1021/acs.inorgchem.8b02423>.
- Wang, J., Song, J., Lu, J., Zhao, X., 2014. Comparison of three aluminum coagulants for phosphorus removal. *J. Water Resour. Prot.* 06, 902–908. <https://doi.org/10.4236/jwarp.2014.610085>.
- Wen, Q., Wu, Y., Zhao, L., Sun, Q., 2010. Production of electricity from the treatment of continuous brewery wastewater using a microbial fuel cell. *Fuel* 89, 1381–1385. <https://doi.org/10.1016/j.fuel.2009.11.004>.
- Ye, Z., Shen, Y., Ye, X., Zhang, Z., Chen, S., Shi, J., 2014. Phosphorus recovery from wastewater by struvite crystallization: property of aggregates. *J. Environ. Sci.* 26, 991–1000. [https://doi.org/10.1016/S1001-0742\(13\)60536-7](https://doi.org/10.1016/S1001-0742(13)60536-7).
- Ye, S., Jing, Y., Wang, Y., Fei, W., 2017. Recovery of rare earths from spent FCC catalysts by solvent extraction using saponified 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (EHEHPA). *J. Rare Earths* 35, 716–722. [https://doi.org/10.1016/S1002-0721\(17\)60968-2](https://doi.org/10.1016/S1002-0721(17)60968-2).
- Yu, H., Gu, G., 1996. Biomethanation of brewery wastewater using an anaerobic upflow blanket filter. *J. Clean. Prod.* 4, 219–223. [https://doi.org/10.1016/S0959-6526\(96\)00036-4](https://doi.org/10.1016/S0959-6526(96)00036-4).
- Żelazny, S., Świnder, H., Białecka, B., Jarosiński, A., 2017. Odzysk pierwiastków ziem rzadkich z popiołów lotnych. *Człł. Wytrącanie z roztworu. Przem. Chem.* 1, 102–108. <https://doi.org/10.15199/62.2017.11.14>.
- Zhang, W., Rezaee, M., Bhagavatula, A., Li, Y., Groppo, J., Honaker, R., 2015. A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. *Int.J.Coal Prep.Util.* 35, 295–330. <https://doi.org/10.1080/19392699.2015.1033097>.
- Zhao, J., Li, B., Yang, C., Rao, X., 2010. Application of Ce(IV) in industrial wastewater treatment. *J. Rare Earths* 28, 37–39. [https://doi.org/10.1016/S1002-0721\(10\)60340-7](https://doi.org/10.1016/S1002-0721(10)60340-7).
- Zhao, Z., Qiu, Z., Yang, J., Ma, B., Li, Z., Lu, S., Xu, Y., Cao, L., Zhang, W., 2020. Recovery of rare earth element cerium from spent automotive exhaust catalysts using a novel method. *Waste Biomass Valoriz.* 11, 4967–4976. <https://doi.org/10.1007/s12649-019-00783-x>.

Article

Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant

Paweł Lejwoda ¹, Barbara Białecka ², Krzysztof Barbusiński ³ and Maciej Thomas ^{4,*}

¹ Department of Energy Saving and Air Protection, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; plejwoda@gig.eu

² Department of Environmental Monitoring, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; bbialecka@gig.eu

³ Department of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland; krzysztof.barbusinski@polsl.pl

⁴ Faculty of Environmental Engineering and Energy, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

* Correspondence: maciej.thomas@pk.edu.pl

Abstract: Due to the high cost and limited sources of cerium coagulants, it is extremely important to take measures to recycle this raw material. This paper presents the new possibility of recovering cerium(III) chloride, cerium(III) sulphate, cerium(IV) sulphate, and potentially phosphate from sewage sludge (101.5 g/kg Ce and 22.2 g/kg total P) through a brewery wastewater treatment process using recycled CeCl_3 as a coagulant. In order to recover the Ce and P, the sludge was subjected to extraction using an HCl solution. Optimal process conditions were determined by means of central composite design and response surface methodology (CCD/RSM) for three input parameters (HCl mass, reaction time, and extractant volume). Under optimal conditions (0.35 g HCl per 1 g of sludge, 40 min reaction time, extractant volume of 25 mL per 1 g of sludge), the highest efficiency obtained was 99.6% and 97.5% for Ce and P, respectively. Cerium(III) oxalate as $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ was precipitated from the obtained solution using $\text{H}_2\text{C}_2\text{O}_4$ (99.97%) and decomposed into CeO_2 (at 350 °C), which was afterwards subjected to a reaction with HCl (30%, m/m) and H_2O_2 (30%, m/m), which led to the crystallisation of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ with a purity of 98.6% and a yield of 97.0%. The obtained CeO_2 was also subjected to a reaction with H_2SO_4 (96%, m/m) and H_2O_2 (30%, m/m), which produced $\text{Ce}_2(\text{SO}_4)_3$ with a yield of 97.4%. The CeO_2 was also subjected to a reaction with only H_2SO_4 (96%, m/m), which produced $\text{Ce}(\text{SO}_4)_2$ with a yield of 98.3%. The filtrate obtained after filtering the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ contained 570 mg/L of P, which enabled its use as a source of phosphorus compounds. The presented processes of Ce and potentially P recovery from sewage sludge originating from brewery wastewater contribute to the idea of a circular economy.



Citation: Lejwoda, P.; Białecka, B.; Barbusiński, K.; Thomas, M. Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant. *Materials* **2024**, *17*, 938. <https://doi.org/10.3390/ma17040938>

Academic Editor: Andrea Petrella

Received: 8 January 2024

Revised: 8 February 2024

Accepted: 13 February 2024

Published: 17 February 2024

Keywords: brewery wastewater; response surface methodology; central composite design; sewage sludge; cerium coagulants



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The decreasing supply of potable water in the world is a consequence of numerous negative factors, including the increasing population, developing industry, and uncontrolled pollutant emissions, which, in the near future, may result in decreased access to potable water, droughts, food shortages, and climate migration on a global scale. Therefore, action aimed at limiting pollutant emissions to the water environment and restoring the quality of polluted water is extremely important. In developed countries, the problem of wastewater emissions to the environment was minimised by transporting waste to treatment plants using elaborate sewage systems or vacuum trucks. As a result of the

processes conducted at waste treatment plants, it is possible to remove physical, chemical, and biological pollutants and restore the original quality of water to a state where it is free of substances harmful to living beings. The number and types of stages forming a waste treatment process depend on multiple factors, some of which include the quantity and composition of the waste, the types and concentrations of pollutants in the waste flowing into the treatment plant, and the required level of waste treatment. While municipal wastewater is characterised by a repeatable composition, industrial waste is considerably varied in terms of the type and concentration of pollutants, depending on the type of activity that generates it, the technological advancement of the industrial plant, the application of processes for minimising water consumption, the presence of a local treatment plant providing preliminary waste treatment, and so on. Heavy industry engaged in metal ore processing generates waste characterised by an increased concentration of heavy metals such as, e.g., Cd, Co, Ni, Cu, and V [1]. Electroplating plants, depending on the types of coating produced, generate waste containing, e.g., Ni, Cr, Pb, Cd, and Sn [2,3], as well as cyanides (CN^-), detergents (anionic, non-ionic, and cationic), etc. On the other hand, waste originating from the tanning industry is characterised by high values of COD and total nitrogen, as well as increased P and Cr contents [4–6]. Unlike waste originating from heavy industry, wastewater from the food industry, as well as domestic sewage, is characterised by increased contents of biogenic elements (C, N, P, and S), whose presence in the water environment contributes to eutrophication; therefore, these pollutants need to be removed with high efficiency. In the case of food industry wastewater originating from breweries [7–9], dairies [10,11], and sugar factories [12,13], the type of pollutants is similar to those found in domestic sewage, though their concentration is much greater. In the case of treatment plants where the primary pollutant stream includes domestic sewage and food industry wastewater, the use of biological processes, such as denitrification, and chemical processes, like coagulation, is often sufficient to treat the waste. In such situations, the treated waste typically fulfils the requirements defined in legal regulations concerning the maximum concentrations of pollutants for treated waste introduced into municipal sewage systems or into the water and soil.

An element linking the various wastewater treatment technologies is the generation of sewage sludge with a complex composition containing a significant amount of phosphorus compounds, which are an important component of fertilisers used to intensify agricultural production. According to various estimations, the extractive resources of this element will be depleted over the next 50–280 years [14,15], while the location of the richest deposits in just a few countries raises the risk of significant price fluctuations on the market as well as limited availability due to the complex political and economic situation in the future, which has currently made sewage sludge an interesting source of this element that also exhibits a high processing potential, which has made it the subject of numerous studies [16,17]. Sewage sludge is generated, e.g., as a result of coagulation processes that occur after the addition of an appropriate reactant (coagulant) to the treated waste. Commonly applied coagulants include Fe^{3+} and Al^{3+} compounds that undergo hydrolysis after their addition to the wastewater, generating hydrated metal hydroxides with a developed active surface that are capable of adsorbing pollutants or partially binding them as a result of direct chemical reactions.

Ferric chloride (FeCl_3) was applied in prior research [18], where it was concluded that the most effective (97%) phosphorus removal occurred at a pH of 6.2. The other work [19] applied FeCl_3 with added tannic acid ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$) to improve phosphorus removal from wastewater. As a result of the tests conducted at a sewage pH of 7.5, up to 95% of the phosphorus was removed, which was bound in a complex of tannic acid—Fe—P and ferric hydroxyphosphate ($\text{Fe}_x(\text{OH})_y\text{PO}_z$). The use of aluminium coagulants such as aluminium chloride (AlCl_3), aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$), or polyaluminium chloride (PAC, $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$) makes it possible to remove up to 74.9% of phosphorus at a pH range of 6.5–8.5, up to 62% at a pH range of 5–9, and even up to 80% at a pH range of 6–8, respectively [20].

Another method for removing phosphorus from wastewater is to precipitate it in the form of poorly soluble salts such as struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), and amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$). The precipitation processes occur at high concentrations of NH_4^+ , Ca^{2+} , and PO_4^{3-} ions and in a pH range of 7.0–10.7. Literature data indicate that the struvite precipitation yield can reach 97%, though it is strongly dependent on the content ratios of P to Mg and P to N. The recovery of phosphorus directly from sewage sludge and eluates is interesting from a scientific and practical perspective, but it generates the risk of introducing pathogens and hazardous organic substances accumulated in the precipitates into the environment. In this case, the sludge must be subjected to hygienisation by applying, e.g., $\text{Ca}(\text{OH})_2$, CaO , CaO_2 , or $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ [21]. A considerable disadvantage of this type of solution is the high cost of the hygienisation processes [22,23].

In the case of more rarely used cerium coagulants that contain Ce^{3+} ions for wastewater treatment (primarily the precipitation of PO_4^{3-}), the pollutant removal process exhibits the highest efficiency at a pH of 7.0–8.5. The removal of PO_4^{3-} occurs primarily as a result of the direct binding of Ce^{3+} ions with PO_4^{3-} ions, generating a CePO_4 precipitate over the course of Reaction (1). Furthermore, the Ce^{3+} cations bind anions such as F^- , OH^- , CO_3^{2-} , and $\text{C}_2\text{O}_4^{2-}$ as a result of chemical Reactions (2)–(5) in the form of poorly soluble salts (1)–(5), whose solubility product constants are presented in Table 1.

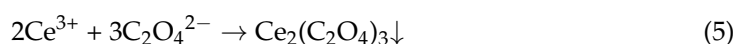
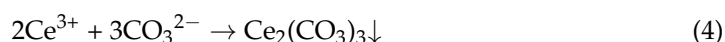


Table 1. Solubility product constants (K_{SP}) of selected cerium compounds.

Compound	Solubility Product Constant, K_{SP}	Source
CePO_4	1.00×10^{-23}	[24]
	$10^{-24.3}$	[25]
	$10^{-26.27}$	[26]
$\text{Ce}(\text{OH})_3$	1.6×10^{-20}	[24]
	10^{-21}	[27]
CeF_3	8.00×10^{-16}	[24]
	1.4×10^{-18}	[28]
$\text{Ce}_2(\text{CO}_3)_3$	$10^{-21.80}$	[29]
$\text{Ce}_2(\text{C}_2\text{O}_4)_3$	1.84×10^{-28}	[30]
	5.9×10^{-30}	[31]

When cerium salts are used, the phosphorus concentration in the treated sewage is lower, and the cost of disposal of the resulting sewage sludge is lower (due to the smaller volume of the resulting sludge) than when using iron or aluminium coagulants [32]. The disadvantage of cerium coagulants is their higher purchase cost compared to substances based on iron and aluminium compounds. This fact prompts the search for alternative sources of cerium compounds that could reduce the cost of their purchase and effectively compete with commonly used coagulants.

Research on brewery wastewater treatment using cerium(III) chloride revealed that the process produces sludge with a high content of cerium (101.5 g/kg) and phosphorus (22.2 g/kg), bound primarily in the form of CePO_4 [9], which suggests the possibility of recovering these elements from the sewage sludge.

This paper presents a processing concept for sewage sludge subjected to extraction using an HCl solution in order to recover cerium and phosphorus and apply them for the preparation of useful products in subsequent stages. The purpose of the tests was to conduct an extraction process and to recover cerium and phosphorus with a high yield, which, in combination with wastewater treatment performed using a cerium(III) chloride solution as a coagulant, could close the cerium circulation within the process. The research presents a new concept of coagulant recovery and complements the gap in research on the recovery of cerium compounds from sewage sludge and fits into the idea of a circular economy.

2. Materials and Methods

2.1. Materials

The material subjected to testing was sewage sludge obtained by brewery wastewater treatment using a cerium(III) chloride (recovered from spent polishing powder) solution as a coagulant, per the brewery wastewater treatment method described in [9]. Before analysis, the sludge was dried at ambient temperature (20 ± 1 °C) to a solid mass (Figure 1).

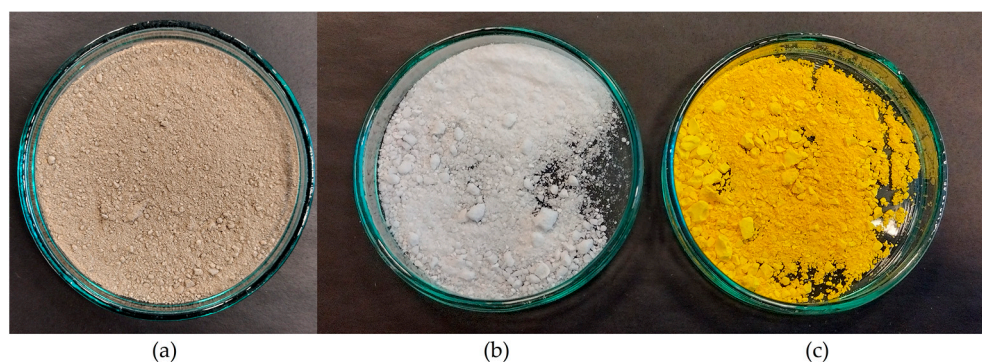


Figure 1. Sewage sludge dried at ambient temperature (a) and obtained $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (b) and $\text{Ce}(\text{SO}_4)_2$ (c) salts.

The chemical composition of the sewage sludge after mineralisation in aqua regia using a standard laboratory method ($\text{HCl}:\text{HNO}_3$, 3:1, v/v) is presented in Table 2.

Table 2. Selected physicochemical parameters of the sludge used in the study.

Parameter	Unit	Result $\pm$ Measurement Uncertainty
Cerium (Ce)	g/kg	101.5 ± 10
Total Phosphorus (P)	g/kg	22.2 ± 2.2
Sodium (Na)	g/kg	3.65 ± 0.37
Magnesium (Mg)	g/kg	1.05 ± 0.11
Calcium (Ca)	g/kg	21.3 ± 2.1
Iron (Fe)	g/kg	3.46 ± 0.35
Manganese (Mn)	g/kg	0.10 ± 0.02
Aluminium (Al)	g/kg	1.23 ± 0.12
Barium (Ba)	g/kg	0.185 ± 0.037
Strontium (Sr)	g/kg	0.084 ± 0.021
Zinc (Zn)	g/kg	0.417 ± 0.083

Nitric acid (60%), hydrochloric acid (30%) (Suprapur[®], Merck, Darmstadt, Germany), sulphuric acid (96%) (analytically pure, Chempur[®], Piekary Śląskie, Poland), 30% hydrogen peroxide (analytically pure, Chempur[®], Piekary Śląskie, Poland), sodium hydroxide (analytically pure, Chempur[®], Piekary Śląskie, Poland), oxalic acid (analytically pure, Warchem Ltd., Zakręt, Poland), a certified multielement standard solution for inductively coupled plasma (ICP) with a concentration of each rare earth element of 50 mg/L (Sigma Aldrich[®], Saint Louis, MI, USA), and certified multielement standard solutions for ICP

with a metal concentration of 10 mg/L and 100 mg/L (AccuStandards[®], New Haven, CT, USA) were also used in the study. A certified multielement anion standard solution for ion chromatography (IC) (AccuStandards[®], New Haven, CT, USA) and deionised water with an electrical conductivity of under 0.05 $\mu\text{S}/\text{cm}$ (Direct-Q3 UV, Millipore[®], Burlington, VT, USA) were used as well.

2.2. Analytical Methods

The metal and non-metal concentration determination in the water solutions and the mineralised sewage sludge was performed according to standard [33] by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 5300DV, Perkin Elmer[®], Waltham, MA, USA). Inductively coupled plasma mass spectrometry (ICP-MS) (NexION 300S, Perkin Elmer[®], Waltham, MA, USA) was used to determine cerium content in the water solutions. The measurement was performed according to standard [34]. The metal and non-metal content determination uncertainty was 10%, 15%, 20%, and 25%, depending on the analysed element concentration, with a coverage factor of 2 and a significance level of 95%. The chloride (Cl^-) determination was performed by ion chromatography according to [35] (DIONEX ICS 5000, Thermo Fisher Scientific[®], Waltham, MA, USA). The pH measurement was performed per standard [36] using the Inolab pH/ION/Cond 750 multi-parameter meter (WTW[®], Weilheim, Germany) with a measurement accuracy of ± 0.1 pH.

Phase identification was performed by powder X-ray diffraction (DSH) in Bragg-Brentano geometry using a Bruker D8 DISCOVER diffractometer (Bruker[®], Billerica, MA, USA), $\text{CuK}\alpha$ radiation, a Ni filter, and a LYNXEYE XE detector. The mineral composition was determined and calculated based on standards licensed in PDF-4+2022 RDB ICDD (International Centre for Diffraction Data), ICSD (Inorganic Crystal Structure Database), and NIST (National Institute of Standards and Technology). DIFFRAC v.4.2, TOPAS v.4.2, and Bruker AXS software (v.6.0) were applied for registration and diagnostics. The Rietveld methodology was used for the quantitative calculations of crystalline phases and the amorphous substance.

Grain surface morphology and chemical composition in micro-areas were analysed by scanning electron microscopy (SEM) and X-ray energy dispersion spectroscopy (EDS) using an SU3500 SEM microscope (Hitachi[®], Tokyo, Japan) working in conjunction with an UltraDry EDS Detector (Thermo Fisher Scientific[®], Waltham, MA, USA) under the following conditions: acceleration voltage –15 keV, detector—BSE, scanning time –40 s, magnification $\times 1000$ – $\times 3000$. The images were taken after spraying the sample with gold.

2.3. Extraction of Cerium and Phosphorus

Central composite design (CCD) and response surface methodology (RSM) were applied to determine the optimal conditions for cerium and phosphorus extraction from the sewage sludge [37–40]. The optimal input parameters were time (min), the liquid/solid ratio (volume/mass), and the mass of HCl as 100% HCl (mg). The input parameters and the quantities of Ce and P are presented in Table 3.

Table 3. Empirical conditions for CCD/RSM and the results (Ce and P) for sewage sludge (HCl 35.0–405.0 mg, liquid:solid mass ratio (7.96–92.0:1), time 6.36–73.6 min); *—centre of the plan.

Run	Experimental Conditions			Experimental Results	
	Liquid:Solid Ratio, x_1	Time (min), x_2	HCl, mg, x_3	P, mg/g	Ce ³⁺ , mg/g
1	25.0	20.0	110	14.24 ± 2.14	67.95 ± 10.19
2	25.0	20.0	330	22.73 ± 3.41	104.5 ± 15.68
3	25.0	60.0	110	14.27 ± 2.14	67.86 ± 10.18
4	25.0	60.0	330	21.80 ± 3.27	101.6 ± 15.24
5	75.0	20.0	110	15.09 ± 2.26	71.73 ± 10.76
6	75.0	20.0	330	20.48 ± 3.07	98.54 ± 14.78
7	75.0	60.0	110	15.54 ± 2.33	72.23 ± 10.84
8	75.0	60.0	330	21.76 ± 3.26	102.6 ± 15.39
9	7.96	40.0	220	18.23 ± 2.73	91.89 ± 13.78
10	92.0	40.0	220	19.91 ± 2.99	91.44 ± 13.72
11	50.0	6.36	220	18.99 ± 2.85	93.18 ± 13.98
12	50.0	73.6	220	19.58 ± 2.94	93.35 ± 14.00
13	50.0	40.0	35	1.014 ± 0.152	11.17 ± 1.68
14	50.0	40.0	405	21.84 ± 3.28	101.4 ± 15.22
15 *	50.0	40.0	220	19.67 ± 2.95	97.03 ± 14.55
16 *	50.0	40.0	220	20.96 ± 3.14	101.1 ± 15.16
17 *	50.0	40.0	220	21.23 ± 3.18	103.2 ± 15.47
18 *	50.0	40.0	220	21.42 ± 3.21	105.3 ± 15.80
19 *	50.0	40.0	220	19.45 ± 2.92	104.8 ± 15.72
20 *	50.0	40.0	220	18.93 ± 2.84	102.2 ± 15.33

2.4. Precipitation of Solid Cerium(III) Compounds

The extract was obtained under the conditions determined in the optimisation process, i.e., time of 40 min, liquid:solid ratio of 25:1, 330 mg HCl. In order to precipitate $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ from the acidic post-extraction solution with a pH of 0.3, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was added, and then the pH was increased to 1.8 with the addition of NaOH solution [41]. The solution was mixed at 250 rpm for 30 min and set aside for 12 h to obtain a coarse crystalline precipitate [42]. The obtained $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ was filtered through a membrane filter (hydrophilic PTFE) with a pore size of 0.45 μm and washed with water to remove the solution residues containing undesired ions. The material was dried at a temperature of $105 \pm 1^\circ\text{C}$ to a solid mass, weighed, and decomposed into CeO_2 in a muffle furnace at a temperature of $350 \pm 5^\circ\text{C}$ [43]. The obtained CeO_2 was weighed and subjected to a reaction with HCl (30% m/m) and H_2O_2 (30% m/m), mixed and heated to a temperature of about 90°C [44], after which the solution was filtered, subjected to crystallisation, and dried at $70 \pm 1^\circ\text{C}$ (process no. 1). The second process (process no. 2) involved a reaction of the CeO_2 with excess H_2SO_4 (96% m/m) to obtain $\text{Ce}_2(\text{SO}_4)_3$. The reactants were mixed and heated at a temperature of $100 \pm 1^\circ\text{C}$ for an hour, and after heating was concluded, they were diluted with deionised water, and the Ce(IV) was reduced to Ce(III) by the addition of H_2O_2 (30%, m/m). The obtained mixture was filtered through a membrane filter (hydrophilic PTFE) with a pore size of 0.45 μm , evaporated, crystallised, and dried at a temperature of $300 \pm 5^\circ\text{C}$.

The third process (process no. 3) involved a reaction of the CeO_2 with excess H_2SO_4 (96% m/m) to obtain $\text{Ce}(\text{SO}_4)_2$. The reactants were mixed and heated at a temperature of $100 \pm 1^\circ\text{C}$ for an hour, after which they were heated in a muffle furnace at $300 \pm 5^\circ\text{C}$, also for an hour, to strip the excess H_2SO_4 .

2.5. Removal of Metals from a Phosphorus-Rich Solution

The removal of metals (Al, Zn, Fe, Cu, and Mn) present in the acidic solution remaining after filtering the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ was conducted by using precipitants such as sodium trithiocarbonate (Na_2CS_3), trimercapto-s-triazine, trisodium salt (TMT),

and dimethyldithiocarbamate (DMDTC) after the prior increase of the solution pH to 9.5 ± 0.1 [3,45,46]. The obtained solutions were filtered through a PTFE membrane filter with a pore size of $0.45 \mu\text{m}$ to remove the colloidal sediments and analysed by ICP-OES.

3. Results and Discussion

3.1. Extraction of Cerium and Phosphate from Sewage Sludge

The statistical analysis performed (in Tables S1–S4 in Supplementary Materials) showed the lack of significance of some of the independent variables ($p > 0.05$). Further analysis was carried out after excluding insignificant linear–linear interaction, quadratic time, and quadratic liquid:solid ratio effects. Following the optimisation of the Ce and P recovery from sewage sludge containing 10.15% Ce and 2.22% P, it was revealed that the most advantageous process conditions required the application of 350 mg of HCl (as 100% HCl) per 1 g of sludge, an extractant volume of 25 mL, and a reaction time of 40 min. Under the adopted optimal conditions determined by the model, 99.6% of Ce and 97.5% of P were extracted. CCD/RSM was applied in the optimisation process, where the calculated coefficient of determination (R^2) after reducing the number of statistically insignificant variables was 0.923, and the adjusted R^2 (R^2_{adj}) was 0.902 (for the cerium extraction optimisation model), which indicated a very good fit of the model to the experimental data. On the other hand, the coefficient of determination (R^2) calculated for the phosphorus extraction optimisation model was 0.896, while the adjusted R^2 (R^2_{adj}) was 0.868, which indicated a good fit of the data included in the model to the experimental data. It is typically assumed that if $0 < R^2 \leq 0.5$, the fit of the model is unsatisfactory; if $0.5 < R^2 \leq 0.6$, the fit of the model is poor; if $0.6 < R^2 \leq 0.8$, the fit of the model is satisfactory; if $0.8 < R^2 \leq 0.9$, the fit of the model is good; and if $0.9 < R^2 \leq 1$, the fit of the model is very good [47]. Pareto charts (Figure 2) present the standardised effect estimators, which were grouped according to their absolute values. The red line in the chart indicates the significance threshold $p = 0.05$, under which the analysed variables are insignificant. The evaluation of the effects and the results of the ANOVA analysis for Ce^{3+} and P (mg/g) are presented in Tables 4–7.

Table 4. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, Ce^{3+} ; $R^2 = 0.923$; $R^2_{\text{adj}} = 0.902$, MS = 48.844.

Parameter	Effect	Standard Error	t(15)	p	CI (−95%)	CI (+95%)	Factor	Standard Error	CI (−95%)	CI (+95%)
Constant value	99.022	1.999	49.547	<0.001	94.762	103.281	99.022	1.999	94.762	103.281
(1) liquid:solid (L) *	0.347	3.782	0.092	0.928	−7.715	8.408	0.173	1.891	−3.858	4.204
(2) time (L)	0.270	3.782	0.071	0.944	−7.792	8.332	0.135	1.891	−3.896	4.166
(3) mg HCl (L)	40.904	3.782	10.814	<0.001	32.842	48.966	20.452	1.891	16.421	24.483
mg HCl (Q)	−28.896	3.649	−7.919	<0.001	−36.674	−21.119	−14.448	1.824	−18.337	−10.560

*—mass ratio, statistically significant if $p < 0.05$.

Table 5. ANOVA analysis results for Ce^{3+} extraction.

Parameter	SS	df	MS	F	p
(1) liquid:solid (L) *	0.410	1	0.410	0.008	0.928
(2) time (L)	0.248	1	0.248	0.005	0.944
(3) mg HCl (L)	5712.425	1	5712.425	116.952	<0.001
mg HCl (Q)	3063.310	1	3063.310	62.716	<0.001
Error	732.661	15	48.844		
Total sum of square	9509.054	19			

*—mass ratio, ANOVA model coefficients after excluding insignificant linear–linear interaction, quadratic time, and quadratic liquid:solid ratio effects, statistically significant if $p < 0.05$.

Table 6. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, total P; $R^2 = 0.896$; $R^2_{adj} = 0.868$, MS = 3.081.

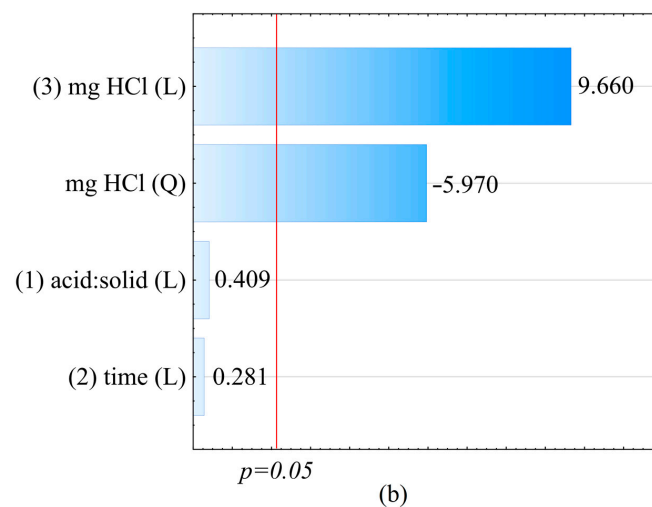
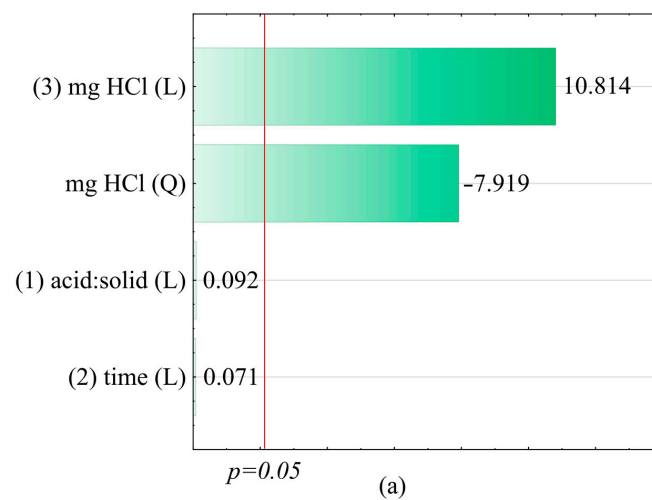
Parameter	Effect	Standard Error	t(15)	p	CI (−95%)	CI (+95%)	Factor	Standard Error	CI (−95%)	CI (+95%)
Constant value	20.226	0.502	40.295	<0.001	19.156	21.296	20.226	0.502	19.156	21.296
(1) liquid:solid (L) *	0.389	0.950	0.409	0.688	−1.636	2.413	0.194	0.475	−0.818	1.207
(2) time (L)	0.267	0.950	0.281	0.783	−1.758	2.291	0.133	0.475	−0.879	1.146
(3) mg HCl (L)	9.177	0.950	9.660	<0.001	7.152	11.202	4.589	0.475	3.576	5.601
mg HCl (Q)	−5.471	0.916	−5.970	<0.001	−7.424	−3.518	−2.736	0.458	−3.712	−1.759

*—mass ratio, statistically significant if $p < 0.05$.

Table 7. ANOVA analysis results for total P extraction.

Parameter	SS	df	MS	F	p
(1) liquid:solid (L) *	0.515	1	0.515	0.167	0.688
(2) time (L)	0.243	1	0.243	0.079	0.783
(3) mg HCl (L)	287.540	1	287.540	93.325	<0.001
mg HCl (Q)	109.810	1	109.810	35.640	<0.001
Error	46.216	15	3.081		
Total sum of square	444.324	19			

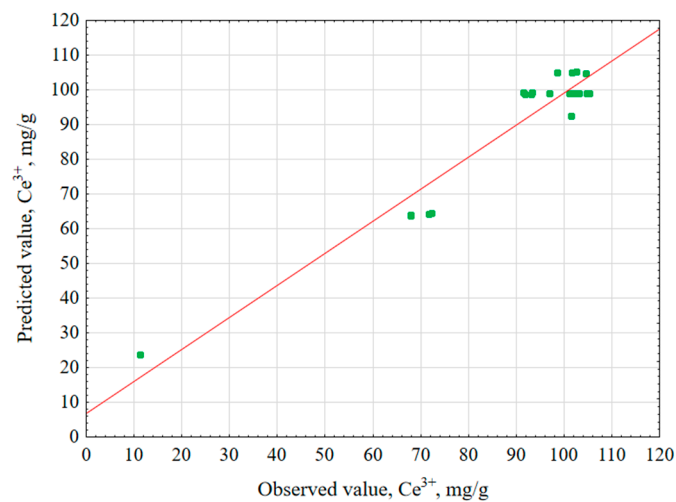
*—mass ratio, ANOVA model coefficients after excluding insignificant linear–linear interaction, quadratic time, and quadratic liquid:solid ratio effects, statistically significant if $p < 0.05$.

**Figure 2.** Pareto charts—absolute standardised assessment values for the effects (mg HCl (L), mg HCl (Q), acid:solid (L), and time (L)) for (a) Ce^{3+} and (b) total P.

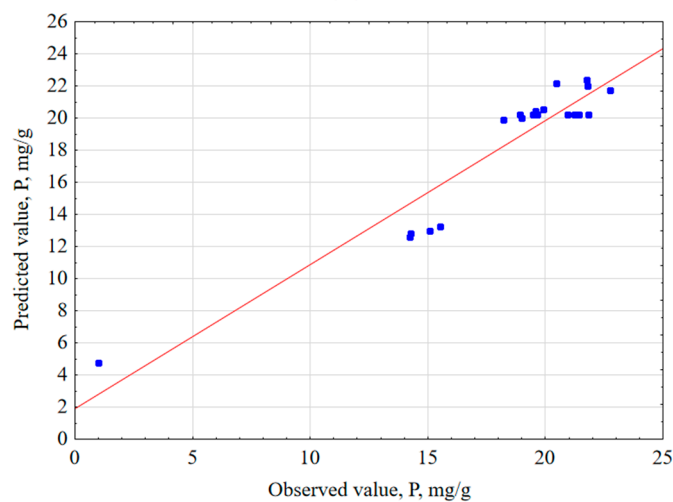
Second-order Equations (6) and (7) were determined based on the obtained mathematical models, describing the predicted Ce^{3+} and total P concentrations after extraction. The predicted concentration values were compared to the values obtained experimentally and compiled in Figure 3.

$$\text{Ce}^{3+} \text{ conc.} = -0.0217 + 0.0069 \times (\text{acid:solid}) + 0.7113 \times (\text{mg HCl}) - 0.0012 \times (\text{mg HCl})^2 \quad (6)$$

$$\text{total P conc.} = -0.2819 + 0.0077 \times (\text{acid:solid}) + 0.1412 \times (\text{mg HCl}) - 0.0002 \times (\text{mg HCl})^2 \quad (7)$$



(a)



(b)

Figure 3. Predicted values vs. observed values for (a) Ce^{3+} ($R^2 = 0.923$, $R^2_{\text{adj}} = 0.902$) and (b) total P ($R^2 = 0.896$, $R^2_{\text{adj}} = 0.868$) extraction experiments.

A graphical interpretation of the response surfaces is depicted in the 3D contour plot in Figure 4.

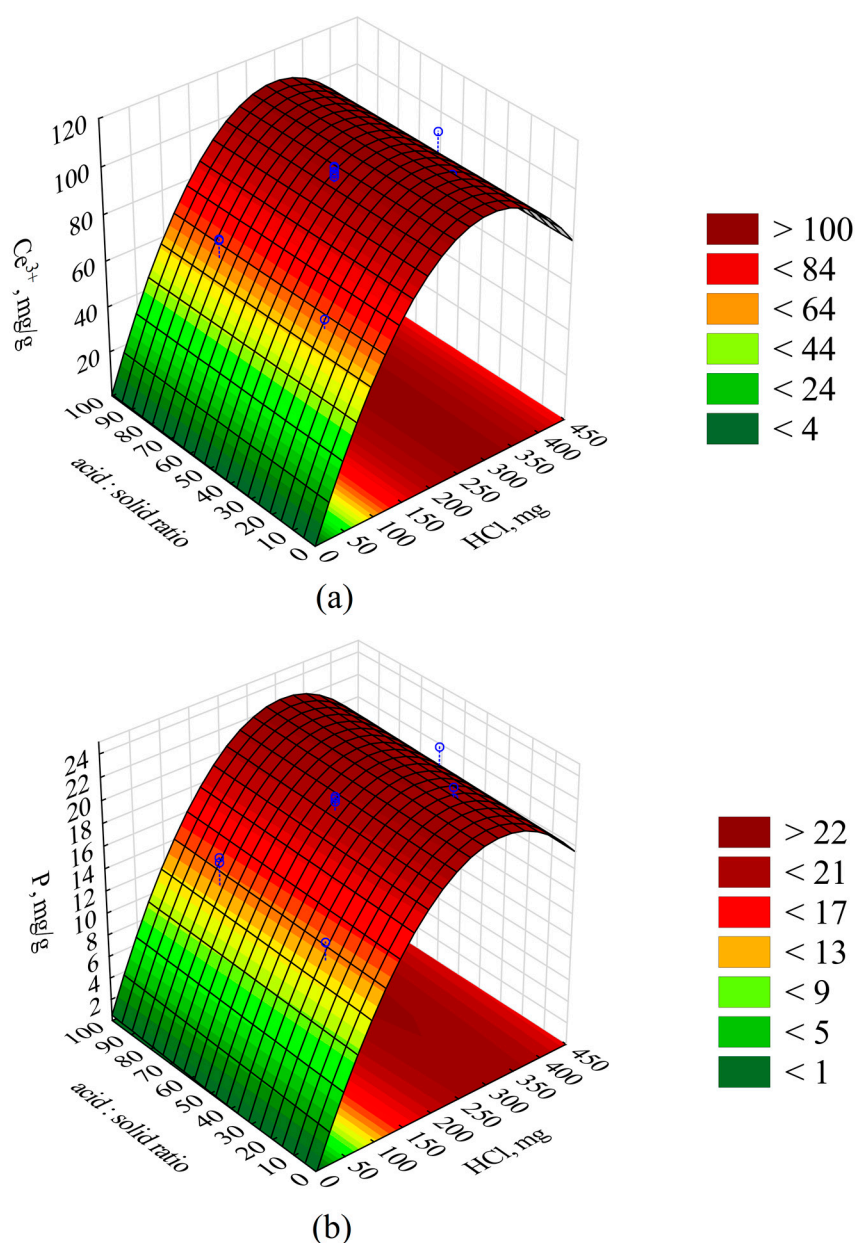


Figure 4. Response surfaces presenting the (a) Ce and (b) P yield depending on the quantity of the applied HCl and the acid:sludge volume ratio. Blue circles—measured points.

Improving the fit (R^2 and R^2_{adj}) of both extraction models described would probably be possible by deriving a higher-order equation. This would require taking into account higher-order effects (e.g., cubic effects) [48], which would probably allow for flattening the response surfaces presented in Figure 4 for the mass of HCl used above 300 mg and obtaining the predicted concentrations of Ce and P at a similar level to the measured values. The model, including quadratic effects, causes the surface to curve downward, suggesting a decrease in Ce and P recovery, which deviates from the measured values. As a result of the conducted analysis, it was concluded that the parameter with the greatest influence on the Ce and P extraction efficiency ($p < 0.05$) is the mass of the HCl applied in the process, and a limit value was defined, above which the leaching of cerium and phosphorus is the greatest. From a statistical perspective, the process efficiency was not significantly dependent on the volume ratio of the reaction solution to the mass of the sludge, but the ratio could significantly influence processes at an industrial scale, such as the pumping of the reaction mixture or its transport via pipelines, due to, e.g., the density of the mixture, the resistance

of flow, etc. The process duration had no significant influence on the degree of cerium and phosphorus leaching. The high degree of extraction of cerium and phosphorus makes the obtained solution a perfect raw material for the recovery of these elements.

3.2. Preparation of Cerium Compounds

An extract with a pH of 0.30 ± 0.01 was obtained following the extraction of cerium (Ce) and phosphorus (P) using an HCl solution under optimal conditions. Table 8 presents the selected physicochemical parameters of the obtained extract.

Table 8. Selected chemical parameters of the extract obtained after acid leaching.

Parameter	Unit	Result $\pm$ Measurement Uncertainty
pH	-	0.30 ± 0.01
Cerium (Ce)	mg/L	3763 ± 376
Total Phosphorus (P)	mg/L	790 ± 79
Sodium (Na)	mg/L	149 ± 15
Magnesium (Mg)	mg/L	36.4 ± 3.6
Calcium (Ca)	mg/L	774 ± 77
Iron (Fe)	mg/L	96.7 ± 9.7
Aluminium (Al)	mg/L	43.6 ± 4.4
Zinc (Zn)	mg/L	14.3 ± 1.4

The extract contained 3763 mg/L of Ce, which was precipitated after adding an $\text{H}_2\text{C}_2\text{O}_4$ solution and increasing the pH to 1.8. The Ce concentration determined in the filtrate (1.10 mg/L) revealed that the precipitation process exhibited a yield of 99.97%. A poorly soluble $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ precipitate was obtained following the precipitation reaction, which was heated in a muffle furnace at a temperature of $350 \pm 5^\circ\text{C}$ in order to obtain CeO_2 . The low decomposition temperature ($350 \pm 5^\circ\text{C}$) was selected to ensure that the obtained CeO_2 would be characterised by a small particle size and thereby a greater reactivity towards acids. The crystalline composition of the obtained compound was analysed by XRD as described in the Analytical Methods section and is presented in Table 9, whereas a diffractogram of this compound is depicted in Figure 5.

Table 9. Chemical composition of the substance after $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ digestion (XRD analysis).

Parameter	Unit	Result $\pm$ Measurement Uncertainty
CeO_2	%	74.0 ± 1.0
$\text{Ce}(\text{CO}_3)_2$	%	1.0 ± 1.0
Amorphous substance	%	24.5 ± 0.5

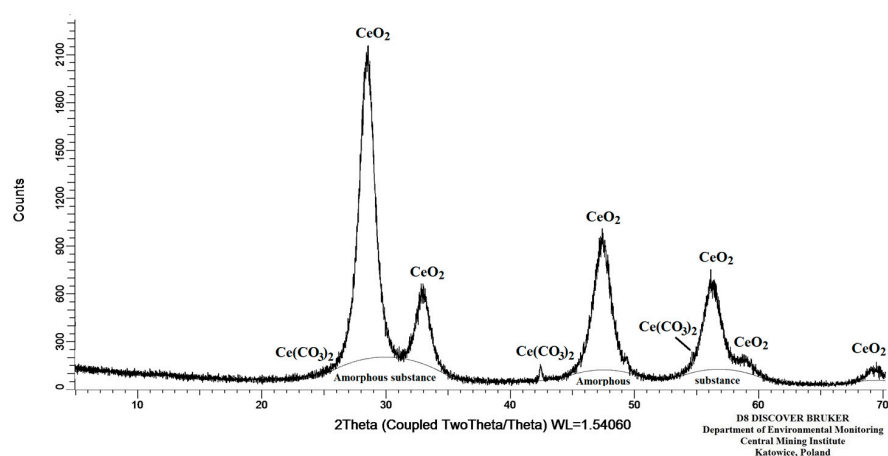


Figure 5. Diffraction pattern of the substance after $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ digestion.

At the same time, the test results revealed explicitly that the primary component of the obtained material was CeO_2 (74.0%), while 24.5% was an amorphous phase, which could also be CeO_2 [43,49,50]. The performed calculations demonstrated that the mass of the obtained oxide constituted 99.5% of the theoretical mass.

Three independent processes were conducted to obtain cerium salts. The first process yielded $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ by mixing CeO_2 with excess HCl (30%, m/m) and H_2O_2 (30%, m/m) [9,44], and heating the solution to a temperature of about $90 \pm 1^\circ\text{C}$, followed by evaporation and crystallisation (Figure 1). Under these conditions, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was obtained with a yield of 97.0%. A sample of the obtained substance was subjected to chemical analysis, which revealed that Ce constituted 98.6% of the analysed cations (30 elements).

The second process yielded $\text{Ce}_2(\text{SO}_4)_3$ by adding excess concentrated H_2SO_4 (96%, m/m) to the CeO_2 , mixing and heating at a temperature of $100 \pm 1^\circ\text{C}$ for 60 ± 1 min, followed by diluting with deionised water and reducing the Ce(IV) to Ce(III) by adding H_2O_2 (30%, m/m) (Figure 1). The obtained mixture was filtered through a membrane filter (hydrophilic PTFE) with a pore size of $0.45 \mu\text{m}$, evaporated, crystallised, and dried at a temperature of $300 \pm 5^\circ\text{C}$. In this case, $\text{Ce}_2(\text{SO}_4)_3$ was obtained with a yield of 97.4%, while a chemical analysis confirmed that Ce constituted 95.9% of all the analysed cations (30 elements) in the $\text{Ce}_2(\text{SO}_4)_3$ sample.

The third process yielded $\text{Ce}(\text{SO}_4)_2$ by subjecting the obtained CeO_2 to a reaction with excess concentrated H_2SO_4 (96%, m/m) relative to the required stoichiometric quantity and heating at a temperature of $100 \pm 1^\circ\text{C}$, followed by heating in a muffle furnace at a temperature of $300 \pm 5^\circ\text{C}$. The process exhibited a $\text{Ce}(\text{SO}_4)_2$ yield of 98.3%. The conducted chemical analysis of the obtained compound confirmed that Ce constituted 97.5% of all the analysed cations (30 elements).

An analysis of the obtained $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3$ and $\text{Ce}(\text{SO}_4)_2$ compositions performed by SEM-EDS, ICP-OES, and IC is presented in Table 10. SEM images obtained for $\text{Ce}_2(\text{SO}_4)_3$ and $\text{Ce}(\text{SO}_4)_2$ are presented in Figure 6. The analysis results confirm the expected obtained cerium salt composition, as the percentage elemental content calculated based on the results of the conducted tests for individual salts exhibits minor differences from the theoretical values calculated based on the chemical formulas of these compounds. All stages of the recovery of each cerium salt were carried out with high efficiency, which resulted in high efficiency throughout the entire process. Furthermore, it can be assumed that expanding the process from the laboratory to a semi-commercial or commercial scale will make it possible to improve the process yield by preventing material losses associated with the conduct of experiments at a small laboratory scale. Analysing the quantity of pollutants in the obtained salts makes it possible to classify them as technically pure substances; however, if they were to be applied as active substances of cerium coagulants, the purity of the obtained compounds could be deemed sufficient.

Table 10. Chemical composition of the obtained cerium salts.

Salt	Parameter	Unit	Result $\pm$ Measurement Uncertainty		
			Theoretical Content	ICP—OES, IC *	SEM—EDS
$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	Ce	%	37.62	37.21 ± 3.72	-
	Cl	%	28.55	29.15 ± 2.92 *	-
	Ce	%	49.30	46.61 ± 4.66	49.6
$\text{Ce}_2(\text{SO}_4)_3$	S	%	16.92	-	16.1
	O	%	33.78	-	33.2
	SO_4^{2-}	%	50.70	52.52 ± 5.25	-
	Ce	%	42.17	41.32 ± 4.13	44.0
$\text{Ce}(\text{SO}_4)_2$	S	%	19.30	-	19.3
	O	%	38.52	-	36.5
	SO_4^{2-}	%	57.82	58.68 ± 5.87	-

* determination made using ion chromatography technique.

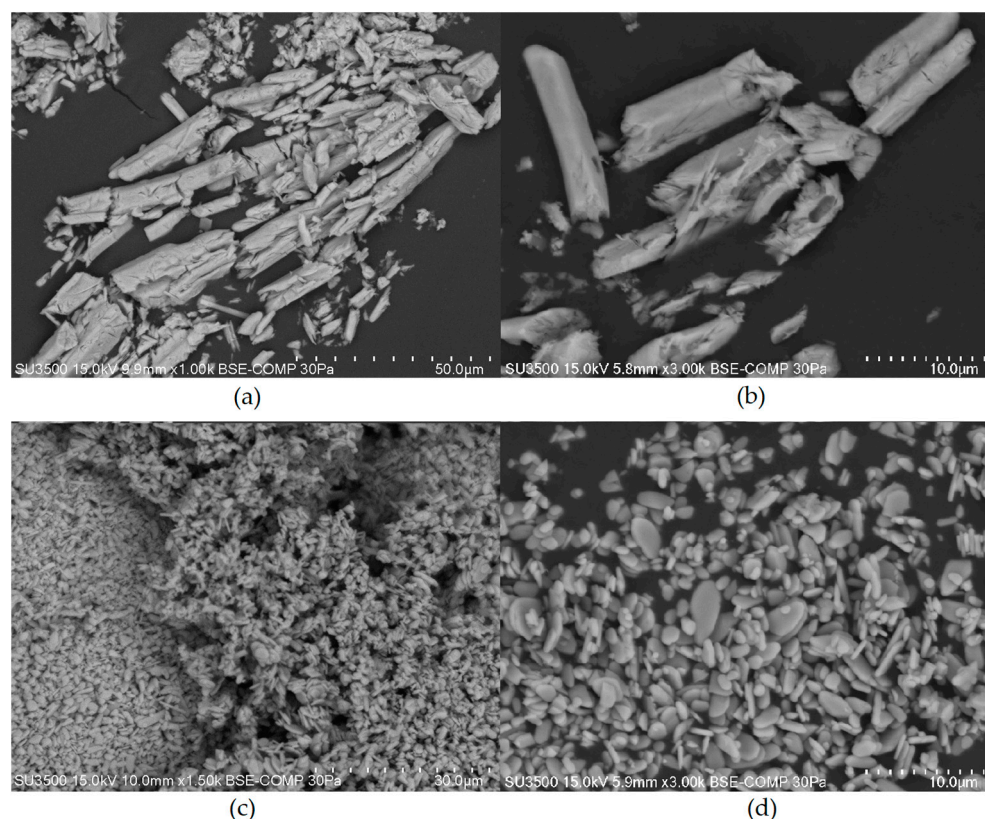


Figure 6. SEM images obtained for $\text{Ce}_2(\text{SO}_4)_3$ at a magnification of $\times 1000$ (a) and a magnification of $\times 3000$ (b), and for $\text{Ce}(\text{SO}_4)_2$ at a magnification of $\times 1500$ (c) and a magnification of $\times 3000$ (d).

Cerium salts obtained in a complex and environmentally harmful production process are an alternative to iron and aluminium compounds but are 3–6 times more expensive [51,52]. Therefore, recovering them from industrial waste such as spent polishing powders (16,000 tons per year; [53]), spent catalysts [54,55] can contribute to a significant reduction in their prices. According to the European Commission reports from 2017–2023, Light Rare Earth Elements (LREE) recycling remains at an extremely low level of approximately 1% [56–58]. Reducing the costs of cerium compounds at the stage of installation operation can also be achieved through the high-efficiency recycling of sewage sludge described in this article, thus largely closing the cerium cycle in the process. Cerium salts needed for the start-up of the installation and to cover any process losses can be replenished with recycled salts [9,44,59].

3.3. Removal of Metals from a Phosphorus-Rich Solution and the Possible Directions of Its Processing and Application

Phosphatic fertilisers for application in agriculture must be characterised by an appropriate level of purity, and they must particularly be free of heavy metals, whose elevated concentrations could negatively impact the environment. In the case of the studied phosphorus-rich eluate, it was revealed to contain metals (Al, Cu, Zn, Fe, and Mn), whose concentrations had to be reduced to safe values. Additional experiments were performed based on literature data [2,3] describing the high efficiency of heavy metal removal from acidic eluates through the application of DMDTC, TMT, and Na_2CS_3 solutions. The metal removal was conducted using four methods, i.e., increasing the pH to 9.5; increasing the pH to 9.5 and applying stoichiometric quantities of one of the three solutions relative to the metal contents (Al, Cu, Zn, Fe, and Mn), i.e., TMT, DMDTC, and Na_2CS_3 . Table 11 presents the results of these tests.

Table 11. Selected chemical parameters of the extract following metal removal by various methods.

Parameter	Unit	Result $\pm$ Measurement Uncertainty				
		The Solution after Filtration $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$	NaOH	TMT	DMDTC	Na_2CS_3
pH	-	1.8 ± 0.1	9.5 ± 0.1	9.5 ± 0.1	9.5 ± 0.1	9.5 ± 0.1
Total Phosphorus (P)	mg/L	561 ± 56	453 ± 45	442 ± 44	438 ± 44	440 ± 44
Copper (Cu)	mg/L	2.20 ± 0.22	1.82 ± 0.18	0.829 ± 0.166	0.071 ± 0.018	1.97 ± 0.20
Iron (Fe)	mg/L	61.0 ± 6.1	44.68 ± 4.47	3.17 ± 0.32	1.85 ± 0.19	1.15 ± 0.12
Manganese (Mn)	mg/L	2.33 ± 0.23	0.22 ± 0.04	0.241 ± 0.048	0.106 ± 0.021	0.136 ± 0.027
Aluminium (Al)	mg/L	49.7 ± 5.0	1.66 ± 0.17	8.40 ± 0.84	5.66 ± 0.57	2.67 ± 0.27
Zinc (Zn)	mg/L	9.71 ± 0.97	0.76 ± 0.15	1.34 ± 0.13	0.97 ± 0.19	1.12 ± 0.11
Lead (Pb)	mg/L	$<0.005 \pm 0.001$	$<0.005 \pm 0.001$	$<0.005 \pm 0.001$	$<0.005 \pm 0.001$	$<0.005 \pm 0.001$

The application of DMDTC yielded an eluate characterised by the lowest concentration of metal cations. Therefore, the initial alkalisating of the eluate (pH 9.5) and the application of a stoichiometric dose of DMDTC relative to the concentrations of the individual metal cations should be considered the most effective method of their removal. The phosphate solution obtained after applying NaOH and DMDTC was characterised by a low metal concentration, which is why it may constitute a valuable resource for obtaining phosphate salts by the application of, e.g., a CaCl_2 solution in an alkaline medium (pH correction is not required due to the alkaline reaction of the post-process solution obtained after removing the metal cations in the form of poorly soluble colloidal precipitates), retaining a 1.5 molar ratio of Ca:P. Furthermore, rinsing the calcium phosphate precipitate with an NaOH solution may remove pollutants such as Al [60]. Another method of obtaining useful phosphate salts may consist of precipitating struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). As demonstrated by prior research [61], increasing the Mg:P ratio may have a beneficial influence on the precipitation of these phosphorus compounds, while conducting the precipitation process at a pH above 9.0 reduces the negative influence of the humic acids that may potentially be present in the solution.

Another work [62] presented the positive influence of brewery sewage sludge applied to increase the agricultural production of maize as a result of supplying the soil with elements such as nitrogen (N), phosphorus (P), and sulphur (S). A problem with the application of this material was the increase in the concentration of lead (Pb) in the soil, which over time may lead to the accumulation of this element and result in exceeded permissible levels of lead (Pb) in the soil and its accumulation in cultivated plant tissue, and consequently in obtaining agricultural products potentially hazardous to health. In this work, as a result of increased pH and the application of DMDTC, the concentrations of Fe, Mn, Al, Cu, and Zn were lowered by 93.8%, 95.4%, 88.6%, 96.8%, and 90.0%, respectively. Therefore, the potential heavy metal contamination risk for the synthesised phosphorus salts (obtained per one of the methods described above) is negligible. Additionally, the performed tests demonstrated that the lead concentration in the filtrate after filtering the $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ as well as after applying the precipitants (NaOH and DMDTC) was <0.005 mg/L and was therefore negligible as a potential pollutant in the phosphate salts obtained using the solution remaining after the prior separation of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. Nevertheless, the presence of undesired metals in the sewage sludge and the solutions after their processing is possible, and in the event of their occurrence, action should be taken to reduce their concentrations to safe levels.

3.4. Potential Application of the Precipitates and Post-Reaction Solutions

The precipitate, composed primarily of organic matter unaffected by the process described in pt. 3.1, could probably be applied for fertilisation purposes, e.g., for degraded post-industrial land reclamation, though it is necessary to perform a series of additional tests regarding its potential biological and chemical risks, which would explicitly determine

the usefulness of this material for the aforementioned applications, but this is outside the scope of this work. However, this study can certainly inspire further interesting research. Prior work [21] demonstrated the usefulness of materials of biological origin in the process of post-industrial land reclamation, but only after the sludge was subjected to hygienisation, which reduced the quantity of hazardous bacteria by means of calcium peroxide (CaO_2) or sodium percarbonate ($2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$), compared to the commonly applied calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium oxide (CaO), and calcium carbonate (CaCO_3). Such a process may also be necessary in the case of the precipitate obtained after the extraction of sewage sludge using an HCl solution. Furthermore, if necessary, the precipitate composition may be modified to increase the concentration of phosphorus originating from the phosphate salts that could be obtained in the processes described in Section 3.3.

The final solution obtained after all the processing stages contained a high quantity of chloride ions and sodium (about 36 g/L NaCl). However, crystalline sodium chloride (NaCl) can be separated from this post-process solution by applying a water desalination process, such as multi-stage flash distillation (MSF) [63], reverse osmosis (RO) preceded by other concentration processes [64], or water evaporation in evaporation ponds [65], and using the crystallised salt as an additive to the road salt used for de-icing. As in the case of extraction sediments, the usefulness of salt should be determined by conducting tests for the content of chemical and biological pollutants.

4. Conclusions

Following an analysis of the chemical composition of brewery sewage sludge obtained by coagulation using recycled CeCl_3 , it was demonstrated that due to the high concentration of Ce and P (101.5 g/kg Ce and 22.2 g/kg P), the waste may serve as a potential raw material for the recovery of these elements and may be subjected to recovery processes. The application of CCD/RSM enabled the determination of optimal extraction process conditions, i.e., 0.35 g HCl as 100% HCl per 1 g of sludge, 40 min reaction time, and an extractant volume of 25 mL per 1 g, with extraction efficiency of 99.6% and 97.5% for Ce and P, respectively. The tests demonstrated excellent recovery of cerium (97.0–98.3%) in the form of cerium chlorides or sulphates, as well as a very good extraction of phosphorus (97.5%), which may be subjected to further processing by precipitating struvite, hydroxyapatite, and calcium phosphate. Based on the performed tests, it can be concluded that the discussed processing concept exhibits potential for development, and the processes could be enhanced for conduction at a greater scale. The by-products obtained in the process, such as a precipitate containing organic matter and a post-process solution with elevated salinity, can find industrial application, but only after the conduction of additional tests and experiments necessary from the perspective of their potential use, which certainly constitutes a field of new, interesting, and comprehensive research related to the recovery of phosphorus from sewage sludge in the context of the prior utilisation of modern coagulants, where the active substances may include cerium, zirconium, or titanium compounds. The proposed method of sewage sludge processing is a new and innovative way of repurposing this waste, where unit processes yield a number of products that could potentially be reused in, e.g., municipal or industrial waste treatment, degraded industrial land reclamation, traffic (road de-icing), and even agriculture. Furthermore, it should be stressed that the presented recovery process concept, together with the proposed applications of individual products and by-products, offers an excellent contribution to the idea of a circular economy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma17040938/s1>, Table S1. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, Ce^{3+} ; $R^2 = 0.938$; $R^2_{\text{adj}} = 0.882$, MS = 59.277. Table S2. ANOVA analysis results for Ce^{3+} extraction. Table S3. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, total P; $R^2 = 0.904$; $R^2_{\text{adj}} = 0.817$, MS = 4.287. Table S4. ANOVA analysis results for total P extraction.

Author Contributions: Conceptualization, P.L., B.B., K.B. and M.T.; Formal analysis, P.L. and M.T.; Funding acquisition, P.L.; Investigation, P.L.; Methodology, P.L. and M.T.; Resources, P.L.; Supervision, B.B., K.B. and M.T.; Writing—original draft, P.L. and M.T.; Writing—review and editing, P.L., B.B., K.B. and M.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Science of the Republic of Poland (Statutory Activity of the Central Mining Institute, Task no. 11331013-331).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Acknowledgments: The authors would like to thank the anonymous reviewers for their helpful comments.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CCD	Central composite design
COD	Chemical oxygen demand
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
RSM	Response surface methodology
Total P	Total phosphorus as P

References

1. Rzymiski, P.; Klimaszyk, P.; Marszelewski, W.; Borowiak, D.; Mleczek, M.; Nowiński, K.; Pius, B.; Niedzielski, P.; Poniedziałek, B. The Chemistry and Toxicity of Discharge Waters from Copper Mine Tailing Impoundment in the Valley of the Apuseni Mountains in Romania. *Environ. Sci. Pollut. Res.* **2017**, *24*, 21445–21458. [\[CrossRef\]](#)
2. Thomas, M.; Białecka, B.; Zdebik, D. Removal of Copper, Nickel and Tin from Model and Real Industrial Wastewater Using Sodium Trithiocarbonate: The Negative Impact of Complexing Compounds. *Arch. Environ. Prot.* **2018**, *44*, 33–47.
3. Thomas, M.; Kozik, V.; Bąk, A.; Barbusiński, K.; Jazowiecka-Rakus, J.; Jampilek, J. Removal of Heavy Metal Ions from Wastewaters: An Application of Sodium Trithiocarbonate and Wastewater Toxicity Assessment. *Materials* **2021**, *14*, 655. [\[CrossRef\]](#)
4. Saxena, G.; Chandra, R.; Bharagava, R.N. Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. In *Reviews of Environmental Contamination and Toxicology: Reviews of Environmental Contamination and Toxicology*; Springer: Cham, Switzerland, 2016; Volume 240, pp. 31–69.
5. García-Valero, A.; Martínez-Martínez, S.; Faz, Á.; Terrero, M.A.; Muñoz, M.Á.; Gómez-López, M.D.; Acosta, J.A. Treatment of Wastewater from the Tannery Industry in a Constructed Wetland Planted with *Phragmites Australis*. *Agronomy* **2020**, *10*, 176. [\[CrossRef\]](#)
6. Zhao, J.; Wu, Q.; Tang, Y.; Zhou, J.; Guo, H. Tannery Wastewater Treatment: Conventional and Promising Processes, an Updated 20-Year Review. *J. Leather Sci. Eng.* **2022**, *4*, 10. [\[CrossRef\]](#)
7. Simate, G.S.; Cluett, J.; Iyuke, S.E.; Musapatika, E.T.; Ndlovu, S.; Walubita, L.F.; Alvarez, A.E. The Treatment of Brewery Wastewater for Reuse: State of the Art. *Desalination* **2011**, *273*, 235–247. [\[CrossRef\]](#)
8. Enitan, A.M.; Adeyemo, J.; Kumari, S.K.; Swalaha, F.M.; Bux, F. Characterization of Brewery Wastewater Composition. *Int. J. Environ. Ecol. Eng.* **2015**, *9*, 1073–1076. [\[CrossRef\]](#)
9. Lejwoda, P.; Białecka, B.; Thomas, M. Removal of Phosphate from Brewery Wastewater by Cerium(III) Chloride Originating from Spent Polishing Agent: Recovery and Optimization Studies. *Sci. Total Environ.* **2023**, *875*, 162643. [\[CrossRef\]](#)
10. Kaur, N. Different Treatment Techniques of Dairy Wastewater. *Groundw. Sustain. Dev.* **2021**, *14*, 100640. [\[CrossRef\]](#)
11. Sirianuntapiboon, S.; Jeeyachok, N.; Larplai, R. Sequencing Batch Reactor Biofilm System for Treatment of Milk Industry Wastewater. *J. Environ. Manag.* **2005**, *76*, 177–183. [\[CrossRef\]](#)
12. Ahmad, S.; Mahmoud, T.A. Wastewater from a Sugar Refining Industry. *Water Res.* **1982**, *16*, 345–355. [\[CrossRef\]](#)
13. Singh, P.K.; Tripathi, M.; Singh, R.P.; Singh, P. Treatment and recycling of wastewater from sugar mill. In *Advances in Biological Treatment of Industrial Waste Water and Their Recycling for a Sustainable Future*; Springer: Singapore, 2019; pp. 199–223.
14. Cordell, D.; Drangert, J.-O.; White, S. The Story of Phosphorus: Global Food Security and Food for Thought. *Glob. Environ. Change* **2009**, *19*, 292–305. [\[CrossRef\]](#)

15. Daneshgar, S.; Callegari, A.; Capodaglio, A.; Vaccari, D. The Potential Phosphorus Crisis: Resource Conservation and Possible Escape Technologies: A Review. *Resources* **2018**, *7*, 37. [\[CrossRef\]](#)
16. Kwapinski, W.; Kolinovic, I.; Leahy, J.J. Sewage Sludge Thermal Treatment Technologies with a Focus on Phosphorus Recovery: A Review. *Waste Biomass Valorization* **2021**, *12*, 5837–5852. [\[CrossRef\]](#)
17. Tan, Z.; Lagerkvist, A. Phosphorus Recovery from the Biomass Ash: A Review. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3588–3602. [\[CrossRef\]](#)
18. Caravelli, A.H.; Contreras, E.M.; Zaritzky, N.E. Phosphorous Removal in Batch Systems Using Ferric Chloride in the Presence of Activated Sludges. *J. Hazard. Mater.* **2010**, *177*, 199–208. [\[CrossRef\]](#)
19. Zhou, Y.; Xing, X.-H.; Liu, Z.; Cui, L.; Yu, A.; Feng, Q.; Yang, H. Enhanced Coagulation of Ferric Chloride Aided by Tannic Acid for Phosphorus Removal from Wastewater. *Chemosphere* **2008**, *72*, 290–298. [\[CrossRef\]](#)
20. Wang, J.; Song, J.; Lu, J.; Zhao, X. Comparison of Three Aluminum Coagulants for Phosphorus Removal. *J. Water Resour. Prot.* **2014**, *06*, 902–908. [\[CrossRef\]](#)
21. Więckol-Ryk, A.; Thomas, M.; Białecka, B. Solid Peroxy Compounds as Additives to Organic Waste for Reclamation of Post-Industrial Contaminated Soils. *Materials* **2021**, *14*, 6979. [\[CrossRef\]](#)
22. Jaffer, Y.; Clark, T.A.; Pearce, P.; Parsons, S.A. Potential Phosphorus Recovery by Struvite Formation. *Water Res.* **2002**, *36*, 1834–1842. [\[CrossRef\]](#)
23. Cieřlik, B.; Konieczka, P. A Review of Phosphorus Recovery Methods at Various Steps of Wastewater Treatment and Sewage Sludge Management. The Concept of “No Solid Waste Generation” and Analytical Methods. *J. Clean. Prod.* **2017**, *142*, 1728–1740. [\[CrossRef\]](#)
24. Dahle, J.; Arai, Y. Environmental Geochemistry of Cerium: Applications and Toxicology of Cerium Oxide Nanoparticles. *Int. J. Environ. Res. Public Health* **2015**, *12*, 1253–1278. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Byrne, R.H.; Kim, K.-H. Rare Earth Precipitation and Coprecipitation Behavior: The Limiting Role of PO₄^{3−} on Dissolved Rare Earth Concentrations in Seawater. *Geochim. Cosmochim. Acta* **1993**, *57*, 519–526. [\[CrossRef\]](#)
26. Liu, X.; Byrne, R.H. Rare Earth and Yttrium Phosphate Solubilities in Aqueous Solution. *Geochim. Cosmochim. Acta* **1997**, *61*, 1625–1633. [\[CrossRef\]](#)
27. Kragten, J. Hydroxide Complexes of Cerium(III). *Talanta* **1978**, *25*, 147–150. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Kury, J.W. *Problems in the Aqueous Chemistry of Cerium(III) Fluoride and Lanthanum(III) Fluoride (Thesis)*; U.S. Atomic Energy Commission: Washington, DC, USA, 1953.
29. Ferri, D.; Grenthe, I.; Hietanen, S.; Salvatore, F.; Powell, D.L.; Suchi, R. Studies on Metal Carbonate Equilibria. 5. The Cerium(III) Carbonate Complexes in Aqueous Perchlorate Media. *Acta Chem. Scand.* **1983**, *37*, 359–365. [\[CrossRef\]](#)
30. Rodríguez-Ruiz, I.; Teychené, S.; Vitry, Y.; Biscans, B.; Charton, S. Thermodynamic Modeling of Neodymium and Cerium Oxalates Reactive Precipitation in Concentrated Nitric Acid Media. *Chem. Eng. Sci.* **2018**, *183*, 20–25. [\[CrossRef\]](#)
31. Crouthamel, C.E.; Martin, D.S. Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution. II. Neodymium and Cerium(III)¹. *J. Am. Chem. Soc.* **1951**, *73*, 569–573. [\[CrossRef\]](#)
32. Kajjumba, G.W.; Fischer, D.; Risso, L.A.; Koury, D.; Marti, E.J. Application of Cerium and Lanthanum Coagulants in Wastewater Treatment—A Comparative Assessment to Magnesium, Aluminum, and Iron Coagulants. *Chem. Eng. J.* **2021**, *426*, 131268. [\[CrossRef\]](#)
33. ISO 11885:2007; Water Quality—Determination of Selected Elements by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). ISO: Geneva, Switzerland, 2007.
34. EN ISO 17294-2:2016; Water Quality — Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) — Part 2: Determination of Selected Elements Including Uranium Isotopes (ISO 17294-2:2016). ISO: Geneva, Switzerland, 2016.
35. EN ISO 10304-1:2009; Water Quality - Determination of Dissolved Anions by Liquid Chromatography of Ions—Part 1: Determination of Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate and Sulfate (ISO 10304-1:2007). ISO: Geneva, Switzerland, 2009.
36. EN ISO 10523:2012; Water Quality—Determination of pH (ISO 10523:2008). ISO: Geneva, Switzerland, 2012.
37. Myers, R.H.; Montgomery, D.C.; Anderson-Cook, C.M. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2009.
38. Aslan, N. Application of Response Surface Methodology and Central Composite Rotatable Design for Modeling and Optimization of a Multi-Gravity Separator for Chromite Concentration. *Powder Technol.* **2008**, *185*, 80–86. [\[CrossRef\]](#)
39. Kokare, M.B.; Ranjani, V.; Mathpati, C.S. Response Surface Optimization, Kinetic Study and Process Design of n-Butyl Levulinate Synthesis. *Chem. Eng. Res. Des.* **2018**, *137*, 577–588. [\[CrossRef\]](#)
40. Bu, X.; Xie, G.; Peng, Y.; Chen, Y. Kinetic Modeling and Optimization of Flotation Process in a Cyclonic Microbubble Flotation Column Using Composite Central Design Methodology. *Int. J. Miner. Process.* **2016**, *157*, 175–183. [\[CrossRef\]](#)
41. Źelazny, S.; Świnder, H.; Białecka, B.; Jarosiński, A. Odzysk Pierwiastków Ziem Rzadkich z Popiołów Lotnych. Cz. II. Wytrącanie z Roztworu. *Przemysł Chem.* **2017**, *1*, 102–108. [\[CrossRef\]](#)
42. Chen, F.; Liu, F.; Wang, L.; Wang, J. Comparison of the Preparation Process of Rare Earth Oxides from the Water Leaching Solution of Waste Nd-Fe-B Magnets’ Sulfate Roasting Products. *Processes* **2022**, *10*, 2310. [\[CrossRef\]](#)
43. Lopez, H.F.; Mendoza, H. Temperature Effects on the Crystallization and Coarsening of Nano-CeO₂ Powders. *ISRN Nanomater* **2013**, *2013*, 208614. [\[CrossRef\]](#)

44. Poscher, A.; Luidold, S.; Schnideritsch, H.; Antrekowitsch, H. Extraction of Lanthanides from Spent Polishing Agent. In Proceedings of the 1st European Rare Earth Resources Conference (ERES 2014), Milos, Greece, 4–7 September 2014; pp. 209–222.
45. Thomas, M.; Bialecka, B.; Zdebik, D. Use of Sodium Trithiocarbonate for Remove of Chelated Copper Ions from Industrial Wastewater Originating from the Electroless Copper Plating Process. *Arch. Environ. Prot.* **2018**, *44*, 32–42.
46. Lejwoda, P.; Świnder, H.; Thomas, M. Evaluation of the Stability of Heavy Metal-Containing Sediments Obtained in the Wastewater Treatment Processes with the Use of Various Precipitating Agents. *Environ. Monit. Assess.* **2023**, *195*, 442. [[CrossRef](#)] [[PubMed](#)]
47. Kuc, J.; Thomas, M.; Grochowalska, I.; Kulczyk, R.; Mikosz, G.; Mrózek, F.; Janik, D.; Korta, J.; Cwynar, K. Determination and Removal of Selected Pharmaceuticals and Total Organic Carbon from Surface Water by Aluminum Chlorohydrate Coagulant. *Molecules* **2022**, *27*, 5740. [[CrossRef](#)]
48. Wang, X.; Bu, X.; Ni, C.; Zhou, S.; Yang, X.; Zhang, J.; Alheshibri, M.; Peng, Y.; Xie, G. Effect of Scrubbing Medium's Particle Size on Scrubbing Flotation Performance and Mineralogical Characteristics of Microcrystalline Graphite. *Miner. Eng.* **2021**, *163*, 106766. [[CrossRef](#)]
49. Um, N.; Hirato, T. Precipitation of Cerium Sulfate Converted from Cerium Oxide in Sulfuric Acid Solutions and the Conversion Kinetics. *Mater. Trans.* **2012**, *53*, 1986–1991. [[CrossRef](#)]
50. Brzyska, W. *Lantanowce i Aktynowce*, 2nd ed.; WNT: Warszawa, Poland, 1996.
51. Kajjumba, G.W.; Marti, E.J. A Review of the Application of Cerium and Lanthanum in Phosphorus Removal during Wastewater Treatment: Characteristics, Mechanism, and Recovery. *Chemosphere* **2022**, *309*, 136462. [[CrossRef](#)]
52. Gupta, C.K.; Krishnamurthy, N. Extractive Metallurgy of Rare Earths. *Int. Mater. Rev.* **1992**, *37*, 197–248. [[CrossRef](#)]
53. Borra, C.R.; Vlught, T.J.; Yang, Y.; Spooren, J.; Nielsen, P.; Amirthalingam, M.; Offerman, S.E. Recovery of Rare Earths from Glass Polishing Waste for the Production of Aluminium-Rare Earth Alloys. *Resour. Conserv. Recycl.* **2021**, *174*, 105766. [[CrossRef](#)]
54. Ilyas, S.; Kim, H.; Srivastava, R.R. Resource Recovery of Cerium from Spent Catalytic Converter Using Aqueous Metallurgy. In Proceedings of the 150th Annual Meeting & Exhibition Supplemental Proceedings, Online, 15–18 March 2021; pp. 1055–1062.
55. Trinh, H.B.; Lee, J.; Kim, S.; Kim, J. Recovery of Cerium from Spent Autocatalyst by Sulfatizing–Leaching–Precipitation Process. *ACS Sustain. Chem. Eng.* **2020**, *8*, 15630–15639. [[CrossRef](#)]
56. European Commission Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs; Grohol, M.; Veeh, C. *Study on the Critical Raw Materials for the EU 2023*; Final Report; Publications Office of the European Union: Luxembourg, 2023. [[CrossRef](#)]
57. European Commission European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs. *Study on the Review of the List of Critical Raw Materials*; Final Report; Publications Office: Luxembourg, 2017. [[CrossRef](#)]
58. European Commission European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs; Blengini, G.; El Latunussa, C.; Eynard, U.; Torres de Matos, C.; Wittmer, D.; Georgitzikis, K.; Pavel, C.; Carrara, S.; Mancini, L.; et al. *Study on the EU's List of Critical Raw Materials (2020)*; Final Report; Publications Office of the European Union: Luxembourg, 2020. [[CrossRef](#)]
59. Wu, Y.; Song, M.; Zhang, Q.; Wang, W. Review of Rare-Earths Recovery from Polishing Powder Waste. *Resour. Conserv. Recycl.* **2021**, *171*, 105660. [[CrossRef](#)]
60. Petzet, S.; Peplinski, B.; Bodkhe, S.Y.; Cornel, P. Recovery of Phosphorus and Aluminium from Sewage Sludge Ash by a New Wet Chemical Elution Process (SESAL-Phos-Recovery Process). *Water Sci. Technol.* **2011**, *64*, 693–699. [[CrossRef](#)] [[PubMed](#)]
61. Zhou, Z.; Hu, D.; Ren, W.; Zhao, Y.; Jiang, L.-M.; Wang, L. Effect of Humic Substances on Phosphorus Removal by Struvite Precipitation. *Chemosphere* **2015**, *141*, 94–99. [[CrossRef](#)] [[PubMed](#)]
62. Alayu, E.; Leta, S. Brewery Sludge Quality, Agronomic Importance and Its Short-Term Residual Effect on Soil Properties. *Int. J. Environ. Sci. Technol.* **2020**, *17*, 2337–2348. [[CrossRef](#)]
63. Thabit, M.S.; Hawari, A.H.; Ammar, M.H.; Zaidi, S.; Zaragoza, G.; Altaee, A. Evaluation of Forward Osmosis as a Pretreatment Process for Multi Stage Flash Seawater Desalination. *Desalination* **2019**, *461*, 22–29. [[CrossRef](#)]
64. Sanmartino, J.A.; Khayet, M.; García-Payo, M.C.; El-Bakouri, H.; Riaza, A. Treatment of Reverse Osmosis Brine by Direct Contact Membrane Distillation: Chemical Pretreatment Approach. *Desalination* **2017**, *420*, 79–90. [[CrossRef](#)]
65. Rodríguez, F.A.; Santiago, D.E.; Franquiz Suárez, N.; Ortega Méndez, J.A.; Veza, J.M. Comparison of Evaporation Rates for Seawater and Brine from Reverse Osmosis in Traditional Salt Works: Empirical Correlations. *Water Supply* **2012**, *12*, 234–240. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.

Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant

Paweł Lejewoda ¹, Barbara Białecka ², Krzysztof Barbusiński ³ and Maciej Thomas ^{4,*}

¹ Department of Energy Saving and Air Protection, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; plejewoda@gig.eu

² Department of Environmental Monitoring, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; bbialecka@gig.eu

³ Department of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland; krzysztof.barbusinski@polsl.pl

⁴ Faculty of Environmental Engineering and Energy, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

* Correspondence: maciej.thomas@pk.edu.pl

Table S1. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, Ce^{3+} ; $R^2 = 0.938$; $R^2_{adj} = 0.882$, $MS = 59.277$.

Parameter	Effect	Standard error	t(10)	p	CI (-95%)	CI (+95%)	Factor	Standard error	CI (-95%)	CI (+95%)
Constant value	102.050	3.140	32.499	< 0.001	95.053	109.046	102.050	3.140	95.053	109.046
(1) liquid:solid (L)	0.347	4.167	0.083	0.935	-8.937	9.631	0.173	2.083	-4.469	4.815
liquid:solid (Q)	-4.633	4.056	-1.142	0.280	-13.670	4.405	-2.316	2.028	-6.835	2.203
(2) time (L)	0.270	4.167	0.065	0.950	-9.014	9.554	0.135	2.083	-4.507	4.777
time (Q)	-3.501	4.056	-0.863	0.408	-12.539	5.536	-1.751	2.028	-6.270	2.768
(3) mg HCl (L)	40.904	4.167	9.817	< 0.001	31.620	50.188	20.452	2.083	15.810	25.094
mg HCl (Q)	-29.631	4.056	-7.305	< 0.001	-38.669	-20.593	-14.816	2.028	-19.334	-10.297
1L relative to 2L	1.887	5.444	0.347	0.736	-10.243	14.017	0.944	2.722	-5.122	7.009
1L relative to 3L	-3.296	5.444	-0.605	0.558	-15.426	8.834	-1.648	2.722	-7.713	4.417
2L relative to 3L	0.178	5.444	0.033	0.975	-11.952	12.308	0.089	2.722	-5.976	6.154

* mass ratio, statistically significant if $p < 0.05$.

Table S2. ANOVA analysis results for Ce^{3+} extraction.

Parameter	SS	df	MS	F	p
(1) liquid:solid (L)*	0.410	1	0.410	0.007	0.935
liquid:solid (Q)*	77.323	1	77.323	1.304	0.280
(2) time (L)	0.248	1	0.248	0.004	0.950
time (Q)	44.167	1	44.167	0.745	0.408
(3) mg HCl (L)	5712.425	1	5712.425	96.369	< 0.001
mg HCl (Q)	3163.284	1	3163.284	53.365	< 0.001
1L relative to 2L	7.123	1	7.123	0.120	0.736
1L relative to 3L	21.731	1	21.731	0.367	0.558
2L relative to 3L	0.063	1	0.063	0.001	0.975
Error	592.765	10	59.277		
Total sum of square	9509.054	19			

* mass ratio, statistically significant if $p < 0.05$.

Table S3. Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, total P; $R^2 = 0.904$; $R^2_{adj} = 0.817$, $MS = 4.287$.

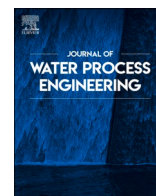
Parameter	Effect	Standard error	t(10)	P	CI (-95%)	CI (+95%)	Factor	Standard error	CI (-95%)	CI (+95%)
Constant value	20.217	0.844	23.942	< 0.001	18.336	22.099	20.217	0.844	18.336	22.099
(1) liquid:solid (L)	0.389	1.120	0.347	0.736	-2.108	2.885	0.194	0.560	-1.054	1.443
liquid:solid (Q)	-0.065	1.091	-0.059	0.954	-2.495	2.366	-0.032	0.545	-1.247	1.183
(2) time (L)	0.267	1.120	0.238	0.817	-2.230	2.763	0.133	0.560	-1.115	1.382
time (Q)	0.088	1.091	0.081	0.937	-2.343	2.518	0.044	0.545	-1.171	1.259
(3) mg HCl (L)	9.177	1.120	8.190	< 0.001	6.680	11.674	4.589	0.560	3.340	5.837
mg HCl (Q)	-5.469	1.091	-5.014	< 0.001	-7.899	-3.039	-2.734	0.545	-3.950	-1.519
1L relative to 2L	0.655	1.464	0.447	0.664	-2.607	3.917	0.327	0.732	-1.304	1.958
1L relative to 3L	-1.105	1.464	-0.755	0.468	-4.367	2.157	-0.553	0.732	-2.184	1.078
2L relative to 3L	-0.034	1.464	-0.023	0.982	-3.296	3.228	-0.017	0.732	-1.648	1.614

* mass ratio, statistically significant if $p < 0.05$.

Table S4. ANOVA analysis results for total P extraction.

Parameter	SS	df	MS	F	p
(1) liquid:solid (L)*	0.515	1	0.515	0.120	0.736
liquid:solid (Q)*	0.015	1	0.015	0.003	0.954
(2) time (L)	0.243	1	0.243	0.057	0.817
time (Q)	0.028	1	0.028	0.006	0.937
(3) mg HCl (L)	287.540	1	287.540	67.080	< 0.001
mg HCl (Q)	107.758	1	107.758	25.139	< 0.001
1L relative to 2L	0.858	1	0.858	0.200	0.664
1L relative to 3L	2.443	1	2.443	0.570	0.468
2L relative to 3L	0.002	1	0.002	0.001	0.982
Error	42.865	10	4.287		
Total sum of square	444.324	19			

* mass ratio, statistically significant if $p < 0.05$.



Holistic insight into the viability of employing cerium(IV) sulphate to oxidise toxic contaminants in effluent from the coal gasification process: Optimisation studies

Paweł Lejwoda^{a,*}, Barbara Białecka^b, Maciej Thomas^c

^a Central Mining Institute in Katowice, Department of Energy Saving and Air Protection, Plac Gwarków 1, Katowice 40-166, Poland

^b Central Mining Institute in Katowice, Department of Environmental Monitoring, Plac Gwarków 1, Katowice 40-166, Poland

^c Cracow University of Technology, Faculty of Environmental Engineering and Energy, Warszawska 24, Cracow 31-155, Poland

ARTICLE INFO

Editor: Laura Bulgariu

Keywords:

Wastewater treatment
Phenol
Benzo(a)pyrene
Dibenz(a,h)anthracene
Benzo[a]anthracene

ABSTRACT

The coal gasification (CG) process, while beneficial for producing syngas, poses environmental risks due to the production of highly toxic wastewater containing high concentrations of polycyclic aromatic hydrocarbons (PAHs), phenolics, and cyanides. This study examines the oxidation of pollutants in wastewater from a simulated underground coal gasification (UCG) process, with initial pollutant levels of pH 1.8, total cyanides 21.00 mg/L, total phenols 61.95 mg/L, heavy metals 7.68 mg/L, PAHs 2459 µg/L, and dissolved organic carbon (DOC) 148.0 mg/L. Three oxidation systems ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$, and Fenton process with $\text{FeSO}_4 + \text{H}_2\text{O}_2$) were used to remove pollutants from wastewater from the coal gasification process. In the first system, the oxidising agent was Ce^{4+} ions, while in the second and third systems, where hydrogen peroxide was added, the oxidising agents were hydroxyl radicals. Using central composite design and response surface methodology (CCD/RSM), the most favourable oxidation conditions were identified for $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (35 min, $\text{Ce}^{4+}:\text{C}$ molar ratio of 5:1, pH 2.5, temp. 40 °C). For the $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$ system DOC: $\text{Ce}^{4+}:\text{H}_2\text{O}_2$ molar ratio of 1:2:10. Results showed significant reduction in pollutants: $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ reduced PAHs, phenols, cyanides, DOC, and heavy metals by 99.40 %, 99.97 %, 97.67 %, 65.34 %, and 90.01 %, respectively; $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$ achieved reductions of 99.91 %, 99.66 %, 98.14 %, 76.35 %, and 81.45 %; and the Fenton process achieved reductions of 99.91 %, 99.95 %, 95.07 %, 56.49 %, and 89.33 %. An application of alternative oxidation processes ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$) is a viable option in removing toxic pollutants with simultaneously cerium recovery.

Abbreviations

AOPs	Advanced oxidation processes
CCD	Central composite design
CFA	Continuous flow analysis
CG	Coal gasification
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
E_h	Redox potential
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
PAHs	Polycyclic aromatic hydrocarbons
REEs	Rare earth elements

RSM	Response surface methodology
UCG	Underground coal gasification

1. Introduction

Coal gasification is a process involving the use of a limited amount of a gasifying agent in the gas phase in relation to coal in the solid phase, which is used to obtain a gas mixture containing H_2 , CO, CH_4 and other compounds. [1–4]. The parameters of the coal gasification process depend on a number of factors, such as the type of coal subjected to gasification [5,6], the type of reactor used [7–9] and the type of gasification agent. The most common gasifying agents include oxygen (O_2), steam ($\text{H}_2\text{O}_{(g)}$), air or their mixture [10]. Ensuring the high efficiency of

* Corresponding author.

E-mail address: plejwoda@gig.eu (P. Lejwoda).

<https://doi.org/10.1016/j.jwpe.2024.106243>

Received 7 August 2024; Received in revised form 20 September 2024; Accepted 24 September 2024

Available online 27 September 2024

2214-7144/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

the process requires the use of catalysts such as potassium carbonate (K_2CO_3), nickel (Ni), iron(II) oxide (FeO), iron(II, III) oxide (Fe_3O_4), and calcium oxide (CaO) [11–16].

The obtained syngas (synthesis gas) is a mixture of hydrogen and carbon monoxide in various ratios that can be used in chemical synthesis after purification and separation. Syngas is usually used in the synthesis of ammonia (NH_3) [17,18], methanol (CH_3OH) [19,20], ethanol (C_2H_5OH) [21,22] or fuel for power engineering purposes [23,24].

Apart from valuable gas products, the coal gasification process generates wastewater containing many toxic (inorganic and organic) pollutants, including heavy metals (derived from coal material and associated rock) [25], polycyclic aromatic hydrocarbons (PAHs), phenols and cyanides.

PAHs are ring-structured compounds obtained in the process of incomplete combustion of hydrocarbons [26,27], in waste combustion processes [28], in the coal gasification process [29], in the coal coking process [30–32], and even during cigarette smoking [33,34]. The 16 PAHs [35] are particularly dangerous due to their confirmed mutagenic [36], carcinogenic [37] and genotoxic properties [38,39]. As indicated by the literature, the content of PAHs in wastewater after the coal gasification process can vary within a wide range, from 362 to even 2808 $\mu g/L$ [40,41]. According to the European Union directive in drinking water, the maximum value of PAH's is 0.10 $\mu g/L$ for the sum of benzo(b)fluoranten, benzo(k)fluoranten, benzo(ghi)perylene and indeno (1,2,3-cd)piren [42] and for surface waters, local regulations are 0.2–1 $\mu g/L$ [43].

Phenols include a number of compounds containing a hydroxyl group (-OH) connected to a benzene ring. In the case of polyphenols, at least two hydroxyl groups are attached to the benzene ring. Many phenolic compounds occur naturally and demonstrate antiseptic properties (eugenol [44] and thymol [45], antioxidant properties guaiacol [46], catechol [47], resveratrol [48], and hydroquinone) [49], a specific colours (anthocyanins [50] and flavonoids [51]), smells and tastes (vanillin [52] and menthol [53]). Unfortunately, a significant number of phenolic compounds (e.g., phenol, o-cresol, m-cresol, and p-cresol) that have toxic effects on plants and animals, especially aquatic plants, aquatic (micro)organisms and (micro)organisms found in activated sludge in sewage treatment plants, can be found in wastewater from the process of coal coking [54], coal gasification [55], and crude oil refining [56]. The content of phenolic compounds (usually determined as total phenols) in industrial wastewater can reach up to 6000 mg/L [57]. In the European Union, the permissible concentration of phenolic compounds in drinking water is 1 $\mu g/L$ [42]. In the case of surface water intended for drinking water, the permissible limits according to local guidelines range from 1 $\mu g/L$ to 100 $\mu g/L$, which directly determines the number of activities necessary to treat this water [43].

Cyanides are used in chemical synthesis, e.g., for the production of acrylonitrile [58], dyes [59], and polymers [60], and in the metallurgical industry for the refining of metals, such as gold (Au) and silver (Ag) [61,62], as well as for the production of metallic coatings in galvanising plants [63,64]. In addition to being intentionally used in industrial processes, cyanides are generated as by-products, among others, in the process of coal gasification [65], coal coking [66] and the combustion of coal fuels, similar to PAHs [67]. The presence of cyanides in the environment is extremely dangerous for both plants and animals [68,69]. In an acidic environment, they form volatile and highly toxic hydrogen cyanide ($HCN_{(g)}$), which has a lethal effect, among other effects, on the respiratory tract, as it blocks pathways for transporting oxygen to tissues [70]. According to the recommendations of the European Union directive, the maximum permissible concentration of cyanides in drinking water is 50 $\mu g/L$ [42]. According to local regulations, similar limits are required for surface waters intended for drinking water [43].

The conventional treatment of wastewater containing PAHs, phenols and cyanides is a complicated process due to the toxicity of these compounds towards (micro)organisms present in activated sludge, but this is possible [71]. However, this approach requires the use of bacteria

resistant to cyanides, which is costly [72–77]. On the other hand, the use of physicochemical methods followed by biological methods allows for more effective treatment of toxic wastewater [78]. In many cases, organic pollutants are resistant to commonly used biological methods for removal; therefore, it is necessary to use additional, more advanced technologies based on chemical oxidation of pollutants. Table S1 presents selected physicochemical properties and the composition of wastewater from the process of gasification of various types of coal. It can be observed that in each of the examples the concentrations of contaminants such as cyanides, phenols and PAHs were high and exceeded the permissible limits.

Advanced oxidation processes (AOPs) are various methods that use hydroxyl radicals ($\bullet OH$) with high oxidising potential for wastewater treatment. An example of such a process using hydroxyl radicals and used for wastewater treatment is the Fenton reaction (1).



In reaction (2), the Fe^{2+} ion is recreated in the reaction of the Fe^{3+} ion with hydrogen peroxide (H_2O_2), which is accompanied by the formation of hydroperoxyl radicals ($HO_2\bullet$), with a much lower oxidation potential than that of hydroxyl radicals ($\bullet OH$). Table S2 presents the potentials of the selected agents.



The reaction of the formed radicals with organic pollutants (RH) occurs, among other reactions, according to formulas (3) and (4).



In addition to the reactions in which pollutants are effectively oxidised, there are a number of side reactions, including reactions between hydroxyl radicals terminating the oxidation process (5), dimerisation reactions between organic radicals (6), and pollution reduction reactions (7).



This method has undergone a number of modifications called Fenton-like processes [79], which include heterogeneous catalysts, such as iron(II,III) oxide (Fe_3O_4), cerium(IV) oxide (CeO_2), metallic silver (Ag), manganese(IV) oxide (MnO_2), manganese(II, III) oxide (Mn_3O_4), and metallic copper (Cu). The formation of hydroxyl radicals, in addition to processes based on the Fenton reaction and its modifications (Fenton-like processes), also involves a number of physical processes, as well as combinations of chemical and physical processes, such as the application of light in the UV/VIS range (photo-Fenton), ionising radiation (gamma radiation), electrochemical processes (electro-Fenton), combinations of oxidising systems, e.g., $O_3/H_2O_2/UV$, and ultrasound [80,81].

Coagulation is also an important part of wastewater treatment methods. Commonly used coagulants in this process are iron(II), iron (III), or aluminium salts, which, when added to wastewater subjected to treatment, as a result of hydrolysis, create sparingly soluble hydroxides that are capable of adsorbing pollutants. Coagulants based on cerium salts are becoming increasingly popular due to their greater effectiveness compared to coagulants based on iron or aluminium. Cerium-based coagulants, such as $CeCl_3$ solution, can be successfully used for the treatment of municipal wastewater as well as wastewater from the brewing industry. High effectiveness was particularly noticeable in the reduction of the phosphate concentration by >99 % due to the direct reaction of Ce^{3+} with PO_4^{3-} ions and the formation of a sparingly soluble

sludge [82–84]. However, the processes for obtaining lanthanides, including cerium, are disadvantageous due to their multi-stage nature, high energy demands, and the use of substantial quantities of chemicals, which have a negative impact on the environment [85]. From an ecological and technological point of view, it is extremely important to obtain these substances from waste materials, where their concentration is frequently much greater than that of the original minerals from which they were obtained. Currently, in the European Union, recycling of cerium (Ce) occurs at negligible level 1 % Ce [86]. Cerium salts for wastewater treatment processes can be successfully obtained from waste, which can improve the recycling rate of this element. Examples of such waste include polishing powders and wastewater sludge after the cerium(III) chloride coagulation process, which can be used to obtain the following salts: cerium(III) chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$), cerium(III) sulphate ($\text{Ce}_2(\text{SO}_4)_3$), and cerium(IV) sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) [84,87–89].

In the fourth oxidation state, cerium is a strong oxidant, which indicates the possibility of its use in the oxidation of pollutants contained in wastewater [90,91]. In the work of [92], Ce^{4+} effectively reduced the values of physicochemical parameters such as chemical oxygen demand (COD), turbidity, arsenic, and cadmium by 96.5 %, 88.5 %, 91.7 %, 98.3 %, respectively. In addition to the direct use of Ce^{4+} in the process of pollutant oxidation, an interesting solution is the possibility of using Ce^{4+} in a system with hydrogen peroxide (H_2O_2), in which case a highly reactive hydroxyl radical ($\bullet\text{OH}$) is formed, as in previously described Fenton-like methods [79].

The above methods are characterised by varying efficiencies of decomposition and removal of pollutants; some of them are at the laboratory or semitechnical research stage and have not been used on an industrial scale. The literature data indicate a significant lack of effective methods for removing pollutants from by-products or industrial waste with the use of green chemistry techniques, which are consistent with the ideas of a circular economy and the concept of sustainable development. The presented research is one of the attempts to fill this gap.

The aim of the research presented in the article is to assess the possibility of using cerium(IV) sulphate in the process of oxidising toxic pollutants contained in acidic wastewater from the hard coal gasification process. The conducted experiments enabled the establishment of the optimal conditions for the process and the determination of the most advantageous addition of an oxidising agent, which allowed for a maximum reduction in the concentrations of highly toxic substances contained in the wastewater to values safe for biological processes in municipal sewage treatment plants. The obtained research results significantly fill the gap in the scope of highly effective methods for treating wastewater from coal gasification processes. The possibility of recovering the radical reaction catalyst from wastewater sludge enabled the closure of the cerium cycle in the purification process, which is consistent with the assumptions of the closed-loop economy policy and will have a positive impact on the economic balance of its application in the process.

2. Materials and methods

2.1. Materials

The tests were carried out for acidic wastewater (pH 1.8) produced in the process of filtering gases from a process simulating the conditions of underground coal gasification (UCG) through a scrubber (Fig. 1) [93]. The wastewater was subjected to physicochemical analyses, and its characteristics are presented in Table 1.

The oxidising mixtures used in the experiments were prepared from cerium(IV) sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), analytically pure (Chempur, Poland), hydrogen peroxide (H_2O_2), 30 % (m/m), analytically pure (Chempur, Poland), iron(II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and analytically pure (Chempur, Poland). pH adjustment was carried out using analytically pure solutions of 30 % hydrochloric acid (HCl) (Suprapur®, Merck,

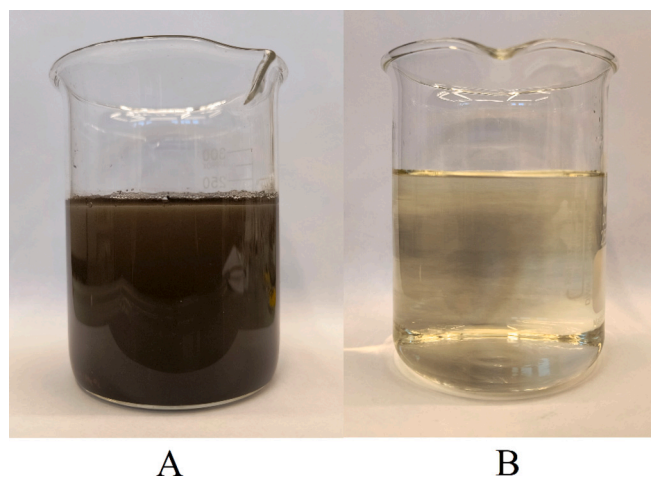


Fig. 1. Raw wastewater (A) and filtered wastewater (B) used in the experiments.

Table 1

Chemical composition of the wastewater used in the experiments.

Parameter	Unit	Raw wastewater
pH	–	1.8 ± 0.1
Redox	mV	480
DOC	mg/L	148.0 ± 22.2
Cerium (Ce)	µg/L	< 0.10 ± 0.15
Iron (Fe)	mg/L	11.537 ± 1.154
Manganese (Mn)	mg/L	0.197 ± 0.039
Cadmium (Cd)*	mg/L	< 0.005 ± 0.001
Chromium (Cr)*	mg/L	2.441 ± 0.244
Copper (Cu)*	mg/L	< 0.020 ± 0.005
Nickel (Ni)*	mg/L	1.088 ± 0.109
Lead (Pb)*	mg/L	1.603 ± 0.160
Zinc (Zn)*	mg/L	2.544 ± 0.254
Total cyanides	µg/L	21,000 ± 2100
Total phenols volatile	µg/L	61,950 ± 4956
Naftalen	µg/L	153.78 ± 38.45
Acenafteen	µg/L	284.56 ± 71.14
Fluoren	µg/L	107.39 ± 26.85
Fenantren	µg/L	263.23 ± 65.81
Antracen	µg/L	93.81 ± 23.45
Fluoranten	µg/L	133.79 ± 33.45
Piren	µg/L	322.10 ± 80.53
Benzo(a)antracen	µg/L	291.30 ± 72.83
Chryzen	µg/L	143.09 ± 35.77
Benzo(b)fluoranten	µg/L	151.23 ± 37.81
Benzo(k)fluoranten	µg/L	85.26 ± 21.32
Benzo(a)piren	µg/L	231.81 ± 57.95
Dibenzo(a,h)antracen	µg/L	51.53 ± 12.88
Benzo(g,h,i)perylene	µg/L	47.85 ± 11.96
Indeno(1,2,3-cd)piren	µg/L	95.40 ± 23.85
Σ PAH	µg/L	2459.11 ± 614.78

* included in the sum of heavy metals.

Germany) and sodium hydroxide (NaOH) (Chempur, Poland). Deionised water (< 0.05 µS/cm) was used for dilutions.

2.2. Analytical methods

The concentrations of metals and nonmetals were determined using the techniques of optical emission spectrometry (ICP-OES) (EN ISO 11885:2009) with Optima 5300DV (Perkin Elmer, USA) and mass spectrometry (ICP-MS) (EN ISO 17294-2:2016) with NexION300s (Perkin Elmer, USA), with a measurement uncertainty of 10–25 %. The determination of dissolved organic carbon (DOC) was performed according to ISO 1484:1999 using high-temperature combustion with infrared detection (TOC-L CPH, Shimadzu, Japan) with a measurement uncertainty of 15 %. The measurement of pH and electrical conductivity

(EC) was conducted according to EN ISO 10523:2012 and EN 27888:1999, with a measurement uncertainty for a pH of ± 0.1 and for an EC of 5 %, using the Inolab pH/ION/Cond 750, WTW, Germany. The concentrations of total cyanides and total phenolics were determined according to ISO 14403-2:2012 and ISO 14402:1999 standards using continuous flow analysis (CFA) with spectrophotometric detection (Skalar San++, Skalar Analytical B.V., Netherlands), with a measurement uncertainty of 10 % for cyanides and 8–30 % for phenolics. The concentrations of polycyclic aromatic hydrocarbons (PAHs) were determined using high-performance liquid chromatography with fluorescence detection (HPLC-FID) (EN ISO 17993:2003; Agilent 1200, Agilent Technologies, Inc., USA), with a measurement uncertainty of 25 %. The digestion of the precipitate formed after the oxidation process was carried out in accordance with ISO 15587-1:2002.

2.3. Process optimisation

The measured portion of wastewater was transferred to 200 mL beakers equipped with a magnetic stirrer, the pH was adjusted, the beakers were heated, and solid cerium(IV) sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) was added in an amount consistent with the values adopted in the experimental plan. Next, the mixture was stirred at a speed of 250 rpm. The wastewater heating was intended to reflect the temperature conditions after leaving the scrubber, where in the analysed case, the temperatures reached a value of up to 90 °C. In addition, it was assumed that the use of waste heat could improve the efficiency of the pollutant oxidation process. The optimisation of process conditions was carried out by performing 29 experiments according to the experimental design presented in Table 2. The number of experiments required to create the response surface (RSM) was conducted following a central composite design (CCD), which allowed for a significant reduction in the number of

Table 2

Empirical conditions for CCD/RSM and the results (DOC) for impurities oxidation (time 5–65 min, Ce^{4+} :DOC molar ratio 2–10, pH 0.5–4.5, temperature 10–90 °C).

Run	Experimental Conditions				Experimental Results
	time (min), x_1	Ce^{4+} :DOC ratio, x_2	pH, x_3	Temperature °C, x_4	DOC, mg/L
1	20	4	1.5	30	63.0 $\pm$ 9.5
2	20	4	3.5	30	64.8 $\pm$ 9.7
3	20	8	1.5	30	67.6 $\pm$ 10.1
4	20	8	3.5	30	68.1 $\pm$ 10.2
5	20	4	1.5	70	73.1 $\pm$ 11.0
6	20	4	3.5	70	78.5 $\pm$ 11.8
7	20	8	1.5	70	81.4 $\pm$ 12.2
8	20	8	3.5	70	81.8 $\pm$ 12.3
9	50	4	1.5	30	69.9 $\pm$ 10.5
10	50	4	3.5	30	70.5 $\pm$ 10.6
11	50	8	1.5	30	78.8 $\pm$ 11.8
12	50	8	3.5	30	70.3 $\pm$ 10.5
13	50	4	1.5	70	72.0 $\pm$ 10.8
14	50	4	3.5	70	81.1 $\pm$ 12.2
15	50	8	1.5	70	75.5 $\pm$ 11.3
16	50	8	3.5	70	83.1 $\pm$ 12.5
17	5	6	2.5	50	67.2 $\pm$ 10.1
18	65	6	2.5	50	62.9 $\pm$ 9.4
19	35	6	2.5	10	68.1 $\pm$ 10.2
20	35	6	2.5	90	107.0 $\pm$ 16.1
21	35	2	2.5	50	68.9 $\pm$ 10.3
22	35	10	2.5	50	81.4 $\pm$ 12.2
23	35	6	0.5	50	62.8 $\pm$ 9.4
24	35	6	4.5	50	77.3 $\pm$ 11.6
25*	35	6	2.5	50	56.7 $\pm$ 8.5
26*	35	6	2.5	50	52.7 $\pm$ 7.9
27*	35	6	2.5	50	51.7 $\pm$ 7.8
28*	35	6	2.5	50	54.5 $\pm$ 8.2
29*	35	6	2.5	50	62.2 $\pm$ 9.3

* – centre of the plan.

experiments compared to the traditional method of examining all combinations of independent variables. To minimise the impact of interfering factors and to eliminate the sequence effect, the experiments were conducted in a random order. The input parameters included a time of 5–65 min, a Ce^{4+} to dissolved organic carbon (DOC) molar ratio of 2–10, a temperature of 10–90 °C, and a pH of 0.5–4.5 [94,95]. Upon completion of the oxidation process, the wastewater was alkalised to pH 8.2 in order to precipitate the oxidant used in the form of, among others, $\text{Ce}(\text{OH})_3$ and/or $\text{Ce}(\text{OH})_4$.

2.4. Oxidation in the $\text{Ce}^{4+} + \text{H}_2\text{O}_2$ and $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ systems

The preparation of the experiments was similar to that described in section 2.3. In this case, 9 experiments were performed using 9 different molar ratios of $\text{DOC}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$, selected on the basis of experiments regarding the application of the Fenton process described in the literature [96,97]. The molar ratio of Ce^{4+} to DOC was assumed to be 1–3, and the molar ratio of H_2O_2 to DOC was assumed to be 5–15. To determine the content of cerium (Ce), the wastewater sludge generated in the process was mineralised in *aqua regia* according to standard ISO 15587-1:2002. Cerium recovery from wastewater sludge through extraction with hydrochloric acid (HCl) was carried out according to the method described by Lejwoda et al. [87].

For comparison, an experiment based on the classic Fenton process was carried out in which the same proportion as that selected for the $\text{DOC}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$ oxidising system was maintained. Similar to the experiment described in point 2.3, the wastewater from the process was alkalised to pH 8.2 to precipitate cerium(III) and cerium(IV) hydroxides from the process in the $\text{Ce}^{4+} + \text{H}_2\text{O}_2$ system and iron(II) and iron(III) hydroxides from the process in the $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ system.

3. Results and discussion

3.1. Optimisation of the process of pollutant oxidation with Ce^{4+} ions

The coal gasification effluents used in the experiment were characterised by high concentrations of harmful substances such as cyanides, phenols, PAHs, heavy metals (cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)) and an acidic pH of 1.8. A series of experiments conducted in accordance with central composite design (CCD) enabled the assessment of the effectiveness of removing pollutants with the use of cerium(IV) sulphate by measuring the DOC concentration. The data contained in Table 2 were used for the statistical analysis performed with Statistica 13 software (TIBCO Software Inc., USA). In the first step, the effects of the independent variables and their linear interactions on the DOC concentration were assessed (Table S3). The variables with the most significant impact on the DOC concentration reduction process were temperature, the molar ratio of Ce^{4+} , pH, and time. In the second step, ANOVA was performed (Table S4). The significance of individual variables was assessed. After eliminating most of the statistically insignificant parameters from the model (linear interactions between pairs of variables 1 L vs 3 L, 1 L vs 4 L, 2 L vs. 3 L, 3 L vs 4 L) the effects were re-evaluated (Table S5). ANOVA analysis (Table S6) was also performed.

A slight deterioration in model fit from $R^2 = 0.909$ to $R^2 = 0.904$ was observed, but the value of the corrected coefficient $R_{\text{adj}}^2 = 0.818$ improved to $R_{\text{adj}}^2 = 0.850$. The R^2 coefficient ranges from 0 to 1, where 0 means no fit, and 1 means a perfect fit. It can be assumed that values in the range of 0.90–1 mean a very good fit, 0.80–0.89 – a good fit, 0.60–0.80 – indicate a satisfactory fit, and 0–0.50 indicate an unsatisfactory fit [98]. In the discussed case, the coefficient $R_{\text{adj}}^2 = 0.850$ means that the model is well fitted to the experimental data, owing to which it explains 85 % of the results.

A graphical interpretation of the effects of individual parameters is presented in the Pareto chart (Fig. 2.). The standardised effects of particular variables were grouped according to their absolute values.

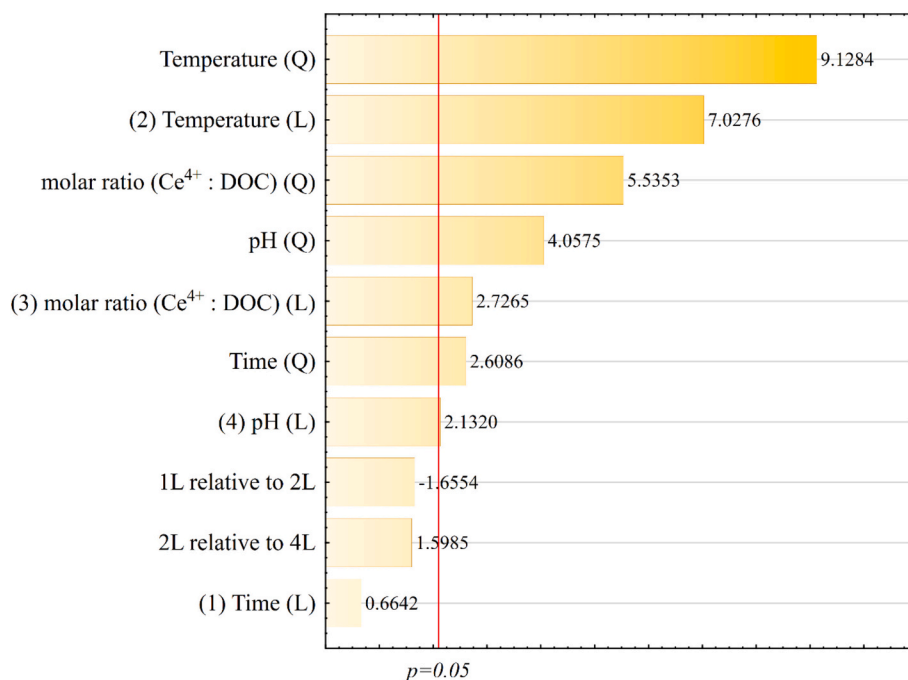


Fig. 2. Pareto chart - the absolute values of the standardised assessments of the effects. (DOC (mg/L), 4 values, 1 block, 29 experiments, MS = 19.313).

The red, vertical line indicates the limit of statistical significance with the assumed value of $p = 0.05$. The results to the right of the line are statistically significant. The parameters with the greatest statistical significance (the greatest impact on the model) were the quadratic and linear effects of temperature, followed by the quadratic effects of the Ce^{4+} :DOC molar ratio and pH, the linear effects of the Ce^{4+} :DOC molar ratio, the quadratic effects of time, and the linear effects of pH. Below the significance threshold were the effects of 1 L relative to 2 L, 2 L relative to 4 L and linear time effects (the smallest impact on the model).

An analysis with a reduced number of independent variables was conducted to create 6 response surface models (RSMs) indicating areas of maximum DOC reduction for individual sets of independent variables (Fig. 3). Particularly noteworthy are graphs D, E, and F in Fig. 3, which present the influence of the most important parameters (Ce^{4+} :DOC ratio and temperature, pH and temperature, pH and Ce^{4+} :DOC ratio) on the reduction in DOC concentration. The 3D plots indicate that the most optimal ranges of process parameters were a pH of 2.0–2.5, a Ce^{4+} :DOC ratio of 4–6, a reaction time of 20–40 min and a temperature range of 30–50 °C.

Fig. 4 shows a summary of the observed versus approximated results. In a situation of perfect fit ($R_{adj}^2 = 1$), the points on the graph would be along the regression line (red line). This would mean that the model explains 100 % of the results obtained. In the discussed case, due to the measurement uncertainty of the analytical methods used and unidentified factors affecting the experiment, the results are concentrated near the regression line (red line); therefore, 15 % of the results remain unexplained by the presented model. The approximated results were determined based on the second-degree eq. (8) obtained along with the creation of the response surface (RSM) (Fig. 3).

Based on the statistical analysis of the collected data, it was assumed that at 35 min, a pH of 2.5, a Ce^{4+} :DOC molar ratio of 1:5 and a temperature of 40 °C, the DOC reduction process was the most effective, allowing for the removal of 97.67 % of the cyanides, 99.97 % of the volatile phenolics, 99.40 % of the PAHs, and 90.01 % of the Σ of the heavy metals.

The reduction in pollutant concentrations is mainly based on their oxidation and, therefore, a reduction of Ce^{4+} ions in accordance with reaction (9).



During the dissolution of $CeSO_4 \cdot 4H_2O$, the solution immediately became cloudy, which could have been caused by the formation of pale yellow, sparingly soluble hydrolysis products, such as basic ceric sulphate $H[Ce(OH)_3SO_4]$. This phenomenon, which depends on various factors, such as, among others, the pH of the solution, Ce^{4+} concentration and temperature, may affect the efficiency of the oxidation reaction due to the inhibition of Ce^{4+} ions [99,100].

Upon completion of the process, the wastewater was alkalisied to pH = 8.2 to precipitate Ce^{3+} and Ce^{4+} . A decrease in the pH of the solution to 5.9 within 60 ± 1 min was an unfavourable phenomenon, which resulted in the dissolution of part of the sludge consisting of, among others, $Ce(OH)_3$ and in secondary contamination of the wastewater with Ce ions, the concentration of which reached 7.655 ± 0.766 mg/L. The above phenomenon suggests that it would be necessary to control and maintain a constant pH of wastewater or to quickly separate the liquid phase (purified wastewater) from the solid phase (sludge) in the case of using the batch process. In order to verify the adopted assumptions, an additional experiment was performed to confirm the optimal param-

$$\begin{aligned} \text{DOC concentration} = & 152.993 - 0.357 \cdot (\text{time}) + 0.010 \cdot (\text{time})^2 - 1.661 \cdot (\text{temperature}) + 0.020 \cdot (\text{temperature})^2 - 13.104 \cdot (Ce^{4+} \\ & : \text{DOC molar ratio}) + 1.194 \cdot (Ce^{4+} : \text{DOC molar ratio})^2 - 19.981 \cdot (\text{pH}) + 3.501 \cdot (\text{pH})^2 - 0.006 + 0.088 \end{aligned} \quad (8)$$

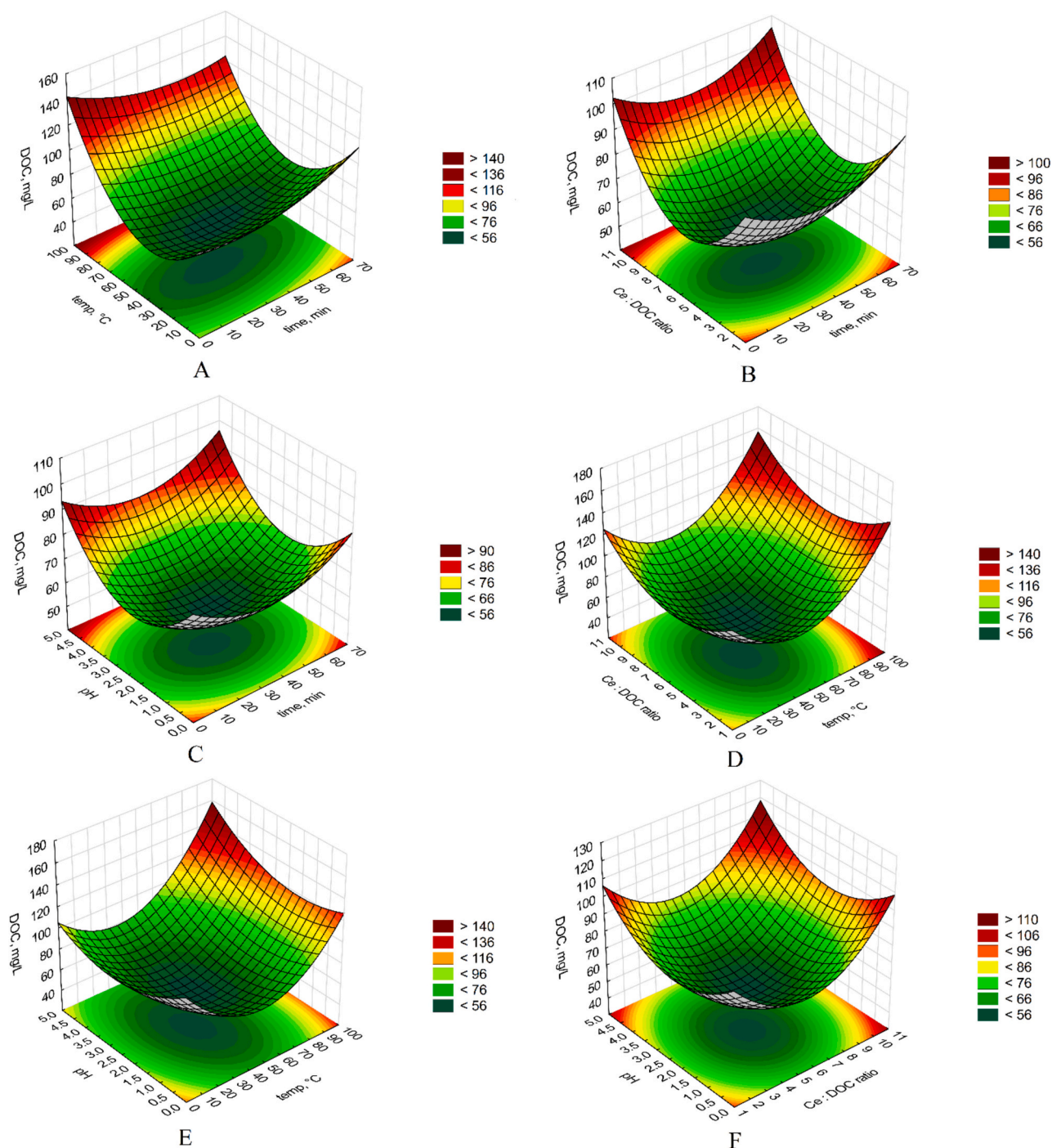


Fig. 3. Response surfaces showing the DOC concentration as a function of individual sets of independent variables, (A) temperature and time, (B) Ce⁴⁺:DOC molar ratio and time, (C) pH and time, (D) Ce⁴⁺:DOC molar ratio and temperature, (E) pH and temperature, (F) pH and Ce⁴⁺:DOC molar ratio.

ters. The results are presented in Table 4. When potassium ferrate(VI) was used by [101] as an oxidiser of pollutants in real produced water from an oil and gas exploration site, 89.73 % of the PAHs were removed. Potassium ferrate(VI) was also used by [102] for removing PAHs from coke wastewater. In an experiment involving a combination of potassium ferrate(VI) and the Fenton process, 84.01 % of phenanthrene was removed, while the use of potassium ferrate(VI) and the Fenton process alone allowed for a reduction of 73.66 and 52.61 %, respectively, of phenanthrene, which, as a PAH, is a typical compound found in coke wastewater.

3.2. Oxidation of pollutants in the Ce⁴⁺ ions + H₂O₂ system

The second process is a modification of that described in section 3.1. The modification consisted of dissolving solid cerium(IV) sulphate in the wastewater (with corrected pH to 2.5) and adding a 30 % hydrogen peroxide solution, the aim of which was to increase the oxidation potential of the system by generating hydroxyl radicals. After solid cerium (IV) sulphate was added to the wastewater, the solution immediately became cloudy which could have been caused by the hydrolysis of the added salt and the formation of compounds, as in the first experiment. In the next step, after adding perhydrol and mixing, the mixture was observed to change its colour to orange. After 35 min, the pH of the

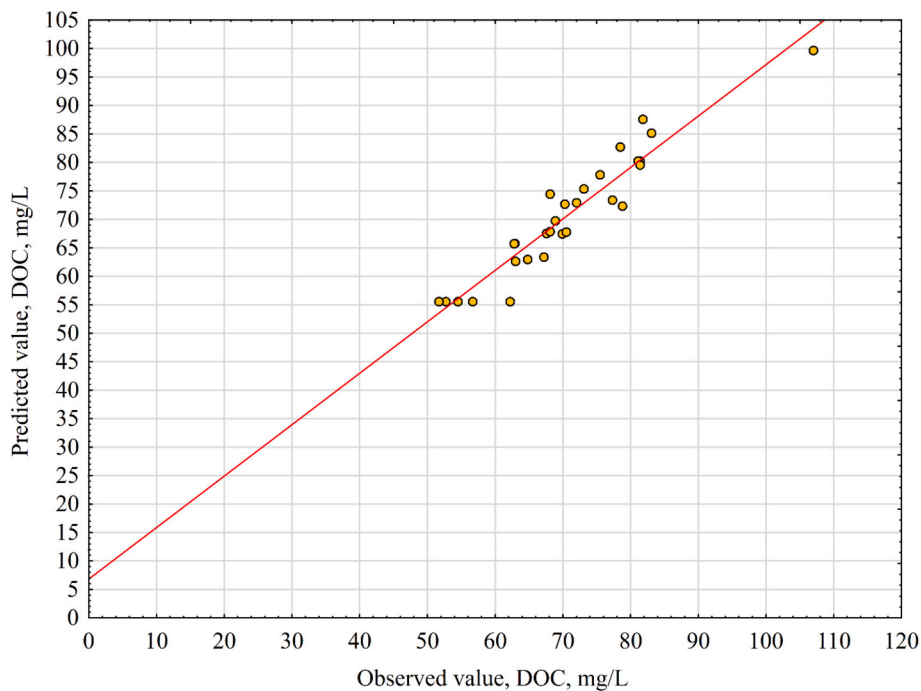


Fig. 4. Predicted values vs. observed values for DOC ($R^2 = 0.904$, $R^2_{adj} = 0.850$) oxidation experiments.

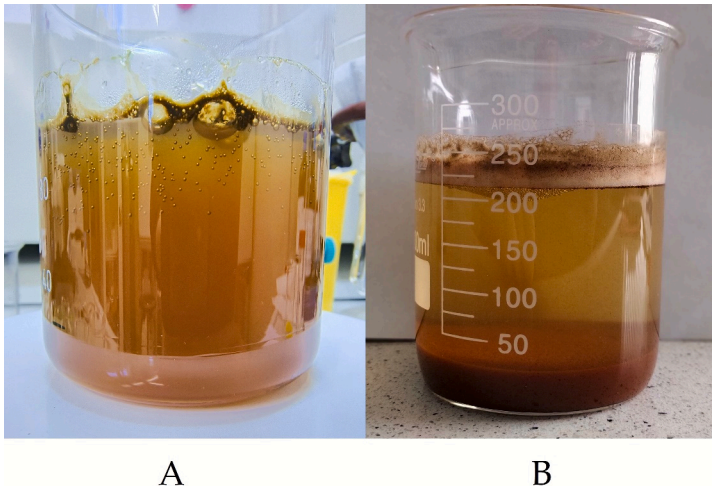


Fig. 5. The solution during the mixing and oxidation process, where the optimal $\text{DOC}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$ molar ratio was 1:2:10 and the time was 35 min (A); the solution after the oxidation and sedimentation process at pH 8.2 (B).

Table 3
DOC concentrations as a function of the amount of added cerium(IV) sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2); wastewater pH = 2.5.

Molar ratio $\text{C}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$	DOC, mg/L
1:1:5	38.7 ± 5.8
1:1:15	37.9 ± 5.7
1:2:2	41.8 ± 6.3
1:2:5	42.4 ± 6.4
1:2:10	37.1 ± 5.6
1:2:15	39.0 ± 5.9
1:3:5	36.7 ± 5.5
1:3:10	41.8 ± 6.3
1:3:15	39.0 ± 5.9

solution was increased to 8.2 by adding NaOH, and mixing was stopped. When the NaOH solution was subsequently added, the colour of the precipitate changed from orange to brown (Fig. 5).

The optimal proportions of H_2O_2 and Ce^{4+} to DOC were determined in a series of tests, in which different molar ratios of $\text{C}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$ reagents were tested. The DOC concentrations after the process for individual proportions of reagents are presented in Table 3.

Due to the lack of large differences between the results of individual tests, a molar ratio of $\text{DOC}:\text{Ce}^{4+}:\text{H}_2\text{O}_2$ of 1:2:10 was arbitrarily chosen as the optimal value, where the values of 2 for Ce^{4+} and 10 for hydrogen peroxide (H_2O_2) were between the tested values. Under optimal conditions, 98.14 % of the cyanides, 99.66 % of the phenols, 99.91 % of the PAHs and 81.45 % of the heavy metals were removed. In order to verify the adopted assumptions, an additional experiment was performed to confirm the optimal parameters. The results are presented in Table 4. Regarding the removal of contaminants by AOP methods, many authors

Table 4
Chemical composition of the wastewater before and after treatment.

Parameter	Unit	Raw wastewater	Ce ⁴⁺	Ce ⁴⁺ + H ₂ O ₂	Fe ²⁺ + H ₂ O ₂
pH	–	1.8 ± 0.1	5.9 ^a ± 0.1	8.7 ^a ± 0.1	7.9 ^a ± 0.1
Redox	mV	480	1153 ^b	585 ^b	559 ^b
DOC	mg/L	148.0 ± 22.2	51.3 ± 7.7	35.0 ± 5.3	64.4 ± 9.7
Cerium (Ce)	µg/L	< 0.10 ± 0.15	7655 ± 766	3.7 ± 0.6	< 0.10 ± 0.15
Iron (Fe)	mg/L	11.537 ± 1.154	0.003 ± 0.001	0.002 ± 0.001	0.003 ± 0.001
Manganese (Mn)	mg/L	0.197 ± 0.039	< 0.005 ± 0.001	< 0.005 ± 0.001	< 0.005 ± 0.001
Cadmium (Cd)	mg/L	< 0.005 ± 0.001	< 0.005 ± 0.001	< 0.005 ± 0.001	< 0.005 ± 0.001
Chromium (Cr)	mg/L	2.441 ± 0.244	0.0010 ± 0.0003	0.91 ± 0.09	0.41 ± 0.08
Copper (Cu)	mg/L	< 0.020 ± 0.005	< 0.020 ± 0.005	< 0.020 ± 0.005	< 0.020 ± 0.005
Nickel (Ni)	mg/L	1.088 ± 0.109	0.766 ± 0.153	0.514 ± 0.103	0.409 ± 0.082
Lead (Pb)	mg/L	1.603 ± 0.160	< 0.050 ± 0.013	< 0.050 ± 0.013	< 0.050 ± 0.013
Zinc (Zn)	mg/L	2.544 ± 0.254	< 0.050 ± 0.013	< 0.050 ± 0.013	< 0.050 ± 0.013
Total cyanides	µg/L	21,000 ± 2100	489 ± 49	390 ± 39	1036 ± 104
Total phenols volatile	µg/L	61,950 ± 4956	18.5 ± 2.8	207.8 ± 31.2	32.5 ± 4.9
Naftalen	µg/L	153.78 ± 38.45	4.64 ± 1.16	0.14 ± 0.04	< 0.050 ± 0.013
Acenaften	µg/L	284.56 ± 71.14	0.36 ± 0.09	0.23 ± 0.06	0.06 ± 0.02
Fluoren	µg/L	107.39 ± 26.85	0.25 ± 0.06	0.78 ± 0.20	< 0.050 ± 0.013
Fenantren	µg/L	263.23 ± 65.81	6.55 ± 1.64	0.36 ± 0.09	0.38 ± 0.10
Antracen	µg/L	93.81 ± 23.45	0.09 ± 0.02	0.42 ± 0.11	0.07 ± 0.02
Fluoranten	µg/L	133.79 ± 33.45	1.22 ± 0.31	0.16 ± 0.04	0.37 ± 0.09
Piren	µg/L	322.10 ± 80.53	0.45 ± 0.11	0.10 ± 0.03	0.45 ± 0.11
Benzo(a)antracen	µg/L	291.30 ± 72.83	0.08 ± 0.02	< 0.050 ± 0.013	0.10 ± 0.03
Chryzen	µg/L	143.09 ± 35.77	0.08 ± 0.02	< 0.050 ± 0.013	0.08 ± 0.02
Benzo(b)fluoranten	µg/L	151.23 ± 37.81	0.09 ± 0.02	< 0.050 ± 0.013	0.08 ± 0.02
Benzo(k)fluoranten	µg/L	85.26 ± 21.32	0.05 ± 0.01	< 0.050 ± 0.013	0.05 ± 0.01
Benzo(a)piren	µg/L	231.81 ± 57.95	0.11 ± 0.03	< 0.050 ± 0.013	0.12 ± 0.03
Dibenzo(a,h)antracen	µg/L	51.53 ± 12.88	0.03 ± 0.01	< 0.050 ± 0.013	0.05 ± 0.01
Benzo(g,h,i)perylene	µg/L	47.85 ± 11.96	0.45 ± 0.11	0.31 ± 0.08	0.36 ± 0.09
Indeno(1,2,3-cd)piren	µg/L	95.40 ± 23.85	0.17 ± 0.04	< 0.050 ± 0.013	0.16 ± 0.04
Σ PAH	µg/L	2459.11 ± 614.78	14.64 ± 3.66	2.25 ± 0.56	2.32 ± 0.58

^a – The pH of the wastewater after treatment was increased to 8.2, and another measurement was performed 1 h after the end of the process.

^b – redox potential after adding an oxidant to the wastewater.

have achieved results similar to those presented in this article. [103] achieved nearly 100 % reduction of phenol in water using copper slag in a Fenton-like process. Similarly, the use of zero-valent iron nanoparticles as catalysts in the Fenton-like process for the purification of real oily produced water, as reported by [104], resulted in an 87.4 % reduction in PAHs.

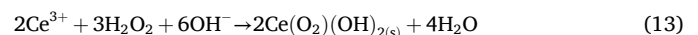
In an acidic environment (such as the analysed wastewater from the coal gasification process), radicals are formed in accordance with reactions (10) and (11) [105]. In the case of an alkaline environment, cerium creates stable peroxide forms, which block the process of producing hydroxyl radicals. Another instance where the oxidising capacity of the system may be hindered is when cerium salts are dissolved and mixed with hydrogen peroxide before the actual process of pollutant oxidation occurs [106].



Experiments carried out under optimal conditions resulted in reductions in pollutants such as cyanides, phenolics, and PAHs of 98.14 %, 99.66 %, and 99.91 %, respectively. Following the oxidation, the wastewater was alkalisied to a pH of 8.2 to precipitate certain metals, including cerium, in the form of hydroxides.

When added to wastewater, cerium(IV) sulphate may undergo hydrolysis and produce the substances described in section 3.1. Some Ce⁴⁺ ions oxidise pollutants and are reduced to Ce³⁺. In addition to the previously described formation of hydroxyl radicals, according to [107], the addition of H₂O₂ in an acidic environment may result in the formation of a Ce³⁺ complex with hydrogen peroxide (12), which, according to [108] in an acidic environment and with increasing pH in subsequent stages, will react to form a series of intermediate products, such as Ce(HO₂)₂²⁺, Ce(O₂)₂²⁺, and Ce(O₂)₂²⁺, to ultimately produce the brown sludge Ce(O₂)(OH)_{2(s)} according to the general eq. (13). Sixty minutes after the conclusion of the process, a subsequent pH

measurement indicated an increase in pH from 8.2 to 8.7. The increase in the solution pH could have been caused by the partial decomposition of Ce(O₂)(OH)_{2(s)} with the release of OH[−] ions.



The wastewater from the coal gasification process used in the experiment was characterised by a low pH of 1.8, which made it ideal for oxidation by the Ce⁴⁺ + hydrogen peroxide method and did not require significant pH correction. It is worth mentioning that the presence of Fe²⁺ and Fe³⁺ ions in wastewater can also initiate the formation of hydroxyl radicals, but in the case of the process in question, their impact is negligible due to the predominant concentration of Ce⁴⁺ ions [109]. As a result of the conducted experiment, the main pollutants in the wastewater were oxidised at an almost identical level as in the first experiment. However, the concentration of DOC was lower than in first experiment, confirming that the Ce⁴⁺ + H₂O₂ system is stronger oxidation agent than the Ce⁴⁺ solution alone. Additionally, the effect of secondary contamination with an oxidant was greatly reduced by binding to cerium in the stable sludge, which was not observed in the first experiment. An increase in the pH of the solution to 8.7 can be interpreted as a positive phenomenon, which results in the binding of some metals in the hydroxide form and minimising the content of Ce³⁺ and Ce⁴⁺ ions to the level of 2.1–4.5 µg/L (a concentration lower by 99.996 % compared to the amount used for the oxidation process). Such a content of Ce in the solution does not pose a threat to aquatic organisms and proves that Ce is effectively bound in the sludge. Attempts should therefore be undertaken to recover this element and, consequently, reduce the costs of the process by reusing Ce(SO₄)₂·4H₂O.

For this purpose, the wastewater sludge was tested for cerium recovery according to the acid extraction methodology described by [87]. The analysis was conducted by dissolving a 0.1 g sample of the sludge in aqua regia to determine the total Ce content according to ISO 15587-

1:2002. The Ce content in the sample dissolved in aqua regia was 624.4 ± 62.4 g/kg, whereas the sample after HCl leaching contained 621.4 ± 62.1 g/kg, which translates to a 99.52 % extraction of cerium from the sludge. This result indicates the possibility of Ce recovery and reuse in the wastewater treatment process after performing additional chemical operations aimed at reducing the pollutant content, i.e., HCl extraction, cerium oxalate precipitation, thermal decomposition of cerium oxalate to cerium(IV) oxide, and dissolution of cerium(IV) oxide in concentrated H_2SO_4 .

3.3. Oxidation of contaminants in the Fe^{2+} ions + H_2O_2 system

The third experiment was a comparison between the well-known, commonly used Fenton method for oxidising pollutants and the rarely used Fenton-like oxidation process in the Ce^{4+} + H_2O_2 system. The Fenton system, consisting of an Fe^{2+} solution with the addition of hydrogen peroxide (H_2O_2), was used in the same molar ratio as in the experiment described in section 3.2 (C: Ce^{4+} : H_2O_2 , 1:2:10). The results of this experiment are presented in Table 4.

In this process, hydroxyl radicals were generated, which, similar to previous experiments, significantly reduced pollutants such as cyanides by 95.07 %, total phenols by 99.95 %, PAHs by 99.91 %, and the Σ of heavy metals by 89.33 %. Other authors, in their studies using the classical Fenton process, obtained results that were worse or similar to those presented in this article. [110] used the Fenton process to treat coke wastewater, which is chemically similar to coal gasification wastewater, and reduced phenol by 88.46 % and cyanide by 79.34 %. In this article, each of the three examined methods allowed for effective pollutant reduction.

3.4. Perspective of using cerium compounds

The conducted studies and comparative analysis with the classical Fenton process have demonstrated that the use of cerium(IV) sulphate is an effective oxidising agent for pollutants present in acidic effluent from the coal gasification process. An additional aspect is the utilisation of waste heat from the gasification process, which enhances the efficiency of pollutant reduction. The possibility of using cerium(IV) sulphate as a pollutant oxidiser complements the previously conducted research,

allowing for the proposal of a cerium cycle scheme in the wastewater treatment process, as shown in Fig. 6. Industrial waste, such as spent polishing agents and wastewater sludge after coagulation with cerium (III) chloride, which contain approximately 82 % CeO_2 and 10 % Ce, respectively, can be valuable sources of cerium. The process of obtaining rare earth elements (REEs) is easier and less burdensome for the environment than the processing of minerals containing REEs. Research on the use of cerium compounds has shown that this element is an effective agent in wastewater treatment technology and can be recycled, thus closing its circulation in the process. Given the abovementioned aspects, the use of cerium compounds in coagulation or pollutant oxidation processes provides an interesting alternative to commonly applied technologies [84,87].

4. Conclusions

The conducted research assessed the ability of selected oxidation systems to reduce the content of pollutants in acidic wastewater from the process of hard coal gasification. The analysed systems, based on Ce^{4+} , Ce^{4+} and hydrogen peroxide, and Fe^{2+} and hydrogen peroxide (classical Fenton method), demonstrated high oxidation efficiency, removing 95.07–98.14 % of the total cyanides, 99.66–99.97 % of the total phenolics and 96.98 – ~100 % of the PAHs, and precipitating 89.0–99.0 % of the heavy metals as a result of alkalisation after the oxidation process. The conducted studies and obtained results showed that the proposed methods are effective and can be applied in the oxidation of highly toxic pollutants. Moreover, the possibility of secondary contamination of the solution with the oxidising agent was assessed. When cerium(IV) sulphate was used, it was more advantageous to carry out the process with the addition of H_2O_2 to produce hydroxyl radicals. After the oxidation process in the Ce^{4+} + hydrogen peroxide system and increasing the pH to slightly alkaline, the sludge demonstrated very good stability by binding 99.996 % of cerium ions, effectively reducing the risk of secondary contamination of the treated effluent. Due to the greater price of cerium compounds compared to iron(II) compounds, attempts have been made to extract cerium compounds from wastewater sludge generated in the oxidation process to produce cerium(III) salts, which are used as coagulants, cerium(IV) salts with oxidising properties, or high-purity cerium compounds for other applications. Studies on the

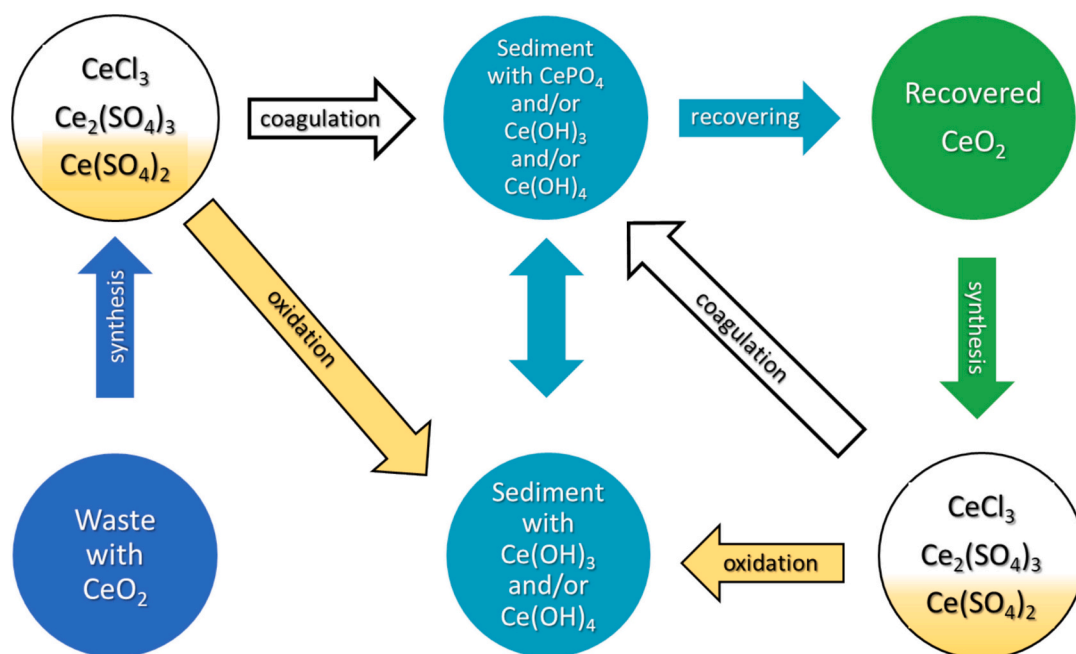


Fig. 6. Schematic diagram of the circulation of cerium compounds in the wastewater treatment process, considering recycling.

extraction of cerium from sludge with the use of hydrochloric acid have revealed its high efficiency, which creates the possibility of recovering cerium and reusing it for pollutant oxidation, thus closing its circulation in the process, which is extremely important from the point of circular economy.

Funding

This work was supported by the Ministry of Science and Education, Republic of Poland (Statutory Activity of the Central Mining Institute, Task no. 11331013–332).

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable

CRediT authorship contribution statement

Paweł Lejwoda: Writing – review & editing, Writing – original draft, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Barbara Bialecka:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization. **Maciej Thomas:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The datasets supporting the conclusions of this article are included within the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2024.106243>.

References

- [1] K. Kapusta, M. Wiatowski, H.R. Thomas, R. Zagorščak, S. Sadasivam, S. Masum, T. Kempka, C. Otto, W. Basa, M. Szyja, K. Stańczyk, Experimental simulations of methane-oriented underground coal gasification using hydrogen - the effect of coal rank and gasification pressure on the hydrogasification process, *Int. J. Hydrogen Energy* 48 (2023) 921–932, <https://doi.org/10.1016/j.ijhydene.2022.10.012>.
- [2] K. Kapusta, M. Wiatowski, K. Stańczyk, R. Zagorščak, H.R., Thomas, large-scale experimental investigations to evaluate the feasibility of producing methane-Rich gas (SNG) through underground coal gasification process, Effect of Coal Rank and Gasification Pressure, *Energies (Basel)* 13 (2020) 1334, <https://doi.org/10.3390/en13061334>.
- [3] R. Zagorščak, S. Sadasivam, H.R. Thomas, K. Stańczyk, K. Kapusta, Experimental study of underground coal gasification (UCG) of a high-rank coal using atmospheric and high-pressure conditions in an ex-situ reactor, *Fuel* 270 (2020) 117490, <https://doi.org/10.1016/j.fuel.2020.117490>.
- [4] K. Kapusta, Effect of lignite properties on its suitability for the implementation of underground coal gasification (UCG) in selected deposits, *Energies (Basel)* 14 (2021) 5816, <https://doi.org/10.3390/en14185816>.
- [5] B. Bielowicz, J. Misiak, The impact of Coal's petrographic composition on its suitability for the gasification process: the example of polish deposits, *Resources* 9 (2020) 111, <https://doi.org/10.3390/resources9090111>.
- [6] M. Wiatowski, W. Basa, M. Pankiewicz-Sperka, M. Szyja, H.R. Thomas, R. Zagorščak, S. Sadasivam, S. Masum, T. Kempka, C. Otto, K. Kapusta, Experimental study on tar formation during underground coal gasification: effect of coal rank and gasification pressure on tar yield and chemical composition, *Fuel* 357 (2024) 130034, <https://doi.org/10.1016/j.fuel.2023.130034>.
- [7] M. Ma, Y. Bai, J. Wei, X. Song, P. Lv, J. Wang, W. Su, Q. Xiong, G. Yu, Decoupling study of volatile-char interaction during coal/biomass co-gasification based on a two-stage fixed bed reactor: insight into the role of O-containing compound species, *Chem. Eng. Sci.* 265 (2023) 118262, <https://doi.org/10.1016/j.ces.2022.118262>.
- [8] B. Liu, X. Tu, Plasma coal gasification for syngas production, in: *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier, 2024, <https://doi.org/10.1016/B978-0-443-15740-0.00037-9>.
- [9] X. Wang, Z. Zhu, K. Wang, K. Yu, Q. Lyu, Experimental study of pilot-scale CFB gasification: effect of gasifying agent and coal feeding modes on the gasification performance, *Fuel* 251 (2019) 603–610, <https://doi.org/10.1016/j.fuel.2019.04.070>.
- [10] E. Aydar, S. Gul, N. Unlu, F. Akgun, H. Livatyali, Effect of the type of gasifying agent on gas composition in a bubbling fluidized bed reactor, *J. Energy Inst.* 87 (2014) 35–42, <https://doi.org/10.1016/j.joei.2014.02.004>.
- [11] Z. Zhao, W. Kong, X. Zhang, M. Liu, P. Cui, Catalytic steam gasification of bituminous coal for syngas production with catalyst derived from calcium-rich construction demolition waste, *Fuel* 359 (2024) 130428, <https://doi.org/10.1016/j.fuel.2023.130428>.
- [12] H. Jüntgen, Application of catalysts to coal gasification processes, Incentives and perspectives, *Fuel* 62 (1983) 234–238, [https://doi.org/10.1016/0016-2361\(83\)90206-5](https://doi.org/10.1016/0016-2361(83)90206-5).
- [13] N.C. Nahas, Exxon catalytic coal gasification process, *Fuel* 62 (1983) 239–241, [https://doi.org/10.1016/0016-2361\(83\)90207-7](https://doi.org/10.1016/0016-2361(83)90207-7).
- [14] T. Popa, M. Fan, M.D. Argyle, M.D. Dyar, Y. Gao, J. Tang, E.A. Speicher, D. M. Kamm, H₂ and CO_x generation from coal gasification catalyzed by a cost-effective iron catalyst, *Appl. Catal. Gen.* 464–465 (2013) 207–217, <https://doi.org/10.1016/j.apcata.2013.05.038>.
- [15] M. Gao, P. Lv, Z. Yang, Y. Bai, F. Li, K. Xie, Effects of Ca/Na compounds on coal gasification reactivity and char characteristics in H₂O/CO₂ mixtures, *Fuel* 206 (2017) 107–116, <https://doi.org/10.1016/j.fuel.2017.05.079>.
- [16] S. Fan, X. Yuan, J.-C. Park, L.-H. Xu, T.-J. Kang, H.-T. Kim, Gasification of Indonesian sub-bituminous coal with different gasifying agents using Ca and K catalysts, *Energy Fuel* 30 (2016) 9372–9378, <https://doi.org/10.1021/acs.energyfuels.6b01329>.
- [17] D.A. Flórez-Orrego, R. Nogueira Nakashima, M.E.G.R. Domingos, M.T. dos Santos, S. de Oliveira Junior, Ammonia Production from Syngas, in: *Advances in Synthesis Gas : Methods, Elsevier, Technologies and Applications*, 2023, pp. 45–91, <https://doi.org/10.1016/B978-0-323-91878-7.00016-2>.
- [18] M. Farsi, Ammonia Production from Syngas: Plant Design and Simulation, in: *Advances in Synthesis Gas : Methods, Elsevier, Technologies and Applications*, 2023, pp. 381–399, <https://doi.org/10.1016/B978-0-323-91879-4.00012-6>.
- [19] G. Liu, H. Hagelin-Weaver, B. Welt, A concise review of catalytic synthesis of methanol from synthesis gas, *Waste* 1 (2023) 228–248, <https://doi.org/10.3390/waste1010015>.
- [20] X. Cui, S.K. Kær, A comparative study on three reactor types for methanol synthesis from syngas and CO₂, *Chem. Eng. J.* 393 (2020) 124632, <https://doi.org/10.1016/j.cej.2020.124632>.
- [21] D.M. Kennes-Veiga, C. Fernández-Blanco, M.C. Veiga, C. Kennes, Ethanol Production from Syngas, in: *Advances in Synthesis Gas : Methods, Elsevier, Technologies and Applications*, 2023, pp. 147–171, <https://doi.org/10.1016/B978-0-323-91878-7.00013-7>.
- [22] G. Liu, G. Yang, X. Peng, J. Wu, N. Tsubaki, Recent advances in the routes and catalysts for ethanol synthesis from syngas, *Chem. Soc. Rev.* 51 (2022) 5606–5659, <https://doi.org/10.1039/D0CS01003K>.
- [23] A.L. Boehman, O. Le Corre, Combustion of syngas in internal combustion engines, *Combust. Sci. Technol.* 180 (2008) 1193–1206, <https://doi.org/10.1080/00102200801963417>.
- [24] Z. Wang, K.G. Burra, M. Zhang, X. Li, X. He, T. Lei, A.K. Gupta, Syngas evolution and energy efficiency in CO₂-assisted gasification of pine bark, *Appl. Energy* 269 (2020) 114996, <https://doi.org/10.1016/j.apenergy.2020.114996>.
- [25] K. Kapusta, K. Stańczyk, Pollution of water during underground coal gasification of hard coal and lignite, *Fuel* 90 (2011) 1927–1934, <https://doi.org/10.1016/j.fuel.2010.11.025>.
- [26] C.-E. Boström, P. Gerde, A. Hanberg, B. Jernström, C. Johansson, T. Kyrklund, A. Rannug, M. Törnqvist, K. Victorin, R. Westerholm, Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air, *Environ. Health Perspect.* 110 (2002) 451–488, <https://doi.org/10.1289/ehp.110-1241197>.
- [27] G.K. Gaurav, T. Mehmood, M. Kumar, L. Cheng, K. Sathishkumar, A. Kumar, D. Yadav, Review on polycyclic aromatic hydrocarbons (PAHs) migration from wastewater, *J. Contam. Hydrol.* 236 (2021) 103715, <https://doi.org/10.1016/j.jconhyd.2020.103715>.
- [28] W.T. Hsu, M.C. Liu, P.C. Hung, S.H. Chang, M.B. Chang, PAH emissions from coal combustion and waste incineration, *J. Hazard. Mater.* 318 (2016) 32–40, <https://doi.org/10.1016/j.jhazmat.2016.06.038>.
- [29] M. Wiatowski, K. Kapusta, Evolution of tar compounds in raw gas from a pilot-scale underground coal gasification (UCG) trial at Wieczorek mine in Poland, *Fuel* 276 (2020) 118070, <https://doi.org/10.1016/j.fuel.2020.118070>.
- [30] Q. Zhang, J. Meng, G. Su, Z. Liu, B. Shi, T. Wang, Source apportionment and risk assessment for polycyclic aromatic hydrocarbons in soils at a typical coking plant, *Ecotoxicol. Environ. Saf.* 222 (2021) 112509, <https://doi.org/10.1016/j.ecoenv.2021.112509>.

- [31] W. Zhang, C. Wei, C. Feng, B. Yan, N. Li, P. Peng, J. Fu, Coking wastewater treatment plant as a source of polycyclic aromatic hydrocarbons (PAHs) to the atmosphere and health-risk assessment for workers, *Sci. Total Environ.* 432 (2012) 396–403, <https://doi.org/10.1016/j.scitotenv.2012.06.010>.
- [32] H. Cao, B. Wulijia, L. Wang, Y. Li, X. Liao, New perspective on human health risk from polycyclic aromatic hydrocarbons (PAHs) on surfaces of structures and buildings for industrial legacy before and after remediation, *J. Clean. Prod.* 379 (2022) 134828, <https://doi.org/10.1016/j.jclepro.2022.134828>.
- [33] S. Dobaradaran, T.C. Schmidt, M. Lorenzo-Parodi, M.A. Jochmann, I. Nabipour, A. Raeisi, N. Stojanović, M. Mahmoodi, Cigarette butts: an overlooked source of PAHs in the environment? *Environ. Pollut.* 249 (2019) 932–939, <https://doi.org/10.1016/j.envpol.2019.03.097>.
- [34] O.A. Adesina, T.I. Olowolafe, A. Igbafe, Levels of polycyclic aromatic hydrocarbon from mainstream smoke of tobacco products and its risks assessment, *Journal of Hazardous Materials Advances* 5 (2022) 100053, <https://doi.org/10.1016/j.hazadv.2022.100053>.
- [35] E. Hussar, S. Richards, Z.-Q. Lin, R.P. Dixon, K.A. Johnson, Human health risk assessment of 16 priority polycyclic aromatic hydrocarbons in soils of Chattanooga, Tennessee, USA, *Water Air Soil Pollut.* 223 (2012) 5535–5548, <https://doi.org/10.1007/s11270-012-1265-7>.
- [36] P.K. Verma, D. Sah, J. Dubey, K.M. Kumari, A. Lakhani, Mutagenic and Cancer risk estimation of particulate bound polycyclic aromatic hydrocarbons from the emission of different biomass fuels, *Chem. Res. Toxicol.* 34 (2021) 743–753, <https://doi.org/10.1021/acs.chemrestox.0c00378>.
- [37] R. Stading, G. Gastelum, C. Chu, W. Jiang, B. Moorthy, Molecular mechanisms of pulmonary carcinogenesis by polycyclic aromatic hydrocarbons (PAHs): implications for human lung cancer, *Semin. Cancer Biol.* 76 (2021) 3–16, <https://doi.org/10.1016/j.semcancer.2021.07.001>.
- [38] N.A. Sopian, J. Jalaludin, S. Abu Bakar, T.R. Hamedon, M.T. Latif, Exposure to particulate PAHs on potential genotoxicity and Cancer risk among school children living near the petrochemical industry, *Int. J. Environ. Res. Public Health* 18 (2021) 2575, <https://doi.org/10.3390/ijerph18052575>.
- [39] F.C. da Silva Junior, M.B.M.C. Felipe, D.E.F. de Castro, S.C. da S. Araújo, H.C. N. Sisenando, S.R. Batistuzzo de Medeiros, A look beyond the priority: a systematic review of the genotoxic, mutagenic, and carcinogenic endpoints of non-priority PAHs, *Environ. Pollut.* 278 (2021) 116838, <https://doi.org/10.1016/j.envpol.2021.116838>.
- [40] S. Sadasivam, R. Zagorščak, H.R. Thomas, K. Kapusta, K. Stańczyk, Characterisation of the contaminants generated from a large-scale ex-situ underground coal gasification study using high-rank coal from the South Wales coalfield, *Water Air Soil Pollut.* 231 (2020) 519, <https://doi.org/10.1007/s11270-020-04888-1>.
- [41] M. Pankiewicz-Sperka, K. Kapusta, W. Basa, K. Stolecka, Characteristics of water contaminants from underground coal gasification (UCG) process—effect of coal properties and gasification pressure, *Energies (Basel)* 14 (2021) 6533, <https://doi.org/10.3390/en14206533>.
- [42] European Commission, DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2020 on THE Quality of Water Intended for Human Consumption (Recast), 2020.
- [43] MINISTER GOSPODARKI MORSKIEJ I ŻEGLUGI ŚRÓDLĄDOWEJ, Rozporządzenie Ministra Gospodarki Morskiej i Żegluga Śródlądowej z dnia 29 sierpnia 2019 r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia przez ludzi, Poland, 2019.
- [44] M.F. Nisar, M. Khadim, M. Rafiq, J. Chen, Y. Yang, C.C. Wan, Pharmacological properties and health benefits of eugenol: a comprehensive review, *Oxid. Med. Cell. Longev.* 2021 (2021) 1–14, <https://doi.org/10.1155/2021/2497354>.
- [45] A. Escobar, M. Pérez, G. Romanelli, G. Blustein, Thymol bioactivity: a review focusing on practical applications, *Arab. J. Chem.* 13 (2020) 9243–9269, <https://doi.org/10.1016/j.arabjc.2020.11.009>.
- [46] T. Gao, Y. Zhang, J. Shi, S.R. Mohamed, J. Xu, X. Liu, The antioxidant Guaiacol exerts fungicidal activity against fungal growth and Deoxynivalenol production in fusarium graminearum, *Front. Microbiol.* 12 (2021), <https://doi.org/10.3389/fmicb.2021.762844>.
- [47] Q. Wu, D. Yan, Y. Chen, T. Wang, F. Xiong, W. Wei, Y. Lu, W.-Y. Sun, J.J. Li, J. Zhao, A redox-neutral catechol synthesis, *Nat. Commun.* 8 (2017) 14227, <https://doi.org/10.1038/ncomms14227>.
- [48] M. Koushki, N. Amiri-Dashatan, N. Ahmadi, H. Abbaszadeh, M. Rezaei-Tavirani, Resveratrol: a miraculous natural compound for diseases treatment, *Food Sci. Nutr.* 6 (2018) 2473–2490, <https://doi.org/10.1002/fsn3.855>.
- [49] R.M. Giner, J.L. Ríos, S. Máñez, Antioxidant activity of natural Hydroquinones, *Antioxidants* 11 (2022) 343, <https://doi.org/10.3390/antiox11020343>.
- [50] H.N. Murthy, K.S. Joseph, K.Y. Paek, S.-Y. Park, Anthocyanin production from plant cell and organ cultures in vitro, *Plants* 13 (2023) 117, <https://doi.org/10.3390/plants13010117>.
- [51] M.C. Dias, D.C.G.A. Pinto, A.M.S. Silva, Plant flavonoids: chemical characteristics and biological activity, *Molecules* 26 (2021) 5377, <https://doi.org/10.3390/molecules26175377>.
- [52] S.S. Arya, J.E. Rookes, D.M. Cahill, S.K. Lenka, Vanillin: a review on the therapeutic prospects of a popular flavouring molecule, *Adv. Tradit. Med.* 21 (2021) 1–17, <https://doi.org/10.1007/s13596-020-00531-w>.
- [53] Z. Li, H. Zhang, Y. Wang, Y. Li, Q. Li, L. Zhang, The distinctive role of menthol in pain and analgesia: mechanisms, practices, and advances, *Front. Mol. Neurosci.* 15 (2022), <https://doi.org/10.3389/fnmol.2022.1006908>.
- [54] W. Zhang, C. Wei, C. Feng, Y. Ren, Y. Hu, B. Yan, C. Wu, The occurrence and fate of phenolic compounds in a coking wastewater treatment plant, *Water Sci. Technol.* 68 (2013) 433–440, <https://doi.org/10.2166/wst.2013.269>.
- [55] Y. Zhao, Composition of phenolic compounds in wastewater from the fixed-bed gasification of Baishihu coal, *Int. J. Coal Sci. Technol.* 8 (2021) 1461–1467, <https://doi.org/10.1007/s40789-021-00425-5>.
- [56] W. Al Hashemi, M.A. Maraqa, M.V. Rao, M.M. Hossain, Characterization and removal of phenolic compounds from condensate-oil refinery wastewater, desalination, *Water Treat* 54 (2015) 660–671, <https://doi.org/10.1080/19443994.2014.884472>.
- [57] J. Shi, N. Wan, L. Li, Z. Li, H. Han, Review on treatment technologies of coal gasification wastewater in China, *J. Clean. Prod.* 333 (2022) 130166, <https://doi.org/10.1016/j.jclepro.2021.130166>.
- [58] S.G. Davey, Sustainability: sweet new route to acrylonitrile, *Nat. Rev. Chem.* 2 (2018) 0110, <https://doi.org/10.1038/s41570-017-0110>.
- [59] L.D. Hansen, W.M. Litchman, G.H. Daub, Turnbull's blue and Prussian blue: KFe(III)[Fe(II)(CN)₆], *J. Chem. Educ.* 46 (1969) 46, <https://doi.org/10.1021/ed046p46>.
- [60] M. Ruiz-Bermejo, J.L. de la Fuente, C. Pérez-Fernández, E. Mateo-Martí, A comprehensive review of HCN-derived polymers, *Processes* 9 (2021) 597, <https://doi.org/10.3390/pr9040597>.
- [61] M.A. Acheampong, R.J.W. Meulepas, P.N.L. Lens, Removal of heavy metals and cyanide from gold mine wastewater, *J. Chem. Technol. Biotechnol.* 85 (2010) 590–613, <https://doi.org/10.1002/jctb.2358>.
- [62] A. Akcil, C. Erust, C.S. Gahan, M. Ozgun, M. Sahin, A. Tuncuk, Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants – a review, *Waste Manag.* 45 (2015) 258–271, <https://doi.org/10.1016/j.wasman.2015.01.017>.
- [63] S.S.M. Hassan, M.S.A. Hamza, A.E. Kelany, A novel spectrophotometric method for batch and flow injection determination of cyanide in electroplating wastewater, *Talanta* 71 (2007) 1088–1095, <https://doi.org/10.1016/j.talanta.2006.06.010>.
- [64] M. Thomas, V. Kozik, A. Bak, K. Barbusiński, J. Jazowiecka-Rakus, J. Jampilek, Removal of heavy metal ions from wastewaters: an application of sodium Trithiocarbonate and wastewater toxicity assessment, *Materials* 14 (2021) 655, <https://doi.org/10.3390/ma14030655>.
- [65] M. Wiatowski, K. Stańczyk, J. Świądowski, K. Kapusta, K. Cybulski, E. Krause, J. Grabowski, J. Rogut, N. Howaniec, A. Smoliński, Semi-technical underground coal gasification (UCG) using the shaft method in Experimental Mine "Barbara," *Fuel* 99 (2012) 170–179, <https://doi.org/10.1016/j.fuel.2012.04.017>.
- [66] Y.M. Kim, D. Park, D.S. Lee, J.M. Park, Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment, *J. Hazard. Mater.* 152 (2008) 915–921, <https://doi.org/10.1016/j.jhazmat.2007.07.065>.
- [67] S. Mahernia, A. Amanlou, G. kiae, M. Amanlou, Determination of hydrogen cyanide concentration in mainstream smoke of tobacco products by polarography, *J. Environ. Health Sci. Eng.* 13 (2015) 57, <https://doi.org/10.1186/s40201-015-0211-1>.
- [68] R. Eisler, S.N. Wiemeyer, Cyanide Hazards to Plants and Animals from Gold Mining and Related Water Issues, 2004, pp. 21–54, https://doi.org/10.1007/978-1-4419-9100-3_2.
- [69] E. Jaszczak, Ż. Polkowska, S. Narkowicz, J. Namieśnik, Cyanides in the environment—analysis—problems and challenges, *Environ. Sci. Pollut. Res.* 24 (2017) 15929–15948, <https://doi.org/10.1007/s11356-017-9081-7>.
- [70] A.R. Allen, L. Booker, G.A. Rockwood, Acute cyanide toxicity, in: *Toxicology of Cyanides and Cyanogens*, Wiley, 2015, pp. 1–20, <https://doi.org/10.1002/9781118628966.ch1>.
- [71] Q. Ji, S. Tabassum, S. Hena, C.G. Silva, G. Yu, Z. Zhang, A review on the coal gasification wastewater treatment technologies: past, present and future outlook, *J. Clean. Prod.* 126 (2016) 38–55, <https://doi.org/10.1016/j.jclepro.2016.02.147>.
- [72] N. Panigrahy, A. Priyadarshini, M.M. Sahoo, A.K. Verma, A. Daverey, N.K. Sahoo, A comprehensive review on eco-toxicity and biodegradation of phenolics: recent progress and future outlook, *Environ. Technol. Innov.* 27 (2022) 102423, <https://doi.org/10.1016/j.eti.2022.102423>.
- [73] V.S. García Rea, B. Egerland Bueno, D. Cerqueda-García, J.D. Muñoz Sierra, H. Spanjers, J.B. van Lier, Degradation of p-cresol, resorcinol, and phenol in anaerobic membrane bioreactors under saline conditions, *Chem. Eng. J.* 430 (2022) 132672, <https://doi.org/10.1016/j.cej.2021.132672>.
- [74] V.S. García Rea, B. Egerland Bueno, J.D. Muñoz Sierra, A. Nair, I.J. Lopez Prieto, D. Cerqueda-García, J.B. van Lier, H. Spanjers, Chemical characterization and anaerobic treatment of bitumen fume condensate using a membrane bioreactor, *J. Hazard. Mater.* 447 (2023) 130709, <https://doi.org/10.1016/j.jhazmat.2022.130709>.
- [75] W. Kong, Y. Li, Y. Zhang, Y. Mei, S. Tabassum, Biological treatment of refractory organic compounds in coal gasification wastewater: a review, *Journal of Water Process Engineering* 60 (2024) 105255, <https://doi.org/10.1016/j.jwpe.2024.105255>.
- [76] N. Mpongwana, S.K.O. Ntwampe, E.I. Omodanisi, B.S. Chidi, L. C. Razanamahandry, Sustainable approach to eradicate the inhibitory effect of free-cyanide on simultaneous nitrification and aerobic denitrification during wastewater treatment, *Sustainability* 11 (2019) 6180, <https://doi.org/10.3390/su11216180>.
- [77] V.J. Inglezakis, S. Malamis, A. Omirhan, J. Nauruzbayeva, Z. Makhtayeva, T. Seidakhmetov, A. Kudarova, Investigating the inhibitory effect of cyanide, phenol and 4-nitrophenol on the activated sludge process employed for the

- treatment of petroleum wastewater, *J. Environ. Manage.* 203 (2017) 825–830, <https://doi.org/10.1016/j.jenvman.2016.08.066>.
- [78] J. Shi, Y. Han, C. Xu, H. Han, Biological coupling process for treatment of toxic and refractory compounds in coal gasification wastewater, *Rev. Environ. Sci. Biotechnol.* 17 (2018) 765–790, <https://doi.org/10.1007/s11157-018-9481-2>.
- [79] S. Hussain, E. Aneggi, D. Goi, Catalytic activity of metals in heterogeneous Fenton-like oxidation of wastewater contaminants: a review, *Environ. Chem. Lett.* 19 (2021) 2405–2424, <https://doi.org/10.1007/s10311-021-01185-z>.
- [80] P. Mahbub, M. Duke, Scalability of advanced oxidation processes (AOPs) in industrial applications: a review, *J. Environ. Manage.* 345 (2023) 118861, <https://doi.org/10.1016/j.jenvman.2023.118861>.
- [81] J. Nawrocki, *Uzdatnianie wody Procesy fizyczne, chemiczne i biologiczne Tom 1, Wydawnictwo Naukowe PWN, Warszawa, 2010.*
- [82] G.W. Kajjumba, D. Fischer, L.A. Risso, D. Koury, E.J. Marti, Application of cerium and lanthanum coagulants in wastewater treatment—a comparative assessment to magnesium, aluminum, and iron coagulants, *Chem. Eng. J.* 426 (2021), <https://doi.org/10.1016/j.cej.2021.131268>.
- [83] G.W. Kajjumba, E.J. Marti, A review of the application of cerium and lanthanum in phosphorus removal during wastewater treatment: characteristics, mechanism, and recovery, *Chemosphere* 309 (2022) 136462, <https://doi.org/10.1016/j.chemosphere.2022.136462>.
- [84] P. Lejwoda, B. Bialecka, M. Thomas, Removal of phosphate from brewery wastewater by cerium(III) chloride originating from spent polishing agent: recovery and optimization studies, *Sci. Total Environ.* (2023), <https://doi.org/10.1016/j.scitotenv.2023.162643>.
- [85] C.K. Gupta, N. Krishnamurthy, Extractive metallurgy of rare earths, *Int. Mater. Rev.* 37 (1992) 197–248, <https://doi.org/10.1179/imr.1992.37.1.197>.
- [86] European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Grohol, M., Veeh, C., Study on the critical raw materials for the EU 2023 – Final report, Publications Office of the European Union, 2023, <https://data.europa.eu/doi/10.2873/725585>, (2023).
- [87] P. Lejwoda, B. Bialecka, K. Barbusiński, M. Thomas, Recovery of cerium salts from sewage sludge resulting from the coagulation of brewery wastewater with recycled cerium coagulant, *Materials* 17 (2024) 938, <https://doi.org/10.3390/ma17040938>.
- [88] A. Poscher, S. Luidold, H. Schnideritsch, H. Antrekowitsch, Extraction of Lanthanides from Spent Polishing Agent., N Proceedings of the ERES2014-1st European Rare Earth Resources Conference (2014) 209–222.
- [89] C. Borra, T. Vlught, Y. Yang, S. Offerman, Recovery of cerium from glass polishing waste: a critical review, *Metals (Basel)* 8 (2018) 801, <https://doi.org/10.3390/met8100801>.
- [90] K.A. Gschneidner, J.-C.G. Bünzli, V.K. Pecharsky, Handbook on the physics and chemistry of rare earths, in (2006), [https://doi.org/10.1016/S0168-1273\(06\)36007-2](https://doi.org/10.1016/S0168-1273(06)36007-2).
- [91] J. Minczewski, Z. Marczenko, *Analytical Chemistry, Wydawnictwo Naukowe PWN, Warsaw, 2022.*
- [92] J. ZHAO, B. LI, C. YANG, X. RAO, Application of Ce(IV) in industrial wastewater treatment, *J. Rare Earths* 28 (2010) 37–39, doi:[https://doi.org/10.1016/S1002-0721\(10\)60340-7](https://doi.org/10.1016/S1002-0721(10)60340-7).
- [93] M. Wiatowski, K. Kapusta, A. Strugała-Wilczek, K. Stańczyk, A. Castro-Muñiz, F. Suárez-García, J.I. Paredes, Large-scale experimental simulations of in situ coal gasification in terms of process efficiency and physicochemical properties of process by-products, *Energies (Basel)* 16 (2023) 4455, <https://doi.org/10.3390/en16114455>.
- [94] M.O. Saeed, K. Azizli, M.H. Isa, M.J.K. Bashir, Application of CCD in RSM to obtain optimize treatment of POME using Fenton oxidation process, *Journal of water, Process. Eng.* 8 (2015) e7–e16, <https://doi.org/10.1016/j.jwpe.2014.11.001>.
- [95] M. Leili, N. Shirmohammadi Khorram, K. Godini, G. Azarian, R. Moussavi, A. Peykoshian, Application of central composite design (CCD) for optimization of cephalixin antibiotic removal using electro-oxidation process, *J. Mol. Liq.* 313 (2020) 113556, <https://doi.org/10.1016/j.molliq.2020.113556>.
- [96] K. Barbusiński, *Intensyfikacja procesu oczyszczania ścieków i stabilizacji osadów nadmiernych z wykorzystaniem odczynnika Fentona, Zeszyty Naukowe Politechniki Śląskiej, Gliwice, 2004.*
- [97] Ç. Çalik, D.İ. Çifçi, Comparison of kinetics and costs of Fenton and photo-Fenton processes used for the treatment of a textile industry wastewater, *J. Environ. Manage.* 304 (2022) 114234, <https://doi.org/10.1016/j.jenvman.2021.114234>.
- [98] J. Kuc, M. Thomas, I. Grochowalska, R. Kulczyk, G. Mikosz, F. Mrózek, D. Janik, J. Korta, K. Cwynar, Determination and removal of selected pharmaceuticals and Total organic carbon from surface water by aluminum Chlorohydrate coagulant, *Molecules* 27 (2022) 5740, <https://doi.org/10.3390/molecules27175740>.
- [99] P. Yu, S.A. Hayes, T.J. O'Keefe, M.J. O'Keefe, J.O. Stoffer, The phase stability of cerium species in aqueous systems, *J. Electrochem. Soc.* 153 (2006) C74, <https://doi.org/10.1149/1.2130572>.
- [100] A. Paulenova, S.E. Creager, J.D. Navratil, Y. Wei, Redox potentials and kinetics of the Ce³⁺/Ce⁴⁺ redox reaction and solubility of cerium sulfates in sulfuric acid solutions, *J. Power Sources* 109 (2002) 431–438, [https://doi.org/10.1016/S0378-7753\(02\)00109-X](https://doi.org/10.1016/S0378-7753(02)00109-X).
- [101] T. Haneef, M.R.U. Mustafa, K. Wan Yusof, M.H. Isa, M.J.K. Bashir, M. Ahmad, M. Zafar, Removal of Polycyclic Aromatic Hydrocarbons (PAHs) 12 (2020) 3132, <https://doi.org/10.3390/w12113132>, from Produced Water by Ferrate (VI) Oxidation, *Water (Basel)*.
- [102] Y.N. Li, Z.H. Duan, Y.F. Wang, Z.J. Yuan, G.Y. Wang, Preliminary treatment of phenanthrene in coking wastewater by a combined potassium ferrate and Fenton process, *Int. J. Environ. Sci. Technol.* 16 (2019) 4483–4492, <https://doi.org/10.1007/s13762-018-2037-8>.
- [103] T. Huanosta-Gutiérrez, R.F. Dantas, R.M. Ramírez-Zamora, S. Esplugas, Evaluation of copper slag to catalyze advanced oxidation processes for the removal of phenol in water, *J. Hazard. Mater.* 213–214 (2012) 325–330, <https://doi.org/10.1016/j.jhazmat.2012.02.004>.
- [104] T. Haneef, M.R. Ul Mustafa, K. Rasool, Y.C. Ho, S.R. Mohamed Kutty, Removal of Polycyclic Aromatic Hydrocarbons in a Heterogeneous Fenton Like Oxidation System Using Nanoscale Zero-Valent Iron as a Catalyst 12 (2020) 2430, <https://doi.org/10.3390/w12092430>, *Water (Basel)*.
- [105] E.G. Heckert, S. Seal, W.T. Self, Fenton-like reaction catalyzed by the rare earth inner transition metal cerium, *Environ. Sci. Technol.* 42 (2008) 5014–5019, <https://doi.org/10.1021/es8001508>.
- [106] E.G. Heckert, A.S. Karakoti, S. Seal, W.T. Self, The role of cerium redox state in the SOD mimetic activity of nanoceria, *Biomaterials* 29 (2008) 2705–2709, <https://doi.org/10.1016/j.biomaterials.2008.03.014>.
- [107] A.E. Hughes, S.G. Hardin, K.W. Wittel, P.R. Miller, *Proceedings of the NACE Meeting: Corrosion/2000, in: Research Topical Symposium: Surface Conversion of Aluminum and Aluminum Alloys for Corrosion Protection, Usa, 2000.*
- [108] F.H. Scholes, C. Soste, A.E. Hughes, S.G. Hardin, P.R. Curtis, The role of hydrogen peroxide in the deposition of cerium-based conversion coatings, *Appl. Surf. Sci.* 253 (2006) 1770–1780, <https://doi.org/10.1016/j.apsusc.2006.03.010>.
- [109] X. Chen, X. Liu, H.-B. Wang, K.-P. Cui, R. Weerasooriya, S.-L. He, G.-H. Li, J. Pan, K. Zhou, Ce³⁺ triggers Fenton-like processes in neutral solutions for effective catechol degradation, *Environmental Engineering Research* 27 (2020) 200519–0, doi:<https://doi.org/10.4491/eer.2020.519>.
- [110] V. Verma, P.K. Chaudhari, Optimization of multiple parameters for treatment of coking wastewater using Fenton oxidation, *Arabian Journal of Chemistry* 13 (2020) 5084–5095, <https://doi.org/10.1016/j.arabjc.2020.02.008>.

Supplementary materials

Holistic insight into the viability of employing cerium(IV) sulphate to oxidise toxic contaminants in effluent from the coal gasification process: Optimisation studies

Paweł Lejwoda ^{a*}, Barbara Białecka ^b, Maciej Thomas ^c

^a Central Mining Institute in Katowice, Department of Energy Saving and Air Protection, Plac Gwarków 1, Katowice 40-166, Poland

^b Central Mining Institute in Katowice, Department of Environmental Monitoring, Plac Gwarków 1, Katowice 40-166, Poland

^c Cracow University of Technology, Faculty of Environmental Engineering and Energy, Warszawska 24, Cracow 31-155, Poland

* **Corresponding author:** Paweł Lejwoda, E-Mail: plejwoda@gig.eu

Table S1

Chemical composition of wastewater from coal gasification processes.

Parameters	Unit	W1	W2	W3	W4	W5	W6
Material		Semi-Anthracite Coal	Semi-Anthracite Coal	Bituminous Coal	Bituminous Coal	Semi-Anthracite Coal	Semi-Anthracite Coal
Process pressure	bar	20	40	20	40	atm.	30
pH	-	6.4	5.2	5.3	4.9	7.3	5.7
Cerium (Ce)	mg/L	nd	nd	nd	nd	nd	nd
Iron (Fe)	mg/L	0.823	0.284	0.131	0.245	0.92	3.0
Manganese (Mn)	mg/L	0.017	0.021	0.018	0.012	0.043	0.07
Cadmium (Cd)	mg/L	< 0.0005	0.001	< 0.0005	< 0.0005	< 0.001	< 0.001
Chromium (Cr)	mg/L	0.013	0.012	0.010	0.006	0.12	0.25
Copper (Cu)	mg/L	0.005	0.010	0.009	0.002	0.006	0.006
Nickel (Ni)	mg/L	0.098	0.312	0.051	0.027	0.97	0.69
Lead (Pb)	mg/L	<0.005	0.064	0.046	0.060	0.007	0.06
Zinc (Zn)	mg/L	0.021	0.499	0.320	0.200	0.10	19.85
Total Cyanides	mg/L	1.11	1.43	1.7	0.87	7.52	0.25
Total phenols volatile	mg/L	8.45	0.87	17.04	24.46	43.8	0.5
Naphthalene	µg/L	1321.25	320.88	905	305.74	2188	10.79
Acenaphthene	µg/L	nd	nd	nd	nd	28.35	418.8
Fluorene	µg/L	nd	nd	nd	nd	436.2	708.8
Phenanthrene	µg/L	nd	nd	nd	nd	1120	19.11
Anthracene	µg/L	nd	nd	nd	nd	122.9	168.2
Fluoranthene	µg/L	nd	nd	nd	nd	252.7	403.6
Pyrene	µg/L	nd	nd	nd	nd	116.1	30.92
Benz(a)anthracene	µg/L	nd	nd	nd	nd	109.4	30.36
Chrysene	µg/L	nd	nd	nd	nd	181.7	9.015
Benzo(b)fluoranthene	µg/L	nd	nd	nd	nd	183.7	1.337
Benzo(k)fluoranthene	µg/L	nd	nd	nd	nd	32.39	2.847
Benzo(a)pyrene	µg/L	nd	nd	nd	nd	46.19	0.7495
Dibenz(a,h)anthracene	µg/L	nd	nd	nd	nd	92.29	0.1723
Benzo(g,h,i)perylene	µg/L	nd	nd	nd	nd	60.95	0.2356
Indeno(1,2,3-cd)pyrene	µg/L	nd	nd	nd	nd	24.91	0.1154
Σ PAH	µg/L	1657.98	361.99	1090.34	407.2	2808	1805
Author	-	[41]	[41]	[41]	[41]	[40]	[40]

nd – no data

Table S2

Redox potentials of selected oxidants.

Oxidant	Eh, V	Source
•OH	2.80	[93]
O	2.42	[94]
O ₃ (acidic conditions)	2.07	[94]
H ₂ O ₂ (acidic conditions)	1.78	[94]
HO ₂ •	1.70	[94]
Ce ⁴⁺ in 1M HClO ₄	1.70	[91]
Ce ⁴⁺ in 1M H ₂ SO ₄	1.44	[91]
Ce ⁴⁺ in 1M HCl	1.28	[91]
O ₂ (acidic conditions)	1.23	[94]

Table S3

Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, DOC; R² = 0.909; R_{adj}² = 0.818, MS = 23.427

Parameter	Effect	Standard error	t(10)	p	CI (-95%)	CI (+95%)	Factor	Standard error	CI (-95%)	CI (+95%)
Constant value	55.560	2.165	25.668	< 0.001	50.917	60.203	55.560	2.165	50.917	60.203
(1) time (L)	1.192	1.976	0.603	0.556	-3.046	5.430	0.596	0.988	-1.523	2.715
time (Q)	4.501	1.900	2.369	0.033	0.425	8.577	2.251	0.950	0.213	4.289
(2) temperature (L)	12.608	1.976	6.381	< 0.001	8.370	16.846	6.304	0.988	4.185	8.423
temperature (Q)	15.751	1.900	8.288	< 0.001	11.675	19.827	7.876	0.950	5.838	9.914
(3) Ce ⁴⁺ : DOC ratio (L)	4.892	1.976	2.476	0.027	0.654	9.130	2.446	0.988	0.327	4.565
Ce ⁴⁺ : DOC ratio (Q)	9.551	1.900	5.026	< 0.001	5.475	13.627	4.776	0.950	2.738	6.814
(4) pH (L)	3.825	1.976	1.936	0.073	-0.413	8.063	1.913	0.988	-0.207	4.032
pH (Q)	7.001	1.900	3.684	0.002	2.925	11.077	3.501	0.950	1.463	5.539
1 L relative to 2 L	-3.638	2.420	-1.503	0.155	-8.828	1.553	-1.819	1.210	-4.414	0.777
1 L relative to 3 L	-0.663	2.420	-0.274	0.788	-5.853	4.528	-0.331	1.210	-2.927	2.264
1 L relative to 4 L	0.087	2.420	0.036	0.972	-5.103	5.278	0.044	1.210	-2.552	2.639
2 L relative to 3 L	0.063	2.420	0.026	0.980	-5.128	5.253	0.031	1.210	-2.564	2.627
2 L relative to 4 L	3.513	2.420	1.451	0.169	-1.678	8.703	1.756	1.210	-0.839	4.352
3 L relative to 4 L	-2.113	2.420	-0.873	0.397	-7.303	3.078	-1.056	1.210	-3.652	1.539

statistically significant if p < 0.05

Table S4

ANOVA results for DOC removal

Parameter	SS	df	MS	F	p
(1) time (L)	8.520	1	8.520	0.364	0.556
time (Q)	131.424	1	131.424	5.610	0.033
(2) temperature (L)	953.820	1	953.820	40.714	< 0.001
temperature (Q)	1609.309	1	1609.309	68.693	< 0.001
(3) Ce ⁴⁺ : DOC ratio (L)	143.570	1	143.570	6.128	0.027
Ce ⁴⁺ : DOC ratio (Q)	591.739	1	591.739	25.258	< 0.001
(4) pH (L)	87.784	1	87.784	3.747	0.073
pH (Q)	317.951	1	317.951	13.572	0.002
1 L relative to 2 L	52.926	1	52.926	2.259	0.155
1 L relative to 3 L	1.756	1	1.756	0.075	0.788
1 L relative to 4 L	0.031	1	0.031	0.001	0.972
2 L relative to 3 L	0.016	1	0.016	0.001	0.980
2 L relative to 4 L	49.351	1	49.351	2.107	0.169
3 L relative to 4 L	17.851	1	17.851	0.762	0.397
Error	327.985	14	23.427		
Total sum of square	3604.567	28			

statistically significant if $p < 0.05$

Table S5

Analysis of the central composite design experiment using Statistica 13. Evaluation of the effects, DOC;
 $R^2 = 0.904$; $R_{adj}^2 = 0.850$, MS = 19.313

Parameter	Effect	Standard error	t(10)	p	CI (-95%)	CI (+95%)	Factor	Standard error	CI (-95%)	CI (+95%)
Constant value	55.560	1.965	28.270	0.000	51.431	59.689	55.560	1.965	51.431	59.689
(1) time (L)	1.192	1.794	0.664	0.515	-2.578	4.961	0.596	0.897	-1.289	2.480
time (Q)	4.501	1.726	2.609	0.018	0.876	8.126	2.251	0.863	0.438	4.063
(2) temperature (L)	12.608	1.794	7.028	0.000	8.839	16.378	6.304	0.897	4.420	8.189
temperature (Q)	15.751	1.726	9.128	0.000	12.126	19.376	7.876	0.863	6.063	9.688
(3) Ce^{4+} : DOC ratio (L)	4.892	1.794	2.727	0.014	1.122	8.661	2.446	0.897	0.561	4.330
Ce^{4+} : DOC ratio (Q)	9.551	1.726	5.535	0.000	5.926	13.176	4.776	0.863	2.963	6.588
(4) pH (L)	3.825	1.794	2.132	0.047	0.056	7.594	1.913	0.897	0.028	3.797
pH (Q)	7.001	1.726	4.057	0.001	3.376	10.626	3.501	0.863	1.688	5.313
1 L relative to 2 L	-3.638	2.197	-1.655	0.115	-8.254	0.979	-1.819	1.099	-4.127	0.489
2 L relative to 4 L	3.513	2.197	1.599	0.127	-1.104	8.129	1.756	1.099	-0.552	4.064

statistically significant if $p < 0.05$

Table S6

ANOVA results for DOC removal

Parameter	SS	df	MS	F	p
(1) time (L)	8.520	1	8.520	0.441	0.515
time (Q)	131.424	1	131.424	6.805	0.018
(2) temperature (L)	953.820	1	953.820	49.387	0.000
temperature (Q)	1609.309	1	1609.309	83.327	0.000
(3) Ce^{4+} : DOC ratio (L)	143.570	1	143.570	7.434	0.014
Ce^{4+} : DOC ratio (Q)	591.739	1	591.739	30.639	0.000
(4) pH (L)	87.784	1	87.784	4.545	0.047
pH (Q)	317.951	1	317.951	16.463	0.001
1 L relative to 2 L	52.926	1	52.926	2.740	0.115
2 L relative to 4 L	49.351	1	49.351	2.555	0.127
Error	347.637	18	19.313		
Total sum of square	3604.567	28			

ANOVA model coefficients after excluding nonsignificant linear-linear interactions, statistically significant if $p < 0.05$

Article

Innovative Integrated Model of Industrial Wastewater Treatment with the Circular Use of Cerium Compounds as Multifunctional Coagulants: Comprehensive Assessment of the Process and Environmental and Economic Aspects

Paweł Lejwoda ^{1,*} , Barbara Białecka ² , Anna Śliwińska ¹ , Piotr Krawczyk ¹  and Maciej Thomas ^{3,*} 

¹ Department of Energy Saving and Air Protection, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; asliwinska@gig.eu (A.Ś.); pkrawczyk@gig.eu (P.K.)

² Department of Environmental Monitoring, Central Mining Institute in Katowice, Plac Gwarków 1, 40-166 Katowice, Poland; bbialecka@gig.eu

³ Faculty of Environmental Engineering and Energy, Cracow University of Technology, Warszawska 24, 31-155 Kraków, Poland

* Correspondence: plejwoda@gig.eu (P.L.); maciej.thomas@pk.edu.pl (M.T.)

Abstract

This article presents an innovative method for phosphate(V) removal from industrial wastewater using cerium(III) chloride as a coagulant, integrated with reagent recovery. The process combines coagulation, acid extraction, and multistage recovery of cerium and phosphorus, enabling partial reagent loop closure. Based on our previously published studies, at an optimised dose (81.9 mg Ce³⁺/L), phosphate(V) removal reached 99.86% and total phosphorus (sum of all phosphorus forms as elemental P), 99.56%, and 99.94% of the added cerium was retained in sludge. Reductions were also observed for TSS (96.67%), turbidity (98.18%), and COD (81.86%). The sludge (101.5 g Ce/kg, 22.2 g P/kg) was extracted with HCl, transferring 99.6% of cerium and 97.5% of phosphorus to the solution. Cerium was recovered as cerium(III) oxalate and thermally decomposed to cerium(IV) oxide. Redissolution in HCl and H₂O₂ yielded cerium(III) chloride (97.0% recovery and 98.6% purity). The HCl used for extraction can be regenerated on-site from chlorine and hydrogen obtained from gas streams, improving material efficiency. Life cycle assessment (LCA) showed environmental benefits related to eutrophication reduction but burdens from reagent use (notably HCl and oxalic acid). Although costlier than conventional precipitation, this method may suit large-scale applications requiring high phosphorus removal, low sludge, and alignment with circular economy goals.

Keywords: industrial wastewater treatment; multifunctional coagulants; cerium coagulants; life cycle assessment; rare earth elements



Academic Editor: Javier Llanos

Received: 21 July 2025

Revised: 15 August 2025

Accepted: 18 August 2025

Published: 20 August 2025

Citation: Lejwoda, P.; Białecka, B.; Śliwińska, A.; Krawczyk, P.; Thomas, M. Innovative Integrated Model of Industrial Wastewater Treatment with the Circular Use of Cerium Compounds as Multifunctional Coagulants: Comprehensive Assessment of the Process and Environmental and Economic Aspects.

Molecules **2025**, *30*, 3428. <https://doi.org/10.3390/molecules30163428>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The Earth's water resources are estimated at 1.385 billion km³, with saline water accounting for 97.5% of the total volume. Freshwater constitutes only 2.5% of the total water resources, which are primarily stored in glaciers and snow cover (approximately 69%), groundwater (30.1%), lakes (0.26%), soil moisture (0.05%), the atmosphere (0.04%), wetlands (0.03%), rivers (0.006%), and biological water (0.003%) [1]. On the one hand, the continuous growth of the global population necessitates addressing the increasing demand for potable water [2]; on the other hand, industrial and domestic human activities contribute to the

contamination of water bodies with a wide spectrum of pollutants, including pesticides [3]; heavy metals such as lead (Pb) [4], cadmium (Cd) [5], nickel (Ni) [6], mercury (Hg) [7], copper (Cu) [8], and chromium (Cr) [9]; arsenic compounds (As) [10]; and microplastics [11]. This presents a significant challenge for ensuring high-quality water resources for both current and future generations.

On the other hand, the utilisation of freshwater, depending on the end user, in most cases results in the generation of wastewater with diverse chemical compositions. Domestic wastewater is typically characterised by elevated concentrations of biogenic elements such as carbon (C), nitrogen (N), and phosphorus (P) [12]. Wastewater from the food industry, such as brewery effluents, has a composition similar to domestic wastewater but contains pollutants at higher concentrations. Industrial wastewater, for example from the coking industry [13,14] or coal gasification processes, is characterised by high concentrations of cyanides, phenols, and polycyclic aromatic hydrocarbons (PAHs) [15]. Electroplating wastewater, depending on the type of metal coating applied, may contain elevated levels of heavy metals such as Cu, Ni, Cr, and Cd [16,17].

The increasing physicochemical complexity of wastewater poses a significant challenge to treatment processes. A variety of methods are employed to remove specific groups of contaminants. Metal removal can be achieved, among other methods, by precipitation methods involving the alkalisation of wastewater, followed by the precipitation of metal hydroxides, or by the formation of metal sulphides, according to general reactions (1) and (2) [18].



However, these methods have several drawbacks, primarily due to their high demand for chemical reagents, significant generation of secondary sludge, and limited effectiveness in the presence of complexed metals (i.e., metals chelated by strong organic ligands such as ethylenediaminetetraacetic acid (EDTA) or natural humic and fulvic acids, commonly found in industrial and municipal wastewater) [19]. Additionally, precipitated sludge often displays low chemical stability. Therefore, to increase metal removal efficiency, various chemical agents, such as sodium dimethyldithiocarbamate (DMDTC) [20], sodium trithiocarbonate (Na_2CS_3) [21], trimercapto-s-triazine (TMT) [22], and 1,3-benzenediamidoethanethiol dianion (BDET) [23], are applied. These compounds improve the precipitation performance by forming stable complexes, reducing the metal solubility over a broad pH range, and decreasing the sludge volume.

The removal of substances responsible for turbidity and colour, as well as the reduction in phosphorus concentrations, can be achieved via coagulation using, among other methods, ferric or aluminium salts. These compounds operate through a similar mechanism involving the adsorption of contaminants onto the surface of hydroxide flocs formed during the process [24,25]. The efficiency of coagulants strongly depends on the pH of the treated wastewater, with the optimal pH range for ferric salts being 5.5–7.0 [26] and that for aluminium salts being 5.7–6.0 [27]. In the case of ferric salts, the phosphate(V) removal efficiency may reach 98%, whereas for aluminium salts, it is typically approximately 83%. A major disadvantage of these coagulants is the formation of large volumes of hydrated sludge, which requires further handling. Following treatment, the effluents are usually discharged into receiving bodies, most commonly surface waters such as rivers.

In cases of insufficient wastewater treatment, eutrophication is observed, resulting from excessive enrichment of water with nitrogen and phosphorus, originating mainly from municipal, industrial, and agricultural runoff. It leads to rapid algal growth, increased water turbidity, and oxygen depletion, which can threaten aquatic ecosystems. This phenomenon is also accompanied by the deterioration of water quality in terms of odour and taste [28,29].

The removal of excess nitrogen and phosphorus from water is challenging for conventional wastewater treatment processes, posing a significant challenge for water treatment technologies. The removal of these elements requires advanced biological processes such as denitrification (nitrogen removal) [30] and chemical processes such as coagulation (phosphorus removal) [31]. Given increasing water pollution, it is crucial to implement effective strategies to manage nitrogen and phosphorus emissions in both agricultural and urban areas to prevent further deterioration of water quality [32,33].

Compared with conventional coagulants, more effective removal of pollutants from water and wastewater can be achieved by using innovative coagulants containing zirconium, titanium or, more recently, cerium compounds. For the removal of phosphorus compounds, the use of cerium coagulants seems to be particularly beneficial. As recent reports have shown, the use of cerium(III) chloride in wastewater treatment has been studied in the context of treating leachates from sewage sludge dewatering [34] and brewing wastewater [35]. In the case of brewery wastewater, 99.86% of the phosphates(V) were removed under optimal treatment conditions, indicating high removal efficiency. Furthermore, under optimal conditions, 99.94% of the applied cerium(III) was bound within the sludge. Cerium compounds have proven to be effective not only in removing phosphates(V) but also in removing other contaminants present in industrial wastewater, such as effluents from the hard coal gasification process, where cerium(IV) sulphate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) is used for the oxidation of PAHs, cyanides, and phenols [15].

The use of cerium compounds for wastewater treatment is promising; however, rare earth elements (REEs) production is limited to a few countries worldwide (Table 1), posing risks to supply chains in the event of adverse geopolitical developments.

Table 1. Contribution of individual producers to REE production and reserves [36].

Country	REEs Production in 2024 (Tonnes)	REEs Reserves (Tonnes)
China	270,000	44,000,000
USA	45,000	1,900,000
Myanmar	31,000	Not available
Thailand	13,000	4500
Nigeria	13,000	Not available
Australia	13,000	5,700,000
Russia	2500	3,800,000
India	2900	6,900,000
Madagascar	2000	Not available
Vietnam	300	3,500,000
Brazil	20	21,000,000
Malaysia	130	Not available
Canada	Not available	830,000
South Africa	Not available	860,000
Greenland	Not available	1,500,000
Tanzania	Not available	890,000
Other countries	1100	Not available

In the European Union, nearly all REEs consumed are imported, and recycling is carried out for only approximately 1% of REEs [37]. Given the higher price of cerium coagulants than of widely used iron and aluminium coagulants, it is important to explore recycling options. Additionally, owing to their initially high effectiveness, further research should be conducted similarly to the previously studied and developed zirconium and titanium coagulants.

Both cerium used as a coagulant and phosphorus removed during the process are classified as critical raw materials for the European Union's economy. Phosphorus, de-

rived from minerals such as fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), is a key component in the production of mineral fertilisers, which are essential for ensuring efficient agricultural output. Similar to REEs, phosphorus deposits are concentrated in a limited number of countries, including Morocco and China. This creates a significant supply risk and necessitates the search for alternative sources, including recovery from waste streams. Due to the EU's near-total dependence on imports of these materials, the implementation of technologies enabling the closure of phosphorus and cerium cycles through recovery from wastewater is of particular importance. Integrating such solutions into wastewater treatment systems supports not only the circular economy but also strengthens the raw material autonomy of the European Union [37].

Our studies on cerium recycling from wastewater sludge [38] demonstrated the effective removal of contaminants from industrial wastewater and the feasibility of recovering cerium(III) chloride, cerium(III) sulphate, and cerium(IV) sulphate with efficiencies of 97.0%, 97.4%, and 98.3%, respectively. The recycling process involved cerium extraction from wastewater sludge via hydrochloric acid, the selective precipitation of cerium(III) oxalate, the thermal decomposition of cerium(III) oxalate to cerium(IV) oxide, and the synthesis of salts via hydrogen peroxide, hydrochloric acid, or sulphuric acid. The recovered salts can be reused for wastewater treatment. These studies and experiments on a laboratory and semitechnical scale allowed us to propose a complementary process of recovery and the use of cerium compounds to remove phosphorus from industrial wastewater.

This paper summarises our studies that demonstrate the usefulness of cerium coagulants and their recycling, enabling the closure of the cerium cycle in wastewater treatment [35,38]. The proposed new process for the recovery and use of cerium compounds should be subjected to comprehensive process, environmental, and economic assessments. The literature review revealed that no such comprehensive assessment has been conducted to date. This paper presents the results of our research along with an assessment of the entire upscaled process. The work includes a 10-stage process design, mass balance, LCA evaluation, and cost analysis performed using the DGC method, thus addressing a knowledge gap in this field. Therefore, this work can be an important step in the discussion, research, development, and evaluation of advanced precipitation, coagulation, and recovery processes for better environmental protection and sustainable development.

2. Results and Discussion

2.1. Process Analysis (Operating Conditions and Initial Assumptions)

The proposed model assumes an influent industrial wastewater flow of 5000 m³ per day, containing phosphate(V) at a concentration of 37 mg/L, corresponding to 185 kg of phosphate(V) ions. It is further assumed that the addition of the cerium-based coagulant occurs in the primary settling tanks, with the resulting sludge subjected to a series of processes aimed at recovering the cerium coagulant for reuse in wastewater treatment. On the basis of the optimal coagulant dose described by Lejwoda et al. [35], with a molar ratio of Ce(III) to phosphate(V) of 1.5:1, the required amount of cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) during start-up is 1088.3 kg, which corresponds to a concentration of 81.9 mg Ce^{3+} /L. Assuming a recovery efficiency of 97.1% in the form of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1057.3 kg), Stage I will require a top-up dose of approximately 31 kg $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ to compensate for losses.

The dewatered sludge obtained in Stage I is assumed to contain approximately 0.62% dry matter, which translates to 4000 kg of dry sludge from 650 m³ of wet sludge. The supernatant and the filtrate generated in Stage II were subjected to nitrification. The sludge is transported by a belt conveyor to reactors, each with a volume of 25 m³.

In Stage III, 4000 kg of sludge is extracted following the addition of 45,333 kg of water and 4667 kg of 30% hydrochloric acid (HCl). The process requires no heating. The total reaction mass of 54,000 kg is divided into two reactors, with two batches per reactor, resulting in four processing cycles of 13,500 kg each. Each cycle is assumed to last 3 h, after which the reaction mixture is pumped to a filter press.

Stage IV involves filtration of the reaction mass (54,000 kg). The insoluble organic residue (suspended solids) is assumed to be approximately 3406 kg and, following separation, is conveyed for agricultural or energy-related applications.

The extract, weighing approximately 50,600 kg and containing cerium, together with an additional 5000 kg of water used for washing the sludge, is transferred to a buffer tank and then to two 25 m³ reactors, where the process is carried out in three consecutive batches per reactor (six batches in total).

Stage V, which includes the precipitation of cerium(III) oxalate (Ce₂(C₂O₄)₃), begins with the addition of approximately 659 kg of oxalic acid dihydrate (H₂C₂O₄·2H₂O)—the total required amount for the entire stage. To optimise the precipitation conditions, the pH of the reaction mixture, initially 0.3, is increased to 1.8 by adding approximately 1077 kg of sodium hydroxide (NaOH). The total water content of the NaOH and H₂C₂O₄ solutions was 24,500 kg. The extract contained 3763 mg/L of Ce, and after precipitation, the concentration in the filtrate was reduced to 1.10 mg/L, resulting in a calculated yield of 99.97%.

The process results in the precipitation of 1049 kg of Ce₂(C₂O₄)₃ (yield: 99.97%). A total reaction mass of 82,281 kg is pumped to a filter press, where Stage VI involves separating the precipitate from the filtrate. Ce₂(C₂O₄)₃ (approx. 1049 kg) is transferred to a furnace for thermal decomposition. The filtrate (approx. 81,232 kg) was transferred to a storage tank.

The acidic solution (pH 1.8) contains phosphate(V) at a concentration of 570 mg/L, which can be recovered by the addition of calcium hydroxide (Ca(OH)₂), which also serves as a neutralising agent. Neutralisation and precipitation of calcium phosphate(V) (Ca₃(PO₄)₂) require the addition of 210.32 kg Ca(OH)₂ per 81,232 kg of filtrate. The resulting suspension is filtered, and the filtrate is pumped to evaporation ponds covering an area of 10 ha.

The thermal decomposition of (Ce₂(C₂O₄)₃) in Stage VII proceeded with an efficiency of approximately 99.5%, yielding approximately 496.0 kg of cerium(IV) oxide (CeO₂). The process was conducted over 3 h at a temperature of 350 °C.

Stage VIII involves the synthesis of cerium(III) chloride (CeCl₃) from the CeO₂ produced in Stage VII. The oxide is transferred to a 10 m³ reactor, where it reacts with HCl and hydrogen peroxide (H₂O₂). In the scenario analysed, 496.0 kg of CeO₂ was subjected to a reaction with 2713.7 kg of 30% HCl and 993.3 kg of 30% H₂O₂. The process, carried out at 90 °C for 3 h, achieves a yield of 98.5%, resulting in the production of 1057.3 kg of CeCl₃. The by-products included approximately 621.1 kg of chlorine gas (Cl₂) and 7.14 kg of unreacted residue.

Stage IX involves heating the solution to evaporate water, which is then recirculated into earlier stages of the process. At this point, the solution may also be concentrated to reach the desired Ce(III) concentration for reuse in Stage I.

To minimise the environmental impact of by-products and reduce the reagents costs, Stage X was expanded to include the recovery of both chlorine (Cl₂) and hydrogen (H₂), enabling the on-site production of HCl and partially eliminating the need for external sourcing. During Stage VIII (CeCl₃·7H₂O synthesis), a gaseous by-product containing chlorine (Cl₂) and oxygen (O₂) is generated. This mixture is separated via a membrane system, which recovers approximately 619 kg/day of pure Cl₂. The chlorine is then directed to an HCl synthesis reactor, where it reacts with hydrogen.

Hydrogen is derived from sewage sludge, which is first subjected to anaerobic digestion, producing biogas (containing methane (CH_4) and carbon dioxide (CO_2)) and digested sludge. The biogas may be utilised for in-house energy generation, reducing reliance on external suppliers. The digested sludge is then gasified to yield synthesis gas containing H_2 (approx. 19.3 kg/day), carbon monoxide (CO), and carbon dioxide (CO_2). Using a membrane separation module, H_2 is isolated and fed into the HCl synthesis reactor. The resulting HCl gas is absorbed in water within an absorption column to produce a 30% HCl solution. This solution (~1819 kg/day) can then be reused in Stage III for cerium extraction from sludge, effectively closing the reagent loop. Hydrochloric acid constitutes a significant portion of the chemicals used in the process. Implementing recovery reduces the demand for external supply by approximately 24.6%. The implementation of this modification significantly enhances the material and energy efficiency of the system while reducing CO_2 and Cl_2 emissions to the atmosphere. Additionally, surplus hydrogen may be utilised as a fuel for the plant's energy needs or sold externally. The use of this hydrochloric acid recovery technology aligns with the principles of the circular economy, increasing the operational independence of the facility and minimising the environmental footprint of the entire wastewater treatment process.

The integration of all the aforementioned processes enables the formation of a nearly closed-loop system for cerium in wastewater treatment (Figure 1), forming the basis for further process, environmental, and economic evaluation of the proposed technology.

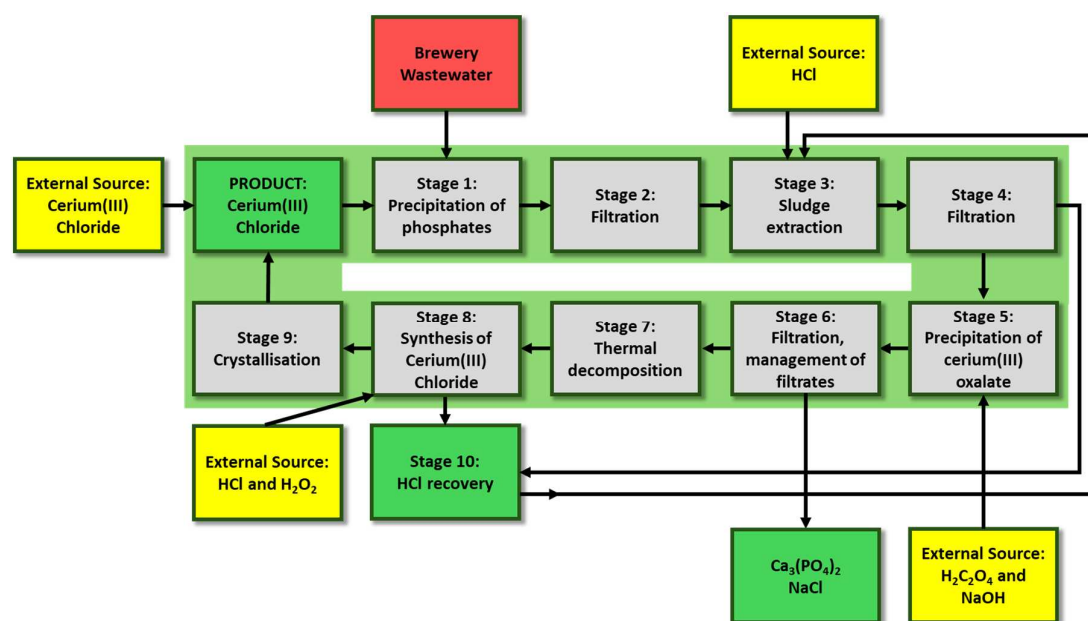


Figure 1. Conceptual diagram of wastewater treatment with cerium coagulant recirculation.

The developed concept comprises ten stages (Table 2), aimed at achieving near-complete closure of the cerium loop within the treatment system.

Table 2. Subsequent stages of the use and recovery of cerium compounds.

Stage No.	Stage
I	Precipitation of phosphates(V) (a)
II	Filtration (a)
III	Sludge extraction (a)
IV	Filtration (a)
V	Precipitation of cerium(III) oxalate (a)

Table 2. Cont.

Stage No.	Stage
VI	Filtration, management of filtrates (a,b)
VII	Thermal decomposition (a)
VIII	Synthesis of cerium(III) chloride (a,b)
IX	Crystallisation (a)
X	HCl recovery (b)

a—results from our previous studies [35,38]. b—results from studies conducted by other authors [39,40].

2.2. Environmental Assessment

Table 3 presents the environmental impact results over the life cycle of the wastewater treatment process with phosphate(V) recovery.

The life cycle assessment (LCA) conducted via the ReCiPe 2016 method allows for the evaluation of various process stages and materials used in relation to their environmental impact. The analysis considers impact categories such as climate change, ozone layer depletion, acidification, eutrophication, toxicity, and resource consumption. The results indicate that $\text{H}_2\text{C}_2\text{O}_4$ and HCl have the greatest impact on multiple categories. Oxalic acid is the dominant contributor to climate change (2.04 kg CO_2 -eq), terrestrial ecotoxicity (5.96 kg 1,4-DCB-eq), and fossil resource depletion (0.479 kg oil-equivalent). Hydrochloric acid significantly affects terrestrial ecotoxicity (5.41 kg 1,4-DCB-eq) and marine ecotoxicity (7.85×10^{-2} kg 1,4-DCB-eq). Oxalic acid and hydrochloric acid along with hydrogen peroxide are main contributors which impact human carcinogenic toxicity. Improving environmental efficiency could be achieved through enhancing the production efficiency of oxalic acid and hydrochloric acid, replacing these substances with alternatives from sustainable sources, and considering less harmful substitutes whenever possible. Additionally, energy consumption at various process stages is a significant source of environmental impact, highlighting the need to improve energy efficiency and transition to renewable energy sources. Figure 2 shows the carbon footprint of the analysed process.

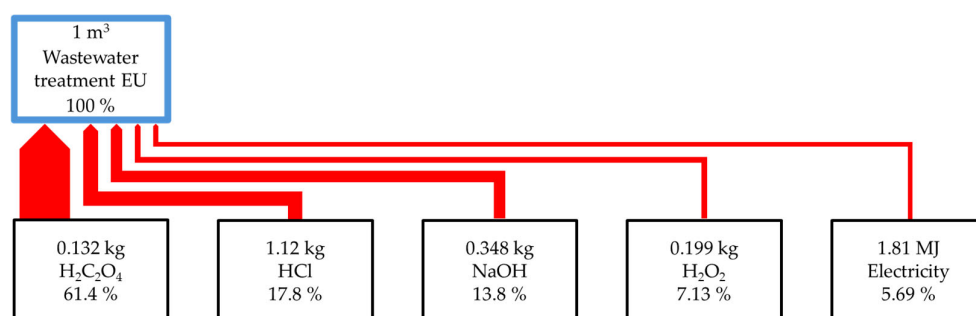


Figure 2. Carbon footprint.

The results indicate that the greatest climate impact is associated with the production of oxalic acid (indirect emission), the calcination of oxalic acid (direct emission), and the consumption of hydrochloric acid.

In the next phase, the normalised results were examined. Normalisation in LCA involves transforming environmental impact results into comparable values by referencing a defined benchmark (e.g., the total environmental impact of a specific region or population). This approach helps determine which impact categories are most significant. Figure 3 presents the normalised environmental impact results calculated via the ReCiPe 2016 midpoint (H/A) method. Normalisation in this method was performed using global per capita reference values derived from annual emissions and resource use data for the year 2010, enabling relative comparison of environmental impacts [41].

Table 3. Results of characterisation—ReCiPe2016 midpoint H.

Impact Category	Unit	Total	1	2	3	4	5	6	7	8	9	10	11
Global warming	kg CO ₂ eq	3.30	2.08×10^{-4}	2.04	5.80×10^{-1}	2.84×10^{-1}	2.35×10^{-1}	6.85×10^{-3}	3.91×10^{-2}	1.88×10^{-1}	-7.86×10^{-2}	0.00	7.67×10^{-3}
Stratospheric ozone depletion	kg CFC11 eq	1.92×10^{-5}	0.00	1.80×10^{-5}	7.94×10^{-7}	2.86×10^{-7}	5.75×10^{-8}	3.83×10^{-9}	1.32×10^{-9}	8.65×10^{-8}	-1.02×10^{-7}	0.00	7.56×10^{-8}
Ionising radiation	kBq Co60 eq	3.75×10^{-1}	0.00	3.93×10^{-2}	1.68×10^{-1}	3.16×10^{-2}	3.28×10^{-2}	3.42×10^{-4}	3.89×10^{-4}	1.08×10^{-1}	-6.13×10^{-3}	0.00	7.91×10^{-4}
Ozone formation, Human health	kg NO _x eq	5.64×10^{-2}	0.00	5.36×10^{-2}	1.30×10^{-3}	7.58×10^{-4}	3.84×10^{-4}	2.71×10^{-5}	2.69×10^{-5}	3.48×10^{-4}	-1.54×10^{-4}	0.00	9.61×10^{-5}
Fine particulate matter formation	kg PM _{2.5} eq	1.25×10^{-2}	0.00	1.02×10^{-2}	1.39×10^{-3}	5.80×10^{-4}	2.12×10^{-4}	1.35×10^{-5}	8.42×10^{-6}	2.88×10^{-4}	-1.94×10^{-4}	0.00	1.67×10^{-5}
Ozone formation, Terrestrial ecosystems	kg NO _x eq	5.67×10^{-2}	0.00	5.38×10^{-2}	1.36×10^{-3}	7.75×10^{-4}	4.22×10^{-4}	2.76×10^{-5}	3.02×10^{-5}	3.60×10^{-4}	-1.64×10^{-4}	0.00	9.75×10^{-5}
Terrestrial acidification	kg SO ₂ eq	3.77×10^{-2}	0.00	3.21×10^{-2}	3.89×10^{-3}	1.04×10^{-3}	5.59×10^{-4}	2.83×10^{-5}	2.28×10^{-5}	7.32×10^{-4}	-6.67×10^{-4}	0.00	4.88×10^{-5}
Freshwater eutrophication	kg P eq	1.15×10^{-3}	0.00	3.94×10^{-4}	3.79×10^{-4}	1.33×10^{-4}	8.81×10^{-5}	3.22×10^{-6}	6.27×10^{-7}	1.75×10^{-4}	-2.78×10^{-5}	-3.31×10^{-5}	3.57×10^{-5}
Marine eutrophication	kg N eq	2.48×10^{-4}	0.00	2.74×10^{-5}	5.53×10^{-5}	1.19×10^{-5}	1.54×10^{-5}	2.29×10^{-5}	3.29×10^{-7}	1.25×10^{-5}	-3.30×10^{-6}	0.00	1.05×10^{-4}
Terrestrial ecotoxicity	kg 1,4-DCB	1.42×10^1	0.00	5.96	5.41	1.25	9.31×10^{-1}	4.96×10^{-2}	1.45×10^{-2}	1.09	-5.30×10^{-1}	0.00	2.40×10^{-2}
Freshwater ecotoxicity	kg 1,4-DCB	1.77×10^{-1}	0.00	6.43×10^{-2}	6.00×10^{-2}	1.49×10^{-2}	1.65×10^{-2}	1.18×10^{-3}	6.60×10^{-5}	2.32×10^{-2}	-4.79×10^{-3}	0.00	1.65×10^{-3}
Marine ecotoxicity	kg 1,4-DCB	2.32×10^{-1}	0.00	8.50×10^{-2}	7.85×10^{-2}	1.96×10^{-2}	2.18×10^{-2}	1.52×10^{-3}	1.00×10^{-4}	2.94×10^{-2}	-6.32×10^{-3}	0.00	2.03×10^{-3}
Human carcinogenic toxicity	kg 1,4-DCB	1.90×10^{-1}	0.00	5.68×10^{-2}	6.40×10^{-2}	1.87×10^{-2}	3.82×10^{-2}	4.92×10^{-4}	1.70×10^{-4}	1.33×10^{-2}	-4.70×10^{-3}	0.00	2.72×10^{-3}
Human noncarcinogenic toxicity	kg 1,4-DCB	3.65	0.00	1.49	1.18	3.31×10^{-1}	3.30×10^{-1}	4.05×10^{-2}	1.70×10^{-3}	3.54×10^{-1}	-9.10×10^{-2}	0.00	1.44×10^{-2}
Land use	m ² a crop eq	5.22×10^{-2}	0.00	1.82×10^{-2}	2.11×10^{-2}	6.82×10^{-3}	4.41×10^{-3}	6.49×10^{-4}	5.39×10^{-4}	6.17×10^{-3}	-5.83×10^{-3}	0.00	1.10×10^{-4}
Mineral resource scarcity	kg Cu eq	1.01×10^{-2}	0.00	4.16×10^{-3}	4.32×10^{-3}	9.88×10^{-4}	9.33×10^{-4}	1.08×10^{-3}	7.84×10^{-6}	7.31×10^{-4}	-2.15×10^{-3}	0.00	3.61×10^{-5}
Fossil resource scarcity	kg oil eq	8.40×10^{-1}	0.00	4.79×10^{-1}	1.79×10^{-1}	6.90×10^{-2}	7.92×10^{-2}	1.55×10^{-3}	3.55×10^{-3}	5.09×10^{-2}	-2.28×10^{-2}	0.00	1.20×10^{-3}
Water consumption	m ³	5.87×10^{-2}	0.00	1.55×10^{-2}	1.92×10^{-2}	6.76×10^{-3}	1.51×10^{-2}	-8.24×10^{-6}	5.30×10^{-5}	3.29×10^{-3}	-1.38×10^{-3}	0.00	1.40×10^{-4}

(1) Wastewater treatment; (2) Oxalic acid, H₂C₂O₄; (3) Hydrochloric acid, HCl; (4) Sodium hydroxide, NaOH; (5) Hydrogen peroxide, H₂O₂; (6) Cerium(IV) oxide, CeO₂; (7) Lime, hydrated, packed, Ca(OH)₂; (8) Electricity; (9) Inorganic phosphorus fertiliser, such as P₂O₅, prevents impact; (10) Phosphorus emission to river—avoided impact; (11) Raw sewage sludge, municipal incineration.

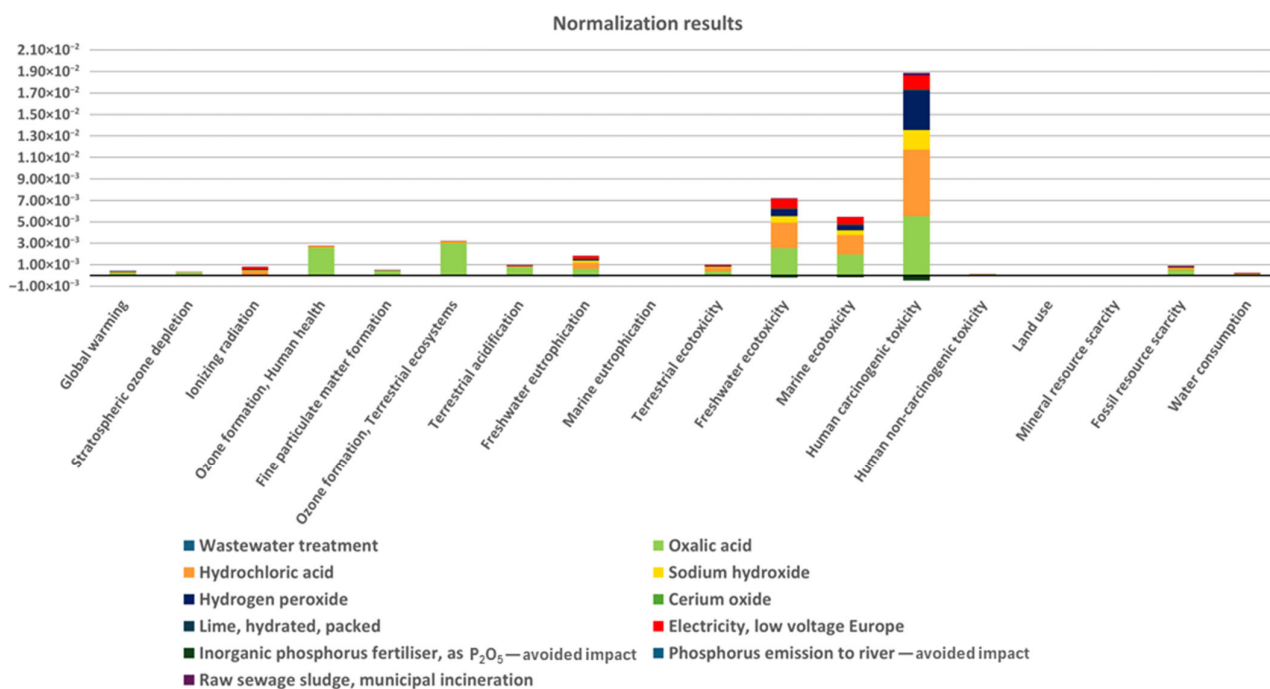


Figure 3. Normalised environmental impact results via the ReCiPe 2016 midpoint (H/A) method.

The highest environmental burden is observed in the category of human noncarcinogenic toxicity, with oxalic acid being the dominant contributor. The next two dominant categories are freshwater ecotoxicity and marine ecotoxicity, and this impact is also associated with the production of oxalic acid, hydrochloric acid, and sodium hydroxide. Although greenhouse gas emissions and resource consumption are important concerns, they are not the dominant issues in the analysed system.

The goal of the analysed process is the recovery of phosphate(V) (PO_4^{3-}) from wastewater, which is one of the main factors causing eutrophication, i.e., the enrichment of aquatic ecosystems with excessive amounts of nutrients, leading to uncontrolled algal growth, oxygen depletion in water, the death of aquatic organisms, the proliferation of toxic cyanobacteria species, and the disruption of aquatic ecosystem balance.

By effectively treating wastewater and reducing phosphate(V) emissions into rivers and lakes, the process significantly reduces the impact in the eutrophication-related category. In the freshwater eutrophication impact category, a negative value (impact reduction) appears, indicating that avoiding phosphate(V) emissions significantly reduces eutrophication. A similar situation occurs in marine eutrophication, where reducing phosphorus emissions lowers the negative impact on coastal ecosystems. Furthermore, phosphorus recovery from wastewater sludge and the reuse of the obtained calcium phosphate(V) as a substitute for phosphate(V) fertilisers reduce the need for phosphate(V) resource exploitation and subsequent environmental emissions. The proposed phosphate(V) emission minimisation technology plays a significant role in protecting freshwater bodies and marine ecosystems from degradation.

2.3. Economic Assessment

Table 4 presents the calculation results for the selected years covered in the economic analysis, which were used to determine the DGC indicator.

Table 4. Calculation results for selected years of the economic analysis used for DGC calculation.

Item	Unit	Construction Period			Plant Operation Period			
		2025	2026	2027	2030	2035	2040	2046
Investment expenditures	USD	1,202,530	1,202,530	0	0	0	0	0
Raw materials, chemicals	USD	0	0	1,700,228	1,846,185	1,916,928	1,935,208	1,952,690
Maintenance and repairs	USD	0	0	16,941	18,396	19,101	19,283	19,457
Electricity	USD	0	0	263,372	287,793	260,142	235,148	208,304
Employee salaries	USD	0	0	114,133	123,268	139,331	156,566	179,454
Monitoring	USD	0	0	19,324	20,983	21,787	21,995	22,193
Total—Costs	USD	1,202,530	1,202,530	2,113,997	2,296,625	2,357,288	2,368,200	2,382,098
Volume of treated wastewater	m ³ /year	0	0	1,825,000	1,825,000	1,825,000	1,825,000	1,825,000
Discount factor	-	1.00000	0.96154	0.92456	0.82193	0.67556	0.55526	0.43883
Discounted costs	USD	1,202,530	1,156,279	1,954,509	1,887,658	1,592,500	1,314,977	1,045,345
Discounted volume of wastewater	m ³ /year	0	0	1,687,315	1,500,017	1,232,905	1,013,358	800,871
Total discounted costs	USD	32,670,246						
Total discounted volume of wastewater	m ³	23,848,409						

The economic analysis conducted via the dynamic generation cost (DGC) method revealed that the cost of phosphate (V) removal from wastewater via cerium(III) chloride and its recovery is 1.37 USD/m³. As of Q1 2025, the average net wastewater fee calculated for 97 major cities in Poland [42] was approximately 2.13 USD/m³. This cost includes not only wastewater treatment but also the transportation of wastewater to treatment plants via the sewage system and the general operational costs of enterprises managing urban wastewater systems. At municipal wastewater treatment plants that use standard phosphate(V) removal methods (typically chemical precipitation), the cost of phosphate(V) removal represents a small fraction of the overall operational cost of the facility. However, precise data on what proportion of the total expenses it constitutes are not readily available.

A review of market prices and literature sources [34,43] indicates that cerium(III) chloride prices can be 2.5 to 14 times higher than those of commonly used iron- and aluminium-based coagulants. Consequently, technology based on cerium(III) chloride and its recovery may be significantly more expensive than simpler chemical precipitation methods. However, the use of cerium-based coagulants reduces the amount of wastewater sludge generated by approximately 20–25% compared with traditional methods. For large wastewater treatment plants, lower sludge production translates into significantly reduced costs associated with its management and disposal. Additionally, the phosphate(V) removal efficiency of over 99.8% achieved with this technology is practically unattainable via conventional chemical precipitation methods. Ultimately, despite the higher purchase costs of the coagulant, this method may be economically justified in wastewater treatment plants where high phosphate(V) removal efficiency and minimised sludge management costs are a priority.

3. Materials and Methods

3.1. Assumptions Underlying the Design of a Cerium-Based Wastewater Treatment Process

On the basis of the results of our previous research on the recovery, synthesis, properties, and application of cerium compounds [15,35,38], which were conducted at both laboratory and semitechnical scales, an innovative solution for industrial wastewater treatment using cerium(III) chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$) as a coagulant has been proposed. Although this concept was developed specifically for brewery wastewater, it may also be suitable for other types of industrial effluents containing phosphorus compounds. Furthermore, it is assumed that the proposed solution can be applied wherever efficient precipitation of phosphorus from contaminated water or wastewater is particularly important. The main objective of this process is the cyclic recovery of cerium from sewage sludge and the management of by-products generated during recycling.

Stage I involves the removal of phosphate(V) from brewery wastewater through the precipitation of poorly soluble cerium(III) phosphate(V), according to reaction (3) [34,44–46]. A molar ratio of $\text{Ce}:\text{PO}_4^{3-}$ equal to 1.5:1 was adopted for calculations on the basis of the study by Lejwoda et al. [35], which ensures efficient phosphate(V) removal with a minimal residual concentration of cerium coagulant in the treated effluent.

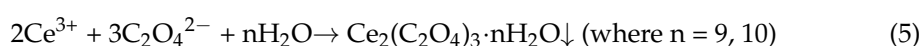


Stage II comprises sedimentation and filtration of the resulting sludge. The sludge obtained contains, on average, 10.15 wt% of cerium and 2.22 wt% of phosphorus, making it a valuable material for recovery. In Stage III, cerium and phosphorus are extracted from wastewater sludge via hydrochloric acid, following reaction (4) [38].



The solubilisation of cerium and phosphorus enables, in Stage IV, the separation of dissolved substances from undissolved organic matter, which is subsequently used as feedstock for the processes described in Stage X.

In Stage V, oxalic acid is first added to the acidic extract (pH 0.3), followed by pH adjustment to 1.8 using sodium hydroxide (NaOH). The selective action of oxalic acid under these conditions leads to the precipitation of poorly soluble cerium(III) oxalate, as shown in reaction (5) [47–49].



Stage VI involves the filtration of the resulting suspension, with the solid cerium(III) oxalate directed to Stage VII, while the acidic filtrate is neutralised, and the phosphate(V) content is removed via precipitation with calcium hydroxide ($\text{Ca}(\text{OH})_2$). The resulting solid is filtered, and the brine is evaporated in solar ponds to recover NaCl.

Stage VII is the thermal decomposition of cerium(III) oxalate at 350 °C to obtain fine-crystalline CeO_2 according to reaction (6), which is more reactive in subsequent processes than the cerium(IV) oxide produced at higher temperatures [38,50,51].



Stage VIII consists of the synthesis of cerium(III) chloride. This is achieved by reducing Ce(IV) to Ce(III) via the use of hydrogen peroxide (30 wt%) in hydrochloric acid (30 wt%) applied in 100% and 200% excess. This allows the conversion of cerium(IV) to cerium(III), followed by the formation of cerium(III) chloride through concentration and crystallization, according to reactions (7) and (8) [38,52].



Depending on the scale of demand, Stage IX may include the concentration of the CeCl_3 solution to the level required in Stage I or complete crystallisation, with the evaporated water being redirected to earlier stages of the process.

To assess the process comprehensively, Stage X is introduced, with a focus on minimising waste streams. The gaseous by-products of Stage VIII (O_2 and Cl_2) are separated via a membrane system [53]. Chlorine can be used for HCl synthesis via reaction with hydrogen (reaction 9), which is obtained through the gasification of organic matter remaining after Stage III.

Fermented and/or gasified sludge may also serve as a source of methane (CH_4) and carbon monoxide (CO), which can be utilised for energy production within the facility.



The concentrations of elements at individual stages of the process (our studies are marked in Table 2) were obtained from laboratory analyses performed using, among others, ICP-OES and ICP-MS techniques, in accordance with EN ISO standards and our own laboratory procedures, covering a total of 50 elements: Ca, Mg, Na, K, Li, Ba, Sr, Fe, Mn, Cd, Be, Ti, Cr, Co, Zr, V, Cu, Mo, Ni, Pb, B, Zn, Al, Sb, Ag, As, Se, Sn, Bi, S, Si, P, Tl, Hg, Te, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Th, Tm, Y, Yb, and U. Measurement uncertainties ranged from 10% to 25%. The concentrations of the vast majority of these elements were below 0.005 mg/L or 0.001 mg/L (for ICP-OES) and 0.05 $\mu\text{g/L}$ or 0.01 $\mu\text{g/L}$ (for ICP-MS); therefore, during the development of the laboratory-scale process, they were omitted as irrelevant from a technical and technological perspective. The analyses were conducted in an accredited laboratory (Central Mining Institute—National Research Institute in Katowice, Poland).

3.2. Process Analysis (Operating Conditions and Initial Assumptions)

A process analysis was conducted as a preliminary assessment of the technological feasibility of the proposed wastewater treatment process employing a cerium-based coagulant and its subsequent recycling. The analysis incorporated realistic operational conditions by scaling the results of previous laboratory- and pilot-scale studies to the conditions of a small wastewater treatment plant with a daily capacity of 5000 m^3 . Initial process assumptions, including pollutant concentrations and reagent doses and concentrations, as well as the efficiencies of individual process stages, were adopted.

Each of the ten stages of the process was examined in terms of reaction implementation, technological parameters, equipment configuration (e.g., reactors, filters, filter presses, and buffer tanks), and the mass balance of reagents and products. The main and by-products—including sludge, filtrates, and gaseous reaction products—were identified and quantified, particularly with respect to their potential environmental impact. The possibility of managing waste streams through hydrochloric acid recovery, the use of residual sludge as an energy source, and the recovery of salts from postreaction waters was assumed, with the aim of minimising pollutant emissions to the environment.

The process analysis was intended not only to confirm the technological coherence and effectiveness of the proposed solution but also to identify potential critical points that could affect environmental performance and operational costs. The results of the analysis were then used for further environmental assessment via the life cycle assessment (LCA) methodology and for economic evaluation via the dynamic generation cost (DGC) indicator.

3.3. Environmental Assessment

The environmental assessment was conducted via the life cycle assessment (LCA) method, following ISO 14040 [54] and ISO 14044 [55] in four phases: (1) goal and scope definition, (2) inventory analysis (LCI), (3) impact assessment (LCIA), and (4) interpretation.

Life cycle assessment (LCA) is a method for identifying potential environmental risks associated with the production, use, and disposal of a product. It evaluates the environmental impact of a product by quantifying raw material and energy consumption as well as emissions of waste and gases into the environment. A key feature of this approach is that it covers the entire product life cycle—from raw material extraction, transport, and processing through manufacturing processes, usage, and, finally, waste management or reuse. The advantage of LCA is its comprehensive approach, which considers all environmental impact factors as well as various ecological mechanisms and environmental issues [56]. An LCA supports decision-making processes, enabling the evaluation of existing processes and products as well as the design of new technological solutions [57]. The greatest environmental and economic benefits can be achieved by reducing the environmental impact at the early stages of production, which is the main goal of eco-design [58].

The purpose of this analysis was to assess the environmental impact associated with operations, material consumption, emissions, and waste generation resulting from the recovery of phosphates(V) from wastewater streams. The functional unit was defined as 1,825,000 m³ of wastewater treated per year, with all results normalised per 1 m³ of wastewater. The ReCiPe 2016 method was applied for impact assessment [41]. ReCiPe 2016 enables the assessment of potential environmental impacts in seventeen various impact categories (midpoints): climate change, ozone depletion, ionising radiation, fine particulate matter formation, and photochemical oxidant formation: terrestrial ecosystems, human health, terrestrial acidification, and freshwater eutrophication; human toxicity: cancer, noncancer, terrestrial ecotoxicity, freshwater ecotoxicity, and marine ecotoxicity; land use, water use, mineral resource scarcity and fossil resource scarcity. The hierarchist perspective was used during calculations, assuming a compromise between long-term and short-term environmental effects.

The system boundaries included the life cycle associated with the production of materials (chemicals) and electricity, as well as the generated wastewater sludge. The analysed system performs two main functions: wastewater treatment and phosphorus recovery. The multifunctionality issue was addressed by expanding the system boundaries—considering the avoided environmental impact associated with the production of phosphate(V) fertilisers. It was assumed that wastewater sludge is neutralised in a waste incineration plant. The system boundaries included in the analysis are illustrated in Figure 4.

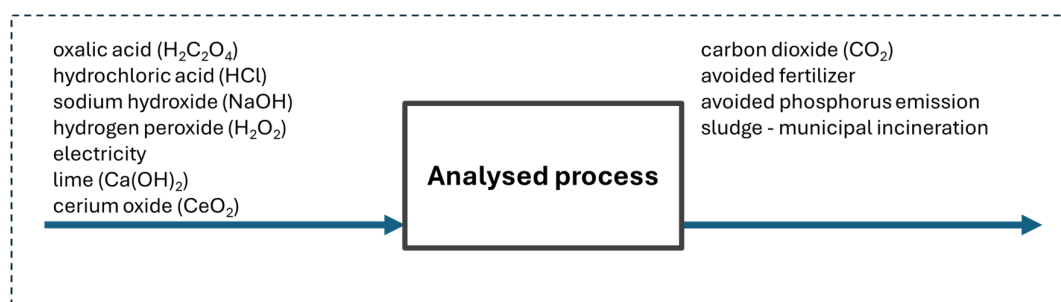


Figure 4. System boundaries.

3.4. Economic Assessment Methodology

Since the analysed technology for phosphate(V) removal using cerium(III) chloride complements the comprehensive wastewater treatment process, it is not possible to charge separate fees for its implementation in treatment plants. Therefore, an economic assessment was conducted via the dynamic generation cost (DGC) method. The dynamic unit cost is equal to the price that allows for discounted revenues to equal discounted costs. DGC demonstrates the technical cost of obtaining a unit of the product (in this project, 1 m³

of treated wastewater). Since it does not consider revenues but includes investment and operational costs (product life cycle), its value reflects the unit life cycle cost of the analysed product or technology. When comparing DGC indicators calculated for different technologies, lower values are considered more favourable. The DGC indicator is calculated via the following formula [59]:

$$DGC = \frac{\sum_{t=0}^n \frac{KI_t + KE_t}{(1+i)^t}}{\sum_{t=0}^n \frac{P_t}{(1+i)^t}}$$

where

KI_t —Investment costs incurred in a given year;

KE_t —Operational costs incurred in a given year;

P_t —Volume of treated wastewater in a given year;

i —Discount rate;

t —Year, ranging from 0 to n , where 0 is the year when the first costs are incurred, and n is the final year of wastewater treatment plant operation.

Investment expenditures were estimated on the basis of the proposed installation concept for phosphate(V) removal via cerium(III) chloride presented in this article, as well as the available online price lists for equipment and technological components. A summary of investment expenditures (price level: Q1 2025) is presented in Table 5.

Table 5. Summary of investment expenditures for the implementation of a phosphate(V) removal installation using cerium(III) chloride with a capacity of 5000 m³/day.

Item	Cost [USD]
Stage I. Phosphate(V) precipitation	
Coagulant preparation tank with mixing	5000
Coagulant dosing pump	4000
Wastewater tank for phosphate(V) removal	50,000
Pump for wastewater discharge into the nitrification process (87% of wastewater)	2000
Pump for sludge discharge to filter press (650 m ³)	2100
Stage II. Filtration	
Filter press × 2	12,000
Pump for filtrate discharge into the nitrification process	2100
Belt conveyor to reactors × 2	2000
Stage III. Sludge extraction	
Acid-resistant reactor for extraction × 2	76,000
30% HCl storage tank for extraction	5000
Acid-resistant pump for HCl	4000
Water storage tank	5000
Water pump	1500
Acid-resistant pump for acidic extract	8000
Stage IV. Filtration	
Acid-resistant filter press	12,000
Belt conveyor for sludge transport for agricultural use	1000
Acid-resistant pump for acidic extract	4000
Acid-resistant reactor for cerium(III) oxalate precipitation × 2	76,000
Stage V. Cerium(III) oxalate precipitation	
NaOH preparation tank with mixing	8000
Alkali-resistant pump	4000
Oxalic acid preparation tank	8000
Acid-resistant pump × 2	8000

Table 5. Cont.

Item	Cost [USD]
Stage VI. Filtration and filtrate management	
Acid-resistant filter press	6000
Belt conveyor for cerium oxalate transport	2000
Acid-resistant pump	8000
Reaction tank with agitator	130,000
Sedimentation tank	70,000
Filter press	75,000
Lime dosing system	30,000
Land preparation, membrane, drainage systems, and barriers	600,000
Stage VII. Thermal decomposition	
Furnace for cerium(III) oxalate decomposition into cerium(IV) oxide at 350 °C	5500
Belt conveyor for cerium(IV) oxide to CeCl_3 synthesis reactor	1000
Stage VIII. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ synthesis	
Acid-resistant reactor	20,000
Acid-resistant pump for HCl	4000
H_2O_2 storage tank	5400
High-resistance pump for H_2O_2	4000
Acid-resistant pump	4000
Stage IX. Crystallisation	
Evaporator for concentration	350,000
Coagulant dosing pump—recirculation after recovery	4000
Stage X. Hydrochloric acid recovery	
Gasification reactor, control system, and pumps	60,000
Membrane module	15,000
High-pressure tanks, compressor	12,260
Tubular reactor, cooling, and control system	82,500
Absorption tower and pumps	55,000
Membrane module for Cl_2 separation	5700
Pressure tank for Cl_2	12,000
Pumps, pipelines, and process control system	25,000
Total—Stages I to X	1,886,060
Additional equipment + piping	200,000
Automation and control system	150,000
Buildings	75,000
Project documentation, administrative decisions, and permits	94,000
Total—CAPEX	2,405,060

Similar to the investment expenditures, the operational costs were estimated on the basis of the proposed installation concept for phosphate(V) removal via cerium(III) chloride, as presented in this article, and available online price lists for chemicals used in the analysed wastewater treatment process. A summary of the operational costs (price level: Q1 2025) is presented in Table 6.

Table 6. Summary of operational costs for phosphate(V) removal installation using cerium(III) chloride with a capacity of 5000 m³/day.

Item	Unit	Amount	Cost [USD/Year]
Electricity	kWh	993,006	248,253
Monitoring	-	-	18,250
Labour	-	-	108,000
Maintenance and repairs	-	-	16,000
$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	kg/year	11,315	16,973
30% HCl solution	kg/year	2,693,956	1,131,461
30% H_2O_2 solution	kg/year	362,555	141,396
Oxalic acid	kg/year	240,535	127,965
NaOH	kg/year	393,105	157,242
Calcium hydroxide	kg/year	76,767	30,707
Total—OPEX	-	-	1,996,247

Recommended Practice 18R-97 of the Association for the Advancement of Cost Engineering International (AACE) describes a Cost Estimate Classification System as applied in Engineering, Procurement, and Construction for the process industries [60]. The techno-economic studies conducted in this article provide cost estimates at the “Study or Feasibility” level (AACE Class 4). Cost estimates in the Class 4 have an expected accuracy range of -15% to -30% on the low side and $+20\%$ to $+50\%$ on the high side.

For the purpose of dynamic generation cost (DGC) analysis of the developed phosphate(V) removal technology, a discount rate of 4% was applied. This value is recommended in the guidelines [61] for financial analyses conducted at constant prices. The analysis covers a 22-year period (2025–2046), including a 2-year investment implementation period and 20 years of plant operation. Throughout this period, the operational costs of the analysed phosphate(V) removal installation were adjusted via the macroeconomic indices presented in the guidelines [62] and the energy price forecasts outlined in the study [63].

4. Conclusions

The wastewater treatment process employing cerium(III) chloride was shown in our previous studies to reduce phosphate(V) concentration by more than 99.86%. The coagulant can also be recovered via acid extraction using hydrochloric acid, with a recovery efficiency of 97.0–98.3%. This enables the reuse of the recovered salt in wastewater treatment processes, with only minimal replenishment required to compensate for losses. An additional advantage of this process is the utilisation of waste materials for energy production or as substrates for the chemical manufacturing required by the treatment plant. The closed-loop reagent cycle in both wastewater treatment and cerium(III) recycling ensures that this innovative technology aligns with the principles of the circular economy.

The conducted life cycle assessment (LCA) demonstrated that the proposed phosphate(V) emission minimisation technology plays a significant role in protecting freshwater bodies and marine ecosystems from degradation. Moreover, the proposed process has adverse environmental impacts, primarily due to the consumption of chemical reagents, notably oxalic acid and hydrochloric acid. The most critical environmental concern identified within the analysed system is related to human carcinogenic toxicity.

The economic analysis revealed that this technology is more expensive than commonly used phosphate(V) removal methods, which are based on chemical precipitation. However, in situations where significantly higher phosphate(V) removal efficiency is needed, the use of cerium(III) chloride becomes an economically justified alternative. The combination of environmental and economic analysis results with the excellent outcomes of experimental studies suggests that this promising technology is worthy of further development and modification to further reduce its environmental impact, lower its operating costs, and improve the utilisation of process by-products.

A recommendation for future research is to compare the efficiency, as well as the environmental and economic aspects, of the proposed solution with other innovative coagulants, such as those based on zirconium or titanium salts, as well as with conventional methods using iron and aluminium salts.

Author Contributions: Conceptualisation, P.L., B.B. and M.T.; methodology, P.L., A.Ś. and P.K.; formal analysis, P.L., A.Ś. and P.K.; investigation, P.L.; resources, P.L.; data curation, P.L., A.Ś. and P.K.; writing—original draft preparation, P.L., A.Ś. and P.K.; writing—review and editing, P.L., B.B. and M.T.; supervision, B.B. and M.T.; funding acquisition, P.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Science of the Republic of Poland (Statutory Activity of the Central Mining Institute, Task no. 11331013-331).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are provided in the article.

Acknowledgments: The authors would like to thank the anonymous reviewers for their helpful comments.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

1,4-DCB-eq	1,4-dichlorobenzene equivalent (used in toxicity assessment)
CAPEX	Capital Expenditures
DGC	Dynamic Generation Cost
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
OPEX	Operational Expenditures
REE	Rare Earth Elements

References

- Kundzewicz, Z.W. Hydrosphere. In *Encyclopedia of Ecology*; Elsevier: Amsterdam, The Netherlands, 2008; pp. 1923–1930.
- Boretti, A.; Rosa, L. Reassessing the Projections of the World Water Development Report. *npj Clean Water* **2019**, *2*, 15. [[CrossRef](#)]
- Navarro, I.; de la Torre, A.; Sanz, P.; Abrantes, N.; Campos, I.; Alaoui, A.; Christ, F.; Alcon, F.; Contreras, J.; Glavan, M.; et al. Assessing Pesticide Residues Occurrence and Risks in Water Systems: A Pan-European and Argentina Perspective. *Water Res.* **2024**, *254*, 121419. [[CrossRef](#)] [[PubMed](#)]
- Ahmad, I.; Asad, U.; Maryam, L.; Masood, M.; Saeed, M.F.; Jamal, A.; Mubeen, M. Treatment Methods for Lead Removal from Wastewater. In *Lead Toxicity: Challenges and Solution*; Springer Nature: Cham, Switzerland, 2023; pp. 197–226.
- Lee, Y.; Lee, C.; Min, K.J.; Park, S. Efficient Cadmium Removal from Industrial Wastewater Generated from Smelter Using Chemical Precipitation and Oxidation Assistance. *Water Environ. Res.* **2024**, *96*, e11059. [[CrossRef](#)]
- Kazmi, S.A.R.; Husnain, S.M.; Khan, A.R.; Qureshi, T.M.; Lemaoui, T.; AlNashef, I.M.; Arafat, H.A.; Shahzad, F. Removal of Nickel Ions from Industrial Wastewater Using Tms-EDTA-Functionalized Ti3C2Tx: Experimental and Statistical Physics Modeling. *J. Hazard. Mater.* **2025**, *490*, 137667. [[CrossRef](#)]
- Suess, E.; Berg, M.; Bouchet, S.; Cayo, L.; Hug, S.J.; Kaegi, R.; Voegelin, A.; Winkel, L.H.E.; Tessier, E.; Amouroux, D.; et al. Mercury Loads and Fluxes from Wastewater: A Nationwide Survey in Switzerland. *Water Res.* **2020**, *175*, 115708. [[CrossRef](#)]
- Liu, Y.; Wang, H.; Cui, Y.; Chen, N. Removal of Copper Ions from Wastewater: A Review. *Int. J. Environ. Res. Public Health* **2023**, *20*, 3885. [[CrossRef](#)]
- Yuan, B.; Yang, Z.; Wu, P.; Yin, X.; Liu, C.; Sun, F.; He, J.; Jiang, W. Efficient Treatment of Chromium-Containing Wastewater Based on Auxiliary Intelligent Model with Rapid-Response Adsorbents. *Sep. Purif. Technol.* **2025**, *363*, 132037. [[CrossRef](#)]
- Khanzada, A.K.; Rizwan, M.; Al-Hazmi, H.E.; Majtacz, J.; Kurniawan, T.A.; Makinia, J. Removal of Arsenic from Wastewater Using Hydrochar Prepared from Red Macroalgae: Investigating Its Adsorption Efficiency and Mechanism. *Water* **2023**, *15*, 3866. [[CrossRef](#)]
- Yang, L.; Kang, S.; Luo, X.; Wang, Z. Microplastics in Drinking Water: A Review on Methods, Occurrence, Sources, and Potential Risks Assessment. *Environ. Pollut.* **2024**, *348*, 123857. [[CrossRef](#)]
- Komorowska-Kaufman, M.; Zembruska, J. Application of Oxidation Processes in Wastewater Quaternary Treatment for Organic Compounds, Antibiotics and Nonsteroidal Anti-Inflammatory Drugs Removal and Disinfection. *Desalination Water Treat.* **2025**, *321*, 101059. [[CrossRef](#)]
- Verma, V.; Chaudhari, P.K. Optimization of Multiple Parameters for Treatment of Coking Wastewater Using Fenton Oxidation. *Arab. J. Chem.* **2020**, *13*, 5084–5095. [[CrossRef](#)]
- Zhang, Q.; Meng, J.; Su, G.; Liu, Z.; Shi, B.; Wang, T. Source Apportionment and Risk Assessment for Polycyclic Aromatic Hydrocarbons in Soils at a Typical Coking Plant. *Ecotoxicol. Environ. Saf.* **2021**, *222*, 112509. [[CrossRef](#)] [[PubMed](#)]
- Lejwoda, P.; Białicka, B.; Thomas, M. Holistic Insight into the Viability of Employing Cerium(IV) Sulphate to Oxidise Toxic Contaminants in Effluent from the Coal Gasification Process: Optimisation Studies. *J. Water Process Eng.* **2024**, *67*, 106243. [[CrossRef](#)]

16. Charazińska, S.; Lochyński, P.; Burszta-Adamiak, E. Removal of Heavy Metal Ions Form Acidic Electrolyte for Stainless Steel Electropolishing via Adsorption Using Polish Peats. *J. Water Process Eng.* **2021**, *42*, 102169. [CrossRef]
17. Rao, D.P.; Krishnasamy, V.D.; Selvaraju, M.; Sundramurthy, V.P.; Kandavalli, S.R.; Chitra, M.S.; Sivasamy, N.; Thirumorthy, P. Adsorptive Removal of Cadmium from Electroplating Wastewater Using Hybrid Composite of Thiol-Grafted Seed Gum of *Tamarindus indica* and Teff Hay Biocarbon. *Z. Phys. Chem.* **2025**, *239*, 633–654. [CrossRef]
18. Pohl, A. Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. *Water Air Soil Pollut.* **2020**, *231*, 503. [CrossRef]
19. Zhang, W.; Rezaee, M.; Bhagavatula, A.; Li, Y.; Groppo, J.; Honaker, R. A Review of the Occurrence and Promising Recovery Methods of Rare Earth Elements from Coal and Coal By-Products. *Int. J. Coal Prep. Util.* **2015**, *35*, 295–330. [CrossRef]
20. Yang, X.; Hu, X.; Kong, L.; Peng, X. Selective Recovery of Cu(II) from Strongly Acidic Wastewater by Zinc Dimethyldithiocarbamate: Affecting Factors, Efficiency and Mechanism. *J. Environ. Sci.* **2023**, *129*, 115–127. [CrossRef]
21. Thomas, M.; Białecka, B.; Zdebik, D. Removal of Copper, Nickel and Tin from Model and Real Industrial Wastewater Using Sodium Trithiocarbonate. The Negative Impact of Complexing Compounds. *Arch. Environ. Prot.* **2018**, *44*, 33–47.
22. Wang, Q.; Zheng, C.; Zhang, J.; He, F.; Yao, Y.; Zhang, T.C.; He, C. Insights into the Adsorption of Pb(II) over Trimercapto-s-Triazine Trisodium Salt-Modified Lignin in a Wide PH Range. *Chem. Eng. J. Adv.* **2020**, *1*, 100002. [CrossRef]
23. Matlock, M.M.; Howerton, B.S.; Atwood, D.A. Chemical Precipitation of Heavy Metals from Acid Mine Drainage. *Water Res.* **2002**, *36*, 4757–4764. [CrossRef] [PubMed]
24. Smith, S.; Takács, I.; Murthy, S.; Daigger, G.T.; Szabó, A. Phosphate Complexation Model and Its Implications for Chemical Phosphorus Removal. *Water Environ. Res.* **2008**, *80*, 428–438. [CrossRef] [PubMed]
25. Mohammed, S.A.M.; Abbas Shanshool, H. Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride. *Iraqi J. Chem. Pet. Eng.* **2009**, *10*, 47–52. [CrossRef]
26. Szabó, A.; Takács, I.; Murthy, S.; Daigger, G.T.; Licskó, I.; Smith, S. Significance of Design and Operational Variables in Chemical Phosphorus Removal. *Water Environ. Res.* **2008**, *80*, 407–416. [CrossRef]
27. Wang, J.; Song, J.; Lu, J.; Zhao, X. Comparison of Three Aluminum Coagulants for Phosphorus Removal. *J. Water Resour. Prot.* **2014**, *6*, 902–908. [CrossRef]
28. Akinawo, S.O. Eutrophication: Causes, Consequences, Physical, Chemical and Biological Techniques for Mitigation Strategies. *Environ. Chall.* **2023**, *12*, 100733. [CrossRef]
29. Owodunni, A.A.; Ismail, S.; Kurniawan, S.B.; Ahmad, A.; Imron, M.F.; Abdullah, S.R.S. A Review on Revolutionary Technique for Phosphate Removal in Wastewater Using Green Coagulant. *J. Water Process Eng.* **2023**, *52*, 103573. [CrossRef]
30. Huang, S.; Fu, Y.; Zhang, H.; Wang, C.; Zou, C.; Lu, X. Research Progress of Novel Bio-Denitrification Technology in Deep Wastewater Treatment. *Front. Microbiol.* **2023**, *14*, 1284369. [CrossRef]
31. Kim, D.W.; Yu, S.I.; Im, K.; Shin, J.; Shin, S.G. Responses of Coagulant Type, Dosage and Process Conditions to Phosphate Removal Efficiency from Anaerobic Sludge. *Int. J. Environ. Res. Public Health* **2022**, *19*, 1693. [CrossRef]
32. Sengupta, S.; Nawaz, T.; Beaudry, J. Nitrogen and Phosphorus Recovery from Wastewater. *Curr. Pollut. Rep.* **2015**, *1*, 155–166. [CrossRef]
33. Zhou, Q.; Sun, H.; Jia, L.; Wu, W.; Wang, J. Simultaneous Biological Removal of Nitrogen and Phosphorus from Secondary Effluent of Wastewater Treatment Plants by Advanced Treatment: A Review. *Chemosphere* **2022**, *296*, 134054. [CrossRef]
34. Kajjumba, G.W.; Fischer, D.; Risso, L.A.; Koury, D.; Marti, E.J. Application of Cerium and Lanthanum Coagulants in Wastewater Treatment—A Comparative Assessment to Magnesium, Aluminum, and Iron Coagulants. *Chem. Eng. J.* **2021**, *426*, 131268. [CrossRef]
35. Lejwoda, P.; Białecka, B.; Thomas, M. Removal of Phosphate from Brewery Wastewater by Cerium(III) Chloride Originating from Spent Polishing Agent: Recovery and Optimization Studies. *Sci. Total Environ.* **2023**, *875*, 162643. [CrossRef] [PubMed]
36. U.S. Geological Survey. *Mineral Commodity Summaries 2025*; U.S. Geological Survey: Reston, VA, USA, 2025.
37. European Commission Directorate-General for Internal Market, Industry; Entrepreneurship and SMEs; Grohol, M.; Veeh, C. *Study on the Critical Raw Materials for the EU 2023—Final Report*; Publications Office of the European Union: Luxembourg, 2023. Available online: <https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1/language-en> (accessed on 5 April 2025).
38. Lejwoda, P.; Białecka, B.; Barbusiński, K.; Thomas, M. Recovery of Cerium Salts from Sewage Sludge Resulting from the Coagulation of Brewery Wastewater with Recycled Cerium Coagulant. *Materials* **2024**, *17*, 938. [CrossRef] [PubMed]
39. Śpiwak, K. Gasification of Sewage Sludge—A Review. *Energies* **2024**, *17*, 4476. [CrossRef]
40. Rodríguez, F.A.; Santiago, D.E.; Franquiz Suárez, N.; Ortega Méndez, J.A.; Veza, J.M. Comparison of Evaporation Rates for Seawater and Brine from Reverse Osmosis in Traditional Salt Works: Empirical Correlations. *Water Supply* **2012**, *12*, 234–240. [CrossRef]
41. Huijbregts, M.A.J.; Steinmann, Z.J.N.; Elshout, P.M.F.; Stam, G.; Verones, F.; Vieira, M.; Zijp, M.; Hollander, A.; van Zelm, R. ReCiPe2016: A Harmonised Life Cycle Impact Assessment Method at Midpoint and Endpoint Level. *Int. J. Life Cycle Assess.* **2017**, *22*, 138–147. [CrossRef]

42. CENY WODY 2025 W POLSCE MIASTA ALFABETYCZNIE I MALEJCO. Available online: <http://www.cena-pradu.pl/woda.html> (accessed on 1 April 2025).
43. Kajjumba, G.W.; Marti, E.J. A Review of the Application of Cerium and Lanthanum in Phosphorus Removal during Wastewater Treatment: Characteristics, Mechanism, and Recovery. *Chemosphere* **2022**, *309*, 136462. [CrossRef]
44. Dahle, J.; Arai, Y. Environmental Geochemistry of Cerium: Applications and Toxicology of Cerium Oxide Nanoparticles. *Int. J. Environ. Res. Public Health* **2015**, *12*, 1253–1278. [CrossRef]
45. Byrne, R.H.; Kim, K.-H. Rare Earth Precipitation and Coprecipitation Behavior: The Limiting Role of PO_4^{3-} on Dissolved Rare Earth Concentrations in Seawater. *Geochim. Cosmochim. Acta* **1993**, *57*, 519–526. [CrossRef]
46. Liu, X.; Byrne, R.H. Rare Earth and Yttrium Phosphate Solubilities in Aqueous Solution. *Geochim. Cosmochim. Acta* **1997**, *61*, 1625–1633. [CrossRef]
47. Rodríguez-Ruiz, I.; Teychené, S.; Vitry, Y.; Biscans, B.; Charton, S. Thermodynamic Modeling of Neodymium and Cerium Oxalates Reactive Precipitation in Concentrated Nitric Acid Media. *Chem. Eng. Sci.* **2018**, *183*, 20–25. [CrossRef]
48. Crouthamel, C.E.; Martin, D.S. Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution. II. Neodymium and Cerium(III) ¹. *J. Am. Chem. Soc.* **1951**, *73*, 569–573. [CrossRef]
49. Żelazny, S.; Świnder, H.; Białecka, B.; Jarosiński, A. Odzysk Pierwiastków Ziemi Rzadkich z Popiołów Lotnych. Cz. II. Wytrącanie z Roztworu. *PRZEMYSŁ Chem.* **2017**, *1*, 102–108. [CrossRef]
50. Lopez, H.F.; Mendoza, H. Temperature Effects on the Crystallization and Coarsening of Nano-CeO₂ Powders. *ISRN Nanomater.* **2013**, *2013*, 208614. [CrossRef]
51. Chen, F.; Liu, F.; Wang, L.; Wang, J. Comparison of the Preparation Process of Rare Earth Oxides from the Water Leaching Solution of Waste Nd-Fe-B Magnets' Sulfate Roasting Products. *Processes* **2022**, *10*, 2310. [CrossRef]
52. Poscher, A.; Luidold, S.; Schnideritsch, H.; Antrekowitsch, H. Extraction of Lanthanides from Spent Polishing Agent. In Proceedings of the ERES2014-1st European Rare Earth Resources Conference, Milos, Greece, 4–7 September 2014; pp. 209–222.
53. Skudaev, V.I.; Solomonov, A.B.; Morozovskii, A.I.; Isakov, N.A. Oxidation of Hydrogen Chloride with Hydrogen Peroxide in Aqueous Solution. *Russ. J. Appl. Chem.* **2008**, *81*, 14–16. [CrossRef]
54. ISO 14040; Environmental Management—Life Cycle Assessment—Principles and Framework. International Standard Organization: Geneva, Switzerland, 2006.
55. ISO 14044; Environmental Management—Life Cycle Assessment—Requirements and Guidelines. International Standard Organization: Geneva, Switzerland, 2006.
56. Kowalski, Z.; Kulczycka, J.; Góralczyk, M. *Ekologiczna Ocena Cyklu Życia Procesów Wytwórczych (LCA)*; PWN: Warszawa, Poland, 2007.
57. Burchart-Korol, D. Zastosowanie Oceny Cyklu Życia (LCA) w Analizie Procesów Przemysłowych. *Probl. Ekol.* **2009**, *13*, 300–305.
58. Kurczewski, P.; Lewandowska, A. *Zasady Projektowania Prośrodowiskowego Obiektów Technicznych Dla Potrzeb Zarządzania Ich Cyklem Życia: Praca Zbiorowa*; Politechnika Poznańska: Poznań, Poland, 2008; ISBN 9788361352204.
59. Rączka, J. *Cost Effectiveness Analysis Based on Dynamic Generation Cost Index. Training Materials Developed Under the TRANSFORM ADVICE PROGRAMME—Investment in Environmental Infrastructure in Poland*; (In Polish: Analiza Efektywności Kosztowej w Oparciu o Wskaźnik Dynamicznego Kosztu Jednostkowego). Available online: <https://www.gov.pl/attachment/ae722d67-2dae-4af0-b269-35fee9faea87> (accessed on 3 April 2025).
60. Advancement of Cost Engineering (ACE) International. *Cost Estimate Classification System—As Applied in Engineering, Procurement, and Construction for the Process Industries*; TCM Framework 7.3—Cost Estimating and Budgeting, AACE International Recommended Practice No. 18R-97; AACE International: Denver, CO, USA, 2005; Revised 29 November 2011. Available online: <https://aheinc.ca/wp-content/uploads/2018/12/AACE-Cost-Estimate-Classification-System.pdf> (accessed on 3 April 2025).
61. Minister Funduszy i Polityki Regionalnej. *Wytyczne Dotyczące Zagadnień Związanych z Przygotowaniem Projektów Inwestycyjnych, w Tym Hybrydowych Na Lata 2021–2027*; Minister Funduszy i Polityki Regionalnej: Warszawa, Poland, 2023.
62. Minister Finansów. *Guidelines on the Use of Uniform Macroeconomic Indicators Constituting the Basis for Estimating the Financial Impact of Draft Laws*; (In Polish: Wytyczne Dotyczące Stosowania Jednolitych Wskaźników Makroekonomicznych Będących Podstawą Oszacowania Skutków Finansowych Projektowanych Ustaw); Minister Finansów: Warszawa, Poland, 2024.
63. Pyrka, M.; Jeszke, R.; Boratyński, J.; Witajewski-Baltvilks, J.; Antosiewicz, M.; Tatarewicz, I.; Rabięga, W.; Wąs, A.; Tobiasz, I.; Lewarski, M.; et al. *VII EW on EU ETS 2050: Changing the Scope of the EU Emissions Trading System*; Krajowy Ośrodek Bilansowania i Zarządzania Emisjami/Instytut Ochrony Środowiska (KOBIZE/IOŚ): Warszawa, Poland, 2023.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.