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 ($CeCl_3 \cdot 7H_2O$) 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 ($Ce_2(C_2O_4)_3 \cdot nH_2O$, where n = 9–10), which was thermally decomposed at 350 ± 5 °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 ($CeCl_3 \cdot 7H_2O$) with a yield of 97.0% and a purity of 98.6%.

In addition, salts such as cerium(III) sulphate(VI) ($Ce_2(SO_4)_3$) with a yield of 97.4% and a purity of 95.9%, and cerium(IV) sulphate(VI) ($Ce(SO_4)_2$) 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) ($Ce(SO_4)_2 \cdot 4H_2O$) 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 $Ce(SO_4)_2 \cdot 4H_2O$ 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 $Ce(SO_4)_2 \cdot 4H_2O + H_2O_2$ 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 ($H_2C_2O_4$). 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.