Application of minerals co-occurring in brown coal deposits to removal of heavy metals from water and wastewater

Summary

For some recent years, the quality of water has been of great concern to the EU legislation, mainly due to the worldwide quest for high quality drinking water sources. Tightening of the standards concerning waters by the EU Directives and growing demand for high quality water force search for more and more effective and ecologically safe methods for water and wastewater purification. One of the more effective methods is using sorbents. However, because the synthetic sorbents are expensive, some alternative, efficient and cost-effective, natural or waste material, mineral or organogenic materials, having high capacity for sorbing heavy metals and other pollutants from liquids, are looked for.

The presented laboratory experiments were to determine the sorption capacity of minerals accompanying brown coal deposits (peats, lignite, brown coal, Tertiary clays) for Cd(II), Zn(II), Cu(II), Ni(II), Cr(III) and Pb(II) ions and for anions of chloride and sulphate. Susceptibility of adsorbed metals to leaching and effects of kind of anions and cations present in solution on amounts of bound metal ions were also determined. The sorption parameters were computed and minerals with the greatest capability for sorbing heavy metals selected. Also conditions for applying these minerals as waste dump barriers or filters for wastewater purification were determined.

The sorption of the minerals was investigated with the use of the “batch” method. The solid phase/solution ratio was 1:10, solution pH was equal to 4, initial concentration of metal ions in the solution was 0.05–25 cmol(+)/dm$^3$. The cation exchange capacity (CEC) of investigated adsorbents was high and in organogenic samples it strongly depended on organic matter content, in clays – on content of aluminosilicate minerals belonging to the smectite group. Main exchangeable cations were Ca$^{2+}$, which besides affecting saturation level of the sorption complex of samples also considerably affected their pH and buffering properties. Very good H$^+$ buffering by peats, brown coal and clay from Belchatów made these minerals resistant to rapid pH changes, for example during reactions with acid sewage or waste dump leachate.

The sorption of metal ions by minerals co-occurring in brown coal deposits depended as well on a kind and initial concentration of metal ions in a solution as on physicochemical properties of investigated material. Among the investigated metal ions (Cr(III), Cu(II), Cd(II), Zn(II), Ni(II), Pb(II)), at pH equal to 4, the greatest affinity to the sorption centres of the minerals had the Cr(III) and Cu(II) ions, and they were bound in amounts exceeding the mineral CEC. Amounts of bound Cd(II) ions were lowest.

The amount of bound ions depended on anion type. In presence of sulphate ions, the sorption capacity of the minerals for the Cd(II), Cu(II), Ni(II) and Zn(II) ions, compared to chloride solutions, increased. The sorption capacity for Cd(II) ions increased most, the lowest increase was of the sorption capacity for Cu(II) ions. Chloride ions in solution, lowering sorption of Cd(II) ions, elevated their liability to leaching. Moreover, at solution pH 4, the chloride ions were not sorbed and the sulphate ions were removed from the solution by reacting with exchangeable Ca$^{2+}$ and precipitating as weakly soluble CaSO$_4$.

Considerable amounts of Cd(II), Ni(II), Zn(II) cations were bound onto the solid phase in the ion exchange reaction, so their binding to the sorption centres was suppressed by competing cations present in the solution. Instead, the Cr(III) ions, and also Cu(II) ones, were strongly bound and of weak mobility. Amorphous
iron oxides also played an important role in binding the Cr(III) and Cu(II) ions.

The sorption capacity of the brown coal related minerals is high and a cost of their obtaining is low. These features predestine these minerals to be cost-effective and efficient sorbents to purify waters and wastewaters.