Summary

SORPTIVE REMOVAL OF DYES FROM WATER AND WASTEWATER USING NEOGENE SMECTITE CLAYS

The European Union legislation concern about the resources of ground and surface waters is motivated by their significance as a source of high quality drinking water.

Since 2000, in the EU, the Water Framework Directive has been in force providing legal instruments to protect waters and aiming at achieving their good quality no later than 2015. Both, the maintenance and improvement of water quality within the assumed period require identification of the threats, assessment of their environmental effects and, where necessary, application of proper remediation measures. In general, the task is realized by imposing limits on discharges of pollutants into waters and water-dependent ecosystems.

Released directly into watercourses and water basins, industrial and municipal waste waters seriously damage the water environment. Many workshops and small industrial plants have no waste treatment stations and, violating the law they release waste waters into sewage systems without any pre-treatment.

An important group of organic pollutants contaminating the water environment is formed by the dyes and pigments coming from various industries, mainly from the dyeing, textile, cosmetic and paper ones. Because of their complex structure and many possible substitutions, the dyes resist physical, chemical or biological degradation. Moreover, their decomposition yields some amounts of toxic and carcinogenic substances.

The adsorption onto porous synthetic materials (activated carbon, ion-exchange resins) is one of the more effective methods for removal of dyes from waters and waste waters, equally at low and high dye concentrations. However, high costs of production and troublesome regeneration of the spent sorbents activate the search for effective and economical, mineral or organic, natural sorbents for dyes.

Two Neogene smectite clays, co-occurring with lignite at "Bełchatów" and "Adamów" Lignite Mines, were examined for their capability of reducing the dye content of water and waste water. The dyes used in the experiment were 14 reactive, direct and acid, anionic and cationic dyes, most common in textile dyeing.

The sorption capacity of the clays depended on the dye properties, the dye chemical composition, number and kind of functional groups, and of the physicochemical properties of the clays themselves. The "Bełchatów" clay had higher sorption capacity for all the examined dyes. Because of good buffering properties of the clays, all the dyes were sorbed at pH higher than the clay point of zero charge, i.e. the colloidal size particles of the clay minerals and quartz had negative charge due to dissociated surface silanol (-SiOH) groups and aluminol ($-Al_2OH$) groups located on the edges of the clay particles.

The greatest sorption capacity both clays showed for cationic dyes (DY-142, AG-16), bound mainly through electrostatic attraction between the dye cations and the surface of the particles of clay minerals. Some anionic dyes (DR-81, AB-9) enhanced the clay capacity for their sorption by polymerizing. The remaining anionic dyes were bound in smaller amounts, through hydrogen bounds between =NH, $-NH_2$, -OH groups (proton donors) in dyes and silanol and aluminol groups (proton acceptors) in clay minerals.

The sorption was classified as surface sorption – the increase of the porosity, specific surface area and the number sorption centers may enhance the sorption capacity of the clays for anionic dyes. It was confirmed by investigating the thermally and chemically modified clays.

The Freundlich equation described the sorption most adequately. The values of Fraundlich's parameter 1/n between 0 and 1 indicated the physical sorption of the anionic dyes, 1/n greater than 1 – chemisorption and creation of many layers of the cationic dyes on the mineral particles. The Freundlich equation was ascertained to describe Giles' type sorption L, S and H. The Langmuir equation describes the L-type sorption, in some cases the S-type sorption, and it does not describe the H-type sorption.

Thermally and chemically modified, the clays sorbed the dyes according to the pseudo-second order equation. The clay modifications changed the reaction rate constants k_2 and the amount $q_{e.}$ of dyes adsorbed in the equilibrium conditions. The intra-particle diffusion played also an important role in the sorption.

The efficiency of the clays in removal of the dyes from the samples of waste water from a textile factory was high and depended on the proportion solid phase : solution. This high efficiency and low costs of the clays co-occurring with lignite deposits allow to consider their application as sorbents for dye removal from waste water released by the dyeing and textile industries.