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REMOVAL OF Cr(III) IONS FROM WATER AND WASTEWATER BY SORPTION ONTO PEATS AND CLAYS OCCURRING IN AN OVERBURDEN OF LIGNITE BEDS IN CENTRAL POLAND

Sorption capacities of low-moor peats and Neogene clays from the overburden of lignite beds in Central Poland for Cr(III) ions as chloride and metalorganic complex ions have been investigated. The binding mechanisms and sorption parameters were determined based on the Freundlich and Langmuir nonlinear sorption isotherms. The sorption capacities of studied materials for Cr(III) ions depended on their properties (porosity, average pore diameters, specific surface area and content of Fe hydroxyoxides) as well as charge of Cr(III) ions, functional groups and their diagonal lengths. Cr(III) ions from chlorides were bound onto sorbents via Coulomb attraction and by Fe hydroxyoxides. However the complex Cr(III) ions were bound to the sorbent surface via hydrogen bonds between the dye –OH groups and =O of the sorbent functional groups. The equation parameters of sorption isotherms indicate cooperative heterogeneous adsorption at low Cr(III) concentrations and chemisorption at high Cr(III) concentrations.

1. INTRODUCTION

The EU Water Framework Directive 2000/60/EC [1] has been in force since the year 2000. It ensures protection of waters and anticipates reaching their at least “good” status no later than 2015. The task involves identification of the risks, evaluation of their environmental effects, and if required, application the remedy procedures.

Despite still improving purifying methods, heavy metals in discharged industrial wastewater still remain an environmental problem. Households and small workshops add to it by contaminating municipal wastewater (30–80% of Ni, Zn, Cu, Pb and 2–30% of Cr and Cd in urban wastewater [2]).

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Toxic chromium and its compounds are released into natural waters in a variety of industrial wastewaters. Its major sources are the electroplating and metal finishing industries, tanning and dyeing textile processes, pigments manufacturing and households. Depending on the source (kind of industry), chromium in wastewater occurs as strongly hydrated ions $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (galvanic wastes) or as complex neutral, anionic or cationic compounds (textile dyeing wastes). Neutral particles (H_2O , NH_3) and anions (OH^- , F^- , SO_4^{2-} , CN^-) may occur as ligands; some organic ligands, natural or synthetic, may occur as well. Depending on pH, Cr(III) occurs as soluble Cr^{3+} and CrOH^{2+} , $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, or $\text{Cr}(\text{OH})_4^-$ ions in aqueous solutions [3, 4]. The Cr coordination number is 6 in all these compounds. Ligands affect the ion ability to interact with the surface of solid phases and the kind of possible bonds by affecting the electric charge and radius of an ion (i.e. the Cartledge ionic potential).

Several treatment technologies have been developed to remove chromium from water and wastewater. Common methods include chemical precipitation, ion exchange, membrane separation, ultrafiltration, flotation, electrocoagulation, sedimentation, dialysis/electrodialysis and adsorption [5–8]. Chemical precipitation has become the most common method, but it generates sludge causing disposal problem. Adsorption onto activated carbon is effective in removal of wide range of contaminants from wastewater [5, 7]. However, application of activated carbon is not economical and its regeneration after the use is troublesome. Due to these troubles with widely used materials, there arises the need of searching the cost effective substitutes with high sorption capacity. They may be sought among minerals, natural materials or wastes, agricultural or industrial by-products, which need only a simple pretreatment to become adsorbents.

Organogenic adsorbents include carbonaceous substances (peat, lignite, oxihumolite, coal). Peat is young Quaternary, mainly Holocene, organogenic sedimentary rock at the first stage of coalification, formed through decomposition of plant material in the presence of weakly acidic humic substances. It is a complex mixture of (mainly) lignin, cellulose, humic substances (fulvic and humic acids), and also mineral substances such as Fe(III) hydroxyoxides and silica [9, 10].

Alkaline and alkaline earth cations may be substituted for H^+ in the peat main functional groups (carboxylic and hydroxyl phenolic groups of humic and fulvic acids) and for $-\text{OH}$ groups in Fe(III) hydroxyoxides. Having the polar character, high total specific surface area, porosity and cation exchange capacity, peats have high sorption capacity for dissolved transition metals and polar organic molecules [11–13].

Poland deals 17th place among the European countries ranked by the percentage of peat bogs in the national area [14]. The peatland area in Poland is 1 255 000 ha [15]. Besides peatlands, peat occurs also in the overburden of lignite deposit in Central Poland (Bełchatów, Konin, Adamów lignite mines). The overburden is dumped during excavation and then used to reclaim terrains devastated by mining.

The best known and commonly used mineral sorbents are clay minerals from the kaolinite, smectite, and illite groups. Mixed-layer clays are built of layers of clays from all these groups (e.g. smectite/illite) [16, 17]. Clay minerals occur very often as fine-grained sedimentary rocks such as bentonites, shale, mudstone. Structure, chemical composition, exchangeable ion type and colloidal size of smectite clays are responsible for several of their unique properties such as high specific area and cation exchange capacity, interlamellar surfaces with unusual hydration characteristics and sometimes the ability to modify strongly the flow behavior of liquids [16].

The sorption capacity of Neogene clays and low-moor peats from the overburden of lignite beds in Central Poland for Cr(III) ions have been presented in the paper. Cr(III) ions were adsorbed from aqueous solutions (the ratio solid:liquid phase was 1:20) of chlorides and metal complex ions – Acid Blue 193 and Acid Black 194 dyes. The binding mechanisms and sorption parameters were determined using the Freundlich and Langmuir nonlinear sorption isotherms.

2. MATERIALS AND METHODS

Sorbents. The sorbents used in the experiment were two low-moor peats and two Neogene clays from the overburden of the lignite deposits in Central Poland:

- Alder peat from the Bełchatów Lignite Mine,
- sedge peat from the Konin Lignite Mine,
- smectite clay from the Bełchatów Lignite Mine,
- smectite/illite mixed layer clay from the Adamów Lignite Mine.

Air-dried and homogenized samples of the sorbents were sieved through a 0.5 mm sieve. Their physicochemical properties are given in Table 1. The methods for determining the physicochemical properties have been described elsewhere [2].

Alder peat and sedge peat had high total specific surface areas (218.98 and 215.26 m²/g), high porosity (0.5211 and 0.5934), their average pore diameters were 10.54 and 13.50 nm. They had high cation exchange capacities (CEC, 124.5 and 117.3 cmol(+)/kg), the dominant exchangeable cations were Ca²⁺, H⁺ and Mg²⁺. Free amorphous iron (Fe_{ox}) content of the peats was high. The main functional groups were carboxyl and hydroxyl groups of phenols in humic acids and hydroxyl groups bound to iron oxides (Fig. 1).

The physicochemical properties of clays, especially the specific surface area and CEC depend on the clay minerals constituting the clays. In clays from the Bełchatów Lignite Mine the main clays are Ca-smectite and kaolinite. The Adamów Lignite Mine clays contain mainly smectite/illite mixed layer clays. The total surface area (208.83 m²/g) and CEC (82.39 cmol(+)/kg) of clays from the Bełchatów Lignite Mine was higher than those from the Adamów Lignite Mine clays, which are 121.43 m²/g and 31.58 cmol(+)/kg, respectively. But the clays had similar porosity (0.2643 and 0.2819) and average pore diameters (6.56 and 7.16 nm).

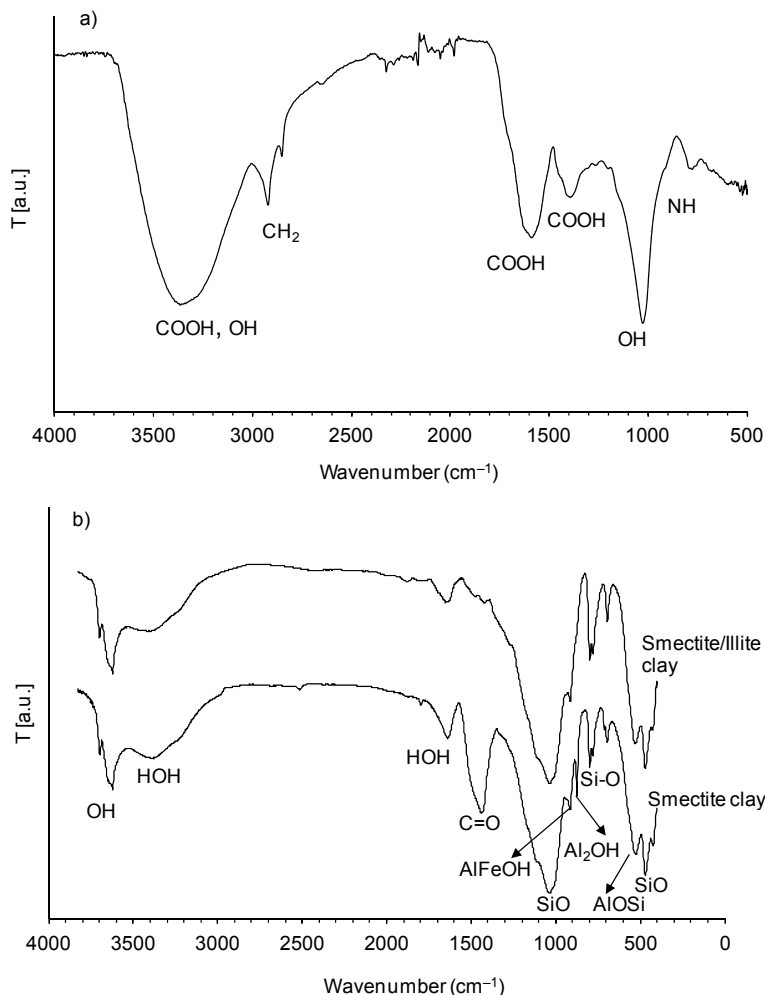


Fig. 1. FTIR spectra of peats (a) and clays (b). Bands originating from main functional groups are described in the picture

The main functional surface groups in the clays are silanol – $-\text{Si}-\text{OH}$ (IR vibrational modes near 1054 and 474 cm^{-1}) and aluminol – $-\text{Al}_2-\text{OH}$ (at 921 cm^{-1}) – groups on the edges of clay mineral molecules. The band at 873 cm^{-1} in IR spectra of smectite clay assigned to $-\text{AlFeOH}$ reflects partial substitution of Al by Fe in octahedral sheets. The clays contained much iron, mainly in the clay mineral structure. The free amorphous iron content of the clays (634.5 – 1014 mg/kg) was lower than that of the peats. The values of pH at the isoelectric point, pH_{PZC} , all the sorbents were within the range 5.77 – 8.92 . At pH lower than pH_{PZC} sorbent surface is positively charged, at higher pH – negatively (Table 1).

