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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).

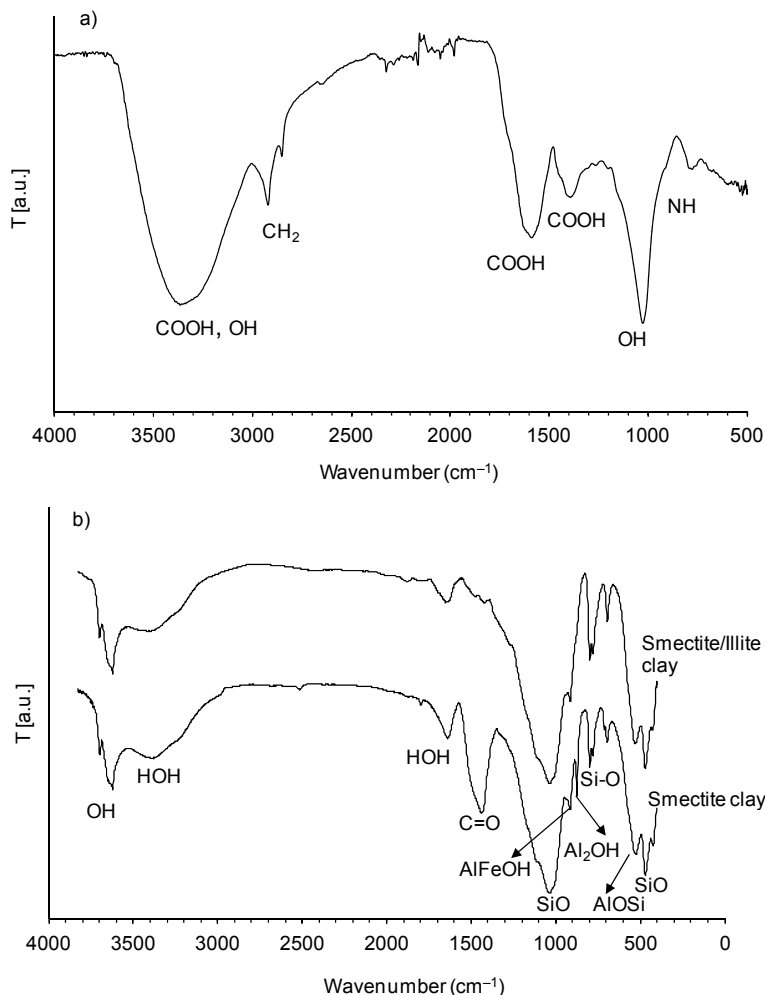


Fig. 1. FTIR spectra of peats (a) and clays (b). Bands originating from main functional groups are described in the picture

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).

Table 1

Physicochemical and chemical properties of the investigated sorbents

Physicochemical properties										
Sample	Porosity	Average pore diameter [nm]	Specific surface [m ² /g]		pH _{H₂O}	pH _{PZC}				
			External	Total						
Alder peat	0.5211	10.54	11.38	218.98	5.62	5.77				
Sedge peat	0.5934	13.50	14.10	215.26	6.33	7.46				
Smectite clay	0.2643	6.56	37.27	208.83	7.85	8.92				
Smectite/illite clay	0.2819	7.16	21.54	121.46	7.53	6.95				
Chemical properties										
Sample	Fe _t	Fe as F _{ox}	-COOH groups	-OH groups	CEC	Exchangeable ions [cmol(+)/kg]				
						Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	H ⁺
	[mg/kg]	[cmol(+)/kg]								
Alder peat	16170	9795	90	115.3	124.5	95.2	7.14	0.20	0.09	21.8
Sedge peat	12470	9092	40	169.8	117.3	104.2	8.91	0.80	0.23	3.04
Smectite clay	45150	634.5	nd	nd	82.39	72.50	8.56	0.08	0.62	0.45
Smectite/illite clay	30590	1014	nd	nd	31.58	24.86	5.82	0.03	0.59	0.10

nd – not determined.

Aqueous solutions. Cr(III) ions were adsorbed from the solutions of:

- CrCl₃·6H₂O,
- Acid Blue 193 (AB-193), C₄₀H₂₂CrN₄O₁₀S_{2.2}Na, chromate(3-),bis[3-hydroxy-4-((2-hydroxy-1-naphthalenyl)azo)-1-naphthalene sulfonato(3-)]-sodium hydrogen),
- Acid Black 194 (ABk-194), C₄₀H₂₀CrN₆O₁₄S_{2.2}Na, chromate(3), bis[₃(hydroxy₆O)₄[[₂(hydroxy₆O)₁naphthalenyl]azo₆N₁]₇-nitro-1-naphthalene sulfonato(3-)]- disodium).

Sorption methods. Sorption capacity was determined by the batch method at room temperature. The initial concentrations of Cr(III) were within 0.5–5000 mg/dm³ in the chloride solutions and 0.06–325 mg/dm³ in the dye solutions. The stock solutions were prepared by dissolving 25.625 g of CrCl₃·6H₂O or 5 g of a dye (AB-193 or ABk-194) in 1 dm³ of distilled water. pH in the stock solutions was adjusted to 4 using 0.1 M HCl. The proportion of the solid phase (*m*) to the solution (*V*) was 1:20, the shaking time was 24 h, the sorbent suspensions were centrifuged at 4000 rpm for 20 min.

The initial (*C*₀) and equilibrium (*C*_{eq}) Cr concentrations in the solutions were determined by the atomic absorption spectrophotometry (Thermo Jerrell Ash model AA Scan 1) under the optimized measurement conditions with the use of a chromium hollow cathode lamp. The signal was background corrected (deuterium lamp) at the optical flame (A–Ac) height.

The amount (S) of adsorbed Cr was calculated from the equation:

$$S = \frac{(C_0 - C_{eq})V}{m} \quad [\text{mg/kg}] \quad (1)$$

pH was measured in the equilibrium solutions using a pH-meter glass electrode, the concentration of Ca^{2+} in the solution was determined by the flame emission spectroscopy (BWB-XP).

Chemical bonding of Cr ions. Sequential extraction (SE) was used to fractionate metals in various environmentally reactive or hydromorphic phases of soil [18], sediment [19] and solid waste [20]. It provides the information about main binding sites and, by separating fractions, the strength of the bonds between metal and solid particles. SE can also be applied to homogenous materials such as organic matter – peats, moss, plants [21].

To fractionate Cr ions, 1 g of dried and homogenized adsorbent containing Cr(III) ions adsorbed from the chloride (at $C_0 = 5000 \text{ mg/dm}^3$) and dye solution (300 mg/dm^3) was subject to the speciation analysis. The fractionation of Cr(III) ions with respect to the major mechanisms of sorption onto peats and clays was done by using the classical seven-step sequential extraction scheme developed by Tessier et al. [22] and modified by Kersten and Förstner [23]. It consists in subsequent treatment of the adsorbent containing Cr(III) by increasingly stronger extractants to determine “pools” (F0–F6) of metal. There are:

- F0 – water-soluble fraction of Cr (in the adsorbent pores),
- F1 and F2 – Cr bound through electrostatic attraction between charged ions and surface of the adsorbent, hydrogen and van der Waals attraction between Cr ions and the surface functional groups or substituted for exchangeable cations,
- F3 and F4 – Cr bound by Mn-Fe hydroxyoxides,
- F5 – Cr bound by organic matter chelating complex formation involving carboxylic –COOH and phenolic –OH groups of humic substances,
- F6 – metals firmly incorporated in the lithogenic crystallites of the mineral fraction (residual fraction); F6 does not occur in pure organic matter.

Each fraction was centrifuged for 20 min (10 000 rpm) to separate solid phase. Cr was determined in all extracts by means of a Thermo Jarrell Ash model AA-Scan-1 atomic absorption spectrophotometer under the optimized measurement conditions using a chromium hollow cathode lamp. The signal measurement was background-corrected (deuterium lamp) at the optical flame (A–Ac) height.

Freundlich and Langmuir adsorption isotherm models. The Freundlich and Langmuir adsorption isotherm models were used to describe the adsorption of Cr ions quantitatively.

The Freundlich isotherm is an empirical one. It is widely applied to describe heterogeneous systems, especially adsorption of organic compounds or highly interactive species onto activated carbon and molecular sieves. The Freundlich equation is:

$$S = K_F C_{eq}^{1/n} \quad [\text{mg/kg}] \quad (2)$$

where the constant K_F (dm^3/kg) expresses the adsorption capacity of the adsorbent and $1/n$ (dimensionless) – favorability of the adsorption process; $1/n < 1$ indicates chemisorption process, $1/n > 1$ – cooperative adsorption, $1/n = 1$ – linear adsorption, the partition between the two phases is independent of the concentration. The value of $1/n$ show also the surface heterogeneity. The closer to zero $1/n$, the sorbent surface more heterogeneous is [24].

The Langmuir isotherm describes homogeneous adsorption, where each molecule possesses constant enthalpy and sorption activation energy (all sites possess the same affinity for the adsorbate), there is no transmigration of the adsorbate within the surface. The adsorbate molecules forming a monolayer on the adsorbent surface do not interact between themselves. It is given by the equation:

$$S = \frac{Q K_L C_{eq}}{1 + K_L C_{eq}} \quad [\text{mg/kg}] \quad (3)$$

where Q (mg/kg) is the maximum sorption capacity of the adsorbent for a dye, K_L (dm^3/mg) is the adsorption equilibrium (Langmuir) constant [25].

K_L enables computing the dimensionless constant separation factor R_L from:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where C_0 (mg/dm^3) is the highest initial concentration of a dye.

The adsorption is unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$, or irreversible if $R_L = 0$.

The adsorption parameters may be estimated from the linear or non-linear equations of the isotherms. In this paper, the linear equations have been used. K_F and $1/n$ are determined from the linear form of the Freundlich isotherm, received by taking the logarithm of the Eq. (2) sides:

$$\log S = \log K_F + \frac{1}{n} \log C_{eq} \quad (5)$$

K_F values were determined from the intercepts, $1/n$ from the slopes of the plots $\log S$ vs. $\log C_{eq}$.

The Langmuir constants, K_L and Q , were determined through the linearization of Eq. (3):

$$\frac{C_{eq}}{S} = \frac{C_{eq}}{Q} + \frac{1}{K_L Q} \quad (6)$$

K_L may be obtained from the intercept $1/K_L Q$, and Q from the slope $1/Q$.

3. RESULTS AND DISCUSSION

3.1. SORPTION OF Cr(III) FROM CHLORIDE SOLUTION

The isotherms $S = f(C_{eq})$ of the sorption of Cr(III) from the chloride solution onto the peats and clays are presented in Fig. 2.

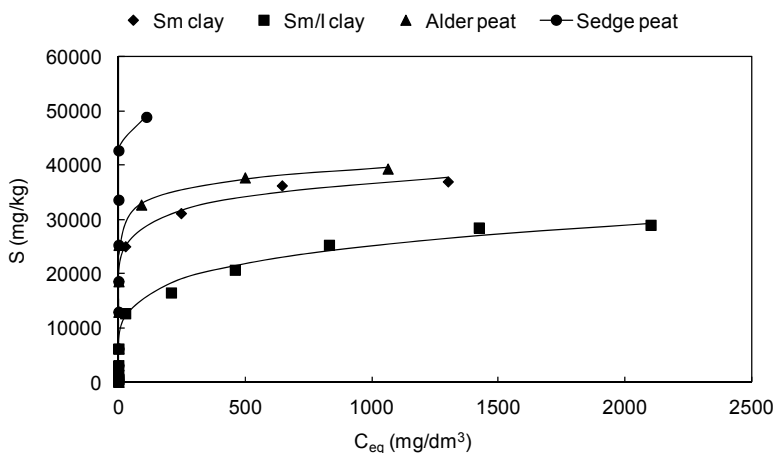


Fig. 2. Isotherms of Cr(III) sorption from chloride solutions onto investigated sorbents

At the initial concentrations of Cr(III) ions (C_0) from 0.5 to 500 mg/dm³, the Cr(III) ion uptake onto all sorbents reached 99–100%. The course of the sorption revealed the peat ability to absorb effectively even more Cr(III). The sorption capacity for Cr at maximum C_0 of alder peat was 39 372 mg/kg, of sedge peat – 48 900 mg/kg, of smectite clay – 37 000 mg/kg, and of smectite/illite clay – 29 000 mg·kg⁻¹. The sorption capacity of clays was lower because of their lower porosity and smaller pores.

The maximum amount of Cr(III) bound by the sorbents was between 1.8 (Alder peat) and 5.5 (smectite/illite clay) times higher than their CEC. The Ca²⁺ concentration in the equilibrium solution after sorption was low, from 183 mg/kg (0.91 cmol(+)/kg) for smectite clay to 1550 mg/kg (7.75 cmol(+)/kg) for sedge peat. It did not depend on

C_0 and was comparable with the Ca^{2+} ion content of the sorbent water extracts [2]. This indicates the Cr(III) specific sorption, not the ion exchange.

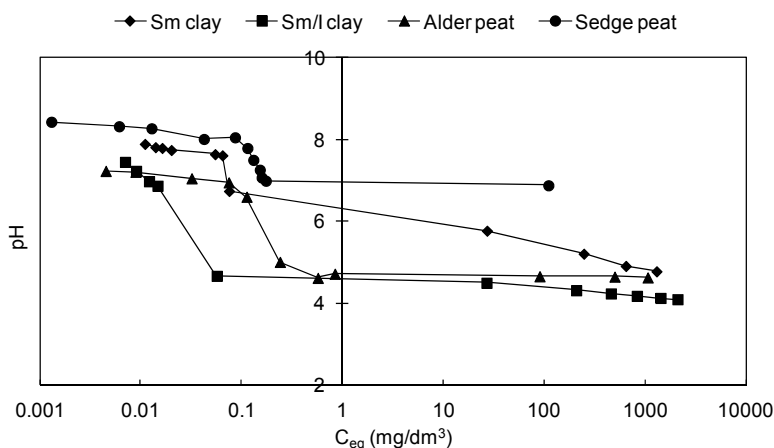
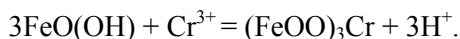


Fig. 3. pH in the equilibrium Cr(III) chloride solution (x axis scaled semi-logarithmically)

pH values in the equilibrium solutions are presented in Fig. 3. From the charts of pH vs. C_{eq} it may be seen that the solution pH was higher than the adsorbent pH_{PZC} at low initial concentrations of Cr(III) ($0.5\text{--}500\text{ mg/dm}^3$) – the surface of the adsorbents was negatively charged. Positively charged Cr(III) ions can be bound through the Coulomb forces onto the negatively charged sorbent surface. Moreover, the Cr(III) ions may precipitate as $\text{Cr}(\text{OH})_3$ at $\text{pH} > 4.5$. At C_0 higher than 500 mg/dm^3 , Cr was sorbed in reaction with functional surface groups of smectite minerals (clays) and carboxyl and hydroxyl groups of phenols in humic acids (peats).

Cr(III) ions can be bound by Fe hydroxyoxides in the reaction



The fractionation of Cr(III) ions in a sorbent depends on the adsorbent nature (organogenic or mineral, Fig. 4). In peats, 61–72% of Cr(III) load was in the F4 “pool” attributed to Fe hydroxyoxides, 12–19% and 10–13% were in F2 and F5, respectively. In clays, 44–50% of the total sorbed Cr(III) was in F2, and 26–36% in F4. The retention capacity of pores (F0) for Cr ions was low in all sorbents. This means that Fe hydroxyoxides play an important role in binding Cr(III) ions, especially in peats.

Cr(III) ions were mainly bound onto the surface. The diagonal length of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is 0.46 nm. The average diameter pore of the peat (10.54 and 13.50 nm) could accommodate up to 22 ions of chromium while the average diameter pore of the clay (6.56 and 7.16 nm) could accommodate up to 15 ions, if the repelling forces between cations were ignored (Table 1).

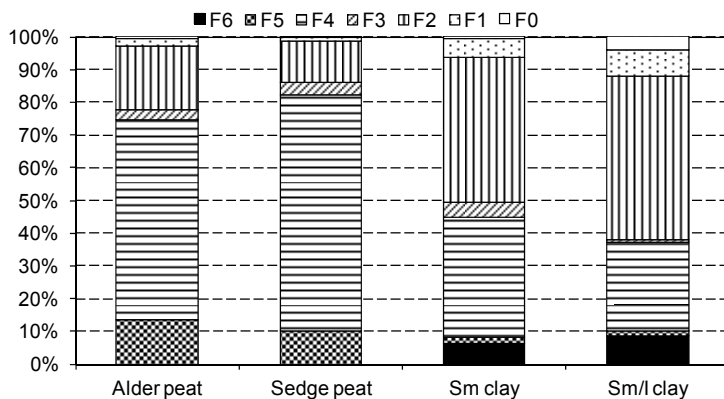


Fig. 4. Forms of chemical bonds of Cr(III) ions in peats and clays after sorption from Cr(III) chloride solutions

Concluding, the sorption capacity of the studied sorbents depended on their textural properties such as porosity, specific surface area and average pore diameter as well as on the chemical composition, especially on Fe oxide-hydroxide content and functional groups.

3.2. SORPTION OF Cr(III) FROM AB-193 AND ABK-194 SOLUTIONS

In the two dyes, AB-193 and ABK-194, Cr(III) occurred in complexes which form anions in water solutions. The structure of the Cr complexes is presented in Fig. 5.

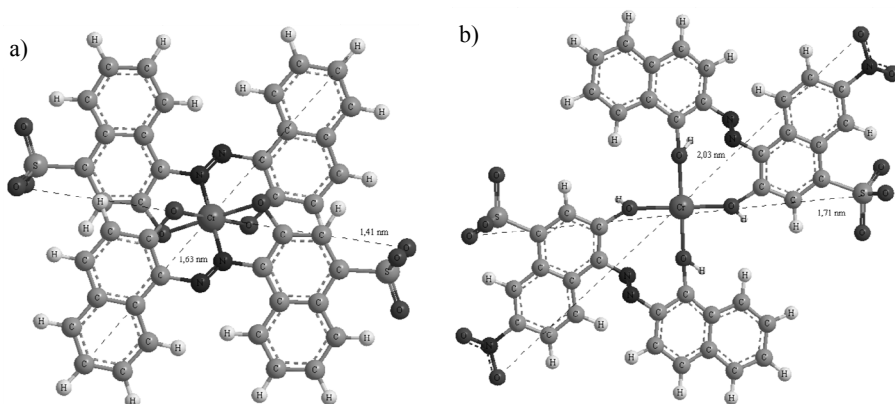


Fig. 5. Molecular structure of Cr in Acid Blue 193 (a) and Acid Black 194 (b)

Because the clay and peat uptakes of the complex Cr ions differed significantly, the isotherms of the sorption onto clays and peats are presented in two separate figures (Figs. 6a and 6b, respectively).

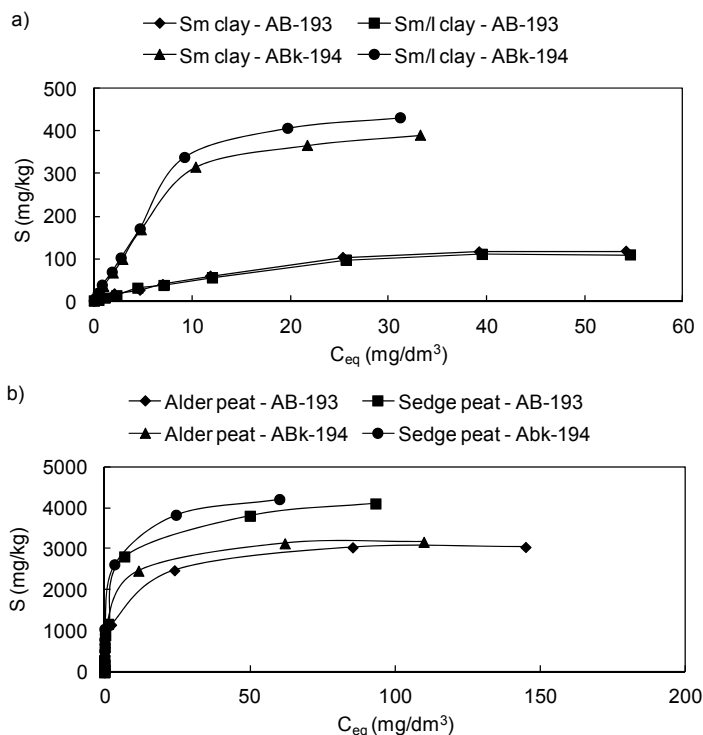


Fig. 6. Isotherms of Cr(III) sorption from dye solutions onto investigated clays (a) and peats (b)

The sorption capacities of smectite and smectite/illite clays for the complex Cr ions from the AB-193 solution were low and close to each other. Their maximum uptakes of Cr were 115 and 109 mg/kg, respectively. The maximum uptakes of Cr(III) from the ABk-194 solution by the clays were higher – 390 and 431 mg/kg.

The clays adsorbed Cr ions from the dye solutions at $\text{pH} \geq \text{pH}_{\text{PZC}}$. The clay surface was electrically neutral or weakly negative (Fig. 7a), therefore the complex Cr(III) anions could not be bound through the Coulomb forces.

The uptakes of the complex Cr(III) ions from the two dye solutions by the peats were 10 times higher than by the clays. The maximum sorption capacity of alder peat for Cr(III) from the AB-193 and ABk-194 solutions was 3047 and 3172 mg/kg, of sedge peat – 4108 and 4214 mg/kg, respectively. The peats, like the clays, adsorbed complex Cr ions at $\text{pH} > \text{pH}_{\text{PZC}}$ (Fig. 7b).

The structure of the complex Cr ions and number and kind of the functional groups suggest that the functional groups in the dyes can be donors or acceptors to protons. Acid Blue 193 contains 14 acceptor locations in sodium sulfate ($-\text{SO}_3\text{Na}$) and azo ($-\text{N}=\text{N}-$) groups. Acid Black 194 contains 4 donor locations in hydroxyl ($-\text{OH}$)

groups and 12 acceptor locations in sodium sulfate ($-\text{SO}_3\text{Na}$), azo ($-\text{N}=\text{N}-$) and nitro ($-\text{NO}_2$) groups. Therefore, Cr(III) can be bound through the hydrogen bonds to $-\text{COOH}$ or $-\text{OH}$ groups in humic matter or $-\text{OH}$ of iron oxides and of the silanol $\text{Si}-\text{OH}$ and aluminol $\text{Al}-\text{OH}$ groups in smectites.

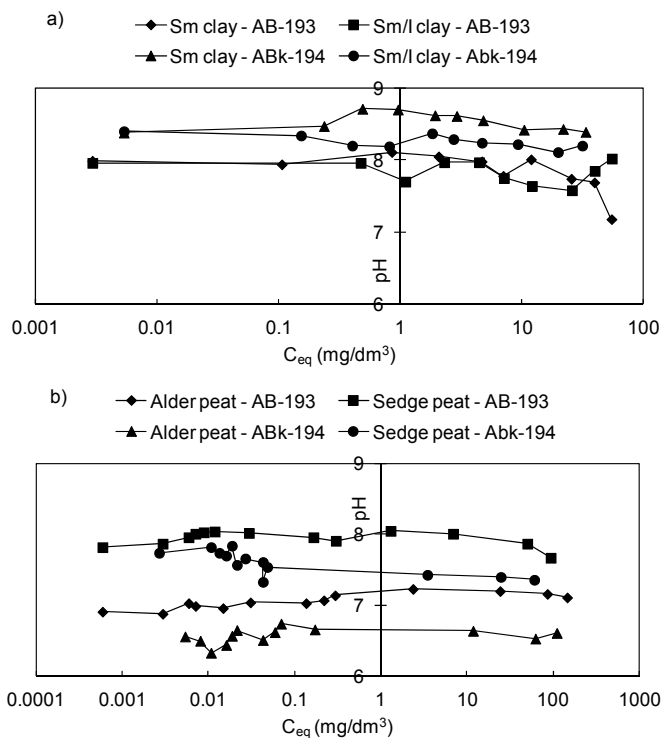


Fig. 7. pH of Cr(III) dyes solutions in the equilibrium: a) clays, b) peats (x axis scaled semi-logarithmically)

Like in sorption of Cr(III) from the chloride solutions, the textural properties (porosity, pore diameter) and the presence of the surface functional groups of adsorbents were important. The higher adsorption capacity for Cr from the ABk-194 solution may be due to formation of hydrogen bonds between the $-\text{OH}$ groups of the dye and $=\text{O}$ of the surface functional groups of the adsorbent. Because of the functional groups, the diagonal lengths of the complex Cr ions in the AB-193 and ABk-194 solutions were high – 1.63 and 2.03 nm, respectively (Fig. 5). Thus the complex Cr ion differed from the simple hydrated $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion not only in the electric charge sign but also in the size. The diagonal length of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is 0.46 nm, the complex Cr ion is 3.5–4.4 times greater, thus the complex Cr ions were not adsorbed so efficiently as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, especially onto clays.

Examinations of the binding strength of Cr complex ions adsorbed onto studied rocks using sequential extraction showed that Cr(III) ions occurred in mobile fractions F0 – 75–82% (clays) and 45–49% (peats) as well as in F1 – 25–18% and 55–41% of Cr(III) load, respectively.

3.3. FREUNDLICH AND LANGMUIR ADSORPTION ISOTHERM MODELS

Isothermal equilibrium data were processed employing the Freundlich and Langmuir isotherm equations. From the intercepts and slopes of the linear plots of $\log S$ vs. $\log C_{eq}$ (Freundlich isotherm, Eq. (5)) and C_{eq}/S vs. C_{eq} (Langmuir isotherm Eq. (6)), K_F , $1/n$, Q and K_L , respectively, were estimated. They were estimated for the whole range of the Cr concentrations (Table 2) and prove the Langmuir isotherm applicability to the sorption of Cr(III) from chloride onto all sorbents. The determined coefficient R^2 was 0.99. The separation factor R_L , calculated from Eq. (4) was below 1 indicating favorable adsorption. Instead, R^2 between 0.5642 and 0.7563 indicates the Freundlich isotherm not fitted very well to the Cr(III) sorption. The value of $1/n$, below 1, indicated chemisorption heterogeneous process. The sorption of the complex Cr ions from the AB-193 and ABk-194 solutions onto the peats and clays is well described by both Freundlich and Langmuir equations (R^2 ranges are similar, Table 2).

Sorption of Cr from chloride and complex ions solution was investigated in a wide range of their initial concentrations C_0 : 0.5–5000 mg/dm³ and 0.06–325 mg/dm³, respectively. The results showed that the experimental points in the plots $\log S$ vs. $\log C_{eq}$ and C_{eq}/S vs. C_{eq} arranged in two different ways (I or II) depending on the initial concentration of Cr ions, pointing to two different adsorption mechanisms (Figs. 8, 9): For Cr ions adsorbed from chloride solutions onto clays the range I was from 0.5 to 2000 mg/dm³ and range II – from 2500 to 5000 mg/dm³ but for Cr(III) ions adsorbed on the peat, the range I extended from 0.5 to 2500 mg/dm³ and II – from 3000 to 5000 mg/dm³. The concentration range I for sorption of complex Cr ions onto clay was from 0.06 to 16 mg/dm³, for range II – from 33 to 65 mg/dm³ and onto peat range I from 0.06 to 150 mg/dm³ and range II – from 176 to 300 mg/dm³.

The adsorption parameters and R^2 for range I of C_0 indicate that the adsorption of Cr(III) from the chloride and complex ion solutions onto peats cannot be described by the Langmuir equation (Table 2, Figs. 8 and 9). Instead, the Freundlich equation describes these adsorptions well – R^2 are between 0.8491 and 0.9805. Values of $1/n$ (Eq. (5)) for the sorption are above 1 indicating cooperative adsorption.

Except for AB-193 and smectite clay, the Langmuir equation cannot describe the sorption of the Cr(III) ions from solutions of chloride, AB-193 and ABk-194 at I range of C_0 , either (Table 2). The Freundlich equation describes it well, R^2 is between 0.8195 and 0.9903. Values of $1/n$ are below 1 for the sorption of Cr from complex ion, but for the sorption of Cr as chloride are above 1 – the binding mechanisms were different.

Table 2

Adsorption isotherms for the adsorption of Cr(III) onto peats and clays

Material	Isotherm	Parameter	Cr from chloride			Cr from AB-193			Cr from ABk-194		
			All C_0	I C_0	II C_0	All C_0	I C_0	II C_0	All C_0	I C_0	II C_0
Alder peat	Freundlich	$1/n$	0.3860	1.0157	0.0762	0.5477	1.0217	0.2401	0.5765	1.9379	0.119
		$K_F, \text{dm}^3/\text{kg}$	6651	41 433	23 289	557.3	3448	1036	593.3	107 969	1857.4
		R^2	0.6828	0.9515	0.9934	0.8492	0.9361	0.9031	0.6248	0.8491	0.9567
	Langmuir	$S_{\text{max}}, \text{mg}/\text{kg}$	39 372	25 312	39 372	3045	1175	3045	3173	1051	3173
		$Q, \text{mg}/\text{kg}$	39 461	200 000	40 000	3067	2000	3165	3278	-21,13	3225
		$K_L, \text{dm}^3/\text{mg}$	0.2889	0.1923	0.0404	0.6996	2.0833	0.2016	0.2883	-18.93	0.5439
R^2		0.9995	0.0131	0.9998	0.9987	0.1524	0.9995	0.9548	0.1693	0.9931	
	R_L	0.0007	–	0.0049	0.0048	–	0.0167	0.0138	–	0.0068	
Sedge peat	Freundlich	$1/n$	0.5699	1.0528	0.7066	0.5854	1.0191	0.2656	0.6471	2.593	0.1701
		$K_F, \text{dm}^3/\text{kg}$	24 827	107 053	4 637 138	824.5	6270.5	1353	939.5	2 484 849	2147
		R^2	0.6357	0.9785	0.9926	0.8368	0.8852	0.8476	0.6376	0.9805	0.9856
	Langmuir	$S_{\text{max}}, \text{mg}/\text{kg}$	48 900	6219	48 900	4178	1175	4178	4214	1053	4214
		$Q, \text{mg}/\text{kg}$	49 067	22 446	48 923	5000	2000	5000	4386	-20.70	4386
		$K_L, \text{dm}^3/\text{mg}$	2.688	-3.315	20.67	0.6667	2.500	0.25	0.3631	-26.88	0.4054
R^2		0.9999	0.5540	0.9999	0.9981	0.1058	0.9999	0.9384	0.4054	0.9994	
	R_L	0.00008	–	0.0000096	0.0003	–	0.0651	0.0101	–	0.0104	
Smectite clay	Freundlich	$1/n$	0.3134	2.1711	0.1059	0.4692	0.4344	0.1816	0.8128	0.8286	0.2138
		$K_F, \text{dm}^3/\text{kg}$	6388	5 345 237	17 657	17.35	16.06	57.98	35.180	35.637	200.95
		R^2	0.5642	0.8442	0.9813	0.9680	0.9602	0.8856	0.9764	0.9701	0.8373
	Langmuir	$S_{\text{max}}, \text{mg}/\text{kg}$	37 000	18 617	37 000	117.8	60.01	117.8	390.1	167.2	390.1
		$Q, \text{mg}/\text{kg}$	37 037	-1150	38 461	140.8	26.95	169.5	588.2	526.2	476.9
		$K_L, \text{dm}^3/\text{mg}$	0.1492	-1.4483	0.0323	0.0930	1.9734	0.048	0.0708	0.0745	0.1381
R^2		0.9989	0.2447	0.9992	0.8910	0.9357	0.9720	0.8205	0.0365	0.9667	
	R_L	0.0014	–	0.0062	0.0104	0.0050	0.0200	0.2667	–	0.1367	

Table 2 continue

Smectite/illite mixed layer clay	Freundlich	$1/n$	1.6969	0.2032	0.5347	0.4749	0.2255	0.8035	0.8325	0.2040
		K_F , dm ³ /kg	1 384 927	6187.3	11.64	10.39	47.02	40.19	41.78	216.5
		R^2	0.6852	0.9649	0.8819	0.8195	0.9462	0.9865	0.9903	0.9784
	Langmuir	S_{max} , mg/kg	6219	29000	109.1	54.98	109.1	430.9	170.1	430.9
		Q , mg/kg	-1692	31250	163.9	88.49	149.25	625.0	370.4	555.6
		K_L , dm ³ /mg	-15.97	0.0068	0.0473	0.0966	0.0577	0.0865	0.1516	0.1208
		R^2	0.1282	0.9933	0.8301	0.1704	0.9595	0.9256	0.4886	0.9705
		R_L	-	0.0285	0.0203	-	0.2889	0.2186	-	0.1432

- means not estimated.

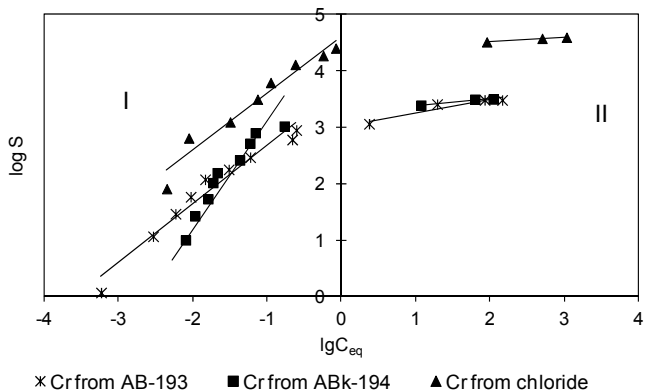


Fig. 8. Freundlich isotherms of Cr(III) binding in chloride and dye solutions onto smectite clay

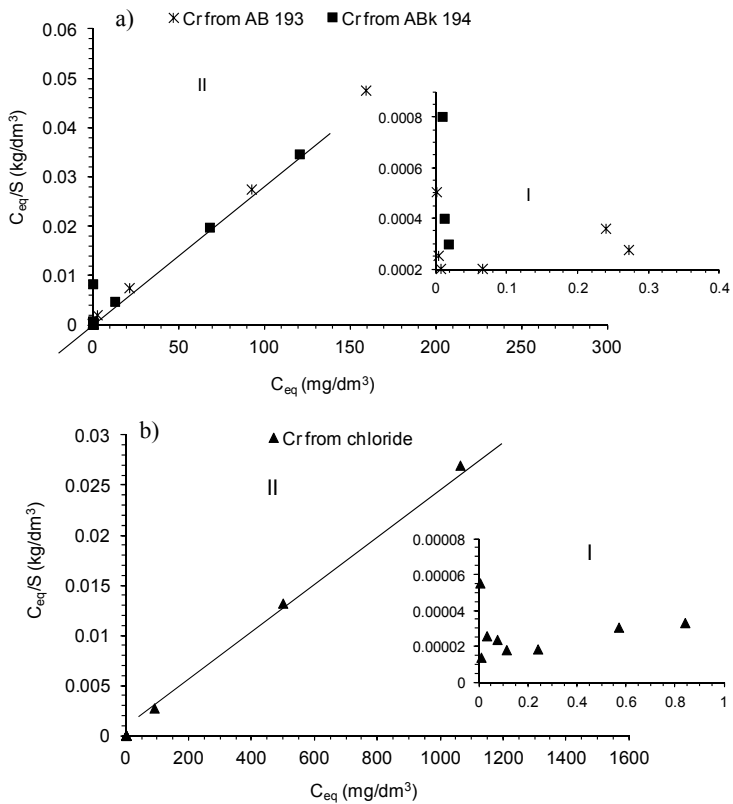


Fig. 9. Langmuir isotherms of Cr(III) binding in dye solutions (a) and chloride (b) onto smectite clay

Sorption of the complex Cr(III) ions from the solutions of AB-193 onto smectite clay is well described by both Freundlich and Langmuir equations at the ranges I and II of C_0 . At the range II of C_0 of the chloride and dye solutions, Cr(III) sorption is well described by both the Freundlich (R^2 between 0.8373 and 0.9856) and the Langmuir (R^2 between 0.9595 and 0.9999) equations. The value of $1/n$ indicated a chemisorption process.

4. CONCLUSIONS

Low-moor peats and clays from the overburden of the lignite beds in Central Poland are good alternatives to expensive activated carbon as effective adsorbents of Cr(III) from chloride and dye solutions at a wide range of the Cr(III) concentrations. They perform better adsorbing Cr(III) from the chloride than from the metal complex solutions. In chloride solutions, their sorption capacity follows the order: sedge peat > alder peat > smectite clay > smectite/illite clay and depends on their textural (porosity, average pore diameter) and chemical (Fe hydroxyoxides content) properties. The positively charged Cr(III) ions were bound onto sorbent surface via Coulomb attraction forces. Fe hydroxyoxides played also an important role in binding Cr.

The complex Cr(III) ions in the dye solutions have higher diagonal lengths and are negatively charged; they were not adsorbed so efficiently. They were bound to the sorbent surface in mobile fraction – via hydrogen bonds between the dye –OH groups and =O of the sorbent functional groups and in pore solution.

The results showed that the binding mechanism of Cr ions depended on their initial concentration. In the range I of Cr(III) concentrations, the sorption was best described by the Freundlich equation; at the range II concentrations, it was described equally well by both the Freundlich and the Langmuir equations.

The equation parameters indicate cooperative heterogeneous adsorption at the range I of Cr(III) concentrations and chemisorption process at the range II of Cr(III) concentrations.

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