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Adsorption of Anionic Dyes on Montmorillonite Modified with Polyhydroxo Complexes of Aluminium and Iron

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Abstract

The sorbents with layered-columnar structure were obtained on the basis of polyhydroxo complexes of aluminium and iron and the montmorillonite clay from the Mukhor-Talinskoye deposit. The texture characteristics of the sorbents were determined by means of low-temperature nitrogen adsorption and XPA. Their adsorption characteristics in aqueous solutions with respect to different anionic dyes were investigated. It was established that modification with polyhydroxo complexes of aluminium and iron causes an increase in the adsorption capacity of montmorillonite with respect to anionic dyes due to an increase in total specific surface and the number of anion-exchange centres.

INTRODUCTION

Materials with layered-columnar structure obtained by means of the substitution of interstitial cations of montmorillonite clays with large hydroxo cations of polyvalent metals, followed by fixation of the silicate layers of clay due to the formation of oxide supports during thermal treatment, are used as sorbents and catalysts of various processes [1–3]. The sorbents with layered-columnar structure (PILC sorbents) have microporous structure and a larger micropore size in comparison with synthetic zeolites. This allows one to use them for adsorption and catalysis of large organic molecules. These sorbents are characterized by high specific surface, as well as by relative cheapness and ecological safety [4]. Layered-columnar materials obtained on the basis of polyhydroxo complexes of aluminium are most frequently used as adsorbents. The modification of clays with aluminium polyhydroxo complexes results in an increase in their affinity to the substances of anionic character, so that they become promising sorbents for the removal of organic compounds of anionic type from water [5, 6]. It was shown in [5] that montmorillonite (MM) modified with aluminium polyoxochlorides possesses rather high sorption capacity with respect to anionic dyes and exceeds expensive active carbon in this parameter. The sorption capacity of the sorbent, obtained by modification of layered aluminosilicate kaolinite with aluminium polyoxo cations, with respect to anion-active compounds (sulphonol and direct scarlet dye) increases by a factor of about 7 in comparison with the initial kaolinite [7]. Publications on the application of layered-columnar clays as the sorbents of organic compounds in aqueous solutions, related mainly to Al-modified clays, provide evidence of their promising character for removal of organic contaminants from the industrial wastewater [4, 5]. Fe-modified clays also are of interest for the adsorption of organic compounds [8]; however, the adsorption properties of these sorbents in aqueous solutions have been investigated insufficiently.

In the present work we report a preparation of the sorbents with layered-columnar structure on the basis of MM from the Mukhor-Talinskoye deposit and polyhydroxo complexes of aluminium and iron as well as mixed Fe/Al polyhydroxo complexes; their adsorption properties in aqueous solutions with respect to various anionic dyes were investigated. The adsorption capacity towards dyes was correlated with the texture characteristics of sorbents as derived from the isotherms of low-temperature adsorption of nitrogen.

EXPERIMENTAL

In order to obtain the sorbents, we used montmorillonite clay from the Mukhor-Talinskoye deposit (Buryatia); the chemical composition of the clay was as follows, mass %: SiO_2 65.50, Al_2O_3 14.30, Fe_2O_3 1.78, MgO 1.42, CaO 1.08, K_2O 0.20, Na_2O 0.10, FeO 0.22, MnO 0.02, TiO_2 0.19, P_2O_5 0.03; calcination loss 15.16. The clay fraction was separated from the solid admixtures by means of elutriation. The diffraction patterns of the elutriated clay fraction exhibited the reflections characteristic of MM (5.7, 17.6, 19.9, and 36^o) and insignificant amount of cristobalite admixture (21.85, 29.1, and 35.5^o) [9].

Modification of MM was carried out by means of intercalation, or pillaring; the method was described schematically in [10], and is illustrated in Fig. 1. The essence of intercalation is the substitution of interstitial cations of the natural form of MM with large polyhydroxo cations (PHC) of metals. Metal PHC are obtained by hydrolysis of metal salt solutions with the solutions of sodium hydroxide or carbonate, followed by aging of the intercalating solutions. The intercalating solution is mixed with clay suspension in order to substitute the exchange cations of clay with metal HPC. The resulting intercalated sorbents are washed from the excess salt anions, dried at room temperature, and subjected to thermal treatment which causes dehydration and dehydroxylation of PHC present in the interlayer space of clay, the formation of metal oxide columns (pillars) and the formation of layered-columnar structure of clay (see Fig. 1).

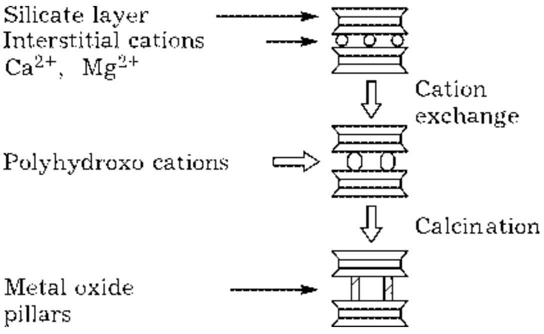

Fig. 1. Scheme of clay intercalation [10].

We obtained clay samples modified with polyhydroxo complexes of iron, aluminium, and mixed polyhydroxo complexes of iron and aluminium.

Preparation of Fe-modified montmorillonite

Fe-containing montmorillonite (Fe-MM) was obtained by means of substitution of the interlayer cations of MM with PHC of iron according to the procedure described in [11]. A suspension of clay in water was made (the ratio of the solid to liquid phase S : L = 1 : 10), left for 24 h for swelling at room temperature. Then the clay suspension was treated with ultrasound (22 kHz) for 3 min to achieve better dispersion of clay particles. We demonstrated previously [12] that the treatment of clay suspension with ultrasound before intercalation stage allows one to obtain the sorbents with larger specific surface in comparison with the clay not treated with ultrasound. The intercalating solution was prepared by mixing 1.0 M $FeCl_3$ and 0.1 M NaOH solutions ($[OH^-]/[Fe^{3+}]$ = 2.0) and aging for 24 h at room temperature. The sol obtained after aging contained about 87 % of mono- and dinuclear complexes of Fe^{3+} and 13 % of polynuclear hydrolysis products [13]; it was added into a 10 % aqueous suspension of clay in such an amount that the concentration of iron was 2.5 mmol Fe/g of clay, and kept for 24 h at room temperature. The resulting Fe-MM was separated from the liquid phase by centrifuging, washed till the negative reaction for chloride ions, dried at room temperature and subjected to thermal treatment at 500 °C. The same preliminary treatment of clay suspension with ultrasound as that applied to obtain Fe-MM was also carried out when synthesizing all the other sorbents.

Preparation of Al-modified montmorillonite

Al-containing montmorillonite (Al-MM) was obtained according to the procedure described in [14]. The intercalating solution was obtained by means of hydrolysis of 0.2 M $AlCl_3$ solution with 0.2 M NaOH solution (the ratio $[OH^-]/[Al^{3+}] = 2.0$, pH 4.3–4.5) at room temperature. The solution was aged for 24 h at 50 °C. PHC $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ is formed under these conditions; its spectrum is recorded at 63.15 ppm [15], which was confirmed by us with the help of NMR spectroscopy of intercalating solution on ^{27}Al nuclei (Fig. 2). In order to obtain Al-MM, the intercalating solution was added to a suspension of clay with S : L = 1 : 100, 80 °C and 3 mmol Al^{3+}/g of clay. Separation, washing, drying and calcination of the resulting Al-MM samples were carried out similarly to the procedure described for Fe-MM.

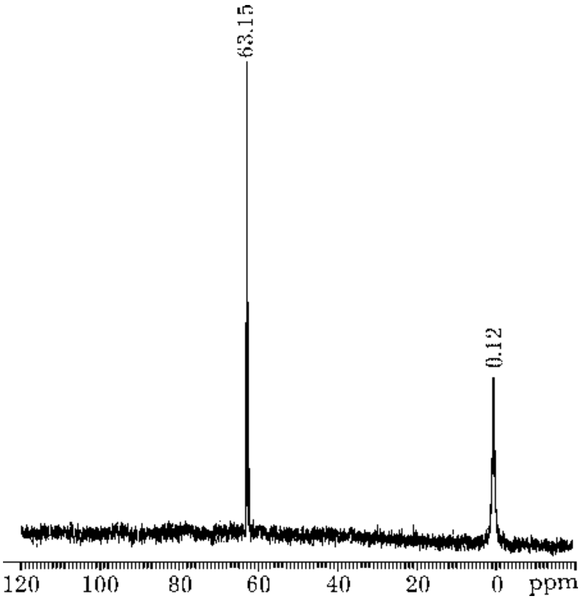

Fig. 2. NMR ^{27}Al spectrum of intercalating solution. $OH^-/Al^{3+} = 2$, pH 4.1.

Preparation of Fe/Al-modified montmorillonite

Clay modified with mixed polyhydroxo complexes of iron and aluminium (Fe/Al-MM) was obtained according to procedure [16] from natural clay taking Fe/Al ratios equal to 1 : 1 and 1 : 10, S : L = 1 : 100. Intercalating solution was obtained by mixing the solutions of 0.1 M $FeCl_3$ and 0.1 M $AlCl_3$ in the amounts necessary for achieving the Fe/Al ratio equal to 1.0 and 0.1 mol/l. A solution of 0.1 M Na_2CO_3 (pH 4–4.5) was added to the mixture of the above-indicated solutions. The resulting sol was aged for two weeks. After aging, the sol was heated for 36 h at 90 °C. According to the data reported in [16], for Fe/Al < 0.5, ferric ions get built into the structure of PHC $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ giving a mixed PHC $[FeAl_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, which was confirmed by the results of NMR spectroscopy of the intercalating solution on ^{27}Al [12]. According to the data reported in [17], for Fe/Al > 0.5 the cations of iron and aluminium are present in the form of PHC $[FeAl(OH)_2(H_2O)_8]^{4+}$. Separation, washing, drying and calcination of the obtained Fe/Al-MM samples were carried out similarly to the treatment of Fe-MM samples. The content of aluminium oxide and ferric oxide in the synthesized sorbents is shown in Table 1.

Texture characteristics of the sorbents were determined by means of low-temperature adsorption of nitrogen (77 K) with ASAP-2400 Micromeritics instrument [14]. Interplanar spacings d_{001} were determined from the diffraction patterns of sorbent powders, recorded with STADI-P instrument of STOE Co. (CuK_{α_1} radiation). The NMR spectra of intercalating solutions were recorded with MSL-400 Bruker spectrometer. The iron content of the sorbents was determined with *ortho*-phenanthroline [18].

When investigating adsorption properties of the sorbents in aqueous solutions, we used anionic organic dyes as the substances to be adsorbed: direct purely blue (DPB) and Congo red (CR); their physicochemical properties were described in [5]. The adsorption capacity of sorbents was determined after equilibrium had been established (96 h) using the procedure described in [5]. According to the data of three parallel experiments, relative arithmetic mean error of the determination of adsorption ca-

TABLE 1

Texture characteristics of the sorbents

Sorbent sample*	Concentration, mass %		S_{BET}, m^2/g	D_{por}, Å	V_{por}, cm^3/g	V_{por}, cm^3/g	S^{**}_{por}, m^2/g	d^{***}_{001}, Å	Δd, Å	V_μ, cm^3/g	S_μ, m^2/g
	Al_2O_3	Fe_2O_3									
MM-400	11.8	1.1	115	96.6	0.278	n/d	n/d	11.4	2.0	<0.002	–
MM-500	11.8	1.1	109	92.7	0.253	n/d	n/d	11.0	1.6	<0.002	–
Fe-500	11.8	6.6	136	76.4	0.271	0.242	95.0	12.4	3.0	<0.002	–
Fe/Al (1 : 1)-400	12.5	4.8	136	63.8	0.235	0.203	90.4	14.5	5.1	<0.002	–
Fe/Al (1 : 1)-500	12.5	4.8	118	63.0	0.212	0.188	85.4	14.0	4.6	<0.002	–
Fe/Al (1 : 10)-400	16.7	2.1	244	72.3	0.249	0.156	59.8	19.2	9.8	0.064	136
Fe/Al (1 : 10)-500	16.7	2.1	219	78.0	0.268	0.189	66.6	18.3	8.9	0.049	104
Al-140	16.3	1.1	274	70.9	0.249	0.141	58.4	19.1	9.7	0.076	160
Al-400	16.3	1.1	242	73.3	0.246	0.156	62.6	17.9	8.5	0.065	135
Al-500	16.3	1.1	192	69.2	0.221	0.155	64.4	17.2	7.8	0.045	95.7

Notes. 1. S_{BET} is total specific surface; D_{por} is mean pore diameter, V_{por} is pore volume, d_{001} is interplanar space, Δd is the width of slit-like micropores, V_μ is volume of micropores, S_μ is the surface area of micropores. 2. n/d – not determined.

*Here and in Tables 2, 3: numbers at sorbent titles mean calcination temperature.

**Volume of pores with $D = 17–3000$ Å.

***Surface area of micropores with $D = 17–3000$ Å.

pacity did not exceed 5 %. The residual concentrations of the dyes in solutions were determined using the calibration dependences of optical density of dye solutions on their concentrations. The optical density of dye solutions was measured with Agilent 8453 UV-Vis spectrophotometer at the wavelength of the maximal absorption of a dye solution. Measurements of pH of aqueous solutions of dyes and sorbent suspensions were carried out with EV-74 pH meter.

RESULTS AND DISCUSSION

The isotherms of low-temperature adsorption of nitrogen on the sorbents under investigation are shown in Fig. 3. The shape of the loop of capillary condensation hysteresis allows us to relate all the isotherms to H3 type according to IUPAC classification; the isotherms are characteristic of mesoporous sorbents with mainly slit-like pores [19]. The isotherms of nitrogen adsorption on Al-MM and Fe/Al-MM (1 : 10) differ from the isotherms of adsorption on Fe-MM and Fe/Al-MM (1 : 1) by a sharper increase for small P/P_0 values, which is due to

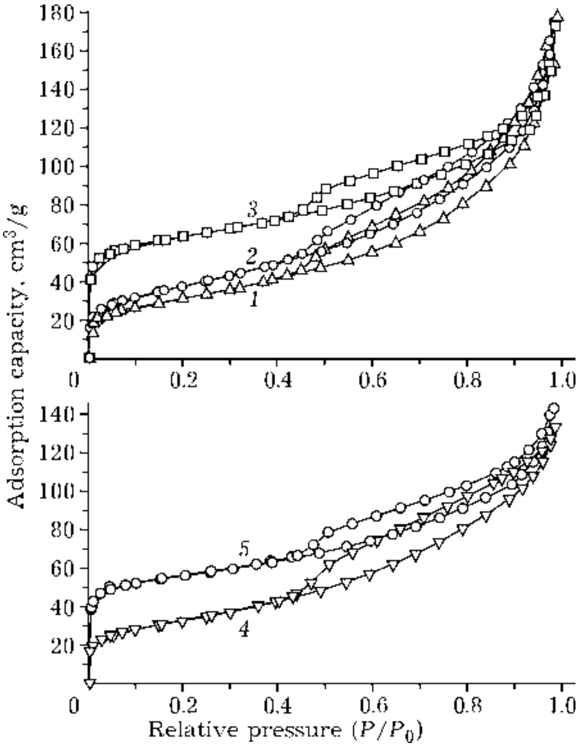

Fig. 3. Isotherms of low-temperature nitrogen adsorption on the sorbents calcined at 500 °C: *1* – natural MM, *2* – Fe-MM, *3* – Fe-Al (1 : 10), *4* – Fe-Al (1 : 1), *5* – Al-MM.

the presence of a large number of micropores in these sorbents [20, 21]. Texture characteristics of the sorbents shown in Table 1 were determined on the basis of isotherms of low-temperature adsorption of nitrogen.

One can see that modification of natural MM with polyhydroxo complexes of iron and aluminium causes an increase in specific surface due to the formation of primary slit-like micropores and the formation of layered-columnar structure. The largest increase in specific surface (up to 274 m^2/g) is observed for MM modification with aluminium polyhydroxo complexes and mixed polyhydroxo complexes of iron and aluminium (1 : 10) which have the structure of Keggin cation as we have demonstrated previously [14, 22]. These sorbents are characterized by the presence of a large number of primary micropores with a size of 7.8–9.8 Å and with the specific surface of 96–160 m^2/g, which accounts for 50-58 % of total specific surface of the sorbents (see Table 1). The pores of natural MM, Fe- and Fe/Al (1 : 1)-MM are mainly mesopores, while the volume of micropores in them does not exceed 0.002–0.003 cm^3/g.

Anion-exchange properties of clays are due to the presence of hydroxyl groups Al–OH, Mg–OH, Fe–OH in their structure; at pH below their isoelectric points they dissociate as bases (pH_i of isoelectric points of the oxides of Al, Fe (III), Mg is 7–9, 6.7–8.8, 12.4, respectively [23]). In the case if pH of the medium is less than pH_i, adsorption of anionic dyes on clays proceeds according to equation

$$S{-}OH + A^- + H^+ \rightleftarrows S{-}A + H_2O$$

(S is a surface cation of the sorbent) and increases with a decrease in pH of the medium, which must be taken into account when comparing the adsorption characteristics of different sorbents. The acidity of the aqueous solutions of DPB dye gives pH 5.5–5.6. Their contact with the sorbents under investigation causes a change in pH which is due to the different combination of hydrolyzed cations Fe(III) and Al in sorbents (see Table 1); the acidity of the suspension of dyes with sorbents is pH 5.1–6.2 (Table 2). To compare adsorption characteristics of the sorbents, their limiting adsorption capacity with respect to DPB and CR dyes was determined at pH 5.6±0.1 and 6.0±0.1, respectively (see Tables 2, 3). Fixed pH was adjusted by adding NaOH or HCl solutions. When obtaining the isotherms of dye adsorption on the sorbents under investigation, pH was not adjusted to exclude the effect of foreign anions.

TABLE 2

Limiting adsorption capacity (a_{max}) of sorbents with respect to DPB

Sorbent	pH	a_{max}*, mmol/100 g
MM-400	6.2	1.3/1.4
MM-500	6.1	0.8/0.91
Fe-MM-500	5.2	3.1/2.8
Fe/Al(1 : 10)-400	5.6	7.5/7.5
Fe/Al(1 : 10)-500	5.6	4.7/4.7
Fe/Al(1 : 1)-400	5.1	4.4/3.9
Fe/Al(1 : 1)-500	5.1	3.7/3.3
Al-400	5.3	5.2/5.0
Al-500	5.4	4.8/4.7

* The first value is the limiting adsorption capacity of a sorbent for the indicated pH value, the second value is for fixed pH 5.6±0.1.

The isotherms of adsorption of a weakly associated DPB dye (association factor for premicellar region ≤ 14 [5]) on the sorbents are shown in Figs. 4, 5. The limiting adsorption capacity values for the sorbents (a_{max}) with respect to DPB dye are shown in Table 2. One can see that natural MM possesses low adsorption capacity for DPB dye, which is due to the insignificant amount of anion-exchange centres Al–OH, Mg–OH in natural MM [24]. Similar results were obtained in [5] for MM from Oglanlinskoye, Pyzhevskoye and Cherkasskoye deposits. Modified MM are characterized by higher affinity to anionic dyes than natural MM samples are. The maximal adsorption capacity is

TABLE 3

Limiting adsorption capacity (a_{max}) of sorbents with respect to CR

Sorbent	pH	a_{max}*, mmol/100 g
Fe-MM-500	5.7	5.6/5.5
Fe/Al(1 : 10)-400	6.3	6.3/6.4
Fe/Al(1 : 1)-400	5.8	6.0/5.9
Al-500	6.1	6.5/6.5

* The first value is the limiting adsorption capacity of a sorbent for the indicated pH value, the second value is for fixed pH 6.0±0.1.

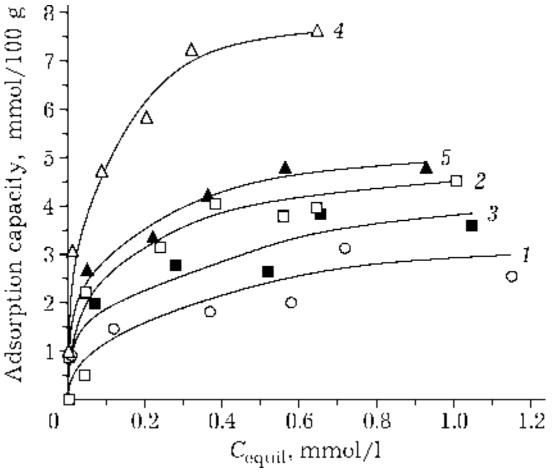

Fig. 4. Isotherms of adsorption of DPB dye on Fe-containing sorbents: *1* – Fe-MM-500, *2* – Fe-Al(1 : 1)-400, *3* – Fe-Al(1 : 1)-500, *4* – Fe-Al(1 : 10)-400, *5* – Fe-Al(1 : 10)-500.

observed for the sorbents Fe/Al (1 : 10)- and Al-MM possessing the largest specific surface and a larger size of primary slit-like micropores (see Table 1). Adsorption of individual anions of DPB dye is likely to occur in the primary micropores of these sorbents, while their associates are sorbed in secondary mesopores and macropores. Adsorption of the anions and associates of DPB dye on natural MM, Fe-MM and Fe/Al (1 : 1) occurs mainly in the mesopores larger than 17 Å in diameter; the surface of the latter pores accounts for about 70 % of the total specific surface of the sorbents. The obtained values of maximal adsorption capacity with respect to DPB agree with the data on total specific surface of these sorbents. The observed increased sorption of DPB on Fe- and Al-containing sorbents in comparison with natural MM can be also explained by the fact that, along with the formation of a layered-columnar structure causing an increase in specific surface, modification also causes an increase in the amount of anion-exchange centres Al–OH and Fe–OH [24]. The introduction of iron into the structure of Al-containing MM samples causes an increase in their sorption capacity with respect to DPB. For instance, Fe/Al (1 : 10)-400 and Al-400 sorbents having almost the same aluminium content, close specific surface values and texture characteristics (see Table 1) differ in adsorption capacity, which is likely to be due to the differences in iron content. Taking into account the possibility of the formation of complexes between dye molecules and Al^{3+} and Fe^{3+} ions, we carried out experiments to study the effect of Al^{3+} and Fe^{3+} ions on the absorption spectrum of DPB dye (Fig. 6). The observed shift of the maximum of the absorption band of DPB dye to longer wavelengths after the addition of the solutions of aluminium chloride and ferric chloride to the dye solution can be an evidence of the formation of complexes between dye molecules and Al^{3+} and Fe^{3+} ions as shown in [5]. The largest shift of the dye absorption band occurs with the addition of Fe^{3+} ions, which is the evidence of the better ability of ferric ions to form complexes with DPB dye.

The isotherms of CR dye adsorption on Al-MM-500, Fe/Al(1 : 10)-400, Fe/Al (1 : 1)-400, Fe-MM-500 sorbents are shown in Fig. 7.

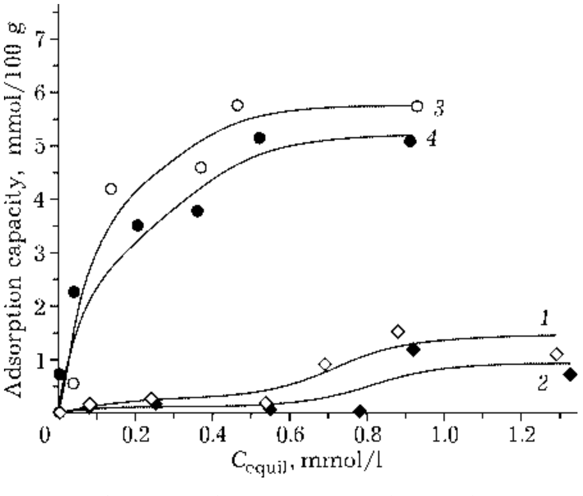

Fig. 5. Isotherms of adsorption of DPB dye on Al-containing sorbents: *1* – natural MM-400, *2* – natural MM-500, *3* – Al-MM-400, *4* – Al-MM-500.

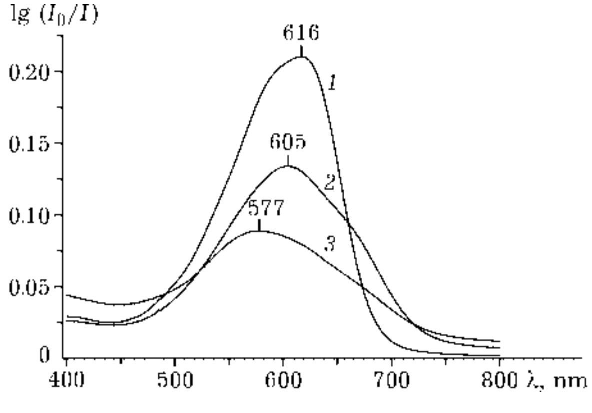

Fig. 6. Absorption spectra of the aqueous solutions of DPB dye: *1* – initial, *2*, *3* – with $AlCl_3$ and $FeCl_3$, respectively.

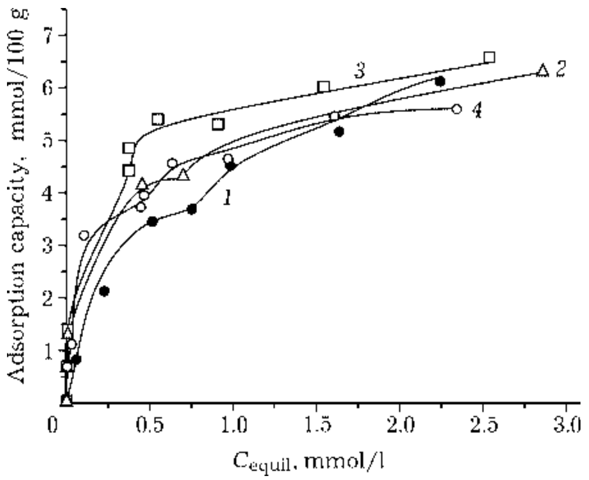

Fig. 7. Isotherms of adsorption of CR dye on calcined sorbents: *1* – Al-MM-500, *2* – Fe-Al(1 : 10)-400, *3* – Fe-Al(1 : 1)-400, *4* – Fe-MM-500.

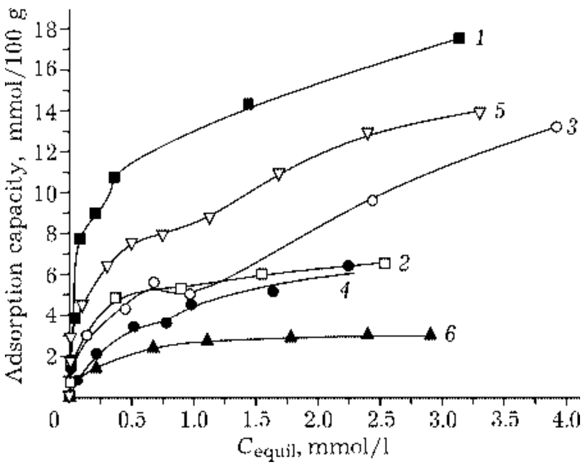

Fig. 8. Isotherms of adsorption of CR dye on sorbents: *1* – Fe-Al(1 : 1)-25, *2* – Fe-Al(1 : 1)-400, *3* – Al-MM-100, *4* – Al-MM-500, *5* – Al-MM-100 (data from [5]), *6* – active carbon KAD-iodine (data from [5]).

The values of a_{max} are shown in Table 3. It follows from these data that all the sorbents are characterized by close values of the limiting adsorption capacity with respect to CR dye. This is an evidence of the fact that micropores in Al-MM-500 and Fe/Al(1 : 10)-400 sorbents are inaccessible for the adsorption of CR dye particles which are large associates (association factor f_1 = 20–50) at concentrations close to critical micelle concentration (CCM) (0.7 mmol/l). For concentrations above CCM, the CR dye forms associates characterized by $f_2 \geq 1000$ [5, 25]. High degree of CR dye association in aqueous solutions hinders the penetration of its aggregates into primary micropores, so that their adsorption occurs in meso- and macropores of Al-MM-500 and Fe/Al (1 : 10)-400 sorbents. For adsorption of large organic molecules from aqueous solutions, the phenomena of this kind are observed for microporous active carbon [26]. This is also confirmed by a decrease in a_{max} for CR, which is observed with an increase in calcination temperature for Al-MM and Fe/Al (1 : 1) sorbents (Fig. 8).

Thermal treatment of Fe/Al(1 : 1) and Al-MM samples (at 400 and 500 °C, respectively) causes the formation of a rigid layered-columnar structure with slit-like micropores which are inaccessible for adsorption of large associates of CR dye; this is the reason of low a_{max} values for calcined sorbents. At the same time, the sorbents dried at 25 and 100 °C conserve the ability to increase interplanar spaces, which simplifies penetration of dye particles into the interlayer space of clays and causes increased sorption of dyes.

Comparison of our results with adsorption data obtained in [5] for CR dye adsorption on MM from the Oglanly deposit, modified with aluminium polyoxochlorides (100 °C), shows that Al-MM sorbent obtained on the basis of MM from Mukhor-Talinskoye deposit has similar adsorption properties and is not worse than active carbon of KAD-iodine grade (see Fig. 8).

CONCLUSION

It may be concluded on the basis of the obtained results that modification of MM with polyhydroxo complexes of iron and aluminium causes an increase in total specific surface and the number of anion-exchange centres, which explains increased adsorption of anionic dyes on modified sorbents. With an increase in the temperature of calcination of modified MM, adsorption of anionic dyes that form large associates in aqueous solutions decreases, which is caused by a decrease in the size of slit-like micropores that become inaccessible for their adsorption.

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