

## Preparation, Texture Parameters and Adsorption Properties of Fe-Montmorillonite

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### Abstract

Layer-pillar pore structured samples of Fe-montmorillonite (Fe-MM) have been obtained through modifying of bentonite by mono- and binuclear iron (III) hydroxocomplexes. The influence of conditions of synthesis and thermal treatment on samples properties has been studied. Texture characteristics obtained through N<sub>2</sub> adsorption measurement at 77 K and X-ray phase analysis results bear witness to formation of great number of mesopores and large interparticle lacunas generated both at the expense of random arrangement of short layer-pillar pore structured regions, and through sintering of clay particles on calcining. Adsorption properties of Fe-MM are determined from extinction of phenols and dyes aqueous solutions. Form of isotherms (S-type for phenol, L-type for resorcin and hydroquinone) allows to argue that phenols adsorption takes place mainly at the surface of Fe-MM and is due to dispersion forces action. Methylene blue cationic dye is adsorbed both on the Fe-MM surface, and in the interlayer space by use of ion-exchange centers remaining active, as well as micropores produced from pillarization. Since the sorbent surface is appreciably dehydroxilated and contains small quantity of active groups capable of holding large associates of anionic dyes, the adsorption of last mentioned occurs largely in secondary mesopores produced on calcining of Fe-MM samples.

### INTRODUCTION

In deciding on methods of recycling water cleansing and sewage treatment it is necessary to minimize expenses for materials and reagents, construction and operation of local purification installations. Maximum use of inexpensive local mineral raw materials, specifically, natural bentonites as materials and reagents for water cleansing may be a factor.

Unique properties of these layered aluminosilicates are caused by high value of specific surface of particles dispersed in the water along with the existence of trade cations, hydroxyl groups and adsorbed water molecules in their structure [1]. Modification of bentonites makes it possible to expand substantially area of their application [2–5]. Modification is performed

through incorporation of Al, Fe, Zr, Cr hydroxopolycations into interlayer space followed by calcining of samples at 110–500 °C. Thus obtained layer-pillar pore structured samples, referred to as pillar-clays, possess well-developed specific surface ( $S_{sp} = 50\text{--}300 \text{ m}^2/\text{g}$ ) and are in routine use by a number of catalytic processes, but are also applicable as sorbents for sewage freeing from flotation agents, pesticides, SSAS, dyes and others. There are practically no works on their application as oxidation catalysts for organic impurities in the sewage.

Despite the fact that many works are published every year on study of layer-pillar aluminosilicate properties, a number of factors still remain to be determined, on which depend texture characteristics of these materials. It is suggested that arrangement of layers in

pillar-clays may be effected by two ways: in the form of parallel regularly packed structures, which form micropores, and randomly arranged in the bulk of material, short layer "shatters", which shape mesopores. The most substantial factors determining properties of layer-pillar structured materials are hydroxopolycations (pillar-agents) type, their concentration in solution, duration and temperature to perform hydrolysis, concentration of slurry, temperature of final drying (calcining) and even circumstances of modified material separation from mother liquor [5, 6–8].

The purpose of the present work is obtaining of layer-pillar structured materials on the basis of montmorillonite modified by iron (III) and examination of their texture characteristics and adsorptive properties.

## EXPERIMENTAL

To produce layer-pillar structured material the bentonite has been used from Tuldon site (Buryatia) represented mostly by montmorillonite (65 %) and kaolinite (5 %).

Naturally occurring mineral (composition, mass fraction, %: 69.0 SiO<sub>2</sub>, 16.7 Al<sub>2</sub>O<sub>3</sub>, 2.6 Fe<sub>2</sub>O<sub>3</sub>, 1.5 CaO, 1.3 MgO, 2.8 K<sub>2</sub>O, 2.2 Na<sub>2</sub>O, 5.6 H<sub>2</sub>O) was suspended in distilled water, solution was clarified, and finely dispersed fractions were separated by centrifugation. Clay modification was carried out in solution of basic iron (III) chlorides obtained by addition of calculated amount of NaOH solution (proportion OH<sup>-</sup>/Fe<sup>3+</sup> = 1.5) to 1 M FeCl<sub>3</sub> solution. The solution was subjected to ageing for 24 h at room temperature. As this took place, polymerization processes occurred to produce polynuclear hydroxo-aqua complexes of iron [Fe<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>6-y</sub>]<sup>(3x-y)+</sup>. Obtained sol containing about 87 % of mono- and binuclear complexes of Fe<sup>3+</sup> and 13 % of polynuclear products of hydrolysis [9] was then added in 10 % water suspension of clay in such a quantity that iron concentration would be 2.5 mmol/g of clay. Iron-hydroxo-aqua complex-modified samples of montmorillonite (Fe-MM) were washed off by water to negative reaction on Cl<sup>-</sup>, condensed by centrifugation, dried first at room temperature, and then calcined during 2 h at 500 °C. Part of samples,

after mother liquor separation, were not washed off by water (Fe-MM-n).

Quantitative determination of Fe in samples was performed by sulfosalicylic acid photometry according to [10].

To determine cation-exchange capacity of natural and modified montmorillonite, the samples were first transformed into sodium form, and then the exchange of Na<sup>+</sup> to NH<sub>4</sub><sup>+</sup> ions was carried out under static conditions.

X-ray patterns registration was performed on STAD/P diffractometer, STOE company, with Ge-monochromator and coordinate detector, and also in Guinier-FR-552 cell, CuK<sub>α1</sub> (λ = 1.54051 Å)

Texture parameters of layer-pillar structured Fe-MM were measured at ASAP-2400 Micromeritics setup by nitrogen adsorption at 77 K according to routine procedure after evacuation at 200 °C during 12–16 h up to remainder pressure less than 10<sup>-3</sup> Torr. Calculation of texture parameters follows the method [11].

Adsorption properties of modified montmorillonite were examined by variable concentrations method on adsorption from aqueous solution of cation type (methylene blue (MB)) and anion type (Direct Sky Blue (DSB) and direct scarlet (DS)) dyes and on adsorption of organic substances of phenol class (phenol, resorcin, hydroquinone). Concentration of dyes and phenols in solution were determined by photometric evaluation using KFK-2 and Specord UV-VIS instruments.

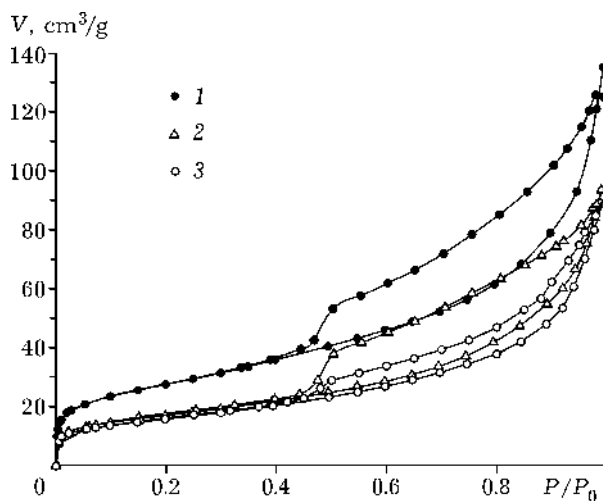


Fig. 1. Sorption isotherms of N<sub>2</sub> on natural and modified montmorillonite: 1 – Fe-MM, 2 – MM, 3 – Fe-MM-n.

TABLE 1

Texture parameters of natural (MM) and modified (Fe-MM) montmorillonite

Sample	$S_{sp}$ , m <sup>2</sup> /g	$C_{BET}$	Mean diameter of pores, nm	Total pore volume, cm <sup>3</sup> /g	Micropores volume, cm <sup>3</sup> /g
MM	60.8	142.7	9.51	0.14	
Fe-MM	99.33	110.6	8.41	0.2018	0.0028
Fe-MM-n	56.23	157.4	10.06	0.1357	0.0033

## RESULTS AND DISCUSSION

### Chemical composition and texture properties

Conditions of Fe-MM synthesis were chosen so that the optimum proportion was achieved between iron quantity incorporated into interlayer space of montmorillonite of specific surface  $S_{sp}$  and volume of pores  $V$ .

A limiting exchange capacity of examined samples of natural montmorillonite (MM), Fe-MM, and Fe-MM-n calcined at 500 °C, on  $NH_4^+$  ions, comprised 0.73, 0.48, and 0.20 mmol/g respectively. Iron content, recalculated to  $Fe_2O_3$ , corresponded to 5.9 % in Fe-MM sample, 6.8 % in Fe-MM-n sample, with consideration of iron content in naturally occurring clay. Increase of iron content in modified montmorillonite with simultaneous substantial decrease of exchange capacity may be evidence for the fact that part of ion-exchange centers in interlayer space of smectite is substituted by polyhydroxocations of iron, which form layer-pillar structured material on calcining.

Form of nitrogen adsorption isotherms of calcined samples of naturally occurring and modified montmorillonite is presented in Fig. 1. The results of texture characteristics measurement have been summarized in Table 1.

The isotherms pertain to type IV of Brunauer classification [12]. Typical for them is well-defined capillary-condensation hysteresis indicative of the structure with transitional porosity. According to [13, 14], such pores in clays are mainly interparticle lacunas. As the failure of interlayer structure in natural montmorillonite is possible even on heating in air at the temperature of 200 °C [15], the formation of such lacunas may be accounted for a partial damage of layered structure of clay even with heating in the course of pre-

paratory procedure of  $N_2$  adsorption measurement.

Increase of surface area  $S_{sp}$  from 60.8, for natural MM, up to 99.3 m<sup>2</sup>/g for montmorillonite samples modified by iron hydroxo-aqua-complexes, washed off from excess of iron ions, and then calcined at 500 °C, can be explained, as expected, by formation of layer-pillar structure (pillarization) with parallel slit-like pores. As sol used for clay modifying contained mostly mono- and binuclear iron hydroxo-aqua-complexes, considerable part of ion-exchange centers of montmorillonite is occupied by iron ions unbonded in oligomers. This provides an explanation for the small quantity of micropores in Fe-MM samples (see Table 1).

Decrease of  $S_{sp}$  to 56 m<sup>2</sup>/g for unwashed Fe-MM-n samples is testimony to formation of a great many mesopores and large interparticle lacunas being generated, presumably, both at the expense of random arrangement of short layer "shatters", and sintering of clay particles on calcining. Such parameters of unwashed

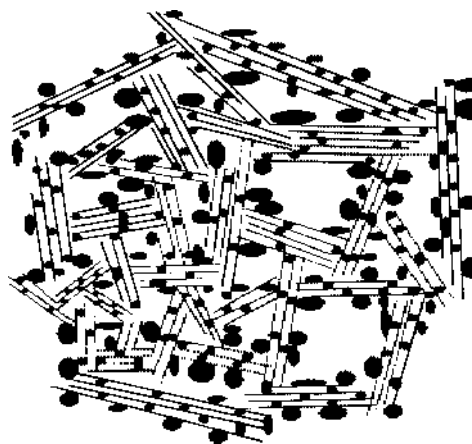


Fig. 2. Texture sketch of layer-pillar pore structured Fe-MM containing particles of iron oxide [7] after calcining at 500 °C.

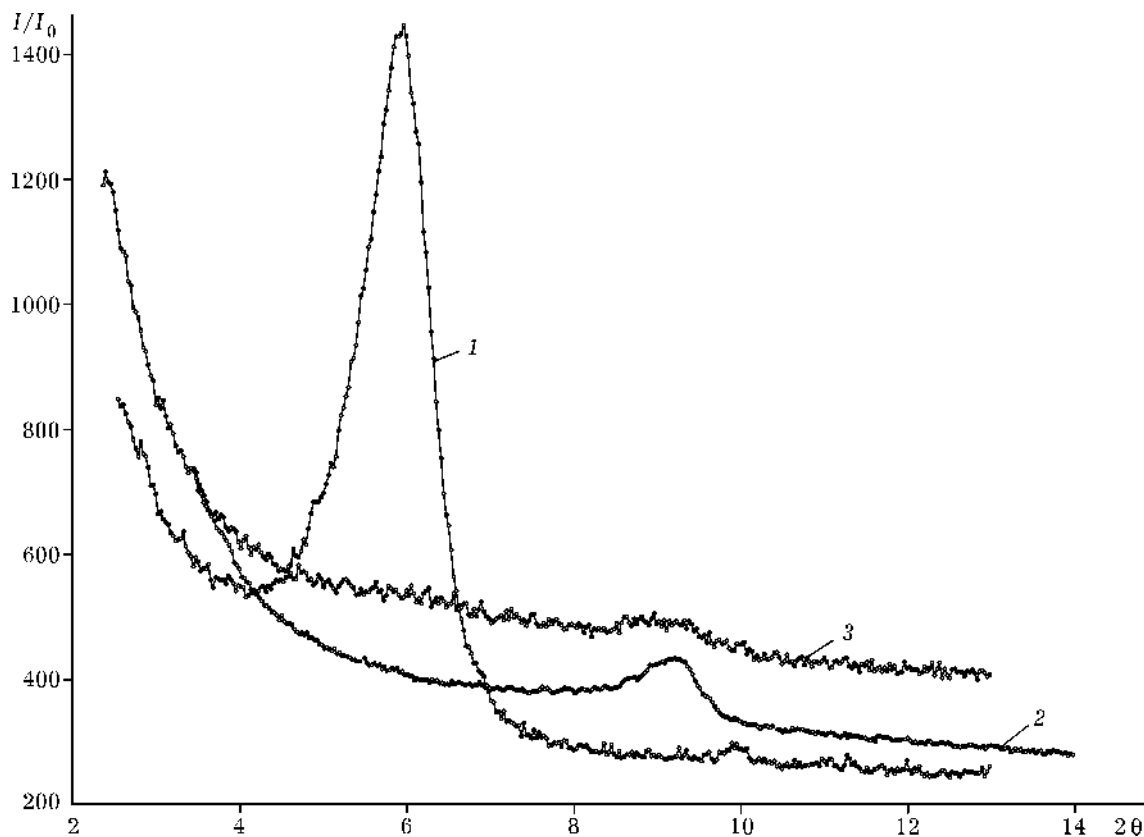


Fig. 3. Diffraction patterns ( $\text{CuK}\alpha$  irradiation) of air-dry montmorillonite (1), calcined at 500 °C montmorillonite (2), and Fe-montmorillonite calcined at 500 °C (3).

samples of modified montmorillonite are favourable for adsorption of large molecules and colloid particles from aqueous solutions. However, further research showed that texture characteristics of Fe-MM-n after calcining at the temperatures of 400–500 °C are poorly reproduced. Summarizing obtained data, one can schematically imagine the layer-pillar structure of Fe-montmorillonite as “a house of cards” [7] (Fig. 2).

#### *X-ray phase analysis*

In Table 2 are presented the values of the first basal reflection ( $d_{001}$ ) of natural and modified montmorillonite samples as a function of thermal treatment conditions, and in Fig. 3 – diffraction patterns of MM and Fe-MM in the range of  $2\theta = 3\text{--}15^\circ$ . Calcining of MM up to the temperature of 500 °C occurs with loss of interlayer water resulting in ‘compressed’ struc-

TABLE 2

Values of the first basal reflection  $d_{001}$  for natural (MM) and modified (Fe-MM) montmorillonite

Sample	Temperature of calcining, °C	$d_{001}$ , Å
MM	Air-dry	14.8139
»	500	9.1379
Fe-MM	Air-dry	14.4061
»	200	14.2993
»	400	9.8250
»	500	9.6759

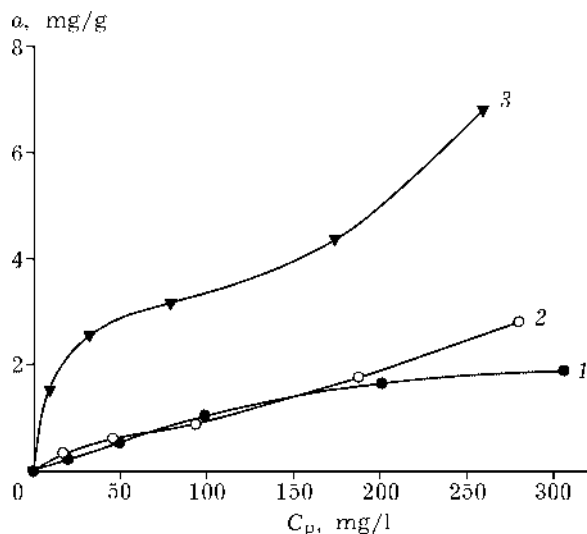


Fig. 4. Adsorption isotherms of phenols on Fe-MM: 1 - phenol, 2 - resorcin, 3 - hydroquinone.

ture such that the value of the first basal reflection  $d_{001}$  changes from 14.8139 to 9.1379 Å.

Table 2 indicates that incorporation of  $[\text{Fe}_x(\text{OH})_y(\text{H}_2\text{O})_{6-y}]^{(3x-y)+}$  hydroxocomplexes into natural clay does not tend to increase interlayer distance (for air-dry sample Fe-MM  $d_{001} = 14.4061$  Å), *i. e.* the moving of interlayer packs apart does not occur as observed, for example, in [5, 16]. It seems likely that under our experimental conditions the cation exchange occurs predominantly between less in size mono- and binuclear complexes  $[\text{Fe}_1(\text{OH})_1(\text{H}_2\text{O})_5]^{2+}$ ,  $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_3]^{4+}$ ,  $[\text{Fe}_1(\text{OH})_2\text{H}_2\text{O}]^+$ ,  $[\text{Fe}_2(\text{OH})_1(\text{H}_2\text{O})_5]^{5+}$  and  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  exchange cations of montmorillonite, concurrent with loss of free interlayer water, which does not result in extreme change of  $d_{001}$  value inherent to naturally occurring montmorillonite. Nevertheless, an influence of polyhydroxocomplexes on the montmorillonite structure can be followed from comparison of  $d_{001}$  values for natural MM ( $d_{001} = 9.1379$ ) and Fe-MM ( $d_{001} = 9.6759$ ), calcined at 500 °C. Calcining of air-dry Fe-MM at 200, 400, and 500 °C, as well as for natural montmorillonite, leads to the loss of interlayer and constitutional water and transition to compressed structure, which is accompanied by gradual decrease of  $d_{001}$  values. Moreover, when calcined, longer two-dimensional structure units of clay rupture and transform into short randomly packed fragments forming the picture, characteristic for semiamorphous species (see Fig. 3).

Detail examination of Fe-MM properties was carried out with samples calcined at 500 °C, since at this temperature complete fixation of iron polyhydroxocomplexes as iron (III) oxides is ensured and the transfer of iron ions into solution is not observed.

#### Adsorption of phenols

Data on adsorption of phenol, resorcin, and hydroquinone by Fe-MM from model aqueous solutions are presented in Fig. 4.

Low values of adsorption capacity of Fe-MM are caused by surface dehydroxylation and formation of rigid spatial structure when heat treated, by concurrent adsorption of water molecules on its surface combined with small quantity of micropores generated in the course of pillarization.

Form of isotherms (S-type for phenol, L-type for resorcin and hydroquinone) allows to argue that phenols adsorption takes place mainly at the surface of Fe-MM and is due to dispersion forces action [17]. Obtained results are consistent with the concept that phenol sorption on the surface of sorbents is the greater, the smaller is their water solubility [18-20]. The statement under discussion is correct at least for hydroquinone - phenol pair. But since the solubility of resorcin is several-fold as great as phenol or hydroquinone solubility (58.4, 8.2,

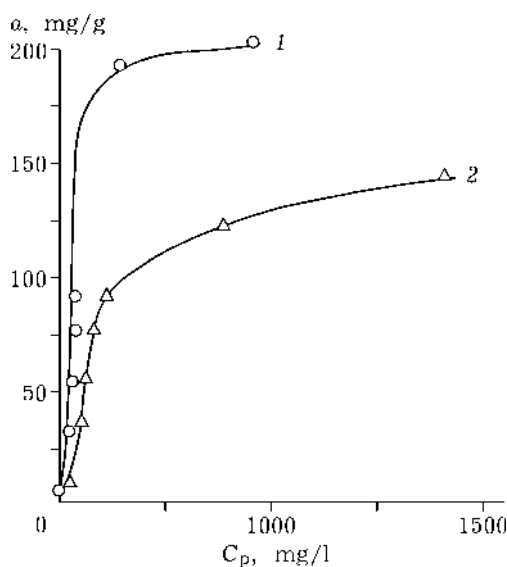


Fig. 5. Adsorption isotherms of methylene blue cationic dye on natural montmorillonite (1) and Fe-montmorillonite (2).

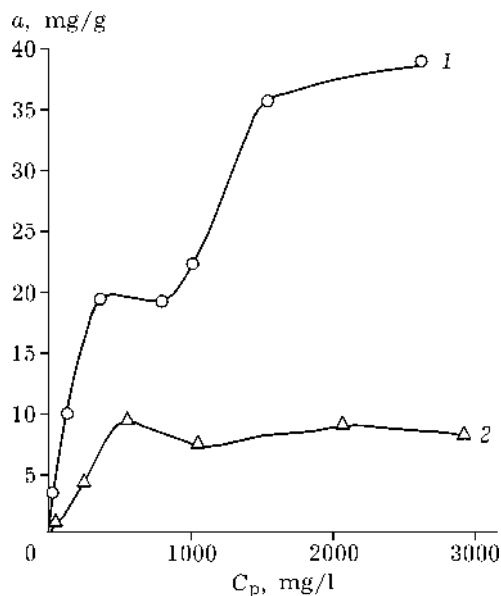


Fig. 6. Adsorption isotherms of direct scarlet anionic dye on natural montmorillonite (1) and Fe-montmorillonite (2).

6.0 %, respectively), it would be expected much less values of this compound adsorption on Fe-MM. Abnormally high values of resorcin adsorption are attributable to the fact that the emergence of the second OH<sup>-</sup> group in this phenol molecule results in parallel, instead of perpendicular, as with phenol, orientation of adsorbed molecules about the surface of sorbent and in stronger interaction (as compared with water molecules) with the montmorillonite surface.

#### Adsorption of dyes

Adsorption data of MB, DSB, and DS dyes on natural MM and Fe-MM are presented in Figs. 5–7. Comparatively high adsorption capacity of Fe-MM in relation to cationic MB dye (see Fig. 5) derives from the fact that MB is adsorbed both on the surface of Fe-MM, and in the interlayer space by use of ion-exchange centers remaining active, as well as micropo-

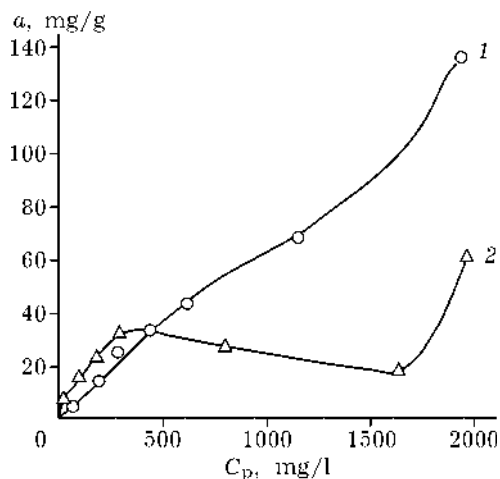


Fig. 7. Adsorption isotherms of Direct Sky Blue anionic dye on natural montmorillonite (1) and Fe-montmorillonite (2).

res produced from pillarization. Such adsorption mechanism is well explicable since MB is dye low-associated in the water with the adsorption site  $\omega = 0.75 \text{ nm}^2$  [21], comparable in size with Fe-montmorillonite pores.

Adsorption isotherms nature of DS and DSB anionic dyes and their adsorption values on natural and Fe-montmorillonite (see Figs. 6, 7) are determined both by quantity and size of primary micropores (<0.97 nm), mesopores and large interparticle lacunas, and by their chemical structure features and thus by their association degree in aqueous solutions in various equilibrium concentrations. Distinct inflections are observed on isotherms of anion type dyes in the field of concentrations close to critical concentration of micellation (CCM).

It is common knowledge that, although DSB has greater molecular mass, it is less associated in solution than DS (association factor  $f_1$  over the pre-micellar region for DSB <4, for DS, 20–50,  $\omega = 2.3$  and  $2.7 \text{ nm}^2$ , respectively [21, 22]). With knowledge of adsorption site values and adsorption capacity of Fe-MM on the adsorb-

TABLE 3

Several parameters describing dye adsorption on Fe-MM

Dye	$M$ , g/mol	$f_1$	$\omega$ , nm <sup>2</sup>	$S$ , m <sup>2</sup> /g
MB	319.9	–	0.75	38.8
DSB	992	<14	2.3	8.5
DS	813	20–50	2.7	3.4

ates in the premicellar region of adsorption isotherms, the values of effective area of sorbent surface occupied by dyes can be calculated:

$$S = 10^{-18}aN\omega$$

where  $S$  is effective specific surface of the adsorbent,  $\text{m}^2/\text{g}$ ;  $a$  is adsorption value before CCM,  $\text{mol}/\text{g}$ ;  $N$  is Avogadro number;  $\omega$  is dye adsorption site,  $\text{nm}^2$ .

Obtained  $S$  values (Table 3) confirm the conclusion that sorbent surface is appreciably dehydroxylated and contains small quantity of active groups, which are capable of holding large associates of anionic dyes. Adsorption occurs largely in secondary mesopores produced on calcining of Fe-montmorillonite samples.

## CONCLUSION

Considering main texture characteristics of materials obtained through modification of natural montmorillonite samples by iron hydroxo-oaqua complexes, and adsorption features of organic substances on Fe-MM, the essential tendencies of their use in practice of sewage treating can be defined, specifically, in catalytic oxidation of organic substrates, for instance, by hydrogen peroxide.

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