АДСОРБЦИЯ КРАСИТЕЛЯ МЕТАНИЛОВЫЙ ЖЕЛТЫЙ НА Fe-МОДИФИЦИРОВАННОЙ БЕНТОНИТОВОЙ ГЛИНЕ

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Получены железосодержащие материалы путем модификации бентонитовой глины месторождения Мухорталинское (Республика Бурятия, Россия) полимерными гидроксокатионами железа и последующего нагрева при 500 °С. Материалы охарактеризованы методами химического анализа, низкотемпературной адсорбции азота и РФА. Содержание железа в образцах составило 14,5-15,8%, их удельная поверхность равнялась 138-143 м²/г. Изучены адсорбционные свойства материалов на примере адсорбции кислотного красителя Метаниловый Желтый из модельных водных растворов. Установлена зависимость адсорбции красителя от физико-химических параметров процесса, таких как pH, содержание сорбента, начальная концентрация красителя. Величина удельной адсорбции красителя на сорбентах возрастала при уменьшении pH и увеличении начальной концентрации водных растворов красителя и при уменьшении загрузки сорбентов. Максимальная адсорбция красителя составила 88,5 мг/г при pH 3,5 и содержании сорбента 1 г/л в интервале начальных концентраций красителя 24- 491 мг/л. Эффективность удаления красителя равнялась 86-95% при его начальной концентрации 84 мг/л и содержании сорбентов 3-10 г/л. Сорбционная емкость полученных сорбентов в отношении изучаемого красителя являлась близкой к сорбционной емкости некоторых углеродных сорбентов. Было показано, что изотерма адсорбции красителя Метаниловый Желтый на сорбентах хорошо описывается моделью адсорбции Фрейндлиха, что указывает на неоднородность поверхности сорбентов. Результаты опытов по десорбции и повторной адсорбции красителя Метаниловый Желтый свидетельствовали о высокой эффективности извлечения красителя и возможности повторного использования сорбентов в адсорбции азокрасителей. Сорбенты могут представлять интерес для применения в процессах очистки сточных вод от кислотных красителей.

Ключевые слова: Fe-модифицированная бентонитовая глина, адсорбция, краситель Метаниловый желтый, десорбция, очистка сточных вод

ADSORPTION OF METHANYL YELLOW DYE ON Fe-MODIFIED BENTONITE CLAY

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Iron-containing materials were obtained by modifying bentonite clay from the Mukhortalinskoe deposit (Republic of Buryatia, Russia) with polymeric iron hydroxocations and subsequent heating at 500 °С. The materials were characterized by chemical analysis, low-temperature nitrogen adsorption, and XRD. The iron content in the samples was 14.5-15.8%. Their specific surface area was 138-143 m²/g. The adsorption properties of materials have been studied using the example

of the adsorption of an acidic dye Metanyl Yellow from model aqueous solutions. The dependence of the dye adsorption on the physicochemical parameters, such as pH, sorbent loading, and the initial dye concentration has been established. The specific dye adsorption on sorbents increased with a decrease in pH and an increase in the initial concentration of the dye aqueous solutions and with a decrease in the loading of sorbents. The maximum dye adsorption was 88.5 mg/g at pH 3.5 and a sorbent loading of 1 g/l in the range of initial dye concentrations 24–491 mg/l. The dye removal efficiency was 86-95% at an initial concentration of 84 mg/L and a sorbent loading of 3-10 g/l. The sorption capacity of the obtained sorbents in relation to the dye was close to the sorption capacity of some carbon sorbents. It was shown that the adsorption isotherm of the Metanyl Yellow dye on sorbents is well described by the Freundlich adsorption model, which indicates the heterogeneity of the sorbent surface. The results of experiments on desorption and re-adsorption of the Metanyl Yellow dye indicated a high efficiency of the dye extraction and the possibility of re-using sorbents in the adsorption of azo dyes.The sorbents may be of interest for use in wastewater treatment processes from acid dyes.

Key words: Fe-modified bentonite clay, adsorption, Metanyl yellow dye, desorption, wastewater treatment

INTRODUCTION

Environmental problems associated with the increasing anthropogenic pollution of the environment have acquired particular importance at the present stage of human development. The total volume of untreated wastewater discharged into surface water bodies is increasing from year to year [1]. For example, the amount of dyes produced annually in the world is about 900 thousand t, of which 10-15% is discharged in the form of untreated wastewater from enterprises of textile, paper, chemical and other industries that use dyes for dyeing products [2]. Adsorption technologies have become quite widespread in the treatment of industrial wastewater due to their high efficiency, the absence of secondary pollution and the simplicity of the used equipment. Active carbon is most often used in industrial wastewater treatment [3-5]. However, the high cost of production and regeneration of this sorbent stimulates the search for alternative effective sorbents from cheap natural raw materials [6]. Bentonite clays, the main clay mineral of which is montmorillonite, have a high affinity for cations and are widely used in wastewater treatment from metal cations and cationic organic dyes [7-8]. However, they are characterized by an insignificant ability to adsorb anions [9]. To develop sorbents capable of absorbing anions, research is needed to modify clays with various compounds and to find the optimal conditions for their use in sorption processes. These issues have not been sufficiently investigated currently. In this work, sorbents were obtained from natural montmorillonite- ontaining clay and polymeric iron hydroxocations and their adsorption properties with respect to the acid azo dye Metanyl Yellow in aqueous solutions were studied, the possibility of extracting the sorbed dye and reusing the sorbents was also studied.

MATERIALS AND METHODS

Preparation of sorbents. The initial material was a finely dispersed fraction (particle size 0.003-0.005 mm) of natural clay from the Mukhortalinskoye deposit (Republic of Buryatia (Russia). The content of montmorillonite (Mt) in this fraction was about 80%. Natural clay was pretreated with 1M NaCl solution to obtain the Na-form of Mt [10]. The chemical composition of the resulting Na-Mt, determined by methods [11, 12], consisted of oxides of the following elements (wt. %): $SiO_2 - 65.6$, $Al_2O_3 - 14.5$, $Fe_2O_3 - 1.44$, FeO $- 0.04$, MnO < 0.01, MgO $- 0.78$, CaO $- 0.07$, $Na_2O - 1.57$, $K_2O - 0.29$, $P_2O_5 < 0.03$, $TiO_2 - 0.17$, CuO $- 0.002$, $H_2O - 15.4$. The synthesis of sorbents was carried out by the method of ion exchange of Na^+ cations for polymeric iron hydroxocations [13]. A modifying solution containing iron polyhydroxocations (PC) was prepared by alkaline hydrolysis of a 0.2M $Fe(NO_3)_3$ solution by adding a 0.2M NaOH solution to molar ratios

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Изв. вузов. Химия и хим. технология. 2022. Т. 65. Вып. 5

Z = [OH⁻]/[Fe³⁺] equal to 1.6 (sorbent S1) and 2.0 (sorbent S2) [14]. Then the modifying solution was added dropwise to the Na-Mt suspension and the resulting suspension was left to stand for 24 h at room temperature. The solid phase was separated from the solution and washed with distilled water. The resulting materials were calcined at 500 °C for 2 h. The concentration of iron ions was determined by a photometric method after treatment of solids with concentrated HCl [15]. The specific surface area of the sorbents was determined using the BET equation [16] from the isotherm of low-temperature nitrogen adsorption using a setup "Thermosorb LP".

Adsorption experiment. The adsorption properties of the materials were studied in aqueous solutions of the azo dye Metanyl Yellow (MY), which is often present in dyeing wastewaters as it is widely used in industry for dyeing wool, nylon, silk, paper, ink, aluminum, detergents, etc [17]. MY refers to acid dyes that dissociate into sodium cations and organic anions in aqueous solutions. The dye adsorption was determined from the difference between the initial concentration and the concentration of the dye solution at the moment of reaching equilibrium (24 h). The dye concentration was determined by a photometric method. Absorbance was measured on a UV-spectrophotometer UV-1800 (Zhimadzu, Japan) at 442 nm (Fig. 1).

The equilibrium dye adsorption (q_e, mg/g) was calculated by the formula:

$$q_e = \frac{C_o - C_e}{m_s} \cdot V \qquad (1)$$

where C_o and C_e – initial and equilibrium dye concentrations in solution, mg/L; V – the solution volume, L; m – the mass of the sorbent, g.

The dye removal efficiency E (%) was calculated by the formula:

$$E = \frac{C_o - C_e}{C_e} \cdot 100 \qquad (2)$$

RESULTS AND DISCUSSION

Physicochemical properties of sorbents. The diffraction pattern of the original clay revealed reflections at 2θ equal to 9.16, 19.82 34.98 and 62.19°, characteristic of montmorillonite, as well as reflections characteristic of cristobalite (21.89, 35.98°) and feldspar (27.63°) [18]. The diffractograms of the sorbents showed a shift of the first basal reflection, characteristic of Mt (9.16 Å), to small angles 2θ (11.48 Å), which was due to the penetration of iron PC into the interlayer space of Mt and the appearance of weak reflections characteristic of hematite (33.18, 36.69 Å), which was formed as a result of the dehydration and dehydroxylation during the calcination at 500 °C [19]. Modification of Mt with iron complexes and its heat treatment led to an

increase in the specific surface area (S_{sp}) from 90 m²/g (initial Mt) to 138 m²/g (S1) and 143 m²/g (S2). The iron content in the initial Mt was 1.04%, and after modification, the iron content increased to 14.2% (S1) and 15.8% (S2).

Study of the dye adsorption. The effect of pH on the dye adsorption was studied in experiments carried out at pH 3.5, 5.7 and 7.0 with the sorbent loading of 1 g/L and MY concentration of 54.3 mg/L. The results are shown in Table 1.
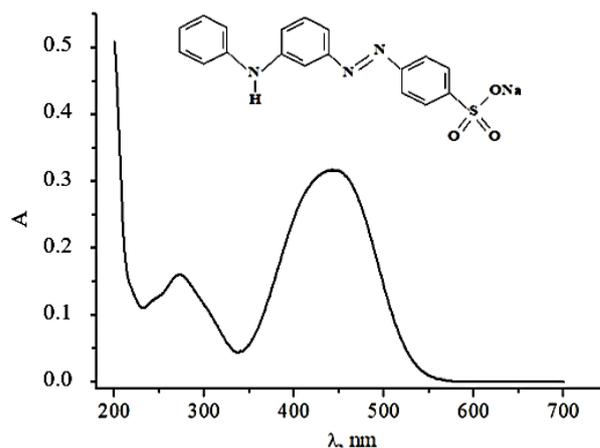

Fig. 1. UV-Vis spectrum and structural formula of Metanil Yellow dye
Рис. 1. УФ-спектр красителя Метаниловый Желтый и его структурная формула

Table 1

Dependence of adsorption q_e on pH
Таблица 1. **Зависимость адсорбции q_e от pH**

Sorbents	pH	q_e, mg/g
S1	3.5	22.5
	5.7	7.7
	7.0	0.2
S2	3.5	24.1
	5.7	11.3
	7.0	0.5

Modification of Mt lead to an increase in the anion-exchange capacity due to an increase in the number of Fe-OH groups. The maximum of dye adsorption was observed at pH 3.5. An increase in pH led to a decrease in the adsorption as the adsorption centers on the surface of oxide sorbents are charged negatively with an increase in the pH of solutions [9].

To study the effect of the MY concentration experiments were carried out with the sorbent loading (S2) of 1 g/L and at the initial dye concentrations 23.6; 52.8; 84.1; 184.4; 278.3; 373.8; 491.0 mg/L at 25 °C and pH = 3.5 (corresponds to maximum adsorption) and pH = 5.7 (natural pH value of the dye and sorbent suspension without acid addition). The obtained dependences of the adsorption values (q_e) on the equilibrium dye concentrations are shown in Fig. 2.
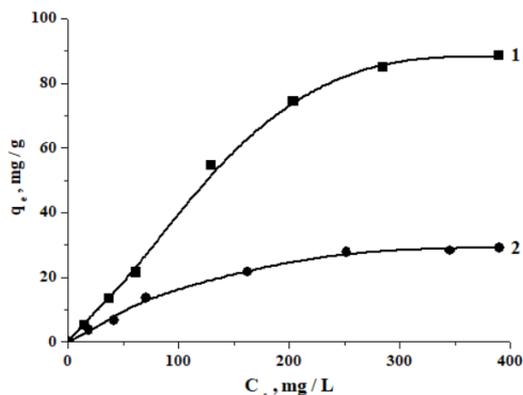
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Fig. 2. Isotherms of MY dye adsorption on sorbent S2 at different pH values: 3.5 (1) and 5.7 (2)

Рис. 2. Изотермы адсорбции красителя MY на сорбенте S2 при разных значениях pH: 3,5 (1) и 5,7 (2)

The experimental data were analyzed using the Langmuir and Freundlich adsorption models, which describe adsorption on a homogeneous and non-uniform surface, respectively [20].

The linear form of the Langmuir isotherm is expressed by equation (3):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (3)$$

where q_m − constant corresponding to the maximum adsorption, mg/g; K_L is a constant depending on the adsorption energy and temperature, L/g.

The linear form of the Freundlich isotherm is expressed by equation (4):

$$\log q_e = \log K_F + \frac{1}{n}(\log C_e) \qquad (4)$$

where K_F is the Freundlich adsorption constant, L/g; n is an experimental constant describing the intensity of adsorption [21].

Figure 3 shows the experimental data on the adsorption of the MY dye in the form of the linear form of the Freundlich equation.
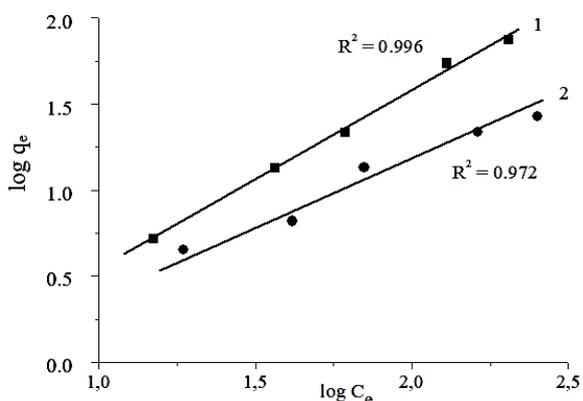

Fig. 3. Experimental data on the dye MY adsorption in the linear form of the Freundlich equation at: pH 3.5 (1) and pH 5.7 (2)

Рис. 3. Экспериментальные данные по адсорбции MY в виде линейной формы уравнения Фрейндлиха при: pH 3,5 (1) и pH 5,7 (2)

The correlation coefficients according to the Langmuir and Freundlich models were 0.203 and 0.996 (pH 3.5); 0.902 and 0.972 (pH 5.7), respectively. The MY adsorption was satisfactorily described by the Freundlich adsorption model (5):

$$q_e = K_F \cdot C_e^{1/n}, \qquad (5)$$

where K_F was 0.535, n was 1.389 (pH 5.7) and K_F was 0.313, n was 0.961 (pH 3.5).

The influence of the sorbents loading was studied at initial dye concentration 84.1 mg/L and pH 3.5. Fig. 4 shows the q_e values and the dye removal efficiency depending on the loading of sorbents.
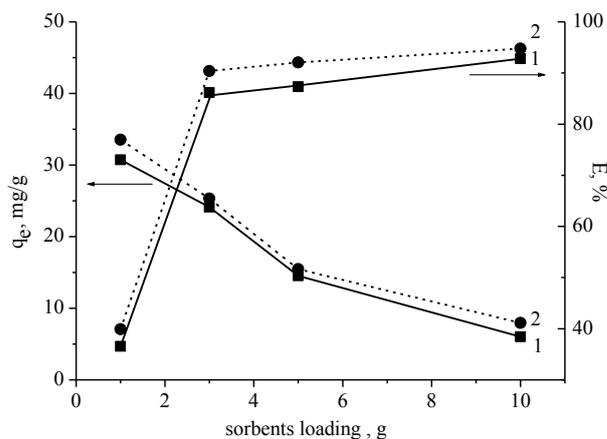

Fig. 4. Dependence of q_e and the efficiency E on the loading of sorbents: S1 (1) and S2 (2)

Рис. 4. Зависимость q_e и E от содержания сорбентов в растворе: S1 (1) и S2 (2)

The number of surface adsorption centers increased with an increase in the of sorbents loading, which led to an increase in the total amount of the dye sorbed and the efficiency of dye removal. The efficiency of MY removal was 86.2 and 90.4% for sorbents S1 and S2, respectively, at loading of 3 g/L. The efficiency of removal increased to 92.8 (S1) and 94.7% (S2) at the loading 10 g/L. The specific dye adsorption (q_e) decreased due to the fact that the number of adsorption centers involved in adsorption decreased with an increase in the ratio of the sorbent loading to the dye concentration. The sorption capacity of the obtained materials was close to the sorption capacity of some carbon materials as shown in the Table 2.

Study of MY dye desorption and re-adsorption. The primary adsorption of the dye was carried out from MY solution with an initial concentration of 85 mg/L at pH 3.5. Desorption was carried out by adding distilled water or an aqueous solution of 0.001 M NaOH to the sorbent S2 containing 23 mg/g of sorbed dye. 10, 20, 30 ml of water or 10 ml of 0.001 M NaOH were added to 0.01 g of the sorbent, the suspension was stirred and left to stand for 24 h. The desorption efficiency was 38.8, 70.5, and 93.3% at a ratio of the

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sorbent mass to the volume of added water of 1.0, 0.5 and 0.3 g/L, respectively. When 0.001M NaOH solution was used, the desorption efficiency was 82.4% in 2 h and 97.2% in 24 h at the ratio of the sorbent mass to the added solution volume 1 g/L. After the dye desorption the sorbent was filtered from the solution, washed by distilled water, dried at 104 °C for 2 h, and reused in the adsorption. Secondary adsorption was carried out under the same experimental conditions as primary adsorption. The adsorption value was 22.1 mg/g. This value was close to the sorption capacity observed at the primary use of the sorbent. The desorption efficiency was 95 and 93% in the second and third desorption cycles, respectively. The efficiency of secondary and tertiary adsorption was equal to 95 and 90% of the primary adsorption. According to these results, the adsorption capacity of sorbent S2 was retained in three repeated cycles. The adsorption capacity decreased in the quaternary use of the sorbent to 70%.

CONCLUSIONS

Adsorption properties of iron-containing materials obtained by modifying the bentonite clay with polymeric iron hydroxocations were studied in the adsorption of Metanil Yellow dye. The dependence of the dye adsorption on the physicochemical parameters (pH, sorbent content, the initial dye concentration) has been established. The results showed that the materials are effective reusable sorbents for acid dyes removal.

Table 2
Comparison of the sorption capacity of materials
Таблица 2. **Сравнение сорбционной емкости материалов**

Sorbents	Dye	q_{max}*, mg/g	References
Activated carbon produced from saw dust	MY	132	22
Activated carbon produced from coconut shell	MY	99.2	22
Activated carbon produced from rise husk	MY	66.2	22
Amino functionalized drapheme	MY	76.3	23
Sorbent S2	MY	88.5	This work
The commercial Activated Carbon supplied by J.T. Baker (Holland)	Acid Red 97 Acid Orange 61 Acid Brown 425	52.1 169.5 222.2	24

*q_{max} - maximum adsorption capacity
*q_{max} - максимальная адсорбционная способность

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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