Research of the activity of Fe-pillared montmorillonites in aqueous dye solution

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Abstract. High specific surface area, large micropore volume, concentration of surface acid sites, and increased density of sorption sites make montmorillonite pillared as an excellent adsorbent and catalyst to remove contaminants from wastewater. The studies are aimed at establishing the adsorption and catalytic activity of Fe pillared montmorillonite based on Krantau and Navbakhor bentonite in relation to dyes from solutions. It has been shown that the introduction of Fe^{3+} ions into the interlayer space of a natural sample increases the activity with respect to the anionic dye by more than 2 folds. Despite the large specific surface area of the original Navbakhor clay, compared to Krantau clay, the activity for Congo red is greater in the pillar of the latter. It has been established that Fe-pillared materials are active catalysts for the oxidation of dyes by hydrogen peroxide in aqueous solutions and lead to its 100% conversion. An increase in the temperature of catalytic oxidation ranged from 25 to 55°C increases the discoloration degree of Congo red solution under homogeneous conditions by 1.5 folds or more, and under conditions of heterogeneous catalysis at least three folds.

1 Introduction

Scientific achievements in the field of green chemistry and engineering are aimed at solving the problem connected to neutralization of the toxic substances in the environment. In recent years, there has been growing interest in the use of columnar clays as nontoxic heterogeneous catalysts in wastewater treatment [1]. Scientists and specialists in this field is of increasing interest in a case of clay minerals using in heterogeneous catalysis [2]. Yet, clay minerals inherently suffer from the inaccessibility of their active sites, which reduces their effectiveness in a case of catalytic reactions. Furthermore, the modification of natural clay minerals with giant particle pillaring has become a promising technology because it allows the opening of clay layers, ensuring high resistance and thermal stability, increased porosity, surface area and basal distance, and other physicochemical behaviors [3].

Pillared clays have been identified as porous materials of the 21st century and have attracted much attention in a view point of an academic and an applied sciences [4, 5]. Their high specific surface area, large micropore volume, concentration of upper acid sites,

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increased hydrophobicity, and increased density of sorption sites make them an excellent adsorbent and catalyst for the removal of pollutants from effluents [6].

Oxidative treatment technology has gained recognition as an alternative wastewater treatment approach compared to conventional ones and is aimed at removing non-biodegradable and toxic organic compounds [7]. The Fenton oxidation process is considered as an effective to eliminate the organic compounds in wastewater [8] and is relatively environmentally friendly due to the fact that no harmful chemicals are used. At the same time, the use of homogeneous Fenton processes requires the creation of acidic environments (pH≤3) and the removal of ferric hydroxide sediment after wastewater treatment. The list of harmful factors also lengthens the complexity of the separation and reuse of these catalysts, which limits the application of this process on an industrial scale.

Recently, in order to improve heterogeneous processes using catalysts, since iron supported on a carrier, etc., clay materials are being studied as a carrier [9]. Columnar clay catalysts were used to remove organic pollutants as phenol and its derivatives, organic dyes, toluene [10], tyrosol, and other persistent compounds [11]. It is reported that these mixed pillared materials can also operate over a wide range of pH and temperature and can be easily separated from aqueous solution and retain their catalytic activity through multiple cycles of use.

Barrault et al. [12] were among the first investigators to study the removal of phenol from wastewater under mild reaction conditions using mixed Al/Fe-pillared clays. Their studies showed that approximately 80% of the phenol present was converted to CO_2 and H_2O within 2 hours of reaction, and even after three reaction cycles, only less than 1 mg/L of iron was leached.

The patent [13] describes a method for purifying wastewater from azo dyes using the example of direct pure blue, acidic chromium dark blue, and acidic chromium blue-black in the presence of a Fe/Al catalyst intercalated with a mixed iron-aluminum complex. Oxidation was carried out at a concentration of dyes of 0.1 mmol/l in the range of pH=2.0-5.7, at a temperature of 30-60 ºC. Depending on the conditions of catalysis, the conversion of dyes in 60-240 minutes reaches 82-99%.

It should be noted that the activity of hydroxyl radicals is extremely high in the absence of selectivity, i.e., $HO^•$ can attack the oxidized substrate simultaneously in different positions, which leads to the formation of a complex of products. The lifetime of hydroxyl radicals is very short, the rate constant of their interaction with organic molecules is about 106–109 $M^{-1} s^{-1}$, which is close to the values of diffusion constants [14].

Thus, the present study is aimed at investigation of the activity of Fe-intercalated montmorillonites based on Krantau (10-FeKr) and Navyubakhor (10-FeNb) [15] in solutions of cationic and anionic dyes.

2 Materials

Fe-pillared materials based on Krantau (Kr) Navbakhor (Nb) bentonite were chosen as objects of the study.

Determination of adsorption activity was carried out using model solutions of cationic - methylene blue (MB) and anionic - Congo red (CR) dyes.

3 Method

Before use, natural clays were enriched by elutriation until complete removal of non-clay impurities. Enriched forms of clays were dried at a temperature of 104±1ºC and milled. Previous studies [17] contributed to the establishment of conditions for the process of
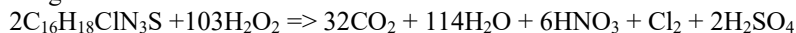
intercalation of montmorillonite with Fe^{3+} polyoxocations, according to which the processes were carried out in the following sequence: calculated amounts of salt $FeCl_3$ $6H_2O$ (10 mmol Fe^{3+} per 1 g of clay) with constant stirring on a magnetic stirrer at room temperature. At that mass ratio of solid and liquid should be 1 : 15.

A 1 M NaOH solution was added dropwise to the resulting suspension at a ratio of $OH/Fe^{3+} = 2$; after thorough stirring (at least 2 h, at a temperature of 50°C), the suspension was allowed to settle at rest at room temperature for 24 h. Before separating the solid phase, the suspension was subjected to sonication at a wave frequency of 50 kHz for 5 min. Afterwards, the resulting mass was washed to a negative reaction from Cl^- ions and dried at a temperature of 100±1ºC. The resulting samples were subjected to grinding and then sifted through 170 mesh sieve. The sieved intercalated materials were calcined at temperatures from 200 to 500°C for 2 hours at a heating rate of 5°C/min. Adsorption isotherms of anionic and cationic dyes from aqueous solutions on the samples were obtained at different temperatures in the concentration range of 0.01^{-1} mmol/g. The amount of adsorbed substance was determined using the Langmuir equation (depending on the type of isotherm obtained and the residual concentrations of dyes in the solution).

The experiments for determining the adsorption capacity were carried out in the following order: first, dye solutions were prepared in water with a concentration of 1 to 100 mg/L, and the optical densities of these solutions were determined. Based on the data obtained, a standard calibration graph was drawn. In solutions with a volume of 50 ml with 7 different concentrations of the dyes, 0.05 g of samples of pillared materials were added in the form of a powder. The flasks were shaken gently, then settled at rest until equilibrium was established. After the adsorption equilibrium was established, the optical densities of the solutions were measured, and their concentrations were calculated using the data from the calibration curve.

The quantitative determination of dyes was carried out by scanning spectrophotometry using a UV/V-5100 spectrophotometer (Shanghai Metash Instruments Co.) at a characteristic wavelength of 660 and 505 nm, respectively, for MB and CR. The catalytic effect of pillared materials was estimated from the change in the characteristic absorption bands (Figure 1) of a solution of MB and CR in the visible part of the spectrum at 501 and 620 nm, respectively, due to $n \rightarrow \pi^*$ transitions of electrons of the azo group, as well as in the UV part in the wavelength range of 320 and 228 nm related to $\pi \rightarrow \pi^*$ transitions in aromatic rings.

The catalytic oxidation reaction of dyes in the aqueous phase was carried out using a 3% solution of H_2O_2 at molar ratios of dye and hydrogen peroxide from 1:1 to 1:10 and at a catalyst flow rate of 1 to 10 g/l. The complete oxidation of MB and CR proceeds according to the following reactions:

$$2C_{16}H_{18}ClN_3S + 103H_2O_2 => 32CO_2 + 114H_2O + 6HNO_3 + Cl_2 + 2H_2SO_4$$
$$C_{32}H_{22}N_6Na_2O_6S_2 + 91H_2O_2 = 32CO_2 + 98H_2O + 6HNO_3 + 2NaHSO_4$$

The activity of the catalyst was determined by the discoloration of the solution and the decrease in the optical density of the dyes at the corresponding wavelength.
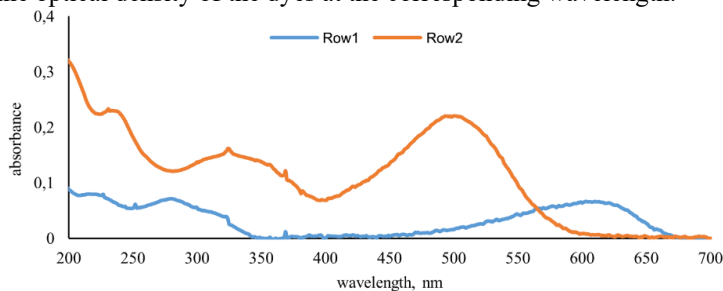

Fig. 1. Electron absorption spectrum of the solution: 1) MB; 2) CR. The concentration of the dye in the solution is 10 mg/L.

4 Result and discussion

Recently, adsorption methods have been widely used to treat industrial wastewater from inorganic and organic pollutants. The use of natural sorbents makes it possible to increase the economic efficiency of sorption technologies. It is known that bentonite clays are effective cation exchangers and the development of anion exchange sorbents based on them continues to be an urgent task. Numerous studies [14] have shown that the intercalation of polyoxocations Fe^{3+} and others in montmorillonites (MM) leads to a decrease in the cation exchange capacity. Due to which there is a decrease in adsorption processes occurring due to the exchange of cations. Therefore, one should expect a decrease in the adsorption activity of the synthesized pillared montmorillonites with respect to cationic MB. The adsorption isotherms obtained are shown in Figure 2, A.

As expected, intercalation did not lead to a decrease in the sorption characteristics for the cationic dye. It can be attributed that the intercalation of Fe^{3+} polyoxocations [Bergay, DOFF] increases negatively charged particles. Therefore, it can be assumed that adsorption in this case proceeds mainly due to the formation of new chemical bonds between the negatively charged surface of the pillared MM and large MB cations.
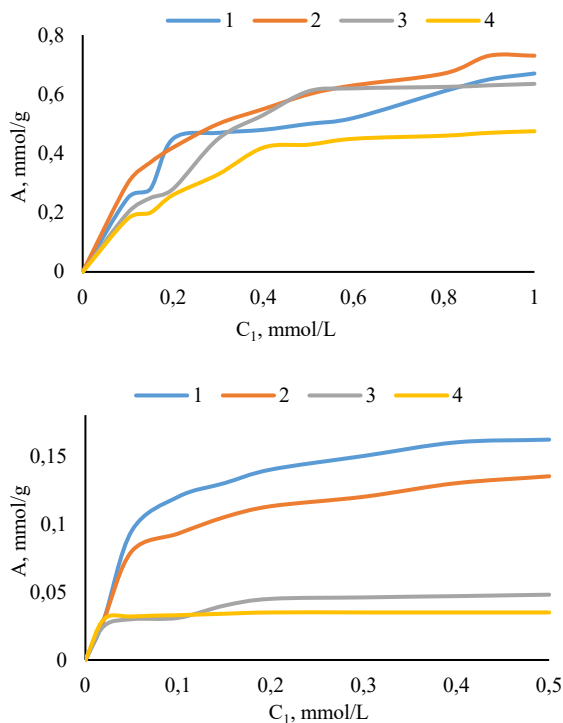

Fig. 2. Adsorption isotherms A) MB and C) CR on pillared MM at 20°C and pH=7: 1) 10-FeKr; 2) 10-FeNb; 3) Nb; 4) Kr.

To improve the stability of intercalated polycations, it is necessary to heat treat them. In this case, the ability to swell montmorillonite in an aqueous medium and wash out interlayer cations is completely lost. Due to this, it is possible to reuse various pillars in adsorption and catalytic processes in an aqueous medium. Natural montmorillonite clays are not resistant to heat treatment. At temperatures above 550°C, the volume of micropores, which are mainly represented by the interlayer space, is much reduced. In pillared MM, the change in the basal space under the influence of temperature is much less pronounced, which can be seen from the data on changes in the amount of adsorption of MB on the pillars. Thus, during heat

treatment, the adsorption capacity A_0 for 10-FeKr and 10-FeNb decreases by 12.0 and 14.2%, while for their natural precursors it is more than 34.3 and 49.8%.

Various models were used to describe the adsorption equilibrium in the studied systems. The experimental data on MB adsorption on the studied objects showed the possibility of describing them by the Langmuir equation up to the equilibrium concentration, which is proved by the high values of the correlation coefficient R^2 (Figure 3).
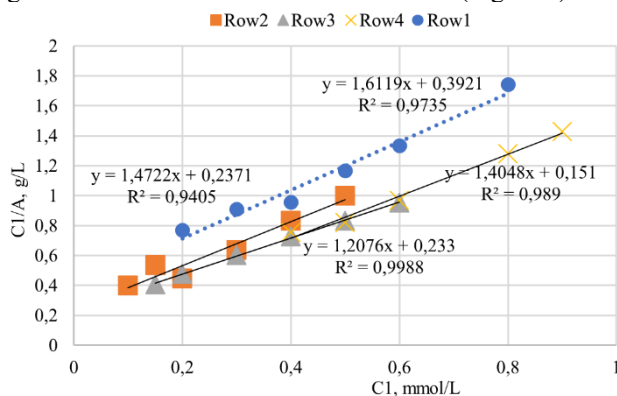
Fig. 3. Isotherms of MB adsorption on intercalated samples: 1) Kr; 2) 10-FeNb; 3) 10-FeKr; 4) Nb in the coordinates of the linear Langmuir equation.

Using the data from the diagram (the tangent of the slope of the straight line and the value of the segment cut off on the y-axis) corresponding to $1/A_\infty$ and $1/A_\infty*K$, the values of K and A∞ were calculated for the first two samples. The data obtained are given in Table. 1.

Experimental results have shown that the sorption capacity of intercalated MMs for an anionic dye is much higher than the values of their natural precursors (Figure 2 B). Probably, the anionic activity of materials is primarily due to the charge of the surface of the material.

Table 1. Parameters of Langmuir isotherms for the studied samples (500°C) by the method of linear regression.

Samples	MB adsorption parameters					Parameters for CR adsorption				
	R^2	A_∞, mmol/g	S, m²/g	ΣV_{pore}, cm³/g	K	R^2	A_∞, mmol/g	S, m²/g	ΣV_{pore}, cm³/g	K
Kr	0.9735	0.62	392.16	0.488	4.111	0.9998	0.036	45.07	0.192	16.01
Nb	0.989	0.71	448.925	0.413	9.325	0.9907	0.053	67.41	0.205	20.02
10-FeNb	0.998	0.828	523.435	0.532	5.183	0.9953	0.143	181.31	0.653	20.35
10-FeKr	0.9988	0.679	429.357	0.492	6.209	0.9983	0.177	223.86	0.612	19.83

The adsorption value of CR on calcined 10-FeKr and 10-FeNb is 2; 2.04 folds higher than in natural forms. Despite the large specific surface area of the initial Nb compared to Kr (143 and 109 m²/g, respectively), the adsorption capacity for CR is higher in 10-FeKr.

Consequently, the adsorption activity according to CR corresponds more to the number of anion exchange centers than to the change in the total specific surface area of these pillar adsorbents. It can be attributed by that the CR dye has relatively large molecular sizes, due to which they are not able to be adsorbed on micropores. Obviously, that the sharp rise in the Fe adsorption isotherms of intercalated MMs is primarily associated not only with the presence of accessible pores, but also with a large amount of surface anion-exchange ions. Nevertheless, the adsorption capacity for CR anions decreases upon calcination starting from 250°C for these sorbents, which is associated with a decrease in anion exchange centers that were introduced into the interlayer space of the MM during intercalation.

Thus, the adsorption studies carried out show that the intercalation of Fe^{3+} ions into the interlayer space of the MM affects their adsorption activity with respect to the anionic dye. The values of the specific surface area for the initial Kr and Nb, calculated on the basis of the CR adsorption isotherm, are 45.07 and 67.41 m^2/g, while for their pillar forms they are 223.86 and 181.31 m^2/g.

As it turned out, in the presence of oxidizers in the dye solution, the studied pillared materials are capable of exhibiting catalytic activity. Wherein, for the initial MMs without active pillars, no significant changes were observed in the interlayer space for dye solutions in the presence of oxidizing agents. It was found that with an increase in the concentration of iron (III), i.e. with an increase in pillared MM in the system, at a constant content of H_2O_2, the discoloration degree of the dye solution increases. The dependence of the conversion degree of MB and CR on time is exponential behaviour (Figure 4).

Indeed, with the consumption of 10-FeKr iron from 2 to 10 g/l, an almost 5-fold increase, the discoloration degree of CR increased from 25 to 91% in 30 min of contact in the oxidizing system. Consequently, the more stable pillared Fe^{3+}, the greater the activity of these materials. When using the 10-FeNb catalytic system, the degree of discoloration of MB and CR solutions was 98 and 94% for 45 min interaction time.

The spectrophotometric analysis of solutions revealed that with an increase in the concentration of Fe^{3+}, a more intense destruction of the molecules of cationic and anionic dyes is observed, as evidenced by a decrease in the intensities of pronounced absorption bands with maxima at 620 cm^{-1} for MB and 517 cm^{-1} for CR, as well as at 322 cm^{-1} corresponding to the coloring azo group and the aromatic ring. The absorption peak of oxidation products in the UV region below 250 nm increased until they completely disappeared.
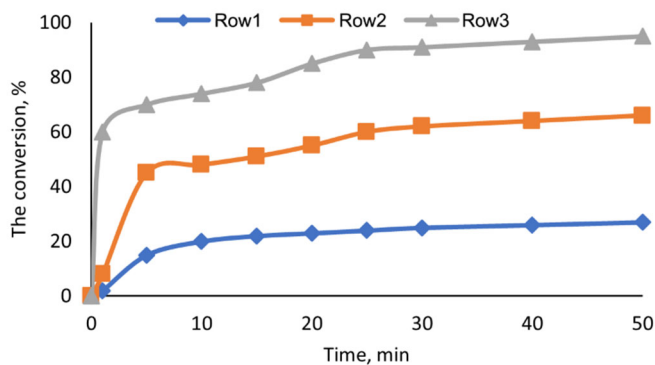
Fig. 4. Dependence of the degree of discoloration (%) of the CR solution (C_{CR}=1 mmol/l) on the duration of the process at various costs of 10-FeKr, g/l: 1) 2; 2) 5; 3) 10.

In all experiments to establish the catalytic activity, forms of pillar clays heat-treated at temperatures above 500°C were used; they are sensitive to an acidic environment and their activity is greatly reduced with an increase in the pH of the medium.

At the same time, the dependence of the catalytic activity of intercalated MMs on the temperature of its calcination was established, a tendency was observed to decrease in activity with increasing temperature, probably due to the deterioration of their surface properties. However, at high ignition temperatures, Fe^{3+} ions are more intensively fixed, preventing their washing out. It turned out that after the oxidative destruction of MB in the system with pillar MM, obtained at temperatures of 400 and 550°C, the Fe^{3+} concentration in the aqueous medium was 0.18 and 0.02 mg/L, respectively (the values obtained in the system with CR differ by approximately 0.6-1%).
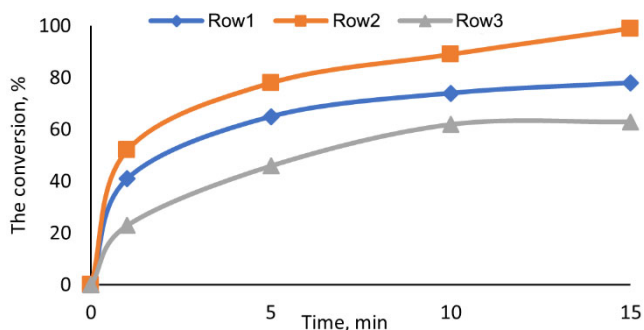
Fig. 5. Dependence of the discoloration degree (%) of a solution of CR with a concentration of 100 mg/L on the duration of the process, at temperatures, °C: 1) 25; 2) 55; 3)75. Catalyst consumption 2 g/l.

A comparative experiment was carried out using a homogeneous catalyst, which was $Fe_2(SO_4)_3$. Comparison of these results showed that at the same consumption of the active components of the catalysts, the rate of CR oxidation in a homogeneous process is higher than in a heterogeneous one. The kinetic curves of concentration change have an induction period that disappears with an increase in the amount of catalyst. Of course, this fact can be explained with the diffusion difficulties of the adsorbate and oxidant molecules on the surface of the adsorbent. Probably, a part of Fe^{3+} in the structure of montmorillonite pillars present in the crystal lattice of montmorillonite is difficult to access for these reagents.

The effect of the process temperature on its rate was studied. It has been established that an increase in the temperature of catalytic oxidation from 25 to 55°C increases the degree of discoloration of the CR solution under homogeneous conditions by 1.5 folds or more, and under conditions of heterogeneous catalysis at least three times. A further increase in temperature practically does not lead to an increase in the degree of CR conversion due to the thermal decomposition of oxidant molecules (Figure 5).

5 Conclusion

Thus, as a result of pillaring, the adsorption activity of MM changes with respect to various adsorbates. If the observed adsorption capacity for MB of natural MM correlates with the amount of cation-exchange capacity and the value of the total specific surface area.

Whereas, during adsorption on the surface of pillared MM, the total negative charge of the surface plays a primary role, due to which ion-exchange adsorption proceeds.

The rate and yield of the process of oxidative degradation of dyes depends on the amounts of pillared clays in the system. The process temperature also affects the rate of catalysis and the clarification degree. A distinction has been found between heterogeneous and homogeneous catalysis. Despite the high rates of dye conversion in a homogeneous process, heterogeneous catalysis has its advantages in the form of multiple cyclic applications in this

process. Fe-pillared MM has been established that are active catalysts for the oxidation of dyes by hydrogen peroxide in aqueous solutions and lead to its 100% conversion. An increase in the temperature of catalytic oxidation from 25 to 55°C increases the degree of discoloration of the CR solution under homogeneous conditions by 1.5 folds or more, and under conditions of heterogeneous catalysis at least three times. A further increase in temperature practically does not lead to an increase in the degree of CR conversion due to the thermal decomposition of oxidant molecules.

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