Purification of aqueous solutions of methylene blue by adsorption on montmorillonite

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Abstract. The adsorption of cationic dye methylene blue on natural and Fe-modified materials obtaining two methods was investigated. It was established that adsorptive capacity of natural and Fe-modified materials depends on their cation-exchange capacity. It was determined that the adsorption capacity of Fe-modified materials with respect to the dye "methylene blue" in aqueous solution depends on the method of obtaining. The adsorption of methylene blue on sorbents describes by Langmuir model (the correlation coefficients are 0.9858-1.0000), which corresponds to monolayer adsorption on a homogeneous surface.

1. Introduction

Currently, intensive pollution of natural waters with organic dyes occurs as a result of wide use of dyes in the textile and paper industry. The dyes at high concentrations are resistant to biodegradation. They are carcinogenic and toxic to aquatic living organisms [1, 2]. Therefore, the discharge of wastewater containing dyes without treatment can cause significant damage to human health and the environment. There are various physical-chemical technologies for removing dyes from aqueous solutions, including chemical oxidation [3], electrochemical methods, photocatalysis, adsorption, etc. [4-6]. Among various available methods for dyes removal from wastewater, adsorption is one of the most widely used due to its applicability to the removal of numerous pollutants and simplicity of design and operation [7].

In an effort to improve the economy of sorption processes the problem of developing efficient and fairly cheap sorbents based on natural materials is becoming actual. Among the natural sorbents the most effective are clay minerals, in particular, montmorillonite. The use of clay minerals can significantly reduce the content of dyes in wastewater, reduce the cost of cleaning, as well as avoid the formation of secondary pollution.

As is known, natural clay minerals are very effective in adsorption of cationic dyes, but it is impossible to extract the dye back. Because is the use of modified clay minerals is more appropriate. The modification of natural clays by various compounds leads to a change in their porous structure and the nature of the surface, which expands the possibilities of their use in sorption processes. We have previously shown that the modification of natural clays with aluminum and iron polyhydroxocomplexes leads to an increase in their adsorption capacity with respect to anionic dyes [8].

In this work the adsorption of the cationic dye methylene blue (MB) on natural and Fe-modified clays was studied.
2. Experimental

In this work, bentonite clay from Tuldon deposit (Buryatia) which was mainly represented by montmorillonite (65%) and kaolinite (5%) and had the following chemical composition: (mass%) SiO₂ - 69.0, A₂O₃ - 16.7, Fe₂O₃ - 2.6, CaO - 1.5, MgO - 1.3, K₂O - 2.8, Na₂O - 2.2, H₂O - 5.7 was used. Montmorillonite (Mt) was separated from impurities and its purity was 95%.

Two forms of Fe-modified clays were prepared on the basis of montmorillonite: Fe-Mt and Fe-Mt (US), which were obtained as follows: a modifying solution containing iron polyhydrocomplexes of the composition [Feₓ(OH)ᵧ(H₂O)₆₋ₐ₋]⁽³ₓ₋ᵧ⁺ was prepared by slowly adding a NaOH solution to 1 M FeCl₃ solution, with vigorous stirring, so that the OH⁻/Fe³⁺ ratio was 1.5. Then the solution was subjected to ageing at room temperature for 24 h to form polyhydroxocomplexes of iron. Then the modifying solution was slowly added to I) a 10% clay slurry (Fe-Mt) and II) a clay slurry treated with ultrasound (US) 22 KHz for 3 minutes (Fe-Mt/US) with a ratio of Fe³⁺/clay 2.5 mmol g⁻¹ clay. Fe-modified clay was kept at room temperature for 24 h, washed off by water to negative reaction on chloride ions, condensed by centrifugation, dried at room temperature and calcined at 500 °C for 2 h.

Textural characteristics of the samples were measured by low-temperature nitrogen adsorption on an ASAP-2400 Micromeritics unit at 77 K using the standard procedure. Adsorption studies were carried out using the limited volume method. When determining the equilibrium adsorption, an aqueous solution of MB with a preset initial concentration (100–3000 mg · l⁻¹) was added to a portion of clay weighing 0.1 g, stirred at 200 rpm for 48 hours (equilibration time) on a shaker LAB-PU-01, then the sorbent was separated from the liquid by centrifuging at 4000 rpm. The concentration of the dye in the aqueous solution was determined spectrophotometrically by using a UV-vis Agilent 8453 spectrophotometer at a wavelength of 490 nm, corresponding to the maximum absorption of the dye. The amount of MB dye adsorbed on natural and modified materials (q, mg · g⁻¹) was calculated by the formula:

\[ q_t = \frac{(C_0 - C_t) \cdot V}{m} \]

C₀ is the initial concentration of MB dye in solution, mg · l⁻¹; Cₜ is the concentration of MB dye in solution at the moment of time t, mg · l⁻¹; V is the volume of MB dye solution, l; m is the weight adsorbent, g.

To determine cation-exchange capacity of the samples was carried out by substitution of exchange cations of natural and modified clays to ammonium cations. The excess of ammonium cations was measured by photometric method using Nessler's reagent and potassium-sodium tartrate. The iron content in the obtaining sorbents was determined by the photometric method with ortho-phenanthroline.

3. Results and Discussions

Textural characteristics of the sorbents, calcined at 500 °C, are presented in Table 1.

|          | Sₘₐ (m² g⁻¹) | Dₚore (nm) | Vₚore (cm³ g⁻¹) | Vₜ (cm³ g⁻¹) | CEC (mg-equiv g⁻¹) |
|----------|--------------|------------|-----------------|--------------|-------------------|
| Mt       | 60.80        | 9.51       | 0.140           | 0.003        | 0.73              |
| Fe-Mt    | 95.05        | 8.02       | 0.191           | 0.033        | 0.33              |
| Fe-Mt (US)| 99.33       | 8.41       | 0.209           | 0.027        | 0.48              |

Sₘₐ – surface area,
Vₚore – pore volume,
Dₚore – pore diameter,
Vₜ – micropore volume.
It can be seen from table 1 that the modification of natural clay with polyhydroxocomplexes of iron and their further calcination at 500 °C leads to an increase in the specific surface area and an increase in the pore volume, as compared to natural clay. However, modification of clay contributes to formation of micropores, but reduces the average pore diameter by 10–15%. These factors indicate the introduction of iron cations into the interlayer space of clays and formation of a layer-pillar structure of Fe-modified clays, which can be schematically presented in the form of "house of cards". When comparing the textural characteristics of Fe-modified clays, it is seen that with ultrasound, there is a slight increase in the specific surface and pore diameter and pore volume by 4-8%, while the volume of micropores decreases by 18% (Table 1).

Adsorption properties of natural and Fe-modified materials have been studied with respect to the aqueous solution of the dye, methylene blue (MB), which belongs to the thiazine series of dyes and has the following structure (Figure 1).

![Figure 1. The chemical structure of MB.](image)

The equilibrium isotherms of dye adsorption on the sorbents: natural Mt, Fe-Mt and Fe-Mt (US) are presented in figure 2. According to the shape of the initial part the isotherms of MB on all sorbents belong to H-type, which are observed at strong adsorption and at low concentrations of the adsorbate, which indicate to a high affinity of sorbents to MB.

![Figure 2. Adsorption isotherms of MB dye on sorbents: 1 – Mt, 2 – Fe-Mt, 3 – Fe-Mt (US).](image)

Adsorption of dye MB on natural montmorillonite calcined at 500 °C occurs on surface of Mt particles and in mesopores formed by voids between contacting particles, because the volume of micropores in a natural Mt is insignificant (less than 0.003 cm³ · g⁻¹). The cation-exchange centers of the natural Mt are represented mainly by the exchangeable cations of sodium, calcium, and magnesium, which are concentrated on the outer basal surfaces and in the interlayer space of clay. It is known [9] that ~ 80% of the cation-exchange capacity of natural Mt is due to exchange cations, the adsorption of which does not depend on pH. A small part of the cations of dye MB can be sorbed on the side faces, replacing the protons in the Si-OH groups, which dissociate to pH 2 according to the acid type.

A comparative analysis of the adsorption isotherms of MB dye on the studied materials (Figure 1) shows that Fe-modified clays have a lower sorption, compared to natural clay, although they are characterized by a higher specific surface. This is due to the fact that the columns of Fe₂O₃ oxides,
formed as a result of the calcination of the modified clays, limit the access of dye molecules, which in aqueous solutions can exist as monomers and dimmers, into the pores of the sorbent. The adsorption capacity of sorbents correlates well with the value of their cation-exchange capacity (CEC), determined by ammonium ions (Table 1). It has been established that the adsorption capacity of Fe-Mt (US) (181.2 mg · g⁻¹) is larger compared to Fe-Mt (76.2 mg · g⁻¹), which is due to the larger specific surface, pore diameter and a large number of mesopores.

The Langmuir and Freundlich models are usually used to describe adsorption mechanisms [10]. The Freundlich isotherm describes multilayer adsorption and assumes that the surface of the sorbent has a heterogeneous character. The correlation coefficients of adsorption of MB on sorbents had the following values: R² - 0.8567 (Mt), R² - 0.6387 (Fe-Mt) and R² - 0.863 (Fe-Mt (US)). It indicates that the experimental data do not correspond to the Freundlich isotherm. The obtained sorption isotherms of MB were also analyzed using the Langmuir model (Figure 3). This model assumes that adsorption occurs on a homogeneous surface of the sorbent, and the adsorption centers of the sorbent are equally accessible and energy equivalent, with each center carrying the same number of molecules and without interaction between the dye molecules [11]. The Langmuir expression and its linearized form are represented by the following equations [11]:

$$q_e = \frac{K_L C_e}{1 + a_L C_e}$$

where qₑ is the amount of MB sorbed per unit mass of the sorbent (mg · g⁻¹); Cₑ is the equilibrium concentration of MB in solution (mg · l⁻¹); K_L and a_L are Langmuir constants found from the intersection and slope of the straight line \(C_e q_e^{-1}\) versus \(C_e\).

![Figure 3. Langmuir plot of adsorption onto Mt (1), Fe-Mt (2) and Fe-Mt (US) (3).](image)

Correlation coefficients closed to 1, calculated from the linear form of the Langmuir isotherm, indicate a monolayer coating by molecules of MB on the surface of sorbent particles, which correspond to the maximum adsorption capacity [12].

4. Conclusion
Thus, it has been established that the modification of natural clay with iron polyhydroxocomplexes leads to an increase in the specific surface and pore volume. Adsorption studies on natural and Fe-modified clays were carried out at different initial dye concentrations. Langmuir and Freundlich models were used to describe adsorption isotherms. Adsorption isotherms were well-fitted by Langmuir model. The high adsorption capacity of Fe-Mt (UZ) shows that this modified clay can be used as a sorbent for the removal of thiazine dyes.
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