Natural clays as effective sorbents of anthropogenic pollutants

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Abstract. In this work, the adsorptive properties the Tuldon deposit were studied using the example of the adsorption of the basic dye “Methyl Green” from aqueous solutions. It has been established that the kinetic regularities of the dye adsorption on clay are consistent with the model of the kinetics of the pseudo-second order, characteristic of chemisorption. The isotherm of the dye adsorption is in good agreement with the Langmuir model. The results of the study allow us to conclude that the clay of the Tuldon deposit can be an effective sorbent for removing basic dyes from aqueous media.

1. Introduction

Currently, an actual environmental problem is the growing pollution of the environment with harmful substances, the appearance of which is caused by human activities. These include synthetic dyes, which are used for dyeing of products of the pulp and paper, paint and varnish, printing and cosmetic industries; and are contained in the wastewater of these industries in high concentrations [1]. The widespread use of synthetic dyes having a complex aromatic structure with the presence of various functional groups is due to their low cost and a wide variety of colours. The high solubility of dyes in water, low biodegradability, the ability to inhibit the process of photosynthesis of plants causes their toxic, carcinogenic and even mutagenic properties, which poses a serious danger to aquatic organisms. In addition to dyes, coloured wastewater also contains other accompanying organic and mineral contaminants, such as surfactants, aromatic hydrocarbons, organic and mineral acids, chlorides, sulphates and heavy metal ions (chromium compounds), which are characterized by high values of chemical oxygen demand. Treatment of coloured wastewater before being discharged into water bodies is necessary to reduce the concentration of pollutants to the maximum permissible values (the maximum permissible concentration for a number of dyes should not exceed 0.1 mg·L⁻¹). For these purposes, there are various methods of purification of coloured wastewater (ion exchange, coagulation, flotation, chemical precipitation, reverse osmosis, membrane filtration, biological decomposition, etc.), but these methods have certain limitations [2-4].

Adsorption on porous materials is recognized as one of the most reliable technologies available for removing organic and inorganic compounds from water, provided the appropriate adsorbents are selected. The most widely used industrial sorbent is activated carbon [5-7]. However, its high cost and the need for an expensive regeneration system make it urgent to search for alternative cheap sorption materials [8]. Materials such as clay minerals [9], peat [10], coconut shells [11, 12], zeolite [13], silica balls [14], sawdust [15] can be used as sorbents. Clay minerals are one of the most promising sorbents for removing pollutants, since they have high sorption activity due to their chemical composition and features of their structure. Their widespread occurrence in nature, the ease of their extraction from a deposit and the possibility of using them in their natural form determine the low cost of clay minerals and the high efficiency of adsorption technologies for water purification based on their use.
2. Models and Methods

A natural clay from the Tuldon deposit (Republic of Buryatia) was used in the work. The clay fraction was preliminarily purified from large impurities by dispersion and settling in a water column, then dried at room temperature. The study of the adsorptive properties of clay was carried out using the example of the dye “Methyl Green” (MG), the structure and absorption spectrum of which are shown in Figure 1.

![Chemical structure and absorption spectrum of the dye Methyl Green.](image1)

Figure 1. Chemical structure and absorption spectrum of the dye Methyl Green.

The amount of dye adsorption was determined from the difference between the initial and equilibrium concentrations of the dye aqueous solutions. The dye concentration was determined from the dependence of the optical density of the dye solution on its concentration. The optical density of the solution was measured on an Agilent 8453 UV-Vis spectrophotometer at a wavelength of 632 nm, which corresponds to the maximum absorption of the dye solution. The equilibrium dye adsorption \((q_e, \text{mg} \cdot \text{g}^{-1})\) was calculated by the formula (1):

\[
q_e = \frac{C_0 - C_e}{m} \cdot V
\]

where \(C_0\) and \(C_e\) – initial and equilibrium dye concentrations in solution, \(\text{mg} \cdot \text{L}^{-1}\); \(V\) – the dye solution volume, \(\text{L}\); \(m\) – the mass of the clay, \(\text{g}\).

3. Results and Discussion

The dye Methyl Green refers to the dyes of the triphenylmethane series (Figure 1). It is the basic dye by the type of dissociation in an aqueous solution, decomposing into a coloured cation and an inorganic anion. Triphenylmethane dyes are widely used in various industries for dyeing textile, leather, cosmetic and plastic products, and are also used in medicine [16, 17].

The mineralogical analysis showed that the clay used in the work consisted mainly of the mineral montmorillonite, which belongs to layered aluminosilicates of the 2:1 type, the structure of which consists of an alumina-oxygen octahedron located between two silicon-oxygen tetrahedrons [18]. This mineral is characterized by the presence of a negative charge of aluminosilicate layers resulting from isomorphic substitutions in octahedra (substitution of \(\text{Al}^{3+}\) for \(\text{Mg}^{2+}, \text{Fe}^{2+}\)) and in tetrahedra (substitution of \(\text{Si}^{4+}\) for \(\text{Al}^{3+}\)). The excess negative charge of the layers is compensated for by sodium, potassium and calcium cations, which readily enter into an ion exchange reaction with other cations present in aqueous solutions. The high sorption activity of clay in relation to cations is due precisely to the presence of these exchange cations in its structure. During the adsorption of basic dyes, exchangeable clay cations are replaced by organic dye cations, the binding energy of which with the clay surface is much higher than that of inorganic cations.
To determine the mechanism of dye adsorption, kinetic studies were carried out. Figure 2 (a, b) shows the obtained dependences of the adsorption value of the dye on natural clay on time at different initial dye concentrations. It can be seen that the mass of the sorbed dye increases rapidly during the first ten minutes of contact, which is explained by the presence of a large number of free adsorption centres at the initial stage, which are available for the adsorption of dye particles (fast stage). The rate of adsorption decreases (slow stage) with time and then adsorption equilibrium sets in, due to the complete saturation of the clay surface adsorption centres with the adsorbate molecules [19, 20]. The contact time required to achieve the adsorption equilibrium of the MG dye on natural clay was 30 min.

To analyse the experimental results on the kinetics of adsorption and determine the limiting stage of adsorption of dissolved substances, it is customary to use the kinetic equations of the pseudo-first order (2) and pseudo-second order (3) [21], which have the following form:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

where \( q_t \) is the adsorption value at time \( t \), \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g\(\cdot\)mg\(^{-1}\)\cdot\)min\(^{-1}\)) are the rate constants of the pseudo-first order and pseudo-second order, respectively.

The parameters of the kinetic model of the pseudo-first order were obtained from the linear graphical dependence of the adsorption values at the initial period, plotted in the coordinates \( \ln(q_e - q_t) \) versus time. To obtain the coefficients of the kinetic model of the pseudo-second order, graphical dependences were built in coordinates \( t/q_t \) versus time. The model correctly describes the experimental data if the value of the correlation coefficient \( R^2 \geq 0.94 \). This condition is fulfilled for the kinetic model of the pseudo-second order, where \( R^2 \) lies in the range of 0.9941 ÷ 0.9997, while the values of \( R^2 \) are in the range 0.8985 ÷ 0.9648 for the pseudo-first order model (Table 1). The agreement of the experimental adsorption kinetics with the pseudo-second order model indicates that chemisorption is the limiting stage of MG dye adsorption [21]. The adequacy of this model was also confirmed by the fact that the calculated values of the maximum specific adsorption \( q_e \) were very close to the experimental data and the difference did not exceed 5.1% (Table 1). At the same time, the discrepancy between the experimental values of \( q_e \) and \( q_1 \) calculated by the pseudo-first order model was more than 60%.

### Table 1. Kinetic parameters for the adsorption of Methyl Green on natural clay.

| [MG], mg\(\cdot\)l\(^{-1}\) | \( q_e \) exp., mg\(\cdot\)g\(^{-1}\) | \( q_1 \), mg\(\cdot\)g\(^{-1}\) | \( R^2 \) | \( q_2 \), mg\(\cdot\)g\(^{-1}\) | \( k_2 \), g\(\cdot\)mg\(^{-1}\)\cdot\)min\(^{-1}\) | \( R^2 \) |
|---------------------|-------------------------------|-----------------|--------|-----------------|-----------------|--------|
| 48.9                | 48.9                          | 12.6            | 0.9225 | 50              | 3.32            | 0.9995 |
| 75.2                | 66.5                          | 14.5            | 0.9425 | 66.7            | 2.38            | 0.941  |
| 100.0               | 85.0                          | 57.5            | 0.8985 | 83.3            | 2.48            | 0.992  |
| 131.1               | 95.5                          | 38.0            | 0.9532 | 100.0           | 1.60            | 0.997  |
| 166.4               | 115.0                         | 114.3           | 0.9342 | 113.6           | 1.55            | 0.991  |
| 210.0               | 127.0                         | 39.8            | 0.9202 | 142.9           | 1.63            | 0.996  |
| 240.0               | 144.6                         | 50.2            | 0.9648 | 139.51          | 1.16            | 0.993  |
| 300.0               | 161.8                         | 58.88           | 0.9409 | 169.49          | 1.41            | 0.991  |

To study the type of adsorption and determine the value of the maximum clay adsorptive capacity, the values of equilibrium adsorption were determined at different dye initial concentrations at 25°C. The obtained experimental dependence of the equilibrium dye adsorption on its equilibrium concentrations in the solution is shown in Figure 3. The adsorption isotherm of the dye MG was type H in shape, which is characteristic of adsorbents with a high affinity for the adsorbed substances.
The adsorption capacity of the clay increases with an increase in the equilibrium dye concentration to 138 mg·L⁻¹, then the value doesn’t change. The maximum value of the adsorption of the MG dye on clay is 161.8 mg·g⁻¹, which indicates a rather high cation exchange capacity of the clay. For comparison, the literature data can be cited: the maximum adsorption of the dye MG on sepiolite clay and kaolinite was 60 mg·g⁻¹ [22, 23], the maximum sorption of MG was 456 mg·g⁻¹ after 7 days of adsorption on the SWy-1 clay, enriched in an industrial way [22], which probably indicates multilayer dye adsorption with increasing contact time.
Figure 3. Isotherm of adsorption of the dye MG on natural clay (25°C).

The experimental adsorption isotherm of the dye on natural clay was analysed using the adsorption models of Langmuir and Freundlich (Figure 4). The Langmuir model assumes that adsorption occurs on a homogeneous sorbent surface (the adsorption centres are equally accessible and are energetically equivalent) and there is no interaction between the adsorbed molecules. The Freundlich isotherm assumes that the adsorbent surface is heterogeneous [24].

The linear forms of the Langmuir (4) and Freundlich (5) isotherms are represented by the following equations:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{4}
\]

\[
\log q_e = \frac{1}{n \log C_e} + \log K_f \tag{5}
\]

where \(q_e\) is the equilibrium amount of MG sorbed per unit mass of the sorbent (mg·g\(^{-1}\)); \(C_e\) is the equilibrium concentration of MG in the solution (mg·L\(^{-1}\)); \(K_L\) and \(a_L\) are constants of the Langmuir equation; \(K_f\) and \(n\) are the adsorption constant and the adsorption rate constant, respectively [24].

The value of the correlation coefficients according to the Langmuir model was equal to \(R^2 = 0.9707\), and for the Freundlich model \(R^2\) was 0.9162 (Figure 4). The experimental adsorption isotherm correlates better with the Langmuir model, which indicates the homogeneity of adsorption centres and monolayer coverage of the clay surface with dye particles.

Figure 4. Experimental data on the adsorption of MG in the linear forms of the Langmuir (a) and Freundlich (b) equations.
Figure 5 shows the dependence of efficiency of the dye removal from aqueous solutions on its initial concentrations. The dye removal efficiency depends on the ratio of the dye concentration and the loading of clay in the solution to be purified. The efficiency decreases from 100% to 85% when the dye concentration increases from 48.9 mg·L⁻¹ to 100 mg·L⁻¹. The concentration of dyes in coloured wastewater usually does not exceed 50 mg·L⁻¹, at this concentration it is enough to add 1 g·L⁻¹ of clay to achieve a high degree of water purification.

4. Conclusion
It can be concluded from the obtained results that the clay of the Tuldon deposit has a high adsorption capacity in relation to the basic dye Methyl Green. It was established that the kinetic regularities of the adsorption of the MG dye on clay are consistent with the model of the kinetics of the pseudo-second order, characteristic of chemisorption. The isotherm of the dye adsorption is in good agreement with the Langmuir model. The results of the study allow us to conclude that the clay of the Tuldon deposit can be an effective sorbent for removing basic dyes from the aquatic environment.

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