Removal of Congo Red Dye from aqueous solutions using natural clay of montmorillonite type

S V Badmaeva

Laboratory of Engineering Ecology, Baikal Institute of Nature Management, 6 Sakhyanova Str., Ulan-Ude 670047, Russia

E-mail: sbadm@mail.ru

Abstract. Natural clay of the montmorillonite type, heated at different temperatures, was studied in removal of the Congo Red anionic dye, which is a component of the wastewater of the dyeing industry by the adsorption method. It was shown that with an increase in the calcination temperature of the clay the specific surface, pore diameter and pore volume decreased. The calcination temperature also affected the adsorption properties of clay. It has been established that the largest sorption capacity with respect to the Congo Red dye is possessed by a sample heated at 104 °C. Sorption isotherms were analyzed using linear Langmuir and Freundlich equations. It was determined that the adsorption of the dye on natural clay was in good agreement with the Langmuir adsorption isotherm with a correlation coefficient of 0.9751-0.9966, which corresponded to monolayer adsorption on a uniform surface.

1. Introduction
The development of the textile industry has a strong environmental impact. Colored industrial wastewater arises as a direct consequence of the production of dye, as well as a result of the activities of the textile, pulp and paper, paint and varnish, printing and cosmetic industries. There are various classes of dyes used to color various substrates, which in most cases are of a synthetic nature. Typically, the dye structure consists of aromatic rings and functional groups (NR₂, NHR, NH₂, COOH, OH, N₂, NO and NO₂) [1], as a result of which they can be toxic, carcinogenic and mutagenic properties. Due to their low biodegradability the dyes pose a significant danger to aquatic organisms and humans [2-4]. Therefore, they must be processed in order to reduce their concentration to an acceptable limit before discharge into water bodies in accordance with the requirements of the law on environmental protection. There are various methods for treating wastewater contaminated with dyes such as ion exchange, coagulation, flotation, chemical deposition, reverse osmosis, membrane filtration, biological decomposition, oxidation), but all of these methods have one or another restrictions [5-6]. Among them adsorption on porous materials (zeolites, activated carbon, clay minerals) with a high specific surface area is recognized as one of the safest technologies available for removing pollutants from water provided that the appropriate adsorbents are selected [7-10]. The advantage of adsorption is the low initial cost of materials, simplicity of construction and maintenance, universality and insensitivity to toxic substances (hydrophobic organic compounds, cationic/anionic dyes, heavy metal). Activated carbon is the most well-known industrial sorbent, but due to its high cost and the need for an expensive regeneration system, the search for effective and cheap sorbents...
based on natural dispersed materials becomes is actual. Clay minerals such as bentonite clay are promising for the removal of organic and inorganic compounds from wastewater due to their high specific surface and cation-exchange capacity, chemical and mechanical stability, prevalence, surface characteristics [11–14], as well as the absence of secondary pollution.

In this work we studied the adsorption of the Congo Red dye using natural montmorillonite as an adsorbent.

2. Experimental
Bentonite clay with the following chemical composition (mass,%) was used as a sorbent: SiO₂-65.5; Al₂O₃-14.3; Fe₂O₃-1.8; CaO-1.5; MgO-1.1; K₂O-0.2; Na₂O-0.1; loss at calcination -15.5 [15]. The major component of the bentonite sample was montmorillonite as could be concluded from the proximate analysis and XRD reports. Some impurities like quartz, mica, and feldspar were also present in bentonite clay. Anionic dye Congo Red contains NH₂ and SO₃ functional groups with chemical formula C₃₂H₂₂N₆Na₂O₆S₂ was used as sorbate. The dye concentration in the aqueous solution was evaluated spectrophotometric method on a UV-Vis Agilent 8453 spectrophotometer (Agilent Technologies, USA) at 498 nm, the measurement accuracy of ± 5%. The value of specific adsorption was determined by the formula (1):

\[
q_t = \frac{C_o - C_t}{m} \cdot V,
\]

where \(q_t\) is the amount of dye adsorbed per 1 g of sorbent at a given time \(t\), (mg·g⁻¹);

\(C_o\) is the initial concentration of the dye solution, mg·L⁻¹,

\(C_t\) is the concentration of the dye solution at time \(t\), mg·L⁻¹,

\(m\) is the mass of the sorbent, g,

\(V\) is the volume of the dye solution, L.

The low-temperature nitrogen adsorption was used on a ASAP-2400 Micromeritics for determine the specific surface area (\(S_{BET}\)) of the materials. Powder X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer STADI P (STOE, Germany) with a Ge-monochromator (CuKα irradiation, 2θ = 4–77°).

3. Results and discussion
The textural characteristics of montmorillonite, determined by the method of low-temperature adsorption / desorption of nitrogen [16], are presented in Table 1. Calcination at 500 °C leads to a decrease in the specific surface and total pore volume, but the pore diameter slightly increases. Also during calcination, adsorption and structural water were removed, which led to a decrease in the interlayer space from 14.9 to 9.4 Å due to the sticking together of silicate layers as shown in Table 1.

|          | \(S_{BET}\), m²·g⁻¹ | \(V_{pore}\), cm³·g⁻¹ | \(D_{pore}\), Å | \(d_{001}\), Å |
|----------|---------------------|-----------------------|----------------|----------------|
| Mt-25°C  | 119                 | 0.27                  | 91             | 14.9           |
| Mt-104°C | 116                 | 0.27                  | 97             | 12.4           |
| Mt-500°C | 109                 | 0.25                  | 94             | 9.4            |

Azo dyes are commonly used for dyeing fabrics in the textile industry, however, many of these compounds pose a health hazard if released into the environment with wastewater. Adsorption properties of natural montmorillonite were carried out using the CR azo dye as an example, the electronic absorption band and the structural formula of which are shown in Figure 1.
Figure 1 shows the adsorption isotherms of the Congo red dye on natural montmorillonite heated at 25, 104 °C and calcined at 500 °C. It can be seen that natural montmorillonite has a fairly good sorption capacity with respect to anionic dyes, since it is known that the anion exchange properties are due to the presence in their structure of hydroxyl groups AlOH, FeOH, MgOH [17]. A sample of Mt-25 °C and Mt-104 °C have a higher adsorption capacity compared to Mt-500 °C at the dye concentration up to 500 mg·L⁻¹. Their increased sorption is primarily due to the fact that the samples retain the ability to swell. With a further increase in the dye concentration, adsorption on Mt-25 °C slows down and reaches a plateau at equilibrium dye concentration 700 mg·L⁻¹, which indicates the saturation of the adsorption centers of the sorbent with dye molecules. However, on the curve of the adsorption isotherm at Mt-104 °C at a concentration above 500 mg·L⁻¹, no plateau is observed, as well as on the curve of the isotherm at Mt-500 °C. The shape of the isotherm is primarily due to the fact that when heated at 104 °C and 500 °C, adsorption and structural water are removed, which gives access to the main hydroxyl groups AlOH, FeOH, MgOH, which are located on the side faces and edges of clay crystallites [17]. It leads to an increase in the anion-exchange properties of layered aluminosilicates. The large adsorption capacity of Mt-104 °C may also be due to the fact that the clay structure still retains the ability to swell in an aqueous solution, as well as to the fact that the dye molecules in an aqueous solution at equilibrium dye concentration above 0.7 mmol·L⁻¹ exist in the form of large associates (f₁ = 20 ÷ 50). The lower adsorption of CR at Mt-500 °C is explained by the fact that when the clay is calcined, the silicate layers stick together, because of which the accessible surface of the clay decreases, which leads to a decrease in its adsorption capacity.

A comparison of the adsorption values of CR on natural montmorillonite and active carbon shows that the samples exceed active carbons in their adsorption capacity as shown in Figure 2 [18]. Thus, dye adsorption depends on the presence of anion exchange centers, the available specific surface area of the sorbent and the nature of the dyes.

Correlation of equilibrium data using various adsorption models is important for interpreting adsorption and predicting the degree of adsorption. Therefore, the obtained experimental adsorption isotherms were analyzed using the most well-known Langmuir and Freundlich models in this work. The Langmuir isotherm describes monolayer adsorption on a homogeneous surface while the Freundlich adsorption isotherm describes multilayer adsorption on an inhomogeneous surface [19].

The linear form of the Langmuir isotherm is expressed by the equation (2):

\[
\frac{C_e}{q_e} = \frac{1}{Q_{\text{max}} \cdot K_L} + \frac{C_e}{Q_{\text{max}}}
\]

where \( Q_{\text{max}} \) - constant corresponding to maximum adsorption, mg·g⁻¹;

\( K_L \) - Langmuir constant, depending on the adsorption energy and temperature, L·g⁻¹.
Figure 2. Sorption isotherms of Congo red dye on natural montmorillonite, calcined at different temperatures: 25 °C (1), 104 °C (2) and 500 °C (3) and CAD-iodine activated carbon (4) [18].

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

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

(3)

where $K_f$ - Freundlich adsorption constant, L·g⁻¹;

$n$ - Freundlich experimental constant describing the intensity of adsorption.

Figure 3 presents graphs of linear functions of the Langmuir and Freundlich isotherms. The values of the correlation coefficients $R^2$ indicate that the adsorption of Congo Red on natural montmorillonite is in good agreement with the Langmuir adsorption isotherm with a correlation coefficient of 0.9751-0.9966, while the coefficient for the Freundlich isotherm is 0.8577-0.9621, which is in agreement with the data [20].

Figure 3. Isotherms of CR adsorption represented in the coordinates of the linearized Langmuir (a) and Freundlich (b) equations on: Mt-25 °C (1), Mt-104 °C (2) and Mt-500 °C (3).

4. Conclusion
The adsorption properties of montmorillonite clay heated at temperatures of 25, 104 and 500 °C with respect to the Congo Red anionic dye in an aqueous solutions are investigated. It was shown that, the clay specific surface, pore volume, and pore diameter decrease with an increase in the calcination temperature of the samples. Adsorption studies were carried out at room temperature in the dye
concentration range of 50–3000 mg·L⁻¹ at pH 6.7. It was established that the sample heated at 104 °C had the highest sorption capacity. The obtained isotherms were analyzed using the Langmuir and Freundlich isotherms. It was determined that the adsorption of the dye on natural clay is in good agreement with the Langmuir adsorption isotherm with a correlation coefficient of 0.9751-0.9966, which corresponds to monolayer adsorption on a uniform surface. Thus, we can conclude that bentonite clay can be used as an inexpensive, natural and effective sorbent for removing of Congo Red dye and it can be an alternative to more expensive materials.

References
[1] Gupta V K, Suhas 2009 J. Environ. Manag. 90 2313
[2] Habiba U, Siddique T A, Joo T C, Salleh A, Ang B C and Afifi A M 2016 Carbohydr. Polym. 157 1568
[3] Tijani J O, Fatoba O O, Madzivire G and Petric L F 2014 Water Air Soil Pollut. 2102 1
[4] Kok Bing Tan B. S., Vakili M, Horri B A, Poh Ph E and Abdullah A Z 2015 Sep. Purif. Technol. 150 229
[5] Khankhasaeva S Ts, Dambueva D V and Dashinamzhilova E Ts 2012 J. Appl. Chem. 85 1095
[6] Nguyen Th A and Juang R-Sh 2013 Chem. Eng. J. 219 109
[7] El Haddad M 2016 J. Taibah Univ. Sci. 10 664
[8] Pires J, Carvalho A, de Carvalho M B 2001 Micropor. Mesopor. Mater. 43 277
[9] Rouquerol J, Llewellyn Ph, Sing K 2014 Adsorption by Powders and Porous Solids (Second Edition) (New York: Academic Press) p 646
[10] Herrera-González A M, Caldera-Villalobos M, Peláez-Cid A A 2019 J. Environ. Manag. 234 237
[11] Chaari I, Feki M, Medhioub M, Bouzid J, Fakhfakh E and Jamoussi F 2009 J. Hazard. Mater. 172 1623
[12] Chaari I, Moussi B and Jamoussi F 2015 J. Alloy. Compd. 647 720, 216
[13] Bentahar S, Dbik A, El Khomri M, El Messaoudi N and Lacherai A 2017 J. Environ. Chem. Eng. 5 5921
[14] Khosla E 2015 J. Chem. Appl. Biochem. 2 1
[15] Badmaeva S V, Khankhasaeva S Ts and Dashinamzhilova E Ts 2019 IOP Conference Series: Earth and Environmental Science 272 032081
[16] Gregg S J and Sing K S W 1982 Adsorption Surface Area and Porosity (New York: Academic Press) p 310
[17] Tarasevich Yu 1988 The Structure and Surface Chemistry of Layered Silicates (Kiev: Naukova Dumka) p 248
[18] Doroshenko V E, Tarasevich Yu I and Rak V S Chemistry and technology of water 1989 11 500
[19] Kennedy Oubagaranadin J U and Murthy Z V P 2010 Appl. Clay Sci. 50 409
[20] Bulut E, Mahmut Özacar M and Şengil I A 2008 J. Hazard. Mater. 154 613

Acknowledgments
The study was carried out under the State assignment to Baikal Institute of Nature Management of Siberian Branch Russian Academy of Sciences.