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Adsorption of Triarylmethane Dye on Ca-Montmorillonite: Equilibrium, Kinetics, and Thermodynamics

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Abstract—The equilibrium, kinetics, and thermodynamics of adsorption of triarylmethane dye, crystalline violet, from aqueous solutions on Ca-montmorillonite have been studied. The regularities of the influence of the physicochemical parameters (suspension pH, clay and dye concentrations, temperature, and contact time) on the specific adsorption value of the dye have been found. It has been shown that Ca-montmorillonite is capable of removing the dye from aqueous solutions in a wide range of concentrations with an efficiency of up to 99.8%. The adsorption of crystalline violet obeys the Langmuir model (the correlation coefficient is 0.999), which corresponds to monolayer adsorption on a homogeneous surface. The kinetics of dye adsorption is described by a pseudo-second-order equation, which is characteristic of chemisorption. The thermodynamic parameters of adsorption, $\Delta H = 40.42$ kJ/mol, $\Delta S = 139.6$ J/mol, and $\Delta G = -4.68$ kJ/mol (323 K), have been determined and lead to the conclusion that the dye adsorption is a spontaneous endothermic process.

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INTRODUCTION

Dyes are widely used for painting products in many branches of industry (light, food, chemical, pulp-and-paper, etc.), as well as in printing. The production and use of synthetic dyes is accompanied by the formation of contaminated wastewater containing water-soluble organic dyes. The most efficient method of wastewater purification from organic dyes is adsorption [1]. The use of sorption methods is economically advantageous in closed water-supply systems of industrial plants, because these methods make it possible to desorb dyes and repeatedly use purified wastewater in a production cycle. Currently, active carbons are most commonly used as adsorbents in industry due to their developed porous structure and surface characteristics [2–5]. However, the wide practical application of active carbons in the processes of wastewater purification from dyes is constrained by their high cost and difficult recovery after use. Results of recent studies have shown that, instead of expensive synthetic sorbents, natural cheap materials (peat, zeolites, clays, and bottom sediments) or production waste (iron-containing sludge; sawdust; activated slag; shells of wheat, nuts, and rice; etc.) can be successfully applied [6–8]. Natural clays are used as sorbents due to their large specific surface area; high ability to sorb cations and polar organic molecules; and availability, low cost, and environmental safety. Bentonite clays, the main mineral of which is montmorillonite (Mt), are the natural clays most commonly used for water purification. Mt belongs to dioctahedral layered aluminosilicates of the 2 : 1 type, the structure of which consists of layers formed by an octahedral oxygen–hydroxyl network ($Al(O,OH)_6$) located between two SiO_4 tetrahedral networks [9]. The negative charge generated in aluminosilicate layers as a result of isomorphic exchange of cations $Al^{3+} \rightarrow Mg^{2+}$ in the octahedral and $Si^{4+} \rightarrow Al^{3+}$ in the tetrahedral networks is compensated by exchangeable Na^+ and/or Ca^{2+} cations located in the interlayer gaps and on the basal planes of Mt particles. The high cation-exchange capacity of Mt is due to the ability of exchangeable cations to be replaced by cations of other metals, as well as the expansion of Mt structural cells upon a contact with water and other polar liquids. The development of sorption technologies for wastewater purification using clays requires the knowledge of adsorption regularities, which are determined by both the properties of adsorbents and substances being adsorbed and the physicochemical conditions of the process.

The aim of this work was to study the kinetic regularities and equilibrium of the adsorption of triarylmethane dye, crystalline violet, on Ca-montmorillonite and to determine the thermodynamic characteristics of the process.

EXPERIMENTAL

An Mt-containing fraction of alkaline-earth bentonite clay with the predominance of exchangeable Ca cations and an Mt content of 90% (Ca-Mt) of the Mukhortal deposit (Buryatia, Russia) was used as an adsorbent. The chemical composition of the clay enriched by the sedimentation method was represented by oxides (wt %): SiO_2, 65.5; Al_2O_3, 15.3; Fe_2O_3, 1.78; CaO, 1.08; MgO, 1.42; Na_2O, 0.1; K_2O, 0.2; and TiO_2, 0.19; its calcination loss was 14.43%. X-ray diffraction analysis performed with a STADI P autodiffractometer (STOE Co.) (Cu$K_{\alpha 1}$ radiation, $2\theta = 3°–77°$) showed that the Ca-Mt diffractogram [10] comprised reflections attributed to Mt, which is the main rock-forming mineral of bentonite clays, and to an impurity mineral, cristobalite [11].

The specific surface area of the clay was determined by the BET method [12] from the low-temperature nitrogen adsorption isotherm, which was obtained using a TermoSorb LP setup (Katakon, Novosibirsk, Russia). The specific surface area of the clay was 80 m^2/g, the total pore volume was 0.253 cm^3/g, and the average pore diameter was 12.7 nm. The cation-exchange capacity of Mt was 0.95 mg-equiv/g.

Being a typical representative of triarylmethane dyes, crystalline violet dye (CV, $C_{25}H_{30}N_3Cl$) belongs to basic dyes and dissociates into organic cations CV^+ and Cl^- anions in aqueous solutions.

Adsorption studies were carried out by the limited volume method at an initial CV solution concentration of 35.2–700 mg/L, a clay weighed portion of 1.0–10 g/L, and pH 3.45–6.45. When determining the equilibrium adsorption, an aqueous solution of CV with a preset initial concentration was added to a calculated weighed portion of clay, and the mixture was stirred at 200 rpm for 4 h (equilibration time) with a LAB-PU-01 device; then, the sorbent was separated from the liquid phase by centrifugation at 8000 rpm. The concentration of the dye in the aqueous solution was determined from the optical density versus dye concentration calibration plot. The optical density of the solution was measured with an UV-Vis Agilent 8453 spectrophotometer (Agilent Technologies, United States) at 590 nm with an error of ±5%. The specific adsorption value was calculated by the following formula:

$$q_t = \frac{C_0 - C_t}{m} V, \tag{1}$$

where q_t is the amount of the dye adsorbed by 1 g of the sorbent at time moment t (mg/g), C_0 is the initial concentration of the dye in the solution (mg/L), C_t is the concentration of the dye in the solution at time moment t (mg/L), m is the mass of the sorbent (g), and V is volume of the dye solution (L).

The efficiency of the removal of the dye from the solution was determined as

$$\mathrm{E} = \frac{(C_0 - C_t) \times 100\%}{C_0}. \tag{2}$$

Kinetic studies were carried out in the following way: clay was placed into several flasks (0.01 g into each flask), and CV solutions (10 mL) with different initial concentrations and $pH_0 = 5.6–5.8$ were added to the flasks. The suspensions were stirred, and samples were taken from them in predetermined time intervals. The liquid phase was separated from the solid phase by centrifugation, and the residual dye concentration was measured in the supernatant. The thermodynamic parameters of the adsorption were determined by performing experiments in a thermostated vessel within a temperature range of 298–323 K.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 shows the dependence of equilibrium adsorption q_e calculated by Eq. (1) at time t corresponding to the establishment of equilibrium on the pH of the CV a solution at 25°C. The adsorption of CV remains almost unchanged upon increasing solution pH from 3.25 to 6.45. This agrees with the mechanism of cation adsorption on Mt. It is known that about 80% of the exchange capacity of Mt is due to the presence of exchangeable cations that are easily replaced by cations of other metals, and the adsorption of cations does not depend on pH, because the lattice charge generated on the basal surface due to heterovalent isomorphism is fixed and independent of the properties of a solution. An insignificant amount of the cations may be sorbed on the lateral faces of Mt particles by replacing protons in Si–OH groups, which, at pH > 2.0–2.5, dissociate via an acidic mechanism and are involved in the exchange for metal cations. In contrast to the cations compensating for the heterovalent substitutions, the number of such protons in the clay structure is variable and depends on the pH of a medium [9].

Effect of Sorbent Content Loading

Table 1 presents the values of equilibrium adsorption and efficiency of CV removal (calculated by Eq. (2)) from an aqueous solution at different sorbent contents. A rise in the Ca-Mt content from 1.0 to 2.0 g/L leads to an increase in the efficiency of dye removal from 70.5 to 98.8% due to a rise in the number of adsorption centers accessible for CV adsorption. A further increase in the sorbent content does not affect the degree of CV removal. Specific adsorption q_e increases from 40.8 to 87.5 mg/g with a decrease in the sorbent content from 3.0 to 1.0 g/L. As the sorbent content is increased above 1.0 g/L, the q_e value

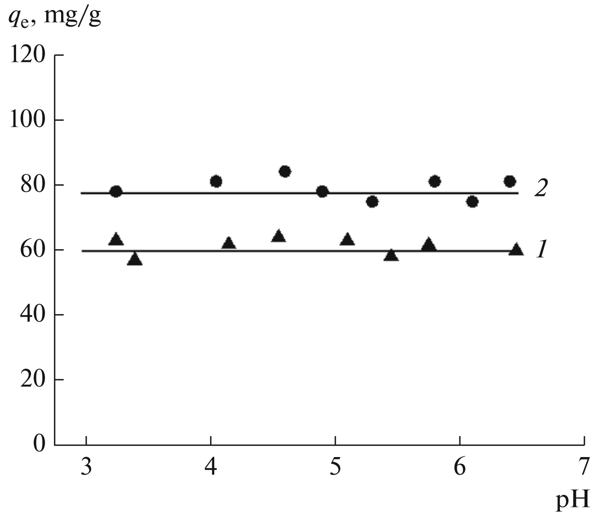

Fig. 1. pH dependences of q_e at different initial concentrations of CV solutions: (*1*) 65 and (*2*) 107.7 mg/L.

decreases due to the fact that, upon increasing the mass ratio between the sorbent and the dye, the involvement of the clay surface decreases, and a significant fraction of the Ca-Mt adsorption centers remains unoccupied.

Effect of Dye Concentration

Figure 2 shows the equilibrium adsorption as depending on the equilibrium concentration of the dye in a solution (adsorption isotherm at 25°C). In the initial region of the isotherm, the adsorption dramatically increases, thereby indicating a high affinity of Mt to CV cationic dye. This agrees with the cation-exchange nature of Mt adsorption centers. Then, the isotherm reaches a plateau, and the value of the equilibrium adsorption ceases to depend on the initial concentration of the dye. The obtained experimental isotherms were analyzed in terms of the models that are used to describe the adsorption of solutes, i.e., the Langmuir isotherm, which describe the monolayer adsorption on homogeneous surfaces, and the Freundlich isotherm, which describes the multilayer adsorption on inhomogeneous surfaces [13].

The linear form of the Langmuir isotherm is expressed by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}},$$

where Q_{max} is a theoretical constant corresponding to the maximum adsorption (mg/g) and K_L is the Langmuir constant, which depends on the adsorption energy and temperature (L/g).

The linear form of the Freundlich isotherm is expressed via the following equation:

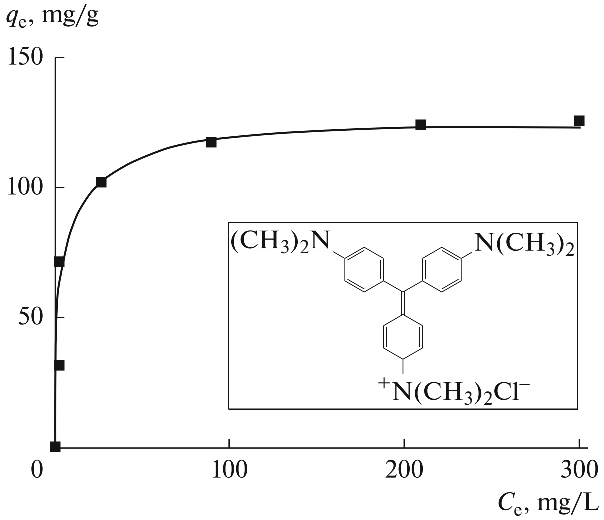

Fig. 2. Isotherm of CV Adsorption on Ca-Mt (sorbent content, 1 g/L; 25°C; and adsorption time, 250 min).

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

where K_F is the Freundlich adsorption constant (L/g) and n is the experimental Freundlich constant describing the adsorption intensity.

The plots of the linear functions of the Langmuir and Freundlich isotherms are presented in Fig. 3. The values of the correlation coefficients indicate that the adsorption of CV on Ca-Mt is in good agreement with the Langmuir adsorption isotherm with a correlation coefficient of 0.9993, while, for the Freundlich isotherm, this coefficient is 0.7477.

Effect of Temperature on the Adsorption of CV Dye

The values of entropy ΔS, enthalpy ΔH, and Gibbs free energy ΔG for the adsorption of CV were deter-

Table 1. The influence of Ca-Mt content on the value of q_e and the efficiency of CV removal from an aqueous solution

Sorbent content, g/L	q_e, mg/g	CV removal efficiency, %
1.00	87.5	70.5
1.50	72.9	89.3
2.00	61.1	98.8
3.00	40.7	99.8

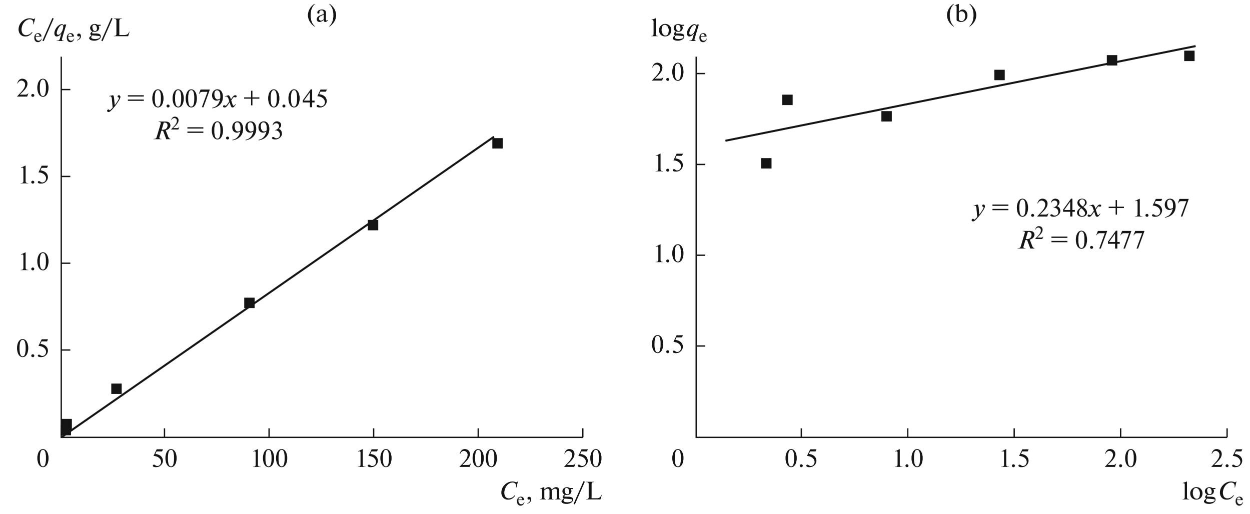

Fig. 3. Isotherms of CV adsorption on Ca-Mt represented in the coordinates of the linearized (a) Langmuir and (b) Freundlich equations.

mined graphically from the dependence shown in Fig. 4,

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT},$$

where $K_d = q_e/C_e$ is the adsorption equilibrium constant.

The following values were obtained for the adsorption of CV on Mt: $\Delta H = 40.42$ kJ/mol and $\Delta S = 139.6$ J/mol, while the ΔG values were −1.88, −3.28, and −4.67 kJ/mol at 30, 40, and 50°C, respectively. The positive value of ΔH shows that the adsorption of CV is an endothermic process; the values of the Gibbs free energy and entropy of adsorption indicate that the dye adsorption on Ca-Mt is a spontaneous process [14].

Adsorption Kinetics

Figure 5 presents the data on the adsorption kinetics of CV at temperatures of 30, 40, and 50°C. Initially, the process is rapid, with 30–70% of the dye being adsorbed over 30 min, depending on temperature. Then, the rate of adsorption gradually decreases. In the case of surface reactions, this effect occurs due to a gradual reduction in the number of adsorption centers on the surface of an adsorbent in the course of

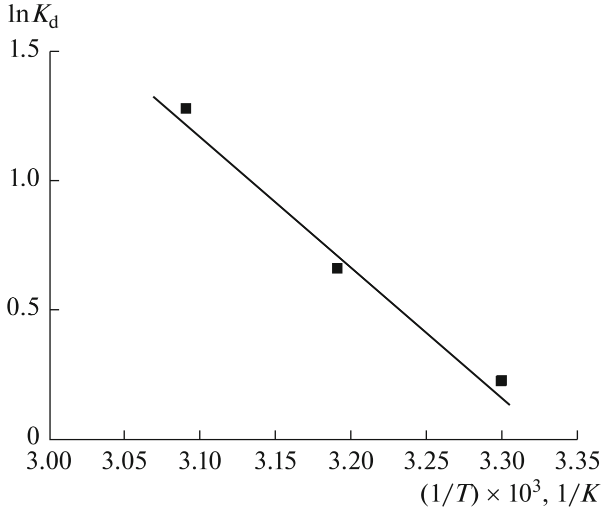

Fig. 4. Dependence of $\ln K_d$ on $1/T$.

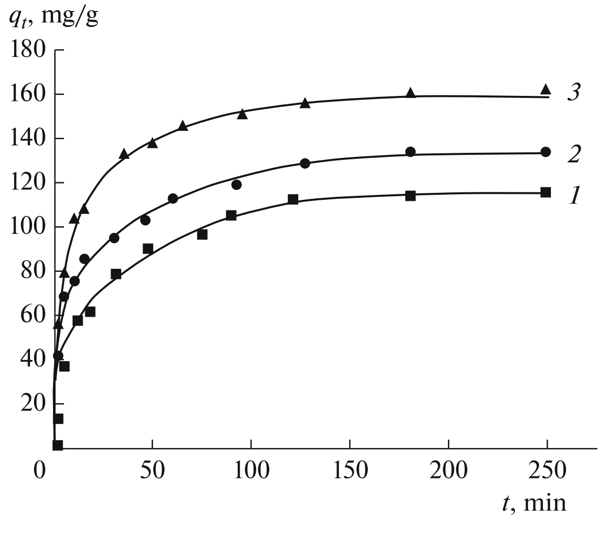

Fig. 5. Kinetic curves for CV adsorption at different temperatures: (*1*) 30, (*2*) 40, and (*3*) 50°C.

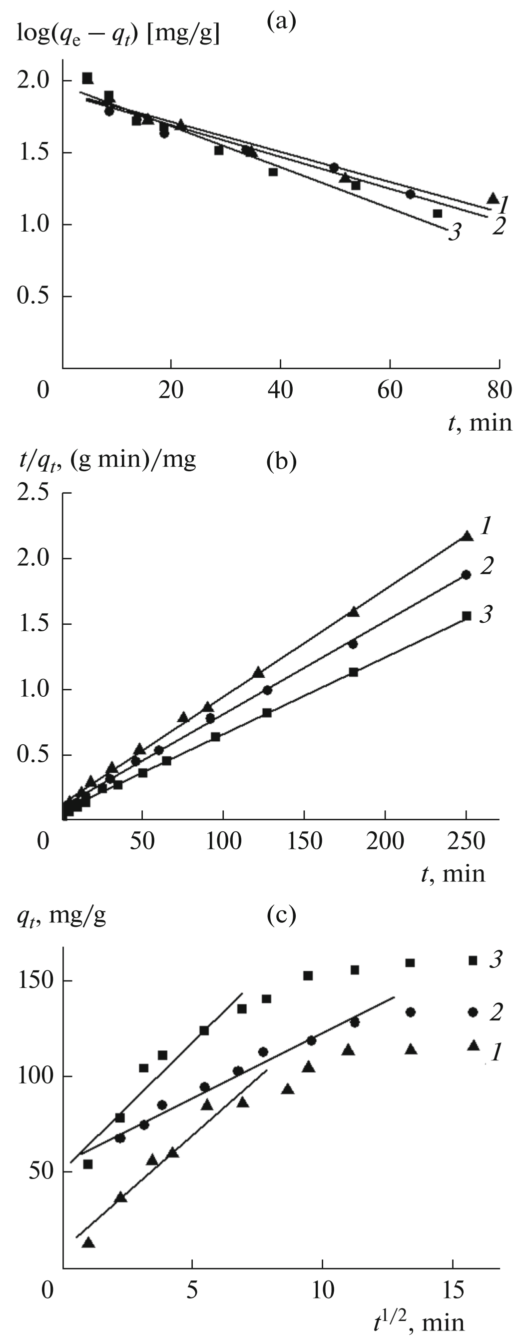

Fig. 6. Plots of (a) pseudo-first- and (b) pseudo-second-order kinetic equations and (c) intraparticle-diffusion equation for CV adsorption on Ca-Mt at different temperatures: (*1*) 30, (*2*) 40, and (*3*) 50°C.

their filling, thereby leading to the establishment of adsorption equilibrium.

The pseudo-first- and pseudo-second-order kinetic models and the intraparticle-diffusion model (Eqs. (3), (4), and (5), respectively) are most suitable for studying the mechanism of adsorption of solutes and determining the rate-limiting step of this process. These equations are widely used to explain experimental data on the adsorption of organic dyes and metal cations from aqueous solutions [15, 16].

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \tag{4}$$

$$q_t = k_i t^{1/2}. \tag{5}$$

In the above equations, k_1 (1/min), k_2 (g/(mg min)), and k_i (mg/(g min$^{1/2}$)) are the rate constants of the pseudo-first and pseudo-second orders and of the intraparticle diffusion, respectively.

Figure 6 presents the experimental data on the rate of dye adsorption on Ca-Mt in the coordinates of the linear forms of the equations of the pseudo-first- and pseudo-second-order kinetic equations, and the intraparticle-diffusion equation. Table 2 shows corresponding correlation coefficients R^2. The values of R^2 lie within ranges of 0.9665–0.9810, 0.9979–0.9985, and 0.8970–0.9852 for the pseudo-first- and pseudo-second-order models and the model of intraparticle diffusion, respectively. The theoretical values of equilibrium adsorption q_2 calculated in terms of the pseudo-second-order model are in good agreement with the experimental q_e values, with the difference being no higher 5.2% (Table 2). The difference between the experimental values of q_e and the value of q_1, calculated within the pseudo-first-order model is as large as 35%. According to the results obtained, the data on the kinetics of CV adsorption are in good agreement with the pseudo-second-order kinetics model, which is confirmed by the high value of correlation coefficient R^2. The correspondence of the experimental adsorption kinetics to the pseudo-second-order model indicates that the rate-limiting step of CV adsorption is chemisorption [15]. Similar results were obtained for the adsorption of acid red 57 dye on calcined alunite [17] and malachite green on bentonite [18].

Thus, it has been found that Ca-montmorillonite is an efficient sorbent for triarylmethane dye, crystalline violet, and makes it possible to remove up to 99.8% of the dye from a solution. The main parameters affecting CV adsorption on Ca-Mt are the amount of the sorbent, the concentration of the dye, and temperature. The specific adsorption of CV on Ca-Mt increases as the sorbent amount decreases and the temperature increases. The isotherm of dye adsorption is described by the Langmuir equation. The kinetic regularities of CV adsorption on the studied sorbent are consistent with the pseudo-second-order model, which is characteristic of chemisorption.

Table 2. Kinetic parameters of CV adsorption on Ca-Mt

Temperature, °C	q_e, mg/g	Pseudo-first-order equation		Pseudo-second-order equation			Equation of intraparticle diffusion	
		q_1, mg/g	R^2	q_2, mg/g	K_2, g/(mg min)	R^2	k_i, mg/g min$^{1/2}$	R^2
30	115.9	106.7	0.9736	121.9	5.651×10^{-4}	0.9984	0.128	0.9852
40	133.6	87.1	0.9810	140.8	6.426×10^{-4}	0.9979	0.149	0.9761
50	160.9	85.1	0.9665	169.8	8.794×10^{-4}	0.9985	0.062	0.8953

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