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Studies on the adsorption behavior of methyl orange from dye wastewater onto activated clay

Qingliang Ma[a], Fangfang Shen[b], Xiaofang Lu[a], Weiren Bao[a,]*, Hongzhu Ma[b]

[a]*Key laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China*
Tel. +86 29 81530726; Fax: +86 29 81530727; email: baoweiren@tyut.edu.cn
[b]*College of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China*

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ABSTRACT

In this study, activated clay was used as adsorbent for the removal of methyl orange (MO) from aqueous solution in a batch system. Experiments were carried out as a function of contact time, initial concentrations of solution, adsorbent dosage, solution pH, and temperature, and consequently, optimum condition of adsorption was obtained. The equilibrium adsorption data of MO on activated clay were analyzed by Langmuir, Freundlich and Temkin isotherm models, the results indicate that Langmuir and Temkin models provide better correlation of the experimental data. The pseudo-first-order, pseudo-second-order and Elovich kinetics models were used to analyze the kinetics data obtained at different concentrations. Among the kinetics models studied, the pseudo-second-order model was the best applicable model to describe the adsorption of MO onto activated clay. The values of Gibbs free energy of adsorption (ΔG°) were found to be $-7.462\,\mathrm{kJ\,mol^{-1}}$, the negative value indicated the spontaneity of the adsorption process of MO onto activated clay. The values of ΔH° and ΔS° were found to be $-12.289\,\mathrm{kJ\,mol^{-1}}$ and $-16.474\,\mathrm{J\,mol^{-1}\,K^{-1}}$, respectively. The negative value of ΔH° reveals the adsorption is exothermic, and the negative value of ΔS° suggests that the confusion degree of adsorption process is decreasing.

Keywords: Activated clay; Methyl orange; Adsorption; Kinetics; Thermodynamics; Wastewater

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1. Introduction

Dye is used in many industries such as food, paper, carpet, rubbers, plastics, and textiles. The discharge of colored wastewater from these industries causes many significant environmental problems. It is reported that approximately 5 ton of dye discharge from dyes and coloration industries every year [1]. Methyl orange (MO) is representative contamination in industrial wastewater and shows poor biodegradability. Hence, treatment technologies, such as biological treatment, adsorption technology, air striping and incineration, have been used to treat wastewater containing this pollutant [2]. Adsorption, as one of physical/chemical methods, is considered

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*Corresponding author.

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superior to other methods. And activated carbon is the most effective adsorbent with high surface and can be regenerated, but it is limited due to the high operation costs, and this is a major economic consideration in any large-scale remediation application [3].

Recently, attention has focused on the development of low-cost adsorbent for the application concerning treatment of wastewater, such as coal fly ash [4], sepiolite [5], montmorillonite [6], agricultural waste [7], unburned carbon [8], low-rank coal [9], and clays [10]. Clay mineral, as a low cost and easily available absorbent, can serve as an alternative for more costly wastewater treatment processes. Clays are a group of microcrystalline secondary minerals consisting of a variety of phyllosilicate minerals rich in variable amounts of structural water with sheet-like structures. They are highly valued for their adsorptive properties, which stem from their high surface area and their tendency to adsorb water in the interlayer sites [11].

The adsorption mechanism of activated clay and resin has been studied in wastewater treatment in these decades. For example, adsorption kinetics and thermodynamic parameters of cationic dyes from aqueous solutions by using a new strong cation-exchange resin [12], studies on the MO adsorption have been also reported on other adsorbents such as modified ultrafine coal powder [13]. However, resin, coal powder, and other adsorbents are expensive, especially the polymer resin. So in this study, activated clay, with extensive sources and low costs, was used as adsorbent for the removal of MO from aqueous solution in a batch system.

In this study, the influence factors of adsorption of MO onto activated clay and the adsorption thermodynamics and kinetics were discussed, and this will provide theoretical basis for industrial application of activated clay in wastewater treatment.

2. Materials and methods

2.1. Reagents

All chemicals and reagents used of analytical grade and employed without further purification. MO (Fig. 1) is obtained from Tianjin Chemical Reagent Co. China. Activated clay was purchased from Huangshan Taike activated bleaching earth, Ltd. China.

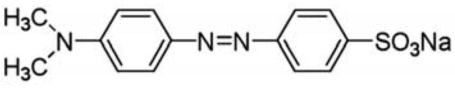

Fig. 1. MO structure.

2.2. Experimental methods

2.2.1. The pretreatment of activated clay

Before use, the activated clay dried at 363 K for 4 h in the DZF-6060 vacuum oven (Shanghai Jinghong Experimental Equipment Co. Ltd.), transferred to the pharmaceutical bottle and sealed.

2.2.2. Analysis method

The concentration of MO solution was determined using a double-beam UV–vis spectrophotometer (UV-7504, Shanghai Xinmao Instruments Co., Ltd., China). The MO solution for 50–250 $\mathrm{mg\,l^{-1}}$ was prepared with volumetric flasks (100 ml) and determined by spectrophotometer at the maximum absorbency visible wavelength (465 nm).

2.2.3. Adsorption process

Adsorption process was performed in a set of Erlenmeyer flasks where solution of MO with certain concentration and amount, and then, activated clays were introduced. When it was reached to equilibrium, the solution was centrifuged with 800-centrifuge (Maximum speed of 4,000 $\mathrm{r\,min^{-1}}$, Shanghai Pudong Physical Optical Factory, China), the absorbance of supernatants was determined by spectrophotometer, and then, the concentration was calculated by the standard curve equation. According to the results and Eqn. (1), the equilibrium adsorption quantity of MO onto the activated clay were calculated.

$$q_e = \frac{(c_o - c_e)V}{m} \tag{1}$$

where q_e ($\mathrm{mg\,g^{-1}}$) was equilibrium adsorption quantity; c_o ($\mathrm{mg\,l^{-1}}$) and c_e ($\mathrm{mg\,l^{-1}}$) are the liquid-phase concentrations of MO at initial and equilibrium, respectively, V the volume of the solution (l), and m is the mass of dry adsorbent used (g).

3. Results and discussion

3.1. Factors of affecting adsorption

3.1.1. Effect of initial pH on adsorption process

The initial solution pH affects not only the existing form of MO molecule in solution but also the surface structure and chemical properties of absorbents. The adsorption behavior of MO on activated clay was studied over a wide pH range of 3.0–11.0. The effect of pH on adsorption of MO was carried out at initial

MO concentration of 250 mg l^{-1} at 293 K as shown in Fig. 2. It was found that the highest adsorption capacity of MO occurred at pH 3–7, and the color removal over 95%. The adsorption capacity and color removal of MO decreased sharply when pH increased higher than 7.0. The effect of solution pH on the removal of MO from aqueous solution by adsorption can be explained by two reasons. On one hand, activated clay was prepared from bentonite by acid activation, according to the preparation principles of activated clay, H^+ in the solution can increase the specific surface area [14] and charge distribution of activated clay, so the solution pH value can affect the adsorption performance of activated clay; on the other hand, the pK_a of MO was 3.46, when solution pH less than pK_a, the existing form of MO was ionic form, and it was easily absorbed by the absorbent with charge, so the adsorption capacity of activated clay was increased [15]. However, considering the wastewater discharge standard, it is more appropriate that the pH of MO solution was 7.0.

3.1.2. Effect of activated clay dosage on MO adsorption

The effect of absorbent dosage on adsorption capacity of activated clay was studied at 0.25, 0.5, 0.75, 1.0, and 1.25 g at initial MO concentration 250 mg l^{-1} at pH 7.0 and 293 K. As seen in Fig. 3, the removal efficiency of activated clay increased with the increasing dosage of the absorbent, indicating that the higher dose of adsorbent, the greater availability of adsorption sites for the pollutant. The color removal of MO on the activated clay increased from 52 to 94% with an increasing in adsorbent dosage from 5 to 25 g l^{-1}. However, it is showed that the adsorption capacity of absorbents was decreased with an increase in adsorbent dosage from 5 to 25 g l^{-1}, suggesting that the utilization efficiency of absorbent was highest when the dosage is 5 g l^{-1}, so activated clay dosage fixed 5 g l^{-1} in the following experiments.

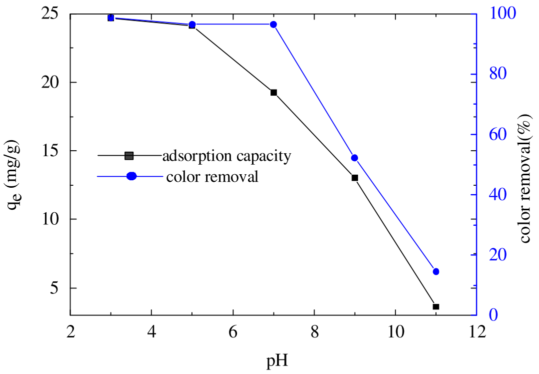

Fig. 2. Effect of pH on MO adsorption onto activated clay.

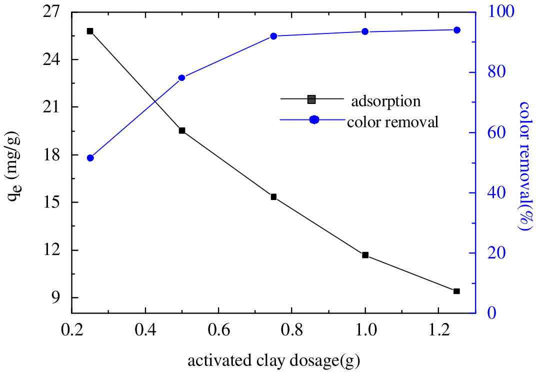

Fig. 3. Effect of absorbent dosage on adsorption capacity.

3.1.3. Effect of initial concentration, temperature, and contact time on MO adsorption

The initial dye concentration provides an important driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phases. Hence, a higher initial concentration of dye will enhance the adsorption process [16]. It should be noted that the initial dye concentration on an effluent was important since a given mass of the adsorbent can adsorb only a fixed amount of dye. The adsorption capacity at equilibrium (q_e) increased from 6.0 to 15.0 mg g^{-1} when the initial MO concentration was increased from 40 to 120 mg l^{-1} (Fig. 4). This is because that the higher the initial concentration of solution, the more the concentration difference between the solution and the absorbent surface, and the more MO molecules were adsorbed. Therefore,

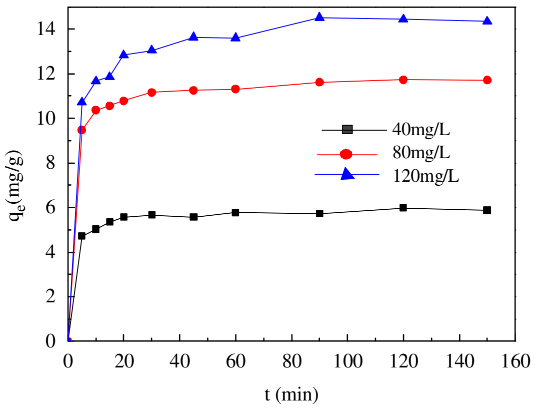

Fig. 4. Effect of initial concentrations on adsorption capacity at 293 K.

increasing the initial concentration of solution would lead to the mass transfer driving force increase.

The effect of temperature on the equilibrium adsorption capacity of absorbent is displayed in Fig. 5. Various temperatures at 293, 303, and 313 K were taken and adsorption of MO was achieved at adsorbent dose 5 g l^{-1} and pH 7.0. The adsorption capacity was reduced with the increasing of temperature, indicating that the adsorption process of MO onto activated clay is exothermic in nature. This is expected due to the fact that the higher temperature of solution, and the more thermal motion of the MO molecules, which then weakening the adsorptive forces between the active sites of the adsorbent and adsorbate species, and also between the adjacent molecules of the adsorbed phase [17]. The adsorption capacities of activated clay were 11.61, 11.59, and 10.79 mg g^{-1} at 293, 303, and 313 K, respectively. The optimum temperature for MO adsorption on activated clay was found to be 293 K within the temperature range studied.

The equilibrium adsorption time of MO on the activated clay was also investigated (Figs. 4 and 5). At the beginning of adsorption, the slope of curve is extremely great, then the process quickly reach equilibrium at almost 30 min for initial concentration less than 80 mg l^{-1} and over 30 min for higher concentration. This may be due to that in the initial of adsorption procedure, all the active sites are vacant, and the competition among MO molecules is weak [18]. So adsorption rate is exceedingly quick and the increasing of adsorption capacity is extremely fast. When the adsorption of the exterior surface reached almost saturation, the MO ions entered into the pores of adsorbent and were adsorbed by the interior surface of the particles. This process takes relatively long contact time. So the adsorption capacity of absorbents keeps almost a constant value. Consequently, the adsorption of dyes was carried out in two distinct stages, a relatively rapid one followed by a slower one.

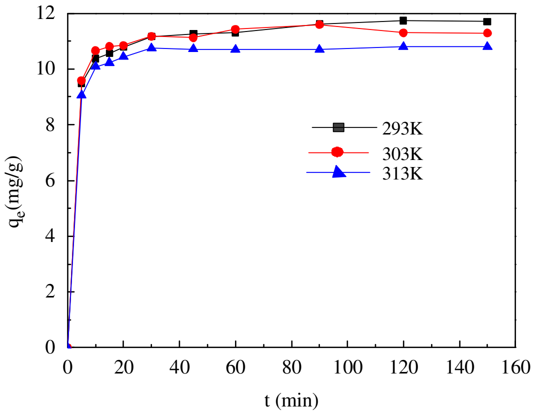

Fig. 5. Effect of temperature on adsorption capacity at 80 mg l^{-1}.

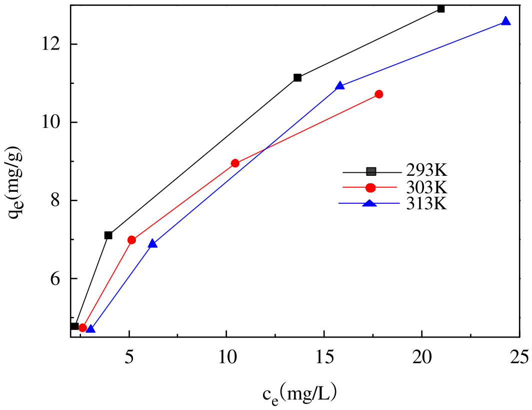

Fig. 6. The adsorption curves of MO onto activated clay at different temperature.

3.2. Adsorption isotherms

It was found that the adsorption capacity at equilibrium (q_e) of MO onto activated clay increased with the increasing of concentration at equilibrium (c_e) as shown in Fig. 6. It can also found that the adsorption capacity of absorbent was reduced with the temperature increasing for the same concentration of MO, which can be explained that the process of adsorption was exothermic. Analysis of equilibrium data is important for developing an equation or a model that can be used to compare different sorbents under different operational conditions and to design and optimize the operating procedure [19,20]. Three isotherm models, Langmuir, Freundlich and Temkin have been used to describe the equilibrium characteristics of adsorption.

The Langmuir sorption isotherm [21] is an idea adsorption equation, which describes the uniform surface, adsorbed molecules without interaction, and monolayer adsorption. Its scope of application is extensive, but it is suitable for physical adsorption. And for the adsorption of solid in the solution, Langmuir sorption isotherm widely used for the sorption of a pollutant from a liquid solution assuming that the sorption takes place at specific homogeneous sites within the adsorbent. It has produced good agreement with a wide variety of experimental data and may be represented as follows:

$$q_e = \frac{q_m K_L c_e}{1 + K_L} \qquad (2)$$

Table 1
The summary of isotherm parameters for MO on activated clay

T (K)	Langmuir				Freundlich			Temkin		
	B (l mg^{-1})	q_m (mg g^{-1})	R_L	R^2	K_F	n	R^2	A	B	R^2
293	0.194	15.85	0.094	0.9975	3.627	2.346	0.9791	2.055	3.536	0.9881
303	0.199	13.63	0.091	0.9982	3.299	2.382	0.9816	1.893	3.083	0.9986
313	0.120	16.78	0.143	0.9974	2.819	2.090	0.9954	0.214	3.850	0.9951

The above equation can be rearranged to the following linear form:

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \tag{3}$$

where c_e is the equilibrium concentration (mg l^{-1}), q_e the amount of adsorbate adsorbed (mg g^{-1}), q_m the monolayer capacity (mg g^{-1}), and K_L is the adsorption equilibrium constant (l mg^{-1}). By plotting c_e/q_e vs. c_e at 293, 303 and 313 K, respectively, the adsorption coefficients could be evaluated. The q_m and K_L thus determined from the Langmuir isotherm were showed in Table 1.

Freundlich isotherm [22] is an empirical formula, and generally, its scope is wider than that of Langmuir isotherm, and its characteristics are not saturated adsorption value. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Freundlich isotherm can be used for the physical adsorption and chemical adsorption. The isotherm is expressed by the following equation:

$$q_e = K_F c_e^{1/n} \tag{4}$$

where K_F ((mg g^{-1}) (mg L^{-1})$^{-1/n}$) and n are the Freundlich constants that point to relative capacity and adsorption intensity, respectively. In general, as the K_F value increases the adsorption capacity of adsorbent for a given adsorbate. When the $1/n$ less than unit, adsorption is easy, otherwise, adsorption is difficult. The Freundlich equation can be linearized by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} c_e \tag{5}$$

The constants can be determined as shown in Fig. 8. And according to the Freundlich isotherm, the value of $1/n$ and K_F were determined as Table 1 shown.

The Temkin isotherm [23] assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm model can be expressed as follows:

$$q_e = A + B \ln c_e \tag{6}$$

where $B = RT/b$, B is the Temkin constant related to heat of sorption (J mol^{-1}), A is the Temkin isotherm constant (l g^{-1}), R is the gas constant

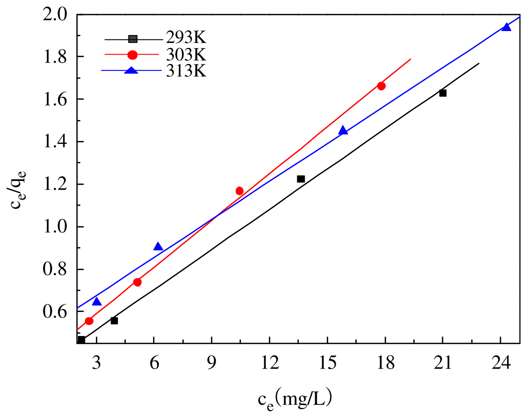

Fig. 7. Langmuir isotherm for MO adsorption onto activated clay at different temperature.

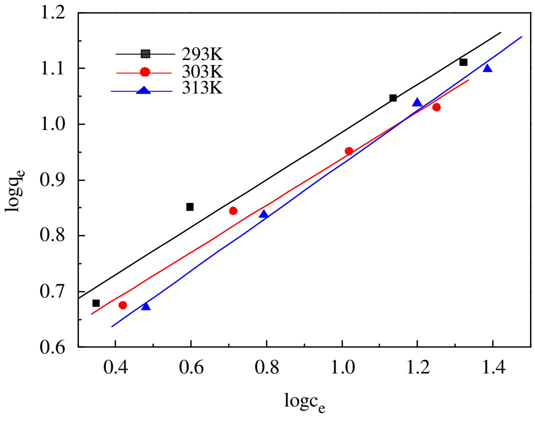

Fig. 8. Freundlich isotherm for MO adsorption onto activated clay at different temperature.

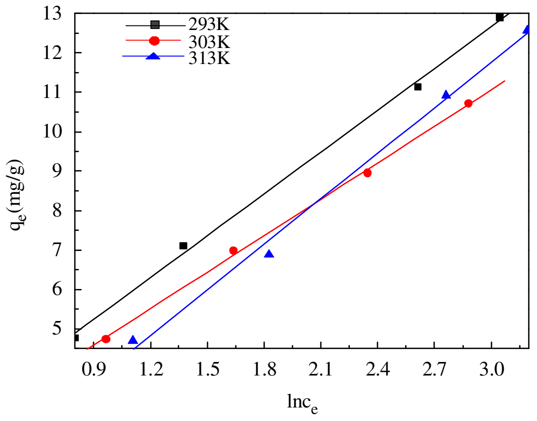

Fig. 9. Temkin isotherm for MO adsorption onto activated clay at different temperature.

(8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Therefore, a plot of q_e vs. ln c_e (at 293, 303 and 313 K, respectively) enables one to determine the constants A and B as shown in Fig. 9. The constants A and B are recorded in Table 1.

Combined with Figs. 7–9 and Table 1, it can be seen that all of R^2 were satisfactory, and R^2 of Langmuir isotherm is higher than that of Freundlich isotherm and revealed that the Langmuir isotherm can descript accurately the adsorption of MO onto activated clay. According to Langmuir equation, the calculated maximum adsorption capacity (q_m) was 13.624–16.779 mg g^{-1} in different temperature range, indicating that activated clay has excellent adsorption performance. In light of Temkin isotherm, its correlation coefficients (R^2) were 0.9881, 0.9986, and 0.9951 at 293, 303, and 313 K, respectively, which confirms the better fit of equilibrium data as compared with the Freundlich isotherm model. But Temkin isotherm model is not as good as Langmuir, as can be seen from the reported values of coefficient of determination (R^2). Summing up, it was deemed that the adsorption of MO onto activated clay is monolayer adsorption. The equilibrium parameter R_L in Table 1 is defined as $R_L = 1/(1 + bc_0)$ [24]. Where c_0 is the initial concentration of adsorbate (mg l^{-1}) and b (l mg^{-1}) is the Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm accordingly: R_L>1, unfavorable adsorption; when $0 < R_L < 1$, the preferential adsorption; $R_L = 0$, the irreversible adsorption; $R_L = 1$, linear adsorption. The values of R_L were 0.0935, 0.0913, and 0.143 at 293, 303, and 313 K, respectively, listed in Table 1 in this experiment has been found $0 < R_L < 1$. Therefore, the sorption process was very favorable and the adsorbent employed exhibited a good potential for the removal MO from aqueous solution [25].

3.3. Adsorption kinetics

In order to further study the mechanism of adsorption, the adsorption capacity of activated clay at different temperature (293, 303, and 313 K) and initial concentration of MO solution (40, 80, and 120 mg l^{-1}) were investigated and the kinetic data were modeled using Lagergren pseudo-first-order [26,27], pseudo-second order [28,29] and Elovich kinetics equations [30].

3.3.1. Lagergren pseudo-first-order kinetics model

The adsorption rate constant was calculated by using Lagergren pseudo-first-order model, equation was expressed as follows:

$$\frac{dt}{dq_t} = K_1(q_e - q_t) \tag{7}$$

where q_e and q_t are the amounts of MO adsorbed at equilibrium and at time t in mg g^{-1}, respectively, and K_1 (1 min^{-1}) is the pseudo-first-order rate constant. The integration of Eq. (7) with the initial condition, $q_t = 0$ at $t = 0$ leads to:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{8}$$

As such, the value of $\log(q_e - q_t)$ were calculated at different temperature (293, 303, and 313 K) and initial concentration of solution (40, 80, and 120 mg l^{-1}) and showed in Figs. 10 and 11, according to the intercept and the slope of line, $q_{e\ \text{cal}}$, K_1 and the correlation coefficient (R^2) was calculated and showed in Table 2. The value of R^2 approximately was equal to 0.7, much less than 0.99, indicated that pseudo-first-order equa-

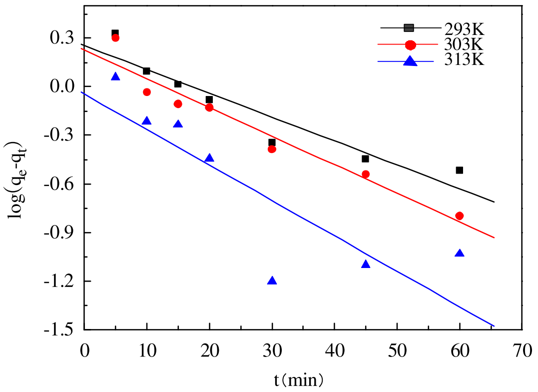

Fig. 10. Pseudo-first-order kinetics for MO at different temperature.

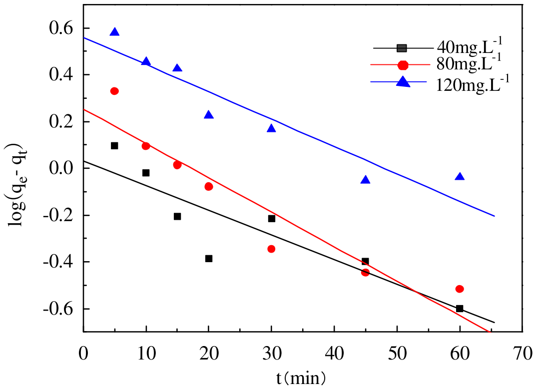

Fig. 11. Pseudo-first-order kinetics for MO at different initial concentration.

Table 2
Kinetic parameters for pseudo-first-order kinetic models

Pseudo-first order kinetic models				q_e (mg g^{-1}) (experimental)
T (K)	K_L	q_e (mg g^{-1})	R^2	
293	0.0525	3.1637	0.7167	11.6144
303	0.0554	3.0301	0.7659	11.5878
313	0.0674	2.0379	0.7205	10.7918
c_0 (mg l^{-1})	K_L	q_e (mg g^{-1})	R^2	q_e (mg g^{-1})
40	0.0375	1.8113	0.6349	5.9757
80	0.0525	3.1637	0.7167	11.6144
120	0.0376	5.5406	0.7343	14.5202

tion can not accurately describe the adsorption process of MO onto activated clay.

3.3.2. *Pseudo-second-order kinetics model*

The pseudo-second-order kinetics model can be represented in the following form:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{9}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively, (mg g^{-1}) and K_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order sorption. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated and rearranged form of Eq. (9) as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

By plotting $t/q_t \sim t$ (Figs. 12 and 13), q_e and K_2 can be determined from slope and intercept and listed in Table 3. The value of correlation coefficient (R^2) over 0.99 was obtained, so the pseudo-second-order kinetics model can describe excellently the adsorption process.

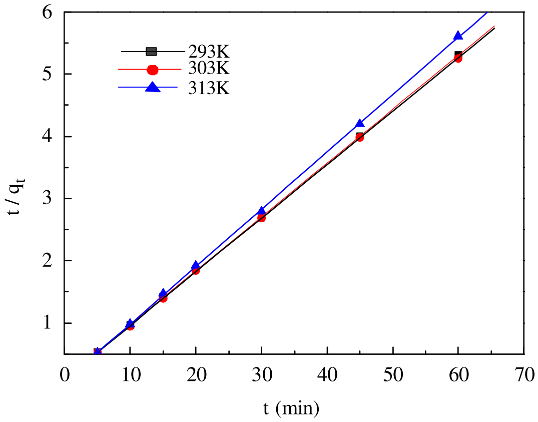

Fig. 12. Pseudo-second-order kinetics for MO at different temperature.

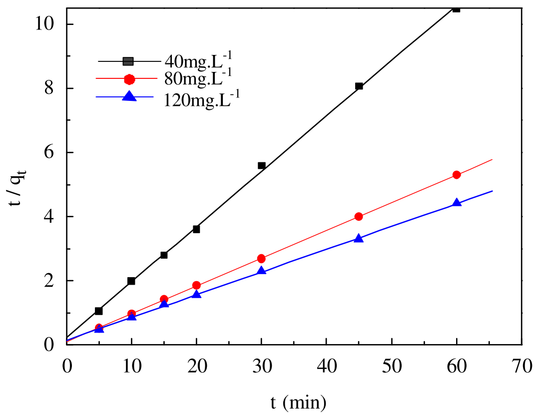

Fig. 13. Pseudo-second-order kinetics for MO at different initial concentration.

Table 3
Kinetic parameters for pseudo-second-order kinetic models

Pseudo-second-order kinetic model				q_e (mg g^{-1}) (experimental)
T (K)	k_2	q_e (mg g^{-1})	R^2	
293	0.1053	11.4377	0.9996	11.6144
303	0.1124	11.5115	0.9997	11.5878
313	0.1988	10.7933	0.9998	10.7918
c_0 (mg l^{-1})	k_2	q_e (mg g^{-1})	R^2	q_e (mg g^{-1})
40	0.1793	5.7392	0.9989	5.9757
80	0.1053	11.4377	0.9996	11.6144
120	0.0495	13.8889	0.9986	14.5202

3.3.3. Elovich kinetics equation

Elovich kinetics equation was expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{11}$$

where α (mg g^{-1} min^{-1}) is the initial adsorption rate and β (g mg^{-1}) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorptions. Eq. (11) is simplified by assuming α, $\beta \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, as given by Eq. (12):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{12}$$

By plotting $q_t \sim \ln t$ at different temperature (293, 303, and 313 K) and different concentration (40, 80, 120 mg l^{-1}), respectively, the results were showed in Figs. 14 and 15. According to the intercept and slope of the curve, the value of α, β, and R^2 were calculated and displayed in Table 4. The values of R^2 indicate that the correlation of Elovich kinetics equation was more moderate than that of pseudo-first-order model, but much poorer than that of pseudo-second-order model.

Based on the above discussion, it was observed that the pseudo-second-order kinetics model can descript the adsorption of MO onto activated clay well. The value of correlation coefficient (R^2) of the pseudo-first-order equation exceeded 0.998. In addition, the adsorption capacity ($q_{e\ \mathrm{cal}}$) that was calculated by the theoretical pseudo-first-order equation was close to the q_e derived from the experiment. So it can be concluded that the adsorption process of MO onto activated clay was more in line with the mechanism of pseudo-second-order model. Moreover, the adsorption rate increased and the adsorption capacity decreased with temperature increasing, this was identical with the result of experiment. In addition, adsorption rate decreased with the increase in initial concentration, it was due to the fact that the adsorption of MO onto activated clay is monolayer adsorption and competition were existed in the dye molecules in solution, when the initial concentration increased the competition intensified, so it resulted in the adsorption rate reduced.

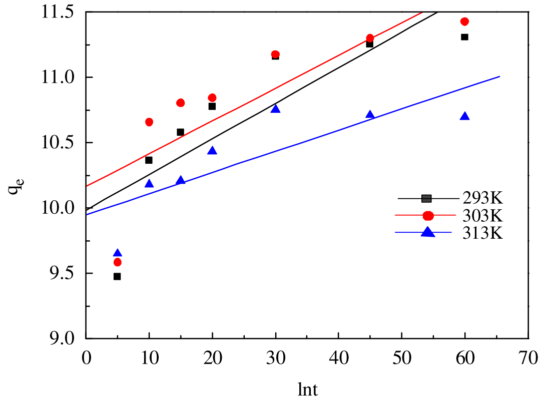

Fig. 14. Elovich kinetics for MO at different temperature.

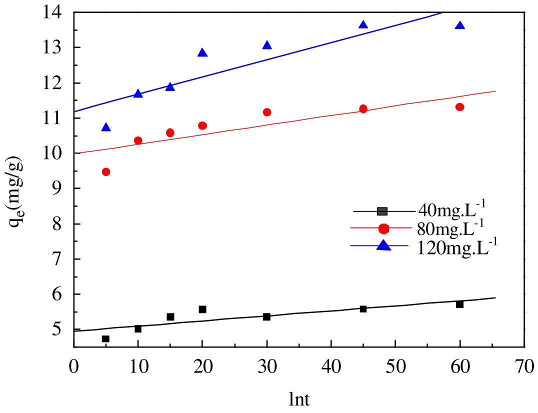

Fig. 15. Elovich kinetics for MO at different initial concentration.

Table 4
Kinetics parameters for Elovich kinetics model

Elovich kinetics model				q_e (mg g^{-1}) (experimental)
T (K)	α	β	R^2	
293	9.66×10^4	1.3816	0.9390	11.6144
303	3.41×10^5	1.4891	0.8928	11.5878
313	4.75×10^8	2.2933	0.8998	10.7918
c_0 (mg l^{-1})	α	β	R^2	q_e (mg g^{-1})
40	2.90×10^4	2.6714	0.8660	5.9757
80	3.41×10^5	1.3816	0.9390	11.6144
120	1.48×10^3	0.8071	0.9605	14.5202

3.4. Determination of thermodynamic parameters

Arrhenius relationship can be used to calculate the activated energy of adsorption, which was expressed as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{13}$$

where k_2 is the pseudo-first-order constant (g mg^{-1} min^{-1}); E_a (kJ mol^{-1}) is the Arrhenius activation energy of adsorption; A is the Arrhenius factor; R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the operated temperature. When ln k_2 is plotted against $1/T$ (Figure was not shown), a straight line with slope $-E_a/R$ was obtained. According to the value of the apparent activated energy of adsorption, the adsorption process that is a physical adsorption or chemical adsorption can be determined. Generally speaking, when E_a was between 5 and 40 kJ mol^{-1}, it was physical adsorption, and if the value of E_a was more than 40 kJ mol^{-1} [31], it was chemical adsorption. In this present experiment, $E_a = 24$ kJ mol^{-1} which was less than 40 kJ mol^{-1}, so it was inferred that the adsorption of MO onto activated clay was physical adsorption.

In order to evaluate the feasibility and the effect of temperature better, for MO adsorption onto activated clay, thermodynamic parameters such as standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were also obtained. The Gibbs free energy change of adsorption process was calculated by using the following equations:

$$K_c = \frac{c_{Ae}}{c_e} \tag{14}$$

$$\ln K_c = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{15}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{16}$$

where K_c is the equilibrium constant, c_{Ae} and c_e (both in mg l^{-1}) are the equilibrium concentration for solute on the sorbent and in the solution, respectively. R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T (K) is temperature.

The plot of ln K_c vs. $1/T$ (Fig. 16) is linear with the slope and the intercept giving values of enthalpy change ΔH° and entropy change ΔS°, the higher correlation coefficient ($R^2 = 0.9995$) prove the credibility of the equation fitting. And the value of ΔH°, ΔS°, and ΔG° calculated was listed in Table 5. The negative value of ΔG° at different temperature indicates the spontaneous nature of MO adsorption onto activated clay, and the absolute term of ΔG° revealed that the adsorption trend decrease with the increase in temperature, this was consistent with the result which the adsorption lessen with increasing in temperature. Enthalpy change ($\Delta H^{\circ} = -12.289$ kJ mol^{-1}) was negative, and it was implied that adsorption process of MO was exothermic. In other words, the high temperature is unfavorable to the progress of adsorption. And the value of ΔH° is lower than the chemical adsorption enthalpy values (40–120 kJ mol^{-1}) [32], and it was proved again that the adsorption process was physical adsorption. The negative value of entropy change ΔS° was explained that the course of MO transfer into adsorbent was decreased in confusion degree.

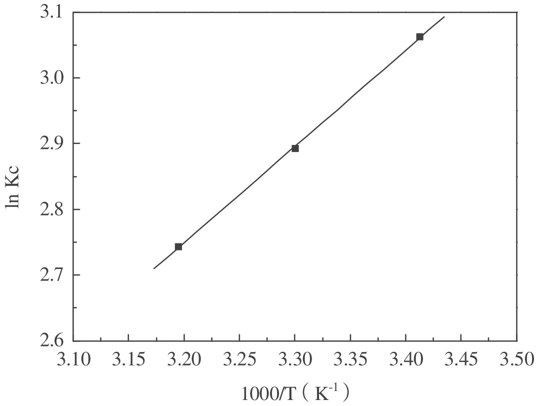

Fig. 16. Plot of ln K_c vs. $1/T$ for MO adsorption on activated clay.

Table 5
Thermodynamic parameters for the adsorption of MO onto activated clay

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})
293	−7.462	−12.289	−16.474	24.0
303	−7.297			
313	−7.050			

4. Conclusions

This present investigation shows that the adsorption of MO from wastewater onto activated clay, including the factors of affecting adsorption, adsorption isotherm, adsorption kinetics, and thermodynamics. The experimental results show that the optimum conditions of adsorption were pH $\leqslant$ 7.0, absorbent dosage 5 g l^{-1} at 293 K for 30 min. Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption behavior of MO onto activated clay, especially, the Langmuir isotherm exhibits the highest correlation with data. The kinetics research has demonstrated that adsorption process of MO is extremely suitable for the pseudo-second-order model and physical adsorption, and equilibrium adsorption capacity decrease with the increasing of temperature. The negative value of ΔG° signifies the adsorption reaction was a spontaneous adsorption. The negative value of ΔH° indicated the adsorption process was exothermic, which may be indicated that activated clay is an effective adsorbent for the removal of MO from aqueous solutions. As a low-cost natural abundant adsorbent material, activated clay may be an alternative to more costly adsorbent materials.

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