Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28118

250 (2022) 266–287
February

Adsorption effect of two modified kaolin materials on wastewater containing multi-component organic dyes

Zike Huang, Jiaqi Bu, Hui Wang*

College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China, Tel. +86 13973138633; email: huiwang1968@163.com (H. Wang), 1018856194@qq.com (Z. Huang), 547702535@qq.com (J. Bu)

Received 7 September 2021; Accepted 1 January 2022

ABSTRACT

Adsorption method is one of the most important methods for the treatment of organic dye wastewater. Since the actual industrial wastewater generally contains multiple organic dyes, it is necessary to develop adsorbents that can remove multiple organic dyes simultaneously and efficiently. Some modified kaolin materials have the potential as adsorbents for the removal of numerous pollutants. In view of this, we prepared the aqueous solution containing methylene blue, rhodamine B and orange II and developed two modified kaolin materials called Fe-kaolin and kaolin, respectively. Then we studied the adsorption properties of the two materials in the solution containing three organic dyes. The results showed that among three organic dyes, both Fe-kaolin and kaolin had the largest adsorption capacity for methylene blue, followed by orange II, and finally rhodamine B. In addition, the quality of adsorbents, time, the concentration of Cl^-, pH and temperature had great impact on the adsorption effect of organic dyes on these two materials. Among these factors, the quality of adsorbents had the greatest influence on the adsorption. Therefore, the regeneration or the best adsorption effect of the two modified kaolin materials on multiple organic dyes can be realized by adjusting these factors. For example, the activation and regeneration of adsorbents was achieved by adjusting pH. This technology had the advantages of simple operation and low cost. Furthermore, the mechanism of the three organic dyes by the modified kaolin materials was studied. The results showed the adsorption of these three organic dyes by the modified kaolin materials was a chemical adsorption process and an endothermic adsorption process. The adsorption of methylene blue by the two modified kaolin materials was monolayer adsorption. But it was difficult to judge whether the other two organic dyes adsorbed by the two modified kaolin materials was monolayer adsorption or multilayer adsorption. Last but not least, the adsorption of methylene blue by these two modified kaolin materials can usually proceed spontaneously while the adsorption of the other two organic dyes by these two modified kaolin materials usually cannot proceed spontaneously. In short, these two modified kaolin materials had the potential in the treatment of wastewater containing multiple organic dyes. This work has certain significance for the recycling applications of kaolin tailings and the development of novel modified kaolin materials that can remove multiple organic dyes in wastewater efficiently.

Keywords: Organic dye wastewater; Adsorption method; Modified kaolin materials; Recycling; Kaolin; Fe-kaolin; Methylene blue; Rhodamine B; Orange II

* Corresponding author.

1. Introduction

Organic dyes have been widely used in numerous fields. There have been many kinds of organic dyes with complex components. For example, methylene blue, a phenothiazine salt, is relatively stable in air. Its aqueous solution is alkaline and toxic [1]. Methylene blue, a cationic dye [2], has been widely used in chemical indicators, dyes, biological stains and drugs [3,4]. Besides, rhodamine B, a cationic dye with a bright pink color [5], can be used as a kind of cell fluorescent staining agent in laboratories. Nowadays rhodamine B has been widely used in industries such as colored glass and special fireworks [6–8]. Orange II, an orange acicular crystal or powder with irritation, is an anionic dye [9] that can be used as acid-base indicator and biological stains. Nowadays orange II has been used in the extraction and photometric determination of cationic surfactants [10,11]. However, many organic dyes have their own toxic effects. For instance, high-concentration methylene blue solution can oxidize hemoglobin and make hemoglobin produce methemoglobin, which causes nausea, abdominal pain, precordial pain, dizziness, headache, sweating, and unconsciousness [12]. Rhodamine B may retard the growth of rats, reduce their reproductive capacity, and reduce the resistance of rats, resulting in decreased longevity of rats [13]. Orange II is a highly toxic anionic organic dye. High-concentration orange II solution can cause adverse reactions such as nausea, abdominal pain, precordial pain, dizziness, headache, sweating and unconsciousness [14]. With the rapid development of the chemical industry, the discharge of organic dye wastewater is also increasing in recent years. Most organic dyes in wastewater are difficult to degrade in natural environment [15]. In addition, the salt content and organic dye concentration in wastewater are usually high [16]. In short, organic dye wastewater has caused great harm to the ecosystem and biological health [17–19]. Therefore, it is urgent to treat organic dye wastewater. Nowadays a lot of methods for treating organic dye wastewater have been developed. At present, the techniques used commonly for the treatment organic dye wastewater mainly include biological method [20], membrane separation method [21], oxidation method [22,23], catalytic degradation method [24], electrocoagulation method [25] and adsorption method [26,27]. Among these methods, adsorption method, as a physicochemical method, has the advantages of simple equipment, low cost, short cycle, simple operation, small pH change and safety. Besides, the adsorbents can be recycled. More importantly, the adsorption method has better removal effect on difficult-to-degrade organic dyes [28]. Based on this, adsorption method has been used widely in the removal of organic dyes in wastewater. The effect of adsorption method depends on the performance of adsorbents because the realization of selective enrichment of pollutants on adsorbents depends on dense pores and huge specific surface area of adsorbents, as well as multiple forces between various functional groups on the surface of the adsorbents and pollutants [29–31]. Inspired by this, various adsorbents for adsorb organic dyes have been developed in recent years [32–34]. For instance, Balarak et al. developed polypyrrole/nanosilica composite (PPN/SiO_2) for the removal of acid orange 7 dyes, and its removal efficiency was as high as 99.4% under optimal conditions [26]. Besides, they developed a novel material called C-Fe_2O_3 by coating magnetite Fe_2O_3 nanoparticles on the surface of chitosan polymer. It was found that the removal efficiency of acid blue 113 dye by C-Fe_2O_3 reached 99.68% under optimal conditions [27].

However, many adsorbents have complex synthetic routes and high cost. In addition, some adsorbents may pollute the environment during the synthesis process. Last but not least, nowadays most studies mainly focused on the adsorption and removal of a pollutant by adsorbents. Thus, low-cost adsorbents prepared from natural materials or some wastes have attracted extensive attention recently [35]. For example, Balarak et al. used *Azolla filiculoides* aquatic fern as a good and an economical biosorption agent for the eradication of reactive black 5 dye in wastewater with acidic pH [36]. In addition, they also utilized canola residue for biosorption of acid orange 7 (AO7) from wastewater [37]. These works have important significance and reference value for the treatment of organic dye wastewater and the recycling of some wastes.

Kaolin, as a natural silicate mineral material, is mainly used in the field of hollow stripping and slicing of glass, ceramics and concrete, and it is less used in other areas [35,38,39]. With the continuous development and utilization of mineral resources, plenty of kaolin tailings have been produced. It is necessary to treat these kaolin tailings with appropriate treatment methods [40]. It is worth noting that kaolin has the potential as adsorbents for the treatment of pollutants due to the advantages of wide source, low price, neutral pH, non-toxic, large specific surface area and large adsorption capacity [41–43]. More importantly, the modification of clay minerals such as kaolin can increase the adsorption sites and functional groups on the surface of the clay minerals, thereby greatly improving the adsorption performance of the clay minerals for environmental pollutants. Based on this, some clay mineral modification methods have been developed in recent years [44]. Utilizing the adsorption properties of kaolin or some modified kaolin materials to remove organic dyes from wastewater is conducive to turning waste into treasure, which has significant social and environmental benefits. For example, some modified kaolin materials have been used for the removal of methylene blue in wastewater [45–47]. However, an adsorbent usually only removes one organic dye in wastewater. But the actual industrial wastewater generally contains multiple organic dyes. The study on the adsorption behavior and mechanism of multiple organic dyes by adsorbents is of great significance for the development of adsorbents that can remove multiple organic dyes. Nevertheless, the studying of the adsorption behavior of multicomponent adsorbates on adsorbents has not attracted enough attention [48].

In view of this, we prepared an aqueous solution containing the three organic dyes mentioned above, that is, the aqueous solution containing methylene blue, rhodamine B and orange II. Besides, two modified kaolin materials named Fe-kaolin and kaolin, respectively, were developed in this paper. Then the two modified kaolin materials were added to the above solution containing three organic dyes, respectively, to study the adsorption properties of the two materials for multiple organic dyes. Besides, the effects of

the quality of adsorbents, time, the concentration of Cl^-, pH and temperature on the adsorption of organic dyes by the adsorbents were studied. Moreover, the activation and regeneration technology of these two modified kaolin materials were also studied. Last but not least, the adsorption behavior and mechanism of these two modified kaolin materials to organic dyes were explored preliminarily through adsorption kinetics, adsorption isotherms and adsorption thermodynamics in this paper.

2. Materials and methods

2.1. Materials

The kaolin used in this study were acquired in Kermel (Tianjin, China), and other solvents and reagents were acquired in Sinopharm (Beijing, China). All the chemicals were of analytical grade and used without further purification.

2.2. Mathematical model of adsorption

The following formulas and models were used to study the adsorption mechanism of organic dyes by adsorbents with reference to some previous studies [26,27].

The adsorption capacity (Q_e) (mg g^{-1}) and removal rate (X) (%) of the modified kaolin materials to organic dyes was calculated by Eqs. (1) and (2), respectively:

$$Q_e = \frac{\left(c_0 - c_e\right) \times V}{m} \tag{1}$$

$$X = \frac{c_0 - c_e}{c_0} \times 100\% \tag{2}$$

where c_0 (mg L^{-1}) represented the concentration of organic dyes before adsorption while c_e (mg L^{-1}) represented the concentration of organic dyes after adsorption. V (L) was the volume of the aqueous solution containing organic dyes. m (g) was the quality of these two modified kaolin materials added.

Moreover, to further understand the adsorption mechanism, the thermodynamics and kinetics of the adsorption of organic dyes by the modified kaolin materials were studied preliminarily in this paper. For this purpose, two well-known kinetic model Eq. (3) (pseudo-first-order) and Eq. (4) (pseudo-second-order) were used to calculate the kinetic parameters of the adsorption process of organic dyes by the modified kaolin materials to obtain the adsorption kinetics fitting curve. The equations of these two dynamic models were described as follows:

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{4}$$

where t (h) represented the adsorption time. Q_e (mg g^{-1}) was the equilibrium adsorption capacity of adsorbents. Q_t (mg g^{-1}) was the adsorption capacity at time t. k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) represented the first-order kinetic constant and the second-order kinetic constant, respectively.

Additionally, adsorption thermodynamic isotherms can be used to evaluate the surface properties and affinity of adsorbents. Langmuir adsorption thermodynamic isotherms [Eq. (5)] and Freundlich adsorption thermodynamic isotherms [Eq. (6)] were used to evaluate the adsorbents:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{5}$$

$$Q_e = K_F \left(C_e\right)^{\frac{1}{n}} \tag{6}$$

where Q_e (mg g^{-1}) was the equilibrium adsorption capacity of adsorbents. Q_m (mg g^{-1}) was the maximum adsorption capacity. C_e (mg L^{-1}) represented the concentration of residual organic dyes in the aqueous solution when the reaction reached equilibrium. K_L represented the adsorption rate constant of Langmuir. The adsorption capacity and intensity constants of the Freundlich model were K_F and n, respectively.

Eqs. (7)–(9) were used to better understand the adsorption mechanism of organic dyes by adsorbents:

$$K_D = \frac{Q_e}{C_e} \tag{7}$$

$$\Delta G = -RT \ln K_D \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

where Q_e (mg g^{-1}) was the equilibrium adsorption capacity of adsorbents. C_e (mg L^{-1}) represented the concentration of residual organic dyes in the aqueous solution when the reaction reached equilibrium. K_D was the adsorption thermodynamic equilibrium constant. ΔG was the standard Gibbs free energy variable of adsorption. R was the gas molar constant. T was the absolute temperature. ΔH was the change of the equivalent adsorption enthalpy. ΔS was the change of adsorption standard entropy.

2.3. Methods

The experiment was divided into six parts in this study:

2.3.1. Synthesis of Fe-kaolin and kaolin materials

First of all, 100 g kaolin was added to the aqueous solution and stirred thoroughly. Meanwhile, 1 g $Fe(NO_3)_3$ and 100 g kaolin were added to the aqueous solution and stirred thoroughly. Then the two systems were aged for about 5 h and some powder materials with irregular shapes were got. After that, these powders were baked in the oven at 120°C for about 1 h. Finally, these powders were put in a muffle furnace and reacted at 450°C for about 2 h to obtain kaolin with white and Fe-kaolin with reddish brown.

2.3.2. Drawing of standard curve of the concentration of organic dyes and absorbance

A series of standard solutions with different concentrations of these three organic dyes were prepared, respectively.

And then the relationship between absorbance (Abs) and concentration of organic dyes (mg L^{-1}) was measured by dual-beam ultraviolet/visible spectrophotometer (UV) (TU-1901, Persee China). Based on this, the standard curve of the concentration of organic dye and absorbance was drawn.

2.3.3. Preparation of aqueous solutions containing three organic dyes

0.12 g methylene blue, 0.12 g rhodamine B and 0.12 g orange II were weighed and added into a beaker. Then deionized water was added into the beaker. After that, this mixed system was poured into a 1 L volumetric flask. Then deionized water was poured into the volumetric flask for constant volume. Thus, 1 L organic dye mother liquor with the concentration of these three organic dyes of 120 mg L^{-1} was successfully prepared. Finally, 5 mL the above mother liquor was diluted with 45 mL deionized water to prepare 50 mL aqueous solution containing these three organic dyes at a concentration of 12 mg L^{-1}.

2.3.4. Characterization of Fe-kaolin and kaolin

The morphology and elemental composition of these two modified kaolin materials was characterized by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) (Oxford Instruments, UK). Besides, some information about chemical bonds and crystal structures of the modified kaolin materials were obtained by X-ray diffraction (XRD) patterns (Ultima IV Japan) and Fourier-transform infrared (FT-IR) spectrometer (PerkinElmer, USA). Besides, the specific surface area, pore size and pore volume of the two modified kaolin materials were analyzed by automatic specific surface area and pore size analyzer (Micromeritics ASAP2460, USA).

2.3.5. Studying of the adsorption behavior and mechanism of multi-component organic dyes on the modified kaolin materials

Fe-kaolin and kaolin were added to the 50 mL aqueous solution containing these three organic dyes at a concentration of 12 mg L^{-1}, respectively. Then these systems were put in a constant temperature water bath oscillator (SHA-B, Suzhou Guofei Experimental Instrument Co., Ltd.) and reacted for about 48 h. After that, the systems were put in a desktop high-speed centrifuge (TQ16-WS, Cence, China) and centrifuged at 5,600 rpm for about 3 min. Then the supernatant was taken. After that, dual-beam ultraviolet/visible spectrophotometer (UV) (TU-1901, Persee China) was used to detect the concentration changes of organic dyes. Finally, the adsorption capacity and removal rate of two modified kaolin materials for these three organic dyes was calculated by Eqs. (1) and (2) for the studying the adsorption of organic dyes on adsorbents. Based on this, Eqs. (3)–(9) were used to study the thermodynamics and kinetics of the adsorption of organic dyes by the modified kaolin materials.

2.3.6. Study on the regeneration performance of the adsorbents

The activation and regeneration technology of adsorbents is of great importance in practical applications. The adsorbents that had adsorbed organic dyes were treated with 5 mL of dilute HCl with a concentration of 0.1 mol L^{-1} in this paper. Then the systems were oscillated at room temperature for about 12 h. However, the "acidosis" of the adsorbents may reduce the re-adsorption capacity of the adsorbent to organic dyes. Thus, 5 mL of dilute HCl with a concentration of 0.1 mol L^{-1} was used to neutralize dilute HCl to the systems and then oscillated at room temperature for about 24 h. Finally, the re-adsorption capacity of the activated and regenerated materials for organic dyes was also studied in this paper.

3. Results

3.1. Characterization of the modified kaolin materials

As can be seen from Fig. 1, the surface morphology of Fe-kaolin and kaolin was quite different from each other. Besides, although both Fe-kaolin and kaolin contained multiple metal elements and Si elements, the content ratio and types of elements in the two materials were quite different from each other. For example, Fe-kaolin contained more Fe and Pt compared with kaolin.

As was shown in Fig. 2, the diffraction patterns of these two modified kaolin materials were basically the same. This indicated that the crystal structures of these two modified kaolin materials used in this study were relatively close. Additionally, the diffraction patterns of these two modified kaolin materials showed that the composition of these two modified kaolin materials was very complex.

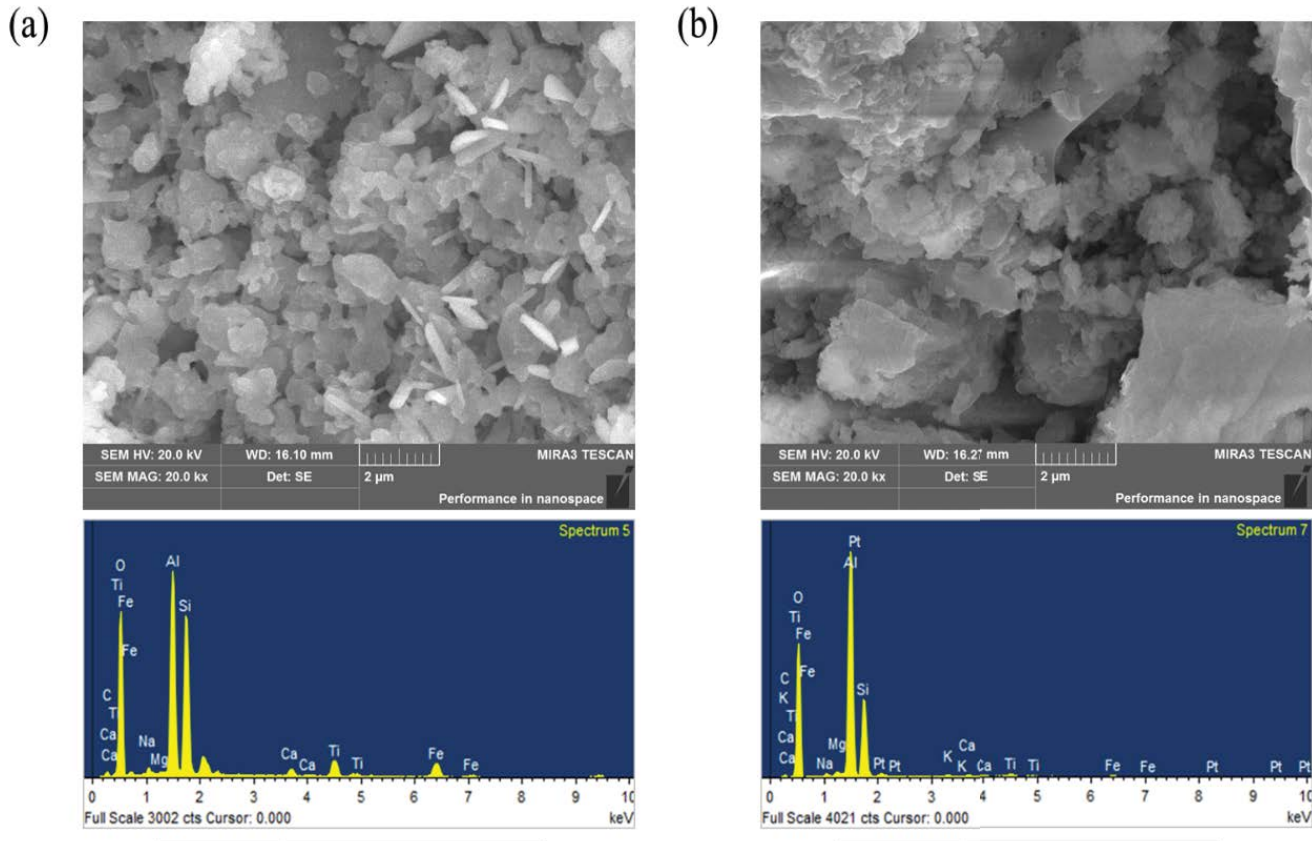
In addition, as can be seen from Fig. 3, the FT-IR spectra of these two modified kaolin materials were slightly different. As can be seen from Fig. 3a, a medium intensity peak at 1,090 cm^{-1} related with Si–O stretching vibration in Fe-kaolin. Besides, a feeble absorption at 812 cm^{-1} related with Al–Mg–OH stretching vibration in Fe-kaolin. And a feeble absorption at 721 cm^{-1} related with Si–O–Al stretching vibration in Fe-kaolin. And a feeble absorption at 552 cm^{-1} related with Si–O stretching vibration in Fe-kaolin [49].

As shown in Fig. 3b, a medium intensity peak at 1083 cm^{-1} related with Si–O stretching vibration in kaolin. And a feeble absorption at 554 cm^{-1} related with Si–O stretching vibration in kaolin [49].

As can be seen from Fig. 4, the adsorption isotherms of Fe-kaolin and kaolin belonged to type III when nitrogen was used as the adsorbate. This indicated that the force between the adsorbents and nitrogen was quite weak. Thus, these two modified kaolin materials had poor adsorption effect on nitrogen. Besides, the adsorption curves of the two modified kaolin materials were basically similar, but the adsorption capacity of kaolin was greater than the adsorption capacity of Fe-kaolin. Moreover, the pore structure parameters of these two modified kaolin materials were shown in Table 1. As can be seen from Table 1, all pore structure parameters of kaolin were greater than that of Fe-kaolin. These results indicated that kaolin may have better adsorption properties than Fe-kaolin.

3.2. Characterization of the adsorption of organic dyes on the modified kaolin materials

The standard curve of the concentration of organic dyes and absorbance is shown in Fig. 5. The concentration of



Element	Weight%	Atomic%
C K	5.73	9.44
O K	50.34	62.25
Na K	0.81	0.70
Mg K	0.11	0.09
Al K	16.42	12.04
Si K	16.35	11.51
Ca K	1.03	0.51
Ti K	3.43	1.42
Fe K	5.77	2.04
Totals	100.00	

Element	Weight%	Atomic%
C K	4.57	7.56
O K	52.64	63.95
Na K	0.50	0.43
Mg K	0.39	0.32
Al K	25.20	18.15
Si K	12.20	8.44
K K	0.38	0.19
Ca K	0.40	0.19
Ti K	0.75	0.31
Fe K	0.72	0.25
Pt M	2.14	0.21
Totals	100.00	

Fig. 1. SEM micrograph of Fe-kaolin and EDS spectrum of the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

methylene blue, rhodamine B and orange II can be obtained through the standard curve formula in Fig. 5. Based on this, the adsorption capacity (Q_e) and removal rate (X) can be calculated for the studying of the adsorption of these three organic dyes on adsorbents.

3.3. Characterization of the adsorption behavior of organic dyes on the modified kaolin materials

As can be seen from Figs. 6 and 7, among these three organic dyes, both Fe-kaolin and kaolin had the largest adsorption capacity for methylene blue. But the adsorption effect on rhodamine B and orange II was relatively poor. Besides, the adsorption capacity of the adsorbents for rhodamine B and orange II in wastewater containing three organic dyes was improved compared with that in the aqueous solution containing one organic dye. This indicated that different organic dyes may promote the adsorption of each other on adsorbents. Therefore, as shown in Figs. 6 and 7, in the aqueous solution containing three organic dyes, the absolute adsorption capacity of methylene blue decreased due to the competition of adsorption sites on the surface of adsorbents. We speculated that stacking, hydrogen bonding and electrostatic attraction may be the adsorption mechanism of organic dyes by the modified kaolin materials.

Additionally, as shown in Figs. 6 and 7, when the quality of the adsorbents added was small, the adsorption sites on the adsorbents were easy to reach saturation at this time. Therefore, the adsorbents had strong adsorption capacity for organic dyes while the removal rate of organic dyes was low. With the increase of the quality of adsorbents added, the adsorption sites of adsorbent gradually increased. The adsorption capacity of organic dyes by adsorbents decreased while the removal rate of organic dyes increased until the organic dyes in wastewater were completely removed.

Last but not least, it was necessary to determine the quality of adsorbents added to further study the adsorption behavior and mechanism. Comprehensively considering the quality of the adsorbents and the removal rate of organic dyes by the adsorbents, the lowest quality of adsorbents when the removal rate of methylene blue reached basically stable was taken. As can be seen from Figs. 6 and 7, the quality of kaolin added was 0.6 g while the quality of Fe-kaolin added was 0.48 g in this study.

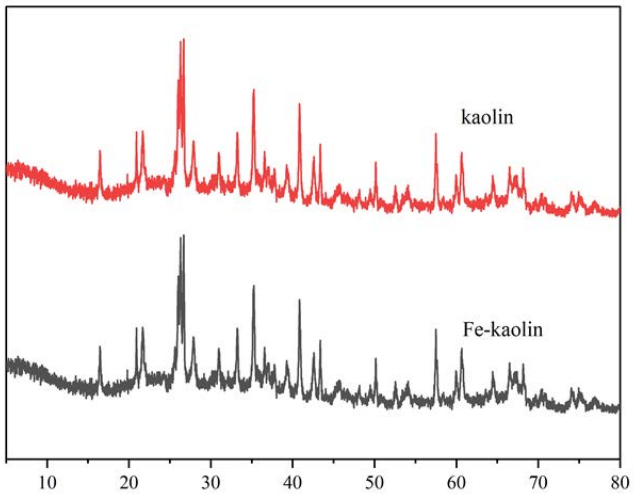


Fig. 2. XRD patterns of the modified kaolin materials.

3.4. Influence of some external factors on the adsorption behavior of organic dyes on the modified kaolin materials

The adsorption time has a great influence on the adsorption effect. With the extension of time, the adsorption capacity of three organic dyes adsorbed by adsorbents increased as shown in Fig. 8. After about 3 h, the adsorption of organic dyes on adsorbents reached equilibrium basically. In order

Table 1
Pore structure parameters of Fe-kaolin and kaolin

Samples	Fe-kaolin	Kaolin
Surface area ($m^2\ g^{-1}$)	4.4199	7.3805
Pore volume ($cm^3\ g^{-1}$)	0.008354	0.034403
Pore size (nm)	7.5603	18.6452

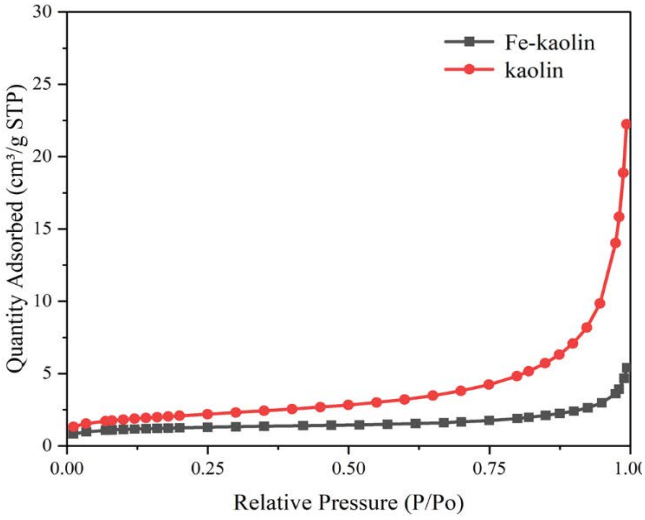


Fig. 4. Nitrogen adsorption isotherms of the modified kaolin materials.

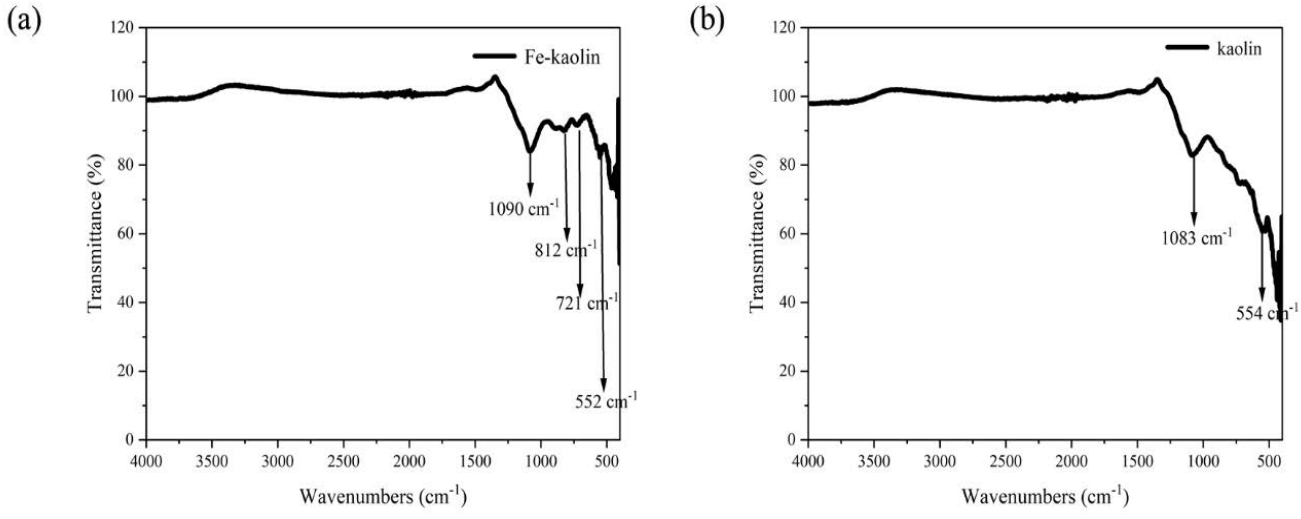


Fig. 3. FT-IR spectra of the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

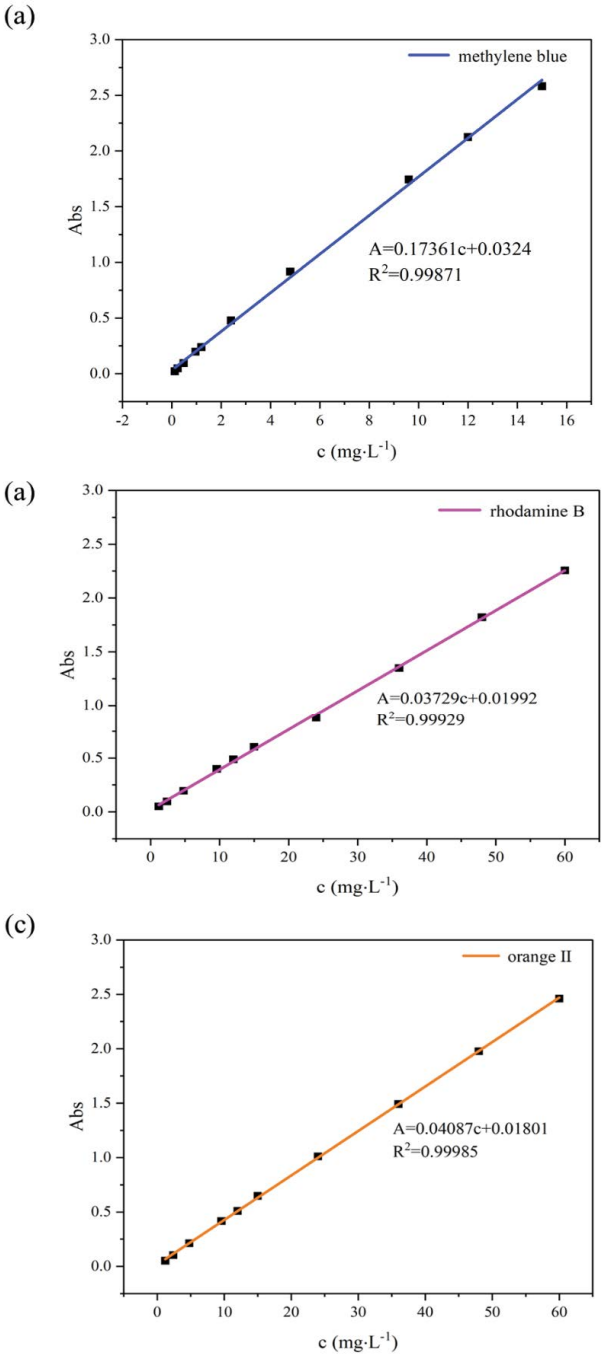


Fig. 5. Standard curve diagram of the concentration of the three organic dyes and absorbance: (a) methylene blue, (b) rhodamine B, and (c) orange II.

to ensure that the adsorption-desorption of organic dyes on the adsorbents had reached equilibrium completely, the time for adsorbents to adsorb organic dyes was set about 24 h. Besides, as shown in Table 2, the two modified kaolin materials had the largest adsorption capacity for methylene blue, followed by orange II, and finally rhodamine B. In addition, the adsorption effect of Fe-kaolin on the adsorption of methylene blue and orange II was better than that of kaolin.

Table 2
The maximum adsorption capacity of the modified kaolin materials for organic dyes (in mg g^{-1})

	Fe-kaolin	Kaolin
Methylene blue	1.0990	0.9570
Rhodamine B	0.1650	0.2660
Orange II	0.7190	0.4720

And the adsorption effect of kaolin on the adsorption of rhodamine B was better than that of Fe-kaolin.

Cl^- is one of the common ions in water. Therefore, it is necessary to study the effect of Cl^- on the adsorption of organic dyes by adsorbents. 5 g L^{-1} NaCl solution were used to adjust the concentration of Cl^- in aqueous solution in this study. As was shown in Fig. 9a, with the increase of the concentration of Cl^-, the adsorption capacity of methylene blue and orange II adsorbed by Fe-kaolin decreased gradually. And when the concentration of Cl^- was relatively low, the adsorption capacity of rhodamine B adsorbed by Fe-kaolin increased with the increase of the concentration of Cl^-. But when the concentration of Cl^- reached a certain concentration, Cl^- inhibited the adsorption of rhodamine B on Fe-kaolin with the increase of the concentration of Cl^-. Nevertheless, when the concentration of Cl^- was relatively high, with the increase of the concentration of Cl^-, the adsorption capacity of rhodamine B increased slightly.

The effect of Cl^- on the adsorption of organic dyes by kaolin was more complicated. As can be shown in Fig. 9b, when the concentration of Cl^- was relatively low, the adsorption capacity of organic dyes adsorbed by kaolin increased with the increase of the concentration of Cl^-. But when the concentration of Cl^- reached a certain concentration, Cl^- inhibited the adsorption of organic dyes on kaolin with the increase of the concentration of Cl^-. However, when the concentration of Cl^- was relatively high, with the increase of the concentration of Cl^-, Cl^- promoted the adsorption of organic dyes on kaolin.

As can be seen from the above experimental results, the regeneration of the adsorbents or the removal of multiple organic dyes can be realized by adjusting the concentration of Cl^- in wastewater.

pH also has a great influence on the adsorption of organic dyes by adsorbents. In order to avoid the interference of Cl^-, dilute HNO_3 and dilute NaOH were used to adjust the pH of wastewater in this study. As can be seen from Fig. 10a, the excessive concentration of H^+ and OH^- inhibited the adsorption of methylene blue by Fe-kaolin. Therefore, the adsorption of methylene blue by Fe-kaolin usually needs to be carried out in a neutral environment. Besides, the excessive concentration of H^+ and OH^- promoted the adsorption of orange II by Fe-kaolin. H^+ promoted the adsorption of rhodamine B on Fe-kaolin while OH^- inhibited the adsorption of rhodamine B on Fe-kaolin.

The change of the pH had little effect on the adsorption of methylene blue by kaolin as shown in Fig. 10b. Besides, the excessive concentration of H^+ and OH^- greatly promoted the adsorption of rhodamine B and orange II by kaolin. Accordingly, the regeneration of the adsorbents or

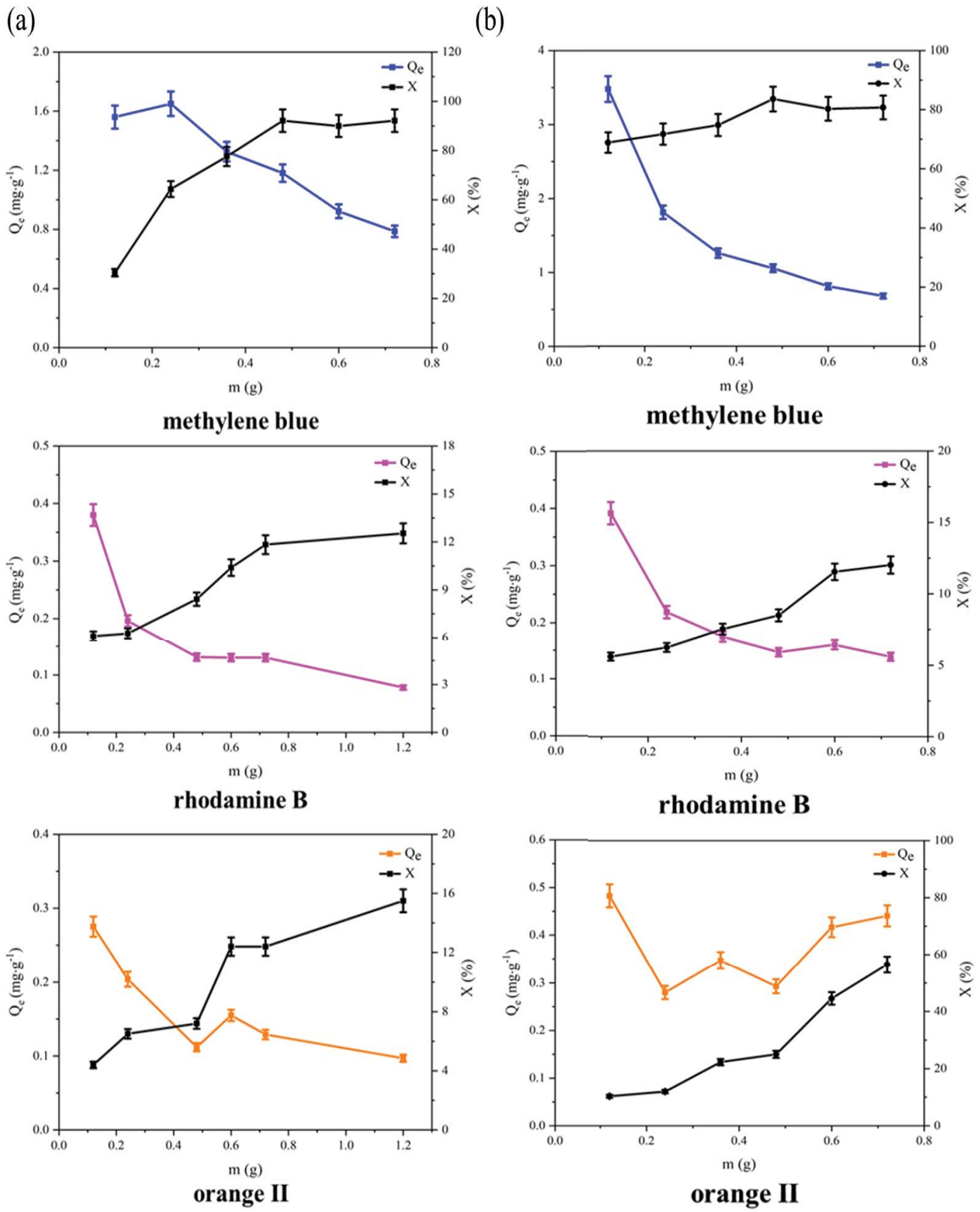


Fig. 6. Effect of the quality of Fe-kaolin on the adsorption: (a) the aqueous solution containing one organic dye and (b) the aqueous solution containing three organic dyes.

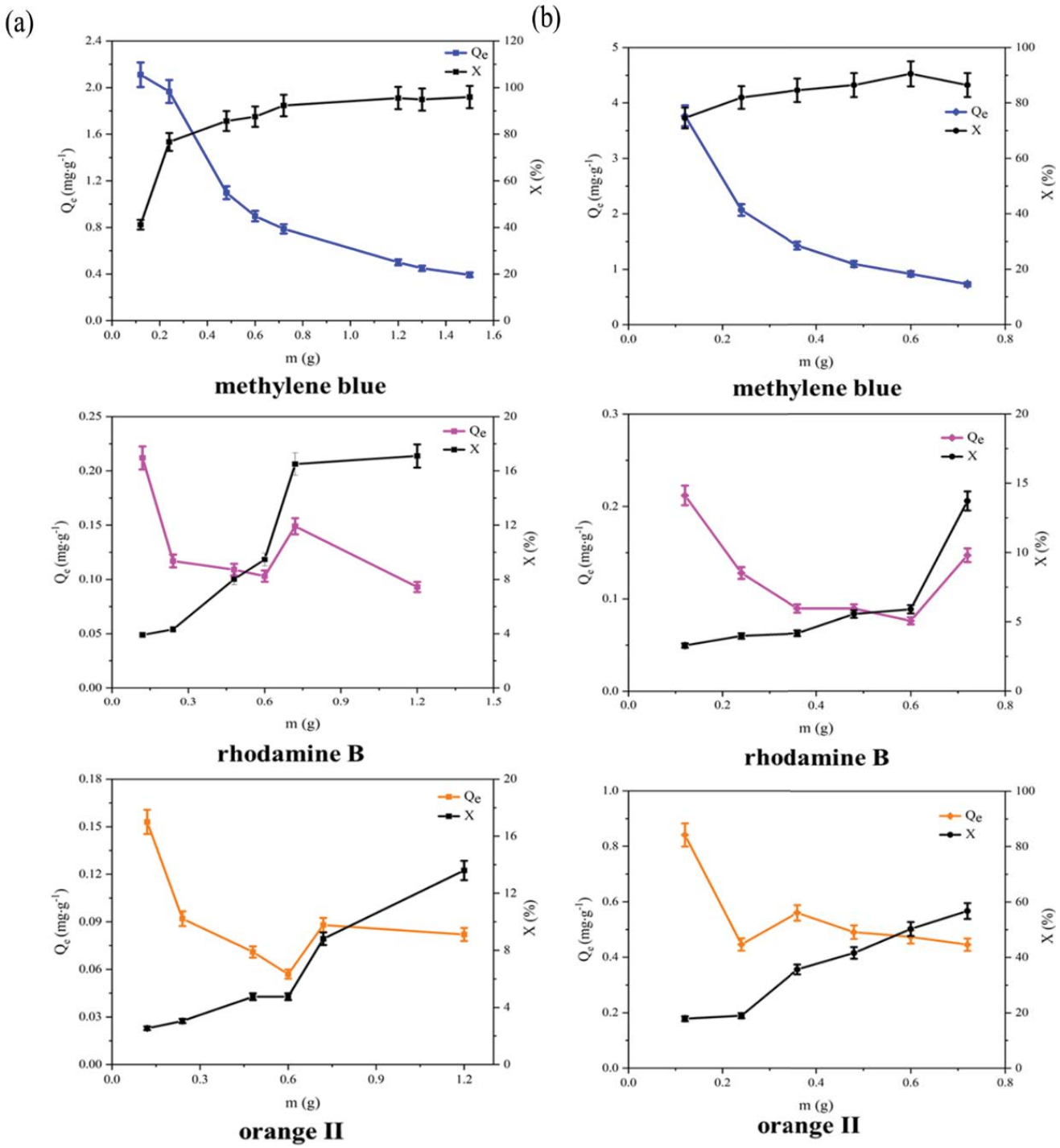


Fig. 7. Effect of the quality of kaolin on the adsorption: (a) the aqueous solution containing one organic dye and (b) the aqueous solution containing three organic dyes.

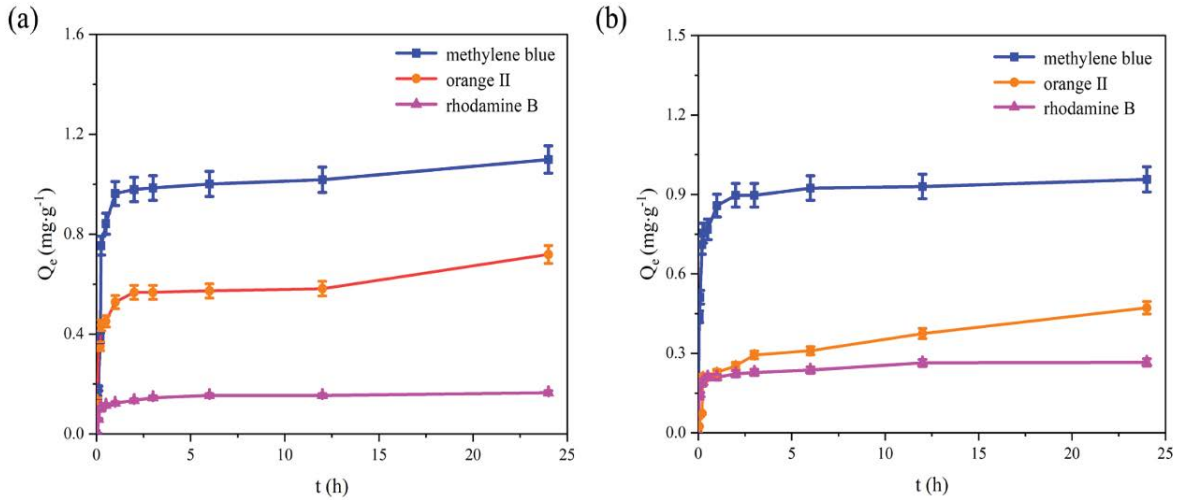


Fig. 8. Effect of time on the adsorption of organic dyes by the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

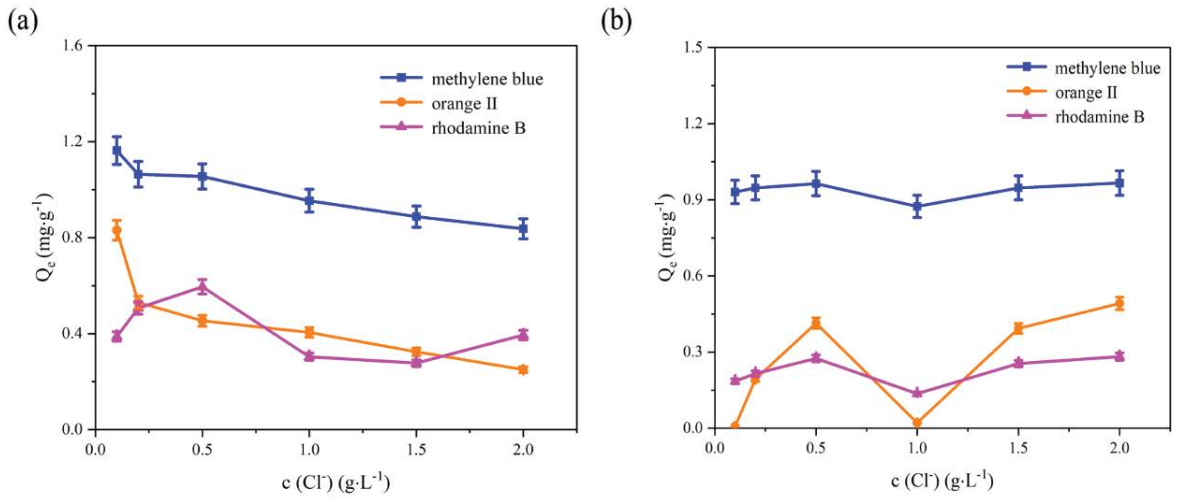


Fig. 9. Effect of the concentration of Cl^- on the adsorption of organic dyes by the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

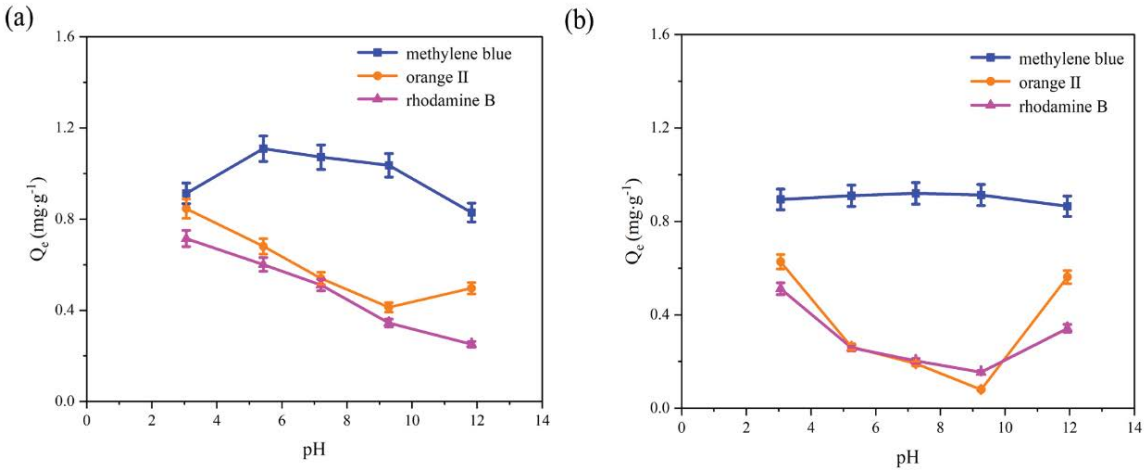


Fig. 10. Effect of pH on the adsorption of organic dyes by the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

the removal of multiple organic dyes can also be achieved by adjusting pH in wastewater.

Temperature usually has great effect on the adsorption process. As can be seen from Fig. 11, the change of temperature had little effect on the adsorption capacity of the two modified kaolin materials to adsorb methylene blue and rhodamine B. And the adsorption capacity of orange II adsorbed by the modified kaolin materials increased with the increase of temperature.

3.5. Adsorption mechanism of organic dyes by the modified kaolin materials

The studying of adsorption mechanism is of great practical significance for the development of efficient adsorbents for organic dyes. As can be seen from Figs. 12–17, compared with the pseudo-first-order kinetics, the points of the pseudo-second-order kinetics distribution of the two modified kaolin materials for adsorbing organic dyes were closer to the oblique line. Besides, as can be seen from Tables 3–8, the adsorption capacity calculated by pseudo-second-order kinetic model was closer to the equilibrium adsorption capacity of organic dyes adsorbed by adsorbents. Moreover, the correlation coefficient of pseudo-second-order dynamics was closer to 1. Therefore, the adsorption mechanism was more in line with the pseudo-second-order adsorption kinetic model. This indicated that the adsorption of organic dyes by the modified kaolin materials was a chemical adsorption process.

Moreover, we also studied the isotherms and adsorption thermodynamics of the two modified kaolin materials for organic dyes. As can be seen from Figs. 18 and 19, the Langmuir isotherms model had a higher linear fit than the Freundlich isotherms model. Moreover, as can be seen in Tables 9 and 10, compared with Freundlich isotherm model, the R^2 value of the Langmuir isotherm model was closer to 1. Accordingly, the adsorption of methylene blue by these two modified kaolin materials was monolayer adsorption.

However, the adsorption isotherms of the two modified materials for the other two organic dyes were different from those of the two materials for methylene blue. As can be seen from Figs. 20–23, the Freundlich isotherms model

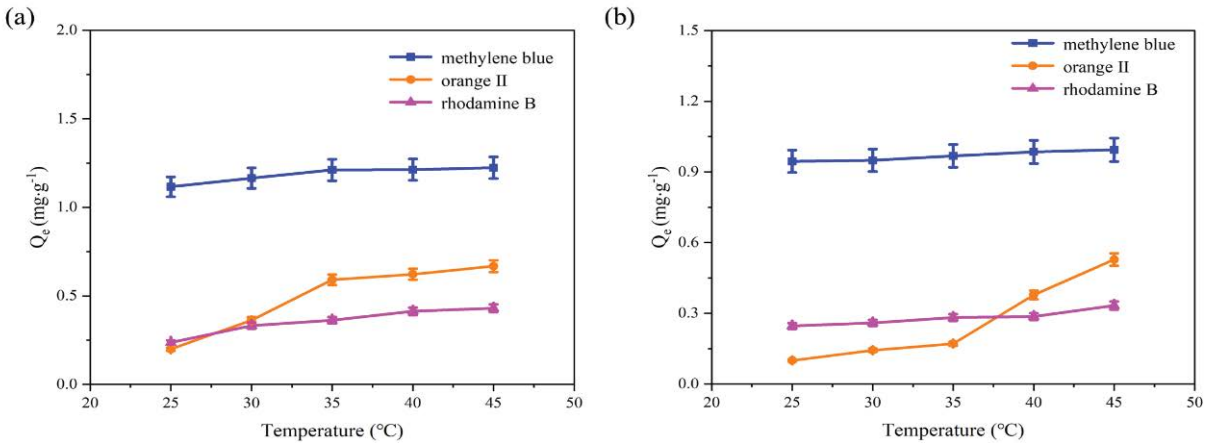


Fig. 11. Effect of temperature on the adsorption of organic dyes by the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

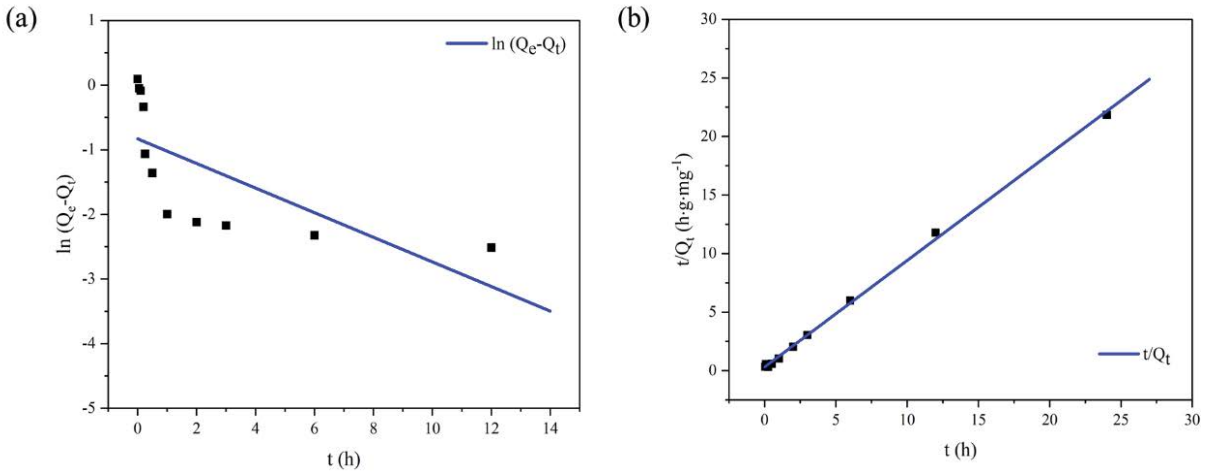


Fig. 12. Kinetic models of adsorption of methylene blue on Fe-kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

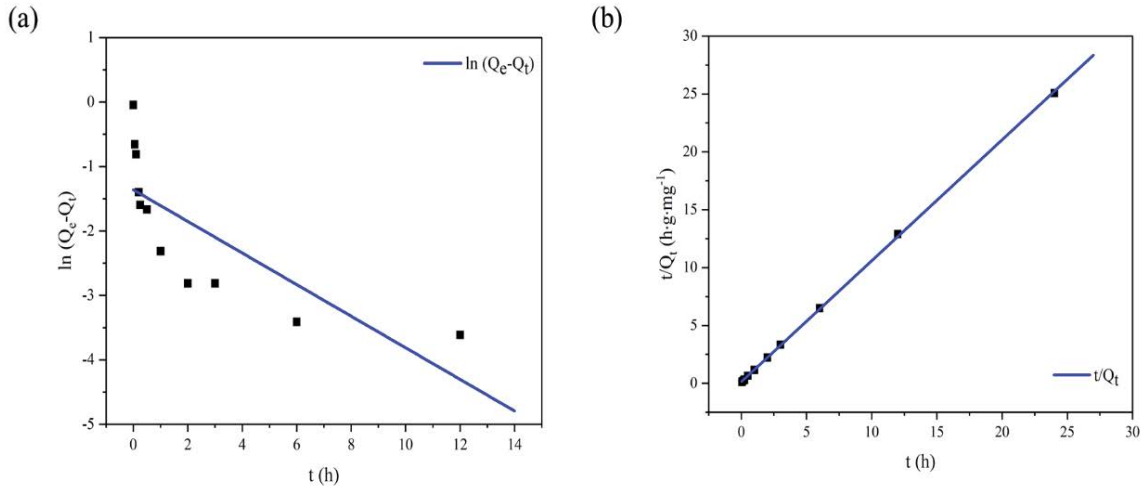


Fig. 13. Kinetic models of adsorption of methylene blue on kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

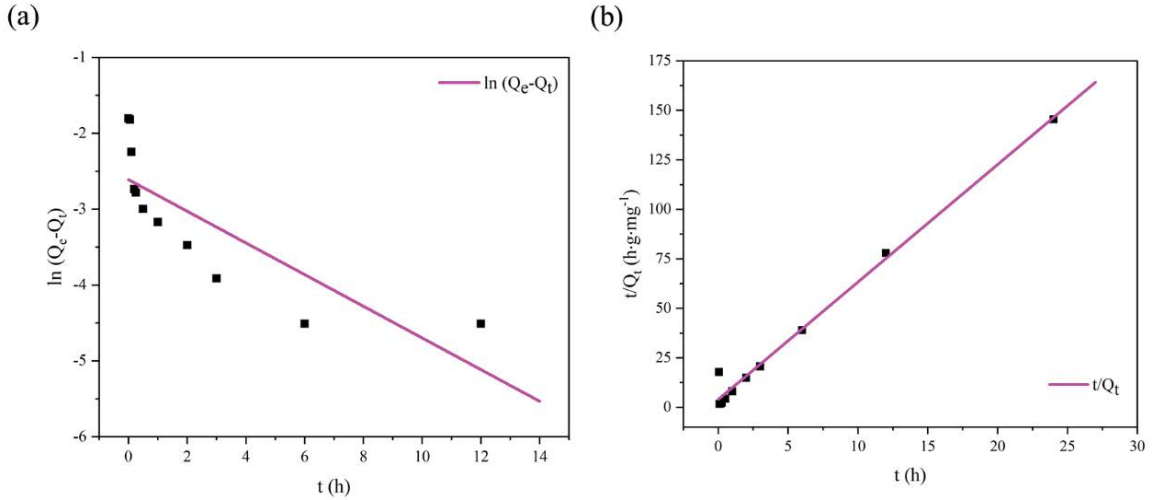


Fig. 14. Kinetic models of adsorption of rhodamine B on Fe-kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

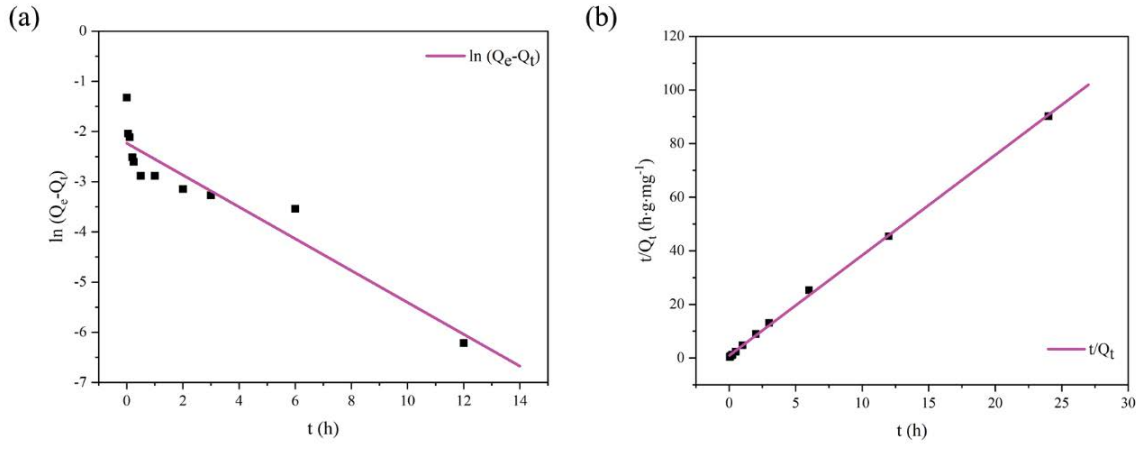


Fig. 15. Kinetic models of adsorption of rhodamine B on kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

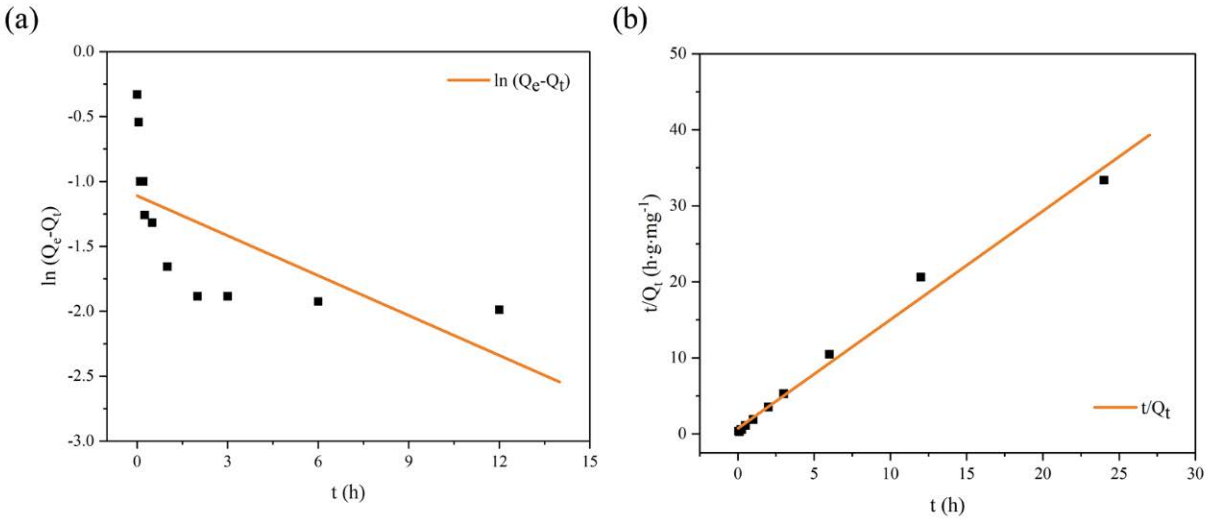


Fig. 16. Kinetic models of adsorption of rhodamine B on Fe-kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

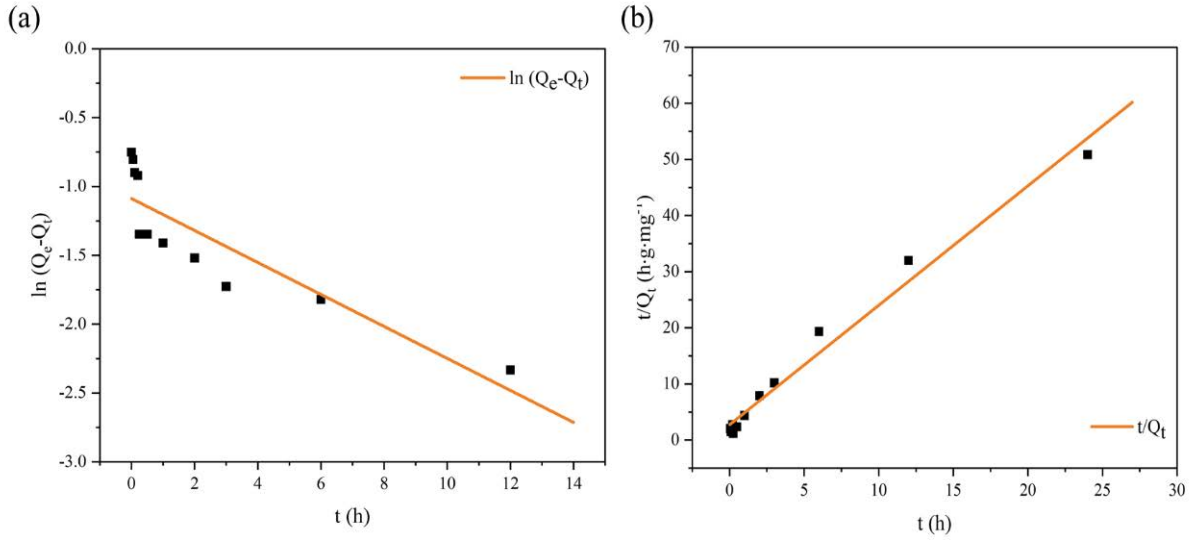


Fig. 17. Kinetic models of adsorption of rhodamine B on kaolin: (a) pseudo-first-order and (b) pseudo-second-order kinetic model.

Table 3
Fitting parameters of the kinetic model for adsorption of methylene blue by Fe-kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	1.0990
Pseudo-first-order	$Q_{e,cal}$ (mg g^{-1})	0.4355
	k_1 (h^{-1})	0.1904
	R^2	0.4782
Pseudo-second-order	$Q_{e,cal}$ (mg g^{-1})	1.0986
	k_2 (h^{-1})	2.6846
	R^2	0.9987

Table 4
Fitting parameters of the kinetic model for adsorption of methylene blue by kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	0.9570
Pseudo-first-order	$Q_{e,cal}$ (mg g^{-1})	0.3210
	k_1 (h^{-1})	0.2451
	R^2	0.6041
Pseudo-second-order	$Q_{e,cal}$ (mg g^{-1})	0.9566
	k_2 (h^{-1})	8.2238
	R^2	0.9998

had a higher linear fit than the Langmuir isotherms model. Moreover, as can be seen in Tables 11–14, compared with Langmuir isotherm model, the R^2 value of the Freundlich isotherm model was closer to 1. Therefore, it was difficult to judge whether rhodamine B and orange II adsorbed by the two modified kaolin materials was monolayer adsorption or multilayer adsorption.

Last but not least, we also studied the adsorption thermodynamics of organic dyes on the two materials. The value of ΔH and ΔS of the adsorption process of methylene blue by the two materials were derived from Fig. 24. The value of ΔH and ΔS of the adsorption process of rhodamine B by the two materials were derived from Fig. 25. And the value of ΔH and ΔS of the adsorption

Table 5
Fitting parameters of the kinetic model for adsorption of rhodamine B by Fe-kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	0.1650
	$Q_{e,cal}$ (mg g^{-1})	0.0735
Pseudo-first-order	k_1 (h^{-1})	0.2088
	R^2	0.6577
	$Q_{e,cal}$ (mg g^{-1})	0.1685
Pseudo-second-order	k_2 (h^{-1})	9.0099
	R^2	0.9882

Table 6
Fitting parameters of the kinetic model for adsorption of rhodamine B by kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	0.2660
	$Q_{e,cal}$ (mg g^{-1})	0.1072
Pseudo-first-order	k_1 (h^{-1})	0.3172
	R^2	0.8819
	$Q_{e,cal}$ (mg g^{-1})	0.2673
Pseudo-second-order	k_2 (h^{-1})	15.3713
	R^2	0.9991

Table 7
Fitting parameters of the kinetic model for adsorption of orange II by Fe-kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	0.7190
	$Q_{e,cal}$ (mg g^{-1})	0.3295
Pseudo-first-order	k_1 (h^{-1})	0.1024
	R^2	0.4299
	$Q_{e,cal}$ (mg g^{-1})	0.6990
Pseudo-second-order	k_2 (h^{-1})	2.8703
	R^2	0.9887

Table 8
Fitting parameters of the kinetic model for adsorption of orange II by kaolin

Kinetic models	Parameters	c_0 = 12.0000 mg L^{-1}
Actual amount of adsorption	$Q_{e,exp}$ (mg g^{-1})	0.4720
	$Q_{e,cal}$ (mg g^{-1})	0.3371
Pseudo-first-order	k_1 (h^{-1})	0.1161
	R^2	0.7686
	$Q_{e,cal}$ (mg g^{-1})	0.4699
Pseudo-second-order	k_2 (h^{-1})	1.6590
	R^2	0.9808

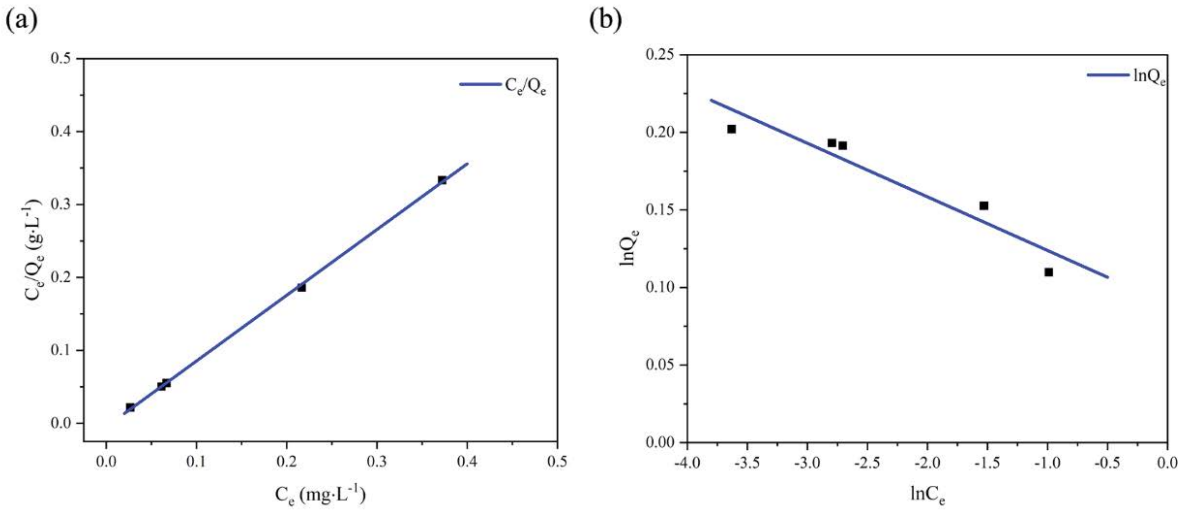


Fig. 18. Thermodynamic models of adsorption of methylene blue on Fe-kaolin: (a) Langmuir and (b) Freundlich isotherms models.

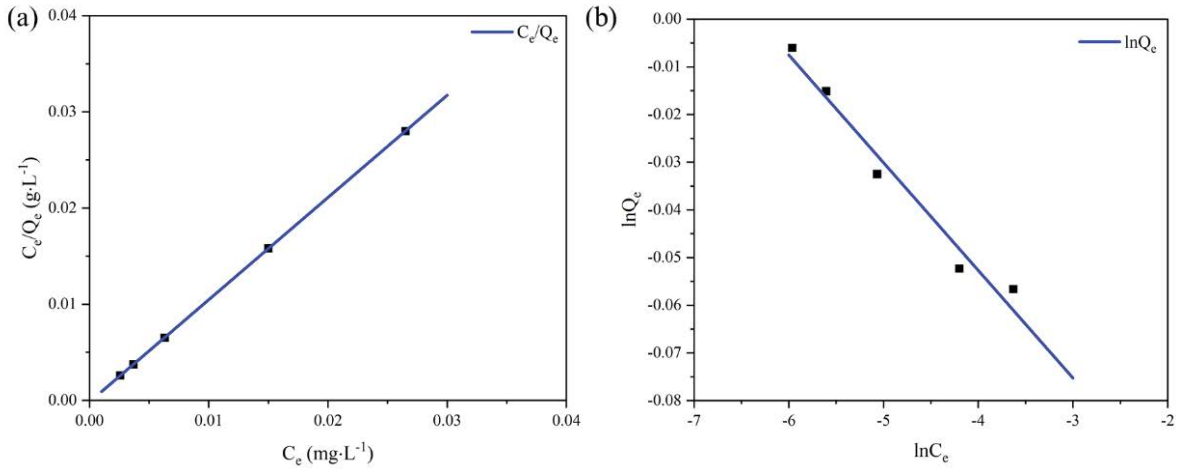


Fig. 19. Thermodynamic models of adsorption of methylene blue on kaolin: (a) Langmuir and (b) Freundlich isotherms models.

Table 9
Fitting parameters of adsorption isotherm for adsorption of methylene blue by Fe-kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	1.1094	–193.8538	0.9995
Freundlich	K_F	n	R^2
	1.0934	–28.9352	0.9018

Table 10
Fitting parameters of adsorption isotherm for adsorption of methylene blue by kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	0.9408	–6,551.6710	1.0000
Freundlich	K_F	n	R^2
	0.8667	–44.2674	0.9701

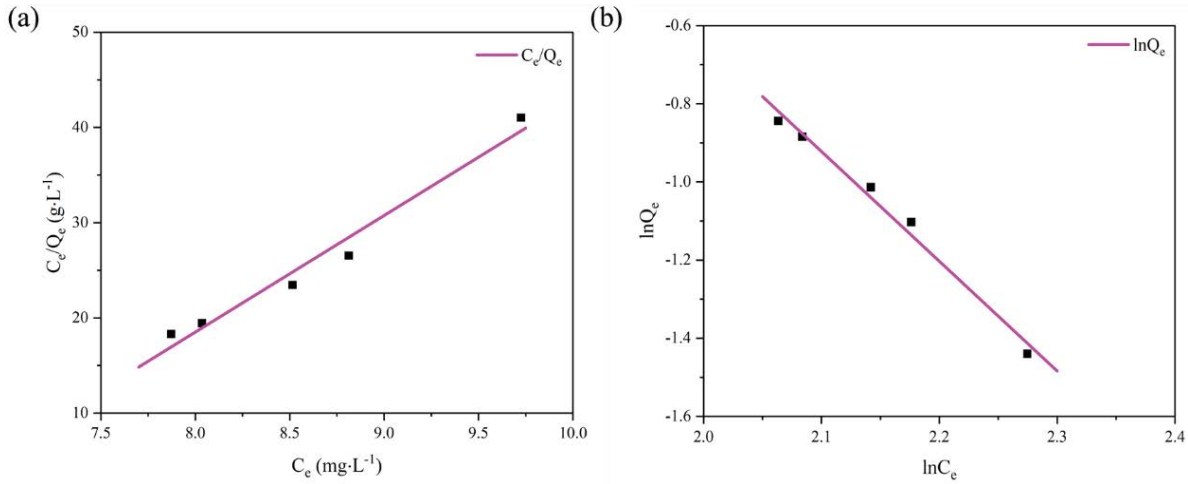


Fig. 20. Thermodynamic models of adsorption of rhodamine B on Fe-kaolin: (a) Langmuir and (b) Freundlich isotherms models.

process of orange II by the two materials were derived from Fig. 26. As was shown in Tables 15 and 16, the adsorption of methylene blue by the two modified kaolin materials can usually proceed spontaneously because ΔG was less than 0. Nevertheless, as can be seen from Tables 17–20, the adsorption of rhodamine B and orange II by these two modified kaolin materials usually cannot proceed spontaneously because ΔG was greater than 0. Besides, as can be seen from Tables 15–20, the value of ΔG of organic dyes adsorbed by adsorbents decreased with the increase of the temperature. Thus, these two modified kaolin materials were more likely to adsorb these three organic dyes spontaneously with the increase of the temperature. Furthermore, the adsorption of organic dyes by these two modified kaolin materials was an endothermic adsorption process because both ΔH and ΔS were greater than 0.

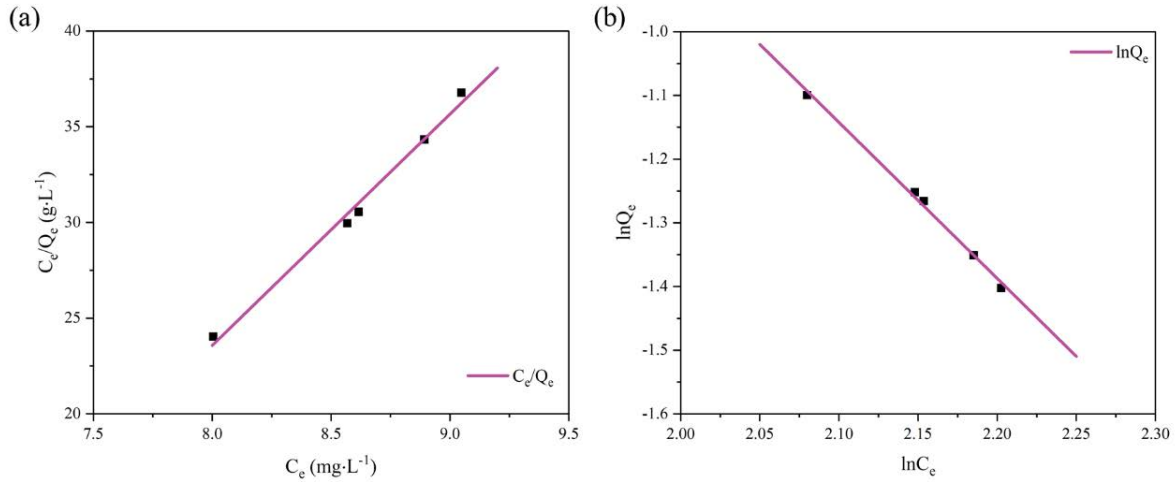


Fig. 21. Thermodynamic models of adsorption of rhodamine B on kaolin: (a) Langmuir and (b) Freundlich isotherms models.

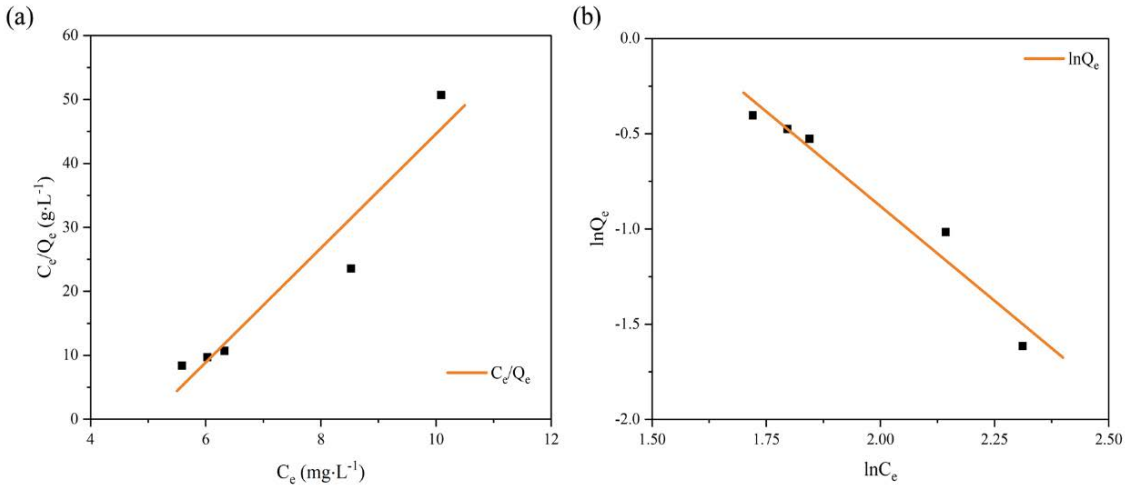


Fig. 22. Thermodynamic models of adsorption of orange II on Fe-kaolin: (a) Langmuir and (b) Freundlich isotherms models.

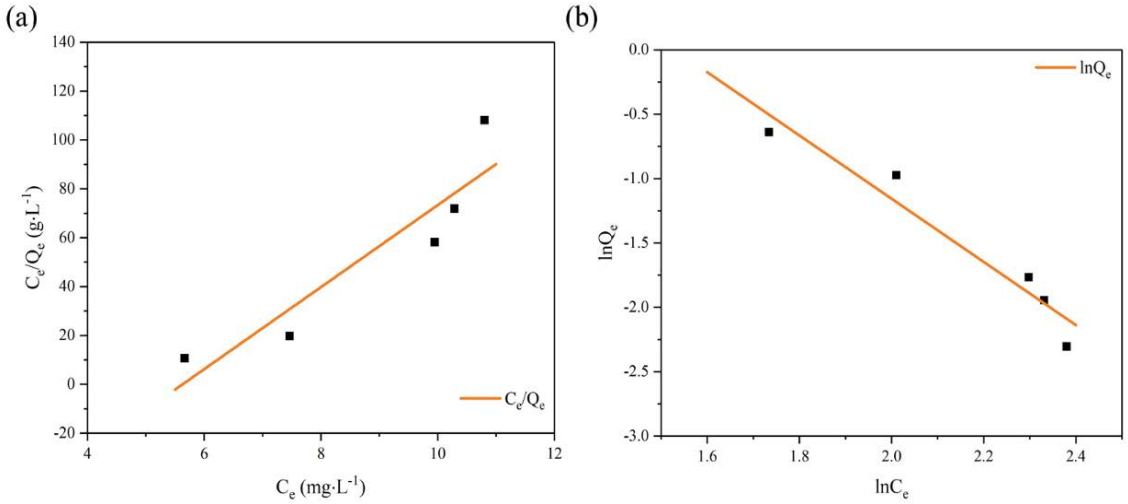


Fig. 23. Thermodynamic models of adsorption of orange II on kaolin: (a) Langmuir and (b) Freundlich isotherms models.

Table 11
Fitting parameters of adsorption isotherm for adsorption of rhodamine B by Fe-kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	0.0817	–0.1541	0.9712
Freundlich	K_F	n	R^2
	145.1068	–0.3560	0.9857

Table 12
Fitting parameters of adsorption isotherm for adsorption of rhodamine B by kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	0.0828	–0.1653	0.9903
Freundlich	K_F	n	R^2
	54.7195	–0.4082	0.9953

Table 13
Fitting parameters of adsorption isotherm for adsorption of orange II by Fe-kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	0.1119	–0.1998	0.9206
Freundlich	K_F	n	R^2
	22.0623	–0.5033	0.9584

Table 14
Fitting parameters of adsorption isotherm for adsorption of orange II by kaolin

Adsorption isotherms			
Langmuir	Q_m (mg g^{-1})	K_L	R^2
	0.0596	–0.1776	0.8539
Freundlich	K_F	n	R^2
	42.8202	–0.4071	0.9364

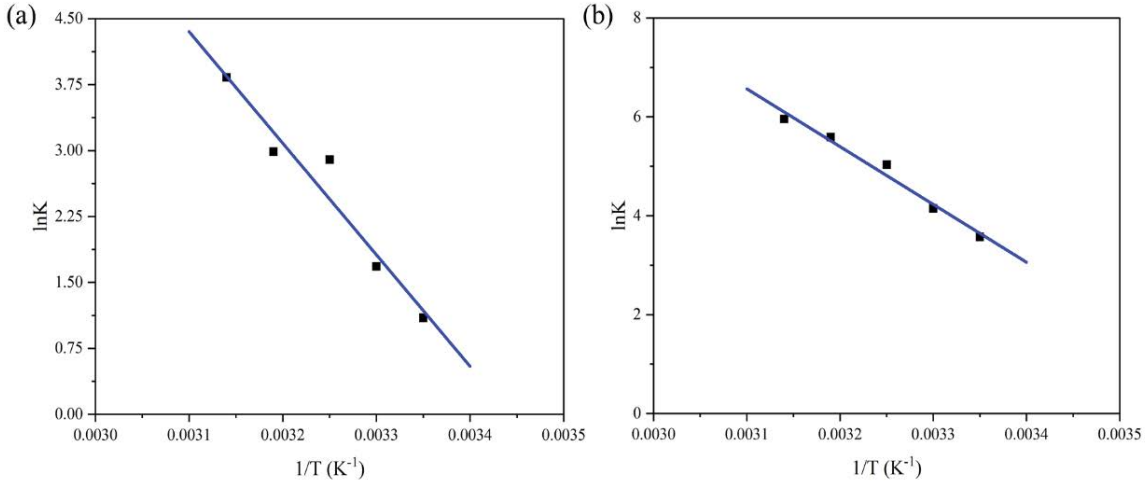


Fig. 24. Thermodynamic analysis of adsorption of methylene blue on the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

3.6. Activation and regeneration technology of the modified kaolin materials

As can be seen from Table 21, combining dilute HCl with dilute NaOH can realize the desorption of most methylene blue and orange II. But the adsorption capacity of rhodamine B increased at this time because the adsorption sites increased at this time. But the adsorption capacity of rhodamine B was still relatively poor.

As shown in Table 22, compared with the results of Table 2, the maximum adsorption capacity of Fe-kaolin after regeneration for methylene blue and rhodamine B increased slightly. But the maximum adsorption capacity of Fe-kaolin after regeneration for orange II reduced greatly. Besides, the maximum adsorption capacity of kaolin after regeneration for methylene blue increased slightly. But the maximum adsorption capacity of kaolin after regeneration for orange II and rhodamine B reduced greatly.

These results indicated that the activation and regeneration technology of the adsorbents had the advantages of simple operation and low cost. Moreover, these two modified kaolin materials after regeneration can be reused to remove organic dyes, especially methylene blue, in wastewater.

4. Discussion

- When the quality of the adsorbents added was small, the adsorption sites on the adsorbents were easy to reach saturation, which limited the total amount of organic dyes adsorbed by the adsorbents. The adsorption sites of adsorbent gradually increased with the increase of

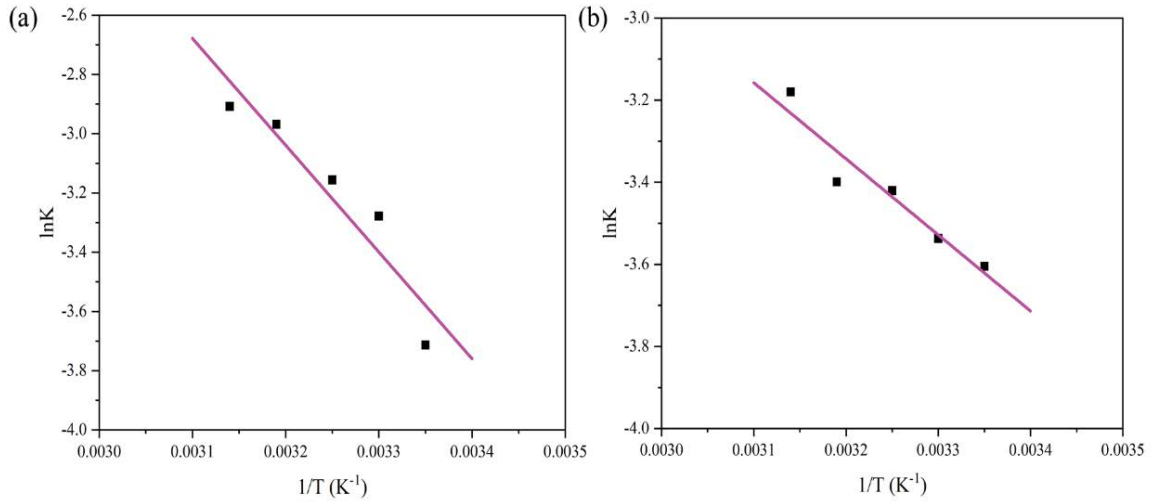


Fig. 25. Thermodynamic analysis of adsorption of rhodamine B on the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

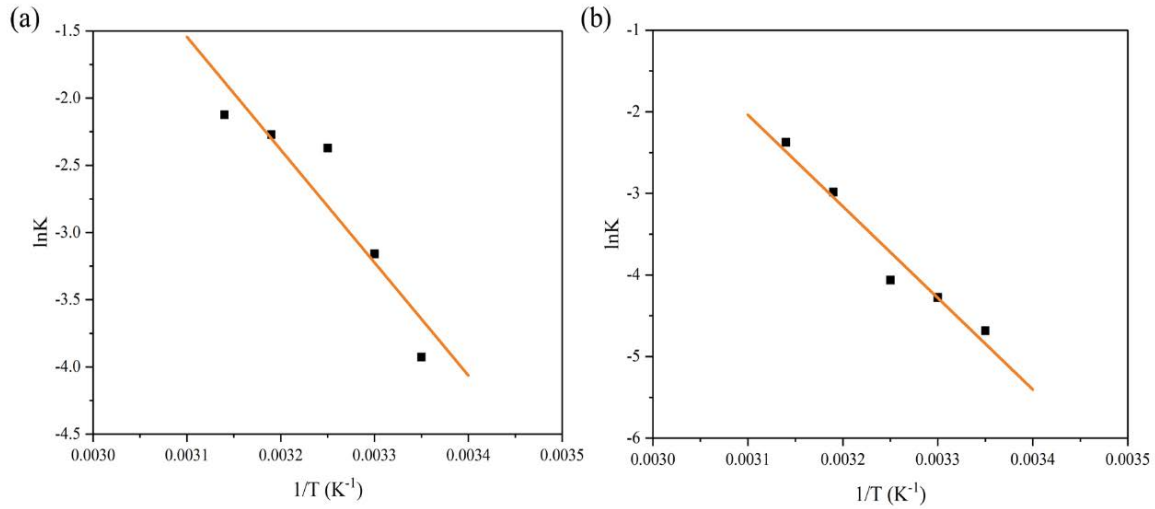


Fig. 26. Thermodynamic analysis of adsorption of orange II on the modified kaolin materials: (a) Fe-kaolin and (b) kaolin.

Table 15
Thermodynamic parameters for adsorption of methylene blue by Fe-kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	1.0983	–2.7225	105.5358	363.3530
303.15	1.6824	–4.2403		
308.15	2.8975	–7.4233		
313.15	2.9883	–7.7801		
318.15	3.8327	–10.1379		

the quality of adsorbents added, which improved the removal rate of organic dyes.

- The minimum mass of Fe-kaolin was about 0.48 g when the removal rate of methylene blue reached basically stable in the aqueous solution containing three organic dyes. And the minimum mass of kaolin was about 0.6 g when the removal rate of methylene blue reached basically stable in the aqueous solution containing three organic dyes.
- These two modified kaolin materials usually had the largest adsorption capacity for methylene blue, followed by orange II, and finally rhodamine B. Stacking, hydrogen bonding and electrostatic attraction may be the

Table 16
Thermodynamic parameters for adsorption of methylene blue by kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	3.5740	–8.8593		
303.15	4.1474	–10.4531		
308.15	5.0347	–12.8987	97.2004	355.9244
313.15	5.5897	–14.5529		
318.15	5.9578	–15.7590		

Table 17
Thermodynamic parameters for adsorption of rhodamine B by Fe-kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	–3.7132	9.2044		
303.15	–3.2781	8.2621		
308.15	–3.1559	8.0853	29.9753	70.6569
313.15	–2.9681	7.7275		
318.15	–2.9077	7.6912		

Table 18
Thermodynamic parameters for adsorption of rhodamine B by kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	–3.6045	8.9349		
303.15	–3.5370	8.9146		
308.15	–3.4204	8.7629	15.4170	21.5420
313.15	–3.3992	8.8499		
318.15	–3.1797	8.4106		

Table 19
Thermodynamic parameters for adsorption of orange II by Fe-kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	–3.9271	9.7346		
303.15	–3.1583	7.9601		
308.15	–2.3709	6.0741	69.8255	203.6221
313.15	–2.2711	5.9129		
318.15	–2.1236	5.6171		

Table 20
Thermodynamic parameters for adsorption of orange II by kaolin

T (K)	ln$K$	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298.15	–4.6831	11.6086		
303.15	–4.2759	10.7769		
308.15	–4.0628	10.4087	93.2993	272.2897
313.15	–2.9838	7.7684		
318.15	–2.3730	6.2768		

Table 21
The adsorption capacity of organic dyes on the modified kaolin material after desorption

	Methylene blue	Rhodamine B	Orange II
Fe-kaolin	0.0701 mg g^{-1}	0.3880 mg g^{-1}	0.0420 mg g^{-1}
Kaolin	0.0725 mg g^{-1}	0.5120 mg g^{-1}	0.00714 mg g^{-1}

Table 22
The maximum adsorption capacity of the modified kaolin materials after regeneration for organic dyes

	Methylene blue	Rhodamine B	Orange II
Fe-kaolin	1.171 mg g^{-1}	0.1921 mg g^{-1}	0.1167 mg g^{-1}
Kaolin	0.9700 mg g^{-1}	0.1506 mg g^{-1}	0.1797 mg g^{-1}

adsorption mechanism of organic dyes by the modified kaolin materials.

- Different organic dyes may promote the adsorption of each other on the modified kaolin materials. Besides, the quality of adsorbents, time, the concentration of Cl^-. pH, temperature had great effects on the adsorption behavior of organic dyes by adsorbents. Among these factors, the quality of adsorbents had the greatest influence on the adsorption.
- The regeneration of the adsorbents can be achieved by adjusting the concentration of Cl^- and pH. Thus, these two modified kaolin materials had the potential in the treatment of wastewater containing multiple organic dyes.
- Combining dilute HCl with dilute NaOH can realize the desorption of most methylene blue and orange II. But the adsorption capacity of rhodamine B increased at this time because the adsorption sites increased at this time. But the adsorption capacity of rhodamine B was still relatively poor.
- The maximum adsorption capacity of Fe-kaolin after regeneration for methylene blue and rhodamine B increased slightly. But the maximum adsorption capacity of Fe-kaolin after regeneration for orange II reduced greatly. The maximum adsorption capacity of kaolin after regeneration for methylene blue increased slightly. But the maximum adsorption capacity of kaolin after regeneration for orange II and rhodamine B reduced greatly. These results indicated that these two modified kaolin materials after regeneration can still be reused to remove organic dyes, especially methylene blue, in wastewater.
- The adsorption mechanism of organic dyes by these two modified kaolin materials was in line with the pseudo-second-order adsorption kinetic model. This indicated that the adsorption of organic dyes by the modified kaolin materials was a chemical adsorption process.
- The adsorption isotherms of the two modified materials for methylene blue was the Langmuir isotherms model. Therefore, the adsorption of methylene blue by the two modified kaolin materials was monolayer adsorption. However, the adsorption isotherms of the two modified materials for the other two organic dyes was the Freundlich isotherms model. Thus, it was difficult to judge whether rhodamine B and orange II adsorbed by the two modified kaolin materials was monolayer adsorption or multilayer adsorption.
- The adsorption of methylene blue by these two modified kaolin materials can usually proceed spontaneously because ΔG was less than 0. But the adsorption of the other two organic dyes by these two modified kaolin materials usually cannot proceed spontaneously because ΔG was greater than 0. This may be the reason why these two modified kaolin materials adsorb methylene blue selectively while the adsorption effect on rhodamine B and orange II was relatively poor.
- The value of ΔG of organic dyes adsorbed by adsorbents decreased with the increase of the temperature. The adsorption of these three organic dyes by the two modified kaolin materials was an endothermic adsorption process because both ΔH and ΔS were greater than 0. Thus, these two modified kaolin materials were more likely to adsorb these three organic dyes spontaneously with the increase of the temperature.

5. Conclusions

In conclusion, we prepared an aqueous solution containing methylene blue, rhodamine B and orange II and developed two modified kaolin materials called Fe-kaolin and kaolin, respectively, in this paper. Then the adsorption properties of the two modified kaolin materials for three organic dyes were studied preliminarily. It turned out that both Fe-kaolin and kaolin had the largest adsorption capacity for methylene blue, followed by orange II, and finally rhodamine B. More importantly, different organic dyes may promote the adsorption of each other on these two modified kaolin materials.

Moreover, time, the concentration of Cl^-, pH and temperature had great impact on the adsorption behavior of organic dyes on these two materials. Therefore, the adsorption effect of the two modified kaolin materials on multiple organic dyes can be optimized by adjusting these factors, thereby achieving efficient treatment of wastewater containing multiple organic dyes. Among these factors, the quality of adsorbents had the greatest influence on the adsorption of organic dyes by adsorbents. It was possible to achieve the of activation and regeneration of these two modified kaolin materials by adjusting the concentration of Cl^- and pH. These two modified kaolin materials after regeneration can be reused to remove organic dyes, especially methylene blue, in wastewater. The activation and regeneration technology has the advantages of simple operation and low cost.

Finally, the adsorption mechanism of these three organic dyes by the modified kaolin materials was studied. The results showed that the adsorption of these three organic dyes by the modified kaolin materials was a chemical adsorption process and an endothermic adsorption process. Besides, the adsorption of methylene blue by the two modified kaolin materials was monolayer adsorption. But it was difficult to judge whether the other two organic dyes adsorbed by the two modified kaolin materials was monolayer adsorption or multilayer adsorption. Furthermore, the

adsorption of methylene blue by these two modified kaolin materials can usually proceed spontaneously while the adsorption of the other two organic dyes by these two modified kaolin materials usually cannot proceed spontaneously.

In short, these two modified kaolin materials had the potential in the treatment of wastewater containing multiple organic dyes. This work not only provides two low-cost and environmentally friendly adsorbents for the treatment of organic dye wastewater, but also provides ideas for the development of fantastic modified kaolin materials and the recycling and reuse of kaolin tailings.

References

[1] J. Clifton, J.B. Leikin, Methylene blue, Am. J. Therm., 10 (2003) 289–291.
[2] C.-H. Weng, Y.-F. Pan, Adsorption of a cationic dye (methylene blue) onto spent activated clay, J. Hazard. Mater., 144 (2007) 355–362.
[3] M. Wainwright, K.B. Crossley, Methylene blue–a therapeutic dye for all seasons?, J. Chemother., 14 (2002) 431–443.
[4] R. Kiesslich, J. Fritsch, M. Holtmann, H.H. Koehler, M. Stolte, S. Kanzler, B. Nafe, M. Jung, P.R. Galle, M.F. Neurath, Methylene blue-aided chromoendoscopy for the detection of intraepithelial neoplasia and colon cancer in ulcerative colitis, Gastroenterology, 124 (2003) 880–888.
[5] C. Junyong, H. Yongmei, L. Yan, G. Jiajia, Magnetic graphene oxides as highly effective adsorbents for rapid removal of a cationic dye rhodamine B from aqueous solutions, RSC Adv., 3 (2013) 7254–7258.
[6] T. Karstens, K. Kobs, Rhodamine B and rhodamine 101 as reference substances for fluorescence quantum yield measurements, J. Phys. Chem., 84 (1980) 1871–1872.
[7] R. Ramette, E.B. Sandell, Rhodamine B equilibria, J. Am. Chem. Soc., 78 (1956) 4872–4878.
[8] I.L. Arbeloa, P.R. Ojeda, Molecular forms of rhodamine B, Chem. Phys. Lett., 79 (1981) 347–350.
[9] S.-A. Ong, L.-N. Ho, Y.-S. Wong, Comparison on biodegradation of anionic dye orange II and cationic dye methylene blue by immobilized microorganisms on spent granular activated carbon, Desal. Water Treat., 54 (2015) 557–561.
[10] S. Ji, Q. Zhang, Y.X. Shen, Screening for colour developer and optimization of reaction conditions for fast determination of basic orange II in foods, Food Sci., 31 (2010) 394–398.
[11] G.V. Scott, Spectrophotometric determination of cationic surfactants with orange II, Anal. Chem., 40 (1968) 768–773.
[12] J. Fu, J. Zhu, Z. Wang, Y. Wang, S. Wang, R. Yan, Q. Xu, Highly-efficient and selective adsorption of anionic dyes onto hollow polymer microcapsules having a high surface-density of amino groups: isotherms, kinetics, thermodynamics and mechanism, J. Colloid Interface Sci., 542 (2019) 123–135.
[13] G. Nainggolan-Sihombing, The toxic effect of rhodamine B in rats, Paediatr. Indones., 24 (1984) 125–138.
[14] S. Antharjanam, R. Philip, D. Suresh, Photocatalytic degradation of wastewater pollutants: titanium dioxide mediated degradation of methyl orange and beta-naphthol orange, Ann. Chim., 93 (2003) 719–728.
[15] S. Yusra, H.N. Bhatti, Factors affecting biosorption of direct dyes from aqueous solution, Asian J. Chem., 22 (2010) 6625–6639.
[16] Y. Zhou, W. Zuo, C. Zhou, R. Zhang, Y. Shen, Optimization for drum spray preconcentration of high-salt organic wastewater, Chin. J. Environ. Eng., 12 (2018) 3099–3108.
[17] P.S. Kumar, M.J.S. Raja, M. Kumaresan, D.K. Loganathan, P. Chandrasekaran, A new electrode reactor with in-built recirculation mode for the enhancement of methylene blue dye removal from the aqueous solution: comparison of adsorption, electrolysis and combined effect, Korean J. Chem. Eng., 31 (2014) 276–283.
[18] J.B. Fathima, A. Pugazhendhi, M. Oves, R. Venis, Synthesis of eco-friendly copper nanoparticles for augmentation of catalytic degradation of organic dyes, J. Mol. Liq., 260 (2018) 1–8.
[19] H. Shu, J. Xie, H. Xu, H. Li, Z. Gu, G. Sun, Y. Xu, Compounds, structural characterization and photocatalytic activity of $NiO/AgNbO_3$, J. Alloys Compd., 496 (2010) 633–637.
[20] A.U. Joshi, A.T. Hinsu, R.J. Kotadiya, J.K. Rank, K.N. Andharia, R.K. Kothari, Decolorization and biodegradation of textile di-azo dye Acid Blue 113 by *Pseudomonas stutzeri* AK6, 3 Biotech., 10 (2020) 214, doi: 10.1007/s13205-020-02205-5.
[21] M.O. Mavukkandy, Q. Zaib, H.A. Arafat, CNT/PVP blend PVDF membranes for the removal of organic pollutants from simulated treated wastewater effluent, J. Environ. Chem. Eng., 6 (2018) 6733–6740.
[22] P. Navarro, J.A. Pellicer, V.M. Gómez-López, Degradation of azo dye by an UV/H_2O_2 advanced oxidation process using an amalgam lamp, Water Environ. J., 33 (2019) 476–483.
[23] C. So, M.Y. Cheng, J. Yu, P.K. Wong, Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation, Chemosphere, 46 (2002) 905–912.
[24] T.J. Al-Musawi, P. Rajiv, N. Mengelizadeh, I.A. Mohammed, D. Balarak, Development of sonophotocatalytic process for degradation of acid orange 7 dye by using titanium dioxide nanoparticles/graphene oxide nanocomposite as a catalyst, J. Environ. Manage., 292 (2021) 112777, doi: 10.1016/j.jenvman.2021.112777.
[25] D. Balarak, F. Ganji, S.S. Choi, S.M. Lee, M.J. Shim, Effects of operational parameters on the removal of acid blue 25 dye from aqueous solutions by electrocoagulation, Appl. Chem. Eng., 30 (2019) 742–748.
[26] M. Sillanpää, A.H. Mahvi, D. Balarak, A.D. Khatibi, Adsorption of acid orange 7 dyes from aqueous solution using polypyrrole/nanosilica composite: experimental and modelling, Int. J. Environ. Anal. Chem., (2021) 1–18, doi: 10.1080/03067319.2020.1855338.
[27] T.J. Al-Musawi, N. Menglizadeh, O. Al-Rawi, D. Balarak, Capacity and modeling of acid blue 113 dye adsorption onto chitosan magnetized by Fe_2O_3 nanoparticles, J. Polym. Environ., (2021) 1–16, doi: 10.21203/rs.3.rs-334767/v1.
[28] K. Bharathi, S.T. Ramesh, Removal of dyes using agricultural waste as low-cost adsorbents: a review, Appl. Water Sci., 3 (2013) 773–790.
[29] D. Dollimore, G.R. Heal, Pore-size distribution in typical adsorbent systems, J. Colloid Interface Sci., 33 (1970) 508–519.
[30] H.H. Lima, R.S. Maniezzo, M.E. Llop, V.L. Kupfer, P.A. Arroyo, M.R. Guilherme, A.F. Rubira, E.M. Girotto, A.W. Rinaldi, Synthesis and characterization of pecan nutshell-based adsorbent with high specific area and high methylene blue adsorption capacity, J. Mol. Liq., 276 (2019) 570–576.
[31] W. Zhang, Z. Xu, B. Pan, C. Hong, K. Jia, P. Jiang, Q. Zhang, B. Pan, Equilibrium and heat of adsorption of diethyl phthalate on heterogeneous adsorbents, J. Colloid Interface Sci., 325 (2008) 41–47.
[32] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions, Waste Manage., 21 (2001) 105–110.
[33] B. Hameed, R. Krishni, S.A. Sata, A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions, J. Hazard. Mater., 162 (2009) 305–311.
[34] J. Yu, W. He, B. Liu, Adsorption of acid orange II with two step modified sepiolite: optimization, adsorption performance, kinetics, thermodynamics and regeneration, Int. J. Environ. Res. Public Health, 17 (2020) 1732, doi: 10.3390/ijerph17051732.
[35] P.M.K. Reddy, S. Mahammadunnisa, B. Ramaraju, B. Sreedhar, C. Subrahmanyam, Low-cost adsorbents from bio-waste for the removal of dyes from aqueous solution, Environ. Sci. Pollut. Res., 20 (2013) 4111–4124.
[36] D. Balarak, T.J. Al-Musawi, I.A. Mohammed, H. Abasizadeh, The eradication of reactive black 5 dye liquid wastes using *Azolla filiculoides* aquatic fern as a good and an economical biosorption agent, SN Appl. Sci., 2 (2020) 1–11.
[37] D. Balarak, H. Abasizadeh, J.-K. Yang, M.J. Shim, S.-M. Lee, Biosorption of Acid Orange 7 (AO7) dye by canola waste:

equilibrium, kinetic and thermodynamics studies, Desal. Water Treat., 190 (2020) 331–339.
[38] P. Zhu, L. Wang, D. Hong, M. Zhou, A study of cordierite ceramics synthesis from serpentine tailing and kaolin tailing, Sci. Sintering, 44 (2012) 129–134.
[39] J. Leite, M. Veras, E. Santos, R. Lima, J. Paulo, M. Pinheiro, Technological characterization of kaolin tailing from small-scale mining in RN and PB states–Brazil, Miner. Eng., 20 (2007) 959–961.
[40] W. Xu, X. Wen, J. Wei, P. Xu, B. Zhang, Q. Yu, H. Ma, Feasibility of kaolin tailing sand to be as an environmentally friendly alternative to river sand in construction applications, J. Cleaner Prod., 205 (2018) 1114–1126.
[41] C.S. Ross, P.F. Kerr, The kaolin minerals, J. Am. Ceram. Soc., 13 (1930) 151–160.
[42] M. Prasad, K. Reid, H.H. Murray, Kaolin: processing, properties and applications, Appl. Clay Sci., 6 (1991) 87–119.
[43] H. Wang, C. Li, Z. Peng, S. Zhang, Characterization and thermal behavior of kaolin, J. Therm. Anal. Calorim., 105 (2011) 157–160.
[44] S. Barakan, V. Aghazadeh, The advantages of clay mineral modification methods for enhancing adsorption efficiency in wastewater treatment: a review, Environ. Sci. Pollut. Res., 28 (2021) 2572–2599.
[45] L. Mouni, L. Belkhiri, J.-C. Bollinger, A. Bouzaza, A. Assadi, A. Tirri, F. Dahmoune, K. Madani, H. Remini, Removal of methylene blue from aqueous solutions by adsorption on kaolin: kinetic and equilibrium studies, Appl. Clay Sci., 153 (2018) 38–45.
[46] K. He, G. Chen, G. Zeng, A. Chen, Z. Huang, J. Shi, M. Peng, T. Huang, L. Hu, Enhanced removal performance for methylene blue by kaolin with graphene oxide modification, J. Taiwan Inst. Chem. Eng., 89 (2018) 77–85.
[47] K. Rida, S. Bouraoui, S. Hadnine, Adsorption of methylene blue from aqueous solution by kaolin and zeolite, Appl. Clay Sci., 83 (2013) 99–105.
[48] H. Rajabi, M.H. Mosleh, T. Prakoso, N. Ghaemi, P. Mandal, A. Lea-Langton, M. Sedighi, Competitive adsorption of multicomponent volatile organic compounds on biochar, Chemosphere, 283 (2021) 131288, doi: 10.1016/j.chemosphere.2021.131288.
[49] A. Kumar, P. Lingfa, Sodium bentonite and kaolin clays: comparative study on their FT-IR, XRF, and XRD, Mater. Today:. Proc., 22 (2020) 737–742.