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FULL PAPER

Study of inorganic doping of kaolin clay, a kinetic study of adsorption of methyl green dye from its aqueous solutions

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The presence of pollutants, including dyes, in water has destructive effects on both human and environment. Therefore, this study includes the removal of a cationic dye (methyl green) from water by both kaolinite clay (kao) mineral and its composite (kao/Al). The kaolinite clay (kao) mineral doping was carried out by alumina molecules in order to increase the adsorption quantity. The changes for kaolinite clay (kao) structure and its composite (kao/Al) were analyzed by XRD, FT-IR, and FESEM technieqes. The kinetic data were achieved by using two different kinetic models and the experimental data which were best fitted to the pseudo-second-order kinetic model. It was also found that the amount of adsorption enhances with increasing temperature to reach a value of 9.0646 mg/g for the surface (kao) and 16.3618 mg/g for (kao/Al), which indicated that the process nature is endothermic for both surfaces, in addition to that it revealed an improvement in the adsorption efficiency of the clay after the inorganic doping process.

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KEYWORDS

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Introduction

The wide use of dyes in different fields of life, especially industry, including textile, is due to their capacities in improving the products properties in terms of quality, age, color stability, and resistance to the surrounding environmental conditions. This makes dyes a major contaminant with long-term damage. Therefore, the processes of discharging dye residues into the environment lead to a negative impact and damage to all kinds of environmental systems, thus it is necessary to treat it and reduce its damage [1,2]. Several treatment technologies are commonly used including adsorption, which is an effective method of pollutant removal due to its ease of design, low cost, and high efficiency [3]. Now the focus has been on the preference for the use of certain types of adsorbents, such as natural and agricultural materials which are environmentally friendly and low in cost, including kaolin clay, which is widely used in pollutants' treatment, including removal of dyes from sewage water [4].

Clays possess encapsulated structure, fine particle size, a large surface area, non-toxic, not expensive, and high cation exchange capacity which qualifies it as a good adsorbent material. Due to their above-mentioned properties, different types of clay have been used to remove dye from their aqueous solutions [5-9].

Considering kaolinite as one of the soil and sediments components when comes into contact with different types of pollutants in

sewage and industrial effluents on the surface of the earth, the pollutant particles can interact with soil particles, including clay, so clay minerals may play a role in purification, causing pollutants to be removed from the environment. Kaolinite has a low ion exchange capacity because it contains few sites of ion exchange and the absence of ion exchange between the clay layers , Thus, it is not expected to be an efficient ion exchanger, but with adsorption it can play a significant role in removing organic and inorganic pollutants from aqueous media [10].

A specific study in this field was concerned with the use of inert kaolin clay catalyzed with sulfuric acid to remove positive dyes from their aqueous solutions in which changes on the clay surface were diagnosed by techniques such as XRD, zeta potential, FT-IR , SEM, BET surface area, and pore size measurements. The kinetic data were analyzed using several different kinematic models and the pseudo-second-order model revealed the best representation of the study data. It also indicated that the process of stimulating the mud with acid resulted in a relative improvement in the efficiency of the mud within the studied thermal range [11].

Another study included the use of the ethiopian medical kaolin clay as an absorbent material (beneficiary, raw powder, and calcined). The chemical and physical properties of the clays as adsorbent surfaces were diagnosed using FT-IR, SEM, XRF, and XRD techniques. The slurry was applied as the adsorbent surfaces for dyes in a batch system for the adsorption process and the factors affecting it such as the initial dye concentrations, pH, temperature, contact time, and adsorbent dose. The results found that these raw and prepared domestic kaolin sorbents have the potential to be low-cost alternatives to remove pigments in industrial wastewater [12].

Other researchers have studied the efficiency of Brazilian kaolin clay as a cheap matting surface for removing Malachite Green (MG) dye from its aqueous solutions. The surface properties changes of the absorbent material were characterized by some techniques such as XRD, FT-IR, SEM, thermogravimetric analysis, particle size distribution, and N_2 absorption isotherms, in which it was applied in the field of batch adsorption to remove MG dye. The adsorption kinetics was studied by using several kinetic models. Elovich's model was best suited to represent the adsorption kinetics, the adsorption efficiency was improved, and this is a satisfactory result in the field of colored effluent removal [13]. Therefore, the purpose of the proposed study was to characterize kaolin clay and its composite by several techniques to determine the kinetic study of MG removal by these surfaces.

Materials and methods

Kaolin clay preparation (kao)

Kaolin clay are pure white blocks prepared from Akashat area in the Western Desert by the General Company for Geological Survey and Mining, Baghdad, Iraq. They were collected and separated from the stones and other heavy particles from the samples, and then they were ground, washed, dried, crushed, and sieved through a 200-mesh sieve to obtain a certain volume of raw kaolin clay (Kao) particles. the clay powder was washed with sufficient quantity of distilled water seven times to remove the material exotic substances which are soluble in water and then dried in an oven (Daihan Labtech Oven LDO- 060E) at (80 °C) about 72 hours.

Kaolin clay modification (kao/Al)

It was prepared from a certain amount of kaolin clay to a solution of sodium hydroxide (0.05 M) (CDH) in a reaction flask of 100 ml capacity with continuous stirring (Hotplate Daihan Labtech Co., LTD, Stirrer) for (1 hour) and at (30 °C). Then, the reaction was transferred to ultrasonic devices (Ultra sonic

Cleaner POWER SONIC-0405S) with the gradual addition of a certain amount of alumina Al_2O_3 (BDH) for (1 hour) and at (30 ºC), and then filtered, washed, and dried in oven (Daihan Labtech Oven LDO 060E) (10 hours) at (100 °C) may be on the second surface (kao/Al).

Adsorbate and adsorption experiment

Methyl green (MG) adsorbate is a cationic dye and belongs to triphenylmethane family pigments, molar mass = 458.47 g·mol^{-1}, and the formula of MG dye is $C_{26}H_{33}Cl_2N_3$ (Figure 1).

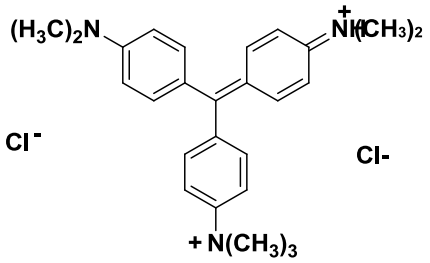

FIGURE 1 Structure of the (MG) dye molecule

Batch adsorption experiments were conducted. A known dose of slurry was introduced into 10 ml of colored water at certain MG concentrations and the solution was in constant agitation shaker (Shaking Water Bath, Labtech) at a fixed speed of 120 rpm for time intervals (1-180) min. Samples were centrifuged (6000 rpm, Hettich (EBA-20) at a speed of 5000 rpm. To measure the MG dye residual concentration which analyzed using a UV-Vis (Shimadzu 1800, Japan) spectrophotometer, remaining MG dye concentrations were measured by using λ_{max} = 632 nm. The amount of the MG dye adsorbed dye was determined by the following equation [14]:

$$q_t = \frac{(C_o - C_e) \times V}{w} \quad (1)$$

In which, q_t is the amount of dye per gram of the adsorbent (mg/g), and C_0 and C_t are, respectively.

Results and discussion

Characterization of kaolnite clay surfaces (kao,kao/Al)

XRD characterization

Kaolin clay surfaces were diagnosed before and after modification (kao, kao/Al) through X-ray diffraction technique within the range (2theta=10-80 degree) through Figures 2 and 3. It was shown that the aluminum oxide modification process led to a relative change in the values of diffraction angles, intensity, and shape of the peaks which indicates that modification process occurred without the clay's composition is deformed or broken, or it loses its crystalline structure [11].

FT-IR spectroscopy characterization (FT-IR)

Kaolin clay surfaces were diagnosed before and after modification (kao, kao/Al) through FT-IR spectra in the range (400–4000) cm^{-1} are depicted in Figures 4 and 5. The strongest characteristic bands of (kao) are recorded as follows. The bands in the wave number ≥ 3000 cm^{-1} correspond to the hydroxyl groups at the end of the clay platelets at the surface of the octahedral layers which interact with the oxygen atoms of the adjacent tetrahedral layers and the internal hydroxyl groups. The bands at 910 cm^{-1} is due to stretching Al–OH groups. The bands within the range of (790-550) cm^{-1} correspond to the vibrations of Si–O–Al groups. The bands within the range of (1500-1000) cm^{-1} correspond to the elongation of Si–O–Si, these bands are typical of kaolinite clay mineral. Furthermore, for kao/Al surface, Figure 5 indicates that modification process led to a relative displacement in the position of all the characteristic peaks of the spectrum except the band at 1635 cm^{-1} is attributed to the vibration of water molecules, because the presence of aluminum is from the composition of kaolin clay. This indicates that the results of FT-IR agree with those by X-ray diffraction [15].

Scanning electron microscopy (SEM)

The surface morphology of these two adsorbents (kao, kao/Al) were observed under SEM analysis (Figures 6 and 7). These images reveal the crust shapes of kaolin clay surface with heterogeneous ones, which are of different sizes, with an approximate size of (27 nm), while the images appear of the clay surface modified by alumina oxide, which demonstrates the crust shapes more homogeneously and larger to be within (46 nm), which confirms the occurrence of a process mud modification (kao/Al) [11].

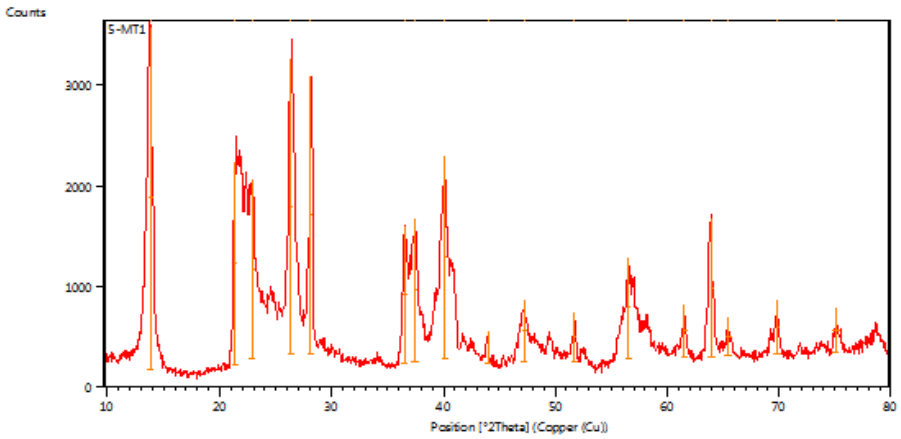

FIGURE 2 XRD spectrum of kao surface

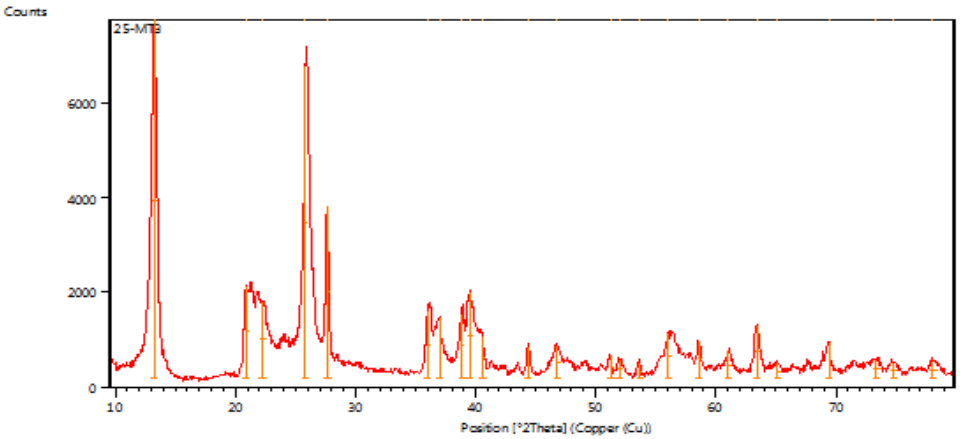

FIGURE 3 XRD spectrum of kao/Al surface

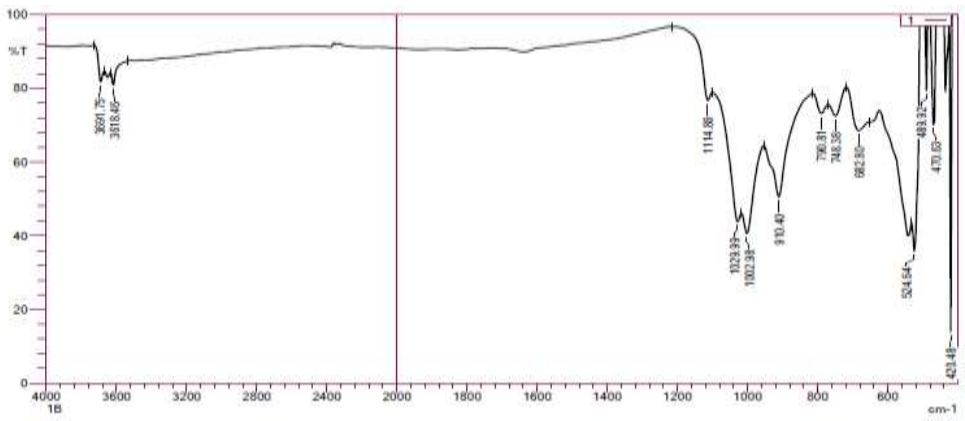

FIGURE 4 FT-IR spectrum of kao surface

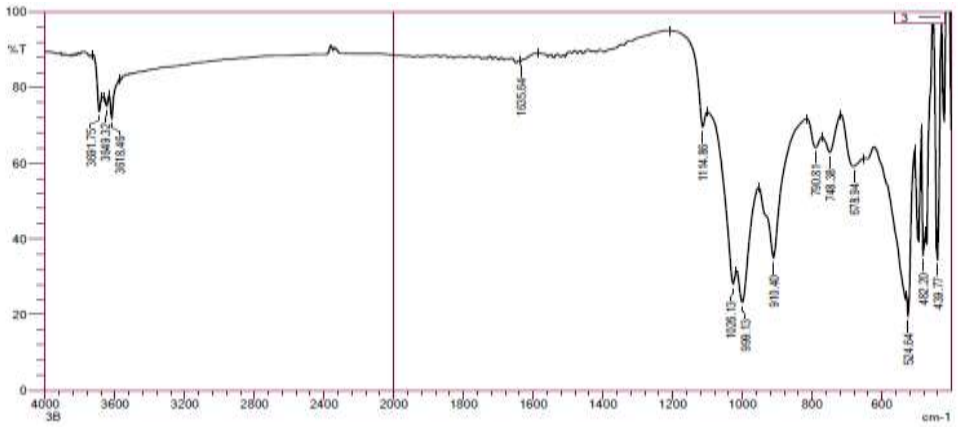

FIGURE 5 FT-IR spectrum of kao/Al surface

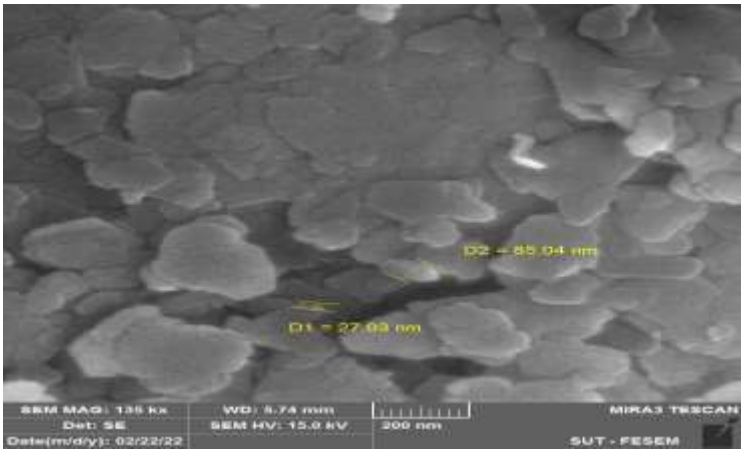

FIGURE 6 FESEM image of kao surface

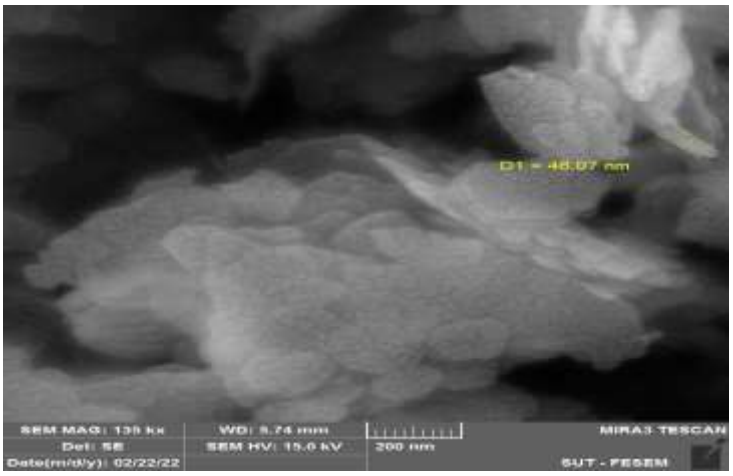

FIGURE 7 FESEM image of kao/Al surface

Effect of contact time and temperature

The effect of contact time on dye adsorption on both kao and kao/Al was studied at initial concentrations of (30 and 50) mg/L of MG dye, 25 °C, pH=7, and 0.035g of (kao, kao/Al), respectively. The capacitance of the MG dye increased over time and reach affixed value at a specified time. It found that the needed time to reach equilibrium is 90 minutes for both

surfaces, as displayed in Figures 8 and 9. The adsorption speed in the primary stage was high because of the availability of vacant positions on the surfaces of the adsorbents and after a certain period of time, the adsorption capacity remains constant due to the lack of effective adsorption sites available. The MG dye absorbed on the surface of kao/Al was faster than the surface of kao [16]. In addition, the surface of kao changed from hydrophilic to hydrophobic after modification of kao/Al [17]. Because temperature is an important parameter for adsorption process and both adsorption studies were carried out at different temperatures. The amount of MG dye adsorption increases with maximizing temperature which indicates that the nature of this adsorption on both surfaces (kao, kao/Al) is a chemical adsorption [18].

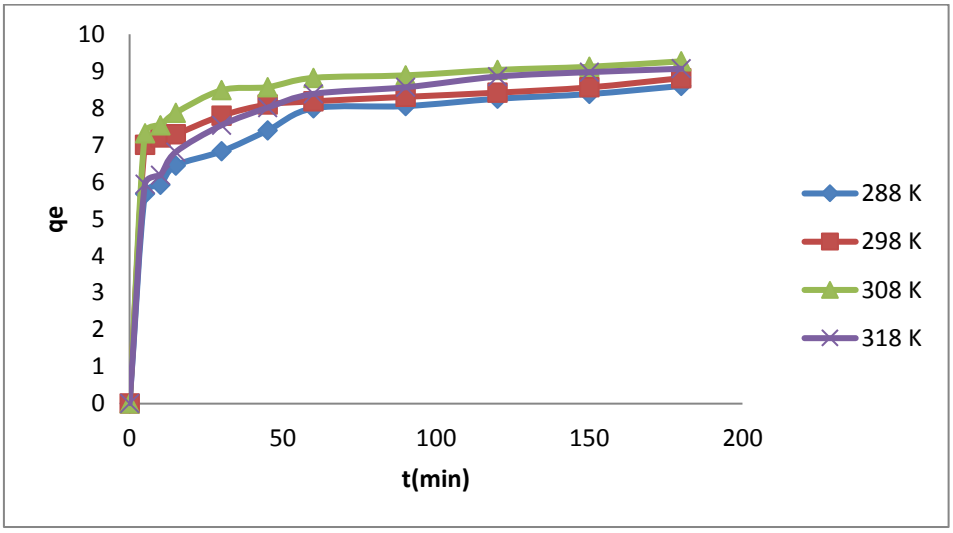

FIGURE 8 Effect of contact time and temperature on MG dye adsorption (30 mg/L) by kao surface

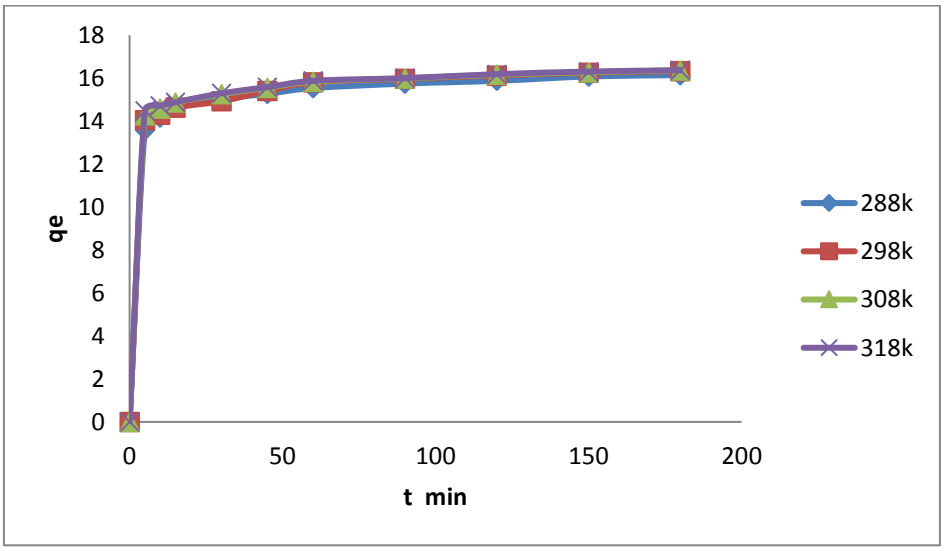

FIGURE 9 Effect of contact time and temperature on MG dye adsorption (50 mg/L) by kao/Al surface

Adsorption kinetics

In order to find the mechanism for the adsorption of (MG) on kao and kao/Al two models were applied to study the adsorption kinetics which is the pseudo-first order known as (Lagergren) equation and the

pseudo – second order known as (Ho and Mckay) equation. The adsorption process was carried out at (288, 298, 308, and 318) K on different times and MV initial concentrations of (30 and 50) mg/L. The linear formula of the pseudo –first order can be represented by the following Equation [19]:

$$\ln(q_e - q_t) = \ln q_e - K_1.t \qquad (2)$$

In which, q_e and q_t (mg/g) are the amounts of (MG) adsorbed at equilibrium, at t time, $K_1(min^{-1})$ is the rate constant of the first order. The amount of K_1 was determined by drawing $\ln(q_e - q_t)$ against t, as displayed in Figures (10 and 11).

The linear formula of the pseudo – second order can be represented by the following Equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q^2_e} + \frac{t}{q_e} \qquad (3)$$

In which, K_2 $(g.\ mg^{-1}.\ min^{-1})$ is the rate constant of the pseudo-second order calculated from the slope of drawing t/q_t versus time, as depicted in Figures 12 and 13. Tables 1 and 2 listed the pseudo-first and second order kinetic parameters. On the other hand, the values of correlation coefficient (R^2) indicate that the adsorption mechanism of (MG) in the kao and kao/Al systems were more fitted to the pseudo-second order than the pseudo-first order [20].

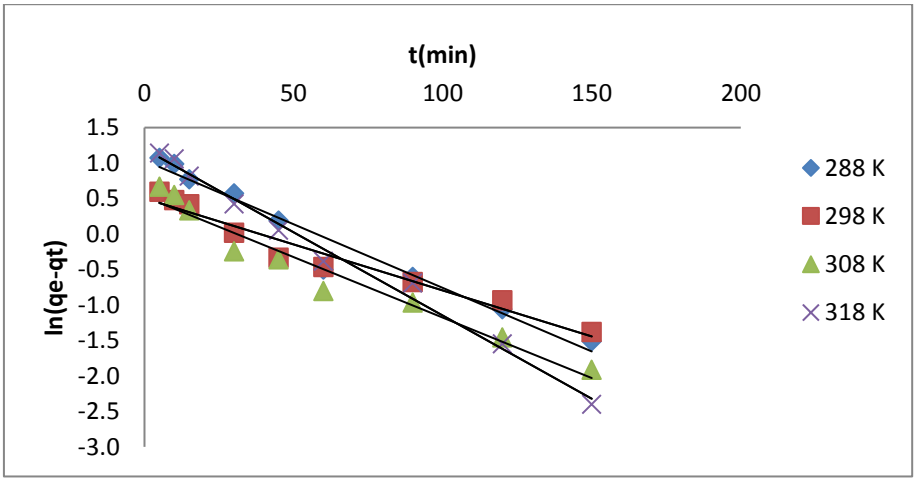

FIGURE 10 The pseudo-first order kinetic of MG adsorption (30 mg/L) by using kao surface

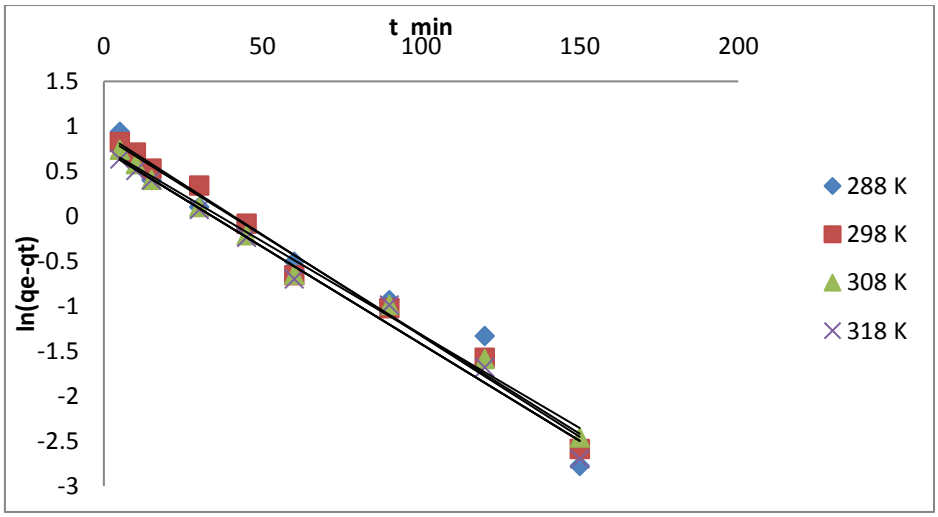

FIGURE 11 The pseudo-first order kinetic of MG adsorption (50 mg/L) by using kao/Al surface

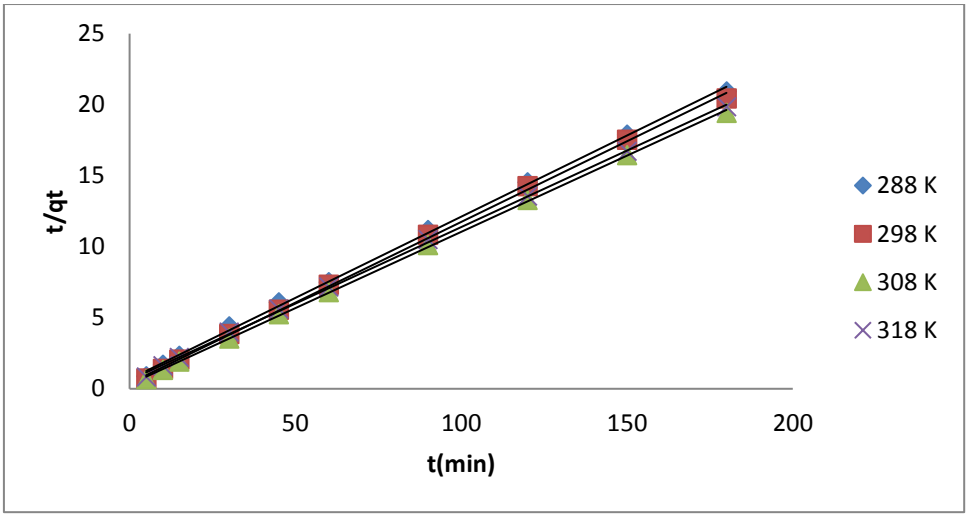

FIGURE 12 The pseudo-second order kinetic of MG adsorption (30 mg/L) by using kao surface

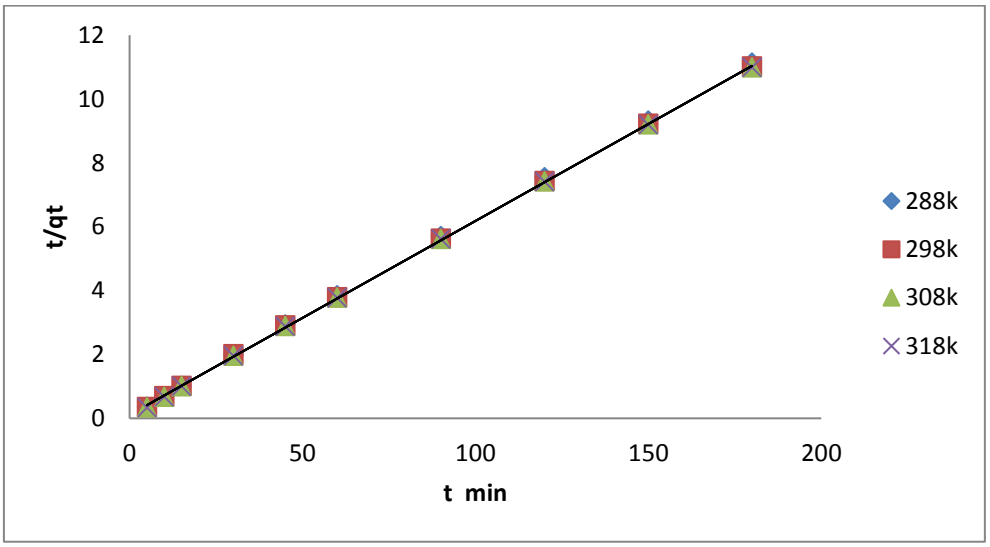

FIGURE 13 The pseudo-second order kinetic of MG adsorption (50 mg/L) by using kao/Al surface

TABLE 1 Kinetic parameters for adsorption of (MG) dye onto kao clay surface based on the pseudo-(first and second) order equations

Model kinetic	Parameter	Temperature/K			
		288	298	308	318
Pseudo-first order	k_1(min^{-1})	0.0179	0.0130	0.0170	0.0235
	q_e(mg/g)	2.8129	1.6515	1.6944	3.3105
	R^2	0.9612	0.9535	0.9556	0.9900
Pseudo-second order	k_2(mg/g.min)	0.0191	0.0334	0.0368	0.0190
	q_e(mg/g)	8.7489	8.8028	9.3197	9.2851
	R^2	0.9989	0.9991	0.9997	0.9995

TABLE 2 Kinetic parameters for adsorption of (MG) dye onto kao/Al clay composite surface based on the pseudo-(first and second) order equations

Model kinetic	Parameter	Temperature/K			
		288	298	308	318
Pseudo-first order	$k_1(min^{-1})$	0.0221	0.0225	0.0207	0.0216
	q_e	2.4332	2.5065	2.1314	2.0901
	R^2	0.9619	0.9881	0.9907	0.9863
Pseudo-second order	k_2(mg/g.min)	0.0302	0.0285	0.0329	0.0341
	q_e	16.2338	16.4474	16.4474	16.4745
	R^2	0.9999	0.9999	0.9999	0.9999

Conclusion

Based on the results of the proposed study and the diagnostic techniques (FT-R, XRD, EDX), it was concluded that the success in modifying kaolin clay process is achieved by using alumina particles (kao, kao/Al). Moreover, it was indicated that the clay efficiency adsorption of MG dye improved from (9) mg/g to (16) mg/g after modification and the application of kinetic systems which are suitable for the pseudo-second order kinetic model.

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