



## Research Article

## Adsorption kinetics of maxilon yellow 4GL and maxilon red GRL dyes on kaolinite

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## ABSTRACT

Kaolinite, a low-costly material, is the most abundant phyllosilicate mineral in highly weathered soils. In this work, the adsorption kinetics of maxilon yellow 4GL (MY 4GL) and maxilon red GRL (MR GRL) dyes on kaolinite from aqueous solutions was investigated using the parameters such as contact time, stirring speed, initial dye concentration, initial pH, ionic strength, acid-activation, calcination and solution temperature. The equilibrium time was 150 min for both dyes. The results showed that alkaline pH was favorable for the adsorption of MY 4GL and MR GRL dyes and physisorption seemed to play a major role in the adsorption process. It was found that the rate of adsorption decreases with increasing temperature and the process is exothermic. The adsorption kinetics followed the pseudo-second-order equation for both dyes investigated in this work with the  $k_2$  values lying in the region of  $1.79 \times 10^4$  to  $107.87 \times 10^4$  g/mol min for MY 4GL and  $3.44 \times 10^4$  to  $72.09 \times 10^4$  g/mol min for MR GRL. The diffusion coefficient values calculated for the dyes were in the range of  $3.76 \times 10^{-9}$  to  $62.50 \times 10^{-9}$  cm<sup>2</sup>/s for MY 4GL and  $1.98 \times 10^{-9}$  to  $44.00 \times 10^{-9}$  cm<sup>2</sup>/s for MR GRL, and are compatible with other studies reported in the literature. The thermodynamic activation parameters such as the enthalpy, entropy and free energy were determined. The obtained results confirmed the applicability of this clay as an efficient adsorbent for cationic dyes.

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## 1. Introduction

Various kinds of synthetic dyestuffs appear in the effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, plastics, etc. [1]. Discharge of dye-bearing wastewater into natural streams and rivers from textile, paper, carpet, leather, distillery, and printing industries poses severe problems because dyes impart toxicity to the aquatic life and cause damage to the aesthetic nature of the environment [2]. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [3]. Such effluents contain a number of contaminants, including acid or caustic, dissolved solids, toxic compounds and color [4]. Considering both volume-discharged and effluent combustion, the wastewater from the textile industry is rated as the most polluting among all industrial sectors [2]. Color is the first contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water is highly visible and undesirable [5].

During the past three decades, several physical, chemical and biological decolorization methods such as aerobic and anaerobic microbial degradation, coagulation, and chemical oxidation,

membrane separation process, electrochemical, dilution, filtration, flotation, softening, and reverse osmosis, have been proposed [2]. However, all of these methods suffered with one or another limitation, and none of these were successful in removing color from the wastewater completely.

Amongst the numerous techniques of dye removal, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [1]. Almost all the work related to adsorption techniques for color removal from industrial effluents was based on studies using activated carbon. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. There is growing interest in using low cost, commercially available materials for the adsorption of dyes. Various low-cost materials have been used for the removal of dyes. Such materials range from industrial waste to agricultural products.

Clays have been used as promising low-cost adsorbents. Kaolinite is the most abundant phyllosilicate mineral in highly weathered soils. It is a 1:1 aluminosilicate comprising a tetrahedral silica sheet bonded to an octahedral sheet through the sharing of oxygen atoms between silicon and aluminium atoms in adjacent sheets. The tetrahedral sheet carries a small permanent negative charge due to isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup>, leaving a single-negative charge for each substitution [6]. Both the octahedral sheet and

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the crystal edges have a pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl (SOH) groups. Kaolinite has a low-cation exchange capacity (CEC) of the order of 3–15 mequiv./100 g and therefore it is not expected to be an ion-exchanger of high order. The small number of exchange sites is located on the surface of kaolinite and it has no interlayer exchange sites. Nevertheless, the small CEC and the adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water [7,8].

In our previous works, we investigated the electrokinetic properties of kaolinite suspensions [8]; and also the adsorption of copper(II) [9] and trivalent chromium ions [7] from aqueous solutions onto kaolinite samples. Therefore, the aim of this study was to determine the adsorption kinetics of cationic dyes such as maxilon yellow 4GL (MY 4GL) and maxilon red GRL (MR GRL) on kaolinite over a range of physicochemical conditions that are important to identify various natural environmental systems. For a successful scale-up of such a process, kinetic studies are essential since they describe the adsorbate removal rate, which in turn controls the residence time in the adsorbent–solution interface. A number of experimental parameters in this study are considered, including the effect of stirring speed, initial dye concentration, initial solution pH, ionic strength, acid activation, calcination and solution temperatures. The thermodynamic activation parameters of the process, such as activation energy, enthalpy, entropy and the free energy, were also determined.

## 2. Materials and methods

### 2.1. Materials

The kaolinite sample was obtained from Güzelyurt (Aksaray, Turkey). Kaolinite was treated before using in the experiments as follows [10]: the suspension containing 10 g/L kaolinite was mechanically stirred for 24 h, after waiting for about 2 min the supernatant suspension was filtered through a white-band filter paper ( $\Phi = 12.5$  cm). The solid sample was dried at 110 °C for 24 h. The particles were crushed using a ball mill to pass through a 100- $\mu$ m metal sieve. The fraction of the particles between 0 and 100  $\mu$ m was used in further experiments.

All chemicals used were of analytical reagent grade and were used without further purification. The chemical structures of maxilon yellow 4GL and maxilon red GRL are illustrated in Fig. 1. The cation exchange capacity of kaolinite was determined as 13 mequiv./100 g by the ammonium acetate method [11]. The

chemical composition of this clay obtained by X-ray fluorescence (XRF) is 53.00% SiO<sub>2</sub>, 26.71% Al<sub>2</sub>O<sub>3</sub>, 0.62% Na<sub>2</sub>O, 0.37% Fe<sub>2</sub>O<sub>3</sub>, 0.57% CaO, 1.39% K<sub>2</sub>O, 0.28% MgO and 17.20% loss ignition [8].

### 2.2. Kinetic experiment

Adsorption kinetic experiments were carried out using mechanic stirrer. All of the dye solution was prepared with ultrapure water. Kinetic experiments were carried out by agitating 2 L of solution of a constant dye concentration with 20 g of kaolinite at a constant agitation speed, 30 °C and natural pH. Agitation was made for 150 min, which is more than sufficient time to reach equilibrium at a constant stirring speed of 400 rpm. Preliminary experiments had shown that the effect of the separation time on the adsorbed amount of dye was negligible. Two millilitres of samples were drawn at suitable time intervals. The samples were then centrifuged for 15 min at 5000 rpm and the left out concentration in the supernatant solution were analysed using UV–vis spectrophotometer (PerkinElmer Lambda 25 UV–vis spectrophotometer) by monitoring the absorbance changes at a wavelength of maximum absorbance (410 and 531 nm for MY 4GL and MR GRL, respectively). Each experiment continued until equilibrium conditions were reached when no further decrease in the dye concentration was measured. Calibration curves were plotted between absorbance and concentration of the dye solution [12]. It was investigated the effects of the following parameters to the removal rate of maxilon yellow 4GL and maxilon red GRL dyes on kaolinite in the experiments.

#### 2.2.1. Effect of stirring speed

The effect of stirring speed on removal rate of maxilon yellow 4GL and maxilon red GRL dyes with kaolinite was investigated at different stirring speeds such as 200, 400 and 600 rpm at the initial dye concentrations of  $5 \times 10^{-4}$  and  $2 \times 10^{-4}$  mol/L at 30 °C and natural solution pH (4.5 and 5.8), respectively.

#### 2.2.2. Effect of initial dye concentration

The initial tested concentrations of dyes were  $3 \times 10^{-4}$ ,  $5 \times 10^{-4}$  and  $7 \times 10^{-4}$  mol/L for MY 4GL and  $1.5 \times 10^{-4}$ ,  $2.0 \times 10^{-4}$  and  $2.5 \times 10^{-4}$  mol/L for MR GRL at 30 °C, natural solution pH and 400 rpm.

#### 2.2.3. Effect of pH

The effect of pH on the rate of color removal was analysed in the pH range from 3 to 9 at 30 °C, natural solution pH, 400 rpm and constant initial dye concentration. The pH was adjusted using 0.1N NaOH and 0.1N HCl solutions by using an Orion 920A pH-meter with a combined pH electrode. pH-meter was standardized with NBS buffers before every measurement.

#### 2.2.4. Effect of ionic strength

The effect of ionic strength to removal rate of dyes on kaolinite was investigated at 0.001–0.100 mol/L KCl salt concentrations at 30 °C, natural solution pH, 400 rpm and constant initial dye concentration.

#### 2.2.5. Effect of acid-activation

In order to obtain the acid-activated kaolinite samples H<sub>2</sub>SO<sub>4</sub> solutions were used. The aqueous suspensions of kaolinite in 0.2, 0.4 and 0.6 M H<sub>2</sub>SO<sub>4</sub> solutions (so that acid/solid ratios were 1/5, 2/5 and 3/5 g/g) were refluxed with a reflux apparatus, then filtered and dried at 110 °C for 24 h [10]. In order to study the effect of acid-activation on removal rate of dyes, the experiments were made using acid-activated kaolinite samples at 30 °C, natural solution pH, 400 rpm and constant initial dye concentration.

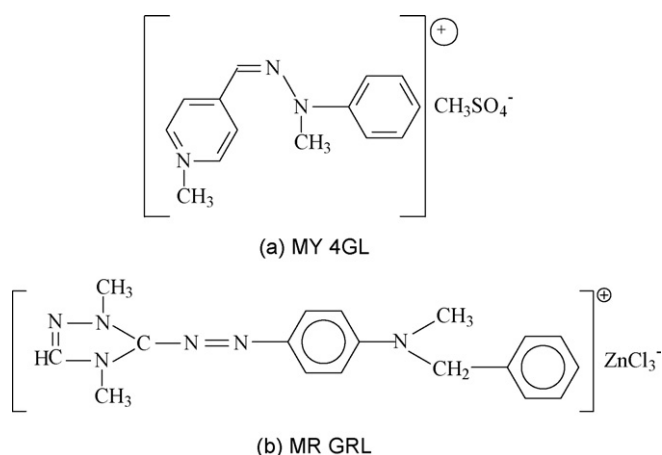


Fig. 1. (a and b) Structures of dyes.

### 2.2.6. Effect of calcination temperature

After cleaning the sample mechanically of the visible impurities, it was ground and sieved to obtain 100  $\mu\text{m}$  size fraction. Then, it was dried at 110  $^{\circ}\text{C}$ , and used in further experiments. Calcinated kaolinite samples have been prepared in the temperature range of 110–800  $^{\circ}\text{C}$  with a Nuve MF-140 furnace [9]. The effect of calcination temperature on the removal rate of dyes was investigated using calcinated-kaolinite samples at 30  $^{\circ}\text{C}$ , natural solution pH, 400 rpm and constant initial dye concentration.

### 2.2.7. Effect of solution temperature

The effect of temperature to the adsorption capacity of kaolinite was carried out at 30, 40, 50 and 60  $^{\circ}\text{C}$  in a constant temperature bath at natural solution pH, 400 rpm and constant initial dye concentration.

## 2.3. Data evaluation

In the kinetic experiments the amount of dyes adsorbed at any time  $t$ ,  $q_t$  (mol/g), was calculated using the following mass balance equation by (1)

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

where  $C_0$  and  $C_t$  are the initial and liquid-phase concentrations at any time  $t$  of dye solution (mol/L), respectively;  $q_t$  is the dye concentration on adsorbent at any time  $t$  (mol/g),  $V$  the volume of dye solution (L), and  $m$  is the mass of kaolinite sample used (g).

## 3. Results and discussion

### 3.1. Adsorption rate

The adsorption of dyes from aqueous phase onto a solid surface can be well described as a reversible reaction under an equilibrium condition established between the two phases [13]. The rate at which the species are removed from solution onto an adsorbent surface is an important factor for designing treatment plants. Thus, in order to characterise the adsorption process of the dyes on kaolinite, in this section, we have discussed the effect of factors such as contact time, stirring speed, initial dye concentration, initial solution pH, ionic strength, acid-activation, calcination and solution temperatures on the removal rate of cationic dyes onto kaolinite from aqueous solution.

#### 3.1.1. Effect of contact time and initial dye concentration

From an economical point of view, the contact time required to reach equilibrium is an important parameter in the wastewater treatment. The adsorption of MY 4GL and MR GRL dyes on kaolinite at different initial concentrations and stirring speed of 400 rpm was studied as a function of contact time in order to determine the equilibrium time. Fig. 2 shows time course of the adsorption equilibrium of MY 4GL and MR GRL onto kaolinite. The removal of dyes was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium. The rapid adsorption observed during the first 5 min is probably due to the abundant availability of active sites on the kaolinite surface, and with the gradual occupancy of these sites, the sorption becomes less efficient. At this point, the amount of dye being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. The time required to attain this state of equilibrium was termed as the equilibrium time and the amount of dye adsorbed at the equilibrium time reflected the maximum dye adsorption capacity of the adsorbent under these particular conditions [14]. It is clear from Fig. 2 that the contact time needed to

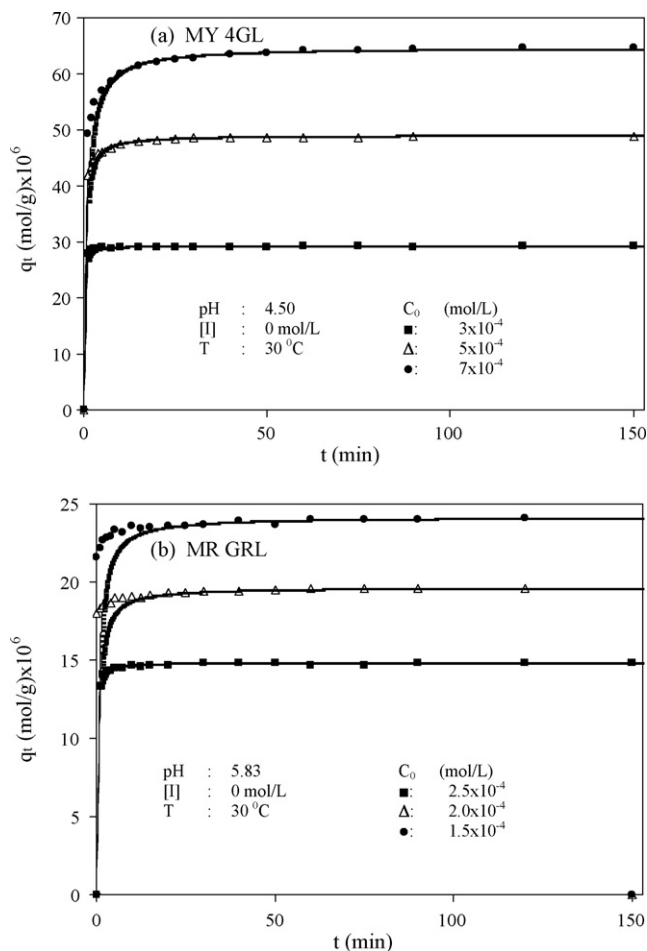


Fig. 2. (a and b) The effect of contact time and initial dye concentration to the adsorption rate of dyes on kaolinite.

reach equilibrium conditions was about 150 min. The time required to reach the equilibrium is in accordance with the results obtained by Kargi and Ozmihci [15] investigating dyestuffs biosorption by powdered activated sludge; by Sun et al. [16] investigating malachite green biosorption by aerobic granules; and by Senthilkumar et al. [17] investigating various dyes adsorption by activated carbon.

The amount of dyes adsorbed,  $q_t$ , increases with time for all initial concentration. However, the uptake rate of the dyes was found to decrease with increase in time until it approaches a pseudo-steady-state value known as the equilibrium loading capacity,  $q_e$ . When the equilibrium conditions are reached the adsorbate molecules in the solutions are in a state of dynamic equilibrium with the molecules adsorbed by the adsorbent. This behaviour indicates negligible further removal of the dye. From Fig. 2, it was clear that the removal of dye was dependent on the concentration of the dye. At low concentrations, adsorption sites took up the available dye more quickly. However, at higher concentrations, dye needed to diffuse to the sorbent surface by intraparticle diffusion. Also, the steric repulsion between the solute molecules could slow down the adsorption process. The equilibrium loading capacity increases at 30  $^{\circ}\text{C}$  from  $2.92 \times 10^{-5}$  to  $6.46 \times 10^{-5}$  mol/L as the initial concentration increases from  $3 \times 10^{-4}$  to  $7 \times 10^{-4}$  mol/L for MY 4GL; and from  $1.48 \times 10^{-5}$  to  $2.41 \times 10^{-5}$  mol/L as the initial concentration increases from  $1.5 \times 10^{-4}$  to  $2.5 \times 10^{-4}$  mol/L for MR GRL, indicating that the initial concentration provided a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases [18]. The shapes of the curves are similar and approx-

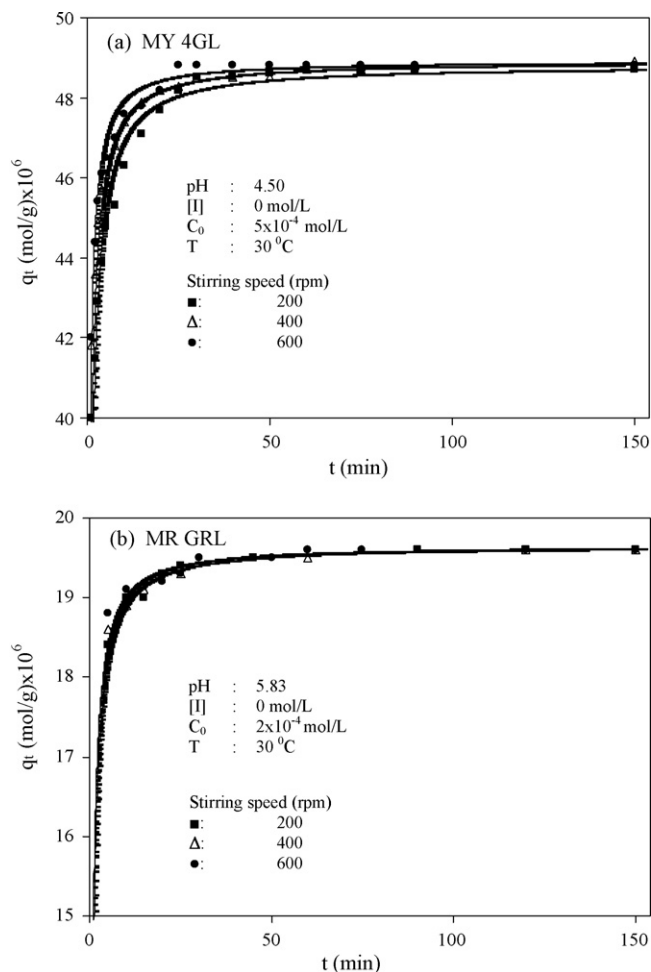


Fig. 3. (a and b) The effect of stirring speed to the adsorption rate of dyes on kaolinite.

imately independent on the initial dye concentration (Fig. 2). This indicates a monolayer formation of the dye on the external surface [19]. A similar trend was reported for the adsorption of dyes such as MG onto treated sawdust [20], reactive dyes onto dried activated sludge [21], metal complex dyes onto pine sawdust [22] and Rhodamine-B onto activated carbon [23].

### 3.1.2. Effect of stirring speed

Fig. 3 shows the effect of stirring speed (i.e., 200, 400 and 600 rpm) on the cationic dye adsorption at initial dye concentrations of  $5 \times 10^{-4}$  mol/L for MY 4GL and  $2 \times 10^{-4}$  mol/L for MR GRL. The difference of adsorption rate was insignificant as the stirring speed increases. Similar phenomena were observed in the kinetic experiments of victoria blue [24], methyl violet [25] and methylene blue [26] on perlite, basic brilliant green on modified peat-resin particle [27], maxilon blue 5G on sepiolite [12] and maxilon blue GRL on sepiolite [28]. Therefore, the stirring speed was taken as 400 rpm in further experiments.

### 3.1.3. Effect of initial pH

Since pH is one of the main variables affecting the adsorption process [29], influencing not only the surface charge of the sorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the sorbent, but also the solution dye chemistry [30]. In this work, the effect of the four initial solution pH (i.e., 3.0, 5.0, 7.0 and 9.0) on the removal rate of MY 4GL and MR GRL dyes by kaolinite was investigated

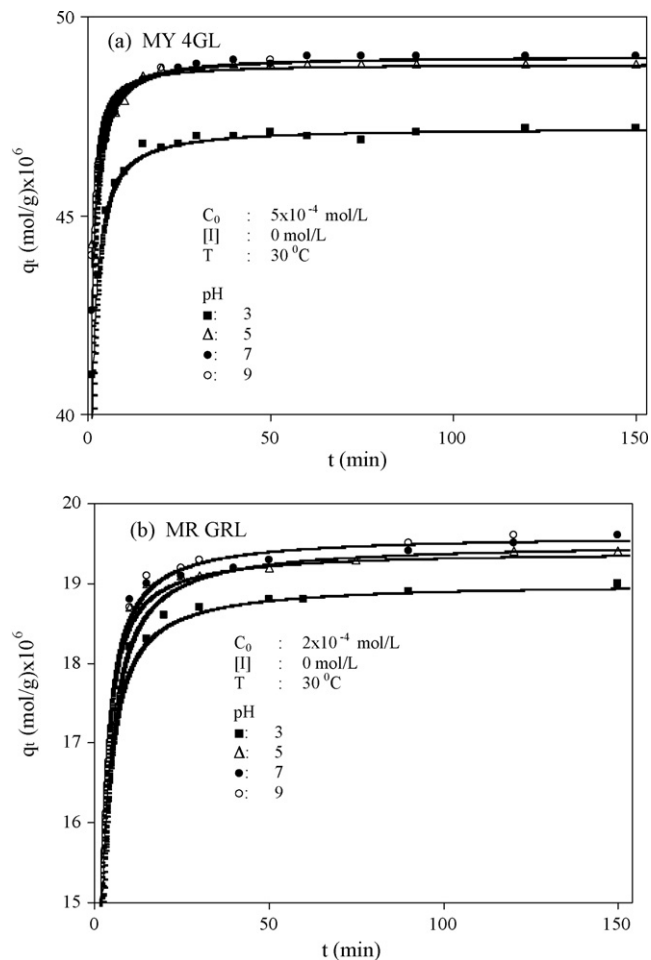


Fig. 4. (a and b) The effect of initial pH to the adsorption rate of dyes on kaolinite.

at stirring speed of 400 rpm and initial dye concentrations of  $5 \times 10^{-4}$  mol/L for MY 4GL and  $2 \times 10^{-4}$  mol/L for MR GRL. As seen from Fig. 4, the adsorption capacity for both dyes increased when the initial pH was increased from 3.0 to 9.0. The adsorption patterns of both dyes were similar in the studied pH range. The pH effect on dye adsorption observed in this study was explained by electrostatic interaction between kaolinite and dye molecules. Maximum adsorption occurs at basic pH (pH 9). In our previously study [8], we found that the charge sign on the surface of kaolinite was negative in a wide pH range (i.e., 3–9). As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. Therefore, the extent of dyes adsorbed on kaolinite tended to increase with the increase of pH values, which can be attributed to the electrostatic attraction between the negatively charged surface and the positively charged dye molecule according to the following reaction:



Also, lower adsorption of cationic dyes at acidic pH is because of the presence of excess  $\text{H}^+$  ions competing with dye cations for the adsorption sites. These observations were similar to earlier findings by other workers for adsorption of methylene blue (i.e., basic blue 9) on kaolinite [31] and perlite [26], and MG onto activated charcoal [32].

### 3.1.4. Effect of ionic strength

Since industrial effluents are always contaminated with various additives such as inorganic salts, it is important to study the



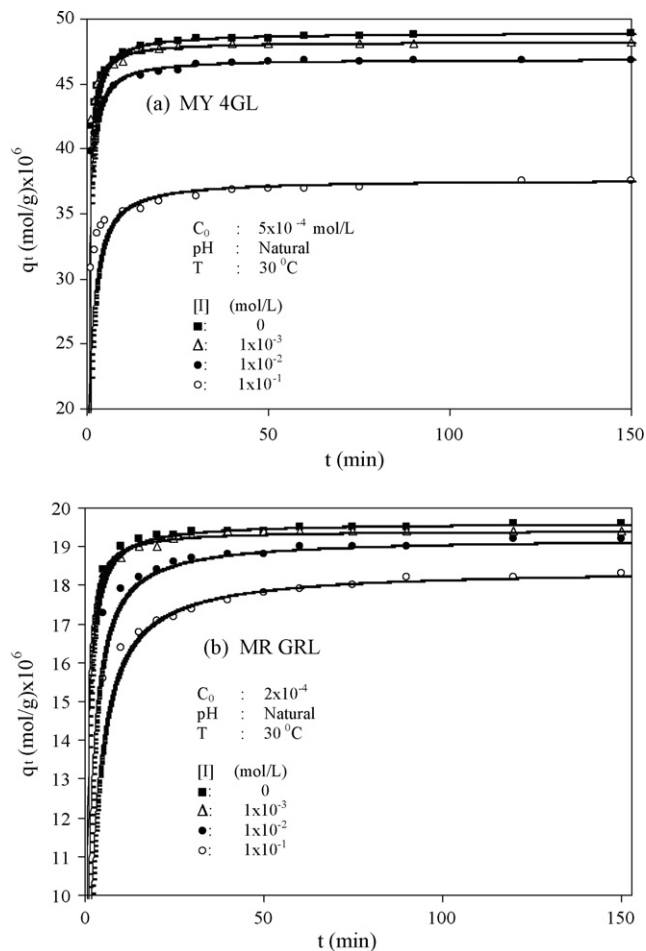


Fig. 5. (a and b) The effect of ionic strength to the adsorption rate of dyes on kaolinite.

effect of these ions on the adsorption property of dye solutions. The adsorption of dye in the presence of salt was therefore carried out. The adsorption of dyes on kaolinite was slightly negatively affected by the presence of KCl (Fig. 5). The concentrations of KCl in solution were in the range of 0.001–0.1 mol/L. Increasing ion strength decreased adsorption capacity when there is the electrostatic attraction between the adsorbent surface and adsorbate ions [33,34]. As ionic strength of solution increases, final pH of suspension decreases. This means that the number of positively charged sites on kaolinite increases. Therefore, the adsorption capacity of dyes on kaolinite decreases. Furthermore, since the salt screens the electrostatic interaction of opposite charges of the oxide surface and the dye molecules, the adsorbed amount will also decrease with increase of KCl concentration [35].

### 3.1.5. Effect of acid-activation

The adsorption rate of MY 4GL and MR GRL dyes on the acid-activated kaolinite samples was investigated at 30 °C and 400 rpm as a function of time. Fig. 6 shows the relationship between the adsorbed dye amount and time. As seen from Fig. 6, the adsorption rate and amount of MY 4GL and MR GRL dyes on the kaolinite surface decreased with increase in acid-activation. The fact that the amount of dyes adsorbed decreases with increase in acid-activation may be due to transforming of SOH groups to SOH<sub>2</sub><sup>+</sup> groups on kaolinite surface according to the following reaction [9]:

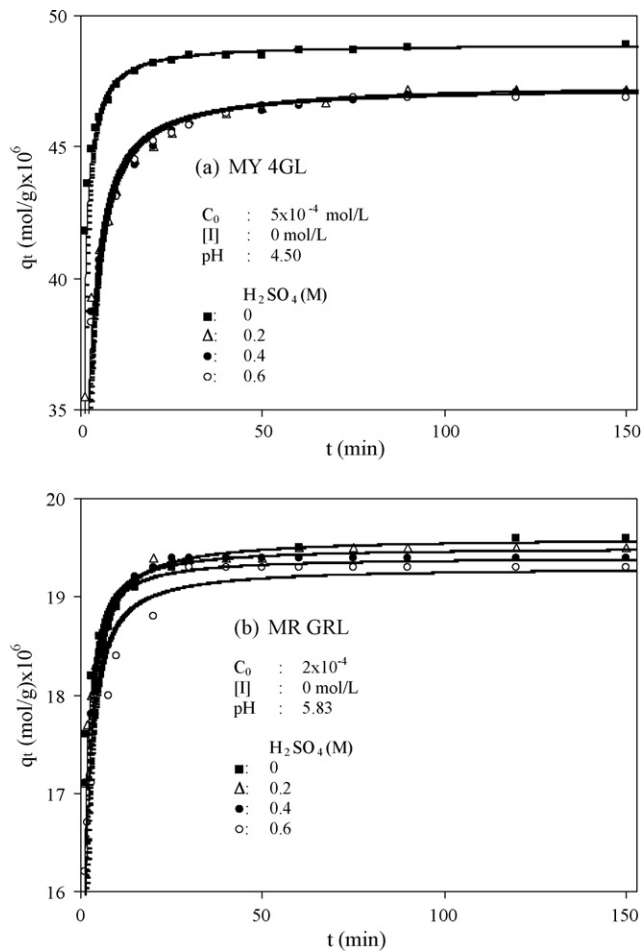


Fig. 6. (a and b) The effect of acid-activation to the adsorption rate of dyes on kaolinite.

### 3.1.6. Effect of calcination-temperature

The removal rate of MY 4GL and MR GRL dyes on calcinated kaolinite samples at 110, 300, 600 and 800 °C was studied at 30 °C and 400 rpm. Fig. 7 shows the plots of adsorbed amount ( $q_t$ ) versus time ( $t$ ). The removal rate of dyes has decreased with increase in calcination temperature. During calcination, the silicon atoms experience a range of environments of differing distortion due to dehydroxylation [36]. In our previous works, we found that the intensity of hydroxyl peaks decreased with increase in calcination temperature [9]. Therefore, the decrease in the amount adsorbed of MY 4GL and MR GRL dyes with increasing activation temperature may be a result of the removal of most of the micropores due to heating the sample and due to the decrease in OH groups in kaolinite during the calcination process.

### 3.1.7. Effect of solution temperature

The degree of adsorption depends on the temperature of the solid–liquid interface. The rates of adsorption were studied in the temperature range of 303 and 333 K. The effect of temperature on the adsorption is shown in Fig. 8. It is observed that at higher temperatures the adsorption is slower, and the adsorption process was exothermic process. The fact that the adsorption capacity of kaolinite for MY 4GL and MR GRL dyes tends to decrease with increase in temperature shows that the adsorption process occurs as a physisorption in this case, in which adsorption arises from the weaker van der Waals and dipole forces which are usually associated with low heat of adsorption. Moreover, careful examination of

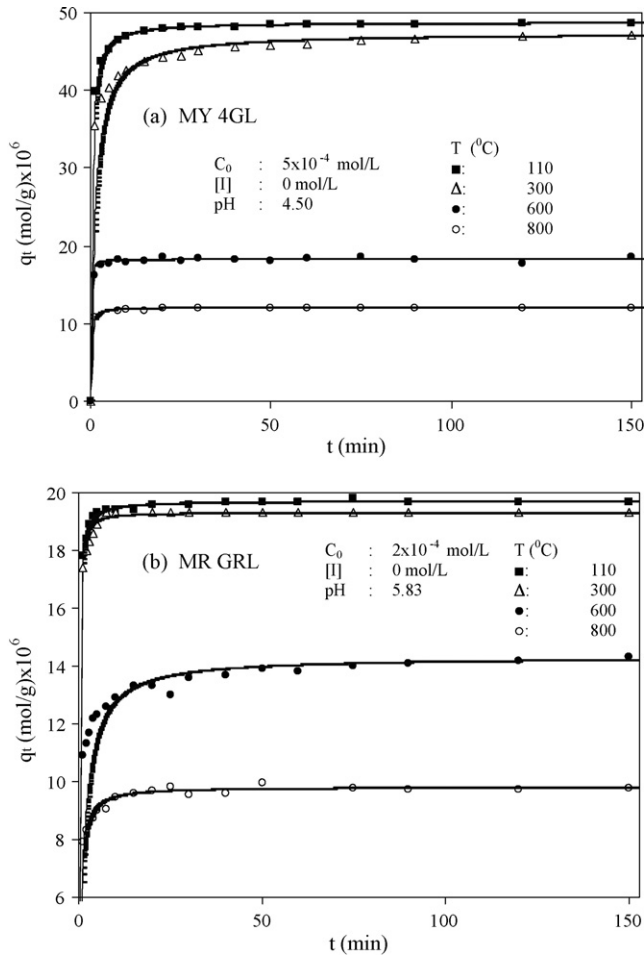


Fig. 7. (a and b) The effect of calcination temperature to the adsorption rate of dyes on kaolinite.

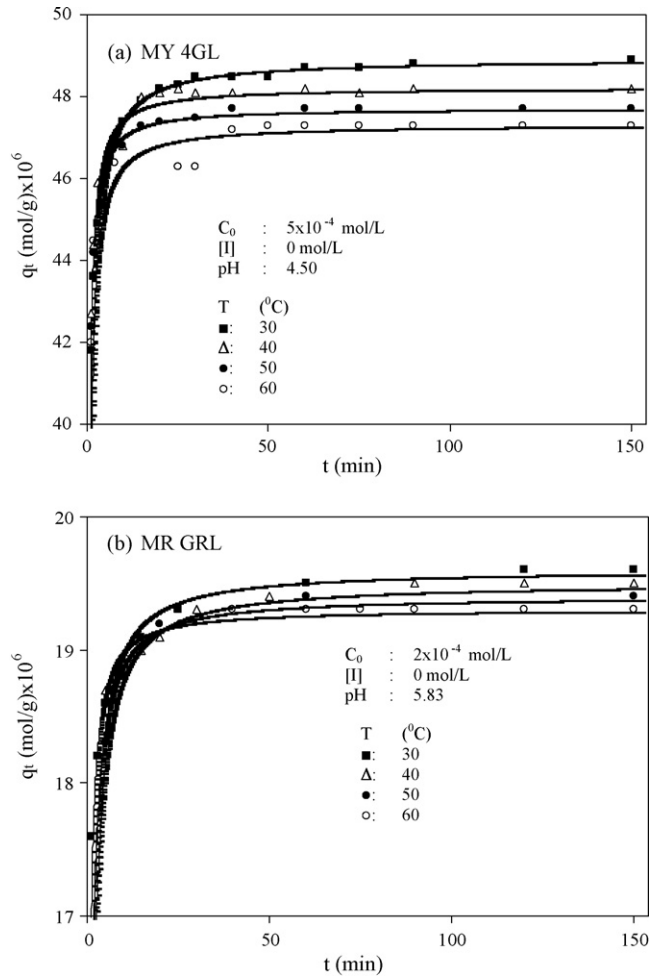


Fig. 8. (a and b) The effect of temperature to the adsorption rate of dyes on kaolinite.

Fig. 8, in particular at high temperatures, reveals that desorption might be occurring. This behaviour could be attributed to either a reversible adsorption or a back diffusion controlling mechanism [37].

### 3.2. Kinetic models

The kinetic study of the adsorption processes provides useful data regarding the efficiency of adsorption and feasibility of scale-up operations. To evaluate the effectiveness of an adsorbate, studies of kinetics of adsorption equilibria are also needed. Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data. The rate constant of the dye removal from the solution by kaolinite was determined using Lagergren pseudo-first-order and pseudo-second-order equations. These equations have been used widely for the adsorption of an adsorbate from aqueous solution.

#### 3.2.1. Lagergren pseudo-first-order equation

The Lagergren pseudo-first-order equation was used to fit the experimental results [38]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where  $q_e$  and  $q_t$  are the amount of dye adsorbed per unit weight of the adsorbent (mol/g) at equilibrium time and time  $t$ , respectively.  $k_1$  is the rate constant for the first-order kinetics. The values

of adsorption rate constant for dyes adsorption on kaolinite were determined from the plots of  $\ln(q_e - q_t)$  against  $t$ .

In many cases the above equation does not fully describes the adsorption kinetics. In such cases, a pseudo-second-order equation can be used.

#### 3.2.2. Pseudo-second-order equation

The pseudo-second-order equation is often successfully used to describe the kinetics of the fixation reaction of pollutants on the adsorbent. The pseudo-second-order kinetics may be expressed as [39]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  is the rate constant of adsorption,  $q_e$  is the amount of dye adsorbed at equilibrium (mol/g) and  $q_t$  is the amount of dye adsorbed at time  $t$  (mol/g). The equilibrium adsorption capacity ( $q_e$ ) and the second-order rate constant  $k_2$  (g/mol min) can be determined experimentally from the slope and intercept of plot of  $t/q_t$  versus  $t$ .

### 3.3. Kinetic analysis

As mentioned above, two kinetic models were used to examine the kinetics of the adsorption process. First, kinetic data were treated with the pseudo-first-order kinetic model. Values of the rate constant ( $k_1$ ), equilibrium adsorption capacity ( $q_e$ ), the corre-

lation coefficient ( $R^2$ ) were calculated from the plots of  $\ln(q_e - q_t)$  versus  $t$  for each individual dye under different conditions and are presented in Tables 1 and 2. The experimental data deviated greatly from linearity. Based on regression coefficient ( $R^2$ ), it appeared that the first-order model was not well fit with the experimental data. In addition, the calculated equilibrium adsorption capacities do not agree with experimental values (these data not given in tables).

Kinetic data were further treated with the pseudo-second-order kinetic model. If the pseudo-second-order kinetics is applicable, the plot of  $t/q_t$  versus  $t$  should show a linear relationship. The correlation coefficients ( $R^2$ ), the second-order rate constants ( $k_2$ ) and calculated ( $q_{cal}$ ) and experimental ( $q_e$ ) equilibrium sorption capacities are shown in Tables 1 and 2 for both dyes. The linear plots of  $t/q_t$  versus  $t$  show that the experimental data agree with the pseudo-second-order-kinetic model for two dyes. In addition, the values of calculated  $q_{cal}$  in the case of the second-order model are very close to the experimental values under all work conditions. The correlation coefficients for the second-order kinetic model are higher than 0.99 in all cases. The values of  $k_2$  and  $q_e$  all increased with increasing concentration of dye presumably due to the enhanced mass transfer of dye molecules to the surface of kaolinite. This observation suggested that the boundary layer resistance was not the rate-limiting step [40]. These results, which confirmed that the adsorption of dyes by kaolinite is best described by the pseudo-second-order model are in agreement with many work in literature [24,26,39].

The half-adsorption time,  $t_{1/2}$ , is another parameter which can be calculated from the equilibrium concentration and the diffusion coefficient rate values. Half-adsorption time,  $t_{1/2}$ , is defined as the time required for the adsorption to take up half as much kaolinite as its equilibrium value. This time is often used as a measure of the adsorption rate. This was calculated by using the following equation [41]:

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{6}$$

The diffusion coefficient largely depends on the surface properties of adsorbents. The diffusion coefficient for the intra particle transport of the two dyes under different conditions were also calculated by using the following relationship [42]:

$$t_{1/2} = \frac{0.030r_0^2}{D} \tag{7}$$

where  $t_{1/2}$  is the half life in seconds as calculated from Eq. (6),  $r_0$  the radius of the adsorbent particle in centimeters and  $D$  is the diffusion coefficient value in  $\text{cm}^2/\text{s}$ . In these calculations, it has been assumed that the solid phase consists of spherical particles with an average radius between the radii corresponding to upper- and lower-size fractions. The value of  $r_0$  was calculated as  $2.5 \times 10^{-3}$  cm for kaolinite samples. Calculated values of  $t_{1/2}$  and  $D$  are given in Tables 1 and 2.  $D$  values for the adsorption of MY 4GL and MR GRL on kaolinite under different conditions are in the range of  $2.65 \times 10^{-9}$  to  $62.5 \times 10^{-9}$  and  $1.98 \times 10^{-9}$  to  $25 \times 10^{-9}$   $\text{cm}^2/\text{s}$ , respectively. The  $D$  values obtained in our study are comparable to those available in the literature [25,26,28,43–46]. Similar results were found for methylene blue on fly ash [43], phenol and benzene on carbon [45], methylene blue and methyl violet on perlite [25,26], and maxilon blue GRL on sepiolite [28]. On the other hand, the  $D$  values obtained for adsorption of reactive dyes on shale oil ash were higher than those in this study [44], whereas our values were lower than those obtained for astrazone blue and telon blue on wood [46].

3.4. Activation parameters

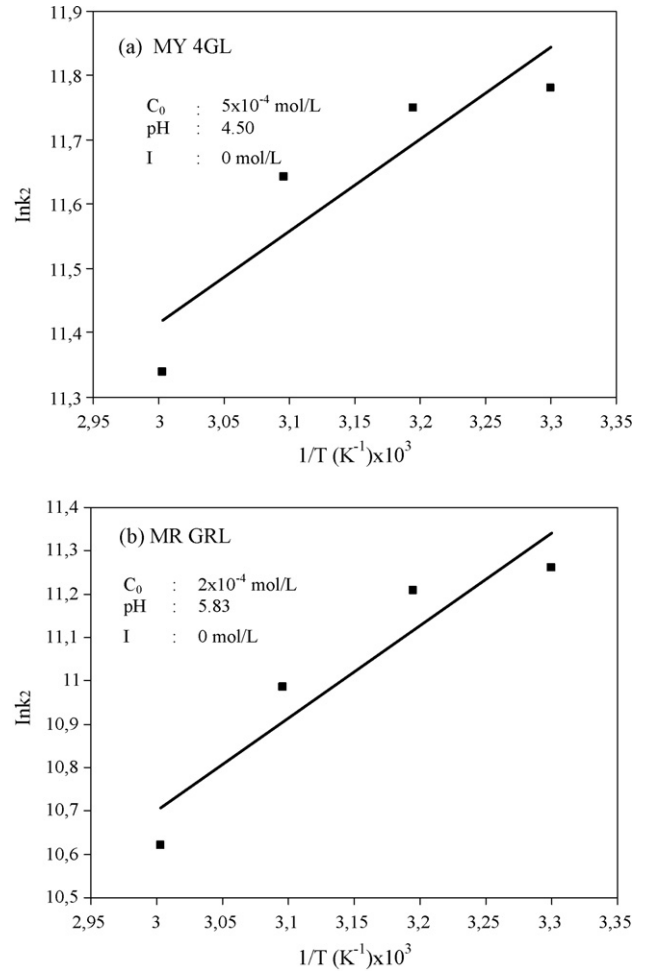
According to the results of the kinetic study the pseudo-second-order model was found to be the best model to describe the

Table 1 Kinetic data calculated for adsorption of MY 4GL on kaolinite.

Parameters	Kinetic models										$D$ ( $\times 10^9$ $\text{cm}^2/\text{s}$ )	$t_{1/2}$ (min)
	$T$ ( $^\circ\text{C}$ )	$[C_0]$ ( $\times 10^4$ mol/L)	pH	Stirring speed (rpm)	Calcination temperature ( $^\circ\text{C}$ )	Acid-activation (mol/L)	First-order $R^2$	Second-order $q_{e(cal)}$ ( $\times 10^5$ mol/g)	$q_e$ ( $\times 10^5$ mol/g)	$k_2$ ( $\times 10^{-4}$ g/mol min)		
30	5	Natural	400	0	0	0.858	4.89	4.89	7.76	0.999	9.98	0.313
40	5	Natural	400	0	0	0.603	4.82	4.83	7.36	0.999	19.10	0.163
50	5	Natural	400	0	0	0.855	4.77	4.78	5.90	0.999	21.10	0.147
60	5	Natural	400	0	0	0.706	4.73	4.75	4.10	0.999	14.20	0.219
30	5	3	400	0	0	0.645	4.72	4.72	9.25	0.999	13.70	0.228
30	5	5	400	0	0	0.926	4.88	4.88	17.51	0.999	26.60	0.117
30	5	7	400	0	0	0.826	4.90	4.90	10.58	0.999	16.20	0.192
30	5	9	400	0	0	0.878	4.90	4.90	11.80	0.999	18.10	0.172
30	5	Natural	200	0	0	0.961	4.87	4.88	5.08	0.999	7.75	0.403
30	5	Natural	600	0	0	0.914	4.88	4.89	10.02	0.999	15.30	0.204
30	3	Natural	400	0	0	0.487	2.92	2.92	34.85	0.999	31.80	0.098
30	7	Natural	400	0	0	0.967	6.46	6.49	2.07	0.999	4.20	0.741
30	5	Natural	400	0	0.001	0.774	4.82	4.82	9.29	0.999	14.00	0.223
30	5	Natural	400	0	0.100	0.884	4.68	4.69	6.87	0.999	10.00	0.310
30	5	Natural	400	0	0.100	0.895	3.76	3.76	3.92	0.999	4.60	0.678
30	5	Natural	400	110	0	0.855	4.86	4.87	6.06	0.999	9.23	0.338
30	5	Natural	400	300	0	0.937	4.72	4.73	1.79	0.999	2.65	1.175
30	5	Natural	400	600	0	0.573	1.85	1.82	107.87	0.999	62.50	0.050
30	5	Natural	400	800	0	0.631	1.20	1.20	57.47	0.999	21.50	0.145
30	5	Natural	400	0	0.2	0.909	4.71	4.73	2.85	0.999	4.21	0.741
30	5	Natural	400	0	0.4	0.946	4.72	4.73	2.66	0.999	3.93	0.792
30	5	Natural	400	0	0.6	0.968	4.72	4.74	2.55	0.999	3.76	0.826

**Table 2**  
Kinetic data calculated for adsorption of MR GRL on kaolinite.

Parameters				Kinetic models				D (×10 <sup>5</sup> cm <sup>2</sup> /s)		τ <sub>1/2</sub> (min)		
T (°C)	[C <sub>0</sub> ] (×10 <sup>4</sup> mol/L)	pH	Stirring speed (rpm)	[I] (mol/L)	Calcination temperature (°C)	Acid-activation (mol/L)	First-order R <sup>2</sup>	Second-order q <sub>e(cal)</sub> (×10 <sup>2</sup> mol/g)	k <sub>2</sub> (×10 <sup>-4</sup> g/mol min)	R <sup>2</sup>		
30	2	Natural	400	0			0.920	1.96	15.77	0.999	9.55	0.327
40	2	Natural	400	0			0.986	1.95	9.52	0.999	8.15	0.383
50	2	Natural	400	0			0.998	1.94	7.63	0.999	11.40	0.272
60	2	Natural	400	0			0.933	1.93	5.34	0.999	18.80	0.166
30	2	3	400	0			0.915	1.96	9.27	0.999	5.68	0.550
30	2	5	400	0			0.973	1.95	7.25	0.999	4.42	0.707
30	2	7	400	0			0.935	1.94	10.36	0.999	6.28	0.497
30	2	9	400	0			0.919	1.90	8.70	0.999	5.17	0.604
30	2	Natural	200	0			0.872	1.96	15.19	0.999	9.32	0.335
30	2	Natural	600	0			0.817	1.96	14.85	0.999	9.11	0.343
30	1.5	Natural	400	0			0.383	1.48	54.70	0.999	25.40	0.123
30	2.5	Natural	400	0			0.843	2.41	7.40	0.999	5.58	0.560
30	2	Natural	400	0.001			0.958	1.94	17.69	0.999	10.70	0.291
30	2	Natural	400	0.010			0.887	1.92	5.49	0.999	3.29	0.947
30	2	Natural	400	0.100			0.957	1.83	3.44	0.999	1.98	1.576
30	2	Natural	400	0	100		0.780	1.97	41.66	0.999	25.80	0.121
30	2	Natural	400	0	300		0.982	1.93	72.09	0.999	44.00	0.071
30	2	Natural	400	0	600		0.937	1.43	5.85	0.999	2.61	1.193
30	2	Natural	400	0	800		0.691	0.98	28.65	0.999	8.77	0.356
30	2	Natural	400	0		0.2	0.780	1.95	21.59	0.999	13.10	0.237
30	2	Natural	400	0		0.4	0.993	1.94	24.44	0.999	14.80	0.210
30	2	Natural	400	0		0.6	0.956	1.93	16.97	0.999	10.20	0.305



**Fig. 9.** (a and b) Arrhenius plot for the adsorption of dyes on kaolinite.

experimental kinetic data for the adsorption of dyes with kaolinite. The second-order rate constants listed in Tables 1 and 2 are used to estimate the activation energy of MY 4GL and MR GRL dyes adsorption on kaolinite using Arrhenius equation:

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \tag{8}$$

where  $E_a$  is the activation energy (J/mol),  $k_2$  is the rate constant of adsorption (g/mol s),  $k_0$  is Arrhenius factor, which is the temperature independent factor (g/mol s),  $R_g$  is the gas constant (J/Kmol), and  $T$  is the solution temperature (K). Accordingly the activation energies of the adsorption of the dyes were calculated using Eq. (8). The value of  $E_a$  was obtained from the slope of the plot of  $\ln k_2$  versus  $1/T$  as shown in Fig. 9.  $E_a$  values were found to be 17.72 and 29.13 kJ/mol for MY 4GL and MR GRL, respectively. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Since the values of the activation energy are lower than 40 kJ/mol [47], this indicates that the adsorption has a potential barrier corresponding to a physisorption. Therefore, the affinity of dyes for kaolinite may be ascribed to Van der Waals forces, electrostatic attractions or hydrogen bonds between the dye and the surface of the particles. These values are consistent with the values in the literature where the activation energy was found to be 43.0 kJ/mol for the adsorption of reactive red 189 on crosslinked chitosan beads [48], 5.6–49.1 kJ/mol for the adsorption of polychlorinated biphenyls on fly ash [49] and 33.96 kJ/mol for the adsorption of maxilon blue GRL on sepiolite [28].



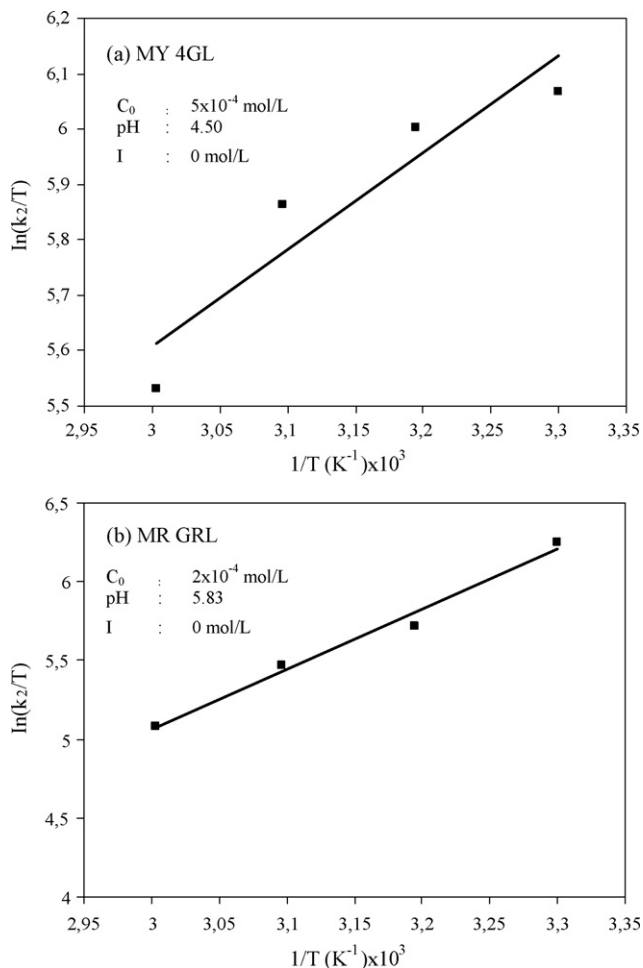


Fig. 10. (a and b) Plot of  $\ln(k_2/T)$  vs.  $1/T$  for adsorption of dyes on kaolinite.

Another aim of this paper is to consider the effect of solution temperature on the transport/kinetic process of dye adsorption. Therefore, the thermodynamic activation parameters of the process such as enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and free energy ( $\Delta G^*$ ) were determined using the Eyring equation [50]:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S^*}{R_g} - \frac{\Delta H^*}{R_g T} \quad (9)$$

where  $k_B$  is the Boltzmann constant ( $1.3807 \times 10^{-23}$  J/K) and  $h_p$  is the Planck constant ( $6.6261 \times 10^{-34}$  J s). Fig. 10 shows the plot of  $\ln(k_2/T)$  against  $1/T$ . The values of  $\Delta H^*$  for MY 4GL and MR GRL dyes are  $-13.64$  and  $-31.77$  kJ/mol, respectively. The value of the activation enthalpy change indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic. At the same time, the low value of  $\Delta H^*$  implies that there was loose bonding between the adsorbate molecules and the adsorbent surface [51]. The values of  $\Delta S^*$  for MY 4GL and MR GRL dyes from Eq. (9) were found as  $-196.2$  and  $-250.7$  J/mol K, respectively. The negative activation entropy change ( $\Delta S^*$ ) value corresponds to a decrease in the degree of freedom of the adsorbed species. The change of activation Gibbs energy is given by following equation:

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (10)$$

The results obtained for the change of Gibbs energy are  $45.80$  and  $44.19$  kJ/mol for MY 4GL and MR GRL dyes, respectively, at  $30^\circ\text{C}$ .

### 3.5. Conclusions

Results of this study provide for a better understanding of the adsorption kinetics of MY 4GL and MR GRL dyes on kaolinite. The adsorption of MY 4GL and MR GRL was highly dependent on initial dye concentration, pH, ionic strength, acid-activation, calcination and solution temperature. An increase in the initial dye concentration enhances the interaction between dyes and kaolinite, resulting in greater adsorption capacity. The dyes adsorption capacity increased with the increase of pH in the range of 3–9. The results showed that the adsorption system could be explained by the electrostatic attraction between the negatively charged surface and the positively charged dye molecule in the basic medium. The addition of salt had a negative effect on the adsorption capacity of kaolinite. The loading capacity of kaolinite decreased with increase in temperature indicating that the adsorption process is exothermic. The adsorption kinetics is fast with 150 min needed to reach equilibrium. Furthermore, the adsorption kinetics of cationic dyes onto kaolinite can be well described by pseudo-second-order reaction model. The kinetic parameters thus obtained from the fittings of the model were dependent on initial adsorbate concentration, pH, ionic strength and temperature. Kaolinite has proven to be a promising material for the removal of contaminants from aqueous phase.

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