The adsorption and mass-transfer process of cationic red X-GRL dye on natural zeolite

Jingjing Tian, Junfang Guan, Huimin Gao, Yafei Wen and Zijie Ren

ABSTRACT

The adsorption behavior of natural zeolite was studied in order to determine the adsorption capacity and mass-transfer process of cationic red X-GRL (C₁₈H₂₁BrN₆) onto the adsorbent. The adsorption tests to determine both the uptake capacity and the mass-transfer process at equilibrium were performed under batch conditions, which showed rapid uptake in general for the initial 5 min, corresponding to 92% total removal. The equilibrium adsorption capacity value (qₑₑₑₑ) in pseudo-second-order kinetics was 13.51 mg/g at 293 K and the whole adsorption process was governed by physical adsorption with an endothermic, endothermic spontaneous nature. Adsorption tests indicated that the zeolite has great potential as an alternative low-cost material in the treatment of X-GRL drainage. However, the mass-transfer process to determine the rate-controlling steps showed that both film diffusion and pore diffusion were important in controlling the adsorption rate. The adsorption process was governed by film diffusion while pore diffusion was poor because the X-GRL molecules could not penetrate into the zeolite easily. The X-GRL molecules were only adsorbed on the external surface of the zeolite. Hence, to improve the adsorption capacity of natural zeolite further, modification to expand its micropores is necessary.

Key words | adsorption capacity, cationic red X-GRL removal, mass-transfer process, natural zeolite

INTRODUCTION

Dyes have been used extensively in many industries such as printing, textiles, leather, paper, plastics, and cosmetics (Zhou & He 2008; Ayad et al. 2012). However, the removal of dye has been a challenge and the discharge of colored wastewater from these industries presents an eco-toxic hazard and introduces the potential danger of bioaccumulation (Ayad et al. 2012; Sahmoune & Ouazene 2012; Sharma & Das 2013). Cationic red X-GRL, one of the most widely used dyes, is barely degradable (Lei & Dai 2007). Treatment processes for X-GRL contaminated wastewater include wet air oxidation (Lei et al. 2007), electrochemical oxidation (Zhou & He 2008), photocatalytic degradation (Stengl et al. 2012; Mahesh & Kuo 2015), Fenton (Du et al. 2008), ozonation (Zhao et al. 2006; Zhao et al. 2011; Wu et al. 2015), joint degradation (electro-Fenton degradation (Lei et al. 2010; Li et al. 2010), wet electrocatalytic oxidation (Dai et al. 2006; Lei & Dai 2007)), microfiltration (Ayad & Abu El-Nasr 2010; Ayad et al. 2012), and biotechnologies (Qiu et al. 2012; Qiu et al. 2014). However, these techniques generate many toxic or carcinogenic degradation intermediates containing benzene rings which are considered to be refractory to further degradation (Lei et al. 2007; Zhou & He 2008; Stengl et al. 2012). Moreover, these techniques are only used for high concentrations of cationic red X-GRL and the treated wastewater still contains a high concentration, which cannot meet the increasingly stringent legislations.

Adsorption of dyes is superior to other techniques in terms of initial cost, high efficiency, simplicity of design, ease of operation, insensitivity to toxic substances (Ayad & Abu El-Nasr 2010; Ayad et al. 2012; Sahmoune & Ouazene 2012) and non-toxicity to the environment (Widiastuti et al. 2011). Microporous and mesoporous materials such as attapulgite (He et al. 2009), active carbon (Li et al. 2011), graphene oxide nanosheets (Sharma & Das 2013), polyaniline nanotubes base (Ayad & Abu El-Nasr 2010; Ayad et al. 2012), sawdust (Sahmoune & Ouazene 2012), rice hull ash, fungi (Sahmoune & Ouazene 2012) and biomass (Das et al. 2006) have been used for dye removal from aqueous solutions. Natural zeolite, among the low-cost adsorbents, is one of the most promising for a number of dyes (Ötker &
Zeolite has a large number of micropores and can effectively perform molecular separations by preferential adsorption and diffusion (Motse et al. 2009). Previous studies have focused on a wide variety of applications in the treatment of dye removal by natural zeolites (Ötker & Akmehmet-Balcıoğlu 2006; Lam & Rivera 2006; Motse et al. 2009; Widiasrututi et al. 2011). Several adsorption kinetics, isotherms and thermodynamics have been reported (Lam & Rivera 2006; Motse et al. 2009; Ayad & Abu El-Nasr 2013; Widiastuti et al. 2012). Despite many studies on thermodynamics through the van’t Hoff equation (Garcia-Delgado et al. 2006; Ai et al. 2011) or Le Chatelier’s principle (Sahmoune & Ouazene 2012; Sharma & Das 2015), there is very little literature published on the comparison of these two methods. In addition, previous studies focused on the two distinct phases (i.e. film diffusion and pore diffusion) (Widiastuti et al. 2011; Sahmoune & Ouazene 2012) in the adsorption process, and limited data are available for adsorption with natural zeolite in terms of the rate-controlling steps in the mass-transfer process.

The overall goals of this research were to understand the performance of natural zeolite in adsorbing X-GRL and the relative mass-transfer process and then provide guidance for the design and operation of zeolite treatment systems that are used for treating X-GRL-contaminated dye water. The two thermodynamic calculation methods were compared to ensure the correct thermodynamic parameters. In addition, this work identified the rate-controlling step in the overall adsorption process to search constraining factors of adsorption. This paper also characterizes the adsorption mechanism of X-GRL onto natural zeolite with appropriate models being proposed.

**MATERIALS AND METHODS**

**Materials**

Natural zeolite was obtained from Huludao, China. The samples were used in their natural state with no further treatments. Its physico-chemical properties are presented in Table 1. Chemical analyses of natural zeolite were characterized using X-ray fluorescence (XRF). Table 1 shows that natural zeolite mainly consists of silica and alumina. The predominant exchangeable cations for the natural zeolite were found to be Ca\(^{2+}\), K\(^+\), Mg\(^{2+}\), Na\(^+\) and Fe\(^{3+}\). The particle size range of the natural zeolite used in this study was 0.074 to 0.038 mm and the mean particle diameter was 0.045 mm. The BET surface area and average pore diameter of natural zeolite were determined from the N\(_2\) adsorption at −196°C by using a surface area and porosity analyzer (P-Sorb 3400, Gold APP Instrument Corporation, China). The BET surface area and the average pore diameter of natural zeolite were 64.0 m\(^2\)/g and 8.0 Å, respectively. Mineralogical analysis of the natural zeolite sample was carried out using X-ray diffraction (XRD). The mineralogical composition of the natural zeolite is given in Figure 1. The results showed that the zeolite is made up of clinoptilolite, heulandite, stilbite and quartz.

X-GRL, a basic dye produced by the Wuhan dyeing factory, was used in all dye adsorption experiments with the chemical molecular formula being C\(_{18}\)H\(_{21}\)BrN\(_6\) (He et al. 2009). The chemical structure of X-GRL is given in Figure 2. Aqueous X-GRL solutions were prepared by dissolving a

<table>
<thead>
<tr>
<th>Chemical weight composition from XRF</th>
<th>Chinese zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)O</td>
<td>0.3</td>
</tr>
<tr>
<td>MgO</td>
<td>1.2</td>
</tr>
<tr>
<td>Al(_2)O</td>
<td>13.4</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>78.5</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>1.2</td>
</tr>
<tr>
<td>CaO</td>
<td>3.9</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe(_2)O</td>
<td>1.0</td>
</tr>
<tr>
<td>Mean particle diameter (μm)</td>
<td>45.0</td>
</tr>
<tr>
<td>BET surface area (m(^2)/g)</td>
<td>64.0</td>
</tr>
<tr>
<td>Average pore diameter (Å)</td>
<td>8.0</td>
</tr>
</tbody>
</table>
known quantity of the basic dye in double-distilled water and used as a stock solution and diluted to the required initial concentration. NaOH and HCl were used for solution pH adjustment.

**Batch sorption studies**

Adsorption was conducted in a conical flask by mixing a required amount of natural zeolite with 50 ml of solutions containing the desired concentration of X-GRL at different temperatures. The mixture was agitated at 200 rpm for the desired time interval (0.5–17 min) and then centrifuged at 4,000 rpm for 5 min. The final X-GRL concentrations in the aqueous solutions were determined spectrophotometrically (UV–vis Shimadzu) at the maximum absorbance wavelength of 530 nm. The effect of adsorbent concentration and solution pH were tested. The adsorbent concentration examined in this study varied from 0.6 to 5 g/L. The solution pH varied from 3 to 11. Batch studies on X-GRL removal by natural zeolite were performed under the conditions shown in Table 2.

The amount of X-GRL absorbed from the aqueous solution was expressed as X-GRL removal capacity per unit mass of the natural zeolite \( (q_e) \) as:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

where \( C_0 \) is the initial X-GRL concentration (mg/L), \( C_e \) is the equilibrium X-GRL concentration (mg/L), \( V \) is the batch volume (L) and \( m \) is the zeolite mass (g). The percentage of X-GRL removal efficiency from the aqueous solution was then calculated from:

\[
\text{Removal efficiency} \% = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}
\]

**Adsorption isotherms**

To study the effect of initial X-GRL concentration on isotherms, batch sorption was conducted by varying the initial X-GRL concentration of 4–20 mg/L. Isotherm studies on X-GRL removal by natural zeolite were performed under the conditions shown in Table 2. Several equilibrium models have been developed to describe adsorption isotherm relationships, the three main isotherm models used in this work being the Langmuir, Freundlich, and Tempkin models.

**Adsorption kinetics**

To study the effect of contact time on kinetics, the X-GRL removal capacity by the adsorbent from aqueous solution was carried out to determine the optimum time required to reach equilibrium. Kinetic studies on X-GRL removal by natural zeolite were performed under the conditions shown in Table 2. Pseudo-first-order, pseudo-second-order, Elovich, and Bangham kinetic models were examined to fit the experimental data in this study.

**Thermodynamic studies**

The thermodynamics provide in-depth information about the energetic changes associated with the adsorption process. While the estimated heats of adsorption are probably not accurate because of the assumptions involved in their calculation, they are considered to be the correct order of magnitude (García-Delgado et al. 2006). For thermodynamic study, the temperature of sorption isotherms was 293, 330

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**Table 2 | Conditions in X-GRL adsorption tests, isotherms and kinetics**

<table>
<thead>
<tr>
<th>Batch studies</th>
<th>Zeolite concentration (g/L)</th>
<th>Initial X-GRL concentration (mg/L)</th>
<th>Contact time (min)</th>
<th>Temperature (K)</th>
<th>Solution pH values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite concentration</td>
<td>0.6–5.0</td>
<td>20</td>
<td>15</td>
<td>293</td>
<td>7</td>
</tr>
<tr>
<td>Solution pH value</td>
<td>1.4</td>
<td>20</td>
<td>15</td>
<td>293</td>
<td>3–11</td>
</tr>
<tr>
<td>Isotherms</td>
<td></td>
<td>1.4</td>
<td>4–20</td>
<td>293–313</td>
<td>7</td>
</tr>
<tr>
<td>initial X-GRL</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
<td>1.4</td>
<td>20</td>
<td>293–313</td>
<td>7</td>
</tr>
<tr>
<td>contact time</td>
<td></td>
<td></td>
<td>0.5–17.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and 313 K. The thermodynamic parameters are mainly calculated by two methods based on the van’t Hoff equation (Garcia-Delgado et al. 2006; Ai et al. 2011) and Le Chatelier’s principle (Sahmoune & Ouazene 2012; Sharma & Das 2013).

Mass-transfer process

To determine the mass-transfer process, sorption kinetics was studied separately in the first 5 min and in the whole sorption process. The mass-transfer process was investigated by the intraparticle diffusion model, the film diffusion model and the pore diffusion model.

RESULTS AND DISCUSSION

Adsorption studies

Effect of zeolite concentration

Figure 3(a) shows the effect of zeolite concentration on X-GRL removal. The initial X-GRL concentration was 20 mg/L. With an increase in zeolite concentration, X-GRL removal increased rapidly at first due to the increase in total available surface area and the adsorbent sites, then levelled off and attained an equilibrium. At the same initial X-GRL concentration, unoccupied surface area and the absorbent sites increased as the zeolite concentration increased. X-GRL was adsorbed completely on the zeolite surface at a certain level of zeolite concentration and the removal reached equilibrium. Taking into account X-GRL removal rate and removal capacity by zeolite, the most appropriate zeolite concentration to treat X-GRL dye effluent with an initial concentration of 20 mg/L was determined to be 1.4 g/L.

Effect of solution pH

Figure 3(b) shows X-GRL removal and X-GRL removal capacity by zeolite as a function of solution pH. As can be seen, the adsorption of X-GRL on zeolite was highly pH dependent and increased with solution pH. Natural zeolite preferentially adsorbs H⁺ ions from solutions and in more acidic conditions, more H⁺ ions are adsorbed from solutions (Motsei et al. 2009; Widiastuti et al. 2011), which explains the lower affinity of natural zeolite for cationic red X-GRL at acidic pH values.

Zeolites are naturally occurring alumino-silicates with a three-dimensional framework structure bearing AlO₄ and SiO₄ tetrahedra. The presence of Al³⁺ in the framework renders it negatively charged, but the charge is compensated by extra framework cations located in the pores, which can be exchanged by other cations. In basic solutions, the extra framework cations (e.g. Na⁺) compensate the negative charge and the interaction with the cationic dye may occur via exchange (Ötker & Akmehmet-Balcıoğlu 2005). As a result, the stronger electrostatic attraction between the cationic red X-GRL and the negatively charged zeolite in alkaline solutions promoted the adsorption of X-GRL and therefore a greater decolorization capacity. Moreover, at higher pH, the line-structured azo-dye chromospheres (–N═N–) of X-GRL are more easily attacked (Xie et al. 2014), resulting in a better dye removal but the refractory intermediates (Lei et al. 2007).

In conclusion, adsorption studies revealed that zeolite removed 92% of X-GRL from an initial X-GRL
concentration of 20 mg/L with zeolite concentration of 1.4 g/L, at solution pH = 7, T = 293 K. Therefore, the zeolite has great potential as an alternative low-cost material in the treatment of X-GRL drainage.

**Adsorption isotherms**

Adsorption isotherms are characterized by certain constant parameters associated with surface characteristics, affinity of the adsorbent and adsorption capacity of the adsorbent, which can be used to evaluate the feasibility of this process for a given application, and determine the adsorbent dosage required (Garcia-Delgado et al. 2006). An additional potential use of adsorption isotherms is for theoretical evaluation and interpretation of thermodynamic parameters (Garcia-Delgado et al. 2006).

In this study, to describe the adsorption equilibrium, Langmuir, Freundlich, and Tempkin isotherm models were used to fit the experimental results for the X-GRL adsorption. All isotherms can be linearized, and then the parameters determined graphically or by linear regression (Garcia-Delgado et al. 2006). The mathematical equations are presented below.

The Langmuir model is given by the following equation (Ötker & Akmehmet-Balcıoğlu 2005; Wang & Zhu 2006; Motsi et al. 2009):

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

where \(q_m\) (mg/g) and \(K_L\) (L/mg) are the Langmuir monolayer capacity and the equilibrium constant, respectively. \(C_e\) is the equilibrium concentration in solution (mg/L) and \(q_e\) represents the amount adsorbed at equilibrium (mg/g). The nature of adsorption can be expressed in terms of a dimensionless equilibrium parameter defined by:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \(C_0\) is the initial concentration of the adsorbate in solution. The values of \(R_L\) indicates the type of isotherm, as irreversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear \((R_L = 1)\) or unfavorable \((R_L > 1)\).

The Langmuir isotherm is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal sorption activation energy.

The Freundlich equation can be written as follows (Ötker & Akmehmet-Balcıoğlu 2005; Wang & Zhu 2006; Motsi et al. 2009):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \(K_F\) (L/g) and \(1/n\) represent the Freundlich capacity factor and the Freundlich intensity parameter, respectively. \(C_e\) is the equilibrium concentration in the solution (mg/L) and \(q_e\) represents the amount adsorbed at equilibrium (mg/g). The magnitude of the exponent \(n\) gives an indication of the favorability of adsorption. Generally \(n\) in the range 2–10 represents good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The Freundlich equation describes heterogeneous systems and reversible adsorption. It is not restricted to the formation of monolayers.

The Tempkin isotherm considers the interaction between adsorbing species and adsorbate, and can be given as the following equation (Widiastuti et al. 2011):

\[
q_e = B_1 \ln K_T + B_1 \ln C_e
\]

where \(K_T\) is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy and constant \(B_1\) is related to the heat of adsorption.

Figure 4 shows the adsorption isotherms of X-GRL on zeolite as a function of equilibrium concentration at different temperatures. The corresponding isotherm properties by fitting Langmuir, Freundlich and Tempkin equations are shown in Table 3. As can be seen, the \(R_L\) values obtained when fitting the Langmuir equation were less than 1, indicating the great affinity of the zeolite for X-GRL. However, the calculated monolayer capacity, \(q_{m,cal}\), decreased as the temperature increased, which conflicted with the experimental monolayer capacity \(q_{m,exp}\) as a function of temperature. So the adsorption does not fit the Langmuir isotherm well.

The correlation coefficients in Table 3 showed that the Freundlich model fitted the results better than the Langmuir model. The Freundlich intensity parameter \(n\) gradually increased with the temperature. At 293 K and 303 K, it is slightly less than 2, while at 313 K, \(n > 2\) indicated that zeolite is a superior adsorbent for X-GRL at higher temperatures.

Table 3 also shows that the maximum binding energy \(K_T\) decreased with increasing temperature, indicating that the adsorption of X-GRL on zeolite was becoming less likely to happen. In addition, both \(B_1\) and \(K_T\) were positive, suggesting the unfavorable thermodynamic adsorption between X-GRL and zeolite. So the adsorption does not fit the Tempkin isotherm well.
In conclusion, the experimental data were best fitted by the Freundlich model, which can be seen from the higher $R^2$ and the compatibility of data and Freundlich curves in Figure 4(b). This is in agreement with previous reports (Widiastuti et al. 2011; Sahmoune & Ouazene 2012). However, other studies (He et al. 2009; Ayad & Abu El-Nasr 2010; Ai et al. 2011; Sharma & Das 2013) have reported that the adsorption isotherm of dye removal could be more generically approximated by the Langmuir model to accommodate the differences in absorbent characteristics such as species, purity, mineral content and chemical composition. In this study, the fact that the data do not fit the Langmuir model well indicates that the zeolite has a heterogeneous surface with a non-uniform distribution of adsorption over the surface.

### Adsorption kinetics

The adsorption kinetics is used to investigate the adsorption process of X-GRL onto zeolite. The kinetic models have been proposed to elucidate the uptake mechanism, depending on the physical and/or chemical characteristics of the...
adsorbent as well as the mass-transport process. Four typical kinetic models widely used to fit single adsorbed experiments, pseudo-first-order, pseudo-second-order, Elovich, and Bangham, were examined to fit the experimental data in this study.

The linear form of pseudo-first-order is determined by the following equation (Wang & Zhu 2006; Widiastuti et al. 2011):

$$\ln(q_e - q_t) = \ln q_e - K_f t$$

where $q_t$ (mg/g) is the amount of adsorbate adsorbed at time $t$ (min), $q_e$ (mg/g) is the equilibrium adsorption capacity (mg/g), and $K_f$ (min$^{-1}$) is the rate constant of the pseudo-first-order model.

The linear pseudo-second-order model can be expressed in the form (Wang & Zhu 2006; Widiastuti et al. 2011):

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t$$

where $K_s$ is the rate constant of the pseudo-second-order model (in g/(mg min)).

The initial sorption rate, $h$ (mg/g min) as $t \to 0$ can be defined as:

$$h = K_s q_e^2$$

The Bangham equation is used to study the step occurring in the present adsorption system and the equation is represented below (Widiastuti et al. 2011):

$$\log \log \left( \frac{C_0}{C_0 - q_m} \right) = \log \frac{K_0 h}{2.303V} + \alpha \log t$$

where $C_0$ is the initial concentration of adsorbate in solution (mg/L), $V$ is the volume of solution (mL), $m$ is the mass of adsorbent per liter of solution (g/L), and $\alpha$ and $K_0$ are constants.

The Elovich equation assumes that the actual solid surfaces are energetically heterogeneous. The linear form of the Elovich equation can be expressed as (Widiastuti et al. 2011):

$$q_t = \frac{1}{\beta} \ln(a\beta) + \frac{1}{\beta} \ln t$$

where $a$ is the initial adsorption rate (mg/(g min)) and the parameter $\beta$ is related to the extent of surface coverage and activation energy (g/mg).

The adsorption of X-GRL from aqueous solutions on zeolite as a function of time is shown in Figure 5. The corresponding parameters when fitting pseudo-first-order, pseudo-second-order, Elovich, and Bangham models are shown in Table 4.

The pseudo-first-order kinetic curves in Figure 5(a) are straight lines and the correlation coefficients are high, from 0.977 to 0.981. The rate constant of the pseudo-first-order model $K_f$ (Table 4) has a higher value at a higher temperature, indicating a higher driving force for adsorption as well as a higher adsorption capacity (Widiastuti et al. 2011). However, the calculated equilibrium adsorption capacity $q_{e,cal}$ values (Table 4) deviate greatly from the $q_{e,exp}$ values, which indicates the inapplicability of the first-order kinetics in fitting the experimental data.

On the contrary, the pseudo-second-order model kinetic curves show much better correlation coefficients, close to 0.999 in all cases. It is worth noting that the $q_{e,cal}$ values approach more closely the $q_{e,exp}$ values calculated from the pseudo-second-order model compared to those of the pseudo-first-order kinetics. Thus, the adsorption of X-GRL on natural zeolite follows pseudo-second-order kinetics.

Bangham and Elovich are also used to study the steps occurring in the present adsorption system. Figure 5(c) and 5(d) present Bangham and Elovich kinetic plots for removal of X-GRL by the zeolite, respectively. The correlation coefficients (Table 4) obtained from a linear fit of the Bangham and Elovich models were lower than that of the pseudo-second-order model, indicating the inapplicability of these two models in fitting the experimental data.

To sum up, the experimental data fitted the pseudo-second-order model best at each temperature, suggesting that the adsorption of X-GRL on zeolite was through a physiosorption process (Lin et al. 2009). It was observed that the affinity of the zeolite for X-GRL increased with temperature. This suggested that X-GRL adsorption by zeolite is an endothermic process (Widiastuti et al. 2011). In order to confirm these conclusions further, the thermodynamics of the adsorption process was calculated by two different methods based on the van’t Hoff equation (Garcia-Delgado et al. 2006; Ai et al. 2011) and Le Chatelier’s principle (Sahmoune & Ouazene 2012; Sharma & Das 2013).

As we can see from Table 4, the specific adsorption at equilibrium $q_{e,cal}$ for pseudo-second-order kinetics is about triple or even quadruple the capacity of the specific adsorption at equilibrium $q_{e,cal}$ for the pseudo-first-order model. Despite wide application of the pseudo-first-order model to explain various adsorption processes, it has limitations because it often fits the kinetic description of the initial
adsorption phase but not for the whole adsorption process. In comparison, the pseudo-second-order model fits well with the whole adsorption process including film diffusion and pore diffusion. Therefore, in this study, to verify the existence of film diffusion and pore diffusion, the mass-transfer process was also studied.

![Figure 5](image)

**Figure 5** The adsorption of X-GRL from aqueous solutions onto zeolite as a function of time at different temperatures: (a) pseudo-first-order kinetics; (b) pseudo-second-order kinetics; (c) Bangham kinetics; (d) Elovich kinetics.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_{e,exp}$ (mg/g)</th>
<th>$K_f$ (min$^{-1}$)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$R^2$</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$h$ (mg/g min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>13.14</td>
<td>0.22</td>
<td>3.55</td>
<td>0.981</td>
<td>13.51</td>
<td>33.33</td>
<td>0.999</td>
</tr>
<tr>
<td>303</td>
<td>13.33</td>
<td>0.22</td>
<td>3.38</td>
<td>0.975</td>
<td>13.70</td>
<td>37.04</td>
<td>0.999</td>
</tr>
<tr>
<td>313</td>
<td>13.41</td>
<td>0.25</td>
<td>3.63</td>
<td>0.977</td>
<td>13.70</td>
<td>38.46</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_0$ (mL/(g/L))</th>
<th>$R^2$</th>
<th>$\alpha$ (mg/(g min))</th>
<th>$\beta$ (g/mg)</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>293</td>
<td>45.10</td>
<td>0.997</td>
<td>0.93</td>
<td>18570.03</td>
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<tr>
<td>303</td>
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<td>0.997</td>
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<tr>
<td>313</td>
<td>48.43</td>
<td>0.997</td>
<td>0.93</td>
<td>20049.60</td>
<td>0.984</td>
</tr>
</tbody>
</table>

**Table 4** Kinetic properties of X-GRL adsorption on natural zeolite when fitting pseudo-first-order, pseudo-second-order, Elovich, and Bangham models.
Thermodynamic studies

The thermodynamic parameters provide in-depth information about the energetic changes associated with the adsorption process. Thermodynamic data, namely enthalpy (\(\Delta H\)), free energy change (\(\Delta G\)) and entropy (\(\Delta S\)), can be obtained from data interpolated using the best fitting isotherms. The isosteric heat of adsorption at different adsorption levels can be calculated from the expression (Garcia-Delgado et al. 2006):

\[
\ln\left(\frac{1}{C}\right) = \ln K_0 + \left(\frac{-\Delta H}{RT}\right)
\]

(12)

where \(C\) is the equilibrium concentration of adsorbate in solution (mg/L). \(\Delta H\) is calculated from the slope of \(\ln(1/C)\) vs \(1/T\). Figure 6(a) shows these curves for the adsorption system and correlation coefficient values were in the range 0.9807–0.9975.

Values of the adsorption \(\Delta G\) can be obtained by using an expression derived from the Gibbs adsorption isotherm (Bell & Tsezos 1987):

\[
\Delta G = -RT \int_0^X q \frac{dX}{X}
\]

(13)

where \(X\) represents the molar fraction of the adsorbate in solutions. \(q\) is then replaced by the Freundlich isotherm equation. The use of the Freundlich isotherm would lead to a value of the free energy independent of \(q\) (Garcia-Delgado et al. 2006).

The change of adsorption entropy can be determined by:

\[
\Delta G = \Delta H - T\Delta S
\]

(14)

In addition to the method above, the thermodynamic parameters can be determined by using the following equations based on Le Chatelier’s principle (Sahmoune & Ouazene 2012; Sharma & Das 2015):

\[
K_d = \frac{q_e}{C_e}
\]

(15)

\[
\Delta G^0 = -RT \ln K_d
\]

(16)

\[
\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

(17)

where \(K_d\) is the distribution coefficient. \(\Delta H\) and \(\Delta S\) are calculated from the slope and intercept of \(\ln K_d\) vs \(1/T\). Figure 6(b) shows some of these curves for the adsorption system. Correlation coefficient values were in the range of 0.9807–0.9975.

The activation energy that the sorption system must acquire before the adsorption can occur also gives information on the adsorption mechanism. A low activation energy value (<42 kJ/mol) indicates a physical adsorption control process while a high activation energy value (>42 kJ/mol) indicates a chemical adsorption control process. Activation energy can be calculated from the Arrhenius equation shown in the following equation (He et al. 2009):

\[
\ln K_s = \ln A - \frac{E_a}{RT}
\]

(18)

where \(E_a\) is activation energy, \(K_s\) is the rate constant of reaction, and \(R\) is the universal gas constant.

Table 5 shows the thermodynamic properties of X-GRL adsorption on zeolite based on the van’t Hoff equation, while Table 6 shows the thermodynamic properties of
X-GRL adsorption on zeolite based on Le Chatelier’s principle. These two sets of thermodynamic values including enthalpy ($\Delta H$), free energy change ($\Delta G$) and entropy ($\Delta S$), display the same trend, positive or negative in the same order of magnitude. Results obtained by different methods also showed the same order of magnitude (Garcia-Delgado et al. 2006).

It can be seen that $\Delta H$ values are always positive, indicating an endothermic nature. Their magnitudes ($10^{-30}$ kJ/mol) suggest a physisorption process. Absolute values decrease as the adsorption increases, which is a common phenomenon when dealing with the adsorption on non-homogeneous surfaces, confirming the results obtained from the isotherm results. The negative $\Delta G$ values indicate the spontaneity of the process. Variations of the $\Delta G$ with temperature as well as with superficial coverage are always small. This confirms the physical character of the adsorption process. The activation energy of cationic red X-GRL is 4.434 kJ/mol, as calculated from the slope of the plot of $\ln K$ vs $1/T$. Here, the X-GRL adsorption on natural zeolite belongs to physical adsorption based on the activation energy values. There is an electrostatic attraction between the cationic, similar to the cationic dye adsorption onto natural attapulgite (He et al. 2009) and methyl green adsorption onto GO nanosheets (Sharma & Das 2015). Finally, the positive values of $\Delta S$ suggest the increasing randomness at the solid-solution interface during adsorption. Absolute entropy values decrease slightly with increasing temperature. This was more obvious when the coverage $q_e$ was increasing.

The batch studies, isotherms and kinetics of X-GRL adsorption on natural zeolite showed that natural zeolite is a promising X-GRL adsorbent with experimental equilibrium adsorption capacity of 13.5 mg/g. However, the adsorption capacity is low compared to other non-zeolitic adsorbents (e.g. activated carbon). So the mass-transfer process was employed to investigate the adsorption-limiting factors in the adsorption process.

### Table 5
Thermodynamic properties of X-GRL adsorption on natural zeolite based on the van’t Hoff equation

<table>
<thead>
<tr>
<th>$q_e$(mmol/g)</th>
<th>$\Delta H$(kJ/mol)</th>
<th>$\Delta G$(kJ/mol)</th>
<th>$\Delta S$(mol.kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293K</td>
<td>303K</td>
<td>313K</td>
</tr>
<tr>
<td>2.0</td>
<td>33.61</td>
<td>-4.41</td>
<td>-5.56</td>
</tr>
<tr>
<td>4.0</td>
<td>25.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>20.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>16.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>13.74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6
Thermodynamic properties of X-GRL adsorption on natural zeolite based on Le Chatelier’s principle

<table>
<thead>
<tr>
<th>$q_e$(mmol/g)</th>
<th>$\Delta G$(kJ/mol)</th>
<th>$\Delta H$(kJ/mol)</th>
<th>$\Delta S$(mol.kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293K</td>
<td>303K</td>
<td>313K</td>
</tr>
<tr>
<td>2.0</td>
<td>-6.12</td>
<td>-7.21</td>
<td>-8.84</td>
</tr>
<tr>
<td>4.0</td>
<td>-4.75</td>
<td>-5.60</td>
<td>-6.79</td>
</tr>
<tr>
<td>6.0</td>
<td>-3.95</td>
<td>-4.66</td>
<td>-5.59</td>
</tr>
<tr>
<td>8.0</td>
<td>-3.38</td>
<td>-3.99</td>
<td>-4.74</td>
</tr>
<tr>
<td>10.0</td>
<td>-2.94</td>
<td>-3.47</td>
<td>-4.08</td>
</tr>
</tbody>
</table>

### Figure 7
X-GRL removal capacity of zeolite as a function of $t^{0.5}$ at different temperatures.

### Table 7
Diffusion coefficients in the mass-transfer process of X-GRL adsorption on natural zeolite

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>293</th>
<th>303</th>
<th>313</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_l$(cm$^2$/s)</td>
<td>1.29$\times 10^{-11}$</td>
<td>1.19$\times 10^{-11}$</td>
<td>1.29$\times 10^{-11}$</td>
</tr>
</tbody>
</table>
Mass-transfer process

The dye adsorption process is governed by two consecutive steps: (1) diffusion across the liquid film surrounding the sorbent particles (film diffusion); and (2) intraparticle diffusion in the liquid contained in the pores and in the sorbate along the pore walls (pore diffusion) (Sahmoune & Ouazene 2012). The overall rate of sorption is controlled by the slowest step, which is either film diffusion or pore diffusion or both.

To investigate the possibility of X-GRL being transported within zeolite pores, the experimental data were fitted by intraparticle diffusion plots.

The intraparticle diffusion model can be expressed as follows (Widiastuti et al. 2011; Sahmoune & Ouazene 2012):

$$q_t = k_{id} t^{1/2} + C$$  \hspace{1cm} (19)

where $k_{id}$ is the intraparticle diffusion rate constant (mg/g min$^{0.5}$), and the values of the intercepts give an indication about the thickness of the boundary layer, i.e., the larger the intercept, the greater the effect from boundary layers.

Figure 7 shows the plots of X-GRL removal capacity by zeolite, $q_t$(mg/g) versus $t^{0.5}$(min$^{0.5}$) at different temperatures. The calculated diffusion coefficients in the mass-transfer process were indicated in Table 7. It can be seen that there are two linear portions in the X-GRL removal capacity curves and the processes tend to follow two distinct phases. This indicates that the sorption of X-GRL onto zeolite is a complex process involving film diffusion and pore diffusion in the rate-limiting step of the sorption. This kind of multilinearity in the intraparticle diffusion plot has also been observed before (Widiastuti et al. 2011; Sahmoune & Ouazene 2012). The initial linear portion of the plot indicates a film-diffusion effect. The second portion is due to pore diffusion. The results indicate that the intraparticle diffusion rate increases with the solution temperature. An increase in temperature will produce higher internal energy, eventually leading to faster diffusion and quicker adsorption.

In phase (I), about 92% of the X-GRL was absorbed by zeolite within 5 min, with an average uptake rate of about 2.48 mg/g min$^{0.5}$. This was attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. Phase (II) was attributed to a very slow diffusion of the adsorbate from the surface film into the adsorbent pores. The intercept deviates from the origin, indicating the importance of film diffusion and the fact that the pore diffusion is not the sole rate-controlling step (Sahmoune & Ouazene 2012).

A commonly used empirical model, the film-diffusion model, was used in this work to calculate the film-diffusion coefficient $\beta$. The model is expressed as (Spahn & Schlünder 1975):

$$\frac{dC}{dt} = \beta S(C - C_i)$$  \hspace{1cm} (20)

where $\beta$ is the film-diffusion coefficient (m/s) and $S$ is the surface area of the adsorbent (m$^2$/g). The coefficients were determined by a simplified equation (below) with some assumptions such as a surface concentration $C_i$ being negligible at $t = 0$, a concentration in solution tending to the initial concentration $C_0$, and also negligible intraparticle diffusion:

$$\left[\frac{d(C/C_0)}{dt}\right]_{t=0} = \beta S$$  \hspace{1cm} (21)

Hence, at $t \to 0$, a plot of $C/C_0$ will yield a slope of $\beta S$ from which $\beta$ can be determined. The slope of this plot can be calculated by assuming that the relationship is linear for the first initial rapid phase (5 min).

The film-diffusion rate constant $\beta$ shown in Table 7 increased as the temperature increased from 293 to 313 K. These values of film-diffusion coefficients are of a similar order of magnitude to those previously obtained (Keith et al. 2001; Sahmoune & Ouazene 2012) for the adsorption of dye ions. This trend was attributed to the competition for available surface area for adsorption between the large numbers of dye molecules, which have more influence on the initial rate of adsorption than the increasing driving force caused by a higher dye concentration.

It is clear that the sorption of X-GRL onto zeolite is a complex process involving film diffusion and pore diffusion in the rate-limiting step of the sorption. To determine the effective pore-diffusion coefficient, $D_i$ (cm$^2$/s) can be simply calculated from the pore-diffusion model (Urano & Tachikawa 1991):

$$- \log \left[1 - \left(\frac{q_t}{q_e}\right)^2\right] = \frac{4\pi^2D_it}{2.3D_p^2}$$  \hspace{1cm} (22)

where $q_t$ and $q_e$ are the solute concentration in the solid at time $t$ and at equilibrium, respectively. $D_p$ is the mean particle diameter (m). The pore diffusion coefficient $D_i$ was computed by plotting $-\log[1 - (q_t/q_e)^2]$ as a function of time.

The comparison of $D_i$ values shown in Table 7 with those of AY (Astrazon Yellow 7 GLL) adsorption in sawdust (Sahmoune & Ouazene 2012) indicates that the process was governed by film diffusion and that pore diffusion was not
the only rate-limiting step. Pore-diffusion coefficients were significantly lower than those obtained in water or porous solids, indicating poor pore diffusion into the pores. According to Lam (Lam & Rivera 2006) and Wang (Wang & Zhu 2006), the average diameter of the cationic dye is approximately 12 Å, greater than the dimensions of the biggest zeolite channel, 7.5 Å × 3.1 Å. Figure 8 shows the stereochemical structure of X-GRL drawn by Chemdraw Ultra 13.0 Trial, suggesting a molecular size of 5.5 Å × 18 Å with 1,024 Å³ molecular volume, greater than the average zeolite pore diameter, 8.0 Å. Therefore, the X-GRL could not penetrate into the zeolite easily. The interaction was therefore on the external surface of the adsorbent and the film diffusion of X-GRL through the particle–liquid film was assumed to be the rate-controlling step in the overall sorption process. Hence, to improve the adsorption capacity of natural zeolite further, modification to expand its micropores is necessary.

CONCLUSIONS

Zeolite is a potential adsorbent in X-GRL removal which was elucidated by: (1) 92% removal efficiency from an initial X-GRL concentration of 20 mg/L with zeolite concentration of 1.4 g/L, at solution pH = 7, T = 293 K; (2) the Freundlich intensity parameter n > 2 in the Freundlich isotherms; (3) the calculated equilibrium adsorption capacity qe,cal values (15.14 mg/g at 293 K) and the experimental equilibrium adsorption capacity qe,exp values (13.51 mg/g at 293 K) from pseudo-second-order kinetics.

The adsorption of X-GRL on zeolite is governed by physiosorption confirmed by: (1) the best fitted Freundlich isotherms which are used to describe heterogeneous and reversible sorption; (2) magnitudes of the ΔH (10–30 kJ/mol); (3) small variations of the ΔG with temperature; and (4) activation energy of 4.434 kJ/mol < 42 kJ/mol.

The adsorption of X-GRL onto zeolite is a complex process involving film diffusion and pore diffusion in the rate-limiting step of the sorption. The process is governed by film diffusion while pore diffusion is poor because the dye molecules cannot penetrate into the zeolite easily.

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