Removal Reactive Blue Dye from Wastewater by Adsorption on White Iraqi Kaolin clay

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Abstract
The adsorption efficiency of kaolin clay by adsorption of reactive blue dye (RB13) at different parameters such as pH, dosage of adsorbent, contact time and solution temperature on the adsorption process were investigated. The experimental results show that the percentage of reactive blue dye removal increases with increasing the dosage of kaolin clay. Equilibrium adsorption data were analyzed by Langmuir and Freundlich isotherm of the results revealed that Langmuir isotherm fitted the experimental results. The thermodynamic parameters ($\Delta H^\circ$, $\Delta G^\circ$, and $\Delta S^\circ$) were also determined from the temperature dependence. The results indicate that the process of adsorption reactive blue dye was spontaneous and exothermic process.

Keywords: adsorption, kaolin clay, Reactive blue RB13, isotherms, thermodynamic.

Introduction
Reactive dyes are widely used in various industries, particularly in the textile, rubber, paper, plastic, leather, cosmetics, and drug industries. Reactive dyes belong to the group of anionic dye due to the sulfo group in its structure and some of them are azo and anthraquinone dyes. Reactive dyes are typically based on the nitrogen chromophors combined with the various types of the reactive groups, for example, vinyl, sulphone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. Azo-reactive dyes are characterized by the presence of one or more azo bonds (-N=N-) (Sayed Ahmed et al., 2012) (Zheng et al., 2002) (Dragan et al., 2011).

Effluents from these dyeing and finishing processes in these industries contains many coloring substances, which are toxic, and their discharge into rivers makes the water and unfit for domestic, agricultural and industrial purposes. Dye wastewater discharged from various industries contributing significantly to the pollution of aquatic ecosystem and environmental problems these dyes are not only toxic to humans, animals and various aquatic life forms, but they also inhibit sunlight penetration and reduce photosynthetic activities of various ecosystems. The biodegradation of others yields carcinogenic products such as aromatic amines. Recently, all governments have been under severe pressure by their people to stop this type of effluent into the public water courses unless it is treated properly (Pajareeya et al., 2012) (O'Neill et al., 1999) (Dizge et al., 2008).
Many researches have been devoted to remove these dyes from wastewaters, using various physicochemical and biological techniques that can be employed to remove dyes from wastewaters such as chemical oxidation (Chengtang et al., 2011), biodegradation (Ong et al., 2005), electro coagulation (Golder et al., 2005), photo degradation (Hussein and Halbus, 2012), solvent extraction (Muthuraman et al., 2009), chemical precipitation (Xiaodong et al., 2012), ion exchange (Pandit et al., 2004), and adsorption (Vargas et al., 2011).

Adsorption techniques have been used widely due to their efficiency in the removal of dyes due to economical and environmentally friendly reasons (Gupta et al., 2009).

Different conventional and nonconventional adsorbents have been cited in the literature for this purpose such as activated carbon (Srivastava et al., 1996), sewage sludge (Pan et al., 2003), silica (Chiron et al., 2003), tree fern (Ho, 2003), fly ash (S. B. Bayat, 2002), and clays (Wingenfelder et al., 2005). Although activated carbons have been most widely used as adsorbents in wastewater treatment processes (Malik, 2003), clay material have been increasingly receiving much attention because it is promising low cost adsorbent (Panneer Selvam et al., 2008).

The clay minerals in soil play the role of a natural scavenger by filtering out pollutants from water through both ion exchange and adsorption mechanisms. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), etc., have made clays excellent adsorbent materials. In the case of kaolinite, the CEC is confined primarily to the surface, in contrast to smectites and illites where a large part of the CEC belongs to interior sites. Therefore, to study purely surface processes, kaolinite may be an ideal material (Bhattacharyya et al., 2006).

The research focused to evaluate the adsorption potential of the white Iraqi kaolin clay in removing reactive blue dye RB13 from aqueous solutions through batch and fixed bed. Experiments were conducted to optimize the system variables and to evaluate the adsorption capacity of RB13 onto white Iraqi kaolin clay.

**Material and Methods**

**Adsorbent:**

Kaolin clay was supplied from the state company for geological survey and mining- Iraq. The chemical composition of kaolin was shown in Table 1. Kaolin was sieved to get a particle size of about 200 mesh. The clay was immersed in 0.001N HCl solution for two hours. The acidified clay was washed with double distilled water and dried in an oven at 115 °C for 24 hours before sieving and that using in the adsorption experiments.

**Table 1: Chemical composition of kaolin clay (L. H. Kadhim, 2005)**

<table>
<thead>
<tr>
<th>Component</th>
<th>(%)</th>
<th>Component</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.57</td>
<td>TiO₂</td>
<td>1.19</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.05</td>
<td>Moisture</td>
<td>0.08</td>
</tr>
<tr>
<td>CaO</td>
<td>0.60</td>
<td>Loss on ignition</td>
<td>12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Adsorbate:

Reactive Blue (C.I. Reactive Blue 13) were supplied by Ciba company and used for this study without any further purification. The structural formula is shown in figure-1. Reactive Blue 13 is highly soluble in water.

![Chemical structure of Reactive Blue 13](image)

Fig.1: The chemical structure of reactive blue 13

Adsorption studies

The adsorption experiments in this work were done for the study the effect of experimental conditions on reactive blue adsorption and determining the conditions that achieve the maximum amount of reactive blue removal. The adsorption tests were conducted in magnetic mixer. The concentration of reactive blue RB13 solution was 10 ppm and the amount of clay was included the ratio 0.05 ,0.1, 0.15, 0.2, 0.25, and 0.3g. In all experiments, the required amount of the adsorbent was suspended in 100 cm$^3$ of aqueous solution of reactive blue. 2 mL was taken from the reaction suspension, centrifuged at 6,000 rpm for 15 minutes in an 800 B centrifuge, and filtered to remove the particles. A second centrifuge was found necessary to remove fine particle of the kaolin clay. After the second centrifuge, the absorbance of the reactive blue was measured at 580 nm , using shimadzu 1650 PC. UV-visible spectrophotometer. The efficiency of reactive blue , % Removal, was calculated as (Guo et al., 2003) (Tan et al., 2008):

\[
\text{% Removal} = \left(1 - \frac{C_f}{C_i}\right) \times 100
\]

(1)

Where $C_i$ is the initial concentration and $C_f$ is the final concentration ,q is the amount of metal adsorbed per specific amount of adsorbent q (mg/g). The sorption capacity at time t, $q_t$ (mg/ g) was obtained as follows:

\[
q_t = \frac{(C_i - C_t) \times V}{m}
\]

(2)

Where $C_i$ is the initial concentration of reactive blue, $C_t$ represents reactive blue concentration at time t, V was the solution volume and m the mass of clay (g). The amount of adsorption at equilibrium, $q_e$ was given by:

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

(3)

Where $C_e$ was the reactive blue concentration at equilibrium.
Results and Discussion

*Calibration Curve of (RB 13)*

The calibration curve of reactive blue (RB 13) was constructed using different concentrations of (RB 13) solutions in distilled water, in the range of (5-40) mg/L. The absorbance were measured at the maximum absorbance wave length (λ max) (580 nm) as shown in figure 2.

![Absorbance vs Concentration](image)

Fig. 2: Calibration curve at different concentration of reactive blue 13.

**Effect of contact time**

Fig. 3 shows the effects of contact time on reactive blue removal. Removal increased with an increase in contact time. Adsorption was very rapid in the first 60 min for kaolin clay, and then increased slowly with time until reaching equilibrium. It was found that the equilibrium time for kaolin clay was more than 60 min. To ensure full equilibration, a shaking time of 100 min was used for all concentrations of kaolin clay in this study (Blanchard et al., 1984).

![Removal vs Time](image)

Fig. 3: Effect of contact time on reactive blue removal by kaolin clay.
Effect of kaolin clay dosage

The effect of kaolin clay dose was studied by varying the dose between 0.05 g and 0.3 g in 100 mL aqueous solutions. These tests were conducted at a temperature of 25 °C, with pH 5 for reactive blue RB13. The initial reactive blue concentration was 10 mg/L. It was observed that the adsorption efficiency percentage of reactive blue RB13 onto the kaolin clay increased rapidly with the increase of adsorbent concentration as shown in Fig. 4. This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.05g to 0.3g, the percentage of reactive blue adsorption increased from 44.06 to 71.14 at higher concentrations. So, 0.3 g/100 mL was considered as optimum dose (Poinern et al., 2010).

![Fig. 4: Effect of clay dosage on the removal efficiency of RB 13.](image-url)

Effect of pH

The pH values during adsorption influenced the surface characteristics of both the kaolin clay and the reactive blue. The adsorption performance was investigated under various pH ranging between 3 to 11, while the dosages of kaolin clay and reactive blue concentration were kept constant at 0.3 g of clay /100 ml and 10 mg/L, respectively. The effect of pH on reactive blue 13 removal by the kaolin clay is illustrated in Fig. 5. It was found that the adsorption of reactive blue onto kaolin clay remained approximately constant in the pH range of 3-11. When the adsorbing species is not ionized, no electrical repulsion will exists, and thus the packing density on the surface can be higher (Isa et al., 2007). Also reported a similar trend for the adsorption of reactive blue RB13 onto kaolin clay surface and the percent removal of reactive dyes remained approximately constant in the pH range of 8-11 (Ramakrishna et al., 1997).
Effect of Temperature and Adsorption Thermodynamics

The adsorption of Reactive Blue 13 on kaolin clay was studied at temperatures of 288, 298, and 308 K. It was observed that the amount of RB13 adsorbed by kaolin clay decreased with an increase in temperature. with these adsorption isotherms being shown in Fig. 6.

Thermodynamic studies, such as the change in standard free energy $\Delta G^\circ$, enthalpy $\Delta H^\circ$, and entropy $\Delta S^\circ$ of adsorption, helped further clarify the effect of temperature on dye removal.

Gibbs free energy of adsorption $\Delta G^\circ$ was calculated based on the equilibrium constant ($Kc$) using the following equation (Namasiyam et al., 2002):

$$\Delta G^\circ = -RT \ln(Kc)$$  \hspace{1cm} (4)
where \( R = \text{gas constant (8.314 J/mol·K)}; \ T = \text{adsorption temperature in Kelvin; and} \ K_c = \text{equilibrium constant (ratio of the concentration of dye ions adsorbed on adsorbent to that of dye ions in the aqueous phase at equilibrium)}. \) From the van’t Hoff equation given as below, the standard enthalpy \( \Delta H^0 \) was estimated from the slope of the linear regression of the plot between \( \ln(K_c) \) and \( (1/T) \) (B.Acemioglu, 2004).

\[
\ln(K_c) = -\frac{\Delta H}{RT} + \text{constant}
\]  

(5)

The plot of \( \ln(K_c) \) versus \( 1/T \) for RB13 adsorption is given in Fig. 7, indicating a linear relationship.

![Fig. 7: Van’t Hoff plot for RB13 adsorption on kaolin clay](image)

The enthalpy \( \Delta S^0 \) could be calculated by using the following equation (B.Acemioglu, 2004):

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]  

(6)

The calculated thermodynamic parameters are presented in Table 2. The negative values of \( \Delta G^0 \), indicated the spontaneity of the adsorption process over the temperature range tested. The negative value of \( \Delta H^0 \) suggested that the adsorption was exothermic which point to the physical nature and the energy stability of the RB13 by kaolin clay, which explained the poor dye removal at increasing temperatures.

The positive value of \( \Delta S^0 \) reflected the affinity of the kaolin clay for RB13 and showed the increasing randomness at the solid/liquid interface during the sorption of RB13 onto kaolin clay. Positive \( \Delta S^0 \) values of RB13 adsorption on clay indicates that increase of the randomness at the clay-solution interface during the adsorption.
Table 2: Thermodynamic parameters of adsorption of Reactive Blue on White Iraqi kaolin clay.

<table>
<thead>
<tr>
<th>ΔH (KJ.mol⁻¹)</th>
<th>ΔG (kJ.mol⁻¹)</th>
<th>ΔS (J.mol⁻¹.K⁻¹)</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.4029</td>
<td>-13.0944</td>
<td>33.6511</td>
<td>288</td>
</tr>
<tr>
<td>-13.3802</td>
<td>33.4809</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>-13.7269</td>
<td>33.5193</td>
<td>308</td>
<td></td>
</tr>
</tbody>
</table>

Adsorption isotherms

The adsorption isotherms are studied through various models such as the Langmuir and Freundlich isotherms. The Langmuir model is based on the assumption of homogeneous monolayer coverage with all sorption sites to be identical and energetically equivalent. The Freundlich model assumes physicochemical adsorption on heterogeneous surfaces. The linear forms of the two models are (Langmuir, 1918) (H. Freundlich, 1985):

\[
\text{Langmuir} \quad \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (7)
\]

\[
\text{Freundlich} \quad \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)
\]

where \( q_e \) (mg/g) is amounts of reactive blue adsorbed at equilibrium, \( q_m \) (mg/g) is the monolayer adsorption capacity, \( K_L \) (L/mg) is the Langmuir adsorption constant related to the free energy of adsorption and \( C_e \) (mg/L) is equilibrium reactive blue concentration in the solution. \( K_F \) and \( 1/n \) are Freundlich adsorption isotherm constants being indicative of extent of adsorption and intensity of adsorption, respectively. The Langmuir isotherm equation was used to estimate the maximum adsorption capacity of the kaolin clay under the conditions of 25°C, pH 5 and 10ppm initial reactive blue RB13 dye concentration while varying adsorbent dose from (0.05 to 0.3 g) and the behavior is shown in Fig. 8. The values of the isotherm constants and \( R^2 \) are given in Table 3. The linear plot is shown in Fig. 9, of \( 1/q_e \) versus \( 1/C_e \) along with high value correlation coefficient indicate that Langmuir isotherm provides a better fit with the equilibrium data. The isotherm parameters as derived from the slope and intercept of the plots are listed in Table 3.

Fig. 8: The linear Freundlich adsorption isotherms for reactive blue adsorption by the kaolin clay.
Fig. 9: The linear Langmuir adsorption isotherms for reactive blue adsorption by the kaolin clay.

Table 3: Langmuir and Freundlich isotherm constants.

<table>
<thead>
<tr>
<th>Isotherm constants</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constants/Correlation coefficients</td>
<td>$R^2$</td>
<td>$q_m$</td>
</tr>
<tr>
<td>Values</td>
<td>0.939</td>
<td>0.584</td>
</tr>
</tbody>
</table>

Conclusions

Kaolin clay was used as an adsorbent for the removal of reactive blue from aqueous solution in the present study. The optimum conditions of adsorption were found to be: a adsorbent dose of 0.3 g in 100 mL of solution. The optimum contact time and pH were 60 min and 5 respectively. The results show that the best fit was achieved with the Langmuir isotherms. Also, application of kaolin clay shows high efficiency for the reactive blue removal in the wastewater. The efficiency of color removed increase with increasing adsorbent dosage, increase with increasing contact time. The removal efficiency of reactive blue was found equal to 71% for kaolin clay. The thermodynamic parameter, enthalpy of adsorption are determined, negative value of enthalpy change indicate the adsorption was exothermic process, value of Gibbs's free energy changes indicate the spontaneous nature of the process, positive $\Delta S^o$ values of RB13 adsorption on clay indicates that increase of the randomness at the clay-solution interface during the adsorption.

References


