Adsorption equilibrium, kinetics and thermodynamics of Rhodamine B dye from aqueous solution using Iraqi Porcellanite rocks

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Abstract - Industrial wastewater and other polluted water need to be treated to make it possible to discharge into rivers and reuse them. Adsorption takes the importance of ways to remove organic and inorganic pollutants in water. The search for materials that are locally available and cheap to use as adsorbent surfaces. The Iraqi porcellanite powder can be used to remove the dye of Rhodamine B in batch method. The effect of various experimental parameters such as contact time, temperature, solution pH, weight of adsorbent initial dye concentration, ionic strength were investigated. The adsorption studies included both equilibrium adsorption isotherms and kinetics. The applicability of Langmuir and Freundlich equations was investigated at different temperature, and the Freundlich isotherm exhibited the best fit with experimental data. The thermodynamic parameters indicated that the adsorption was a spontaneous process (\(\Delta G\) was negative), the negative value of \(\Delta H\) indicate endothermic and \(\Delta S\) was positive value (random), the kinetic data well described by Pseudo-second order kinetic model with intra particle diffusion as one of the rate limiting steps.

Key Words: Adsorption, Rhodamine B, Thermodynamic and Kinetic.

Introduction

Environmental pollution due to speedy development of industries causes harmful effect on human health and ecosystem. The textile dyeing industries have generated a massive pollution problem because it is considered one of the most industries which used a wide range of dyes in their production Consequently, it is the most polluting water sources (Kant, 2012). The basic dyes are the brightest class of soluble dyes used by the textile industry, but their tinctorial value is very high In addition to their use in the dyeing of various products, such as Rhodamine B dye are widely used in the paper industry, cosmetics, food and biomedical laboratories (Inbaraj and Sulochana, 2006).

To reduce the dyes in industrials water effluents chemical, physico-chemical, and biological methods such as photocatalytic degradation, extraction, chemical oxidation, microbiological decomposition, ion exchange, adsorption on activated carbon, combined of adsorption and degradation and ultrasonic decomposition were applied with highly cost (Ahmed and Kumar, 2010).

Among all these methods the cheapest and simplest is the physic-chemical adsorption. Activated carbon was regarded as the most effective material for removal the dyes (Walker and Weatherley, 1997), but due to its high cost and 10-15 % loss during regeneration, unconventional adsorbents like, wood (HO and Mckay,
1998), silica (Lee et al., 2007), clay and activated clay (Bennani Karim et al., 2011; Ho and Chiang, 2001) and agricultural residues (Robinson et al., 2002) have attracted the attention of several investigations for the removal of dyes. The use of clay materials over commercially available adsorbents was becoming popular due to their low-cost, abundant availability, non-toxicity and potential for ion exchange. A number of clay materials: sepiolite (Alkan et al., 2007), kaolinite (Kamel et al., 1991), montmorillonite (Wang et al., 2004), smectite (Tonle et al., 2008), bentonite (Ozcan et al., 2004) and zeolite (Ozdemir et al., 2004) have been investigated for removal of dyes. These clay minerals are of interest according to their variety of structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity (Ozcan et al., 2005).

In this present study, we investigated the adsorption of Rhodamine B dye on the surface of Iraqi porcellanite. The system variables studied include sorbent dose, contact time, initial concentration of the dye, pH, FTIR analysis, ionic strength and temperature.

Materials and Methods

Rhodamine B (abbreviation: RhB). Molecular formula: C_{28}H_{31}N_{2}O_{3}Cl was procured from Sigma-Aldrich. Rhodamine B (molecular weight: 479.01 g mol\(^{-1}\)); IUPAC Name N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene] diethyl ammonium chloride, which is a highly water soluble, was used as a model solute. The molecular structure of RhB was shown in Figure (1). RhB solutions were prepared by dissolving 0.1 g of dye in 1 L of distilled water. This stock solution was used to prepare the 100 mg/l then dilution to required concentration. Wave length at maximum absorbance (\(\lambda_{\text{max}}\)) was determined by scanning the wavelength and found to be 553.5 nm.

![Figure 1. Chemical Structure of Rhodamine B.](image)

Experimental:

Adsorben Material:

Natural porcellanite samples were obtained from the Ministry of Industry and Minerals (The general company for Geological survey and mining), the clay in
powder forms were washed with distilled water to remove impurities and dispose of disposable materials, water soluble salts and other, dried samples for three hours in the oven (at 600 °C) and then crushed and sieved to a particle size of 75 μm and then used for experimental work.

Adsorbent Characterization:
In order to elucidate the particle properties (e.g., surface morphology and particle size) of the resulting porcelainite powders the powder texture was observed by the scanning electron microscope (SEM).
Chemical functional groups were examined by FT-IR apparatus type Shimadzu using KBr pellet method of room temperature. The spectra were retrieved in the wave number range from 400 to 4000 cm⁻¹.

Adsorption Studies:
Batch equilibrium experiments had been carried out to find the optimum pH, contact time and equilibrium isotherms. A series of 100 ml stopper conical flasks were used by adding 0.5 gm of Porcellanite particle size of (75 μm) to 50 ml of 50 mg/l of dye.
All experiments were done at room temperature, after gentle shaking for desired time at 120 rpm. The mixture was then centrifuged and the concentration of the dye determines using UV-Vis spectrophotometer (UV-1200 Spectrophotometer). The removal efficiency and the equilibrium uptake of RhB dye were calculated according to the equations.

\[
\% \text{ Removal} = \left( 1 - \frac{C_e}{C_0} \right) \times 100 \quad \ldots \ldots \ldots 1
\]

\[
Q_e = \frac{V_{sol}(C_o - C_e)}{m} \quad \ldots \ldots \ldots \ldots \ldots 2
\]

Where Co is concentration of dye before the adsorption (mg/l), Ce is equilibrium concentration (mg/l), m (g) adsorbent weight and V solution volume in liter, Qe is the equilibrium adsorption capacity (mg/g).

Kinetic Study:
Kinetic of Rhodamine B on Porcellanite was carried out with (0.5 g) of the porcellanite powder transferred into 100 ml screw cupped conical flask containing 50 ml of 50 mg/l of tested dye, different samples were shaken at (120 rpm) for (10, 20, 30 and 40 °C) by using isothermal water-bath shaker then the mixture solution was taken out at different periods of time. The mixture was centrifuged then measure the amount of the adsorbed dye spectrophotometrically at 553.5 nm, and estimated by eq.(2).

Results and Discussion
Characterization of the Adsorbent:
The FT-IR spectrum as show in Figure (2) and Chemical functional in the porcellanite characteristic bands.
The results of the FTIR spectrum of the porcellanite rock powder (Fig. 2) showed the presence of the main absorption bands. We observe a strong band confined between 3460-3620 cm$^{-1}$ resulting from the stretching vibration of the hydroxyl groups. The absorption band at (1138.00 cm$^{-1}$) belongs to Si-O group. The spectrum also showed peak at (467 cm$^{-1}$) represent Absorption of the group (Fe-O). The spectrum shows an absorption band at (792.7 cm$^{-1}$) and represents the absorption of the group (Al-O). These chemical groups represent effective sites where the adsorption process occurs because of its negative charge, which gives these groups the ability to form chemical bonds or physical bonds because they contain an electronic pair or an electrostatic charge that you can share to form a physical link (Salman and Al-Saad, 2012).

Scanning Electron Microscope (SEM):

The morphology of porcellanite were investigated using SUPRA 55VP analytical Scanning Electron Microscope (SEM). This SEM has resolution of 1.0 nm at 15kV, and 1.7 nm at 1 kV at high vacuum mode (HV). 100 V to 30 kV represents the wide range of the accelerating voltage used on the machine with capability of imaging insulating samples at the lower end of the spectrum. Electromagnetic beam and aperture alignment enables rapid changing between the six beam defining apertures. The GEMINI column employs a Schottky field emitter electron source using a single condenser with a cross over-free beam path. The machine is equipped with a Everhardt Thornley secondary electron (SE) detector, a variable pressure secondary electron (VPSE) detector for use at variable pressure mode with real time automatic contrast/brightness and manual override, a backscatter detector as well as a through the lens SE detector in Figure (3). Scanning Electron Microscope photograph before adsorption revealed the surface morphology and the different
level of porosity in porcellanite. The surface after RhB adsorption shown in Figure (4) however shows that porcellanite is loaded with RhB dye.

Figure 3. SEM image of porcellanite before RhB adsorption.

Figure 4. SEM image of porcellanite after RhB adsorption.

Effect of Contact Time:
The removal of RhB dye by adsorption on porcellanite rocks was studied as a function of contact time at different period (1/4-24 hrs.) at (25 °C), and percentage removal plotted against time (Fig. 5) shows the adsorption rate of RhB onto Porcellante which is fast at the beginning and become constant after (4 hrs.). The removal percentage of dye on porcellante was found to be 86.41 %.
Figure 5. The effect of contact time on adsorption of RhB dye onto porcellanite

Effect of pH on Adsorption of RhB dye:

The pH of the dye solution plays an important role in the adsorption capacity, where it affects both the degree of ionization of the dye as well as the surface properties of the adsorbent (Elkady et al., 2011). In this work the influence of pH on the dye adsorption was studied while the initial dye concentration, contact time, temperature, and amount of porcellanite were fixed (50 mg/l), 4 hrs., (25 °C), (0.5 g) respectively. The effect of pH on adsorption of dye was studied within pH range (2-11). The pH was adjusted by adding a small amount of 0.1M HCl and/or 0.1 M NaOH; The results obtained showed that the removal percentage decreased from 94.2 % to 78.0 % for RhB removal when pH increased from 2 to 11 (see Fig. 6), the pH value of (4) was found to be 97.2 %. Thus, the pH value of 4 was selected as the optimum for performing the adsorption studies. No further significant decrease was observed beyond pH 6. At solution pH <4.0, the RhB molecules exist in cationic and monomeric forms and it forms dimer at solution pH >4.0 due to RhB molecule exists in zwitterionic form (Venkatraman et al., 2012).

Despite RhB molecule being positively charged in pH 4 and the removal of RhB dye was higher than the rest of the pH range. This was suggested that electronic interaction might not be the major force in the interaction between the adsorbate and adsorbent. Also, the smaller monomeric RhB may diffuse into the micropores of the adsorbent particle more readily than the dimer form (Deshpande and Kumar, 2002; Gad and El-Sayed, 2009).

Figure 6. Effect of pH on adsorption of RB dye onto porcellanite surface.
Effect of Initial Dye Concentration:

The effect of initial dye concentration was studied by varying initial dye concentration from (10-100 mg/l) at (25 °C). The result revealed that the percentage adsorption of dye was decrease with increases in initial concentration. The availability of free adsorption sites reduced by increasing the initial concentration of dye therefore the removal percentage decreasing (Almeida et al., 2009). The Figure (7) revealed that the 10 mg/l was the ideal initial concentration of RhB.

![Figure 7. Effect of initial dye concentration on adsorption of RhB dye onto porcellanite.](image)

Effect of Adsorbent Dose:

The influence of different weight of porcellanite on RhB percentage removal at a contact time (4 hrs.) was investigated by ranged the porcellanite weight from (0.25-2 gm) in 50 mg/l RhB solution. Figure (8) shows an increased percentage removal with increasing of porcellanite stone weight and that was because more surface area implies greater number of adsorbent sites attained by increase the weight of porcellanite stone (Inbaraj and Sulochana, 2006).

![Figure 8. Effect of adsorbent dose on adsorption of RhB dye onto porcellanite](image)

Effect of the ionic strength on the adsorption of Rhodamine B on porcellanite:

The effect of ionic strength on adsorption of the dye was studied by the addition various concentrations of salt of sodium chloride to the solution. The concentration of the salts were kept in the range of 0 to 0.08 M. As shown in Figure (9), increasing
the ionic strength of the solution caused decrease in adsorption capacity of the dye. This could be attributed to the competition phenomenon between the dye molecules and the ions for the same sites of the adsorbent. On the other hand, ionic atmosphere may be progressively formed around RhB molecules with increased NaCl concentration and result in the reduction of RhB adsorption onto porcellanite (Sathishkumar et al., 2012).

Figure 9. Effect of ionic strength on adsorption of RhB dye onto porcellanite.

Adsorption Isotherm:

The analysis and design of the adsorption process requires the relevant adsorption equilibrium, which is the most important piece of information in understanding an adsorption process. The adsorption of dye from aqueous solution on porcellanite has been studied at different temperatures (10, 20, 30 and 40 °C) the general shape of dye adsorption isotherm are show in Figure (10) where the quantities adsorbed on porcellanite (Q_e) are plotted as a function of equilibrium concentration (C_e) at (10, 20, 30 and 40 °C).

Figure 10. Adsorption isotherm of dye onto porcellanite at different temperatures.

The shape of the adsorption isotherm of RhB dye on porcellanite consistent with (S 3 type) on the Giles classification. This type, indicative of vertical or flat orientation of adsorbed, there is strong inter-molecular attraction within the
adsorbed layer, and the adsorbate is monofunctional. In the initial part of an S-curve, the more solute was already adsorbed, the easier it is for additional amounts to become fixed (Adrien, 1973). The experimental adsorption data were applied to both the theoretical Langmuir isotherm equation and empirical Freundlich equation. The results of applying Langmuir (eq. 3) and Freundlich (eq. 4).

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad \ldots \ldots 3
\]

Where Q_m is the maximum adsorption capacity (mg/g) and b is related to the adsorption energy.

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots \ldots 4
\]

Where K_f is a function of the adsorption capacity and n is the intensity of adsorption.

Table 1. Results of application of Langmuir & Freundlich isotherm on the system studied.

<table>
<thead>
<tr>
<th>RhB dye</th>
<th>Temp. (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Qm (mg/g)</td>
<td>B (l/g)</td>
</tr>
<tr>
<td>10</td>
<td>5.61</td>
<td>0.035</td>
<td>0.810</td>
</tr>
<tr>
<td>20</td>
<td>7.63</td>
<td>0.096</td>
<td>0.918</td>
</tr>
<tr>
<td>30</td>
<td>11.11</td>
<td>0.025</td>
<td>0.850</td>
</tr>
<tr>
<td>40</td>
<td>13.15</td>
<td>0.059</td>
<td>0.959</td>
</tr>
</tbody>
</table>

The Langmuir and Freundlich isotherms are applied on the experimental data of the adsorption of RhB dye on porcellanite by plotting (C_e/q_e) versus (C_e) and (logq_e) versus (logC_e) respectively (Figs. 11 & 12).

The results of Table (1) show that the value of (Q_m) increased with increasing in the temperature because the adsorption was endothermic, the value of n increased from 0.763 to 1.176 and this is consistent with previous studies (Postai et al., 2016), (K_f) is a function of the adsorption capacity and (n) is a function of the strength used adsorption material.

Value of n low showed adsorption bond is weak, when the value of n < 1 the adsorption coefficient increases with increasing concentration of the solution led to an increase in hydrophobic surface characteristics after monolayer. When the value of n>1 K_f decreases with concentration (Ghazi et al., 2003). The results also show that the Freundlich isotherm is better fitted on this system than the Langmuir isotherm as show by the linear relationship of (log q_e) versus (log C_e) (Fig. 12).
Figure 11. Linear form of Langmuir isotherm of RhB dye on porcellanite at different temperatures.

Figure 12. Linear form of Freundlich isotherm of RhB dye on porcellanite at different temperatures.

Thermodynamic Study:
In order to study the nature of adsorption, the thermodynamic studies play an important role. The effect of temperature was investigated for temperatures ranging from 10 °C to 40 °C using different initial concentration, the thermodynamic parameters free energy change (ΔG), enthalpy change (ΔH) and entropy (ΔS) of the
Adsorption equilibrium, kinetics and thermodynamics of Rhodamine B dye

system were evaluated. The values of ΔH and ΔS were estimated by using the van't Hoff plot by using the following equation:

\[
\Delta G = -RT \ln K
\]

\[ K = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \]

\[ \ln K = \frac{(\Delta S)}{R} - \frac{(\Delta H)}{RT} \]

Where ΔG is the Gibbs energy change (KJ.mol⁻¹), K is the equilibrium constant, Csolid is the solid phase concentration at equilibrium (mg/l), Cliquid is the liquid phase concentration at equilibrium (mg/l), T is the temperature in Kelvin and R is the gas constant (0.008314 KJ. mol⁻¹. K⁻¹).

The ΔG obtained have negative sign that indicates the adsorption process was spontaneous and from slope and intercept of van’t Hoff plot (Fig. 13), ΔH and ΔS are calculated.

The thermodynamic results summarized in Table (2) which shows positive value of enthalpy indicates endothermic adsorption reaction and positive value of entropy indicate increase in randomness.

Table 2. Thermodynamic function for adsorption of studied dye.

<table>
<thead>
<tr>
<th>RhB dye</th>
<th>Co mg/l</th>
<th>Equilibrium constant K</th>
<th>-ΔG KJ.mol⁻¹</th>
<th>-ΔH KJ.mol⁻¹</th>
<th>ΔS Jmol⁻¹K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature °C</td>
<td>Temperature °C</td>
<td>Temperature °C</td>
<td>Temperature °C</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.095</td>
<td>3.007</td>
<td>4.347</td>
<td>7.264</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.603</td>
<td>3.415</td>
<td>5.369</td>
<td>6.874</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.937</td>
<td>3.470</td>
<td>4.870</td>
<td>7.310</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>3.219</td>
<td>3.694</td>
<td>4.714</td>
<td>5.944</td>
</tr>
</tbody>
</table>

The plots of lnK versus 1/T were found to be liner with a correlation coefficient (R² =0.988–0.981) (Fig. 13).

Kinetics of Adsorption:

To understand the mechanism of adsorption reaction, the kinetics experimental observation data was fitted to pseudo-first order (Lagueren equation), and (Ho and McKay) pseudo-second order. The linear form of Lagueren equation formulated as the following (Al-Kinani, 2016).

Where Qe and Qt the adsorption capacity at equilibrium and time t respectively and (kt) (hr⁻¹) is the rate constant of the first-order adsorption. From the plot of ln(Qe-Qt) against the time t) for 50 mg/L 'concentration of RhB dye at different temperatures in the range from 10-40 °C. (Fig. 14). The value of rate K, constant, calculated equilibrium uptake and correlation coefficient obtained and listed in Table (3).

The pseudo-second order equation written as follows (Ho and Mckay, 1999).
\[ \frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \ldots \]

Where \((K_2)\) (g mg\(^{-1}\) hr\(^{-1}\)) is the rate constant of the second order adsorption. A linear plot of \(\frac{t}{Q!}\) against time give the straight line and from the slope and intercept value of \(K_2\) and \(Q_e\) can be calculated. The results obtained are given in Table (3) and shown in Figure (15).

![Figure 13. plot of van't Hoff relationship between lnK and 1/T.](image)

![Figure 14. Linear form of Pseudo-First-Order (Lagergren) Kinetic model of RhB dye on Porcellante at different temperatures.](image)
Table 3. First order and Second order kinetic rate constant, calculated and experimental $Q_e$ values and $R^2$.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Pseudo-First-Order</th>
<th>Pseudo-Second-Order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_e$ exp. mg/g</td>
<td>$Q_e$ Cal. mg/g</td>
</tr>
<tr>
<td>10</td>
<td>4.80</td>
<td>2.68</td>
</tr>
<tr>
<td>20</td>
<td>4.82</td>
<td>2.87</td>
</tr>
<tr>
<td>30</td>
<td>4.86</td>
<td>3.09</td>
</tr>
<tr>
<td>40</td>
<td>4.90</td>
<td>3.44</td>
</tr>
</tbody>
</table>

Figure 15. Linear form of Pseudo-Second-Order Kinetic model of RhB dye on porcellanite at different temperatures.

From Table (3), the results show that the theoretical $Q_e$ (cal.) are lower than the experimentally $Q_e$ (exp.) for pseudo-first-order equation while it can be seen that the correlation coefficients $R^2$ are (0.999), the calculated $Q_e$ values are in agreement with experimental $Q_e$ values. This indicates that the pseudo-second-order model provided the best correlation with experimental data. Hence, the adsorption kinetic of RhB on porcellanite occurred by chemisorption and internal diffusion mechanism based on the assumption in the pseudo-second-order kinetic model.

**Conclusion**

The results obtained show that porcellanite is an efficient sorbent in the removal of RhB from aqueous solutions. The results suggested that the percentage removal of Rhodamine B on porcellanite increased with decreased pH. The maximum percentage removal of (86.41 %) occurred at pH 4. The adsorption capacity of RhB
decreased with increased ionic strength but increased with increased temperature. The experimental equilibrium data obeyed for Langmuir as well as Freundlich isotherms with better fit to Freundlich isotherm, Thermodynamic studies shows the adsorption process spontaneous and endothermic, Adsorption kinetic was found to followed the pseudo second order kinetics rate expression.

References
Adsorption equilibrium, kinetics and thermodynamics of Rhodamine B dye


توازن أمتصاز وحركية وثرموديناميكية صبغة الرودامين

B من محاللها

المانية باستخدام صخور البورسلينات العراقية

ميثاق إبراهيم عبود١ و طارق إبراهيٌّم جاسم²

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المستخلص - إن مياه الصرف الصناعي والمياه الملوثة بحاجة إلى معالجة لجعلها ممكنة الطرح في الأنهار وإعادة استعمالها، إذ يأخذ الأمتصاز أهمية بين طرق إزالة الملوثات العضوية وغير العضوية في المياه. من هنا جاء البحث عن مواد متوفّرة محليًا
ورخصة الثمن لاستعمالها كسطح مادة. جرى في هذه الدراسة إمكانية استخدام مسحوق البورسلينات العراقية لإزالة صبغة الرودامين B بطريقة الدفعات. تم دراسة تأثير العوامل المختلفة مثل زمن الإتزان، درجة الحرارة، الدالة الحامضية للمحلول، وزن المادة المزنة، التركيز الابتدائي للصبغة المدروسة، والقوة الأيونية. كما تضمنت دراسة الإمزاج كلاً من أيزوثيرمات الإمزاج وحركية الإمزاج. طبقت معاذتنا لانكماش وفرينديش على النظام المدروس في درجات حرارية مختلفة، ووجد أن معادلة فرينديش أكثر انتباهًا مع النتائج التجريبية. كذلك بينت الدراسة الترموديناميكية أن عملية الإمزاج للصبغات المدروسة كانت ثالثية من قيم ΔG السالبة وأن تفاعل الإمزاج للصبغتين ماص للحرارة (Endothermic) من خلال قيم ΔH الموجبة بينما دلت القيم الموجبة لـ ΔS على زيادة العشوائية أو اللاانظام لعملية الإزلاء. نتائج الدراسة الحركية وصفت من خلال معادلة المرتبة الثانية الكاذبة حيث كانت أكبر ملائمة لنظام المدروس.