Removal of Basic Red 2 from Industrial Effluents Using Natural Iraqi Material

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ABSTRACT

The use of natural Iraqi porcellanite as a cheap, abundantly and ecofriendly adsorbent has been studied as an alternative substitution of activated carbon for the removal of dye from industrial wastewater. This material was successfully used to remove the basic red 2 dye from aqueous solution in a batch equilibrium adsorption technique.

Various factors such as adsorbent dose, contact time, pH, initial dye concentration and particle size of adsorbent were taken into account at room temperature, and promising results were obtained.

The well known Langmuir and Freundlich isotherm models were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated. The monolayer saturation capacity for adsorption basic red 2 was found to be 66.22 mg/g adsorbent.

Keywords: adsorption, dye, natural material, isotherm

1. INTRODUCTION

The large quantity of dyes released into natural water bodies by industries causes serious environmental problems due to impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities.

The different methods of colour removal from industrial wastewater include biological treatment, coagulation, flotation, adsorption, oxidation. Among the treatment methods, adsorption appears to have considerable potential(Weber, 1978) for the removal of colour from industrial wastewater.

Activated carbon is most widely used as adsorbent for the removal of many organic contaminants. But the high initial cost of activated carbon coupled with problems associated with regeneration, has the search for alternate adsorbents.

Many investigations have study the economic feasibility of using inexpensive alternative materials such as fly ash, rice husk, tree bark and human hair have been tested and reported to give encouraging results in several areas of application (Malik et al., 2003), other different adsorbents such as chitin(Mckay et al., 1982), perlite(Dogan and Alkan, 2003), natural clay(El-Geundi, 1991), fly ash(Sumanjit et al., 1998), rice husk(Sumanjit and Prasad, 2001 ; Malik, 2003), orange peel (Namasivayam et al., 1996).

The purpose of this work is to study the potential of Iraqi rocks (Porcellanite) as low cost alternative adsorbent to activated carbon to remove the basic red 2 dye from aqueous solution.

2. EXPERIMENTAL SECTION

2.1 Materials and methods

2.1.1 Adsorbent preparation

The adsorbent, natural Iraqi porcellanite (rocks) was supplied by the General Establishment for Geological Survey and Mineralogy Ministry of Industry and Mineral(GEGSM), from the Akashat site in the western region of Iraq.

Table(1) represents the chemical and physical analysis of Iraqi porcellanite.
Table 1. Chemical and physical analysis of porcellanite used in this study, (GEGSM)

<table>
<thead>
<tr>
<th>Chemical Composition %</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>L.O.I</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>83.57</td>
<td>0.62</td>
<td>4.45</td>
<td>0.01</td>
<td>1.82</td>
<td>1.46</td>
<td>0.5</td>
<td>0.16</td>
<td>0.22</td>
<td>5.9</td>
<td>98.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specific gravity (SG)</th>
<th>Range for 5 Sample</th>
<th>Average (SG)</th>
<th>Recommendation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5-1.61</td>
<td>1.554</td>
<td>Ok</td>
</tr>
</tbody>
</table>

| Porosity              | 0.52               |

It was crushed and sieved to get granular porcellanite with range of particle size of (100-2500 µm) to be used in present study as shown in Figure(1a,b).

![Figure 1. Natural Iraqi porcellanite used in this study](image1)

Then, the granular porcellanite was washed with distilled water and dried in an electrical oven at 120°C.

It was placed in desiccators for cooling and stored until used.

2.1.2 BR-2 solution

The dye, Safranin-O is a basic red dye stuff (Basic Red 2(BR-2)) IUPAC name as 3,7-Diamino -2,8-dimethyl -5- Phenyl Phenazinium Chloride is a cationic dye which structure is described in Figure (2).

![Figure 2. Structure of Basic Red 2](image2)

The physiochemical properties of BR-2 dye can be shown by Table(2).
Table 2. Physiochemical properties of BR-2 dye

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>350.85 g/mol</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₂₀H₁₉N₄Cl</td>
</tr>
<tr>
<td>C.I. Name</td>
<td>50240</td>
</tr>
<tr>
<td>Absorption maxima</td>
<td>520 nm</td>
</tr>
<tr>
<td>Nature</td>
<td>Basic red (cationic dye)</td>
</tr>
<tr>
<td>Solubility</td>
<td>Water + Alcohol</td>
</tr>
<tr>
<td>Class</td>
<td>Azinium</td>
</tr>
<tr>
<td>Dye content</td>
<td>95%</td>
</tr>
</tbody>
</table>

The stock solution 1000 mg/l was prepared by dissolving accurately weighted amount of BR-2 in distilled water. The working solutions were obtained by diluting the stock solution to get the solution with appropriate concentration.

Concentrations of the dye solutions were determined by measuring the absorbance of the solution at the characteristic wavelength (λ max. = 520 nm) of BR-2 using a double beam UV-Vis spectrophotometer (UV/VIS-1650 PC SHIMATZU). Final concentration was then determined from the calibration curve already prepared by plot of absorbance versus concentration at maximum wavelength of 520 nm. The pH was controlled using either 0.1N HCl or NaOH.

2.2 Adsorption experiments

2.2.1 Batch equilibrium method

Batch adsorption experiments were conducted in order to evaluate the effects of adsorbent dosage, contact time, pH, initial BR-2 concentration and particle size of adsorbent. In each batch experiment, 100ml dye solution was taken in 250ml of standard flask at the ambient temperature.

To study the effect of adsorbent dose on the amount of dye adsorbed was studied by adding different amounts (0.05-0.3g) of adsorbent with dye concentration of 50mg/l and particle size of adsorbent of (100 µm). The samples were agitated for specified time.

For studying the effect of contact time, the experiments was performed at different mixing time ranging from 20 to 250 min., the adsorbent dose used was obtained the best value received from previous experiments, with initial dye concentration of 50mg/l, and particle size of adsorbent of 100 µm.

In order to determine the effect of pH on the adsorption capacity, solutions were prepared at different pH values ranging 3 to 12.

The initial dye concentration was 50mg/l with particle size of adsorbent of 100 µm. This experiments operate at optimum adsorbent dosage and contact time obtained from previous experiments.

To examine the effect of initial dye concentration, the removal of dye was examined for different concentration of dye solution (10-100mg/l) at optimum conditions obtained from previous experiments.

To study the influence of particle size of adsorbent, particle size range from (100-2500 µm) with initial dye concentration of 50mg/l at optimum parameters obtained from previous experiments.

After reaching equilibrium, the mixture was filtered. The dye filtrate was then analyzed.

2.2.2 Adsorption isotherms

For adsorption isotherm, dye solutions of different concentrations (10-100mg/l) were shaken with the optimum amount of adsorbent (0.2g) and particle size of 100 µm till the equilibrium was achieved, and then, the residual BR-2 concentration of the solution was determined.

2.2.3 Formula and calculations

2.2.3.1 Calculation of uptake capacity
Dye uptake capacity ($q_e$) of adsorbent is dye adsorbed per unit mass of the adsorbent (mg/g), $q_e$ was calculated by using mass equilibrium equation (Ranjana et al., 2009; Lalhruaitluarga et al., 2010).

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

Where $q_e$ is adsorption capacity (mg/g), $C_i$ and $C_e$ (mg/l) are the concentration of BR-2 solutions before and after adsorption respectively, $V$(l) is the volume of the dye solutions, and $W$ is the weight of adsorbent in gram.

The amount of BR-2 removal (%) was calculated using Eq.(2):

$$\text{Removal (R%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Meaning of $C_i$ and $C_e$ is the same as mentioned above.

2.3 Adsorption isotherms data analysis

The relationship between the amount of substance adsorbed at constant temperature and its concentration in the equilibrium solution is called adsorption isotherm.

The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent.

The experimental adsorption equilibrium data were analyzed using Langmuir, Freundlich isotherms model. The best-fitting isotherm and the applicability of isotherm model is compared by judging the correlation coefficients can be obtained by using linear regression.

**Langmuir model**

is based on the assumption that adsorption energy is constant and independent of surface coverage where the adsorption occurs on localized sites with pattern on the homogeneous surface without interaction between adsorbed molecules and that maximum adsorption occurs when the surface is covered by a monolayer of adsorbate (Mohd et al., 2001; Singh et al., 2005; Kundu and Gupta, 2006).

The Langmuir non-linear model is expressed as followed:

$$q_e = \frac{Q_mK_aC_e}{1 + K_aC_e} \quad (3)$$

Where $q_e$ is the amount adsorbed per unit mass of sorbent at equilibrium (mg/g); $Q_m$ is a constant and reflect a complete monolayer(mg/g); $K_a$ is adsorption equilibrium constant(l/mg) that is related to the apparent energy of adsorption; $C_e$ is the equilibrium dye concentration (mg/l). For good adsorbents, values of "$Q_m$" should be high and values of "$K_a$" should be low (Kratochvil and Volesky, 1998).

The linear form of Langmuir model can be obtained by plotting of $C_e/q_e$ versus $C_e$ and they should indicate a straight line of slope $1/Q_m$ and the intercept $1/(K_aQ_m)$.

$$\frac{C_e}{q_e} = \frac{1}{Q_mK_a} + \frac{C_e}{Q_m} \quad (4)$$

To confirm the favorability of the adsorption process, the separation factor ($R_L$) was determined. RL is a dimensionless constant which can be defined as (Weber and Chakravorti, 1974).

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

Co is the initial concentration of BR-2 (mg/l); $b$ is the Langmuir isotherm constant. The parameter RL indicates the shape of isotherm as follows:

- $R_L > 1$ unfavorable adsorption, ($R_L = 1$) linear, (0 < $R_L < 1$), indicating the favorable adsorption, ($R_L = 0$) irreversible.

**Freundlich model**

is an empirical equation based on adsorption on a heterogeneous surface or surface supporting sites of varied affinities.

The Freundlich non-linear model is expressed as followed:

$$q_e = K_fC_e^{1/n} \quad (6)$$

Where $K_f$ is a constant for the system related to the bonding energy.

$K_f$ can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration.
n is indicating the adsorption intensity of dye onto the adsorbent or surface heterogeneity.

In general n>1 illustrates that adsorbate is favorably adsorbed on the adsorbent whereas n<1 demonstrates the adsorption process is chemical in nature (Tunc et al., 2009).

The values of $K_F$ and n were obtained by plotting the linear plot of $\log q_e$ versus $\log C_e$.

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e$$

(7)

3. RESULTS AND DISCUSSION

Figure(3) explains the optimization of the adsorbent dose for the removal of BR-2 from its aqueous solutions. It is clear from Figure that, the removal of dye increases with increase in the amount of adsorbent from 0.05-0.3g. The removal increased from 64.67% at 0.05g/100ml to 97.26% at 0.3g/100ml. from Figure, it can be noticed that the removal efficiency become constant at doses of more 0.2g/100ml. So that, it can be considered that the dose of 0.2g of natural porcellanite is the optimum and economical dose for a good removal. Increase in adsorption with the adsorbent dose can be due to increased surface area for adsorption of the dye molecule on the surface and the availability of more adsorption sites. Similar facts were reported by (Mohan et al., 2001; Taha et al., 2009; Taha and Samaka, 2013).

![Graph](image-url)

$\text{Fig. (3) : Adsorption BR-2 by natural porcellanite as a function of adsorbent dose at initial concentration of 50 mg/l and 100\mu m particle size}$

The influence of contact time can be shown from Figure(4) for the dye. One can be noticed that the extent of adsorption is rapid in the initial stages and becomes slow later stages till saturation is obtained.

The final concentration of dye did not vary significantly after 30min. from the start of adsorption process. This means that equilibrium can be achieved at 30min.. This result is expected because a large number of surface sites are available for adsorption at the initial stages and after 30min., the remaining surface site are difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phases (Poots et al., 1976).

The curve are smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the adsorption (Senthikumar et al., 2005; Taha et al., 2009; Taha and Samaka, 2012).
The influence of pH can be shown by Figure(5). There was no significant change in percentage removal over the entire pH range of (3-12).

Other studies for different ionic dyes were also found to be independent of pH (Low et al., 1995; Hu et al., 2010).

This indicates there is such a strong interaction between the dye and natural porcellanite that neither H\(^+\) nor OH\(^-\) could influence the adsorption capacity. In other words, the adsorption of BR-2 dye on natural porcellanite dose not involve an ion-exchange mechanism.

![Figure 5. Percentage uptake of BR-2 onto natural porcellanite as a function of solution pH at initial dye concentration of 50 mg/l and adsorbent dose of 0.2g](image)

The influence of initial BR-2 concentration on the adsorption on natural porcellanite is shown in Figure(6). It can be seen that the adsorption capacity increased from 4.89 to 46.70mg/g as the initial concentration varied from 10 to 100mg/l.

The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases (Ho et al., 2005).

A similar observations were observed by (Gupta et al., 2006; Hameed et al., 2007; Lata et al., 2007; Taha et al., 2009).
The effect of particle size of adsorbent can be explained by Figure(7). It can be cleared that the adsorption capacity increased with decreasing the particle size of the adsorbent. This indicate that the smaller particle size of natural porcellanite for a given mass, the more surface area is available and the greater number of binding sites available (Mckay et al., 1980; Yuh-Shan et al., 2001).

From Figure, it can be seen that 100 µm is considered as optimum particle size with higher adsorption capacity.

3.1 Adsorption isotherms

Figure(8) shows Langmuir isotherm for BR-2 adsorption over natural porcellanite and Figure(9) represent Freundlich isotherm for BR-2 adsorption.
The calculated isothermal adsorption parameters of Langmuir and Freundlich of BR-2 is summarized in Table(3).

### Table 3. Adsorption isotherm parameters for BR-2 removal

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th></th>
<th>Freundlich</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(95% Confidence level)</td>
<td></td>
<td>(95% Confidence level)</td>
<td></td>
</tr>
<tr>
<td>Q&lt;sub&gt;m&lt;/sub&gt; (mg/g)</td>
<td>66.22</td>
<td></td>
<td>K&lt;sub&gt;f&lt;/sub&gt;(mg/g)(l/mg)&lt;sup&gt;1/n&lt;/sup&gt;</td>
<td>15.47</td>
</tr>
<tr>
<td>K&lt;sub&gt;a&lt;/sub&gt; (l/mg)</td>
<td>0.34</td>
<td></td>
<td>l&lt;sup&gt;1/n&lt;/sup&gt;</td>
<td>0.65</td>
</tr>
<tr>
<td>R²</td>
<td>0.9843</td>
<td></td>
<td>R²</td>
<td>0.9812</td>
</tr>
<tr>
<td>Standard error of the estimate(S.E.)</td>
<td>0.0043</td>
<td></td>
<td>Standard error of the estimate(S.E.)</td>
<td>0.0454</td>
</tr>
<tr>
<td>R&lt;sub&gt;L&lt;/sub&gt;</td>
<td>(0.027 -0.222 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Equation**  

\[
q_e = 22.51 C_e /1 + 0.34 C_e
\]

**Equation**  

\[
q_e = 15.47 C_e^{0.65}
\]

![Figure 8. Linearized Langmuir model adsorption isotherm model of BR-2 onto natural porcellanite](image)

![Figure 9. Linearized Freundlich model adsorption isotherm model of BR-2 onto natural porcellanite](image)
By Langmuir isotherm, the maximum adsorption capacity (Qm) was 66.22 mg dye per gram of the natural porcellanite. The applicability of Langmuir isotherm suggested a monolayer coverage of dye on the surface of natural porcellanite.

The separation factor (R_L) values can be shown by Figure (10), which they are in the range of 0-1, indicating that the adsorption was favorable process (Han et al., 2005; Senthilkumar et al., 2005; Bhatnagar, 2007; Hameed, Ahmad and Aziz, 2007).

From Freundlich isotherm, the value of 1/n, the Freundlich parameter, which was between (0-1) also confirmed that the adsorption was favorable and beneficial as low cost adsorbent (Namasivayam and Yumuna, 1992).

The larger value of K_F, the higher the adsorption, because, this value indicates to more heterogeneous the surface when it will closer the zero (Azira et al., 2004).

The natural porcellanite, studied as adsorbent for removal of BR-2, proved that it works well.

The adsorption obeyed both Langmuir and Freundlich isotherms exhibiting heterogeneous surface conditions and monolayer adsorption (Lee et al., 1999).

Figure (11) explains the deviation of these models from the experimental data. It appears that the adsorption of BR-2 on natural porcellanite could be well fitted by the tow isotherms.
4. CONCLUSIONS

The results of this investigation show that natural Iraqi porcellanite has a suitable adsorption capacity for the removal of cationic dye (BR-2) from aqueous solutions.

The ability of natural porcellanite to adsorb BR-2 dye was investigated as a function of adsorbent dosage, contact time, pH, initial dye concentration, and particle size of adsorbent.

The removal of BR-2 increases with increase of adsorbent dose used. The adsorption capacity increased with increased of contact time and achieves equilibrium at 30 minutes. There was no significant change in percentage removal of dye over the studied pH range. The adsorption capacity decreases with increase of adsorbent dosage, but increases with increase of initial dye concentration.

The experimental data correlated reasonably well with the Langmuir and Freundlich adsorption isotherms and the respective isotherm parameters were calculated.

Monolayer equilibrium adsorption capacity, based on a Langmuir analysis, of 66.22 mg/g for BR-2 dye.

As the material is easily and abundantly available, the use of it as adsorbent would also solve their disposal problem.

5. REFERENCES


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