Short communication

Removal of congo red from aqueous solution by adsorption onto acid activated red mud

Ali Tor\textsuperscript{a,},*, Yunus Cengeloglu\textsuperscript{b}

\textsuperscript{a} Selcuk University, Department of Environmental Engineering, Campus, 42031 Konya, Turkey
\textsuperscript{b} Selcuk University, Department of Chemistry, Campus, 42031 Konya, Turkey

Received 22 December 2005; received in revised form 7 April 2006; accepted 11 April 2006
Available online 16 June 2006

Abstract

The objective of this study is to remove the congo red (CR) anionic dye, from water by using the acid activated red mud in batch adsorption experiments. The effects of contact time, pH, adsorbent dosage and initial dye concentration on the adsorption were investigated. The pH of the dye solution strongly affected the chemistry of both the dye molecules and activated red mud in an aqueous solution. The effective pH was 7.0 for adsorption on activated red mud. It was found that the sufficient time to attain equilibrium was 90 min. The adsorption isotherms were analyzed using the Langmuir, the Freundlich, and the three parameter Redlich–Peterson isotherms. The Langmuir isotherm was the best-fit adsorption isotherm model for the experimental data obtained from the non-linear chi-square statistic test.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Activated red mud; Congo red; Adsorption; Isotherm; Chi-square test

1. Introduction

Synthetic dyestuffs can be exist in the effluents of wastewater from different industries, i.e. textiles, paper, leather, plastics, etc. \cite{1}. Discharge of wastewater into natural streams and rivers from the industries using dyes poses severe environmental problems. Even small quantities of dyes can color large water bodies, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. In addition, most of dyes are either toxic or mutagenic and carcinogenic \cite{2,3}. For these reasons, the removal of dyes from process or waste effluents becomes environmentally important.

Conventional wastewater treatment plants are not suited to remove the dyes due to their non-biodegradable features \cite{4}. Therefore, alternative methods have been developed to remove the dyes from wastewater, namely, coagulation and flocculation \cite{5}, membrane separation \cite{6}, oxidation or ozonation \cite{7,8}, electro-coagulation \cite{9}, and adsorption \cite{10,11}.

Among these methods, adsorption currently appears to offer the best potential for overall treatment \cite{12}. Although activated carbon is the most widely used adsorbent for wastewater treatment, it is very expensive and has high operating costs due to the high price of the activated carbon and to the high water flow rate always involved, and these costs can be greatly increased when there are no carbon regeneration units locally \cite{3,13}. Therefore, in recent years, considerable attention has been devoted to the study of different types of low-cost materials in order to remove the pollutants from aqueous phase \cite{14,15}. Many workers have employed the perlite \cite{16}, biomaterial \cite{17}, recycled alum sludge \cite{18}, zeolites \cite{19}, clay \cite{20}, agricultural waste residues \cite{21}, bagasse fly ash \cite{11}, peanut hull \cite{3} for removing the dyes from wastewater.

Red mud (bauxite wastes of alumina manufacture) emerges as an unwanted byproducts during alkaline-leaching of bauxite in Bayer process, which is used for the production of alumina from bauxite. In most refineries, the ground bauxite is initially slurried with a caustic liquor and held at approximately 100 °C for a number of hours (pre-desilication). The slurry is then digested at temperature, usually between 150 and 250 °C, to dissolve the soluble aluminium species (gibbsite and/or boehmite; digestion). The resulting sodium aluminate solution – ‘pregnant’ or ‘green’ liquor – is then separated from the solid impurities (‘red mud waste residue’; mud settling and filtration) and the gibbsite precipitated after cooling and addition of seed material (precipi-
2. Materials and methods

2.1. Red mud and activation procedure

Red mud was supplied from the Etibank Seydişehir Aluminium Plant (Konya, Turkey). The grain size of red mud was mostly (＞94%) less than 10 μm and average composition of the red mud was determined according to the procedure described in Ref. [34] by using ICP-AES (Varian, Vista/AX CCD Simultaneous ICP-AES) and result was given in Table 1. The alkaline red mud was suspended in distilled water with a liquid to solid ratio of 2/1 on a weight basis, stirring it until the equilibrium pH is 8.0–8.5, and drying. Later activation of red mud was boiled in 200 ml of 20 wt.% HCl for 20 min. The equilibrium pH is 8.0–8.5, and drying. Later activation of red mud was boiled in 200 ml of 20 wt.% HCl for 20 min. The BET surface area of activated red mud (mg/g) was 20.7 m²/g, respectively [27].

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt.%) [n = 3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>18.71 ± 0.59</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>39.70 ± 0.67</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.90 ± 0.54</td>
</tr>
<tr>
<td>Na₂O</td>
<td>8.82 ± 0.96</td>
</tr>
<tr>
<td>CaO</td>
<td>4.47 ± 0.56</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.52 ± 0.37</td>
</tr>
<tr>
<td>LOI⁴</td>
<td>8.15 ± 0.40</td>
</tr>
</tbody>
</table>

² Loss on ignition.

Congo red (CR) contains NH₂ and SO₃ functional groups (see Fig. 1). It has a maximum absorbency at wavelength 500 nm on a UV–vis spectrophotometer. The chemical formula and molecular weight of CR is C₃₂H₂₂N₆Na₂O₆S₂ and 696.7 g/mol, respectively.

2.3. Batch adsorption procedure

The dye solutions were prepared from stock solutions (1000 mg/l) to desired concentrations. The adsorption experiments were carried out by a batch method. All experiments were carried out at a constant ionic strength of 0.01 M maintained with NaCl. A known amount of activated red mud and dye solution were taken in a 100 ml stoppered conical flask. Sodium chloride was added to maintain ionic strength, and pH was adjusted to the desired level with 0.1 M NaOH or 0.1 M HCl solutions. pH of the solution was determined by using Orion EA940 ionmeter. The final volume was adjusted to 50 ml with distilled water and agitated at constant speed (700 rpm) with magnetic stirrer at room temperature over a period of time and the dye solution was separated from the adsorbent by at 10,000 rpm for 20 min. The CR concentration of supernatant was determined by using UV spectrophotometer (λ = 500 nm) (Shimadzu UV-160 A). Calibration curves were plotted between absorbance and concentration of the standard dye solutions.

The amount of CR adsorbed was calculated from the following equation:

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

where \( q \) is the amount of dye adsorbed per unit weight of activated red mud (mg/g); \( C_0 \) the initial concentration of CR (mg/l); \( C_e \) the concentration of CR in solution at equilibrium time (mg/l); \( V \) the solution volume (l); \( m \) is the activated red mud dosage (g).

Blank runs, with only the sorbate in 50 ml of distilled water, were conducted simultaneously at similar conditions to account for adsorbed by glass containers.

The experimental parameters studied are adsorbent amount (1–10 g/l), contact time (10–240 min), initial dye concentration (10–90 mg/l), and pH (6–10).

3. Results and discussion

3.1. Effect of contact time

The variation of CR adsorbed with time is shown in Fig. 2. It was observed that as the contact time increases, the amount of CR adsorbed increases with time and then attained a
constant value after 90 min. The time to reach equilibrium conditions appears to be independent of initial CR concentrations. The adsorption of CR decreased from 85 to 50% by increasing CR concentration from 10 to 90 mg/l. Further, it was observed that the removal curves are smooth and continuous indicating the possibility of the formation of monolayer coverage on the surface of activated red mud by dye molecules.

3.2. Effect of pH

The initial pH values of dye solutions affect the chemistry of both a dye molecule and an adsorbent. In this study, blank studies for CR were done in the pH range of 3–13. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was found out. It is found that the color is stable at initial pH around 7. Fig. 3 shows the color removal without activated red mud over a pH range of 3–13. The results indicated that the molecular form of CR in solution medium changed markedly in the pH range 3–5, and at a high alkaline pH of 12, e.g., the color of CR changes from dark blue at pH 3–5 to red at pH 12. In addition, the red color is different from the original red in the pH range 10–12. Similar result was reported in Ref. [35]. Therefore, the pH of the solution were examined between 6 and 10 in the presence of activated red mud.

The solution pH relative to the point of zero charge (pHpzc) for the activated red mud also needs to be considered. At pH values above the pHpzc of the adsorbent, the surface of adsorber particles is negatively charged and as the pH rises above the pHpzc, adsorption of CR decreases. The pHpzc for activated red mud has been reported as about 8.5 in Ref. [27]. The effect of pH is presented in Fig. 3. The percentage removal of dye was maximum in the pH range of 6–8 and decreased with further increase in pH. This result is in agreement with previous publications [11,35]. At a pH above 8, a decrease in adsorption takes place due to repulsion between anionic dye molecules and negatively charged adsorbent surface.

3.3. The isotherm analysis

The relationship between the amount of CR adsorbed and the CR concentration remaining in solution is described by an isotherm. The three most common isotherm types for describing this type of system are the Langmuir, the Freundlich, and the Redlich–Peterson isotherm. The most important model of monolayer adsorption came from the work of Langmuir [36]. This isotherm is given as

$$q_e = \frac{Q_0 C_e}{1 + b C_e}$$  \hspace{1cm} (2)

where $Q_0$ and $b$ are characteristics of the Langmuir equation and can be determined from a linearized form of Eq. (2).

Langmuir : \hspace{1cm} \frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \hspace{1cm} (3)

where $C_e$ is the concentration of CR (mg/l) at equilibrium, $Q_0$ the monolayer capacity of the adsorbent (mg/g) and $b$ is the Langmuir adsorption constant (l/mg).

The Freundlich isotherm [37] is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as

$$q_e = k C_e^{1/n}$$  \hspace{1cm} (4)

The equation may be linearized by taking the logarithm of both sides of Eq. (4) and linear form of Freundlich isotherm can be given as

$$\log q_e = \log k + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)
where \( C_e \) is equilibrium concentration, \( k \) the sorption capacity (mg/g) and \( n \) is an empirical parameter.

The Redlich–Peterson isotherm [38] has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentrations and is in accord with the low concentration limit of the Langmuir equation. Furthermore, the Redlich–Peterson equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to its high versatility. The Redlich–Peterson equation is

\[
q_e = \frac{K_RC_e}{1 + a_RC_e^β}
\]  
(6)

where \( K_R \) is Redlich–Peterson isotherm constant (l/mg), \( a_R \) also a constant (l/mg) and \( β \) is the exponent which lies between zero and one. For \( β = 1 \), Eq. (6) reduces to Langmuir equation and for \( β = 0 \), it reduces to Henry’s equation. Eq. (6) can be converted to a linear form by taking logarithms:

\[
\ln \left( \frac{K_RC_e}{q_e} \right) - 1 = \ln a_R + β \ln C_e
\]  
(7)

The values of the constants for isotherms were obtained from the slope and intercept of the plots of each linear form of isotherm. The monolayer sorption capacity, \( Q_0 \), and sorption equilibrium constant, \( b \), are 7.087 mg/g and 0.130 l/mg, respectively, for Langmuir linear equation. The Freundlich sorption isotherm constant \( k \) is 1.072 and \( n \) is 1.956; the Redlich–Peterson isotherm constant \( K_R \) is 0.821, \( a_R \) is 0.107 and \( β \) is 0.983. The coefficients of determination (\( R^2 \)) for linear form of isotherm models were calculated by using the equation below [39,40].

The value of \( R^2 \) ranges between 0 and 1. A \( R^2 \) of 1 shows that 100% of the variation of experimental data is explained by the regression equation:

\[
R^2 = \frac{S_{xy}^2}{S_{xx}S_{yy}}
\]  
(8)

where \( S_{xx} \) is the sum of squares of \( X \).

\[
S_{xx} = \sum_{i=1}^{n} x_i^2 - \frac{\sum_{i=1}^{n} x_i^2}{n}
\]  
(9)

where \( S_{yy} \) is the sum of squares of \( Y \).

\[
S_{yy} = \sum_{i=1}^{n} y_i^2 - \frac{\sum_{i=1}^{n} y_i^2}{n}
\]  
(10)

where \( S_{xy} \) is the sum of squares of \( X \) and \( Y \).

\[
S_{xy} = \sum_{i=1}^{n} x_iy_i - \frac{\left( \sum_{i=1}^{n} x_i \right) \left( \sum_{i=1}^{n} y_i \right)}{n}
\]  
(11)

The \( R^2 \) value for linear form of isotherms are presented in Table 2. As seen in Table 2, the Redlich–Peterson isotherm best represents the equilibrium adsorption of CR on activated red mud. The Langmuir isotherm also shows comparable fit with the experimental data (see Table 2).

Due to the inherent bias resulting from linearization of isotherm models, chi-square (\( χ^2 \)) error function was employed in this study to find out the best-fit isotherm model to the experimental equilibrium data. \( χ^2 \) analysis is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models [41]. The mathematical statement of chi-square test can be given as below:

\[
χ^2 = \sum \left[ \frac{(q_e - q_m)^2}{q_m} \right]
\]  
(12)

where \( q_m \) is the equilibrium capacity obtained by calculating from the model (mg/g), and \( q_e \) is experimental data of the equilibrium capacity (mg/g). Small number of \( χ^2 \) indicates that data from the model is close to the experimental data. Whereas, large number of \( χ^2 \) indicates that data from the model is different from experimental data. Therefore, there is need for the analysis of the data using the chi-square test to confirm the best-fit isotherm for the sorption system [42]. According to the \( χ^2 \) values (Table 2), the best-fit isotherm model was the Langmuir isotherm model.

Under the basic condition of the CR sorption system, it was estimated to be more likely to approach the Langmuir form; this can be seen from the data that the values of \( β \) tend to unity (\( β = 0.983 \)). Inversely, linear regression has denoted different outcomes. However, linear regression and the non-linear chi-square analysis gave different models as the best-fitting isotherm for the given data set, thus indicating a significant difference between the analytical methods. As most of the chemical analysis still mostly relied on linear regression due to its simplicity compared to the non-linear chi-square analysis, this may have led to an inaccurate conclusion. Therefore, chi-square (\( χ^2 \)) analysis can be used a method for the determination of the best-fit isotherm due to its unified axial setting [42]. Fig. 4 shows the non-linear adsorption isotherms. Consequently, the Langmuir isotherm was the most suitable model for the sorption system of CR on activated red mud. Comparison of monolayer sorption capacity (\( Q_0 \)) for the adsorption of CR by non-conventional adsorbents are presented in Table 3.

The fit of the data to Langmuir isotherm model may indicate the homogeneous of the adsorbent surface. This is also supported by the equilibrium constant (\( K_D \), m\(^2\)/kg) values, which reflects the binding ability of the surface for an element. The \( K_D \) of a system mainly depends on the applied pH and type of surface used. The equilibrium constant \( K_D \) values for dye and red mud at

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>( R^2 )</th>
<th>( χ^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>0.993</td>
<td>0.078</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.930</td>
<td>0.761</td>
</tr>
<tr>
<td>Redlich–Peterson</td>
<td>0.995</td>
<td>0.128</td>
</tr>
</tbody>
</table>

Table 2
Comparison of linear regression coefficients of determination (\( R^2 \)) and non-linear chi-square (\( χ^2 \)) analysis
pH 7 were calculated according to the following equation [46]:

\[ K_D = \frac{C_s}{C_w} \]  

(13)

where \( C_s \) is the concentration of dye in the solid particles (mg/kg) and \( C_w \) is the equilibrium concentration of dye in the solution (mg/m³). As can be seen from Fig. 5, \( K_D \) does not change with increasing activated red mud dose at constant pH that implies the homogenous surface of the activated red mud. If the surface is heterogeneous, the \( K_D \) values at a given pH should increase with increase of adsorbent concentration [47].

3.4. Effect of red mud dosage

The percentage of CR adsorption with varying amounts of activated red mud is presented in Fig. 6. In general, the increase in adsorbent dosage increased the percent removal of adsorbate. This is consistent with the expectation that higher adsorbent dosages will result in lower \( q \) values. The concentration of surface hydroxyl groups is related to red mud concentration through surface site density [48]. Therefore, percent of adsorption increased with red mud dosage, whereas \( q \) decreased since the unit of \( q \) is milligram of dye per gram of activated red mud (Fig. 6).

### Table 3
Comparison of monolayer sorption capacity \( (Q_0) \) for the adsorption of CR by non-conventional adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( Q_0 ) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Fe(II)/Cr(III) hydroxide</td>
<td>44.00</td>
<td>[43]</td>
</tr>
<tr>
<td>Waste orange peel</td>
<td>22.44</td>
<td>[44]</td>
</tr>
<tr>
<td>Biogas waste slurry</td>
<td>9.50</td>
<td>[45]</td>
</tr>
<tr>
<td>Activated red mud</td>
<td>7.08</td>
<td>Present work</td>
</tr>
<tr>
<td>Waste red mud</td>
<td>4.05</td>
<td>[23]</td>
</tr>
</tbody>
</table>

4. Conclusion

In the present study, the removal of CR from synthetic wastewater was investigated by using activated red mud with respective different parameters. The other point, the utilization of activated red mud as adsorbent for removal studies was considered. The following results can be summarized as:

(i) The adsorption equilibrium was attained within 90 min.
(ii) The Langmuir isotherm was the best-fit adsorption isotherm with regard to the Redlich–Peterson and the Freundlich isotherms. This indicates that the homogenous adsorp-
The pH affects the adsorption capacity and the effective pH for the adsorption was found to be 7.

Because the red mud is discarded as waste in bauxite processing industry, its utilization as adsorbent for removal of dye is expected to be economical.

Acknowledgement

The authors are grateful for kindly financial support provided by Selcuk University Research Foundation (SAUF).

References


