The Removal of Composite Reactive Dye from Dyeing Unit Effluent Using Sewage Sludge Derived Activated Carbon

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Abstract

Activated carbon was prepared from dried municipal sewage sludge and batch mode adsorption experiments were conducted to study its potential to remove composite reactive dye from dyeing unit effluent. Adsorption parameters for the Langmuir and Freundlich isotherms were determined and the effects of effluent pH, adsorbent dosage, contact time and initial dye concentration were studied. The toxicity characteristic leaching protocol (TCLP) was used to assess the acceptability of sewage sludge derived activated carbon from the environmental point of view.

Key words: Reactive dye, Sludge derived activated carbon, Commercial activated carbon, Adsorption isotherms, TCLP.

Introduction

Almost every industry uses dyestuffs to dye their products and the residual and unspent substances are usually discharged into the aquatic environment. Discharge of such effluents imparts color to the receiving water and interferes with its intended beneficial use. In addition, recent reports suggest that several color-causing substances are micro-toxic to aquatic biota (Lee et al., 1999; Kadirvelu et al., 2000; Kadirvelu et al., 2003).

Amongst the different industrial wastewaters with different types of color-causing substances, synthetic textile organic dye wastes occupy a prominent position. Over 7 x 10^5 t and approximately 10,000 different types of dyes and pigments are produced worldwide annually. It is estimated that 10% to 15% of the dye is lost in the effluent during the dyeing process (Young et al., 1997; Danis et al., 1998).

Increasingly stringent legislation on the decontamination of wastewater has created interest concerning the use of activated carbons for this purpose (Shukla et al., 2002; Chiou and Li, 2003; Garg et al., 2003; Ozacar and Sengil, 2003; Malik, 2003). However, activated carbons are expensive and therefore their use may imply carrying out regeneration and reactivation procedures (Rozada et al., 2003). In recent years, this has prompted growing research interest in the production of carbon-based adsorbents from a range of residues, mainly industrial or agri-
cultural by-products. The production of activated carbon from residues helps in saving nonrenewable natural resources and producing a valuable product with potential applications in pollution control.

Reactive dyes are used extensively in the textile industry, due to their superior dyeing properties, especially in terms of fastness. Azo, Anthraquinone and Pthalocyanin are major classes of reactive dyes. The use of reactive dyes is increasing and was estimated to reach a market share of 50% in 2004 (Phillips, 1996). However, only a limited number of studies on the removal of reactive dyes have been found in the literature.

The focus of this research is the evaluation of the adsorption potential of sewage sludge derived activated carbon for composite reactive bearing wastewater and comparison with a commercial activated carbon as a reference. The effects of dose of solids loading, pH, contact time and initial dye concentration on the adsorption of composite reactive dye wastewater on to sludge derived and commercial activated carbon were investigated. The Langmuir and Freundlich isotherm models were used to represent the equilibrium data. The toxicity characteristics leaching protocol (TCLP) was used to determine the leachability of toxic elements from sludge derived activated carbon to assess its acceptability from the environmental point of view.

Materials and Methods

Anaerobically digested and dewatered sewage sludge collected from Koyembedu Sewage Treatment Plant, Chennai, was used for making the activated carbon using the procedure shown in Figure 1. The pyrolysis of the sludge was carried out in a muffle furnace in the absence of oxygen. The activation of pyrolyzed sludge was performed by impregnating 10 g of pyrolyzed sludge sample into 25 ml of activating agent solution (ZnCl$_2$ (3 M)) for 24 h at room temperature. Later activating agent was drained and the wet activated carbon was dried at 105 °C for 24 h. Before utilizing for adsorption studies, the activated carbon sample was washed with distilled water to remove residual activating agents and dried at 105 °C in hot air over 24 h.

Characteristics of sewage sludge derived activated carbon in comparison with commercial activated carbon (locally available) are presented in Table 1.

<table>
<thead>
<tr>
<th>Activated Carbon</th>
<th>Apparent Density (g/l)</th>
<th>Iodine Number</th>
<th>Surface Area (m$^2$/g activated carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage Sludge</td>
<td>873.2</td>
<td>886.9211</td>
<td>928.26</td>
</tr>
<tr>
<td>Commercial</td>
<td>291.7</td>
<td>1249.753</td>
<td>1083.42</td>
</tr>
</tbody>
</table>

Figure 1. Schematic process flow diagram of activated carbon preparation from sewage sludge (Sreedhar Reddy, 2004).

Table 1. Properties of activated carbons used in the investigation.

The synthetic composite reactive dye wastewater was prepared as a mixture of 3 reactive dye formulations (Table 2), as per the procedure suggested by Sreedhar Reddy et al. (2005). According to the information obtained from the local dyeing industries, usually 20% of the dyestuffs (hydrolyzed and/or un-fixed form) and 100% of all assisting chemicals remain in the exhausted dye-bath. The composition of a suitably diluted exhausted dye-bath is presented in Table 3. The dye-bath was suitably diluted to represent the typical strength of effluents from the above-mentioned textile manufacturing plant.

Adsorption experiments were carried out by agitating a suitable adsorbent dosage with 100 ml of dye solution of the desired concentration and pH at 100 rpm in a horizontal bench shaker (Labnet Scientific) at room temperature.
Table 2. Properties of dyes used in the investigation.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Procion Brilliant Blue M-R</th>
<th>Procion Brilliant Red H-8G</th>
<th>Procion Turquoise Blue M-G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>Powder</td>
<td>Powder</td>
<td>Powder</td>
</tr>
<tr>
<td>Color Index</td>
<td>Bright Blue (Rb4)</td>
<td>Red</td>
<td>Bright Greenish Blue (Rb140)</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
<td>Odorless</td>
<td>Odorless</td>
</tr>
<tr>
<td>Chromophore</td>
<td>Anthraquinone</td>
<td>Anthraquinone</td>
<td>Copper Phthalocyanine</td>
</tr>
<tr>
<td>Color Index Number</td>
<td>61205</td>
<td>-</td>
<td>74180</td>
</tr>
<tr>
<td>Reactive Group</td>
<td>Dichlorotriazine</td>
<td>Monochlorotriazine</td>
<td>Dichlorotriazine</td>
</tr>
<tr>
<td>pH Value</td>
<td>7 (10 g/l at 25 °C)</td>
<td>7 (10 g/l at 25 °C)</td>
<td>7 (10 g/l at 25 °C)</td>
</tr>
</tbody>
</table>

Table 3. Characteristics and composition of synthetic composite reactive dye wastewater.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameter</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dye</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>pH</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>Total solids</td>
<td>7500</td>
</tr>
<tr>
<td>4</td>
<td>Total suspended solids</td>
<td>320</td>
</tr>
<tr>
<td>5</td>
<td>Total dissolved solids</td>
<td>7180</td>
</tr>
<tr>
<td>6</td>
<td>BOD$_5$ at 20 °C</td>
<td>560</td>
</tr>
<tr>
<td>7</td>
<td>COD</td>
<td>3200</td>
</tr>
<tr>
<td>8</td>
<td>Chlorides (as Cl$^-$)</td>
<td>3800</td>
</tr>
<tr>
<td>9</td>
<td>Sodium (as Na$^+$)</td>
<td>7900</td>
</tr>
</tbody>
</table>

Note: All the values except pH are in mg/l.

The pH of the dye solutions was adjusted with dilute HCl or NaOH solution using a pH meter. Dye concentration was determined colorimetrically at the wavelength corresponding to maximum absorbance ($\lambda_{max}$), using a spectrophotometer. The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifugation at 5000 rpm for 15 min. The absorbance of supernatant solution was measured. The leaching characterization of sewage sludge derived activated carbon was evaluated using TCLP by suspending 1 g of activated carbon in 20 ml of distilled water for 24 h in an oven shaker (Labnet Scientific) at a rolling speed of 50 rpm. Later, distilled water was separated from the activated carbon using filter paper and analyzed for heavy metals like chromium, cadmium, nickel and zinc using an atomic adsorption spectrophotometer.

Results and Discussion

Effect of pH

To study the influence of pH on the adsorption capacity of sewage sludge derived activated carbon and commercial activated carbon for composite reactive dye, experiments were carried out using different initial solution pH values, varying from 3 to 11. As pH is changed, with no adsorbent present, the color intensity of composite reactive dye changes. Therefore, the initial color intensity of dye was measured at the beginning of each experiment, when the initial solution pH was adjusted to the desired value. The obtained results are presented in Figure 2, which shows that the adsorption capacity increases significantly with a decrease in the pH. At acidic pH, the positively charged species start dominating and the surface tends to acquire a positive charge, while the adsorbate species are still negatively charged. As the adsorbent surface is positively charged the increasing electrostatic attraction between negatively
charged adsorbate species and positively charged adsorbent particles would lead to increased adsorption of composite reactive dyes (Shukla et al., 2002).

The maximum removal of composite reactive dye with sludge derived activated carbon and commercial activated carbon was hence observed at pH 3, when the negative charge on the surface was very much reduced due to the excess of protons in solution. For sludge derived activated carbon and commercial activated carbon, the amount of dye adsorbed increased from 7.2 to 11.3 mg/g and from 8.28 to 11.88 mg/g, respectively, with a decrease in pH from 11 to 3.

Effect of Adsorbent Dosage

Figure 3 shows the adsorption of composite reactive dye as a function of dosage of sludge derived activated carbon and commercial activated carbon. It is apparent that by increasing the adsorbent dose the percentage of dye removal increases, but adsorption density, the amount adsorbed per unit mass, decreases. It is readily understood that the number of available adsorption sites increases by increasing the adsorbent dose and it therefore results in an increase in the percentage of dye adsorbed. The decrease in adsorption density with an increase in the adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process (Shukla et al., 2002; Yu et al., 2003). Another reason may be the inter-particle interaction, such as aggregation, resulting from high adsorbent dose. Such aggregation would lead to a decrease in the total surface area of the adsorbent and on an increase in diffusional path length (Shukla et al., 2002).

Effect of Contact Time and Initial Dye Concentration

Effects of contact time and initial dye concentration on adsorption of composite reactive dye by commercial activated carbon and sewage sludge derived activated carbon are presented in Figures 4 and 5. The amount of dye adsorbed increased with an increase in contact time and reached equilibrium after 120 min for the initial dye concentrations of 60, 80, 100 and 120 mg/l used in this study. The equilibrium time is independent of initial dye concentration. However, in the first 30 min, the initial rate of adsorption was greater for higher initial dye concentrations, because the diffusion of dye molecules through the solution to the surface of adsorbents is affected by an increase in the dye concentration. An increase in the dye concentration accelerates the diffusion of dyes from the dye solution on to adsorbents due to the increase in the driving force of the concentration gradient (Sun and Xu, 1997; Ozacar, 2003). Hence, the amount of dye adsorbed at equilibrium increased from 49.2 to 62.4 mg/g for sludge derived activated carbon and from 54.6 to 73.2 mg/g for commercial activated carbon as the initial dye concentration was increased from 60 to 120 mg/l.
Equilibrium Studies

The successful representation of the dynamic adsorptive separation of solute from solution on to an adsorbent depends upon a good description of the equilibrium separation between the 2 phases. By plotting solid phase concentration against liquid phase concentration graphically it is possible to depict the equilibrium adsorption isotherm. In order to optimize the design of a sorption system to remove dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curve.

The equilibrium studies conducted at a fixed initial concentration and varying adsorbent dose were fitted into the linearized Freundlich adsorption isotherm, which is of the form

$$\log(\frac{X}{M}) = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (1)$$

where $X$ is the amount of dye removed (mg), $m$ is the weight of adsorbent used (g), $C_e$ is the equilibrium concentration, and $K_f$ and $n$ are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. The linear plot of $\log(\frac{X}{M})$ versus $\log C_e$ showed that the adsorption obeyed a Freundlich isotherm (Figure 6). Freundlich constants $K_f$ and $n$ were 9.2 mg/g and 2.45 for commercial activated carbon, 4.6 mg/g and 2.116 for sludge derived activated carbon, respectively. It has been shown by McKay et al. (1982) that an $n$ value between 2 and 10 indicates beneficial adsorption.

The Langmuir isotherm, which is in the form

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

was applied for adsorption equilibrium, where $C_e$ is the equilibrium concentration (mg/l), and $q_e$ is the amount of dye adsorbed per gram at equilibrium (mg/g). $Q_o$ and $b$ are Langmuir constants. The linear plot of $\frac{C_e}{q_e}$ versus $C_e$ showed that the adsorption obeyed a Langmuir isotherm model (Figure 7). $Q_o$ and $b$ were determined from the slope and
intercept of the plot and found to be 33.5 mg/g and 0.070 l/mg for commercial activated carbon, and 25 mg/g and 0.44 l/mg for sludge derived activated carbon, respectively. The adsorption capacity obtained in this experiment is in agreement with the results reported in the literature. The adsorption data obeyed both Freundlich and Langmuir models, exhibiting heterogeneous surface conditions and monolayer adsorption (Lee et al., 1995).

\[ y = 30.327x + 664.2 \]
\[ R^2 = 0.9711 \]

\[ y = 22.926x + 285.94 \]
\[ R^2 = 0.9415 \]

Figure 7. Langmuir isotherm for commercial and sludge derived activated carbons.

The favorable nature of adsorption can be expressed in terms of a dimensionless parameter \( R_L \) that is given by the equation

\[ R_L = \frac{1}{1 + bC_o} \]  

(3)

where \( b \) is the Langmuir constant (l/mg) and \( C_o \) is the initial dye concentration (McKay et al., 1982). All \( R_L \) values obtained using Eq. (3) for dye adsorption are greater than zero and less than unity, showing favorable adsorption of dye onto sewage sludge derived activated carbon and commercial activated carbon.

Leachate testing of sludge derived activated carbon

The results of the TCLP leaching test are presented in Table 4. Sludge derived activated carbon generated leachates with values lower than the United States Environmental Protection Agency (EPA) requirements for the disposal of hazardous metals (Federal Registrar, 1990).

This is mainly due to the conversion of metals in the raw sludge to metal oxides during the pyrolysis. The results of TCLP tests indicated that activated carbons derived from sewage sludge are non-hazardous.

Table 4. TCLP of activated carbon derived from sewage sludge: contents of metals in leachates.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration in leachate (mg/l)</th>
<th>EPA regulatory level (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>0.027</td>
<td>0.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.018</td>
<td>-</td>
</tr>
<tr>
<td>Zinc</td>
<td>3.45</td>
<td>25</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.11</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Conclusion

The results of the present investigation show that sludge derived activated carbon has considerable potential for the removal of composite reactive dye from dyeing unit effluents, over a wide range of concentrations. The adsorbed amount of reactive dye increased as the surface area increased with an increasing adsorbent mass. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. A decrease in the pH of solution leads to a significant increase in the adsorption capacities of reactive dye on to commercial activated carbon and sludge derived activated carbon. The adsorbed amounts of reactive dye increased with an increase in contact time and reached equilibrium in 120 min.

The equilibrium time is independent of the initial dye concentration. The equilibrium data were analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients were determined from graphs of their linear equations. Both Langmuir and Freundlich isotherms were demonstrated to provide a meaningful correlation for the adsorption of reactive dye on to sludge derived activated carbon and commercial activated carbon. The results of TCLP tests indicate that sludge derived activated carbons generate leachates with values lower than the EPA requirements for trace metals for the disposal of hazardous materials and are considered non-hazardous.
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References


