Removal of reactive dyes from aqueous solution using bagasse fly ash

Manaskorn Rachakornkij, Sirawan Ruangchuay, and Sumate Teachakulwiroj

Abstract

Rachakornkij, M., Ruangchuaya, S. and Teachakulwiroj, S.
Removal of reactive dyes from aqueous solution using bagasse fly ash

Bagasse fly ash, a waste from the sugar industry, was investigated as a replacement for the current expensive methods of removing reactive dyes (Remazol Black B; RBB, Remazol Brilliant Blue R; RBBR, and Remazol Brilliant Red F3B; RBRF3B) from aqueous solutions. Bagasse fly ash was collected from a local sugar factory in Saraburi province, Thailand. It was oven dried at 110°C overnight and sieved to the desired particle size of 150 µm or smaller. The 50 mL plastic conical tubes containing solution and bagasse fly ash were shaken at room temperature (27±2°C). The pH values of solutions were adjusted by addition of HNO3 and NaOH. The batch study indicated that initial pH of aqueous solutions did not affect dye removal. While the removal efficiency decreased with increasing initial concentration, it increased with increasing adsorbent concentration. The best adsorptions were obtained under condition of 50 mg/L concentration, original pH solution of about 5, and 240, 300, and 240 minutes contact time for RBB, RBBR, and RBRF3B, respectively. Most adsorption experiments showed in the range of about 50% to 98% removal; that is, the efficiencies of RBB, RBBR, and RBRF3B adsorption were found to be between 58.48-98.03%, 46.15-93.47%, and 46.30-94.60%, respectively. For the linear and nonlinear forms of the Langmuir and Freundlich models, the results indicated that the Langmuir adsorption isotherm fitted the data better than the Freundlich adsorption isotherm. Adsorption of these dyes onto bagasse fly ash was favorable sorption. Therefore, bagasse fly ash, the low-cost agricultural waste in Thailand, is suitable for use as adsorbent for RBB, RBBR, and RBRF3B under this investigation.

Key words : bagasse fly ash, reactive dye, adsorption, adsorbent

1Ph.D. (Civil Engineering), 2M.Sc. (Environmental Technology), 3B.Eng. (Mining Engineering), National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM)/Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330 Thailand.
Corresponding e-mail: manaskorn.r@chula.ac.th
Received, 11 March 2004             Accepted, 12 May 2004
Removal of dyes using bagasse fly ash
Rachakornkij, M., et al.

Removing dyes using bagasse fly ash is an important method in the field of environmental management. Various methods, such as oxidation, membrane separation, electrochemical treatment, filtration, flotation, hydrogen peroxide catalysis, and reverse osmosis, have been proposed from time to time. Municipal aerobic treatment systems, dependent on biological activity, were found to be ineffective in removing these dyes (Lazaridis et al., 2003). There are two major technologies available for dye removal, i.e., oxidation and adsorption. Oxidation methods are possibly the best technologies to totally eliminate organic carbons, but they are only effective for wastewater with very low concentrations of organic compounds (Sun and Xu, 1997). Thus, dilution is necessary as a facility requirement. It is known

Reactive dyes, the type considered in this work, are known to have low absorbability on a wide range of adsorbents (Khraisheh et al., 2002). Discharge of dyes into natural streams and rivers from the industries poses severe problems, as dyes give toxicity to the aquatic life and are damaging to the aesthetic nature of the environment (Mohan et al., 2002).

In general, reactive dyes are the most problematic among other dyes, as they tend to pass through conventional treatment systems unaffected (Lazaridis et al., 2003). Various methods of dye removal, including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, flotation, hydrogen peroxide catalysis, and reverse osmosis, have been proposed from time to time. Municipal aerobic treatment systems, dependent on biological activity, were found to be ineffective in the removal of these dyes (Lazaridis et al., 2003). There are two major technologies available for dye removal, i.e., oxidation and adsorption. Oxidation methods are possibly the best technologies to totally eliminate organic carbons, but they are only effective for wastewater with very low concentrations of organic compounds (Sun and Xu, 1997). Thus, dilution is necessary as a facility requirement. It is known

...
that adsorption is one of the most efficient methods for removal of colors, odor, oils, and organic pollutants from process or waste effluents. Also, activated carbon is the most widely used adsorbent due to its excellent adsorption capability (Juang et al., 2002). However, its use is often limited due to high cost, making this method unfavorable for the needs of developing countries like Thailand.

Thailand generates a lot of bagasse fly ash each year because Thailand is one of the largest sugar exporters in the world. In addition, the cogeneration project of The Energy Policy and Planning Office (EPPO) supports small power producers (SPPs) that use renewable fuel to produce and sell electricity to the Metropolitan Electricity Authority (MEA) and the Provincial Electricity Authority (PEA). As many as 22% of the producers use bagasse as a fuel (http://www.nepo.go.th/encon/encon-spp-renewb2.html, 2002). Therefore, bagasse will become fly ash. Utilization of agriculture waste residues for the wastewater treatment at least has the following advantages: 1) there are available abundantly at no or low cost, 2) disposal of the wastes is a serious environmental problem in the area which has extensive agricultural activities such as Thailand. The aim for this research is to study the utilization of bagasse fly ash as adsorbents for removal of three types of reactive dye; Remazol Black B (RBB), Remazol Brilliant Blue R (RBBR), and Remazol Brilliant Red F3B (RBRF3B). The structures of these reactive dyes (Rughachart, 2001) are shown in Figures 1 (a), (b), and (c). The experiments were

![Figure 1. The structures of reactive dye Remazol Black B (a), Remazol Brilliant Blue R (b), and Remazol Brilliant Red F3B (c)]
carried out batches. The effect of contact time, pH, initial concentrations, and adsorbent dose were studied. In addition, suitable condition to remove reactive dyes, and isotherm models were investigated.

Materials and Methods

1. Fly ash collection and adsorbent development

Bagasse fly ash was collected from a local sugar factory in Saraburi province. It was oven dried at 110ºC overnight and sieved through sieve No. 100 (150 μm). The sieved bagasse fly ash was then stored in a vacuum desiccator for further use.

2. Equipment

A UV spectrophotometry was used for dye analysis. The pH measurements were obtained using a digital pH meter Consort model C 830. An IKA HS 501 shaker was used for all adsorption experiments.

3. Adsorption experiments

Adsorption studies were performed by the batch technique. A series of 50-mL plastic conical tubes were used. The tubes were shaken at room temperature (27±2°C) and the shaking speed was 125 rpm. The pH values of solutions were adjusted by addition of HNO₃ and NaOH. The following adsorption experiments were carried out:

Experiment 1. The effect of contact time or shaking time: contact time ranged from 15-420 minutes, initial concentration was 50 mg/L, initial pH solution was 7 and adsorbent dose was 20 g/L.

Experiment 2. The effect of initial pH and initial concentrations: pH ranged from 5 to 9. The initial concentration ranged from 50 to 200 mg/L, and adsorbent dose is 20 g/L. This experiment operates at optimum contact time which result form experiment 1.

Experiment 3. The suitable condition to remove dye. Equilibration time was determined at the optimum initial pH and initial concentrations obtained in experiment 2.

Experiment 4. The effect of adsorbent dose: adsorbent dose ranged from 20 to 120 g/L at optimum contact time from experiment 3 and optimum initial pH and initial concentrations from experiment 2.

Experiment 5. Adsorption isotherms for reactive dyes onto bagasse fly ash: Experiment was set at the suitable condition found in the previous experiment. This study used Langmuir and Freundlich isotherms to describe the reactive dyes adsorption onto bagasse fly ash.

Langmuir isotherm has been used by many workers to study sorption of a variety of compounds (Gupta and Ali, 2001). The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Gupta and Ali, 2001). The Langmuir isotherm relationship is of a hyperbolic form as shown in Equation (1). The Langmuir relationship can be linearized by plotting ether 1/qₑ vs 1/Cₑ.

The linear form of the Langmuir isotherm is given by Equation (2).

\[ qₑ = Qₒ b Cₑ / (1+b Cₑ) \]  \hspace{1cm} (1)  

\[ 1/qₑ = 1/Qₒ + 1/b Qₒ Cₑ \]  \hspace{1cm} (2)  

Where: \( qₑ \) is the amount of dye adsorbed per unit weight of adsorbents and \( Cₑ \) is the equilibrium concentration of the adsorbate (mg/L). Langmuir constants, \( Qₒ \) and \( b \) are related to maximum adsorption capacity and energy of adsorption through the Arrhenius equation, respectively. \( Qₒ \) can also be interpreted as the total number of binding sites that are available for sorption. When m/x or 1/qₑ is plotted against 1/Cₑ, a straight line with slope 1/b \( Qₒ \) is obtained and intercept is correspond to 1/Qₒ.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, \( r \), which describes the type of isotherm and is defined by Equation (3).

\[ r = 1 / (1+b Cₒ) \]  \hspace{1cm} (3)
Removal of dyes using bagasse fly ash

Rachakornkij, M., et al.

Where: $b$ is a Langmuir constant and $C_0$ is the initial concentration of dye (Gupta and Ali, 2000).

If, $r > 1$ unfavorable
$r = 1$ linear
$0 < r < 1$ favorable
$r = 0$ irreversible

The Freundlich isotherm relationship is exponential, given by the Equation (4). The linear form of the Langmuir isotherm is given by Equation (5).

$$Q = K_f C_e^{1/n}$$  \hspace{1cm} (4)

$$\log q_e = \log K_f + 1/n \log C_e$$  \hspace{1cm} (5)

where $K_f$ and $n$ are the Freundlich constants that are associated with adsorption capacity and adsorption intensity, respectively. The value of $n$ between 2 and 10 shows good adsorption. The other parameters have been defined as in equation (1) and (2). A plot of $\log q_e$ against $\log C_e$ gives a straight line, the slope and intercept of which correspond to $1/n$ and $\log K_f$, respectively (Gupta and Ali, 2001).

Result and Discussions

1. Characterization

Chemical analyses of bagasse fly ash are shown in Table 1. Analysis was performed are using an X-ray Fluorescence Spectrometer (XRF), Philips model PW 2400. The major constituent, Silica, was measured at 51.96 % by weight of bagasse fly ash. This is consistent with the results of Rao et al., (2002) and Gupta and Ali (2000 and 2001). The loss on ignition (LOI) was found to be 33.17 % by weight.

Table 1. Chemical characteristics of bagasse fly ash.

<table>
<thead>
<tr>
<th>Content ( % by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
</tr>
<tr>
<td>0.89</td>
</tr>
</tbody>
</table>

2. Effect of contact time

The time-dependent behavior of dye adsorption between adsorbate and adsorbent was measured using conditions that were previously described in Experiment 1. The results are plotted in Figure 2. Removals for each reactive dye were found constant starting at 240 minutes for RBB and RBRF3B, and between 300 minutes for RBBR. Therefore, contact periods of 240, 240 and 300 minutes were finally selected for all of the equilibrium tests for RBB, RBRF3B and RBBR respectively.

3. Effect of pH

The adsorption of reactive dye on bagasse fly ash was studied at conditions described in Experiment 2. It was observed that the removal of RBB, RBBR, and RBRF3B on low-cost adsorbent exhibited similar trend, that is, it did not change with varied pH values at all concentrations because the final solution pH’s of all conditions was about 12. The efficiencies to remove RBB, RBBR, and RBRF3B were between 58.48-98.03%, 46.15-93.47%, and 46.30-94.60%, respectively. Especially, at low concentrations, efficiency of more than 90% could be obtained for all dyes. This can be explained by considering the zero point of charge of the bagasse fly ash. The pH at the zero point of charge (pH$_{zpc}$) is reported to be 8.2 and 2.3 for alumina and silica, respectively (Mohan et al., 2002). The composite pH$_{zpc}$ of the bagasse fly ash is 2.4 (Gupta and Ali, 2001). Thus, for pH values above 2.4, the negative charge density on the surface of the bagasse fly ash increases, thus increasing available sites for the adsorption of dyes. The results are given in Figures 3 (a), (b), and (c) for RBB, RBBR and RBRF3B adsorption, respectively.
Figure 2. Effect of contact time on the rates of adsorption of reactive dye. Initial concentration = 50 mg/L, pH = 7, bagasse fly ash dose = 20 g/L, room temperature (27±2°C) and agitation speed 125 rpm.

Figure 3. Effect of pH on adsorptions of RBB (a), RBBR (b) and RBRF3B (c) by bagasse fly ash. Bagasse fly ash dose = 20g/L, room temperature (27±2°C) and agitation speed 125 rpm. Contact time = 240, 240 and 300 minutes for RBB, RBRF3B and RBBR, respectively.
4. Effect of initial concentration

The adsorption experiments were carried out in the conditions explained in Experiment 2. The results are given in Figures 4 (a), (b), and (c) for adsorption of RBB, RBBR, and RBRF3B, respectively. The figures showed the percent removal of dye as a function of initial concentration at different initial pH values. It was observed that, percent removal of dye decreased with increasing initial concentration from 50 to 200 mg/L. For example, at initial pH solution of 5, RBB removal dropped from 97.05% to 58.91% when the initial dye concentration varied from 50 to 200 mg/L with a constant adsorbent dose 20 g/L. In case of RBBR and RBRF3B, removal efficiency of more than 50% removal was observed when the initial concentration was less than 150 mg/L at all pH’s. While, for RBB at all initial concentration, a removal efficiency of more than 50% was found.

5. The equilibration time on dye adsorption

The adsorption data for the uptake of re-

![Graphs of initial concentration effects on dye removal](image-url)

**Figure 4.** Effect of initial concentration on adsorptions of (a), RBBR (b) and RBRF3B (c) by bagasse fly ash. Bagasse fly ash dose = 20g/L, room temperature (27±2°C) and agitation speed 125 rpm. Contact time = 240, 240 and 300 minutes for RBB, RBRF3B and RBBR, respectively.
active dye onto bagasse fly ash versus contact time are shown in Figure 5. This experiment was carried out under the optimum condition that includes initial pH of about 5 and initial concentration of is 50 mg/L. From the figure, the adsorption of reactive dye increased with increasing contact time and became almost constant after 240, 300, and 240 minutes for RBB, RBBR, and RBRF3B, respectively. These results were not different from the result of Experiment 1.

6. Effect of Adsorbent concentration

The results are plotted in Figure 6. It was found that the removal efficiency of dyes increased with increasing adsorbent concentration. That is, in the case of RBB the removal efficiency increased from 96.66% at 20 g/L to 99.10% at 120 g/L. For RBBR, the adsorption increased from 93.52% at 20 g/L to 97.83% at 120 g/L. While, RBRF3B, the adsorption increased from 94.32% at 20 g/L to 98.18% at 120 g/L. Moreover, the
removal efficiency almost became constant at the doses of more than 60, 80, and 40 g/L for RBB, RBBR, and RBRF3B, respectively. It was apparent that the removal efficiency of reactive dye increased rapidly with increase in the concentration of the adsorbent due to the greater availability of the exchangeable sites or surface areas at higher concentrations of the adsorbent.

7. Isotherm

 Isotherms for the removal of dyes onto bagasse fly ash are shown in Figure 7. Figures 8 (a) and (b) showed linearized Langmuir and Freundlich isotherm for the removal of dyes, respectively.

 Regression values ($R^2$) presented in Table 2, indicate that the adsorption data onto bagasse fly ash fitted well with the Langmuir isotherm for all dyes. Therefore, the recommended isotherms were presented in Langmuir equation as shown in Table 2. The values of $q_e$, separation factor, were found to be 0.3556, 0.3688, and 0.5382 for RBB, RBBR and RBRF3B, respectively. These indicate favorable adsorption. The value of $Q_o$ appeared to be more for RBBR followed by RBRF3B and RBB (Table 2). Table 3 lists the comparison of maxi-

![Figure 7. Isotherms for reactive dyes on bagasse fly ash.](image1)

![Figure 8. Linearized Langmuir isotherms (a), and Freundlich isotherms (b) for reactive dye on bagasse fly ash.](image2)
Removal of dyes using bagasse fly ash

Rachakornkij, M., et al.

Table 2. Values of Langmuir and Freundlich isotherm constants for sorption of dye.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
<th>Recommended isotherm, ( q_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_o )</td>
<td>( b )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>RBB</td>
<td>16.420</td>
<td>0.110</td>
<td>0.993</td>
</tr>
<tr>
<td>RBBR</td>
<td>32.468</td>
<td>0.019</td>
<td>0.906</td>
</tr>
<tr>
<td>RBBRF3B</td>
<td>18.282</td>
<td>0.047</td>
<td>0.966</td>
</tr>
</tbody>
</table>

Table 3. Comparison of the maximum monolayer adsorption capacities of some dyes on various adsorbents.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Adsorben</th>
<th>Maximum monolayer adsorption capacities (g/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBB</td>
<td>Activated carbon (300-500 µm)</td>
<td>434</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>RBB</td>
<td>Activated carbon (500-600 µm)</td>
<td>333</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>RBB</td>
<td>Activated carbon (600-700 µm)</td>
<td>278</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>RBB</td>
<td>Fungus</td>
<td>286-588</td>
<td>Aksu and Tezer, 2000</td>
</tr>
<tr>
<td>RBB</td>
<td>Rice husk</td>
<td>130</td>
<td>Low and Lee, 1997</td>
</tr>
<tr>
<td>RBB</td>
<td>Activated sludge</td>
<td>250</td>
<td>Aksu, 2001</td>
</tr>
<tr>
<td>RBB</td>
<td>Earth</td>
<td>260</td>
<td>Lee et al., 1999</td>
</tr>
<tr>
<td>RBB22</td>
<td>Chitosan (non-cross-linked)</td>
<td>1009</td>
<td>Wu et al., 2001</td>
</tr>
<tr>
<td>RBB22</td>
<td>Chitosan (non-cross-linked)</td>
<td>54-87</td>
<td>Juang et al., 1997</td>
</tr>
<tr>
<td>Acid Blue 29</td>
<td>Peat, fly ash</td>
<td>14,15</td>
<td>Ramakrishna and Viraraghavan, 1997</td>
</tr>
<tr>
<td>Basic Blue 29</td>
<td>Peat, fly ash</td>
<td>46,54</td>
<td>Ramakrishna and Viraraghavan, 1997</td>
</tr>
<tr>
<td>Telon Blue</td>
<td>Activated carbon</td>
<td>~160</td>
<td>McKay, 1983</td>
</tr>
<tr>
<td>Astrazone Blue</td>
<td>Silica</td>
<td>~25</td>
<td>McKay, 1984</td>
</tr>
<tr>
<td>Remazol Red</td>
<td>Activated carbon (300-500 µm)</td>
<td>400</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>Remazol Red</td>
<td>Activated carbon (500-600 µm)</td>
<td>333</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>Remazol Red</td>
<td>Activated carbon (600-700 µm)</td>
<td>213</td>
<td>Al-Degs et al., 2000</td>
</tr>
<tr>
<td>RR 189</td>
<td>Chitosan bead</td>
<td>1189</td>
<td>Chiou and Li, 2002</td>
</tr>
<tr>
<td>RR 222</td>
<td>Chitosan (non-cross-linked)</td>
<td>299-380</td>
<td>Juang et al., 1997</td>
</tr>
<tr>
<td>RR 222</td>
<td>Chitin</td>
<td>~100</td>
<td>Juang et al., 1997</td>
</tr>
<tr>
<td>RR 222</td>
<td>Activated carbon</td>
<td>~50</td>
<td>Juang et al., 1997</td>
</tr>
</tbody>
</table>

The benefit of using bagasse fly ash is two-fold since the problems associated with management of the waste are also ameliorated. Recovery and regeneration of some adsorbent is difficult, whereas the bagasse fly ash in form of adsorbent could be disposed off safely by burning after drying (Rao et al., 2002).
Conclusions

The objective of this paper was utilization of bagasse fly ash as adsorbent materials for reactive dye removal. The following conclusions have been drawn from the above investigations:

1. The removal efficiencies of RBB, RBBR, and RBRF3B through adsorption onto bagasse fly ash were found to be between 58.48-98.03%, 46.15-93.47%, and 46.30-94.60%, respectively.

2. The initial pH’s of aqueous solutions did not affect reactive dye removal. On the other hand, percent removal of reactive dye decreased with increasing initial concentration but increased with increasing adsorbent concentration.

3. The best adsorptions were obtained under the condition of 50 mg/L dye concentration and original pH solution. The suitable contact time was 240, 300, and 240 minutes for RBB, RBBR, and RBRF3B, respectively.

4. Adsorption isotherm can be described by Langmuir equation. The equation, \( q_e = \frac{(16.420\times0.110C_e)}{(1+0.11C_e)} \), \( q_e = \frac{(32.468\times0.053C_e)}{(1+0.053C_e)} \), and \( q_e = \frac{(18.282\times0.047C_e)}{(1+0.047C_e)} \) for RBB, RBBR, and RBRF3B, respectively.

5. The adsorption of RBB, RBBR, and RBRF3B onto bagasse fly ash was favorable sorption. The values of \( r \), separation factor, were found to be 0.3556, 0.6131, and 0.5382 for RBB, RBBR, and RBRF3B, respectively.

6. Bagasse fly ash has the potential for use as adsorbent for dye wastewater containing RBB, RBBR, and RBRF3B. Removal efficiencies of more than 50% can be achieved.

Acknowledgment

This research was funded by the Rajabhat Suan Dusit Institute and the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM) Chulalongkorn University.

References


