Fly ash as an adsorbent for the removal of reactive blue 25 dye from aqueous solutions: optimization, kinetic and isotherm investigations

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Abstract. Fly ash obtained from a thermal power station was used as an adsorbent for the adsorption of reactive blue 25 dye from aqueous solutions. The parameters affecting the batch adsorption studies were optimized for this system. Lagergren’s kinetic models were used for the analysis of the kinetics of dye adsorption by fly ash. It was observed that dye adsorption followed pseudo-second-order kinetics. Batch adsorption experimentation data were fitted to two well-known isotherms: the Langmuir and Freundlich models. Regression analysis showed a good fit of the Freundlich isotherm model. Based on the adsorption studies it can be concluded that the fly ash can be used as an effective adsorbent for the removal of dye from aqueous solutions.

Key words: adsorption, adsorbent, fly ash, isotherms, kinetics.

INTRODUCTION

Industries such as pulp and paper, leather, cosmetic, food, dyeing, etc. discharge effluents containing dyes as major pollutants into water bodies (Bhatnagar and Jain, 2005). Water bodies containing dyes are toxic to aquatic life (Lee et al., 1999) as well as to human beings. As they are carcinogenic and mutagenic in nature, dyes affect the functioning of kidneys, liver, and brain (Papic et al., 2000; Rajeshwari et al., 2001; Kadirvelu et al., 2003). Hence, the treatment of industrial effluents containing dyes is important in protecting habitats. Removal of residual dye from aqueous pollutants by the adsorption process has been a topic of interest for past several years (Ofomaja and Ho, 2008).

Adsorption is a simple operation and widely used in the tertiary wastewater treatment stage for polishing the incoming influent before its final discharge into water bodies (Yin et al., 2008, 2009). Even though activated carbon is regarded as an efficient adsorbent, several researchers are focusing their research interest towards using agricultural and industrial solid waste materials as adsorbents. Fly ash, one of the industrial wastes originating from burning biomass and coal, can be utilized as an adsorbent for the treatment of industrial effluents containing dyes.

India is ranked 4th in the world in the generation of fly ash as a by-product waste and 75% of the total...
power in India is generated by coal-fired thermal power stations (Senapati, 2011). One of the coal-based power stations in India, Raichur thermal power station situated 20 km north of Raichur, Karnataka, India, generates 1.19 mtpa fly ash, out of which 0.47 mtpa (39.38%) is utilized by the cement industry (0.39 mtpa) and brick manufacturers (0.08 mtpa) (Singh, 2015). This shows the abundant availability of fly ash and the need to utilize it in an effective manner.

In the present investigation, fly ash, an industrial waste, was used as the adsorbent for the adsorption of reactive blue 25 dye from aqueous solutions. The Langmuir and Freundlich isotherms were used for the analysis of adsorption equilibrium data. The kinetics of the reactive blue 25 dye adsorption was analysed by using Lagergren’s pseudo-first-order and pseudo-second-order kinetics. The following sections describe the characteristic studies of fly ash and the effect of various factors (solution pH, initial dye concentration, dye–fly ash contact period, and fly ash dosage) on reactive blue 25 dye removal along with isotherm and kinetic studies.

MATERIALS AND METHODS

Adsorbent

Fly ash used in the present study was supplied by Raichur thermal power station (RTPS), a coal-based electric power station located 20 km north of Raichur in the state of Karnataka, India. The fly ash was washed thoroughly with water and dried. The mass fraction passing through 100 µm and retained on 50 µm was used for the adsorption studies. Scanning electron microscopy (SEM) (Zeiss Supra 55 PP) together with energy dispersive X-ray (EDX) spectroscopy (Oxford INCA) were used to characterize the surface morphology (Fig. 1) and elemental composition of the fly ash, respectively. The elemental chemical composition of the fly ash was evaluated using an X-ray fluorescence spectrometer (XRF) (Philips PW2400) and is summarized in Table 1. Fly ash comprises oxides of silicon, aluminium, iron, and calcium. Various other oxides are also present but in meagre proportions. The fly ash (Class F) used in the present study contains 89.98 wt% SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ and 5.66 wt% calcium oxide. SEM observations reveal a spherical shape of particles (Convery et al., 2010). The N2 BET method (Narkis and Ben-David, 1985) employing a Quantasorb surface analyser, QS/7, mercury intrusion porosimeter, Micrometric model 9310 (Orumwense, 1996) was used to measure the surface area and porosity of the fly ash. The fly ash had a specific surface area of 0.4 m$^2$/g and porosity of 0.15 cm$^3$/g.

Table 1. Chemical composition of the fly ash used

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mass, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>63.55</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>22.71</td>
</tr>
<tr>
<td>CaO</td>
<td>5.66</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.72</td>
</tr>
<tr>
<td>MgO</td>
<td>1.48</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1.34</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.60</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.46</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.26</td>
</tr>
<tr>
<td>MnO$_4$</td>
<td>0.16</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Chemicals used

Analytical Reagent (AR) grade chemicals potassium nitrate, hydrochloric acid, and sodium hydroxide, products of MERK India, were used in the present study. Reactive blue 25 dye was kindly supplied by Forbes Campbell Knitwear, Belagavi. Stock solutions were prepared and used in the diluted form for further batch adsorption experiments.

General batch adsorption experiments

All adsorption experiments were conducted in batch mode in conical flasks. The solution pH was adjusted using NaOH/HCl. A measured quantity of fly ash was added. The contents in the flask were agitated in a LABLINE rotary shaker. At regular intervals of time, samples were drawn, centrifuged using a REMI laboratory centrifuge, and the dye concentration was analysed by spectro-photometric analysis (APHA, 1980) using a UV-Vis Spectrophotometer (Elico-BL 198) at 600 nm. The batch adsorption experiments were conducted varying one variable at a time (OVAT) to investigate effects of parameters such as pH, initial dye concentration, fly ash dosage, and agitation time on dye removal.

RESULTS AND DISCUSSION

Point of zero charge

The experiment to determine the point of zero charge (pH\(_{\text{PZC}}\)) of the fly ash was carried out as described by Ofomaja and Ho (2008) and is illustrated in Fig. 2. The adsorbent fly ash had pH\(_{\text{PZC}}\) at 5.8.

Effect of the solution pH

Figure 3 depicts the effect of the solution pH on dye adsorption. Batch adsorption studies were performed at pH values ranging from 2 to 10. Other factors: dye

![Fig. 2. Change in solution pH versus initial pH.](image)

![Fig. 3. Effect of the solution pH on reactive blue dye adsorption.](image)
initial concentration, adsorbent dosage and adsorbate–adsorbent contact period were maintained constant as 10 mg/L, 1 g/L, and 1 h, respectively. It can be seen that the amount of dye adsorbed at equilibrium ($q_e$) was 8.17 mg/g at the solution pH of 2. The corresponding dye removal efficiency was 81.65%. As the solution pH was increased to 4, the amount of dye adsorbed was drastically reduced to 4.57 mg/g with the corresponding dye removal efficiency of 45.67%. With further increase in the solution pH, the amount of dye adsorbed decreased and at pH 10 it was 3.67 mg/g (36.73% removal). Irem et al. (2013), Argun et al. (2014), and Tabak et al. (2009) observed similar trends of decreasing removal efficiency with rising solution pH. Irem et al. (2013) reported a maximum reactive navy blue dye removal of 82% at pH 2 with orange waste and Argun et al. (2014) observed a maximum reactive blue 114 dye removal efficiency of 85% at pH 2 using pomelo peel as adsorbent. Tabak et al. (2009) in their study of adsorption of reactive blue 15 anionic dye onto Turkish Sepiolite observed that the removal of dye was maximum below pH 3. In the present investigation a significant dye adsorption was achieved at pH < pH_{pzc} as reactive blue dye is anionic in nature. Similar observations were also made by Reddy et al. (2014) for anionic Congo red dye adsorption onto Bengal gram seed husk.

### Effect of the reactive blue 25 dye concentration

The effect of the initial reactive blue 25 dye concentration on dye adsorption is shown in Fig. 4. The batch adsorption experiments to investigate the effect of the initial dye concentration on dye adsorption by fly ash were carried out by varying the initial reactive blue 25 dye concentration from 10 to 90 mg/L whereas other factors were held constant: solution pH 2 (optimum value obtained from experiments), adsorbent dosage 1 g/L, and contact period between dye and fly ash 1 h. It was observed that at an initial reactive blue dye concentration of 10 mg/L $q_e$ was 8.17 mg/g (the corresponding dye removal efficiency, 81.65%). It increased with an increase in the initial dye concentration and $q_e$ at 90 mg/L was 30.63 mg/g with the corresponding dye removal efficiency of 34.04%. The increase in $q_e$ with increasing dye concentration is mainly due to the decreased mass transfer resistance as a result of an increase in the initial dye concentration/driving force and also due to the availability of adsorbent sites. It can also be observed that the dye removal efficiency decreased with an increase in the initial dye concentration.

Argun et al. (2014) conducted experiments with varying initial reactive blue dye 114 concentrations of 1 mg/L to 200 mg/L and observed decreased removal efficiency from 89% to 20%. Aksu and Isoglu (2006) varied the initial Gemazol turquoise blue-G reactive dye concentrations from 51 mg/L to 788 mg/L and observed a decrease in the dye adsorption from 77% to 28%.

The results obtained from the batch adsorption experiments conducted to study the effect of the initial dye concentration on dye adsorption were used to investigate the adsorption capacity of fly ash for reactive blue 25 dye through the well-known Langmuir and Freundlich adsorption isotherms.

![Fig. 4. Effect of the initial dye concentration on dye adsorption.](image-url)
The Langmuir adsorption isotherm (physical adsorption model) assumes monolayer adsorption and the linear form of the Langmuir isotherm is (Langmuir, 1918)

$$\frac{c_e}{q_e} = \frac{c_e}{Q_o} + \frac{1}{bQ_o}$$

(1)

where $c_e$ is equilibrium concentration of adsorbate (mg/L), $Q_o$ is adsorption capacity (mg/g), $b$ is constant (L/mg), and $q_e$ is the amount adsorbed at equilibrium (mg/g).

The Langmuir adsorption is usually expressed based on the dimensionless constant, $R_L$. This is given as

$$R_L = \frac{1}{1 + b c_0}$$

(2)

where $R_L$ is dimensionless constant and $c_0$ is the initial concentration of the adsorbate. The values of $R_L$ between 0 and 1 indicate favourable adsorption.

The Langmuir constants along with the Root Mean Square Deviation (RMSD) value are presented in Table 2. The adsorption capacities of activated carbons prepared from various biomass materials for different dyes are summarized in Table 3. The maximum adsorption capacity is 131.93 mg/g in the adsorption of reactive blue 4 onto activated carbon prepared from Enteromorpha prolifera (Sun et al., 2013) and the minimum is 3.53 mg/g in the adsorption of reactive orange by activated carbon prepared from walnut shell (Aygun et al., 2003). The fly ash had an adsorption capacity of 37.04 mg/g suggesting that it was an effectual adsorbent for the removal of reactive blue 25 dye.

The Freundlich isotherm empirical model in its linear form can be expressed as (Freundlich, 1906)

$$\log q_e = \log k_f + \frac{1}{n} \log c_e$$

(3)

where $k_f$ is adsorption capacity (mg/g) and $n$ is constant.

The Freundlich constants along with RMSD value are also summarized in Table 2. It was observed that the RMSD value of the Langmuir isotherm model was 5.04 and for the Freundlich isotherm model the RMSD value was 4.32. Based on the RMSD values, it is concluded that the dye adsorption onto fly ash follows the Freundlich isotherm.

### Table 2. Langmuir and Freundlich isotherm constants

<table>
<thead>
<tr>
<th>Dye concentration, mg/L</th>
<th>$R_L$</th>
<th>Langmuir constants</th>
<th>$Q_o$, mg/g</th>
<th>$b$, L/mg</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.40</td>
<td>37.04</td>
<td>0.05</td>
<td>5.04</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>0.18</td>
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</tbody>
</table>

### Freundlich constants

<table>
<thead>
<tr>
<th>$k_f$, mg/g</th>
<th>$n$</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.51</td>
<td>2.63</td>
<td>4.32</td>
</tr>
</tbody>
</table>

### Table 3. Comparison of adsorption capacities on activated carbons prepared from biomass materials

<table>
<thead>
<tr>
<th>Dye</th>
<th>Biomass material/adsorbent</th>
<th>Maximum adsorption capacity, mg/g</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid yellow 36</td>
<td>Rice husk</td>
<td>86.9</td>
<td>Malik, 2003</td>
</tr>
<tr>
<td>Basic blue 9</td>
<td>Coconut coir</td>
<td>15.59</td>
<td>Sharma and Upadhyay, 2009</td>
</tr>
<tr>
<td>Direct blue 106</td>
<td>Pomegranate peel</td>
<td>58.14</td>
<td>Salleh et al., 2011</td>
</tr>
<tr>
<td>Reactive blue 171</td>
<td>Enteromorpha prolifera</td>
<td>71.94</td>
<td>Sun et al., 2013</td>
</tr>
<tr>
<td>Reactive blue 4</td>
<td>Enteromorpha prolifera</td>
<td>131.93</td>
<td>Sun et al., 2013</td>
</tr>
<tr>
<td>Basic blue 9</td>
<td>Walnut shell</td>
<td>3.53</td>
<td>Aygun et al., 2003</td>
</tr>
<tr>
<td>Basic blue 9</td>
<td>Apricot shell</td>
<td>4.81</td>
<td>Aygun et al., 2003</td>
</tr>
<tr>
<td>Reactive blue 25</td>
<td>Fly ash</td>
<td>37.04</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Effect of the adsorbate–adsorbent contact time

Figure 5 depicts the effect of the adsorbate–adsorbent (dye–fly ash) contact time on reactive blue dye adsorption. Experiments were carried out by keeping the initial dye concentration (10 mg/L), adsorbent dosage (1 g/L), and solution pH (2). After every 10 min of contact time the dye adsorbed by fly ash was calculated. It was observed that 6.7 mg/g of dye (67% removal) was adsorbed by fly ash after 10 min of contact and equilibrium was achieved at 50 min of contact time (dye adsorbed = 8.17 mg/g and removal efficiency = 81.65%). Argun et al. (2014) observed optimum removal efficiency of reactive blue 114 dye at 90 min of contact between adsorbate and adsorbent (pomelo peel) and Irem et al. (2013) observed that the adsorption capacity of orange waste increased sharply for reactive navy blue dye and attained equilibrium after 120 min of contact time.

The experimental data so obtained were further utilized to investigate the adsorption kinetics. The kinetics of reactive blue dye adsorption by fly ash was analysed by using Lagergren’s pseudo-first-order and pseudo-second-order kinetics.

The linear form of Lagergren’s pseudo-first-order kinetic equation is given as (Lagergren, 1898)

$$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}$$

where \( q \) is the amount of the adsorbate adsorbed (mg/g), \( t \) is the agitation time (min), and \( K_1 \) is Lagergren’s pseudo-first-order rate constant (min\(^{-1}\)).

The linear form of the pseudo-second-order kinetic equation is (Ho and McKay, 1999)

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where \( K_2 \) is Lagergren’s pseudo-second-order rate constant (g/(mg min\(^{-1}\)).

Table 4 lists Lagergren’s pseudo-first-order and pseudo-second-order kinetic model parameters. It can be concluded, based on calculated \( q_e \) and \( q_e \) from experiments, that the reactive blue dye adsorption by fly ash follows pseudo-second-order kinetics.

<table>
<thead>
<tr>
<th>( q_e ), experiment, mg/g</th>
<th>Pseudo-first-order kinetic model parameters</th>
<th>Pseudo-second-order kinetic model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 ), min(^{-1})</td>
<td>( q_e ), mg/g</td>
<td>( K_2 ), (g/mg) min(^{-1})</td>
</tr>
<tr>
<td>8.17</td>
<td>0.094</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Fig. 5. Effect of the adsorbate–adsorbent contact time on reactive blue dye adsorption.
Effect of the fly ash dosage

The effect of the adsorbent quantity on reactive blue 25 dye adsorption is shown in Fig. 6. In order to investigate the effect of the adsorbent dosage on dye adsorption, experiments were carried out by varying fly ash quantities as 1, 1.5, 2, 2.5, 3, and 5 g/L whereas the solution pH, initial dye concentration, and adsorbate–adsorbent contact time were maintained constant as 2, 10 mg/L, and 1 h, respectively. The dye removal efficiency of 81.65% was achieved at an adsorbent dosage of 1 g/L and it increased with an increase in the adsorbent dosage. Dye removal efficiency of 88.56% was achieved at an adsorbent dosage of 2.5 g/L. With further increase in the adsorbent dosage, the dye removal efficiency was negligible. This may be due to the overlapping of adsorbent active sites because of the overcrowding of adsorbent particles (Namasivayam et al., 1998).

The optimum parameters obtained from the batch adsorption experiments are given in Table 5 for an initial dye concentration of 10 mg/L.

Table 5. Optimum parameters for the adsorption of reactive blue dye by fly ash at an initial dye concentration of 10 mg/L

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimum conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2</td>
</tr>
<tr>
<td>Adsorbent dosage, g/L</td>
<td>2.5</td>
</tr>
<tr>
<td>Adsorbate–adsorbent contact time, min</td>
<td>50</td>
</tr>
</tbody>
</table>

CONCLUSIONS

An industrial solid waste fly ash was used as an adsorbent for the adsorption of reactive blue dye from aqueous solutions. A series of batch adsorption experiments were conducted by adopting standard methodologies reported in the literature and optimum parameters affecting the adsorption of dye were obtained. It was found that the dye removal efficiency was maximum at the solution pH 2, fly ash dosage 2.5 g/L, and dye–fly ash contact time 50 min for the initial dye concentration of 10 mg/L. The experimental data were used to fit the isotherm models and to analyse the kinetics of dye adsorption by fly ash. It was observed that dye adsorption followed the Freundlich isotherm model and pseudo-second-order kinetics based on the regression analysis. The results indicate that fly ash can be utilized as an effectual adsorbent.

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REFERENCES


Lendtuhk adsorbendina Reactive Blue 25 värvi eraldamiseks vesilahustest:
adsorptsioonikineetika ja isotermid ning süsteemi parameetrite optimeerimine

Umesh B. Deshannavar, Basavaraj G. Katageri, Mohanad El-Harbawi, Ambika Parab ja Kiran Acharya