Removal of Hazardous Organic Pollutants Using Fly Ash

Ahmed Eteba¹, M. Bassyouni²³*, Mamdouh Saleh¹

¹Sanitary and Environmental Engineering, Department of Civil Engineering, Faculty of Engineering, Port Said University, Egypt
²Department of Chemical Engineering, Faculty of Engineering, Port Said University, Egypt
³Materials Science Program, University of Science and Technology, Zewail City of Science and Technology, Egypt

Received June 6, 2021; Revised July 28, 2021; Accepted August 22, 2021

Abstract This study aims to achieve the highest removal efficiency of direct blue dye using a low-cost adsorbent. The adsorption of direct blue 78 dye (DB78) with commercial name (Tubantin blue GLL 300) from a synthetic wastewater using a raw coal fly ash was studied. The ability of coal fly ash (industrial by product) as cost-effective adsorbent to remove dyes from textile wastewater effluent was investigated in detail. A series of batch experiments were conducted in terms of adsorbent dose, contact time, pH, and initial concentration of dye. The raw coal fly ash was characterized by physico-chemical analysis namely; X-ray diffraction (XRD), X-ray fluorescence (XRF) and Brunauer–Emmett–Teller (BET). It was found that the major phases for coal fly ash are quartz and hematite. Loss of ignition percentage and surface area are 36% and 9.6113 m²g⁻¹ respectively with average particles size 624 nm. The adsorption tests showed that the removal efficiency increases with increasing adsorbent dosage and contact time. Removal efficiency decreases at high initial concentration of direct blue 78 dye. The maximum capacities for dyes removal reached to 99.1% with initial concentration 10 mg/l and fly ash dose 3 g/l. Dyes removal (98.4%) was obtained using initial concentration 20 mg/l and fly ash dose 4 g/l. At higher initial concentration (30 mg/l) using fly ash dose 5 g/l, lower removal efficiency was obtained with 97.2%. The Langmuir isotherm model was shown to have a higher coefficient of determination R² than the Freundlich isotherm model in representing the fly ash adsorption process.

Keywords Fly Ash, Adsorption, Organic Hazardous, Wastewater

1. Introduction

Water pollution by chemicals has become a main source of concern and a priority for society and public authorities and more critically for the whole industrial world. Water pollution can be defined in many ways. Water pollution occurs when one or more substances that will modify the water in negative fashion are discharged in it. These substances can cause problems for people, animals and their habitats and also for the environment. Textile industry is considered as one of the most popular industries that causes water pollution. An enormous amount of toxic liquid wastes which contain complex pollutants have been produced as a result of increasing of textile dyeing industries [1]. It was reported that approximately 100 tons of dyes are discharged into waste streams by textile industries by year [2]. Dyes are considered a horrible type of pollutant on aquatic environment because they give an un-desirable color to the water [3], which reduce light penetration and photosynthesis and represent a main threat to the environmental ecology and public health if left without proper treatment process [4-11]. Most of these dyes are considered to be non-biodegradable substances by traditional physical and biological treatment processes [12, 13].
Amongst several dyes removal treatment processes, adsorption is considered as one of the most adaptable treatment technologies. Activated carbon is commonly used as adsorbent because of its availability and remove efficiency for different types of toxic pollutants from water and wastewater effluent. However, its high cost and reusing draw the attention of the researchers to find alternative materials and low-cost adsorbents. Therefore, several efforts have been made to find out available, low cost and effective adsorbent using a various material [14-19].

Many solid waste materials as by products are generated from several industrial activities. Several studies have been conducted to find out a better low-cost adsorbents such as fly ash, saw dust, municipal solid waste, red mud, zeolites and sugar industry waste. Coal fly ash (CFA) amongst many industrial solid wastes (by-product) is considered a very encouraging low-cost adsorbent because of its aptitude to abstraction of different types of venomous non-biodegradable dyes from colored effluents [20]. The research on utilization of fly ash related to dyes removal and wastewater treatment by adsorption as of increasing importance as can be shown from the number or yearly published papers shown in Figure 1.

The novelty of this study is to treat textile industrial wastewater efficiently using coal fly ash as a low-cost adsorbent.

2. Materials and Methods

2.1. Adsorbent Materials and Dyes

A sample of a raw coal fly ash (RCFA) was obtained from a cement factory based on coal in Egypt. The RCFA samples was sieved and only the particles have size less than 75 µm has been used in this study. RCFA sample was washed using a distilled water, filtered and left to dry at 110°C for 12 hours, however. The final solids particles then subjected to physico-chemical analysis.

The direct blue 78 (DB78) dye with commercial name (Tubantin GLL 300), relative molecular mass 1059.95, max wave length $\lambda_{max}$=604 nm and solubility up to 10 g/l at 25°C, has been selected for adsorption tests. The chemical structure is displayed in Figure 2. Three synthetic dye solutions with differing dye concentration (10, 20 and 30mg/l) respectively was prepared for adsorption studies.

![Figure 2. Chemical structure of direct blue 78 dye (Tubantin blue GLL 300).](image)
Direct dyes have a high harmful effect on environment because it has a high water solubility leading to difficulty on pollutants removal using conventional methods. The presence of chromophoric groups in the direct blue 78 dye makes it easy to be dispersed in wastewater. These colors disrupt the water bodies aesthetically, contributing to a decline in the rate of photosynthesis and dissolved oxygen levels affecting the entire aquatic biota [21].

2.2. Characterization of Adsorbent

The phases of the raw coal fly ash samples were investigated by XRD analysis (Bruker D8 diffractometer, Germany) with aid of Empyrex diffractometer system. Copper as an anode material was operated at 45 KV and 30 mA over the range 5-90° with step size of 0.026, scan step time 21.42 second and Goniometer radius 240 mm. These measurements are conducted at temperature 25°C.

The chemical composition of coal fly ash was determined using XRF analysis (Axios advanced, Sequential WD_XRF Spectrometer, Panalytical 2005, Malvern, UK).

The surface area of the raw coal fly ash samples was measured in the presence of N₂ adsorption at -195.65°C using surface area analyzers (Autosorb-l-C-8, Quantachrome, USA.). Prior to adsorption studies, the samples were degasified at 200°C for 4 hours. By applying BET (Brunauer-Emmett-Teller) equation to adsorption data, the BET surface area for the sample was determined.

The colorimetric analysis was done in this study using (LAMOTTE smart spectrophotometer v3 2000-01-MN, USA).

The pH of the raw coal fly ash samples were determined by mixing of 0.1g from sample with 100 of distilled water, mixing speed was 100 r.p.m, for period 3 hours and temperature 25°C using (Digital pH meter, Omega CDS107, Taiwan).

2.3. Adsorption Studies

These study was conducted using dis-continuous batch adsorption system (lab scale) on a single component synthetic wastewater. Coal fly ash samples used in this study were (1-7) g in 1000 ml of synthetic wastewater with differing initial concentration (10, 20 and 30) mg/l was mixing at 500 rpm for contact time (0.105) min at a room temperature (25 ± 2°C).

The spectrophotometrically analysis was applied to determine the removal efficiency by measuring dyes concentration before and after adsorption process at \( \lambda_{\text{max}} = 600 \text{ nm} \) for DB78.

3. Results and Discussion

3.1. Characterization of Adsorbent

From X-ray diffraction curve for RCFA with a particle size \( \leq 75 \mu \text{m} \) seen in the diffractogram Figure 3. It has been found that the RCFA sample consists of some crystalline sharp peaks resulted from the presence of some minerals phases such as quartz, mullite, hematite and lime and some amorphous phases caused by the presence of a chemically stable glassy surface layer forming by quartz which characterized by a very strong intensity and mullite.

![XRD pattern for raw coal fly ash sample.](image-url)
The chemical compositions of raw coal fly ash (RCFA) are 33.14% lime (CaO), 2.35% silica (SiO₂), 0.44% alumina (Al₂O₃), 0.04% titanium dioxide (TiO₂), 6.73% magnesium oxide (MgO), 0.43% hematite (Fe₂O₃), 3.41% sodium oxide (Na₂O), 8.42% potassium oxide (K₂O), 3.59% phosphorus pentoxide (P₂O₅), 2.22% sulfur trioxide (SO₃), 2.61% chlorine (Cl) and LOI (36.16%) as listed in table 1. Trace metal oxides such as MnO, NiO, CuO, ZnO, PbO and SrO were detected.

<table>
<thead>
<tr>
<th>Main constituents</th>
<th>% Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.35</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.44</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.43</td>
</tr>
<tr>
<td>MgO</td>
<td>6.73</td>
</tr>
<tr>
<td>CaO</td>
<td>33.14</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.41</td>
</tr>
<tr>
<td>K₂O</td>
<td>8.42</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>3.59</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.22</td>
</tr>
<tr>
<td>Cl</td>
<td>2.61</td>
</tr>
<tr>
<td>LOI</td>
<td>36.16%</td>
</tr>
</tbody>
</table>

Table 2 presents some of physico-chemical properties of RCFA sample. The BET surface area is generally increase with increasing of unburnt carbon, in this study the BET surface area is about 9.6113 m²g⁻¹. The high percentage of unburnt carbon in RCFA sample lead it to have a highly porous structure, the maximum volume of its pores is about 0.0149 cm³g⁻¹ with median pore width 25.636 nm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area S_BET</td>
<td>9.6113 m²g⁻¹</td>
</tr>
<tr>
<td>Maximum pore volume</td>
<td>0.0149 cm³g⁻¹</td>
</tr>
<tr>
<td>Average particles size</td>
<td>624.26 nm</td>
</tr>
<tr>
<td>Median pore width</td>
<td>25.636 nm</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>36.16 %</td>
</tr>
</tbody>
</table>

3.2. Adsorption Tests

3.2.1. Effect of adsorbent dose on dye removal efficiency

It has been experimentally observed from Figure 4 that the removal of dye from solution increases with increasing of adsorbent quantity until reaching the maximum removal percentage and then approximately reach a constant value. Experiments were also made by varying the amount of RCFA from 1 to 7 g/l on DB78 dye solution with different initial concentration (10, 20 and 30) mg/l at fixed pH, temperature, mixing speed and contact time.

It was observed from batch adsorption tests that solution with initial dye concentration 10 mg/l, the maximum removal percentage was 99.1% by using adsorbent dose 3 g/l and equilibrium loading 3.3 mg/g. For solution with initial dye concentration 20 mg/l, the maximum removal percentage was 98.4% by using adsorbent dose 4 g/l and equilibrium loading 4.9 mg/g. For initial dye concentration 30 mg/l, the maximum removal percentage was 97.2% by using adsorbent dose 5 g/l and equilibrium loading 5.8 mg/g.

Figure 4. (a) Effect of quantity of adsorbent RCFA on dye removal efficiency (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min and particles size <75µm). (b) Effect of quantity of adsorbent RCFA on adsorbent loading (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min and particles size <75µm).

3.2.2. Effect of contact time on dye removal efficiency

Figure 5 shows the effect of contact time on both percentage of dye removal and adsorbent maximum loading. It is experimentally observed that, the percentage of dye removal increase with increasing of contact time even reach the optimum removal efficiency (equilibrium concentration Cₑ) at this time the adsorbent is reaching its maximum loading capacity (equilibrium loading qₑ). For 60 min contact time, 2 g/l as adsorbent dose of RCFA, the equilibrium concentration decreased to 0.3 mg/l with dye removal efficiency 96.85% and optimum loading capacity 4.84 mg/g for initial dye
concentration of 10 mg/l solution, the equilibrium concentration decreased to 1.9 mg/l with dye removal efficiency 90.35\% and optimum loading capacity 9 mg/g for initial dye concentration of 20 mg/l solution and the equilibrium concentration decreased to 10.1 mg/l with dye removal efficiency 66.3\% and optimum loading capacity 9.95 mg/g for initial dye concentration of 30 mg/l solution.

The adsorbent capacity is also effected by initial dye concentration. Figure 6(b) shows that the adsorbent loading increase with increasing of initial dye concentration at constant adsorbent dose and contact time. For adsorbent dose 1 g/l, the adsorbent capacity increase from 8.4 to 11.6 mg/l. For adsorbent dose 2 g/l, the adsorbent capacity increase from 4.8 to 9.9 mg/l, for adsorbent dose 3 g/l, the adsorbent capacity increase from 3.3 to 9 mg/l and For adsorbent dose 4 g/l, the adsorbent capacity increase from 2.4 to 7.1 mg/l. Respectively with increasing of initial concentration from 10 to 30 mg/l.

3.2.3. Effect of dye initial concentration on removal efficiency

The direct blue 78 (DB78) dye solutions having initial concentrations of 10, 20 and 30 mg/l have been verified to examine effect of initial dye concentration on percentage of dye removal. Figure 6(a) shows that for adsorbent dose 1 g/l, the removal efficiency was (84, 54 and 39), for adsorbent dose 2 g/l, the removal efficiency was (96.9, 90.4 and 66.3), for adsorbent dose 3 g/l, the removal efficiency was (99.1, 97.4 and 90.2) and for adsorbent dose 4 g/l, the removal efficiency was (99.6, 98.4 and 95.1). Respectively for (10, 20 and 30) mg/l as dye solutions initial concentration. Based on figure 6(a), the adsorption process is highly dependent on initial concentration of dyes.

3.2.4. Effect of pH on removal efficiency

It has been experimentally observed from Figure 7 that the removal of dye from solution increases with increasing of solution pH until reaching the maximum removal percentage and then started to decrease again. Experiments were also made by varying the solution pH from 3 to 10 on DB78 dye solution with initial concentration 10 mg/l at fixed adsorbent dose, temperature, mixing speed and contact time.

It was observed from adsorption tests that for solution with initial dye concentration 10 mg/l, the maximum removal percentage was 85 \% by using adsorbent dose 1 g/l and solution pH range (8:9).
3.3. Adsorption Isotherm

As shown in figure 8, the adsorption isothermal model indicates the quantity of adsorbate DB78 dye that can be adsorbed by the adsorbent RCFA qe in comparison to the adsorbate concentration in the liquid state (Ce). These are essential considerations in the design of adsorption systems. Also, the form of the equilibrium curve helps to describe other phenomena linked with the adsorbent-adsorbate interaction. The equilibrium curves are identified in four main classes according to the primary slope and subgroups are described for each Class, based on upper parts shapes and slope changes. (a) S curves or vertical orientation isotherm. (b) L curves or normal or “Langmuir” isotherms. (c) H curves or high affinity isotherms. (d) C curves or constant partition isotherm. [22]

The initial shape of the equilibrium curve (L shape) in figure 8 follows the basic premise that the higher the solute concentration, the greater the adsorption capacity until the number of adsorption site clearance is limited, occurring competition between solute molecules for the available sites. This isotherm type indicated that the adsorption occurs due to relatively weak forces, such as "van der Waals forces". There are several isothermal models (equations) are available and the two important isotherms are selected in this study, the Freundlich and Langmuir isotherms.

The Freundlich isotherm believes that the adsorption happens on a heterogeneous surface, and the adsorbed mass increases exponentially with an increase in concentration [23]. This isotherm explains equilibrium on heterogeneous Surfaces and hence capacity is not presumed monolayer. In liquid phase, this isotherm is given by Eq. (1):

$$Q_e = K_f C_e^{1/n_f}$$  

(1)

Where $k_f$ is the Freundlich fixed value ($k_f$ unit = mg/g where $c = 1 / n_f$ is the heterogeneity factor). This isotherm focuses on integrating the role of adsorbent – adsorbate surface interactions. Figure 9 indicates the application of equilibrium data according to Freundlich isotherm. The Freundlich constant $k_f$ values were (7.48, 7.04 and 6.57) and the heterogeneity factor $1/n$ values was (0.38, 0.37 and 0.19) respectively for solution with initial concentration (10, 20 and 30) mg/l.

![Figure 7. Effect of solution pH on dye removal efficiency. (temperature 20 °C, dose 1 g/l, mixing speed 500 r.p.m, contact time 60 min, and particles size <75µm).](image)

Figure 7. Effect of solution pH on dye removal efficiency. (temperature 20 °C, dose 1 g/l, mixing speed 500 r.p.m, contact time 60 min, and particles size <75µm).

![Figure 8. Adsorption isotherm of RCFA for direct blue 78 dye removal. (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min, adsorbent dose (1.7) g/l, initial dye concentration (10, 20 and 30) mg/l and particles size <75µm).](image)

Figure 8. Adsorption isotherm of RCFA for direct blue 78 dye removal. (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min, adsorbent dose (1.7) g/l, initial dye concentration (10, 20 and 30) mg/l and particles size <75µm).

The Langmuir isotherm believes that sorption occurs within the adsorbent at different homogeneous sites and has been successfully applied to several processes of sorption. The isotherm's physical simplicity is based on some assumptions [24]. Adsorption cannot occur beyond monolayer coverage. Each site can hold only one adsorbate molecule. All sites are energetically equivalent and the surface is uniform. The linear form of Langmuir isotherm is given by the following equation Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{C_e}{Q_0}\right)$$  

(2)

Where $C_e$ is the equilibrium concentration (mg / l), $q_e$ the mass adsorbed at equilibrium (mg / g), $Q_0$ the adsorbent loading (mg / g) and b is the adsorption energy (Langmuir fixed value 1 / mg). The values of $Q_0$ and b were determined from the slope and intercept of the linear plots $C_e / q_e$ versus $C_e$, resulting in a straight line of slope $1 / Q_0$ corresponding to the total coverage of Monolayer (mg / g) and the intercept is $1/Q_0b$ [25].

![Figure 9. Freundlich adsorption isotherm of RCFA for direct blue 78 dye removal. (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min, adsorbent dose (1.7) g/l, initial dye concentration (10, 20 and 30) mg/l and particles size <75µm).](image)

Figure 9. Freundlich adsorption isotherm of RCFA for direct blue 78 dye removal. (temperature 20°C, pH (9.2), mixing speed 500 r.p.m, contact time 60 min, adsorbent dose (1.7) g/l, initial dye concentration (10, 20 and 30) mg/l and particles size <75µm).
Removal of Hazardous Organic Pollutants Using Fly Ash

Figure 10. Langmuir adsorption isotherm of RCFA for direct blue 78 dye removal. (temperature 20°C, pH 9.2, mixing speed 500 r.p.m., contact time 60 min, adsorbent dose (1:7) g/l, initial dye concentration (10, 20 and 30) mg/l and particles size <75 µm).

Figure 10 indicates the application of equilibrium data according to Langmuir isotherm. The adsorbent loading values (Q0) were (8.9, 11.3 and 11.7) mg/g. Langmuir fixed value (b) values was (7.3, 2.53 and 0.135) l/mg. respectively for solution with initial concentration (10, 20 and 30) mg/l.

As listed in table 3, adsorption isothermal models equilibrium results followed closely Freundlich and Langmuir isotherm but the latter isotherm better suited the results.

4. Conclusion

Removal of direct blue 78 dye (Tubantin GLL 300) from aqueous solutions by adsorption with RCFA has been experimentally examined using a single component synthetic wastewater applied in batch experiments and the following observations are made: The dye removal efficiency increase with increasing RCFA dosage, improve with increasing contact time and reduce with increasing initial dye concentration. It is observed from the experimental studies that the maximum capacities for dyes removal were respectively, 99.1% (Initial concentration 10 mg/l), 98.4% (Initial concentration 20 mg/l) and 97.2% (Initial concentration 30 mg/l), the raw coal fly ash adsorption capacity was (3.3, 4.9 and 5.8 mg/g) respectively for solution with initial concentration (10, 20 and 30 mg/l). Equilibrium studies have shown that the initial shape of the equilibrium curve (L shape) which means that the adsorption process resulted from electrostatic interaction between dyes molecules and fly ash particles (physical forces). And Langmuir isothermal model best suited the equilibrium results. Even though the contact times and dosages required for fly ash are more than the conventional adsorbents. Taking high costs of conventional adsorbents into consideration fly ash can be used as a cost-effective adsorbent for dyes removal for colored effluents.

Acknowledgment

Corresponding author would like to acknowledge the assistance provided by the Science and Technology Development Fund (STDF) for funding the project, No. 41902 (Center of Excellence in Membrane- based Water Desalination Technology for Testing and Characterization).

<table>
<thead>
<tr>
<th>Initial concentration (mg/l)</th>
<th>Langmuir isothermal</th>
<th>Freundlich isothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q0 (mg/g)</td>
<td>b (1/mg)</td>
</tr>
<tr>
<td>10</td>
<td>8.99</td>
<td>7.318</td>
</tr>
<tr>
<td>20</td>
<td>11.3</td>
<td>2.528</td>
</tr>
<tr>
<td>30</td>
<td>11.75</td>
<td>0.135</td>
</tr>
</tbody>
</table>
REFERENCES


