Adsorption technology involving use of low cost adsorbent provides an economical and eco-friendly option for treating dye wastewaters studded with different type and concentration of various organic pollutants. Present work focuses on various activation techniques of fly ash and its use as an adsorbent. An activation technique of fly ash includes heat treatment (CFA 600), Alkali treatment (CFA NaOH) and Acid treatment (CFA HCl). From experimental study it was observed that raw coal fly ash CFA and CFA HCl had superior adsorbing ability than two modified coal fly ashes (CFA-600 and CFA-NaOH) for the dye Acid Orange 7 (AO7). The adsorption capacities followed the order CFA HCl > CFA> CFA-600 > CFA-NaOH. The adsorptions of AO7 onto CFA, CFA-600, CFA HCl and CFA-NaOH all followed pseudo-second-order kinetics. The isotherm for the adsorption of AO7 onto the raw and modified coal fly ash fits the Temkin isotherm. This study includes the application of these adsorbents in batch application by varying the parameters such as dosage of adsorbent, contact time, initial concentration, and pH.

Key words: Adsorption, Coal fly ash, Kinetics, Isotherms, AO7.

Introduction

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. In principle adsorption can occur at any solid fluid interface. Adsorption is one of the established unit operations used for the treatment of contaminated water i.e. raw water and/or wastewater. Adsorption studies are usually conducted over batch studies and column studies. Activated carbon is the most used adsorbent. Due to its high cost and considering the enormous quantity of effluent produced by textile industries, researches are turning toward the use of alternative adsorbents, also called non-conventional low-cost adsorbents.

Many industries like plastics, paper, textile and cosmetics use dyes to color their products. These dyes are common water pollutants and they may be frequently found in trace quantities in industrial wastewater. Their presence in water, even at very low concentrations, is highly visible and undesirable. In addition, many dyes are difficult to degrade due to their complex aromatic structure and they tend to persist in the environment and creating serious water quality and public health problems. Therefore, it would be advantageous to develop technologies to eliminate them. Dyes can be effectively removed by adsorption process in which dissolved dye compounds were attached to the surface of adsorbents [26].

Numerous studies have been conducted to assess the harmful impacts of colorants on the ecosystem. It was found that dyes may cause problems in water in several ways:

i. Dyes can have acute and/or chronic effects on exposed organisms with this depending on the dye concentration and on the exposure time.

ii. Dyes are inherently highly visible, minor release of effluent may cause abnormal coloration of surface waters which captures the attention of both the public and the authorities.

iii. The ability of dyes to absorb/reflect sunlight entering the water, this has drastic effects on the growth of bacteria and upsets their biological activity.

iv. Dyes have many different and complicated molecular structures and therefore, are difficult to treat and interfere with municipal waste treatment operations.

v. Dyes in wastewater undergo chemical and biological changes, consume dissolved oxygen from the stream and destroy aquatic life.
Increasing demand for energy throughout the world has led to an increase in the utilization of coal and, subsequently, in producing large quantities of fly ash as a waste product [6].

The disposal of coal fly ash from coal-based power plant is a problem of global concern today. In India, most of the utility thermal power and sub-bituminous coal with high ash content (30-50%) resulting in the huge quantity of fly ash. Only a small portion of this huge quantity is used as a raw material for concrete manufacturing and construction purposes, remainder being simply dumped on the landfill sites. Currently, more than 90 million tons of fly ash is being generated annually in India, with 65000 acres of land being occupied by ash ponds. Without proper disposal options, such a huge quantity of ash has posed a great threat to the environment [37].

Since fly ash is enriched with SiO₂ and Al₂O₃, this waste product can be transformed into zeolite-like crystalline materials as a result of chemical treatment. Zeolite is porous material with large surface area and cavities of the basket-like frame. Hence, it has been used for various purposes, e.g., absorbent and ion exchanger in water and wastewater treatment [6].

Materials and methods
Preparation of Adsorbents
Dry coal fly ash is collected from coal fired boiler with the help of electrostatic precipitators or bag house filter. It is being stored and used directly as adsorbent or used for activation or modification to use it as adsorbent.

Modification of Fly ash
Heat treatment
One portion of the coal fly ash sample is washed for removal of soluble impurities and oven dried for 105°C for 24 hours and then used as adsorbent(CFA).

Another portion of the coal fly ash sample was treated in a furnace at 600 °C for 4 h and then stored in a desiccator prior to use (CFA- 600) [41, 43].

Alkali treatment
The CFA sample is treated with 1 M sodium hydroxide (NaOH) solution in 10:1 (NaOH:CFA) ratio and then the mixture was kept on a hot plate at 100 °C for 24 h. After agitation, the solid was recovered by filtration and washed thoroughly with water to remove excess NaOH. The recovered product, termed as modified fly ash, was dried at 105 °C for 24 h and used for the adsorption study (CFA-NaOH) [34, 35, 41].

Acid treatment
The sample was oven-dried at 105 °C for 24 h before use. The fly ash was treated in a 1 M solution of HCl at a solution to fly ash ratio of 2:1 by weight. The mixture was then incubated at 100 °C for 24 h. At the end of the treatment, the mixture was filtered, washed thoroughly and oven-dried at 105 °C for 24 h. The final solid products were then subjected to adsorption studies (CFA-HCl) [6, 35, 33, 41].

Preparation of Adsorbate
Acid Orange dye C.I 7 was used as the adsorbate in this study. AO7 has maximum UV-Vis absorbance at a wavelength of 490 nm. An accurately weighed quantity of the dye was dissolved in distilled water to prepare a stock solution (1000 mg/L). Experimental solutions of the desired concentrations were obtained through successive dilutions with distilled water.

Experimental Method
Dye adsorptions on the prepared adsorbents were carried out in a batch system to determine their dye removal capacity. A desired amount of adsorbent is added to the synthetic dye solution of known concentration and known quantity. This practical is carried out at different pH for determining optimal pH at which adsorbent give best result. pH is adjusted using 0.1 M HNO₃ and 0.1 M NaOH. The solution was agitated by the use of magnetic stirrer at room temperature. The samples were withdrawn from the experimental flask at pre-determined time intervals. Then the dye solution is separated from the adsorbent by using filter paper to ensure the solution is free from adsorbent before measuring the residual dye concentration.

Adsorption kinetics and isotherm experiments for the various CFA samples were undertaken in a batch equilibrium system. For kinetics studies, the adsorption of AO7 was studied.
after adding the adsorbent into an aqueous solution containing AO7 (10–30 mg/L) and stirred at various reaction times. The equilibrium, which was determined by dynamic adsorption studies, was established within 1–1.5 h; therefore, the contact time was fixed at 1.5 h. The adsorption isotherms of AO7 were studied after adding adsorbent into the aqueous solution containing a desired AR1 concentration (10–30 mg/L).

**Analytical method**

The UV scans of the samples were done using UV-visible spectrophotometer which range is 200 nm to 800 nm. Decolourization was determined by measuring the absorbance of the solution at the 490 nm wavelength. The decolourization of dye was detected using a spectrophotometer and the decolourization ratio was calculated from the following equation.

\[
\text{Color Removal (\%)} = \left( \frac{A_i - A_f}{A_i} \right) \times 100
\]

where,

\(A_i\) = Absorbance before Treatment, \(A_f\) = Absorbance after Treatment.

The adsorption capacity of dyes was then calculated from

\[Q_e = \frac{V \Delta C}{m}\]

Where, \(V\) is the volume of the liquid phase, \(m\) is the mass of the solid, and \(\Delta C\) is computed simply from the difference between initial and final concentration obtained from UV readings.

**Results and discussion**

**Effect of Initial pH of dye solution**

The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying the initial pH of dye solution and keeping the other process parameters as constant. Maximum color removal obtained at lower pH for CFA sample. At Higher pH value i.e at pH 12 both activation CFA 600 and CFA HCl gives maximum removal. Activation CFA NaOH yield maximum color removal at neutral pH.

**Figure 3.1** Graphs Showing Effect of pH


[417-429]
Effect of Adsorbent dosage

For dye concentration of 15 mg/L effect of dosage of different adsorbent were studied by varying dosage from 0.1 to 0.3 gm/100 ml, keeping pH and initial dye concentration as constant. The results are shown in the figure. For CFA and CFA HCl activation 0.25 gm of adsorbent dosage gives 100 percent dye removal within one hour. Further increase in dosage was not required. This can be seen from nearly constant percentage removal obtained for higher dosages. It is obvious that an increase in adsorbent dosage increases available surface area and active cites.

Effect of Initial dye concentration

The effect of initial dye concentration on percentage removal is shown in figure. It is seen from figure that dye adsorption increases with increase in initial concentration of dye. Same figure also indicates that the percentage removal was found to decrease with increase in the initial concentration of dye while the amount of dye adsorption increases with increase in initial concentration. The reason may be that there exists reduction in immediate solute adsorption owing to lack of active sites required for high initial concentration of dye.
Adsorption Isotherm

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Langmuir and Freundlich isotherms were used to describe the equilibrium characteristics of adsorption. An accurate isotherm is important for design purposes. Linear regression is commonly used to determine the best fit model, and the method of least squares has been widely used for obtaining the isotherm constants.

One of the most popular adsorption isotherms used for liquids to describe adsorption on a surface having heterogeneous energy distribution is Freundlich isotherm. It is given as:

\[ q_e = K_F C_e^{1/n} \]

Freundlich isotherm is derived assuming heterogeneity surface. \( K_F \) and \( n \) are indicators of adsorption capacity and adsorption intensity, respectively. Rearranging Equation we get,

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

A plot of log \( q_e \) versus log \( C_e \) yields a straight line, with a slope of \( 1/n \) and intercept of \( \ln K_F \). The value of Freundlich constant \( n \) should lie in the range of 1–10 for favourable adsorption.

Langmuir isotherm, applicable for homogenous surface adsorption, is given as:

\[ q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \]

Above equation can be rearranged into linear form:

\[ \frac{1}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} \]

By plotting \( 1/q_e \) versus \( 1/C_e \), the Langmuir constants can be obtained. The essential characteristics of Langmuir isotherm can be expressed by a separation or equilibrium parameter, which is a dimensionless constant defined as:

\[ R_L = \frac{1}{1 + K_L C_0} \]

\( R_L \) indicates the nature of adsorption as indicated below:

- Unfavourable \( R_L > 1 \);
- Linear \( R_L = 1 \);
- Favourable \( 0 < R_L < 1 \);
- Irreversible \( R_L = 0 \).

Temkin Adsorption Isotherm model is given by,

\[ q_e = \ln A + \ln C_e \]

It’s linear expression, \( q_e = \ln A + \ln C_e \)

Where \( A \) is the equilibrium binding constant related to the heat of adsorption. The plot of \( q_e \) Vs \( \ln C_e \) is used to determine the isotherm constant \( A \). The basic assumptions of this model are that the heat of adsorption of the ions in a layer decreases linearly due to the adsorbent – adsorbate interaction and that the binding energies are uniformly distributed.

**Nomenclature**

- \( C_0 \): initial dye concentration in aqueous solution (mg/dm³)
- \( C_e \): equilibrium dye concentration in liquid phase (mg/dm³)
- \( C_t \): dye concentration in aqueous solution at time \( t \) (mg/dm³)
- \( D \): adsorbent dosage (g/dm³)
- \( K_1 \): pseudo-first-order rate constant (min⁻¹)
- \( K_2 \): pseudo-second order rate constant (g mg⁻¹ min⁻¹)
- \( K_F \): Freundlich constant (mg g⁻¹ (dm³/mg)¹/n)
- \( K_i \): intraparticle diffusion rate constant (mg g⁻¹ min⁰.⁵)
- \( K_L \): Langmuir adsorption constant (dm³ mg⁻¹)
- \( 1/n \): Freundlich parameter
- \( q_e \): equilibrium dye concentration in liquid phase (mg g⁻¹)
- \( q_{esp} \): equilibrium dye concentration in solid phase (mg g⁻¹)

The values of $Q_m$, $K_L$, $R_L$, $K_F$, $n$, $A$ and the linear regression correlations for the Langmuir, Freundlich

and Temkin isotherms are given in Table 1. Because the regression coefficients ($R^2$) for the Langmuir, Freundlich and Temkin isotherm were 0.3791–0.8428, 0.6597–9557 and 0.7448–0.9796, respectively, it appears that the Temkin model yielded a much better fit than the Langmuir and Freundlich model. For the four adsorbents, the maximum adsorption capacities ($Q_m$) at various concentrations decreased in the order 30 > 15 > 10 mg/L.

![Temkin Isotherm for CFA](image)

![Temkin Isotherm for CFA 600](image)
### Table 1

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye Conc.</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFA</td>
<td>10</td>
<td>2.19</td>
<td>2.15</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>4.48</td>
<td>9.38</td>
<td>0.01</td>
</tr>
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<td></td>
<td>30</td>
<td>6.11</td>
<td>0.84</td>
<td>0.04</td>
</tr>
<tr>
<td>CFA 600</td>
<td>10</td>
<td>2.40</td>
<td>0.02</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.78</td>
<td>9.29</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.58</td>
<td>0.49</td>
<td>0.06</td>
</tr>
<tr>
<td>CFA HCl</td>
<td>10</td>
<td>2.65</td>
<td>5.82</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>3.54</td>
<td>1.88</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>6.74</td>
<td>0.98</td>
<td>0.03</td>
</tr>
<tr>
<td>CFA NaOH</td>
<td>10</td>
<td>1.58</td>
<td>1.41</td>
<td>0.07</td>
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<tr>
<td></td>
<td>15</td>
<td>1.94</td>
<td>0.96</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>3.51</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table I: Langmuir, Freundlich and Temkin constants for CFA, CFA-600, CFA HCl and CFA-NaOH
Adsorption kinetic studies

The transient behaviour of the dye sorption process was analysed by using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Application of a single kinetic model to sorption on solid adsorbents may be questionable because of the heterogeneity of adsorbent surfaces and diversity of adsorption phenomena.

3.5.1 Pseudo-first-order model

The pseudo-first-order kinetic model has been widely used to predict dye adsorption kinetics. The pseudo-first-order rate expression suggested originally by Lagergren based on solid capacity is expressed as follows.

\[ \frac{dq_i}{dt} = K_1(q_e - q_i) \]

Integrating and applying boundary conditions \( q(i=0) = 0 \) and \( q(i=\infty) = q_e \), we get,

\[ \ln(q_e - q_i) = \ln(q_e - q_0) - K_1t \]

Values of \( q_e \) and \( K_1 \) can be obtained from the slope and intercept of the plot \( \ln(q_e - q_i) \) versus \( t \).

3.5.2 Pseudo-second order model

Pseudo-second order model is expressed by the equation.

\[ \frac{dq_i}{dt} = K_2(q_e - q_i)^2 \]

Integrating and applying boundary conditions \( q(i=0) = 0 \) and \( q(i=\infty) = q_e \), we get,

\[ \frac{1}{q_e - q_i} = \frac{1}{q_e} + K_2t \]

We can rearrange above equation as:

\[ \frac{t}{q_i} = \frac{1}{K_2q_e} + \frac{t}{q_e} \]

Values of \( q_e \) and \( K_2 \) can be obtained from the slope and intercept of the plot \( t/q \) versus \( t \).

3.5.3 Intraparticle diffusion studies

It is necessary to identify the steps involved during adsorption in order to interpret the mechanism of adsorption. It is assumed that the adsorption process consists of several steps. Migration of the dye from the bulk of the solution to the sorbent surface, diffusion of the dye through the boundary layer, intraparticle diffusion, and adsorption of the dye on the internal sorbent surface.

The intraparticle diffusion rate can be expressed in terms of the square root time. The mathematical dependence of \( q_t \) versus \( t^{0.5} \) is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution. The root time dependence, the intraparticle diffusion model is defined as follows:

\[ q_t = K_t t^{0.5} + I \]

The plot \( q_t \) versus \( t^{0.5} \) is given by multiple linear regions representing the external mass transfer followed by intraparticle or pore diffusion.

The experimental data for the different CFA samples were fitted using the pseudo-first-order, pseudo-second-order kinetics, and intraparticle diffusion models. Table 2 lists the parameters obtained using each of the models. The pseudo-first-order and intraparticle diffusion models did not represent the kinetics well; i.e., their regression coefficients were lower than those obtained using the second-order kinetics model. The linearity of the plots of \( t/Q \) versus \( t \) (linear regression coefficients: >0.980) confirmed the pseudo-second-order nature of the process.

![Pseudo Second order kinetics for CFA](image)

Pseudo Second order kinetics for CFA 600

\[
y = 0.2855x + 0.9184 \\
R^2 = 0.9993 \\
y = 0.1936x + 0.8779 \\
R^2 = 0.9978 \\
y = 0.1005x + 1.0147 \\
R^2 = 0.9952
\]

Pseudo Second order kinetics for CFA HCl

\[
y = 0.2385x + 0.7003 \\
R^2 = 0.9988 \\
y = 0.1548x + 0.7715 \\
R^2 = 0.9987 \\
y = 0.083x + 0.5021 \\
R^2 = 0.9988
\]
Conclusions

The conclusions drawn from the present study are summarized as follows:

1. The adsorption capacities of CFA, CFA 600, CFA HCl and CFA NaOH toward AO7 were 4.37-12.72, 3.50-9.95, 4.19-12.05 and 3.14-10.08 mg/g respectively.

2. The experimental adsorption data is reasonably follows the freundlich and Temkin Isotherms and follows pseudo second order rate kinetics.

3. The equilibrium between Dye solution and adsorbent surface is established within 1.5 hours.

4. The amount of adsorbate adsorbed increases with an increase in adsorbent dosage as well as increases with increase in initial dye concentration.

5. It is also confirmed that untreated fly ash and HCl modified fly ash has greater dye removal capacity than other activation.

Reference


Table 2 Kinetic parameters of AO7 on CFA, CFA-600, CFA HCl and CFA-NaOH at various Concentrations

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye Conc.</th>
<th>Pseudo first Order kinetics</th>
<th>Pseudo second Order kinetics</th>
<th>Intraparticle Diffusion</th>
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<tr>
<td></td>
<td></td>
<td>K₁</td>
<td>Qₑ</td>
<td>R²</td>
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<tr>
<td>CFA</td>
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<td>0.0506</td>
<td>6.73</td>
<td>0.9822</td>
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<td>0.0574</td>
<td>2.00</td>
<td>0.9657</td>
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<td>30</td>
<td>0.0823</td>
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<td>0.8793</td>
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<tr>
<td>CFA 600</td>
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<td>0.1157</td>
<td>1.44</td>
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<tr>
<td></td>
<td>15</td>
<td>0.0406</td>
<td>1.6</td>
<td>0.9364</td>
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<td>0.0615</td>
<td>5.23</td>
<td>0.9778</td>
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<td>CFA HCl</td>
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<td>0.9339</td>
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<td>0.1019</td>
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<td>CFA NaOH</td>
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<td></td>
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<td></td>
<td>30</td>
<td>0.0491</td>
<td>6.76</td>
<td>0.9399</td>
</tr>
</tbody>
</table>

Pseudo Second order kinetics for CFA NaOH

\[ y = 0.3184x + 2.6379 \quad R^2 = 0.9929 \]
\[ y = 0.1808x + 3.899 \quad R^2 = 0.9848 \]
\[ y = 0.0992x + 1.8259 \quad R^2 = 0.9798 \]
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