Removal of Dyes from Waste Water Using Commercial Activated Carbon (CAC) as Adsorbent with Kinetic Aspect

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(Received on 17/2/2008) (Accepted for publication 9/6/2008)

Abstract
In this study, the removal of dyes which are present in the industrial wastewater from Diwaniyaa textile factory, by commercial activated carbon (CAC) was investigated as a function of temperature and pHs, residual amount of colored wastewater determined using uv-visible technique at maximum wavelength 370 nm.

Adsorption process was attained to the equilibrium within 60 minutes, the adsorbed amount of mixture dyes were found increased as temperature and pHs decreased.

Kinetics of adsorption was studied by using Lagergreen’s equation at different pHs and the adsorption rate constant K_ad was calculated. The kinetic result indicates that the adsorption process is pseudo first order. Activation energy was calculated using Arrhenius equation which depends on the nature of the adsorbent surface.

Introduction
Water pollution is any human-caused contamination of water that reduces its usefulness to humans and other organisms in nature. Pollutants such as herbicides, pesticides, fertilizers, and hazardous chemicals can make their way into our water supply. When our water supply is contaminated, it is a threat to human, animal, and plant health unless it goes through a costly purification procedure.
Colour removal from textile effluents has been the subject of great attention in the last few years, not only because of its toxicity but mainly due to its visibility. (1) Through hundreds of years, the scale of production and the nature of dyes has changed drastically, consequently the negative impact of dyes on the environment has increased. (2) Adsorption processes which produce good quality effluents that are low in concentration of dissolved organic compounds, such as dyes, (3,4) are rapidly gaining importance as treatment processes.

Dyeing and finishing processes are two important steps in the textile manufacturing process (5, 6). The steps involve the dyeing of man-made or, natural fibers to the desired permanent colours and processing of these fibers into commercial products, subsequently discharging the wastewater.

Before directing these waters away from the industry, they should be treated to remove organic wastes and colouring agents. For this adsorption has evolved as one of the most effective and economical, physical; processes for de-colourization of textile wastewa(7,8). Synthetic dyes represent a relatively large group of organic chemicals which are encountered in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on humans. In order to minimize the possible damage to people and the environment arising from the production and application of dyes, several studies have been conducted around the world (10-14).

The best adsorbent surface for removal of pollutants is activate carbon, which have surface properties are both hydrophobic and hydrophilic; that is, they “hydrophobic” water but “hydrophilic” oil. (15) Organic chemicals are often responsible for taste, odor, and color problems, activated carbon can generally be used to remove such impurities. (16, 17)

Activated carbon has a high adsorption capacity or reactivity which arises from the complexity of the chemical surface groups compared to other surfaces. The surface of carbon materials can contain not one but, at least, five markedly different types of surface groups such as carboxylic, lactonic, phenolic, carbonyl and etheric types. This diversity of surface groups makes the surface chemistry (acid-base character) much more versatile than that of other adsorbents. (18, 19)

The present work involves removal of industrial waste water by commercial activated carbon at different temperatures and pHs.

**Materials and methods**

**Materials:**

Mixture of dyes which are present in the industrial waste water, was taken from Diwaniyaa textile factory. Carbon powder activation: - which was taken from Babylon university, college of engineering, after grinding and sieving, then drying, the powder in the oven at (150 °C) for (1 hour). The purpose of this stage is to burn out the organic materials if were existed. In additional to that the reactivity of carbon powder will be gained which is affected by mechanical work (crushing and sieving) at 90 (µm),have properties as shown in table 1.
Table 1: Properties of the used activated carbon.

<table>
<thead>
<tr>
<th>Test</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension (granular)</td>
<td>12x40 mesh (0.4-1.6)mm</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>460-480</td>
</tr>
<tr>
<td>Void fraction</td>
<td>0.45</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>1100-1130</td>
</tr>
<tr>
<td>Hardness (%)</td>
<td>98</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>5 (max.)</td>
</tr>
<tr>
<td>Microporos</td>
<td>high</td>
</tr>
</tbody>
</table>

Spectronic – 21 mode u.v-visible single beam with 1 cm cells Bausch and lomb (USA) was used for all absorbance measurements, pH measurements were made with Knick digital pH meter (England), Shaker water bath, SB. 4, Tecam were used.

Methods:
The adsorption rate data at different temperatures and initials pH values have been obtained by allowing the commercial activated carbon – solute (0.02 gm of CAC / 20 ml of solute) to be mixed in the shaker water bath, by taken the initial absorbance at each pHs then solution was treated with the adsorbent surface. During these experiments, samples of the solution have been periodically withdrawn at a definite time period (10, 20, 30, 40, 50, 60, 70 and 80 min.). then was filtered and the residual amount of colored mixture dyes were determined spectrophotometry by depending on Beer-Lambert law at 370 nm, which measured at each time using u.v-visible technique, the same treatment was applied at different pHs and temperatures.

Results and Discussion

Effect of contact time
The experimental results of adsorption of colored mixture of dyes on the CAC was studied with different times and the equilibrium data shown in Figures (1-3) at different temperatures and pHs.

The equilibrium is reached after 60 minutes for all the conditions applied [i.e: pH= (5, 7 and 9)], and temperature (290K, 300K and 310K), reveal that the adsorption percent increases with increasing time until equilibrium achieve (20-22).
Figure 1: Effect of contact time by using percentage adsorbed of Mixture dyes on CAC at different temperature and pH 5.

Figure 2: Effect of contact time by using percentage adsorbed of Mixture dyes on CAC at different temperature and pH 7.
Mechanism behavior of adsorption of mixture dyes

The wastewater from industry usually contains more than one dye, in order to investigate the mechanism of sorption, kinetic models have been used to test experimental data. The kinetic model in this study includes the pseudo – first order equation, to study the removal of dye mixture.

The pseudo–first order equation of Lagergreen is generally expressed as follows:

\[ \frac{dQ_t}{dt} = k(Q_e - Q_t) \]  

Where \( A_0 \), \( A_t \), and \( A_e \) are absorbency of colored dye at before adsorption, at time \( t \) and at equilibrium, also \( Q_e \) and \( Q_t \) are the sorption capacity at equilibrium and at time \( t \), respectively, and \( k \) is the rate constant of pseudo first order sorption (min\(^{-1}\)). After integration and applying boundary conditions \( t=0 \) to \( t = t \) and \( Qt=0 \) to \( Qt=Qt \), the integrated form of eq(2) becomes:

\[ \ln(Q_e - Q_t) = \ln Q_e - kt \]  

The value of rate constant for the pseudo first order reaction is

![Percentage of removal vs Time (min.)](image-url)
calculated experimentally by plotting $\ln(Q_e - Q_t)$ against time of the adsorption of colored mixture dyes into (CAC) according to eq (5), results are shown in Figures (4-6) and values of rate constants are illustrated in table (2).

Figures below show increased in rate constant with temperature increase, this may be due to the tendency for the colored mixture dyes molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution.\(^{24-26}\)

![Figure 4: Pseudo-first order adsorption kinetic of colored mixture dyes on the CAC surface at different temperatures and pH 5.](image-url)
Figure 5: Pseudo-first order adsorption kinetic of colored mixture dyes on the CAC surface at different temperatures and pH 7.

Figure 6: Pseudo-first order adsorption kinetic of colored mixture dyes on the CAC surface at different temperatures and pH 9.
The value of rate constant $K_{ad}$ are calculated experimentally from Figures (5, 6 and 7), were found to be increased when temperature increased from 290 to 310K, at different pHs, also the best result of rate constants were found at low pH, and the values of rate constants are illustrated in table (2).

### Table 2: Rate constants for effect of different temperatures on the sorption of coloured waste water.

<table>
<thead>
<tr>
<th>pH 5</th>
<th>T/ K</th>
<th>$K_{ads}$ (min$^{-1}$)$\times10^2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td></td>
<td>6.834</td>
<td>0.9241</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>7.070</td>
<td>0.9354</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td>7.506</td>
<td>0.9193</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH 7</th>
<th>T/ K</th>
<th>$K_{ads}$ (min$^{-1}$)$\times10^2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td></td>
<td>5.880</td>
<td>0.9654</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>6.217</td>
<td>0.9503</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td>7.071</td>
<td>0.9079</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH 9</th>
<th>T/ K</th>
<th>$K_{ads}$ (min$^{-1}$)$\times10^2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>290</td>
<td></td>
<td>4.329</td>
<td>0.9756</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>5.079</td>
<td>0.9359</td>
</tr>
<tr>
<td>310</td>
<td></td>
<td>5.381</td>
<td>0.9504</td>
</tr>
</tbody>
</table>

The sorption rate constant may be expressed as a function of temperature by following the relationship$^{(27,28)}$:

$$\ln k = \ln A - \frac{E_a}{RT} \ldots \ldots (6)$$

Where $k$ is the rate constant of sorption (min$^{-1}$), $E_a$ is the activation energy of sorption (kJ mole$^{-1}$), $R$ is the gas constant (0.008314 kJ K$^{-1}$ mole$^{-1}$), $T$ is solution temperature (K).

The logarithm of $k_a$ values for the pseudo first order were plotted as a function of reciprocal of the Kelvin temperature. Linear variation were observed and are shown in Figure (7), values of activation energy and oscillator factor are illustrated in table (3).

It would be expected that an increase in solution temperature would result in a decrease in adsorption capacities, which leads that the adsorption process is exothermic$^{(20)}$. 


Table 3: values of activation energy and oscillator factor for adsorption of coulored mixture dyes by CAC at different pHs.

<table>
<thead>
<tr>
<th>pH</th>
<th>$E_a$ (kJ mole$^{-1}$) $\times 10^3$</th>
<th>oscillator constant $[A]$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.542</td>
<td>0.284</td>
<td>0.9718</td>
</tr>
<tr>
<td>7</td>
<td>7.119</td>
<td>1.107</td>
<td>0.9493</td>
</tr>
<tr>
<td>9</td>
<td>8.029</td>
<td>1.283</td>
<td>0.9372</td>
</tr>
</tbody>
</table>
Conclusion
The colored wastewater was strongly sorbed by CAC, this could be explained by adsorption interaction between the adsorbed dye molecules and CAC.

The pseudo first-order kinetic model fits very well with the dynamical adsorption behavior of this compound in solution with different temperatures and at different pHs.

High values of rate constant were found at high temperature and low pH.

From values of activation energy explained the adsorption process is exothermic.

References
24. V. K. Gupta, D. Mohan and S. sharmay , *a sugar industry waste