Efficiency of Multi Walled Carbon Nanotubes for Removing Direct Blue 71 from Aqueous Solutions

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ABSTRACT
Dye wastewater produced from industrial activity is usually toxic, resistant to biodegradation and persistent in the environment. The aim of this study was to evaluate the efficiency of multiwalled carbon nanotubes (MWCNTs) for decolorization of Direct Blue 71 (DB71). In this experimental study, the effect of various variables including contact time, solution pH, adsorbent dose, and initial dye concentration was evaluated in a batch reactor. The adsorption and kinetic models were evaluated to explain the adsorbed dye and dynamic reaction. The results of this study showed that the efficiency of dye removal increased, as the contact time and adsorbent dose increased, but as pH and initial dye concentration increased, removal efficiency decreased. The maximum efficiency of Direct Blue 71 removal was observed at acidic solution (pH=3), contact time of 90 minutes, adsorbent dose of 0.6 g/l and initial dye concentration of 25 mg/l. The adsorption of direct blue 71 best fitted the Langmuir isotherm (R²=0.87) and pseudo first order kinetic equation (R²=0.99). According to the results obtained, multiwalled nanotubes was offered as an effective adsorbent for removing direct blue 71.

Keywords: carbon nanotubes, dye wastewater, adsorption isotherms, kinetic study

INTRODUCTION
The rapid development of industries and release of industrial wastewater in the environment has led to major concerns in regard to surface and underground water contamination as well as destruction of the environment [1]. Dyes are well known pollutants that are produced by the textile, printing, ink and other related industries such as food production, leather, paper, polishing oil, medicine and cosmetic industries [2, 3]. Discharge of colored wastewater leads to serious problems due to its high toxicity and its probable accumulation in the environment [4]. The discharge of this wastewater in the environment leads to disturbance in aqueous solutions, because it prevents sunlight pass aqueous environments, slows down photosynthesis, and therefore threatens the synthesis activity of aqueous plants and the whole ecosystem [5-7].
The direct blue 71 dye belongs to the direct dye category and is similar to acidic dyes because it contains sulfonic acid or sodium salts groups, and is generally a sulfonated azo compound [8].

Azo dyes are known with azo bonds (\( N = N \)) in their structure and they are classified into monoazo, diazo, and triazo categories based on the number of azo bonds [9, 10]. Nowadays, treating dye wastewater has been used by various processes such as adsorption, ion exchange, inverse osmosis, coagulation and flocculation, biologic processes, chemical deposition, and advanced oxidation processes [11-17]. Adsorption is one of the most important processes in removing environmental pollutants and is the most appropriate technique for removing dye pollutants from wastewater and improving the quality of industrial wastewater for reuse. Advantages of this process include low cost, easy design, ease of operation and non-sensitivity to toxins [18-21].

Nanotubes can be used for treatment and converting pollutants to less harmful material because of their small size, extended surface, and crystal shape [22-28]. Carbon nanotubes are built from carbon layers with the thickness of just one atom and in the form of hollow cylinders. They were discovered in 1991 by Sumio Iijima. Unique characteristics including high Young's modulus and good tensile strength, as well as the carbon nature of the nanotubes have led to important research about its efficiency and improvements in its production [29]. Nanotubes are classified in two groups, single walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs)[30]. Nowadays, carbon nanotubes are considered as a kind of adsorbent for pre-treatment of environmental pollutants including various organic and non-organic compounds and also radio nucleotide materials in high volumes of wastewater and has attracted more attention all over the world [31].

Shirmardi et al. (2010) studied the removal of acid red 18 dye by using multiwalled carbon nanotubes and showed that MWCNTs can act as an efficient adsorbent for removing dyes [4]. In Leo et al. research about adsorption of Neutral Red halloysite nanotubes, the hallow site nanotubes showed a high efficiency in adsorbing neutral red [32]. Considering the fact that dye is one of the dilemmas of industrial wastewater and especially in the textile industry, the efficiency of MWCNTs in removing direct blue 71 from synthetic wastewater has been evaluated in this research.

**MATERIAL AND METHODS**

**Instruments and Chemicals**

This study was conducted in a batch reactor. The carbon nanotubes used in this study (MWCNTs), were obtained from Pishgaman Nanomavad Company, Iran. The specific area and electrical conductivity of CNTs were 233 m²/g and 100 S/m, respectively. The internal and external diameters of these CNTs were in the range of 5-15 nm and 3-5 nm, respectively. The purity of these CNTs was more than 98%. All of the chemicals used in this study were provided from Merck Company, Germany. The chemical structure of DB71 is \( \text{C}_{40}\text{H}_{23}\text{N}_{7}\text{Na}_{4}\text{O}_{13}\text{S}_{4} \) and was purchased from the Alwan Sabet Company, Iran. The chemical structure of this dye has been illustrated in Figure 1.

The destruction of the dye molecules was determined by measuring the solution absorption at 587 nm using a UV-visible spectrophotometer. The stock solution of dye was prepared by dissolving a certain amount of dye in distilled water. In all experiments, incubator shaker was used to maintain nanotubes suspended and increase adsorption efficiency. At the end of each stage, the solutions were centrifuged at 4000 rpm for 10 minutes. Then they were passed through filters (0.25 μm). The concentration of the remaining DB71 dye was measured by the spectrophotometer UV/Vis (CECIL7250). All the adsorption experiments were done at 25 °C. NaOH and HCl (0.1N) were used for pH adjustment.
**Batch Study and Procedure**

The adsorption tests were carried out in a batch reactor using 250 ml laboratory flasks containing 100 ml of dye solution. The effect of contact time on dye adsorption was evaluated using initial dye concentration of 25 mg/L and 0.6 g/L of adsorbent at pH of 3. The contact time was varied from 5 to 240 min. The effect of pH on dye removal was performed at 0.6 g/L of MWCNT adsorbent and 25 mg/L of dye solution at contact time of 90 min. The effect of sorbent dose was carried out by agitating different dosages of adsorbent (0.1, 0.2, 0.4, and 0.6 g/L) in dye solution (25 mg/L) at pH of 3 and contact time of 90 min. The effect of initial dye concentration on dye adsorption was conducted using 0.6 g/L of adsorbent onto various concentrations of dye solution (25, 50 and 100 mg/L) at pH of 3 and contact time of 90 min. The removal efficiency and adsorption capacity of dye at the equilibrium time was calculated based on Eqn. 1 [1]:

\[
\text{Removal Efficiency (\%) } = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

In this equation, \(C_0\) and \(C_e\) are the initial concentration and the equilibrium concentration of the DB71 dye, respectively. All analyses were done using the Excel software.

**RESULTS**

**The Characteristics of Adsorbent**

The SEM image of the adsorbent has been shown in Figure 2. SEM and TEM are widely used to make distinctive morphology as well as dimensions of the adsorbents. The electron micrographs present well-formed plate. According to Figure 2, it is observed a good level of uniformity and homogeneity of nanotubes.

**The Effect of Contact Time**

The effect of contact time on the adsorption of Direct Blue 71 by MWCNTs has been shown in Figure 3. As contact time increases, the efficiency of dye removal increases as well, until it reaches the equilibrium at 90 minutes.

**The Effect of Initial pH**

As depicted in Figure 4, by increasing pH of the solution, the efficiency of dye removal decreases. The optimum pH was 3. Therefore the rest of the experiments were conducted at pH of 3.

**The Effect of Adsorbent Dose**

The results of the effect of adsorbent dose on dye removal has been shown in Figure 5 and shows that as the dosage of MWCNTs increases from 0.1 g/L to 0.6 g/L, the efficiency of Direct Blue 71 dye removal increases from 84% to 96.44%. The optimum amount of adsorbent was 0.6 g/L.
Figure 3. The effect of contact time on the efficiency of Direct Blue 71 removal (adsorbent dose: 0.6 g/l, initial dye concentration: 25 mg/l and pH=3)

Figure 4. The effect of pH on the efficiency of Direct Blue 71 dye removal (adsorbent dose= 0.6 g/l , initial concentration of dye= 25 mg/l and contact time = 90 minutes)

Figure 5. The effect of adsorbent dosage on the efficiency of Direct Blue 71 dye removal (contact time=90 minutes, initial dye concentration= 25mg/l, and pH=3)
The Effect of Initial Dye Concentration

Figure 6 shows the effect of the initial concentration of Direct Blue 71 on efficiency of dye removal by the MWCNTs adsorbents. As the initial dye concentration increased from 25 mg/L to 100 mg/L, the dye removal efficiency decreased.

Adsorption Isotherms

The adsorption isotherms are very important because they determine interactions between the adsorbate and adsorbent, explain distribution the adsorbed molecules between liquid and solid phases, and also provide important information about optimizing adsorption system design [4].

The Langmuir and Freundlich isotherms were used to describe the adsorption of Direct Blue 71 from aqueous solutions by MWCNTs at pH of 7.

Langmuir Isotherm

The Langmuir isotherm is the most commonly used adsorption isotherm which is widely used for removing pollutant from aqueous solutions [33, 34]. This isotherm describes the monolayer adsorption on active sites of adsorbent in homogenous structures [4, 35]. The equation of the Langmuir isotherm is as follows [36]:

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

(2)

Here, \(C_e\) is the equilibrium of dye in the solution (mg/l), \(q_e\) is adsorption capacity, \(q_m\) is the theoretical saturation capacity of monolayer (mg/g), \(k_L\) is the Langmuir constant (L/mg) which is calculated by plot \(C_e\) versus \(\frac{C_e}{q_e}\).

Freundlich Isotherm

The Freundlich isotherm is an empirical equation and is related to the heterogeneous surfaces [4]. The Freundlich equation has been described in Eqn. 3.

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]  

(3)

In this equation \(k_f\) and \(n\) are the constant values of the Freundlich isotherm which are derived from the \(\log q_e\), \(\log C_e\) plot.
Figure 7 and Figure 8 show the Langmuir and Freundlich isotherms for removing Direct Blue 71. Correlation coefficients of adsorption isotherms have been shown in Table 1.

### Table 1. Freundlich isotherm for direct blue 71 removal onto MWCNT

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$K_L$ (Lµg$^{-1}$)</td>
<td>0.0504</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.876</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$ (mg g$^{-1}$)</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.825</td>
</tr>
</tbody>
</table>

Adsorption Kinetics

The reaction pathways, along times to reach the equilibrium is explained by adsorption kinetic [37-39]. Studying the adsorption kinetics is so important to understand the adsorption reactions dynamic and predicting the adsorption rate, which is useful for process design and modeling. In this study, the pseudo first and second order kinetic were studied for adsorption of Direct Blue 71 onto MWCNTs. Figure 9 summarizes the constants and the plot of studied kinetic that can be obtained from the kinetic models. Pseudo first order kinetics gave better results than pseudo second order kinetic model. The $R^2$ value of pseudo first order model is 0.99.

DISCUSSION

In this study, the efficiency of dye removal increased with increase in contact time. The high and fast removal at the beginning is likely due to the presence of many empty sites on the surface of the adsorbent. As these sites get occupied by the dye molecules and the adsorption rate decreases, occupying the remaining spaces becomes difficult.
because of the repulsive forces between the dye molecules [4]. In a study of Shirmardi et al. in 2010 on removing the acid red 18 dye using oxidated multiwalled carbon nanotubes, removing acid red 18 reached equilibrium at 150 min [4]. In another study done by Luo et al. on removing neutral red using halloysite nanotubes, as contact time increased, the amount of dye removal increased and 30 minutes was equilibrium time, and the maximum amount of dye removal was in the initial 10 minutes of the process [32].

Experiments showed the Direct Blue 71 removal by carbon nanotubes depends on initial pH of the solution. The maximum amount of dye removal by carbon nanotubes was observed at pH=3. The direct blue 71 dye is among the anionic dyes, and the reason of increasing dye removal at low pH is related to increasing the concentration of H⁺ ion and decreasing the concentration of OH⁻ ion on the adsorbent surface. This leads to increase in the electrostatic forces between the dye molecules and the surface of the adsorbent [40]. Similar results were achieved in studies conducted by Mishra et al. for removing azo dyes using MWCNTs. In this study as pH decreased, the efficiency of dye removal increased [41]. In the study done by Xue et al. for removing radioactive dye by furnace ash, the highest amount of anionic dye removal was observed with adsorbents at acidic environments including positive charge [42].

Another important parameter effective on the removing process is the amount of adsorbent. In this study, as the amount of adsorbent increases from 0.1 to 0.6 g/L in the solution, the efficiency of dye removal increased. Increasing dye removal efficiency with enhancing the amount of adsorbent is explained by the fact that in the high amount of adsorbent, a larger adsorption area is available [4]. Similar results were achieved in the study on cationic dyes removal using composite multiwalled carbon nanotubes. As the dose of the adsorbent increased from 0.3 to 0.9 g/L, the removal efficiency increased. The reason for high efficiency at high adsorbent dose is attributed to increase in the van der Waals forces and electrostatic adsorption power between the MWCNTs and the dye molecules [43]. These results are in line with previous study [32].

Dye concentration is one of the variables that can be effective in the dye removal. While the initial dye concentration increases, the efficiency of dye removal by the adsorbent decreases. This is due to the adsorbents have a limited number of active sites which would have saturated by dye molecules [44, 45]. In higher concentration of dye, the amount of adsorption capacity (q_e) (mg/g) increased. This is due to the driving force of high dye concentrations and using more active site available for adsorption [4]. This result is confirmed by Garg et al. for the adsorption of methylene blue dye applying sawdust modified by sulfuric acid [46].

The Freundlich and Langmuir isotherms were evaluated in regard to the adsorption of Direct Blue 71 by carbon nanotubes. The results of these studies showed that the Langmuir isotherm equation best fitted with dye removal onto carbon nanotube (R²=0.87).

Figure 9. The plot and constant of studied kinetics for Direct Blue 71 removal onto MWCNTs

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Pseudo-First Order</th>
<th>Pseudo-Second Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>k (min⁻¹)</td>
<td>0.0320</td>
<td>0.0003</td>
</tr>
<tr>
<td>R²</td>
<td>0.9924</td>
<td>0.9809</td>
</tr>
</tbody>
</table>

Compliance with the Langmuir isotherm equation shows that physical adsorption is dominant for adsorption of dye molecules onto carbon nanotube and adsorption of dye molecules are monolayer. Mishra et al. study showed that azo dye removal by functional MWNTs (f-MWNTs) follows the Langmuir isotherm equation [41]. In another study done by Xue et al. for removing radioactive dyes using modified furnace ash, the process also followed the Langmuir isotherm equation [42].
First order kinetic model best fitted to find the potential rate controlling steps involved in the process of adsorption of Direct Blue 71 onto MWCNTs. Using this model can be comprehended the adsorption reactions dynamic and predicting the adsorption rate, which is useful for process design and modeling.

CONCLUSION

The results showed that carbon nanotubes at low doses have a high efficiency for removing high concentrations of dye and with increasing the dosage of adsorbent and contact time, removal efficiency increases; but by increasing the initial dye concentration and solution pH, removal efficiency decreases. The maximum efficiency of Direct Blue 71 dye removal fell out at optimum pH of 3, contact time of 90 min, adsorbent dose of 0.6 g/L and initial dye concentration of 25 mg/L. Direct Blue 71 adsorption on MWCNTs is best fitted by Langmuir adsorption equation.

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REFERENCES


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