Dye Removal from Single and Quaternary Systems Using Surface Modified Nanoparticles: Isotherm and Kinetics Studies

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ABSTRACT
In this paper, dye removal ability of the surface modified nanoparticle (SMN) (copper ferrite) using surfactant (cetyl trimethyl ammonium bromide (CTAB)) from single and quaternary systems was investigated. Acid Blue 92 (AB92), Direct Green 6 (DG6), Direct Red 23 (DR23) and Direct Red 80 (DR80) were used as model compounds. The effect of surfactant concentration, adsorbent dosage, dye concentration and pH on dye removal was evaluated. The adsorption isotherm and kinetic were also studied. The maximum dye adsorption capacity \( Q_0 \) was 178.571 mg/g AB92, 49.261 mg/g DG6, 39.841 mg/g DR23 and 43.290 mg/g DR80 for SMN. It was found that dye adsorption onto SMN followed Langmuir isotherm. Adsorption kinetic of dyes was found to conform to pseudo-second order kinetics. 

1. Introduction

Treatment of colored wastewaters is one of the main concerns of environmental scientists and engineers because some dyes produce toxic and carcinogenic byproducts via hydrolysis, oxidation, etc. [1-10]. Dye removal using adsorbents is one of the wastewater treatment methods. Natural polymers such as chitosan are used to remove dyes. Chitosan is the N-deacetylated derivative of chitin [11, 12]. Some adsorbents have low dye adsorption capacity and poor separation ability. Thus, researchers interest to conquer these adsorbent limitations.

The magnetic nanoparticles as adsorbents could be separated based on their nanostructures since the ease of direction of magnetization would vary depending on the ordering of atoms in the magnetic structure [13-19]. The main limitation of some magnetic adsorbents is their low pollutant removal potential. To conquer this disadvantage, the surface of magnetic nanoparticles was modified using surfactants. The surface properties of nanoparticles can be greatly modified with a surfactant. This is favored by van der Waals interaction between surfactant and the reduced solvent shielding of the ions in the interlamellar environment. In addition, surfactant provides corrosion inhibition effect [20].

A literature review showed that surface modified nanoparticle (SMN) (copper ferrite) using cetyltrimethylammonium bromide (CTAB) was not used to remove dyes from Quaternary systems.

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In this paper, dye removal ability of surface modified copper ferrite nanoparticle (SMN) from single and quaternary systems is investigated. Acid Blue 92 (AB92), Direct Green 6 (DG6), Direct Red 23 (DR23) and Direct Red 80 (DR80) are used as model compounds. The effect of operational parameters (i.e. surfactant concentration, adsorbent dosage, dye concentration and pH) on dye removal is evaluated. The isotherm and kinetics of dye adsorption are also studied.

2. Experimental
2.1. Materials
Acid Blue 92 (AB92), Direct Green 6 (DG6), Direct Red 23 (DR23) and Direct Red 80 (DR80) were obtained from Ciba and used without further purification. The chemical structure of dyes is shown in Figure 1. Other chemicals were of analytical grade and obtained from Merck.

2.2. Synthesis of copper ferrite and SMN
2.2.1 Synthesis of copper ferrite
4.90 g copper nitrate and 13.4 g iron nitrate was dissolved in 50 mL distilled water which was then added to an aqueous mixed solution of 4.2 g NaOH in 70 mL distilled water and 3 mL ethylene diamine (EG). This solution was heated at 90 °C for 1 h to achieve complete chelation. The powder was calcined on alumina crucible at 500 °C for 1 h, with a heating rate of 10 °C/min [21].

![Figure 1: The chemical structure of dyes: (a) AB92, (b) DG6, (c) DR23 and (d) DR80.](image-url)
2.2.2 Synthesis of SMN
CTAB (0.4 g) was added to a solution containing 10 mL acetone, 125 mL distilled water and 1 g copper ferrite. The mixture was stirred in a mixer for 1 h. The organo-modified copper ferrite was separated from the mixture by magnetic force and then was washed with distilled water [21].

2.3. Adsorption procedure
The dye adsorption measurements were conducted by mixing of adsorbent in jars containing 250 mL dye solution (50 mg/L). The solution pH was adjusted by adding H$_2$SO$_4$ or NaOH. The absorbance of all samples were monitored and determined at certain time intervals during the adsorption process. At the end of the adsorption experiments, the adsorbent particles were removed from the solution by magnetic separation using a magnet and the dye concentration was determined. The results were verified with the adsorption kinetics and isotherms.

UV-Vis Perkin-Elmer Lambda 25 spectrophotometer was employed for absorbance measurements of samples. The maximum wavelengths ($\lambda_{\text{max}}$) used for determination of residual concentration of AB25, DG6, DR23 and DR80 in supernatant solution using UV–VIS spectrophotometer were 580 nm, 632 nm, 500 nm and 540 nm, respectively. The solution pH was adjusted by adding H$_2$SO$_4$ or NaOH.

The isotherm and kinetics of dye adsorption on SMN were studied by contacting 250 mL of dye solution with initial dye concentration of 50 mg/L for 60 min at different amounts of SMN.

The effect of surfactant concentration on dye removal was investigated by contacting 250 mL of dye solution with initial dye concentration of 50 mg/L for 60 min. The effect of adsorbent dosage on dye removal was investigated by contacting 250 mL of dye solution with initial dye concentration of 50 mg/L for 60 min. The effect of initial dye concentration (50-200 mg/L) on dye removal was investigated by contacting 250 mL of dye solution with SMN for 60 min. The effect of pH on dye removal was investigated by contacting 250 mL of dye solution with initial dye concentration (50 mg/L) for 60 min.

3. Results and discussion
3.1. Effect of operation parameters on dye removal
3.1.1. Effect of surfactant concentration
The dye removal (%) versus time (min) at different surfactant concentrations is shown in Figure 2. The increase in dye adsorption with surfactant concentration is due to higher availability of adsorption sites. An electrostatic attraction exists between the positively charged (–N$^+$) surface of the SMN by surfactant and negatively charged anionic dyes.

3.1.2. Effect of adsorbent dosage
The dye removal (%) versus time (min) at different SMN dosages (g) is shown in Figure 3. The increase in dye adsorption with adsorbent dosage is due to the increasing of adsorbent surface and availability of more adsorption sites. However, if the adsorption capacity was expressed in mg adsorbed per gram of material, the capacity decreases by increasing the amount of adsorbent. It can be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length [22].

3.1.3. Effect of dye concentration
Adsorption can generally be defined as the accumulation of material at the interface between two phases [22]. The influence of initial dye concentration on adsorption efficiencies onto SMN was assessed. The results are shown in Figure 4. It is obvious that the higher the initial dye concentration, the lower the percentage of dye adsorbed. The amount of the dye adsorbed onto SMN increases with the initial dye concentration in solution if the amount of adsorbent is kept unchanged due to the increase in the driving force of the concentration gradient with the higher initial dye concentration. The adsorption of dye by SMN is very intense and reaches equilibrium very quickly at low initial concentrations. At a fixed SMN dosage, the amount of adsorbed dye increased with increasing the solution concentration, but the percentage of adsorption decreased. In other words, the concentration of residual dye will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye moles to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration [22].
Figure 2: The effect of surfactant concentration on the modification of nanoparticles to remove dyes from single and quaternary systems.
Figure 3: The effect of SMN dosage on dye removal using SMN from single and quaternary systems.
3.1.4. The effect of pH

The effect of pH on the adsorption of dyes onto SMN is shown in Figure 5. At various pH values, the electrostatic attraction as well as the organic property and chemical structure of dye molecules and SMN could play very important roles in dye adsorption on SMN. The adsorption capacity does not change when the pH changes. It can be attributed that positively charged group of surfactant does not changed with the solution pH.

![Graphs of dye removal vs. time for different dye concentrations and pH values.](image)

**Figure 4:** The effect of dye concentration on dye removal using SMN from single and quaternary systems.
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**Figure 5:** The effect of pH on dye removal using SMN from single and quaternary systems.
3.3. Adsorption isotherms

The relation between the mass of the dye adsorbed at a particular temperature, pH, particle size and liquid phase of the dye concentration is evaluated using adsorption isotherms [23-25]. The current research presents a method of direct comparison of the isotherm fit of several models (the Langmuir, Freundlich and Tempkin models) to enable the best-fit and the best isotherm parameters to be obtained.

The Langmuir isotherm explains the adsorption of dye into adsorbent. A basic assumption of the Langmuir theory is that adsorption takes place at specific sites within the adsorbent [26]. The Langmuir equation can be written as follows:

\[ q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (1)

where \( q_e \), \( C_e \), \( K_L \) and \( Q_0 \) are the amount of dye adsorbed at equilibrium (mg/g), the equilibrium concentration of dye solution (mg/L), Langmuir constant (L/g) and the maximum adsorption capacity (mg/g), respectively. The linear form of Langmuir equation is:

\[ \frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \]  \hspace{1cm} (2)

The Freundlich model can also be used for evaluating isotherm data [27]:

\[ q_e = K_F C_e^{1/n} \]  \hspace{1cm} (3)

where \( K_F \) is adsorption capacity at unit concentration and \( 1/n \) is adsorption intensity. Eq. (3) can be rearranged to a linear form:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} (4)

The Tempkin isotherm is given as [28]:

\[ q_e = B_1 \ln K_T + B_1 \ln C_e \]  \hspace{1cm} (5)

where

\[ B_1 = \frac{RT}{b} \]  \hspace{1cm} (6)

A plot of \( q_e \) versus \( \ln C_e \) enables the determination of the isotherm constants \( B_1 \) and \( K_T \) from the slope and the intercept, respectively. \( K_T \) is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant \( B_1 \) is related to the heat of adsorption.

To study the applicability of the Langmuir, Freundlich and Tempkin isotherms for the dye adsorption onto SMN at different adsorbent dosages, linear plots of \( C_e/q_e \) against \( C_e \), \( \log q_e \) versus \( \log C_e \) and \( q_e \) versus \( \ln C_e \) are plotted. The values of \( Q_0 \), \( K_L \), \( K_F \), \( 1/n \), \( K_T \), \( B_1 \) and \( R^2 \) are listed in Table 1.

The \( R^2 \) values show that the dye removal isotherm using SMN does not follow the Freundlich and Tempkin isotherms (Table 1). The linear fit between the \( C_e/q_e \) versus \( C_e \) and the calculated \( R^2 \) values for Langmuir isotherm model shows that the dye removal isotherm can be approximated as Langmuir model (Table 1). This means that the adsorption of dyes takes place at specific homogeneous sites and a one layer adsorption onto SMN surface.

Table 1: Linearized isotherm coefficients for dye adsorption onto SMN at different adsorbent dosages.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 )</td>
<td>( K_L )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>AB92</td>
<td>178.571</td>
<td>0.024</td>
<td>0.573</td>
</tr>
<tr>
<td>DG6</td>
<td>49.261</td>
<td>0.227</td>
<td>0.935</td>
</tr>
<tr>
<td>DR23</td>
<td>39.841</td>
<td>0.353</td>
<td>0.963</td>
</tr>
<tr>
<td>DR80</td>
<td>43.290</td>
<td>0.285</td>
<td>0.984</td>
</tr>
</tbody>
</table>
4.3. Adsorption kinetics

Adsorption kinetic was determined using pseudo-first order equation, pseudo-second order equation and intraparticle diffusion model [29] in order to investigate the mechanism of dye adsorption onto SMN.

A linear form of pseudo-first order model is [29]:

\[ \log (q_e - q_t) = \log (q_e) - \left( \frac{k_1}{2.303} \right) t \]  \hspace{1cm} (7)

where \( q_t \) and \( k_1 \) are the amount of dye adsorbed at time \( t \) (mg/g) and the equilibrium rate constant of pseudo-first order kinetics (1/min), respectively.

Linear form of pseudo-second order model is defined as [29]:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left( \frac{1}{q_e} \right) t \]  \hspace{1cm} (8)

where \( k_2 \) is the equilibrium rate constant of pseudo-second order (g/mg min).

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model as [29]:

\[ q_t = k_p t^{1/2} + I \]  \hspace{1cm} (9)

where \( k_p \) and \( I \) are the intraparticle diffusion rate constant and intercept, respectively.

To understand the applicability of the pseudo-first order, pseudo second-order and intraparticle diffusion models for the dye adsorption onto SMN at different adsorbent dosages, linear plots of \( \log(q_e - q_t) \) versus contact time \( t \) (Figure 6), \( t/q_t \) versus contact time \( t \) (Figure 7) and \( q_t \) against \( t^{1/2} \) (Figure 8) are plotted. The values of \( k_1 \), \( k_2 \), \( k_p \), \( I \), \( R^2 \) (correlation coefficient values) and the calculated \( q_e \) ((\( q_e \))Cal) are shown in Table 2. \( R^2 \) demonstrates that pseudo-first order and intraparticle diffusion kinetic models do not play a significant role in the uptake of the dye by SMN (Table 2). The linear fit between the \( t/q_t \) versus contact time \( t \) and the calculated \( R^2 \) values for pseudo-second order kinetics model show that the dye removal kinetic can be approximated as pseudo-second order kinetics (Table 2). In addition, the experimental \( q_e \) ((\( q_e \))Exp) values agree with the calculated ones ((\( q_e \))Cal) obtained from the linear plots of pseudo-second order kinetics (Table 2).

![Figure 6: Pseudo-first order kinetics of dye removal by SMN.](image-url)
Figure 7: Pseudo-second order kinetics of dye removal by SMN.

Figure 8: Intraparticle diffusion kinetics of dye removal by SMN.
4.4. Dye removal mechanism by SMN

Copper ferrite has negative charge on its surface and thus not suitable for adsorption of anionic dyes. Thus, its surface should be modified. The surface modification of copper ferrite by adsorption of cationic surfactant has four steps. In step I, when the surfactant concentration is low (much lower than the critical micelle concentration (CMC) of the surfactant), surfactant moieties are adsorbed to the negatively charged substrate almost exclusively by ion exchange mechanism. Thus, the counter ions in the diffuse double layer just outside the surface are exchanged for surfactants with the same charge. This ion exchange leads to a higher surfactant concentration at the surface than that in the bulk. Step II involves a strong lateral interaction between adsorbed monomers as a result of hydrophobic interactions between alkyl tails of the surfactants, resulting in the formation of primary aggregates. The previous published papers have shown that the surfactants are adsorbed with head-groups facing towards the surface while the hydrocarbon tail-groups protrude into solution [30-33]. This creates hydrophobic patches on the surface. By increasing the concentration of surfactant in the solution, the packing at the surface increases as can be seen in step III. At concentrations above CMC, the surfactants form a double layer (step IV) [30]. The modification of copper ferrite with CTAB (SMN) provides many cationic sites at the surface of the particles which can be used for adsorption of anionic dyes by electrostatic attraction.

4. Conclusion

Dye removal ability of SMN from single and quaternary systems was investigated. Acid Blue 92 (AB92), Direct Green 6 (DG6), Direct Red 23 (DR23) and Direct Red 80 (DR80) were used as model compounds. It was found that dye adsorption onto SMN followed the Langmuir isotherm. Adsorption kinetics of dyes was found to conform to pseudo-second order kinetics. It can be concluded that the SMN as a magnetic material might be a suitable alternative to remove dyes from colored aqueous solutions.
6. References


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