Modified magnetite nanoparticles with cetyltrimethylammonium bromide as superior adsorbent for rapid removal of the disperse dyes from wastewater of textile companies

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ABSTRACT: This paper reports application of cetyltrimethylammonium bromide (CTAB) coated magnetite nanoparticles (Fe\textsubscript{3}O\textsubscript{4} NPs) as a novel adsorbent for removal of two types of disperse dyes, including disperse red 167, and disperse blue 183, from wastewater of textile companies. The effect of parameters including type of surfactant, pH of solution, surfactant concentration, and amount of salt, was investigated and optimized. The obtained results showed that the ratio of initial dye concentration to CTAB amounts has critical effect on removal processes so that removal efficiencies higher than 95\% can be achieved even at high concentration of dyes as high as 500 mg l\textsuperscript{-1} when the ratio is optimum. Removal of dyes is very fast, and equilibrium is reached at times less than 10 min even for high concentration of the dyes. Very high adsorbent capacity (as high as 2000 mg g\textsuperscript{-1}) was yielded for maximum tested concentration of the dyes (500 mg g\textsuperscript{-1}). The obtained result was confirmed by thermogravimetric analysis data. This study showed that CTAB coated Fe\textsubscript{3}O\textsubscript{4} NPs is a very efficient adsorbent for removal of dyes from wastewater of textile companies and has high capacity under optimum conditions.

Keywords: Magnetite nanoparticles; Disperse dyes; Removal; Disperse red 167; Disperse blue 183

INTRODUCTION

Treatment and disposal of dye-contaminated wastewater is among the most serious environmental problems faced by the textile, dyeing, printing, ink, and related industries. Dyes are known as pollutants that not only affect aesthetic merits of environment, but also reduce light penetration and photosynthesis, and some of them are considered toxic and even carcinogenic to human health [1]. The presence of minute amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2]. Over 100,000 commercially available dyes exist and more than 7 × 10\textsuperscript{5} tones are annually produced [3,4]. Among different dyes, disperse dyes are widely used in variety of industries, such as textiles, paper and leather. Disperse dyes are non-ionic aromatic compounds, scarcely soluble in water but soluble in organic solvents. The majority of them are Azo and anthraquinone dyes. In addition, these dyes can be used to synthesize fibers such as polyester, nylon, acetate, cellulose and acrylic [5].

As the regulations of worldwide have grown stricter, the effluents of textile and related industries have to be treated carefully before discharge. This has resulted in a demand for environmentally friendly technologies to remove dyes from effluents. Numerous approaches, including biological treatment [6], coagulation/flocculation [7], ozone treatment [8], oxidation [9], membrane filtration [10], electrochemical processes [11], photocatalytic degradation [12] and adsorption [13], have been developed to remove these compounds from colored effluents. Among them, adsorption techniques offer significant advantages over other removal techniques, since the former methods are

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more economical, simpler [14], and capable of efficiently treating dyes in more concentrated form [15]. Also, especially based on environmental point of view, adsorption techniques do not lead to secondary sludge disposal problems [16,17]. Although activated carbon is widely used as an efficient adsorbent for dye removal from colored waters owing to its excellent adsorption abilities, it suffers from several drawbacks such as high price of both its manufacturing and regeneration, and it is also ineffective against disperse and vat dyes [18,19]. Hence, instead of activated carbon, alternative low-cost, novel locally available adsorbents are currently used for removal of textile dye effluents from aqueous solutions. Sepiolite [20,21], zeolite [22], waste metal hydroxide sludge [23], smectite [24], bentonite [25], Sorrel’s cement [26], modified mesoporous silica [27], orange peel [28], polymethylacrylate grafted chitosan [29], magnetic alginate beads [30] and modified magnetic nanoparticles [31,32] are some adsorbents used in this respect.

Recently, nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [33]. These materials have been used in various scientific fields such as biotechnology, engineering, biomedical, environmental, and material sciences [34-37]. Application of nanoparticles (NPs), as novel adsorbents for pollutant removal, is gaining research interest [38-42]. Compared with micrometer-sized particles, NPs offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high extraction capacity, rapid extraction dynamics, and high extraction efficiencies [43,44]. Super paramagnetic NPs such as Fe$_3$O$_4$ are attracted to a magnetic field but retain no residual magnetism after the field is removed. This property makes them particularly suitable for pollutant removal since no centrifugation or filtrations of the sample are then needed after treatment (in comparison with non-magnetic NPs).

In order to enhance commercial application of magnetic nanoparticles (MNPs) as adsorbents in batch contact and column processes for removal of dyestuffs, several chemical modification methods, such as magnetic silica modified with amine group [45], magnetic multi-wall carbon nanotube nanocomposite [46], cetyltrimethylammonium bromide (CTAB) coated magnetic nanoparticles [47], and magnetic alginate beads [48] have been applied to improve its removal efficiency as well as its selectivity. For removal and recovery of dyes from solution, surfactant coated MNPs such as CTAB offer several potential advantages such as high extraction capacity, rapid separation, easy elution and recovery of dyes, and simple and convenient procedures.

In this study, adsorption efficiency of CTAB coated MNPs as a cationic surfactant was investigated for removal of two disperse dyes (disperse red 167 and disperse blue 183) from aqueous solution. For this purpose, first the effects of variables influencing the removal of dyes were evaluated. Then, under optimum conditions, removal of dyes was investigated in wastewater samples from textile industry.

**EXPERIMENTAL**

**Chemicals and Apparatus**

In this study, all of the used chemicals were analytical reagent grade. Disperse red 167 and disperse blue 183 were obtained from Department of Colorant Manufacture, Iran Color Research Center (Tehran, Iran), with analytical grade and were used without further purification. The chemical structure and $\lambda_{\text{max}}$ of the dyes are tabulated in Table 1. Ferric chloride (FeCl$_3$·6H$_2$O), ferrous chloride (FeCl$_2$·4H$_2$O), sodium dodecyl sulfate (SDS), CTAB, triton X-114 (TX-114), methanol, acetone and hydrochloric acid were prepared from Merck Company (Darmstadt, Germany). The water used throughout this work was double distillated water. The dye stock solution was prepared by dissolving accurately weight of dyes in double distillated water. The working solutions were obtained by diluting the stock solution to the required concentrations in water. In order to adjust the acidity of solutions, sodium hydroxide or hydrochloric acid solutions were used.

All pH measurements were performed with a WTW Inolab pH meter (Weilheim, Germany). A thermogravimetric analyzer PL-STA from PL-Thermal Science Company (London, England) was utilized to confirm high capacity of the adsorbent. The spectrophotometric measurements were carried out with UV-Vis. spectrophotometer CECIL CE-7200 (Cambridge, England) at the respective $\lambda_{\text{max}}$ value of each dye, 559 nm for disperse blue 183 and 469 nm for disperse red 167. The dye solutions were stirred using a motor-stirrer (Heidolph,
Germany) by glassware stirrer. A temperature-controlled shaker was applied for shaking at the constant temperature. A super magnet with 1.4 Tesla magnetic fields (10 × 5 × 4 cm) was used for magnetic separation.

**Synthesis of MNPs**

The MNPs were synthesized by chemical co-precipitation method, using a reactor designed in our research group recently [49]. First, 10.4 g of FeCl₃·6H₂O, 4.0 g of FeCl₂·4H₂O and 1.7 ml of HCl (12 M) were dissolved in 50 ml of deionized water in a beaker degassed with nitrogen bubbling for 20 min. Five hundred ml of 1.5 M NaOH solution was degassed (15 min) and heated to 80 ºC in the reactor. Then, the acidic solution was added dropwise into the NaOH solution in 30 min under the nitrogen gas protection and vigorous stirring (1000 rpm) using the glassware stirrer. During the whole process, temperature of the solution was maintained at 80 ºC and nitrogen gas was used to prevent intrusion of oxygen. After completion of the reaction, the obtained MNPs precipitate was separated from the reaction medium by magnetic field. It was subsequently washed with 500 ml of deionized water four times. Finally, the obtained NPs were re-suspended in 500 ml of the degassed deionized water. The pH of obtained suspension was 11.0 and concentration of the generated NPs in suspension was estimated to be about 10 mg ml⁻¹. The obtained NPs were stable at least for one month. The synthesized MNPs were characterized using a scanning electron microscope (SEM), infrared radiation (IR) and X-ray diffraction (XRD) as discussed previously [49].

**Dye Adsorption Procedure**

Extraction of dyes was carried out according to the following procedure: (1) 40 ml aqueous solution of the dyes (40 mg l⁻¹) was prepared in a 100 ml beaker by addition of the appropriate amount of stock solution of the dyes; (2) 1.0 ml of the NPs suspension (containing 10 mg of Fe₃O₄ NPs) was added to the dye solution; (3) pH of the solution was adjusted to the desired value and surfactant was then added into the dye solution; (4) the mixture of solution was stirred to enhance the efficiency of dye adsorption by increasing mass transfer; (5) by the use of a strong magnet after dye adsorption, Fe₃O₄ NPs was separated quickly (1 min) from the sample solution; (6) the residual dye concentration in the

**Table 1. Chemical Structures and λ\text{max} of the Examined Dyes**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical structure</th>
<th>λ\text{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disperse red 167</td>
<td><img src="image1" alt="Chemical structure" /></td>
<td>469</td>
</tr>
<tr>
<td>Disperse blue 183</td>
<td><img src="image2" alt="Chemical structure" /></td>
<td>551</td>
</tr>
</tbody>
</table>
supernatant clear solution was determined spectrophotometrically using the calibration curves. The following equation was applied to calculate the efficiency of dye removal in the treatment experiments:

\[
\text{Dye removal efficiency (\%) = } \left( \frac{C_0 - C}{C_0} \right) \times 100
\]

where \(C_0\) and \(C\) are the initial and residual concentrations of the dye in the solution (mg l\(^{-1}\)), respectively.

**RESULTS AND DISCUSSION**

**Effect of pH**

Surface charge of MNPs can be changed as a function of sample pH. Thus, at various pH conditions, different mechanisms can occur. In the present study different surfactants including cationic (CTAB), anionic (SDS), and non-ionic (TX-114) were used to evaluate removal efficiency of the dyes as a function of samples pH. So, the influence of pH on adsorption efficiency of dyes was studied over a range of pH values from 4 to 11 for TX-114 coated MNPs, from 3 to 8 for SDS coated MNPs, and from 5 to 11 for CTAB coated MNPs. The adsorption efficiency of the dyes is illustrated in Fig. 1a to Fig. 1c for different surfactant coated MNPs. Figure 1a indicates that the maximum adsorption efficiency of SDS coated MNPs is achieved at pH = 3. By increasing the pH, the sorption amount decreased. This can be attributed to the fact that when the pH level is below its zero point charge (PZC 6.5), the surface of MNPs is positively charged [50]. In this condition, SDS molecules can be easily adsorbed on positively charged surface of MNPs via electrostatic attraction forces. By increasing pH, the Fe\(_3\)O\(_4\) surface becomes negatively charged such that the strong electrostatic repulsion can occur between SDS molecules and the negatively charged MNPs surface.

Figure 1b demonstrates that the adsorption efficiency of TX-114 coated MNPs is independent of pH. This parameter remains nearly constant (lower than 50%) over the initial pH ranges of 4-11. This can be attributed to the fact that the surface of MNPs is positively or negatively charged under acidic or alkaline conditions, respectively. Under this circumstance, non-ionic surfactants such as TX-114 cannot easily interact with the charged surface.

Figure 1c shows removal efficiency of CTAB coated MNPs as a function of sample pH. The result indicates that maximum adsorption efficiency occurs at pH = 8. By increasing pH from 5 to 8, the sorption efficiency increased dramatically before reaching its maximum value at pH = 8.
When pH increases, the MNPs surface becomes negatively charged so that the strong electrostatic attraction between CTAB molecules and the negatively charged MNPs surface is high enough to produce a great adsorption affinity for disperse dyes.

In conclusion, maximum removal efficiency can be achieved at pH = 3 with SDS and pH ≥ 8 with CTAB. Removal under alkaline conditions is most favorable. Stability of MNPs in acidic pH is lower than that in alkaline conditions and MNPs can be easily oxidized under acidic condition and lose their magnetization up to 35% [51].

**Influence of CTAB Concentration**

Adsorption of ionic surfactants such as CTAB onto the surface of metal oxides is a favorable process. Depending on the amount of added surfactants, it can form different structures on surface of metal oxides [39,40]. Figure 2 depicts the adsorption efficiency of disperse dyes as a function of the amount of CTAB added. At low concentrations of CTAB, the adsorption efficiency of the disperse dyes on the surface of MNPs is low. In contrast, by increasing CTAB concentration, the adsorption efficiency increases remarkably. An increase in adsorption efficiency can be explained by the gradual formation of hydrophobic hemimicelles on the surface of MNPs which can increase the adsorption efficiency of the dyes. Similar results have been reported in the literature [52-54]. Hemimicelles consist of monolayer of surfactant adsorbing head down on a positively charged mineral oxide surface. Maximum removal was obtained when CTAB concentration was $5.0 \times 10^{-5}$ M for disperse blue 183 and $2.5 \times 10^{-5}$ M for disperse red 167. These results suggest that the removal behaviors of the disperse dyes are related to their hydrophobic properties. By increasing the number of chloro-substitutes, these properties raise.

**Kinetic of the Adsorption Process**

In order to study the adsorption kinetic, removal of dyes under optimum conditions (pH = 8.0 and CTAB concentration were $5.0 \times 10^{-5}$ M for disperse blue 183 and $2.5 \times 10^{-5}$ M for disperse red 167) was investigated by fixing adsorbent dose, and contact times were varied in the range of 5-60 min. Also, the dye concentrations were varied between 80-200 mg l$^{-1}$. Figure 3 shows removal efficiency of disperse red 167 as a function of contact time in different initial dye concentrations. Same results were obtained for disperse blue 183. It is evident that removal efficiency of the dye decreases when initial dye concentration in the solution increases. On the other hand, the results showed that removal rates of dyes are very fast and adsorption equilibrium is reached in 5 min for all of the five...
concentrations tested. Thus, the obtained results cannot be treated with conventional kinetic models. Therefore, it can be concluded that saturation of adsorbent may occur at short times or there is a correlation between amount of CTAB and initial dye concentration. It is worthy to note that for initial dye concentrations, amount of adsorbed dye was almost constant (40 mg l\(^{-1}\)). So, this hypothesis was considered in further studies.

**Effect of Dye-to-CTAB Ratio on the Adsorption Efficiency**

Optimization of CTAB concentration was accomplished for 40 mg l\(^{-1}\) of the dyes. Further studies showed that there is a correlation between initial dye concentration and CTAB concentrations.

Therefore, optimum CTAB concentration was investigated for higher initial concentration of the dyes (≥40 mg l\(^{-1}\)). The result showed that the ration of dye to CTAB should be kept constant at optimum value to achieve high removal efficiency (≥95%). Figure 4 shows the amount of CTAB needed for removal efficiency of ≥95% for different concentrations of the dyes. Under this circumstances, maximum amount of tested dyes (500 mg l\(^{-1}\)) can be removed with removal efficiency of ≥95. In this condition, the adsorbent capacity of the MNPs of the dyes can be 2000 mg g\(^{-1}\). In order to confirm the high capacity of the adsorbent, thermogravimetric analysis (TG) was done on the dry adsorbent which already was contacted with 500 mg l\(^{-1}\) of the dyes (Fig. 5). Obtained results showed that at temperatures lower than 450 °C, near 70 mass% loss occurs. This observation can be explained by thermal decomposition of the dye and CTAB. Since amount of CTAB is very low, it can be concluded that mass loss in TG process is due to degradation of the dyes adsorbed on the surface of the adsorbent. This phenomenon is a unique event which completely differs from the literature data.

**Salt Effect**

Generally, effluents of textile and dyeing industries contain a high concentration of salts, which may affect the removal efficiency of the dye [51]. Therefore, influence of salt concentration in range of 0-10% (w/v) on removal efficiency of the dyes was considered. The results revealed that removal efficiency of the dyes remained constant at even high concentration of the salt (10% (w/v)). This result could be very valuable, because the method can be applied to removal of dye from effluents containing high concentrations of salt without dilution.

**Desorption and Regeneration Studies**

Desorption of the dyes from the CTAB coated MNPs was studied using different kinds of organic solvents.

![Graph showing desorption efficiency comparison for different eluents for dyes from surface of MNPs.](image)

**Fig. 6.** Comparison of desorption efficiency of different eluents for the dyes from surface of MNPs.

(methanol, acetone, 50% (v/v) methanol in 0.1 M HCl, and 50% (v/v) acetone in HCl 0.1 M). The obtained results are demonstrated in Fig. 6. Desorption ability of methanol was found higher than that of the other solvents. This can be explained by suitable solubility of CTAB and the disperse dyes in methanol. Desorption efficiencies higher than 99% were obtained in a short time (1 min) and in a one-step elution using 2 ml of methanol. Further experiments showed that MNPs can be regenerated by methanol and reused for seven successive removal processes with removal efficiency higher than 99%. Under higher removal cycles, removal efficiency decreased maybe due to oxidation, losing and/or dissolving some amounts of the NPs during the successive steps.

**Removal of Dyes from Textile Wastewaters**

Under optimum conditions, removal of the disperse dyes was studied from a dyeing vat. The dyeing vat contained 2.5 x 10^{-3} M of acetic acid. The results showed that these dyes can be removed from the matrix with removal efficiency higher than 99%. Therefore, the proposed method can be directly applied to removal of the disperse dyes without further treatment.

**CONCLUSIONS**

In the present study, the CTAB coated MNPs as an efficient adsorbent were successfully applied to remove the disperse dyes from aqueous solutions. The amount of dye adsorbed was found to be dependent on solution pH, surfactant concentration, and ratio of initial dye concentration to surfactant concentration. The results showed that initial dye to CTAB concentration ratio is very important to achieve high removal efficiency (≥95%) at high concentrations of the dyes. Under this circumstances, maximum tested dyes (500 mg L^{-1}) can be removed with removal efficiency higher than 95%. In this condition, the adsorbent capacity can be as high as 2000 mg g^{-1}. When a simulated textile effluent was used as adsorbate, the adsorption efficiency did not change. Also, MNPs can be reused for more than seven times without any loss in absorption efficiency. Finally, the magnetic properties of the MNPs allow their separation from the effluent by a simple magnetic field, and lead to the development of a clean and safe process for water pollution remediation in accordance with the new requirements of ‘’green chemistry’’.

**REFERENCES**
