The Surface Functionalization of Fe$_3$O$_4$ Nanoparticles by CTAB as Adsorbent for Methyl Orange Elimination in Water

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Abstract. Adsorption is the most extensively used technique for elimination of dye in contaminant water. Magnetically separation of toxic pollutant is becoming a potential method for water purification and obtained more effective and simple compared to conventional method of treatment. The surface-functionalized magnetic iron oxide nanoparticles with cetyl trimethyl ammonium bromide (CTAB-coated CTAB) has been investigated. CTAB-coated Fe$_3$O$_4$ were synthesized by precipitation of ferrous/ferric chloride (mole ratio 2:1) in CTAB/ammonium hydroxide solution mixture. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption-desorption isothermal and Fourier transforms infrared spectroscopy. The CTAB-coated Fe$_3$O$_4$ nanoparticles exhibited ability significantly to eliminate methyl orange in water compared to uncoated Fe$_3$O$_4$. Dye adsorption equilibrium state data were fitted well to the Langmuir isotherm were obtained the favorable of constant separation factor value (RL) (0.005-0.03). The CTAB coated Fe$_3$O$_4$ followed the pseudo-second-order kinetic model, resulting in the rate constant adsorption value for the elimination of methyl orange was 0.0694 g.mg$^{-1}$.h$^{-1}$. CTAB coated Fe$_3$O$_4$ nanoparticles have relatively high saturation magnetization, which allowed their highly-efficient magnetic separation from wastewater. This investigation was concluded than CTAB-coated Fe$_3$O$_4$ nanoparticles was efficient to eliminate dye from wastewater

1. Introduction

Iron oxide magnetic nanoparticles with novel properties and functions have many unique magnetic properties such as superparamagnetic, high coercivity, high surface area to volume ratios, low Currie temperature and high magnetic susceptibility. It is great potential in electronics, magnetic storage, biomedical, optoelectronic, ferrofluid, separation and environmental application [1,2]. The superparamagnetic material can response external magnetic field but retain no residual magnetism after the field has been removed. This property is to be used as possible utilized as carrier adsorbent to remove pollutant from wastewater. Magnetically separation of magnetic particles is considered as a quick and effective technique for many application in biochemistry, analytical chemistry, mining ores and environment [3]. Adsorption procedure combined with magnetic separation has been used extensively in water treatment and environmental cleanup which considerable advantages with respect to fast separation of adsorbent via employing a strong external magnetic field and cost savings for decontamination of wastewater without centrifugation or filtration treatment (versus non-magnetic) [4].

Iron oxide magnetite, Fe$_3$O$_4$, Fe$^{II}$Fe$^{III}$O$_4$, ferrimagnetic possesses superparamagnetic behavior in size less than 15 nm. Accordingly experimental, saturation magnetization value of magnetite nanoparticles have been reported 30-80 emu/g, lower than that bulk magnetite of 100 emu/gr.
However, this value is still sufficient for magnetic separation with a magnet. On the other hand, Fe$_3$O$_4$ exhibits adsorption characteristics, possessing the capability to treat a large volume of wastewater and being convenient for magnetic separation [2]. Several experiments show that Fe$_3$O$_4$ nanoparticles have been undertaken to examine the removal efficiency of inorganic and organic contaminants [5]. It recommended that Fe$_3$O$_4$ nano sorbent were effective and economical adsorbents for rapid removal and recovery of metal ions from wastewater effluents.

To increase its performance, surface modification of Fe$_3$O$_4$ with inorganic shell or organic molecules have been reported [5]. It is in order to not only stabilize the nanoparticles and eventually prevents the oxidation but also enhance the capacity or selective for uptake contaminants in water treatment. The surface functionalized magnetite for environmental application have been utilized such as Fe$_3$O$_4$/silica for methylene blue and Zinc removal [6, 7], biopolymer functionalized iron Oxide for antimicrobial activity [8].

Cetyltrimethylammonium bromide (CTAB), a cationic surfactant has been widely used for the extraction of DNA and synthesis of nanoparticles (sphere, rods, bipyramid, mesoporous). Previous studies found that modification of some adsorbents with CTAB could greatly enhance the sorption of pollutants. For example, dextrin-oxalic acid/CTAB-montmorillonite for heavy metal remediation [9]. CTAB-modified graphite for adsorption bisphenol A [10].

Previous studies, we found that modification of magnetite surface with cetyltrimethylammonium bromide (Fe3O4@CTAB). In general, there are two step synthesis of Fe$_3$O$_4$@CTAB. In the first step, preparation of Fe$_3$O$_4$ nanoparticles by co-precipitation. In the second step, coating prepared Fe$_3$O$_4$ with CTAB. For example, Jin et al. (2012) [11] reported that Fe$_3$O$_4$ nanoparticles carried out by precipitation of a mix Fe(II)/Fe(III) solution with a Fe(II)/Fe(III) of 0.5 in alkali condition. The obtained Fe$_3$O$_4$ was then transferred into CTAB solution under sonification. The founded Fe$_3$O$_4$@CTAB was used for removal of arsenate. Wang et al. (2012) [12] reported that Fe$_3$O$_4$-CTAB was prepared by a facile one-pot solvothermal method in using an autoclave. Series of Fe$_3$O$_4$ morphologies are obtained by controlling the concentration of CTAB for removal of dyes.

In this study, Fe$_3$O$_4$-CTAB was prepared simply by one step (in-situ) process where the mixture of Fe(II)/Fe(III) was dropped in alkali-containing CTAB. This method has a shorter time in the synthesis process. The structural properties and morphology of obtained material were investigated in detail. Adsorption properties of Fe$_3$O$_4$-CTAB for the elimination of methyl orange in water were evaluated using Langmuir isotherms and kinetic adsorption equation.

2. Experiment

2.1. Materials and Reagents
All reagents used were of analytical reagent grade, i.e., ferric chloride (FeCl$_3$.6H$_2$O), ferrous chloride (FeCl$_2$.4H$_2$O), cetyltrimethylammonium bromide (CTAB), ammonium hydroxide (NH$_4$OH), hydrochloric acid, methyl orange. All reagents were purchased from Merck and used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of Fe$_3$O$_4$-CTAB
Amount 5.2 g FeCl$_3$.6H$_2$O and 2 g FeCl$_2$.4H$_2$O (mol ratio of Fe(III):Fe(II) = 2:1) were dissolved in 10.3 mL of 1 N HCl and diluted to 25 mL with deionized water under vigorous stirring. On the other hand, 0.36445 g CTAB was dissolved in 250 mL of 1.5 M ammonium hydroxide solution under vigorous stirring. The iron salt solution was dropped into CTAB/ammonia solution. The mixture was subsequently shaken for 8 hours. The formed black-colored precipitates were separated by helping magnetic bar and washed with deionized water. The obtained black-solid were dried in the oven at 60°C overnight and then 100°C for 2 hours.

2.3. Characterization
The synthesized samples were subsequently characterized by X-ray diffractometer (XRD, Empyrean Panalytical with Cu-K$\alpha$ radiation, $\lambda$=1.154 Å), vibrating sample magnetometer (VSM, Oxford type 1.2 T at room temperature), transmission electron microscope (TEM, JEM-14000 JOEL), Fourier
transform infrared-attenuated total reflection (FTIR-ATR Bruker TENSOR 27), N\textsubscript{2} adsorption-desorption isotherms (Quanitasorb SI-4-Kr/MP, Quantachrome Instruments at the liquid nitrogen temperature (77K)). Before measurement, the samples were degassed at 150°C for 8 hours.

2.4. Adsorption evaluation
All studies were conducted on the batch adsorption. The amount of Fe\textsubscript{3}O\textsubscript{4}-CTAB was inserted into methyl orange solution and stirred by shaker at room temperature for 4 hours. The effects of contact time, pH solution, adsorbent dose and concentration dye on adsorption were investigated. The adsorbed amount of methyl orange was calculated by the difference between the initial and final concentration in the equilibrium solution. The concentration of methyl orange was determined in the UV-Lambda 25 Spectrometer Perkin Elmer at 469 nm.

3. Result and Discussion
In order to determine crystal phase of iron oxide particles, the samples were analyzed by powder X-ray diffractometer (XRD). The XRD patterns of the samples were measured from 20 to 90° (2θ) and revealed the natural of the sample. Figure 1 showed XRD patterns of Fe\textsubscript{3}O\textsubscript{4} without and coated CTAB. The peaks of Fe\textsubscript{3}O\textsubscript{4} was clearly observed in diffractograms which similar to the standard diffraction pattern of magnetite in JCPDS file no. 03-0863 with 2θ at 30.167, 35.451, 43.253, 56.781, 62.726. Thus, the particles can be indexed to the pure phase of magnetite (Fe\textsubscript{3}O\textsubscript{4}) structure. The XRD pattern of Fe\textsubscript{3}O\textsubscript{4}-CTAB is identical with Fe\textsubscript{3}O\textsubscript{4} pattern. This result indicated that Fe\textsubscript{3}O\textsubscript{4} structure phase was no change after coated with CTAB.

![Figure 1. XRD pattern of Fe\textsubscript{3}O\textsubscript{4}-CTAB and Fe\textsubscript{3}O\textsubscript{4}](image)

The morphology and microstructure of Fe\textsubscript{3}O\textsubscript{4}-CTAB were investigated by transmission electron microscopy (TEM). Fig 2 (a) shown that the Fe\textsubscript{3}O\textsubscript{4}-CTAB nanoparticles tend to aggregate form around with size 200 nm. The particle of Fe\textsubscript{3}O\textsubscript{4} is observed possess particles size diameter less than 20 nm. (Fig. 2 (b). In this case, beneficial for magnetic separation due to retaining the superparamagnetic nature of individual nanoparticles, while aggregations of magnetic nanoparticle have relatively large volume enables their effective high-gradient magnetic separation (HGMS).
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Figure 2. Transmission electron microscope (TEM) of Fe$_3$O$_4$-CTAB (a) image on bar scale 100 nm (b) image on bar scale 20 nm.

The isotherms of nitrogen adsorption and desorption in sample Fe$_3$O$_4$ and Fe$_3$O$_4$-CTAB are presented in Fig. 3. The shape of the isotherms are attributed to type –IV curves according to the IUPAC classification. The pattern of the isotherms suggests that the founded Fe$_3$O$_4$ possess characteristic mesoporous materials. Mesoporous samples generally show hysterisis in the adsorption and desorption branches above P/P$_0$ = 0.4, attributed to multilayer formation and especially, capillary condensation in mesopores [13]. Mesoporous was occurred on Fe$_3$O$_4$ nanoparticles because of formation of inter-particles spaces of Fe$_3$O$_4$ agglomeration. There was no significant difference the total pore volume value for both Fe$_3$O$_4$ and Fe$_3$O$_4$-CTAB. However, the average pore diameter of Fe$_3$O$_4$-CTAB is higher than that Fe$_3$O$_4$ (Tabel 1). It is caused by the inter-particles space is rather broad due to the existence of CTAB attached on the surface of Fe$_3$O$_4$.

Figure 3. Nitrogen adsorption-desorption isothermal of Fe$_3$O$_4$ and Fe$_3$O$_4$-CTAB

Figure 4. FTIR spectra of Fe$_3$O$_4$ and Fe$_3$O$_4$-CTAB

| Sample     | BET surface area (m$^2$/g) | Total Pore volume (cc/g) | Average pore diameter (nm) |
|------------|----------------------------|--------------------------|----------------------------|
| Fe$_3$O$_4$| 172                        | 0.3050                   | 7.086                      |
| Fe$_3$O$_4$-CTAB | 146                      | 0.3008                   | 8.204                      |
The binding of CTAB to Fe₃O₄ nanoparticles surface was investigated by FTIR-ATR analysis as shown in Fig. 4. On CTAB curve, the asymmetric and symmetric vibration of CH₂ frequencies observed in 2914 and 2850 cm⁻¹, respectively. The asymmetric vibration of (CH₃-N⁺) and C-N stretching observed around at 3015 and 960 [14]. The bending vibration bands of the head [N(CH₃)]₃ methyl group at 1489 and 1429 cm⁻¹ and (CN⁻) stretching vibrations at 904 [15]. On Fe₃O₄ curve is appear a peak 3400- 3400 cm⁻¹. It is not from water, but it is attributed to the stretching vibrations of -OH groups which are assigned to surface OH group of Fe₃O₄ nanoparticles. This peak is wide due to the formation of hydrogen bond on hydroxyl group. While the peak at 1462 and 1627 is the plane and out of plane bonds of O-H groups [16]. On the Fe₃O₄/CTAB curve, the binding of CTAB to Fe₃O₄ nanoparticles surface result shift the spectrum IR bands peaks of CTAB vibration from 2850 to 2933 cm⁻¹, 2914 to 2980 cm⁻¹ and 1489 to 1452 cm⁻¹ suggesting an interaction between the Fe₃O₄ nanoparticles surface and the chemisorbed CTAB molecule [17]. In addition, the spectrum of CTAB-coated nanoparticles indicated a small shift in the positions of the main peaks in comparison with the bare nanoparticles. This could be ascribed to the alterations in the surface environment of the particles after modification.

Room-temperature magnetic hysteresis of Fe₃O₄ and Fe₃O₄-CTAB were measured by VSM (Fig. 5). It has a typical ferromagnetic behavior. The value of saturation magnetization (Ms) is 62.3 emu/ for Fe₃O₄. According, experimental value for Ms in magnetic iron oxide nanoparticles have been range the 30-80 emu/g. The experiments are lower than that bulk magnetic value 100 emu/g due to Fe₃O₄ nanoparticles are not very stable under ambient condition and easily change to Fe₃O₃ [2]. The saturation magnetization (Ms) of Fe₃O₄-CTAB is 55.9 emu/gr, lower than that Fe₃O₄ pure. This result is reasonable due to the present of non-magnetic material containing (CTAB) on samples. The magnetic remanence (Mr) and coercivity (Hc) value are 11.7 emu/gr and 138 Oe for Fe₃O₄ and 8.49 emu/gr and 116.7 Oe for Fe₃O₄-CTAB. The magnetic remanence and coercivity value of Fe₃O₄-CTAB is lower than that Fe₃O₄. It is favorable due to the degree of its superparamagnetic properties is increase. This alteration of magnetic properties may be caused by several factors, including particles size, structure, morphologies, etc.

![Figure 5](image1.png)  
**Figure 5.** M-H hysteresis curves of Fe₃O₄ and Fe₃O₄-CTAB

![Figure 6](image2.png)  
**Figure 6.** The adsorption of methyl orange on Fe₃O₄ and Fe₃O₄-CTAB

Fig. 6 shows the experiment result of methyl orange (MO) adsorption on Fe₃O₄ and Fe₃O₄-CTAB. The data presented a plot of C/Co (%) MO versus contact time, where C= concentration of MO in sampled water at t time, Co= concentration of MO initial. As shown in this figure, methyl orange was no adsorbed by Fe₃O₄ surface. The surface of Fe₃O₄ nanoparticles is negatively charged and the methyl orange containing –SO₃ group are negative too. So, the dyes can not directly interaction with Fe₃O₄ nanoparticles surface. Next curve, the methyl orange can be adsorbed drastically on CTAB coated Fe₃O₄ (Fe₃O₄/CTAB) which are adsorbed over 90% for 4 hours processes. CTAB containing
\[ S^- \] group is the type of cationic surfactant. The functionalization of Fe\(_3\)O\(_4\) surface with CTAB has altered into a positively charged. Since the Fe\(_3\)O\(_4\)-CTAB surface and methyl orange contain positive group and negative group \[ S^- \] and \[ -SO_3^- \] respectively, electrostatic interactions will occur both materials. This result indicates that CTAB plays an important role in the dye adsorption mechanism. The methyl orange is adsorbed via CTAB on the surface of Fe\(_3\)O\(_4\) nanoparticles. In addition, Sun et al. (2014) [18] reported that methyl orange could interact with alkyl chain of CTAB through hydrophobic intermolecular interaction which can contribute methyl orange adsorbed on the surface of Fe\(_3\)O\(_4\)-CTAB.

Initial pH solution is an important parameter to control the adsorption process. The pH of the solution can change adsorption capacity of adsorbent due to (1) the surface change of the adsorbent, (2) the degree of ionization of the adsorptive molecule and (3) extent of dissociation of functional groups on the active sites of the adsorbent [19]. The adsorption capacity (\(q\)) of adsorbent was calculated by the following equation:

\[
q = \frac{(C_0 - C_e)V}{m}
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium concentration of methyl orange (mg/L), \(m\) is the mass of composite (g) and \(V\) is the volume of solution (L). The adsorption of methyl orange onto Fe\(_3\)O\(_4\)-CTAB was investigated in range pH from 4 to 12 at initial methyl orange concentration of 15 mg/L and the contact time of 4 hours. As shown in figure 7, the methyl orange uptake tends to decrease with increasing pH solution. As described previously, the methyl orange is a dye anionic. The decrease in the adsorption of methyl orange with an increase of pH value is due to the competition between the anionic dye and excess OH- ion in the solution.

![Figure 7](image)

**Figure 7.** pH effect of adsorption methyl orange on Fe\(_3\)O\(_4\)-CTAB

The effect of the adsorbents dose was necessary in order to observe the effective of adsorbent used and also shows the maximum adsorption stochiometric. The effect of adsorbent dosage gives an idea for the ability of a dye adsorption to be adsorbed with the smallest amount of adsorbent. The influence of Fe\(_3\)O\(_4\)-CTAB dose on the adsorption capacity of methyl orange was shown in figure 8. The amount of Fe\(_3\)O\(_4\)-CTAB in the solution was varied from 0.5 to 2.5 g/L in solution with the constant of the initial methyl orange concentration of 20 mg/L. It can see that an adsorbent dose of 1.5 g/L is sufficient for optimal removal of methyl orange. Increasing the dose further did not affect, instead of decrease the adsorption capacity. Generally, increase in the solid concentration increase the surface area of the adsorbent, which in turn increase the number of binding sites. Thus the total amount of dye is removed increase. The adsorption capacity was low at high dose rate and vice versa. The increasing adsorbent concentration can result in a low specific site uptake, due to interference between binding sites. When the mass of the adsorbent in the liquid phase is higher, the interaction between adsorbent
particles become more important. It may cause physical blockage of some adsorption sites, decreasing the adsorption efficiency [20].

The interactive behavior between solutes and adsorbent was described in the equilibrium adsorption isotherm. The equilibrium adsorption data are analyzed using Langmuir isotherms model the following formula:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$  \hspace{1cm} (2)

where $q_e$ is the amount adsorbed at equilibrium (mg.g$^{-1}$), $C_e$ is the equilibrium concentration of the methyl orange (mg.L$^{-1}$), constant $b$ is related to the energy of adsorption (L.mg$^{-1}$), $q_m$ is the Langmuir monolayer adsorption capacity (mg.g$^{-1}$). If $C_e/q_e$ is plotted against $C_e$, one will get a straight line with a slope of $1/q_m$. Figure 9 shows adsorption isotherm and of methyl orange adsorption onto Fe$_3$O$_4$-CTAB, plotting $C_e/q_e$ against $C_e$, one would then obtain a high regression correlation coefficient with $R^2$ value of 0.9941. This indicates that the Langmuir model is suitable for describing the adsorption equilibrium of methyl orange by the Fe$_3$O$_4$-CTAB. The maximum monolayer capacity value which is determined from the Langmuir isotherm was found to have a value of 7.58 mg.g$^{-1}$. The characteristic of the Langmuir isotherm can also be illustrated in a dimensionless constant separation factor $R_L$ that is given by

$$R_L = \frac{1}{1+b C_0}$$  \hspace{1cm} (3)

where $C_0$ is the initial concentration in the liquid phase (mg.L$^{-1}$). The values of calculated Langmuir constants $b$, $q_m$ and $R_L$ are listed in Table 2. The value of $R_L$ indicates the shape of the isotherm to be either unfavorable ($R_L$>1), linear ($R_L$=1), favorable (0<$R_L$<1) or irreversible ($R_L$=0). The obtained $R_L$ value is in the range of 0.005-0.03, indicating that the adsorption is a favorable process.

![Figure 9. Langmuir isotherms of methyl orange adsorption onto Fe$_3$O$_4$-CTAB](image)

![Figure 10. Pseudo-second-order kinetics of adsorption methyl orange onto the Fe$_3$O$_4$-CTAB](image)

Kinetic parameters, which are useful for the prediction of the adsorption rate, give an important information for designing and modeling the adsorption processes. The adsorption mechanism of methyl orange onto the adsorbent was investigated by a pseudo-second-order kinetic model which was expressed in followed equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (4)

where $q_e$ and $q_t$ are the amounts of dye adsorbed (mg.g$^{-1}$) at equilibrium and at time $t$ (h) and $k_2$ (g.mg$^{-1}$.h$^{-1}$) is the rate constant of the pseudo-second-order adsorption. Kinetic constants obtained by linear regression for a pseudo-second-order kinetic model with $R^2$ value of 0.9907 (figure 10). The rate constant of pseudo-second-order adsorption ($k_2$) is 0.0694 g.mg$^{-1}$.h$^{-1}$ as showed in Table 2. The $q_e$(cal)
value close to the $q_{e,\text{exp}}$ (7.21 mg/g), which indicates the applicability of the second-order model to describe the adsorption process of methyl orange onto the Fe$_3$O$_4$-CTAB.

**Table 2.** Adsorption isotherm and kinetic parameters of methyl orange adsorption onto Fe$_3$O$_4$-CTAB

| Sample          | $q_m$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $R_L$ (mg g$^{-1}$) | $q_e$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ h$^{-1}$) | $R^2$ |
|-----------------|---------------------|------------------|-------|---------------------|---------------------|-------------------------|-------|
| Fe$_3$O$_4$-CTAB| 7.58                | 6.5024           | 0.9941| 0.005-0.03          | 11.905              | 0.0694                  | 0.9907|

**Table 3.** Comparison of the maximum monolayer adsorption ($q_m$) of methyl orange onto various adsorbents

| Sample                  | $q_m$ (mg/g) | Reference |
|-------------------------|--------------|-----------|
| Fe$_3$O$_4$-CTAB        | 7.6          | This study|
| Goethite                | 55           | [21]      |
| MoSe$_2$ Microsphere    | 36.9         | [22]      |
| Stratum Landform-like composite | 41.65 | [23]      |
| Wheat Bran              | 12           | [24]      |
| Cork powder             | 17           | [25]      |

The removal of methyl orange by various adsorbents has been studied extensively, and dye adsorption capacity was reported in the literature [21-25]. Table 3 compares the adsorption capacities of composite obtained in this work with different adsorbents previously used for removal methyl orange. It can be seen that the adsorption capacities of the Fe$_3$O$_4$-CTAB for methyl orange are lower slightly than that of many other previously reported adsorbents, indicating that the prepared composite has potential application in dye removal from aqueous solution.

**4. Conclusion**

We have demonstrated the synthesizing of the Fe$_3$O$_4$-CTAB on a simple one step (in-situ) process. The founded material has good adsorbent for methyl orange removal. The sorption capacity for methyl orange was 7.58 mg g$^{-1}$. The optimal sorption pH was 4-6. The adsorbent dose of 1.5 g/L is sufficient for optimal removal of methyl orange. The dimensionless constant separation factor ($R_L$) was in the range 0.005-0.03, meaning that the adsorption is a favorable process. The kinetic parameter was applicable for pseudo-second-order adsorption with rate constants of 0.0694 g mg$^{-1}$ h$^{-1}$. The synthesized Fe$_3$O$_4$-CTAB could easily recollect from water by the magnetic bar. So, they could be utilized as a convenient and effective adsorbent for methyl orange elimination from the water.

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