Silica-coated Magnetite Nanoparticles Prepared by the One-step Electrochemical Method for Dye Removal

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Abstract: In this paper, the synthesis of silica-coated magnetite nanoparticles using a one-step electrochemical method and their application for dye removal are presented. In this method, pure iron in a dilute aqueous sodium silicate solution that served as a silica precursor was electro-oxidized. The silica-coated magnetite nanoparticles produced by this method is nearly spherical with the size of approximately 10 nm and follows the spinel structure of Fe3O4. The silica-coated magnetite nanoparticles exhibit nearly superparamagnetic properties and excellent performance to remove methylene blue from wastewater. The adsorption capacity of the nanoparticles was approximately 24.2 mg methylene blue/g adsorbent, which was much higher than that of pure magnetite nanoparticles (1.1 mg methylene blue/g adsorbent). Also, the percentage removal was higher than 90% with the initial concentration of methylene blue up to 40 mg/L. It can be regenerated and reused with an only slight reduction in percentage removal.

Keywords: magnetite nanoparticles; electrosynthesis; magnetic properties; adsorption; dye removal

1. Introduction

Synthetic dyes are extensively used in various industries including dyestuff, pulp, and paper, plastics, textile, rubber, leather, and cosmetics [1]. The release of dye-containing industrial effluents to a natural water body causes serious environmental and health hazards [2]. The synthetic dyes are typically very intractable to microbial degradation and block the penetration of sunlight and oxygen that essential for the survival of various aquatic forms. Most synthetic dyes are toxic and highly resistant to light and oxidizing agents due to their complex chemical structure [3]. Therefore, the removal of dyes from dye-containing wastewater is of great importance before releasing it to the natural water body.

Several methods have been explored to remove dyes from wastewater, such as chemical oxidation [4], photocatalytic degradation [5], biological treatment [6], coagulation [7], and adsorption [8]. Among the methods, adsorption appears to be the most widely used because of its simplicity, high efficiency, and economy. The most commonly used adsorbents for dye removal are alumina [9], activated carbon [10,11], zeolites [12] and silica gel [13]. However, there are some limitations on their applications such as low...
adsorption capacity and difficulty in separating adsorbent from solution. Therefore, it is of great importance to developing new and cost-effective adsorbent materials for wastewater treatment.

Magnetic nanoparticles have attracted considerable attention for use as an adsorbent in wastewater treatment and are considered as one of the effective methods [14]. Among them, magnetite (Fe₃O₄) provides a convenient approach for separating and removing contaminants, e.g., pentachlorophenol, arsenic, and mercury, from industrial effluent by applying external magnetic fields [15-19]. It has been known that bare magnetite nanoparticles exhibit strong adsorption capacity and have properties of being readily separated and collected by an external magnetic field [16,20]. However, they are susceptible to air oxidation and acid dissolution and are easily aggregated in aqueous systems that make them difficult to recycle [21]. Surface modification has been widely used as a feasible solution to overcome the limitations. Different coating layers for magnetite nanoparticles have been successfully applied for the purpose, including 3-glycidoxypropyltrimethoxisilane [22], multi-wall carbon nanotubes [23], methylene blue [24] and silica [17]. Silica appears to be the most promising coating layers from the viewpoint of its reliable chemical stability, high surface area and facile surface modification [25]. Also, silica contains abundant silanol (−SiOH) groups on its surface, allowing it to be easily modified with many functional groups such as amines, thiols, and carboxyl.

We have successfully synthesized nearly monodispersed magnetite nanoparticles using an electrochemical method with a sacrificial iron anode and demineralized water as the electrolyte [26]. The surface of the particles can be modified with silica by merely changing the electrolyte with a very dilute sodium silicate solution to produce silica-coated magnetite nanoparticles [27, 28]. The silica layer can serve as an excellent protective layer against acidic and high-temperature environments. Moreover, the presence of silica on the magnetite surface has a notable effect on the magnetic properties of the nanoparticles. It changes from ferromagnetic to nearly superparamagnetic properties. These properties are beneficial for the application of novel separation process of adsorbent using an external magnetic field [29]. As mentioned above, silica is one of the most commonly used adsorbents for removal of various kinds of contaminant including dyes. Hence, silica on the surface of magnetite nanoparticles was assumed to enhance the adsorption capacity of the adsorbent.

Starting from our developed method for the preparation of silica-coated magnetite nanoparticles using a one-step electrochemical method [27]. In this work, the composite nanoparticles are investigated as a suitable adsorption material to remove dyes from wastewater. The adsorption equilibrium and kinetics are analyzed experimentally and mathematically. The analysis is very important for the design of the separation process. Regeneration is also examined to evaluate the reusability of this new type of adsorbents.

2. Materials and Methods

2.1. Preparation of silica-coated magnetite nanoparticles

Silica-coated magnetite nanoparticles were prepared using a one-step method by electro-oxidation of iron in demineralized water or dilute sodium silicate solution as previously reported [27,28,30]. Briefly, two iron plates of the same size (23 × 13 mm) were used as the electrodes (the anode and the cathode). The anode was connected with the positive terminal of a DC power supply, and the cathode was with the negative terminal. The electrodes were set parallel with an interelectrode distance of 2 cm. The electro-oxidation was carried out for 20 h at an applied potential of 20 V. For the case of particle preparation in sodium silicate solution, the concentration was 150 ppm and 200 ppm. The particles produced were filtered, washed with demineralized water and dried. The magnetic nanoparticles (MNP) prepared in water and sodium silicate solution with a concentration of 150 and 200 ppm will be referred to, respectively, as MNP, Si150-MNP, and Si200-MNP.

2.2. Characterizations

The morphology of particles was observed using scanning electron microscopy (SEM; JSM-6335F, JEOL). The X-ray diffraction (XRD) patterns of particles were determined using an X-ray diffractometer (X-Pert, Philips). The infrared (IR) spectra were recorded using a Fourier transform infrared (FTIR) spectrophotometer (FTIR 8400s, Shimadzu). The Brunauer–Emmet–Teller (BET) specific surface area of the particles was determined using multi-point nitrogen adsorption at its boiling point (Nova 1200,
Quantachrome). Magnetic characterization was performed using a SQUID magnetometer (Quantum Design MPMS-5T) at 300 K.

2.3. Adsorption isotherm experiments

The dye used in the present study was methylene blue (MB) (Merck, p.a.) and it was used without further purification. 0.5 g of adsorbent was kept in contact with 10 ml of MB solution of different concentrations (5–50 mg/L) to study the adsorption isotherm. An accurately weighed quantity of MB (100 mg/L) was dissolved in demineralized water to prepare a stock solution. Solutions of different concentration were obtained by successive dilution of the stock solution. All sorption experiments were carried out in duplicate in reaction tubes placed in an orbital shaker for 48 h at room temperature. The MB concentration in the equilibrium condition was measured by a UV–vis spectrophotometer (UV1100, Technocomp) at a wavelength of 600 nm.

2.4. Adsorption kinetic experiments

To study the kinetics of adsorption, ten reaction tubes containing 0.5 g of adsorbent and 10 ml of 20 mg/L MB solution was shaken continuously using an orbital shaker. At suitable time intervals, shaking was arrested, and at each time interval, one tube was taken for the determination of the MB concentration remaining in solution. The progress of adsorption at various time intervals was measured by a UV-vis spectrophotometer (UV1100, Technocomp) at a wavelength of 600 nm. The amount of MB adsorbed on the adsorbent was determined by the difference between the initial and the remaining concentrations of MB solution.

3. Results and Discussion

3.1. Characteristics of particles

Figure 1 shows the SEM images of the three samples prepared by the above method: MNP, Si150-MNP, and Si200-MNP. For all cases, the particles are nearly spherical. The mean particle size of sample MNP (prepared in water) is approximately 20 nm. The particle size decreases significantly to approximately 10 nm for samples Si150-MNP and Si200-MNP (both prepared in sodium silicate solution). The surface area of sample MNP is approximately 52 m²/g and increases significantly to approximately 117 m²/g for sample Si150-MNP and 135 m²/g for sample Si200-MNP. The increase in surface area may come from both the decrease in particle size and the silica layer on the particle surface. It is generally true that the smaller the particles are, the higher the specific surface area is. Moreover, the silica layer formed by a sol-gel method has a typical porous structure [18]. The structure makes the layer has a high surface area. The mean size of magnetite particles estimated from the specific surface area by assuming the particles to be spherical and dense is in good agreement with those estimated from SEM. The result suggests that the nanoparticles are well dispersed, not agglomerated. These properties make the silica-coated magnetite nanoparticles useful as adsorbents in water and wastewater treatment.

![Figure 1. SEM images for samples: (a) MNP, (b) Si150-MNP and (c) Si200-MNP.](image)

Observing the XRD patterns of the particles shown in Fig. 2, all particles have seven characteristic peaks which match the standard pattern of the spinel structure of Fe₃O₄ (JCPDS 19-0629). In these diffraction patterns, no trace of other compounds can be observed. To understand the effect of sodium silicate on the particles formed, the infrared spectrum of the particles was detected using an FTIR
spectrophotometer. Figure 3 shows the FTIR spectrum of samples MNP, Si150-MNP and Si200-MNP. The FTIR spectrum of silica is also presented for comparison. For all cases, two main bands (580 and 442 cm\(^{-1}\)) corresponding to Fe\(_3\)O\(_4\) can be observed. The bands are metal–oxygen bands that correspond to the intrinsic stretching frequencies of the tetrahedral and octahedral sites, respectively, of the inverse cubic spinel of Fe\(_3\)O\(_4\) [27, 31]. For samples Si150-MNP and Si200-MNP, other bands (1080, 996 and 624 cm\(^{-1}\)) that can be attributed to Si-O-Si and Si-O stretching corresponding to SiO\(_2\) appear [32,33]. Moreover, the band at 561 cm\(^{-1}\) is possibly due to the Fe–O–Si stretching vibrations caused by perturbation of the metallic ion in SiO\(_4\) [27]. The bands at 1,630 and 3,430 cm\(^{-1}\) can be attributed to O–H bending and stretching of the associated water molecules. The peaks at 3,443 and 1,629 cm\(^{-1}\) correspond to -OH on the silica surface [34]. These results clearly indicate the existence of silica in the magnetite particles although it is not detected in the XRD analysis. This may be caused by the form of silica as a thin layer on the particle surface.

![Figure 2. XRD pattern for samples: (a) MNP, (b) Si150-MNP and (c) Si200-MNP.](image1)

![Figure 3. FTIR spectra for samples: (a) MNP, (b) Si150-MNP, (c) Si200-MNP and (d) silica.](image2)

The magnetic properties of particles were examined with VSM at room temperature. Figure 4 shows the magnetization curve for samples MNP, Si150-MNP and Si200-MNP. The results suggest that all magnetite particles, regardless of silica-coated or uncoated, likely possess ferromagnetic properties. The magnetization curve indicates a hysteresis loop typically observed for ferromagnetic materials. The saturation magnetization of the uncoated magnetite nanoparticles (MNP) is approximately 71 emu g\(^{-1}\),
which is less than that of Fe$_3$O$_4$ bulk materials (Ms = 92 emu g$^{-1}$). It decreases to 45 emu g$^{-1}$ (Si150-MNP) and 39 emu g$^{-1}$ (Si200-MNP) when they are coated with silica. The reduction may be attributed partly to the small particle size and the high surface area, which lead to surface effects such as spin canting. The coercivities of the nanoparticles have values of approximately 360 Oe (MNP), 150 Oe (Si150-MNP) and 130 Oe (Si200-MNP), which is in agreement with the expected value of randomly oriented, uniaxial and non-interacting particles of magnetite. The magnetic properties of the coated ones approach nearly superparamagnetic as indicated by the low values of coercivities.

![Image](https://via.placeholder.com/150)

**Figure 4.** Magnetization curve at room temperature for samples: (a) MNP, (b) Si150-MNP and (c) Si200-MNP; separation of Si200-MNP from the solution under an external magnetic field (inset).

### 3.2. Adsorption isotherms

The contact time used to study the adsorption isotherms was selected from preliminary experiments by measuring the change of MB concentration with time. Figure 5 shows the change of the normalized concentration of MB, $C(t)/C_0$ as a function of time. The initial concentration of MB was 20 mg/L. As can be seen, the equilibrium was established in 20–30 h for all cases. Equilibration for longer times, that is, between 30 and 48 h, gave practically the same concentration. Therefore, the contact time was set at 48 h in all equilibrium tests. After this period, the solution was filtered using Whatman No. 42 filter paper and analyzed for the MB concentration remaining in the solution by a UV-vis spectrophotometer. The distribution of MB between the adsorbent and the solution at equilibrium condition is essential to establish the adsorbent capacity for the MB.

Initial concentrations of 5–50 mg/L were used with the adsorbent at 50 mg in 10 mL MB solution to derive data for the adsorption isotherm. Isotherms of the adsorption of MB on the magnetite (MNP) and silica-coated magnetite (Si150-MNP and Si200-MNP) adsorbents are presented in Fig. 6. The adsorption capacity of MB onto MNP is low (~1.25 mg MB/g adsorbent). It increased significantly to approximately 13 and 17 mg MB/g adsorbent for, respectively, Si150-MNP and Si200-MNP. It is apparent that the presence of silica on the surface of magnetite particles is greatly enhanced the adsorption capacity. Moreover, the surface area of the nanoparticles has also a significant effect on the adsorption performance. The adsorption capacity increases with the increase of surface area. As discussed before, the surface area of MNP, Si150-MNP, and Si200-MNP is, respectively, 52, 113 and 135 m$^2$/g. It is likely that the large surface area allows for binding at a high number of active sites distributed within the particle surface, and as a result, the adsorption capacity increases.
Figure 5. The change of the normalized concentration of MB, \( C(t)/C_0 \), as a function of time.

Figure 6. Isotherms of the adsorption of MB on the synthesized adsorbents. The lines are the corresponding Langmuir model with the constants shown in Table 1.

The adsorption isotherms of magnetite nanoparticles presented in Fig. 6 showed a typical form of Langmuir type of isotherm. This type is characterized by a relatively rapid initial rise in the amount of MB adsorbed with increasing MB concentration and then approaches saturation. Therefore, the experimental data of adsorption were fitted to the Langmuir equation that may be expressed as

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

(1)

In this equation, \( q_e \) is the adsorption capacity of the adsorbent at equilibrium, \( C_e \) is the equilibrium concentration of solute in solution, \( q_m \) is the monolayer adsorption capacity, and \( b \) is the constant related to the free energy of adsorption. The fitted parameters of adsorption were calculated from the linear regression of the linear form of Eq. (1), namely

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

(2)
As expected, the Langmuir model adequately described the adsorption data for all magnetite samples. The Langmuir parameters as calculated from the linear form for all samples are given in Table 1. It can be seen from the table that the values of the maximum adsorption capacity ($q_m$) are found to be higher in the case of the silica-coated magnetite nanoparticles (Si150-MNP and Si200-MNP). The values of $q_m$ for Si150-MNP and Si200-MNP are 14.2 and 24.2 mg MB/g adsorbent, respectively, which are much higher compared to 1.1 mg MB/g adsorbent for the uncoated one (MNP).

The above results demonstrate that the silica-coated magnetite nanoparticles can adsorb MB with high efficiency. The presence of silica on the particle surface enhances the effectiveness of MB uptake. In addition to the surface properties of silica, the enhancement may also be caused by the higher surface area of the silica-coated magnetite nanoparticles.

Several MB solutions were prepared at different concentrations to evaluate the adsorption efficiency of MB on the surface of silica-coated magnetite nanoparticles in more detail. Figure 7 shows the effect of initial concentration on the amount of MB removal. The amount of MB removal for MNP without silica coating is very low (<50%). It increased significantly for silica-coated magnetite nanoparticles (Si150-MNP and Si200-MNP), which could reach approximately 95% at MB concentration of approximately 20 mg/L. The results show that silica-coated magnetite nanoparticles are very effective adsorbent in removing MB.

### Table 1. Parameter values of the Langmuir model fitted to the experimental data.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_m$ (mg/g)</th>
<th>$b$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP</td>
<td>1.063</td>
<td>0.219</td>
<td>0.593</td>
</tr>
<tr>
<td>Si150-MNP</td>
<td>14.225</td>
<td>0.157</td>
<td>0.985</td>
</tr>
<tr>
<td>Si200-MNP</td>
<td>24.213</td>
<td>0.227</td>
<td>0.885</td>
</tr>
</tbody>
</table>

![Figure 7. Effect of initial concentration on the amount of MB removal.](image)

3.3. **Adsorption kinetic**

The adsorption kinetics was studied for the silica-coated magnetite nanoparticles (Si150-MNP and Si200-MNP) adsorbent in MB concentration of 20 mg/L. Two models were used to study the adsorption kinetics, pseudo-first-order, and pseudo-second-order. The pseudo-first-order model may be expressed as

$$\ln(q_e - q) = \ln q_e - k_1 t$$  \hspace{1cm} (3)$$

and the pseudo-second-order is
\[
\frac{t}{q} = \frac{1}{k_1 q_e} + \left(\frac{1}{q_e}\right) t
\]

(4)

In Eqs. (3) and (4), \(q_e\) is the amount of adsorbed MB at equilibrium, \(q\) is the amount of MB adsorbed on adsorbent at time \(t\), \(k_1\) is the pseudo-first-order rate constant, and \(k_2\) is the pseudo-second-order rate constant of adsorption.

Figure 8 shows the time dependence of the amount of MB adsorbed and the corresponding pseudo-first-order and pseudo-second-order kinetic models. Based on the figure and correlation coefficients in Table 2, the kinetics for the removal of MB fitted well with the pseudo-second-order model. It suggests that the surface silanols can interact with MB molecules and corroborated further by the fact that the calculated \(q_e\) values match with the experimental data. The \(k_2\) value increases from 0.099 to 0.211 g/(mg min) as the sodium silicate concentration during electrolysis was increased from 150 ppm (Si150-MNP) to 200 ppm (Si200MNP). As discussed above, the surface area of Si200-MNP is higher than that of Si150-MNP. It indicates that the surface area clearly influences the adsorption rate.

Figure 8. Time dependence of the amount of MB adsorbed and the corresponding pseudo-first-order and pseudo-second-order kinetic models.

Table 2. Parameter values of the kinetics models fitted to the experimental data.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_1) (min(^{-1}))</td>
<td>(R^2)</td>
</tr>
<tr>
<td>Si150-MNP</td>
<td>0.126</td>
<td>0.570</td>
</tr>
<tr>
<td>Si200-MNP</td>
<td>0.112</td>
<td>0.828</td>
</tr>
</tbody>
</table>

3.4. Regeneration and Reusability

Evaluating the reusability of the adsorbents is essential. The evaluation is performed by regenerating the adsorbents and measuring the adsorption performance in a series of further identical solutions. The regeneration was carried out by desorbing MB from the adsorbent surface by washing thoroughly with de-ionized water. In the repeated experiments, the used adsorbent was separated from solutions with a centrifuge, washing thoroughly with de-ionized water to removed adsorbed compounds and then dried before being reused in the next adsorption cycle. Figure 9 shows the reusability of the Si150-MNP and Si200-MNP adsorbents for three cycles. As shown in the figure, %removal decreased during reuse but remained a high value after three cycles. The adsorbents are therefore well suited to
being reused. The behavior may come from the blocking of the porous surface with MB molecules in each cycle and decreases the adsorption capacity in the next cycles.

Figure 9. Reusability of the Si150-MNP and Si200-MNP adsorbents during three adsorption/desorption cycles.

4. Conclusions

Silica-coated magnetite nanoparticles as a novel magnetic sorbent have been prepared using a one-step electrochemical method in a dilute sodium silicate solution as the silica precursor. The particles are nearly spherical with the size of approximately 10 nm and likely possess ferromagnetic properties. The silica-coated magnetite nanoparticles exhibited good performance to remove methylene blue from waste-water. The adsorption capacity of the nanoparticles was approximately 24.2 mg methylene blue/g adsorbent, which was much higher than that of pure magnetite nanoparticles (1.1 mg methylene blue/g adsorbent). Also, the percentage removal was higher than 90% with the initial concentration of methylene blue up to 40 mg/L. It can be regenerated and reused with an only slight reduction in percentage removal.

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