Preparation of Fe$_3$O$_4$@SiO$_2$@PLL Core-Shell Nanoparticles for Potential Application for Heavy Metal Ion Removal

Yi-han Ma, Qing-han Zhou$^*$

**Abstract**—The Fe$_3$O$_4$@SiO$_2$@PLL core-shell nanoparticles were prepared by functionalization of magnetic Fe$_3$O$_4$ nanoparticles with 3-amidyl trimethoxane (APTMS) and Poly(L-lysine) (PLL) as a novel sorbent for heavy metal ion removal in water. The Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles were prepared by a three-step process: (i) surface modification of Fe$_3$O$_4$ nanoparticles by APTMS to form Fe$_3$O$_4$@SiO$_2$, (ii) surface functionalization of Fe$_3$O$_4$@SiO$_2$ nanoparticles by ring opening polymerization to form a Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles, and (iii) deprotection of PLL to form the Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles. The chemical structure of the Fe$_3$O$_4$ @ Fe$_3$O$_4$@SiO$_2$, Fe$_3$O$_4$@SiO$_2$@PLL, and Fe$_3$O$_4$@SiO$_2$@PLL was characterized by FT-IR and XRD. The core-shell nanoparticles were analyzed by DLS and SEM. The core-shell nanoparticles will be further studied on their removal efficiency for heavy metal ions such as Cr$_{2}$O$_7^{2-}$ (VI) from the aqueous medium, and the effects of different factors such as initial adsorbent concentration, adsorption time, adsorption dosage, pH, and temperature in the adsorption experiment will be furtherly studied.

**Index Terms**—Poly(L-lysine), adsorbent, magnetic nanoparticles, removal of heavy metal ions.

I. INTRODUCTION

It is still challenging to provide adequate clean water for the world’s growing population, which is one of the major challenges mankind faces. In last decades, enormous amounts of contaminated aqueous effluents have been generated by industrial activities. Among the contaminated aqueous effluents, heavy metals are the most common pollutants that harm the aqueous environment and damage health of human, animals and plants, because they are non-biodegradable and may cause metabolic and physiological problems. Therefore, international organizations such as the World Health Organization (WHO) and Centre for Disease Control (CDC) regulate heavy metal ions as hazardous substances. Thus, many approaches have been utilized to remove heavy metal ions, including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, and flocculation. Among these methods for removal of heavy metal ions, adsorption is considered as a promising technique owing to its high removal efficiency, low cost, ease of operation, and reusability. Therefore, adsorption method has been extensively used in various water purification processes. Some efficient adsorbents have been employed in heavy metal ion adsorption, such as carbon, zeolit clay, graphene, carbon nanotubes, bio-adsorbents, and various metal oxides. However, a more efficient waste water treatment system with novel adsorbents that can be removed quickly and recycled is necessary.

Magnetic separation is a low-cost and efficient method of separating magnetic materials from aqueous systems through the application of an external magnetic field. Although there have been many significant developments in the application of magnetic nanoparticles, maintaining the stability of these particles for a long time without agglomeration or precipitation is still a challenge. Moreover, bare magnetite nanoparticles are rather susceptible to air oxidation, which hindered the further development in wastewater treatment. Recently, polymeric chelating materials are widely used in the removal of metal ions due to their high adsorption capacities and selectivity. Thus, the nanosorbent with chelating polymer coatings and inorganic magnetic inner core, have attracted much more attention for water treatment due to the facile collection under a magnetic field without contamination.

In this study, Fe$_3$O$_4$@SiO$_2$@PLL was prepared by a three-step process. The magnetic nanosorbent and related nanoparticles were characterized by FT-IR, DLS, and SEM. Finally, based on the experimental results the as prepared Fe$_3$O$_4$@SiO$_2$@PLL core-shell nanoparticles were considered as a promising magnetic nanosorbents for potential use in removal of heavy metal ions from water.

II. EXPERIMENTAL

**Materials**

Ferric trichloride (FeCl$_3$ • 6H$_2$O) and Ferrous chloride (FeCl$_2$ • 4H$_2$O) were purchased from Chengdu xindu MuLan town industrial development zone, Hydrobromic acid in glacial acetic acid (HBr/AcOH , 33% w/v)), 3-amidyl trimethoxane (APTMS), trifluoroacetic acid (TFA) were purchased from Beijing J&K Chemical, ammonium persulfate, citric acid, ammonium hydroxide, nitric acid, hexyl hydrid, ethyl alcohol, ethyl acetate and solvents were purchased from Chengdu kelon chemical reagent company. PZLL-NCA was synthesized by our group.

Yihan Ma. College of Chemical and Environment Protection, Southwest Minzu University, Chengdu, China

Qing-han Zhou. College of Chemical and Environment Protection, Southwest Minzu University, Chengdu, China

$^*$ corresponding author.
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Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

$\text{FeCl}_3\cdot\text{H}_2\text{O}$ 2.70 g and $\text{FeCl}_3\cdot\text{H}_2\text{O}$ 1.00 g were added into a three-necked flask, and then 60.00 mL of deionized water was added under nitrogen atmosphere, and mechanically stirred (700 t/min) at 80 °C. After 30 min stirring, 20.00 mL ammonia was added to adjust the pH to 9–10, and underwent another 30 min stirring under N$_2$ protection. Finally, 2.00 mL citric acid was added, the reaction was carried out at 90 °C for 90 min. When cooled to room temperature, the upper layer liquid was removed, and washed with ethanol and deionized water for several times. The obtained $\text{Fe}_3\text{O}_4$ colloid was placed into a vacuum oven, and dried for 3 h to obtain $\text{Fe}_3\text{O}_4$ magnetic nanoparticles.

Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles

0.13 g $\text{Fe}_3\text{O}_4$ magnetic nanoparticles were added to a three-necked flask containing 15.00 mL of ethanol and 15.00 mL of deionized water. The mixed solution was ultrasonically dispersed for 10 min, and then mechanically stirred (250 t/min) for 30 min at 80°C. 1.00 mL of APTMS were added into the three-necked flask. And the reaction was carried out at room temperature for 3.5 h under N$_2$. Then, the supernatant was removed by centrifugation, and washed with deionized water for several times. The obtained colloid was placed in a vacuum oven at 50 °C for 24 h to obtain the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles.

Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$ magnetic nanoparticles

0.10 g $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles were added into 10.00 mL of DMF and ultrasonically dispersed for 10 min. PZLL-NCA (2.00 g, 4.00 mmol) was added into three-necked flask at room temperature with gently stirring for 36 h. Finally, the solvent was removed, and the product solution was precipitated in diethyl ether. The raw product was then washed with distilled water and ethanol for several times, and was dried by vacuum to obtain the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$ magnetic nanoparticles.

Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$

$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ (0.70 g, 0.07 mmol) was added into 25.00 mL of NaOH solution. The reaction was carried out for 12 h under N$_2$ at room temperature. Then the solvent was removed under reduced pressure, the obtained solid was further dispersed in distilled water, and then washed with diethyl ether for several times. Then the raw product was dried by vacuum to obtain a white powder.

III. RESULTS AND DISCUSSION

Preparation and characterization of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ magnetic nanoparticles

The $\text{Fe}_3\text{O}_4$ nanoparticles were prepared by co-precipitation method. Then APTMS was used to decorate the surface of the $\text{Fe}_3\text{O}_4$ nanoparticles to obtain a -NH$_2$ modified magnetic nanoparticles. By the ring opening polymerization, the PZLL-NCA was used to synthesize the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$ magnetic nanoparticles. Finally, the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ was prepared via deprotection of the PZLL by a hydrolysis reaction. Each step of the preparation process was characterized by FT-IR.

The FT-IR spectra of $\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ were shown in Fig. 2. As shown in Fig. 2, the peak around 580 cm$^{-1}$ could be ascribe to the stretching vibration of Fe-O. In the FT-IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, it was indicated that the absorption peak at 1020 cm$^{-1}$ could be ascribed to the stretching vibration of Si-O. For the FT-IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$, the absorption peak around 1128, 1651, and 1700 cm$^{-1}$ corresponded to the C-O-C group, C=O group in the amide bond, and C=O group in the ester bond. The peak at 3290 cm$^{-1}$ can be ascribed to the N-H stretching vibration. For the FTIR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$, the peak at 1020 cm$^{-1}$ corresponded to Si-O. The peak at 1637 cm$^{-1}$ and 3430 cm$^{-1}$ could be ascribed to C=O and N-H group. Based on the FTIR spectra, it was suggested that the nanoparticles of $\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$ were successfully prepared.

![Fig. 1 Synthetic scheme for the preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$](image1)

![Fig. 2 FT-IR spectra of $\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PZLL}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PLL}$](image2)
The XRD results suggested the successful preparation of Fe$_3$O$_4$@SiO$_2$@PLL, and the lower crystallinity of the Fe$_3$O$_4$ particles in Fe$_3$O$_4$@SiO$_2$@PLL samples can be explained by the polymer modification on the surface of Fe$_3$O$_4$ nanoparticles.

The zeta potential was further investigated to characterize the surface property of each sample. The zeta potential of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$, Fe$_3$O$_4$@SiO$_2$@PLL was 24 mV, 32 mV, and 1.46 mV, which indicated the positively charged Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles were successfully prepared.

As shown in the Fig. 5, the size change of the nanoparticles was investigated by DLS. Fig. 5 revealed that Fe$_3$O$_4$ nanoparticles exhibited a constant average size of 110 nm, and Fe$_3$O$_4$@SiO$_2$ nanoparticles showed an average size of 120 nm after the modification by APTMS, which proved that SiO$_2$ was successfully coated onto the surface of Fe$_3$O$_4$ magnetic nanoparticles. Finally, the Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles were of ~190 nm. It was indicated that the Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles were successfully prepared by with PLL coating.

The SEM photos of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$@PLL were shown in Fig. 6. The size of Fe$_3$O$_4$ magnetic nanoparticles is about 80 nm. The size of Fe$_3$O$_4$@SiO$_2$@PLL nanoparticles were about 160nm, which proved that SiO$_2$ and PLL was successfully coated onto the surface of Fe$_3$O$_4$ magnetic nanoparticles. The SEM results were consistent with the DLS measurement indicating the successfully modification of the Fe$_3$O$_4$ magnetic nanoparticles.

IV. CONCLUSION

In this experiment, the novel magnetic nanosorbent, Fe$_3$O$_4$@SiO$_2$@PLL, was prepared by a three-step process. The chemical structures and morphology of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$, and Fe$_3$O$_4$@SiO$_2$@PLL were fully characterized by FT-IR, DLS, and SEM. Based on the experimental results, the as prepared magnetic nano-adsorbent can be used as a promising reusable nano-materials for potential use in heavy metal ion removal.

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REFERENCES


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