

Preparation of Novel Magnetic PGA@SiO₂@Fe₃O₄ Composite Nanoparticles for Heavy Metal Ion Removal

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Abstract—The novel magnetic adsorbent was prepared by functionalization of magnetic nanoparticles with Poly- γ -glutamate (PGA), and the sorbent is named as PGA@SiO₂@Fe₃O₄. The composite nanoparticles were further used in retrieval of heavy metal ions such as Pb(II) from the aqueous medium. The preparation of PGA@SiO₂@Fe₃O₄ involves a two-step process: (i) surface modification of Fe₃O₄ nanoparticles by ethyl orthosilicate (TEOS) to form SiO₂@Fe₃O₄, (ii) surface functionalization of SiO₂@Fe₃O₄ nanoparticles by free radical copolymerization to form a cross-linking magnetic PGA@SiO₂@Fe₃O₄ nanoparticles. The chemical structure of the PGA, Fe₃O₄, SiO₂@Fe₃O₄, and PGA@SiO₂@Fe₃O₄ was characterized by ¹H-NMR, and FTIR. The nano-size and surface morphologies of the adsorbent were analyzed by SEM and DLS. Finally, the adsorbent was used to adsorb Pb (II), and the effects of different factors such as initial concentration, adsorption time, adsorption dosage, pH, and temperature on the adsorbent and adsorption were studied.

Index Terms— Absorbent, Magnetic nanoparticles, removal of heavy metal ions, polypeptide.

INTRODUCTION

It is still challenging to protect the water resources for preservation of the environment^[1,2]. In last decades, enormous amounts of contaminated aqueous effluents have been generated by industrial activities. Especially, battery enterprises produce effluents with high levels of toxic metals, such as Pb(II), Cd(II), Sb(III) by using large amounts of water^[3-5]. These species are not biodegradable and can be bio-accumulated in the environment. Moreover, Pb(II) can be absorbed and accumulated in the central nervous system of human body when in contact with the gastrointestinal tract, leading to irreversible brain damages. According to the United States Environmental Protection Agency (EPA), low levels of Pb(II) exposure have been associated with damage to the central and peripheral nervous system in children, and higher levels of Pb(II) raise the probability of cardiovascular diseases and even death^[6,7].

Among the method for protection of the water, adsorption is considered as promising technique, and it has been extensively used in various water purification processes^[8]. Compared with traditional sorbents, nanosorbents demonstrate effective adsorption property with high surface area, plentiful sorption sites, tunable pore size and surface, and short intraparticle diffusion distance^[9]. On the other

hand, smagnetic separation is a low-cost and efficient method of separating magnetic materials from aqueous systems through the application of an external magnetic field^[10]. Therefore, magnetic Fe₃O₄ nanoparticles are good candidates for connecting chelating materials to their surfaces because of their inertness to surrounding environment, ease of surface modification with specific functional groups, and high surface area-to-volume ratio leading to enhancement of adsorption capacity. Recently, the nanosorbents 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^[11].

In this study, PGA@SiO₂@Fe₃O₄ was prepared by a two-step process. 1) magnetic nanoparticles Fe₃O₄ were coated with SiO₂ by using TEOS, and 2) The PGA@SiO₂@Fe₃O₄ magnetic nanoparticles adsorbent was prepared by free radical copolymerization with PGA as copolymerization component, ammonium persulfate as initiator, and EGDMA as crosslinking agent. The magnetic nanosorbent, PGA@SiO₂@Fe₃O₄, was characterized by ¹H-NMR, FT-IR, SEM, and DLS. Finally, The PGA@SiO₂@Fe₃O₄ magnetic nanosorbents was used in removal of metal ions from water by using batch adsorption experiments.

EXPERIMENTAL

Materials

Ferric trichloride (FeCl₃ · 6H₂O) and Ferrous chloride (FeCl₂ · 4H₂O) were purchased from Chengdu xindu MuLan town industrial development zone, Hydrobromic acid in glacial acetic acid (HBr/AcOH, 33% w/v), ethyl orthosilicate (TEOS), trifluoroacetic acid (TFA), ethyleneglycol dimethacrylate (EGDMA) were purchased from Beijing J&K Chemical, ammonium persulfate, citric acid, ammonium hydroxide, nitric acid, hexyl hydride, ethyl alcohol, ethyl acetate and solvents were purchased from Chengdu kelon chemical reagent company.

Synthesis of Fe₃O₄ nanoparticles

FeCl₃ · 6H₂O 2.70 g and FeCl₂ · 4H₂O 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 r/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 N₂ 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

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times. The obtained Fe₃O₄ colloid was placed into a vacuum oven, and dried for 3 h to obtain Fe₃O₄ magnetic nanoparticles.

Preparation of SiO₂@Fe₃O₄ magnetic nanoparticles

0.40 g Fe₃O₄ magnetic nanoparticles were added to a three-necked flask containing 40.00 mL of ethanol and 8.00 mL of deionized water were. The mixed solution was ultrasonically dispersed for 10 min, and then mechanically stirred (600 r/min) for 20 min. 2.00 mL of aqueous ammonia and 1.60 mL of TEOS were added into the three-necked flask. And the reaction was carried out at room temperature for 3.5 h under N₂. 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 60 °C for 3 h to obtain the SiO₂@Fe₃O₄ magnetic nanoparticles.

Preparation of PGA

PBLG (0.70 g, 0.07 mmol) was added into 25.00 mL of trifluoroacetic acid under magnetic stirring, and HBr/AcOH (3.80 ml, 30.00 mmol HBr) was drop-wisely added. The reaction was carried out at room temperature for 18 h under N₂. Then the solvent was removed under reduced pressure, the obtained solid was further dispersed in distilled water. the pH of the mixed solution was adjusted to 7 by NaOH solution, and then dialyzed (MWCO 3500 g/mol) against distilled water for 12 h, and freeze-dried for 24 h to obtain a white powder.

Preparation of PGA@SiO₂@Fe₃O₄ magnetic nanoparticles

0.20 g SiO₂@Fe₃O₄ magnetic nanoparticles were added into 80.00 mL of distilled water and ultrasonically dispersed for 10 min. PGA (0.50 g, 1.00 mmol), EGDMA (38.60 μL 0.20 mmol, wt 20% of PGA), and ammonium persulfate (25.00 mg wt 5% of PGA) were added into three-necked flask at 70 °C under refluxing conditions for 2 h. Finally, the solvent was removed, and the product solution was washed with distilled water and ethanol for several times. The raw product was dried by vacuum to obtain the PGA@SiO₂@Fe₃O₄ magnetic nanoparticles.

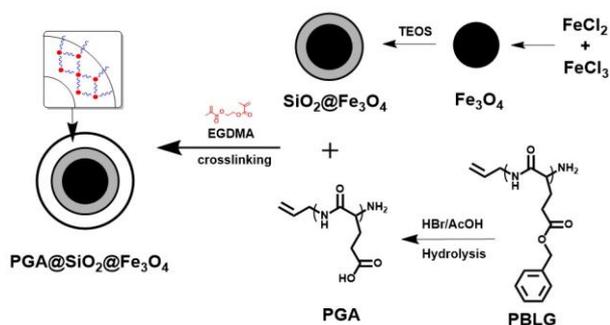


Fig. 1 Synthetic scheme for the preparation of copolymer.

RESULTS AND DISCUSSION

Preparation and characterization of the PGA@SiO₂@Fe₃O₄ magnetic nanoparticles

The PBLG was prepared by the ring opening polymerization of acrylamide with benzyl glutamate NCA. Then PBLG was then hydrolyzed to obtain PGA. Finally,

the PGA@SiO₂@Fe₃O₄ magnetic nanoparticles was prepared by free radical copolymerization using PGA as copolymerization component, ammonium persulfate as initiator and EGDMA as crosslinking agent. The PBLG and PGA structure was characterized by ¹H-NMR.

As shown in the Fig.2(a), δ(ppm)=7.8-8.0 corresponds to the hydrogen on the main chain N-H. δ(ppm)=5.2-5.5 corresponds to the hydrogen on the benzene ring in PBLG. δ(ppm)=5.0-5.2 corresponds to the hydrogen on the benzyl group. δ(ppm)=4.4-4.5 corresponds to the hydrogen on the main chain methylene group. δ(ppm)=2.7-2.9 corresponds to the hydrogen of the methylene group on the initiator residue. δ(ppm)=2.3-2.5 corresponds to the hydrogen on the branched chain β-methylene group. δ(ppm)=1.8-2.3 corresponds to the hydrogen on the branched chain α-methylene group. The ¹H-NMR spectrum of PBLG showed that the synthesis of PBLG was successful. In the Fig.2(b), δ(ppm)=1.9-1.8 corresponds to hydrogen on C-H. δ(ppm)=2.1-2.2 can be ascribed to the carboxyl group. δ(ppm)=4.2-4.1 corresponds to NH₂ group. The ¹H-NMR spectrum of PGA showed that the hydrolysis of PBLG was successful.

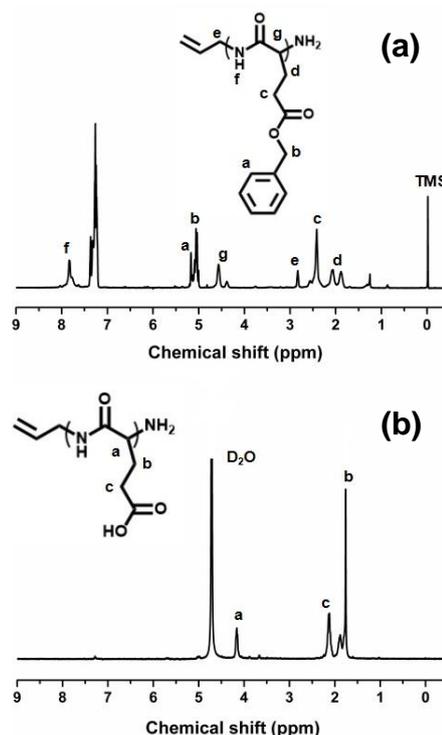


Fig. 2. ¹H NMR spectrum of PBLG in CDCl₃ and PGA in a D₂O.

The FTIR spectra of Fe₃O₄, SiO₂@Fe₃O₄, and PGA@SiO₂@Fe₃O₄ were shown in the Fig.3. In Fig.3(a) the peak at 580 cm⁻¹ could be ascribe to the stretching vibration of Fe-O. Fig.3(b) was the FTIR spectrum of SiO₂@Fe₃O₄, it was indicated that the absorption peak at 1180 cm⁻¹ could be ascribed to the stretching vibration of Si-O. Fig.3(c) was the FTIR spectrum infrared spectrum of PBLG, the absorption peak around 1080-1210, 1750, and 2900 cm⁻¹ corresponded to the C-O-C group, C=O group, and benzene ring C-H stretching vibration. The peak at 3230 cm⁻¹ can be ascribed to the N-H stretching vibration. Fig.3(d) is the FTIR spectrum of PGA. The

peak at 1210 cm^{-1} corresponded to C-O-C. The peak at 1700 cm^{-1} and $3200\text{-}3500\text{ cm}^{-1}$ could be ascribed to C=O and N-H group. Fig.3(f) is the FTIR spectrum of $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ magnetic nanoparticle. Based on the FITR spectra, it was suggested that the preparation of Fe_3O_4 , $\text{SiO}_2\text{@Fe}_3\text{O}_4$, and $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ were successful.

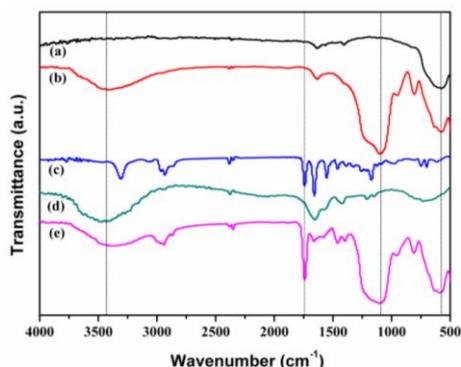


Fig. 3 FT-IR spectra of (a) Fe_3O_4 , (b) $\text{SiO}_2\text{@Fe}_3\text{O}_4$, (c) PBLG, (d) PGA and (e) $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$.

The SEM photos and DLS measurements of Fe_3O_4 , $\text{SiO}_2\text{@Fe}_3\text{O}_4$, and $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ were shown in Fig.4. The size of Fe_3O_4 magnetic nanoparticles is about 20~30 nm. The size of $\text{SiO}_2\text{@Fe}_3\text{O}_4$ nanoparticles were about 120nm, which proved that SiO_2 was successfully coated onto the surface of Fe_3O_4 magnetic nanoparticles. The Size of $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ magnetic nanoparticles were about 170 nm, which is higher than $\text{SiO}_2\text{@Fe}_3\text{O}_4$. It was indicated that the $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ nanoparticles were successfully prepared by with PGA coating. And the DLS measurements also showed the sized change of the Fe_3O_4 , $\text{SiO}_2\text{@Fe}_3\text{O}_4$, and $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ nanoparticles in Fig. 4(d).

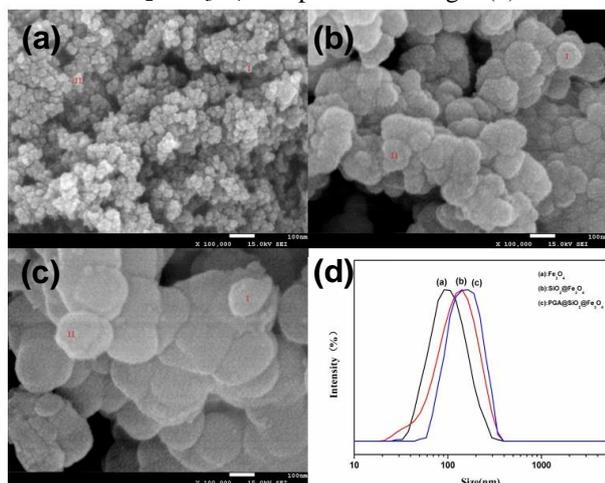


Fig. 4 SEM photos of (a) Fe_3O_4 , (b) $\text{SiO}_2\text{@Fe}_3\text{O}_4$, (c) $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$, and and DLS measurements (d).

CONCLUSION

In this experiment, the preparation of $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ involves a two-step process: (i) surface modification of Fe_3O_4 nanoparticles by TEOS to form $\text{SiO}_2\text{@Fe}_3\text{O}_4$, (ii) surface functionalization of $\text{SiO}_2\text{@Fe}_3\text{O}_4$ nanoparticles by free radical copolymerization to form a cross-linking magnetic $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ nanoparticles. The chemical structures and morphology of PGA, PBLG, Fe_3O_4 , $\text{SiO}_2\text{@Fe}_3\text{O}_4$, and $\text{PGA@SiO}_2\text{@Fe}_3\text{O}_4$ were fully characterized by $^1\text{H-NMR}$, FT-IR, DLS, and SEM. The as

prepared magnetic nanoparticles can be used as a promising reusable nanosorbent with structural stability, good biocompatibility, and efficient adsorption performance.

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