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Dedoped Fe_3O_4/PPy nanocomposite with high anti-interfering ability for effective separation of Ag(I) from mixed metal-ion solution

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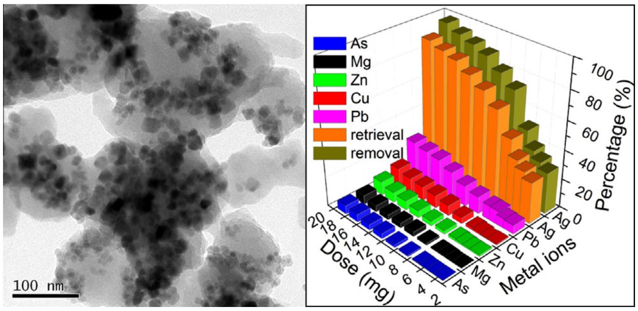
HIGHLIGHTS

- Facile and scalable synthesis of dedoped Fe_3O_4/PPy nanocomposite is presented.
- The magnetic nanocomposite possesses superparamagnetism and a soft-base surface.
- The nanocomposite has a high anti-interfering ability to selectively adsorb Ag(I).
- The nanocomposite shows excellent reusability for selective separation of Ag(I).
- The maximum adsorption capacity of Ag(I) upon the nanocomposite is 143.3 mg g^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic nanocomposites have been well recognized as promising candidates for enzyme immobilization, DNA extraction, targeted drug delivery, and removal of various metal ions. In this paper, dedoped Fe_3O_4/PPy nanocomposite has been obtained by simple ammonia-washing of the newly-formed Fe_3O_4 nanoferrofluid/PPy derived from *in situ* polymerization approach. The magnetic nanocomposite is characterized with XRD, FT-IR, TEM, BET, zeta potential, and magnetometry techniques, and further tested in the role of separating Ag(I) from mixed metal-ion solutions containing Ag(I), Mg(II), Cu(II), Zn(II), As(III), and Pb(II). The adsorption of Ag(I) upon dedoped Fe_3O_4/PPy is an endothermic and spontaneous chemisorption process, ensuring rapid separation of Ag(I) from aqueous solution. The maximum adsorption capacity of Ag(I) upon dedoped Fe_3O_4/PPy is 143.3 mg g^{-1}. The total adsorption process preferably follows the Langmuir model and the pseudo-second order kinetics. Mg(II), Cu(II), Zn(II), and As(III) have minor effects whereas Pb(II) has a relatively remarkable effect on selective separation of Ag(I) from solutions. The magnetic nanocomposite is featured with superparamagnetism, a multicore–shell structure, a soft-base surface, excellent reusability, and a high anti-interfering ability for selective separation of Ag(I) from multiionic solutions, presenting a promising candidate for practical application in selective separation of Ag(I) from silver-containing emissions.

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1. Introduction

As one of the precious metals, silver (Ag) has wide applications in the fields of photography [1], electronics [2], catalysis [3], and antibiotics [4], and so on. Statistically, thousands of tons of silver are annually emitted to land and water since 2007 [5]. In view of the scarcity of silver natural resource, there has been increasing interest in recovery of silver from the emissions produced by electronic, photographic, metallurgic, and silver-gilt industries [6–18]. On the other hand, there is grave concern for the potential detriment of monovalent ionic silver, Ag(I), to the health of human and ecosystem [5]. From the viewpoint of economy and environmental protection, it is necessary to develop an efficient approach for recovery of Ag(I) from emissions.

So far, many approaches have been designed for separation of Ag(I) from solution, such as liquid–liquid extraction [15], cloud point extraction [11,12], solid phase extraction [6,9,10,13,16,17], and membrane technique [7,8,14]. Among these approaches, solid phase extraction is recognized to be superior to the others, in terms of simplicity, flexibility, time-saving, and low cost [6,8]. Recently, solid phase extraction with magnetic composites has been subjected to extensive research, because of their wide applications in enzyme immobilization [19], DNA extraction [20], targeted drug delivery [21], and pre-concentration/removal of various metal ions [6,16,17,22–27].

In the case of magnetic separation, two important factors regarding magnetic adsorbent should be concerned, i.e., magnetism and surface functionality. Magnetic adsorbent with high magnetization approaching to that of pristine magnetite (60–80 emu g^{-1}) facilitates rapid magnetic separation. In particular, it is highly desired to acquire magnetic adsorbent with both high magnetization and superparamagnetism, which enable the adsorbent to be easily separated from and uniformly redispersed into solution by switching on/off an external magnetic field, a situation that is necessary for a high throughput [28]. Theoretically, magnetic nanoparticles with size smaller than 25 nm possess superparamagnetism [29]. However, monodisperse magnetic nanoparticles are difficult to be separated from solution by a simple way using a hand-held magnet, because the randomly directed forces of Brownian motion are stronger than the magnetic forces [28]. Considering that the magnetic force directing particles toward magnet is proportional to magnetic field gradient as well as to magnetization and volume of the particles [28,30], encapsulation of magnetite nanoparticles into nonmagnetic matrix is an alternative strategy to construct magnetic composites with enhanced volume, and hence high magnetization and superparamagnetism. As for surface functionality, amino groups upon magnetic composites have been well documented to facilely combine with metal clusters [31], metal ions [22–28], drug [32], and biomolecules [20]. In view of polyaniline (PANI) and polypyrrole (PPy) being eco-friendly and wealthy in amino groups, Fe_3O_4/PANI and Fe_3O_4/PPy composite microspheres with core–shell structure and superparamagnetism have attracted much attention on the basis of their excellent performance in DNA extraction [20] and metal ion removal [24–26]. Although Fe_3O_4 microspheres constructed by self-assembly of Fe_3O_4 nanospheres with size smaller than 30 nm possess high magnetization and superparamagnetism [20,24,25], the synthesis of Fe_3O_4 microspheres is hard to be scalable, due to the relatively high polyalcohol reduction temperature at ca. 200 °C [33].

In this paper, we report on facile synthesis of Fe_3O_4/PPy nanocomposite and selective separation of Ag(I) from solutions containing altervalent metal ions by using dedoped Fe_3O_4/PPy nanocomposite as the adsorbent. The synthesis of Fe_3O_4/PPy nanocomposite is scalable on the basis of using Fe_3O_4 nanoferrofluid as the magnetic component. By eluting the newly-formed magnetic composite in dilute ammonia water at room temperature, it is easy to obtain dedoped Fe_3O_4/PPy nanocomposite with a soft-base surface. This results in high affinity between the adsorbent surface and Ag(I) on the basis of soft-hard-acid-base (SHAB) theory [34], a situation that facilitates selective separation of Ag(I) from mixed metal-ion solutions.

2. Materials and methods

2.1. Preparation of Fe_3O_4/PPy nanocomposite

Fe_3O_4 nanoferrofluid was prepared by the chemical co-precipitation approach [35]. Briefly, 8.94 mmol $FeCl_3{\cdot}6H_2O$, 5 mmol $FeSO_4{\cdot}7H_2O$, and 80 mL distilled water were added into a three-neck flask with capacity of 250 mL. The mixture was bubbled with N_2, accompanying with agitation to form a clear solution. The reaction temperature was raised to 50 °C, followed by dropwise addition of 40 mL of 1.125 M NaOH aqueous solution. Then, the mixture was heated at 90 °C for 1 h with constant stirring and N_2 bubbling, and then allowed to cool to room temperature. The precipitate was collected by a hand-held permanent magnet, washed twice with distilled water, and redispersed into 100 mL of ethanol aqueous solution ($C_2H_5OH/H_2O = 2:3$, v/v) to produce 0.01 g mL^{-1} Fe_3O_4 nanoferrofluid.

For the synthesis of Fe_3O_4/PPy nanocomposite, 50 mL of the as-obtained ferrofluid, 10 mL of 0.4 M HCl aqueous solution, 20 mg of sodium dodecyl sulfate (SDS) were added into a three-neck flask with capacity of 250 mL. Then, the mixture was subjected to ultrasonic treatment for 5 min, and agitated at room temperature for 0.5 h under N_2 atmosphere, followed by addition of 0.9 mL of redistilled pyrrole. After agitation at room temperature for 1 h, the temperature of the mixture was decreased to 5 °C by using an ice bath. Subsequently, 20 mL of 0.775 M $FeCl_3$ aqueous solution was slowly added into the above mixture. The polymerization reaction was kept at 5–7 °C for 3 h with constant stirring and intermittent ultrasonication. The precipitate was magnetically separated, washed with distilled water and ethanol, and collected by filtration. Finally, the resulting product was dried in a vacuum oven at 40 °C.

To obtain the dedoped Fe_3O_4/PPy, the as-prepared Fe_3O_4/PPy in doping state was redispersed into 1 M ammonia water and agitated at room temperature for 3 h. After magnetic decantation, the precipitate was collected by filtration, washed with distilled water and ethanol, and finally dried in a vacuum oven at 40 °C.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å), operating at 40 kV and 40 mA with a step size of 0.3° $2\theta\ s^{-1}$. Crystallite size (S) of the sample was calculated from the XRD data, according to the Scherrer equation, i.e. $S = 0.9\lambda/\beta\cos\theta_B$, where λ is the X-ray radiation wavelength, β is the full line width at half-maximum height of the corresponding peak after subtraction of the equipment line broadening, and θ_B the Bragg angle. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G20 transmission electron microscope. Fourier transform infrared (FT-IR) spectra were collected on a Shimadzu IRPrestige-21 infrared spectrometer using pressed KBr discs. The FT-IR spectra were recorded with a resolution of 4 cm^{-1} over the range of 4000–400 cm^{-1}. Magnetization measurements were performed on a Quantum Design MPMS XL-7 superconducting quantum interference magnetometer at room temperature. Nitrogen