Short Communication

Removal of Mercury (II) from Wastewater by Magnetic Solid Phase Extraction with Polyethylene Glycol (PEG)-Coated Fe₃O₄ Nanoparticles

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Abstract

The presented study investigates application of polyethylene glycol (PEG)-coated Fe₃O₄ nanoparticles as a magnetic nanoadsorbent for magnetic solid-phase extraction (SPE) and the selective removal of toxic heavy metals such as mercury (II) from aqueous solutions and their determination using graphite furnace atomic absorption spectrometry (GF-AAS). The Fe₃O₄ magnetic nanoparticles were synthesized using co-precipitation and characterized by Scanning electron microscopy (SEM), X-ray diffraction (XRD) and vibrating-sample magnetometer (VSM). The influences of analytical parameters including pH and eluent type, concentration and volume have been studied and optimized. The optimum pH required for maximum adsorption was found to be 6 for mercury. SEM images showed that the particle size was about 24 nm and no marked aggregation occurred. XRD indicated the sole existence of inverse cubic spinel phase of Fe₃O₄ magnetic nanoparticles. VSM patterns indicate superparamagnetic of Fe₃O₄ magnetic nanoparticles. The results obtained from the recovery test showed the capability and reliability of the method for the removing mercury (II) from wastewater.

Keywords: Hg(II), Polyethylene glycol (PEG-4000) coated Fe₃O₄ Magnetic nanoparticles, Co-precipitation, Wastewater.

1. INTRODUCTION

Mercury is one of the most toxic metals known to man. During the 20th century mercury ion and its organometallic species are considered to be highly toxic to the environment, especially the aquatic system. Metal-processing wastewater often contains a considerable amount of divalent mercury which can pose a severe threat to public health and environment if discharged without adequate treatment. USEPA recommends that the levels of mercury in drinking water should be reduced to 0.002 mg·L⁻¹. Main contamination sources of waste waters by mercury ions are battery, paper and pulp, chlor-alkali production, oil refinery and paint manufacturing industries. There are some other minor sources of pollution [1-3]. Removal of toxic heavy metals from wastewater achieved principally by the application of several processes such as cloud point extraction, precipitation /co-precipitation, liquid–liquid extraction, and solid-phase extraction (SPE) [4]. Among these techniques, SPE procedures, are considered superior to other procedures for their simplicity, consumption of small volumes of organic solvent, and ability to achieve a higher enrichment factor. It is commonly acknowledged that the adsorption materials play a very important role in SPE, because adsorption materials
determine the analytical sensitivity, precision and selectivity in SPE techniques. The current researches in SPE are mainly focused on the development of new sorbents such as nanometer-sized material [5]. Nanometer-sized materials have attracted substantial interest in scientific community because of their special properties. Fe₃O₄ magnetic nanoparticles, as a new kind of nanometer-sized materials are attractive because they can exhibit an array of novel and specified properties such as large surface area, potential for high specificity, high reactivity, catalytic potential, and absence of internal diffusion resistance, which are promising to develop new or improve existing technologies in wastewater treatment. These particles are superparamagnetic, which means that they are attracted to a magnetic field, but retain no residual magnetism after the field is removed. Therefore, suspended are superparamagnetic particles adhered to the target can be removed very quickly from a matrix using a magnetic field, but they do not agglomerate after removal of the field [6-10]. Present work introduces an efficient removal of Hg²⁺ ion from wastewater using modified magnetic iron oxide nanoparticles with polyethylene glycol (PEG) that can from strong complex with Hg (II) ion. The major advantages of technology are its effectiveness in reducing the concentration of heavy metal ions such as Hg²⁺, avoid the generation of secondary waste, produced no contaminants, has the capability of treating large amount of wastewater within a short time, good selectivity and the adsorption materials employed in this method can be recycled and used easily on an industrial scale.

2. MATERIALS AND METHOD

2.1 Materials
All chemicals were of analytical reagent grade and used without further purification. Ferric chloride hexahydrate (FeCl₃.6H₂O), ferrous chloride tetrahydrate (FeCl₂.4H₂O), ammonium hydroxide (NH₄OH), Oleic acid and polyethylene glycol (PEG-4000) were purchased from Merck. The Hg²⁺ stock solution (100 µg mL⁻¹) was prepared daily from HgCl₂ (Merck, Darmstadt, Germany). Mercury samples were obtained by dilution of the stock solution. For pH adjustment throughout the experiment, hydrochloric acid (0.1 M) and/or sodium hydroxide (0.1 M) solutions were used as necessary. All acids used were of the highest purity available were obtained from Merck.

2.2 Instrumentation
A graphite furnace atomic absorption spectroscopy (GF-AAS, Shimadzu model AA-670G) was used for the determination of trace element in the samples. The size of the particles were characterized by X-ray diffraction (XRD, Philips model Expert) with Ni-filtered Cu Kα radiation (CuKα₁ = 0.154 nm) and Scanning electron microscopy (SEM, Philips model XL30), respectively. Magnetic properties of the particles were assessed with a vibrating-sample magnetometer (VSM, Homemade 2 tesla). A magnet (Φ 17.5×20 mm, 5500 Oe) was utilized for the collection of magnetic particles.

2.3 Synthesis of PEG-Coated Magnetic Nanoparticles
The Fe₃O₄ was prepared by the conventional chemical co-precipitation method [11]. Briefly, (FeCl₂.4H₂O) and (FeCl₃.6H₂O) were dissolved in deionized water as the solvent. The solution of FeCl₃ and FeCl₂ was mixed with molar ratio of Fe³⁺/Fe²⁺=2. Co-Precipitation occurred with the addition of ammonium hydroxide (NH₄OH) as precipitating agent to the solution under nitrogen atmosphere with vigorous stirring. The color of solution changed to black immediately. The black magnetic precipitate obtained were washed twice with deionized water. For coating magnetic mixture of water and Fe₃O₄ nanoparticles were stirred and heated at 70 °C for 30 min under a nitrogen atmosphere, and then a solution of 25 ml oleic acid was
The suspension was then cooled slowly down to 45 °C with constant stirring. The polyethylene glycol (PEG-4000) solution was then added to the suspension. Then, mixture was kept at 45 °C under vigorous stirring and a nitrogen atmosphere for 1 h. Then, it was cooled down to room temperature. The above solution was slowly added into deionized water for 2 days to allow the formation of hydrophilic nanoparticles and to remove organic solvents. The repulsive force between hydrophobic surfactant molecules coated on single particles can prevent them from agglomeration. Then, polyethylene glycol (PEG-4000) coated nanoparticles were collected by magnetic field separation with a permanent magnet and were dried at room temperature in air atmosphere to form polyethylene glycol-coated Fe₃O₄ nanoparticles powders.

2.4 General procedure

The procedure for the magnetic solid-phase extraction is presented and the removal of Hg²⁺ ion from wastewater using magnetic (Fe₃O₄) nanoparticles is demonstrated in follows: a portion of sample solution containing 100 mg Hg²⁺ ion was transferred to a 200 mL beaker, the pH value was adjusted to 6 with 0.1 molL⁻¹ HCl and 0.1 molL⁻¹ NaOH, and the final volume was diluted to 200 mL. Then 10 mg of PCMNPs were added, and the solution was mixed for 5 min to facilitate adsorption of the metal ion onto the nanoparticles. Then the magnetic adsorbent was separated easily and quickly using a magnet and the supernatants were decanted directly. The magnet was removed, and a solution containing 0.5 molL⁻¹ HNO₃ was added as eluent and mixed again for 5 min. Finally, the magnet was used again to aggregate the magnetic nanoparticles, and eluate was injected to GF-AAS for subsequent analysis (Fig. 1).

3. RESULTS AND DISCUSSION

3.1 Characterization of PEG Coated Magnetic Nanoparticles

Figure 2 shows the Scanning electron microscope (SEM) image. The Scanning electron microscopy was used for investigating size of the prepared magnetic Fe₃O₄ nanoparticles that in this study were about 24 nm. The X-ray diffraction (XRD) pattern of the Fe₃O₄ nanoparticles is presented in Fig. 2(a). The XRD peaks of Fe₃O₄ are compared with the standard peaks. A series of characteristic peaks for Fe₃O₄ 2θ = 30.29°, 35.69°, 43.30°, 53.69°, 57. 38°, and 62.98°, which corresponds to (220), (311), (400), (422), (511), and (440) Bragg reflection, respectively, in Figure 2(a) agree with standard magnetite (Fe₃O₄) XRD patterns, identify that the Fe₃O₄ nanoparticles are cubic spinel structure. Also X-ray diffraction (XRD) was used for structural phase identification (Fig. 2(b)).

The XRD measurements indicated that magnetite (Fe₃O₄) was the dominant phase for the sample. The magnetic properties of MNPs was measured by using vibrating-sample magnetometer (VSM). The hysteresis loop of the Fe₃O₄ nanoparticles, which was measured in the powder state, is shown in Fig. 3 which provided evidence that all the MNPs were superparamagnetic at room temperature, with no hysteresis.

3.2 Effect of pH

Metal sorption is critically linked with pH and the effect of pH of a solution is an important controlling factor in the sorption experiment.
The pH value plays a very important role in the use of nano-adsorbents as supports in the metal ion adsorption process. The number of adsorption sites available for heavy metal ions decreased as the number of protonated metal-binding absorbent groups increase. The pH in solution has been identified as the most variable governing metal adsorption on sorbent. This is partly due to the fact that hydrogen ions themselves are strongly competing adsorbents. The pH solution influences the specification of metal ions and the ionization of surface functional groups. Effect of different pH on the adsorption of Hg$^{2+}$ ions are showed in Fig. 5. In order to determine the optimal pH, the effect of pH is investigated at the pH ranges 2–9 with model solutions keeping the other parameters constant. It can be seen that the adsorption behavior of metal ions is sensitive to pH change. As observed in the graph, the removal efficiency of Hg$^{2+}$ ions from water samples by the magnetic Fe$_3$O$_4$ nanoparticles is clearly pH dependent and Maximum adsorption efficiency is obtained at pH 6 at room temperature. The decrease in signal at pH <6 may be due to competition of hydronium ion toward complexation with poly ethylene glycol (PEG). In an acidic solution the protonation of PEG occurs and there is a weak tendency for reaction between mercury (II) and PEG, which leads to the decrease in the extraction yield. High adsorption at higher pH values implies that metal ions interact with PEG-CNPs by chelating.
with lapse of time. About 98% of total Hg (II) is adsorbed within the first 5 min. And the time ($t_{1/2}$) of 50% adsorption is less than 2 min. One factor could be used to explain the obtained results. One is that PEG has favorable coordination capacity and selectivity for Hg (II). The adsorption increases with time and attains maximum value after 5 min with a stirring speed of 400 rpm is enough for complete adsorption an initial Hg (II) concentration of 100 mg/L.

![Figure 6. The effect of contact times on Hg$^{2+}$ adsorption on Fe$_3$O$_4$ magnetic nanoadsorbents.](image)

3.4 Effect of Elution

The choice of a suitable eluent is another important task in the recovery of analytes. As can be seen from Figure 6, the extraction of these metal ions is negligible at pH<4, in the presence of dilute HCl and HNO$_3$. The elution of the adsorbed metal-chelates on the solid phases is an important step for solid phase extraction studies. Due to this point, various eluent solutions (HNO$_3$, CH$_3$COOH, HCl and H$_2$SO$_4$) were used for desorption of ions complexed with polyethylene glycol (PEG)-Coated Fe$_3$O$_4$ nanoparticles. Quantitative recoveries for Hg (II) ions were obtained only with HNO$_3$. Recoveries were not quantitative for other eluents used in the present study. For this reason, HNO$_3$ is the best eluent for quantitative desorption of Hg (II) ions and was chosen as eluent and effect various concentrations and volumes of HNO$_3$ on the recoveries of the analytes was also studied by using HNO$_3$; it was found that quantitative recoveries could be obtained with 2.0 mL of 0.5 molL$^{-1}$ HNO$_3$.

4. CONCLUSIONS

In the presented study, the superparamagnetic polyethylene glycol coated iron oxide nanoparticles (Fe$_3$O$_4$) with cubic spinel structure and an average particle size of 24 nm were successfully synthesized by the co-precipitation method. Synthesized nanoparticles could be used as a high removal efficiency within a very short time alternates to the conventional adsorbents for the removal of metal ions from wastewater. The removal of Hg$^{2+}$, as a typical metal ion commonly presents in wastewater, by adsorption onto Fe$_3$O$_4$ magnetic nanoparticles was successfully accomplished. It also showed that adsorption was highly dependent on pH value. Maximum removal efficiency was achieved at pH 6 at room temperature. Therefore, the method is accurate, and economical and Fe$_3$O$_4$ magnetic nanoparticles were recommended as fast, effective, and inexpensive nanoadsorbents for rapid removal and recovery of high concentration of Hg$^{+2}$ ions from such wastewaters.

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