



Preparation and Characterization of Fe₃O₄@C Microspheres and Their Application in Enrichment and Analysis of Cadmium in Water Samples

ZHUXING TANG*, JIAN PENG and YIN CHEN

Department of Environmental and Chemical Engineering, Shenyang Ligong University, Shenyang 110159, P.R. China

*Corresponding author: E-mail: tangzhuxing@163.com

Received: 3 July 2014;

Accepted: 11 September 2014;

Published online: 26 May 2015;

AJC-17226

A novel approach for analysis of trace Cd(II) in water sample was developed. Fe₃O₄@C magnetic microspheres were synthesized *via* two-steps method and first applied in trace Cd(II) preconcentration prior to analysis with flame atomic absorption spectrometry. Enrichment ability of Fe₃O₄@C microspheres toward Cd(II) was investigated. The experimental results showed that static adsorption capacity was 35 mg g⁻¹ at pH 7.5 and 35 °C. Adsorbed Cd(II) could be eluted by using 4 mL 0.01 mol L⁻¹ EDTA-Na₂. The detection limit of this method was 0.036 mg mL⁻¹ (n = 11) and the relative standard deviation was 3.65 % (n = 6). Some environmental samples were determined using this method and results were satisfactory as recovery in the range of 95-101 %.

Keywords: Fe₃O₄@C magnetic microspheres, Cd(II), FAAS, Preconcentration.

INTRODUCTION

Cadmium(II) is one of toxic heavy metals and can harm the human body and difficult to be eliminated¹. Cadmium(II) is easy to be enriched through food chain and accumulated in liver, kidney and bone of human organisms²⁻⁴. Moreover, Cd(II) ion can reduce immunity of body and lead to osteoporosis or skeletal deformation, to the extent to death. Diseases such as, itai-itai disease, one of the ten largest environmental pollution incidents, was caused by Cd(II) pollution arising. Therefore, it was very important to develop accurate and sensitive determination method for trace Cd(II) in environmental water.

In daily life, flame atomic absorption spectrometry (FAAS) is one of the most widely methods in measurement of trace heavy metals. FAAS exhibits higher sensibility, expanded linear range and low interference⁵. However, precision and accuracy meet the challenge of analysis at low concentrations in complex substrate. Preconcentration is indispensable to analysis work of trace element in environmental water^{5,6}. Therefore, a novel approach of separation and enrichment for trace heavy metal ions and determination by FAAS was developed in this study.

At present, several methods have been used for separation and enrichment of element such as ion exchange process, coprecipitation method, liquid-phase microextraction and adsorption, *etc*⁷⁻¹³. Among these methods, because adsorption method is simple, low-cost and effective in removing heavy metal ions from wastewaters, this method has always received much attention in recent years.

In recent years, great interest has been devoted to the development of magnetic particles and the improvement of their applicability in different areas¹⁴. Among various magnetic particles, iron oxides have received the most attention owing to their strong magnetic responsiveness and biocompatibility¹⁵. Additionally, advances in material synthesis have enabled the preparation of magnetic core-shell materials with iron oxide cores and functional outer shells of polymers, silica and carbon for a wide range of applications in chemical separation, environmental remediation and monitoring, biotechnology and medicine¹⁶⁻¹⁹.

Carbon nanoadsorbents have been widely studied recently, because carbon nanoadsorbents have several merits, such as high adsorption capacity, easy regeneration and fast adsorption kinetics²⁰⁻²². Carbon nanoadsorbents have been applied in treating various pollutants, including heavy metals, organic dyes and antibiotics²³⁻²⁵.

In this study, nanosized Fe₃O₄@C magnetic microspheres were prepared by two-steps method and applied in trace Cd(II) preconcentration prior to analysis with FAAS.

EXPERIMENTAL

Magnetic microspheres were synthesized in KH-100 mL hydrothermal synthesis reactor (Gongyi Limited Liability Company). The size and morphology of Fe₃O₄@C nanoparticles were observed by scanning electron microscope (SEM, S-3400N, Hitachi in Japan) and transmission electronic microscopy (TEM, TECNAIG20, FEI company in USA). The

structural properties of magnetic powder obtained were analyzed by X-ray diffraction (XRD, Rigaku in Japan, D/MAX). The FT-IR spectrum was obtained on TENSOR 27 FT-IR spectroscopy of Bruker Optics. Magnetic properties of nanoparticles were measured by VSM-220 vibrating sample magnetometer (VSM, Yingpu Magnetism and Electricity Technology Company). A TAS-990 model atomic absorption spectrometer (Beijing Purkinje General Instrument Co.) was used to measure the concentration of cadmium.

All the other reagents including ferric chloride hexahydrate, anhydrous sodium acetate, glucose, glycol, ethyl alcohol, sodium hydroxide, hydrochloric acid, nitric acid, acetic acid and ethylenediamine-tetraacetic acid disodium salt (EDTA-Na₂), were purchased from the national chemical corporation.

Preparation of Fe₃O₄@C nanoparticles: Fe₃O₄@C magnetic microspheres were synthesized using two-steps method. The first step is preparation of Fe₃O₄ nanoparticles by solvothermal method. In this method 1.35 g FeCl₃·6H₂O crushed was dissolved into 75 mL glycol and 3.6 g anhydrous sodium acetate was added into the solution. When all of that were dissolved completely the mixture was ultrasonicated for 5 min and transferred to an autoclave and then heated at 200 °C for 12 h. After that, obtained product was cooled and washed with distilled water and ethanol in turn for several times and dried at 50 °C for 4 h. Fe₃O₄ nano-particles were obtained so far.

In the following step, Fe₃O₄@C magnetic microspheres were synthesized²⁴: 0.4 g Fe₃O₄ microspheres were dissolved by 0.1 mol/L HNO₃ solution, followed by ultrasonicated for 5 min and washed with distilled water. The microspheres were put into 80 mL glucose aqueous solution (0.5 mol/L) under ultrasonic for 5 min. Next, the mixture was transferred to an autoclave and heated at 180 °C for 6 h. When it was cooled to room temperature the Fe₃O₄@C microspheres were isolated with magnet, followed by washed with distilled water and ethanol. Finally, the obtained microspheres were dried at 50 °C.

Absorption and desorption: First of all, the pH of Cd(II) solution was adjusted either using an appropriate concentration of 0.1 M HCl or 0.1 M NaOH solution. A certain amount of the Fe₃O₄@C nanoparticles was added in Cd(II) solution, followed by ultrasonicated for a while. After equilibrium was reached, nanoparticles were removed from solution using magnet by magnetic separation (Fig. 1) and concentrations of residual clear Cd(II) solution by FAAS. The equilibrium adsorption capacity (q) and adsorption rate η(%) of Fe₃O₄@C nanoparticles could be calculated by the following equations:

$$q = (C_0 - C)V/W \quad (1)$$

$$\eta = (C_0 - C)/C_0 \times 100 \% \quad (2)$$

where C₀ and C are the initial and equilibrium concentrations of Cd(II) (mg/L), V is the volume of Cd(II) solution (L) and W is the mass of nanoparticles.

The Cd(II) adsorbed Fe₃O₄@C nanoparticles were washed thoroughly with distilled water and desorption was performed by putting the nanoparticles into EDTA-Na₂ aqueous solution. After desorption, nanoparticles were removed from solution using magnet and the concentration of Cd (II) in liquid solution was measured by FAAS. The elution rate ψ (%) and recovery μ (%) of Fe₃O₄@C nanoparticles were calculated by the following equations:

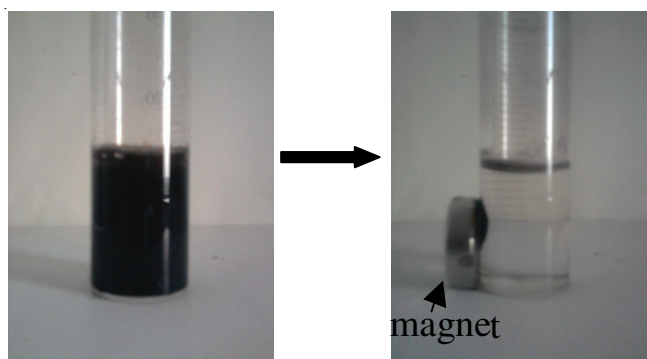


Fig. 1. Procedure of magnetic separation

$$\psi = C'V'/\eta C_0 V \times 100 \% \quad (3)$$

$$\mu = C'V'/C_0 V \times 100 \% \quad (4)$$

where C₀ and C are the initial and equilibrium concentrations of Cd(II) (mg/L), V is the volume of Cd(II) solution (L), C' is the concentrations of Cd(II) in elution (mg/L), V' is the volume of elution (L).

RESULTS AND DISCUSSION

Characterization: The morphology of Fe₃O₄@C nanoparticles were observed by SEM image. Fig. 2 shows the SEM images of Fe₃O₄@C microspheres. These magnetite nanoparticles are monodisperse and diameter of magnetic microspheres had a narrow range.

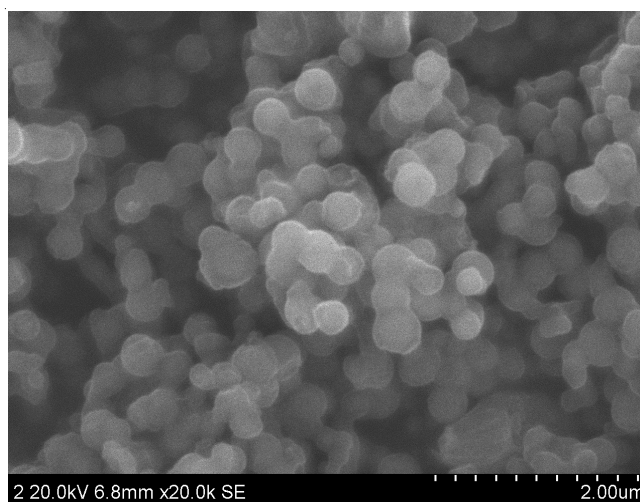


Fig. 2. SEM images of Fe₃O₄@C magnetic nanoparticles

The TEM images of magnetic microspheres are shown in Fig. 3 and more details about tiny ball-shape Fe₃O₄ and Fe₃O₄@C nanoparticles could be seen. One might see, now, some of the stark differences by contrast. Fig. 3a shows Fe₃O₄ microspheres were black microspheres and appeared to be well distributed with an average size of about 200 nm, however, Fig. 3b shows a distinguished core-shell structure. The light-coloured layer of carbon about 30 nm of thickness was successful encapsulated on the magnetic Fe₃O₄ microspheres. It illustrates that Fe₃O₄@C magnetic microspheres with the same diameter could be synthesized successfully.

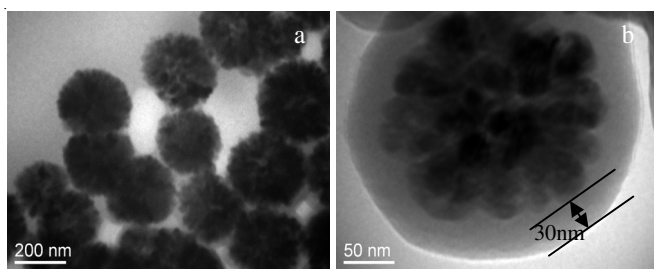


Fig. 3. TEM images of magnetic nanoparticles: (a) Fe₃O₄, (b) Fe₃O₄@C

The crystal structure of Fe₃O₄ and Fe₃O₄@C microspheres were investigated at diffraction angles from 20° to 90°. As shown in Fig. 4, the Fe₃O₄@C and Fe₃O₄ microspheres had similar locations of diffraction peak, which match with characteristics of Fe₃O₄ (JCPDS 79-419) with no impurity peak, so that the synthesized Fe₃O₄@C microspheres had same crystal structure as uncoated microspheres.

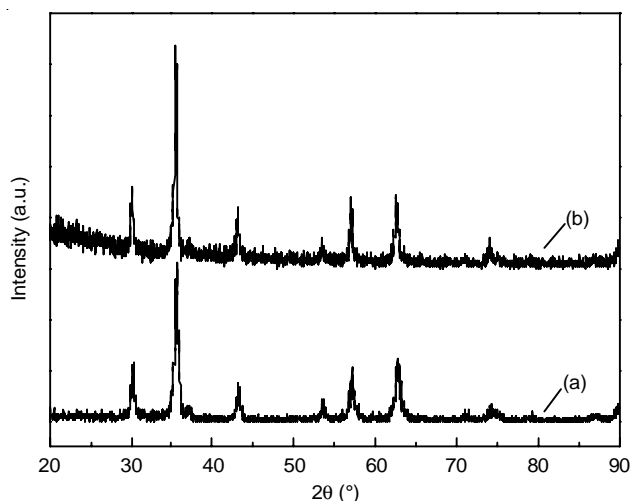


Fig. 4. XRD patterns of magnetic nanoparticles: (a) Fe₃O₄, (b) Fe₃O₄@C

The infrared spectra of Fe₃O₄ and Fe₃O₄@C microspheres were shown in Fig. 5. The most intense signal at 570 cm⁻¹ was Fe-O stretching of Fe₃O₄ and bonds in 1700-1550 cm⁻¹ region illustrated the successful coating of carbon on magnetite microspheres. It demonstrated the successful coating carbon on the magnetic core.

In order to study synthesized Fe₃O₄ and Fe₃O₄@C magnetic behaviour, the magnetic properties were measured at room temperature with a vibrating sample magnetometer (VSM). Fig. 6 shows the hysteresis loops of the samples. The saturation magnetization of Fe₃O₄ and Fe₃O₄@C microspheres were found to be 72 emu g⁻¹ and 33 emu g⁻¹. Coercivity being zero and no reduced remanence indicated that Fe₃O₄ microspheres and Fe₃O₄@C microspheres were superparamagnetic.

Effect of pH: Solution pH is an important parameter that affects adsorption of heavy metals, so a batch of experiments was carried out at different pH values. At room temperature, according to test plan, Fe₃O₄@C microspheres were put into solution with an initial Cd(II) ion concentration of 5 μg mL⁻¹ in the pH range from 2 to 7.5. At low pH the reaction solution would be positively charged so that the surface of adsorbents would be surrounded by the hydrogen ions which competed with sorbent. That may result in a decrease in the amount of

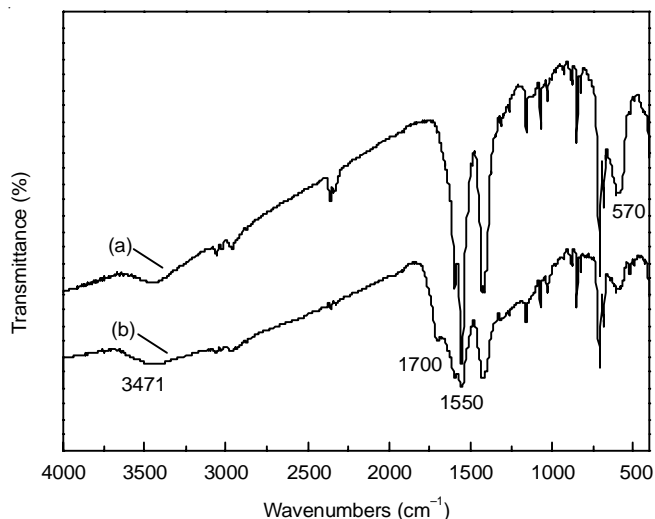


Fig. 5. FT-IR spectrum of nano-Fe₃O₄ (a) and nano-Fe₃O₄@C (b)

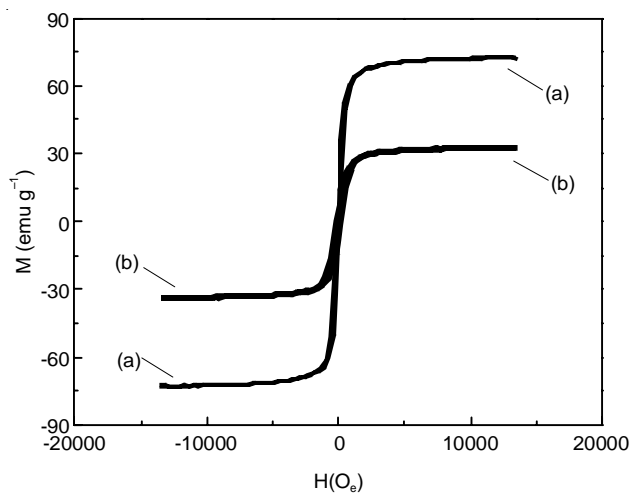


Fig. 6. Hysteresis loops of nano-Fe₃O₄ (a) and nano-Fe₃O₄@C (b)

Cd(II) ion adsorbed. The results showed that adsorption rate of Cd(II) had a lower value at a solution pH below 4. Adsorption rate increases obviously with increasing solution higher than pH 4 and a maximum was found at pH 7.5. When pH value up to 8 the Cd(II) ion concentration descended rapidly and might be attributed to heavy metal was easy to react with hydroxyl ion and product precipitate at higher solution pH. Therefore, pH 7.5 was selected as optimal pH value.

Effect of temperature: To investigate the effect of temperature on adsorption, according to test plan, 5 μg mL⁻¹ of Cd(II) solution was shaken with a certain amount of Fe₃O₄@C nanoparticles from 15 to 50 °C. The experimental result indicated that different temperature resulted in different adsorption effects. As shown in Fig. 7, adsorption increased with increasing the temperature from 15 to 35 °C and reached a maximum value at 35 °C. So temperature played key roles on the adsorption process and following operations. 35 °C were selected as optimal temperature.

Adsorption equilibrium time: Fig. 8 shows the effect of time on the equilibrium of Cd(II) adsorption by Fe₃O₄@C microspheres. The removal efficiency increases within 5 min and adsorption process reached equilibrium after 5 min. The adsorption equilibrium was reached within few minutes for

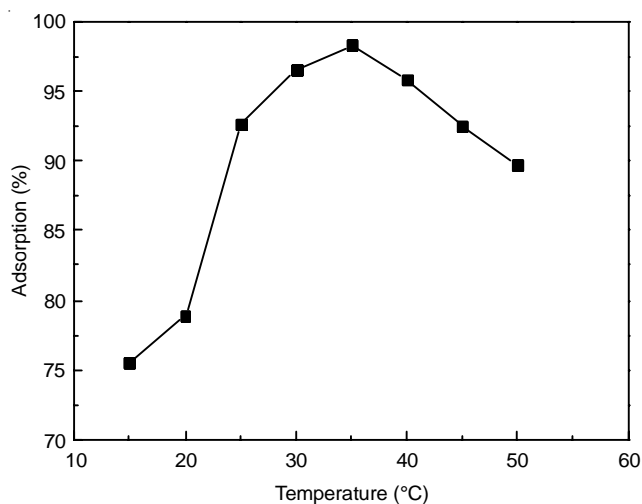


Fig. 7. Effect of temperature on the adsorption of Cd(II)

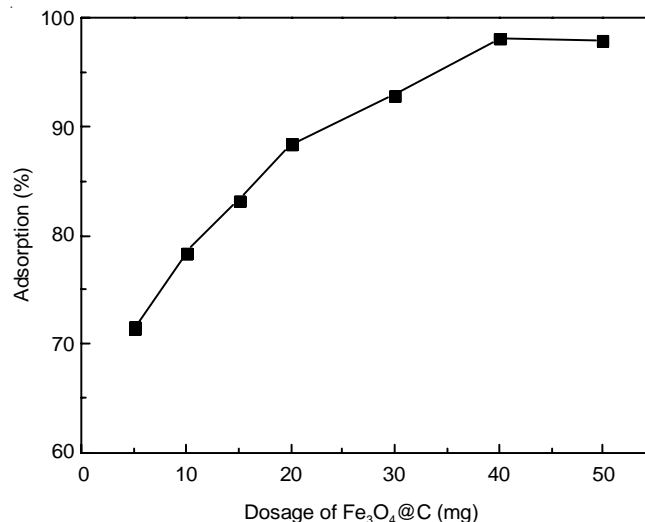


Fig. 9. Effect of amount on the adsorption of Cd(II)

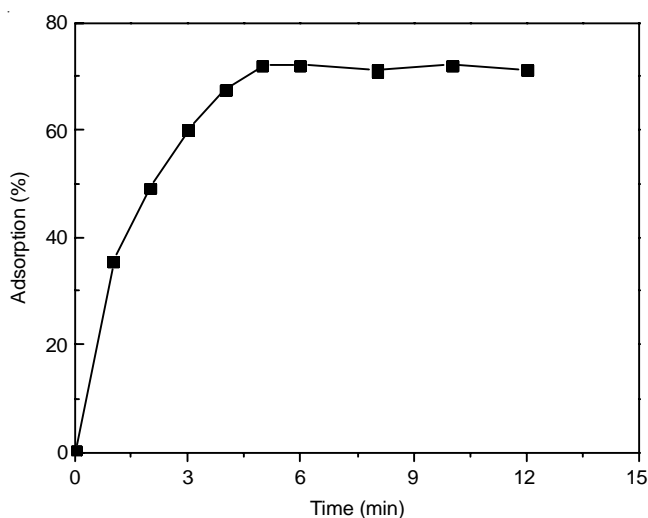


Fig. 8. Effect of time on the adsorption of Cd(II)

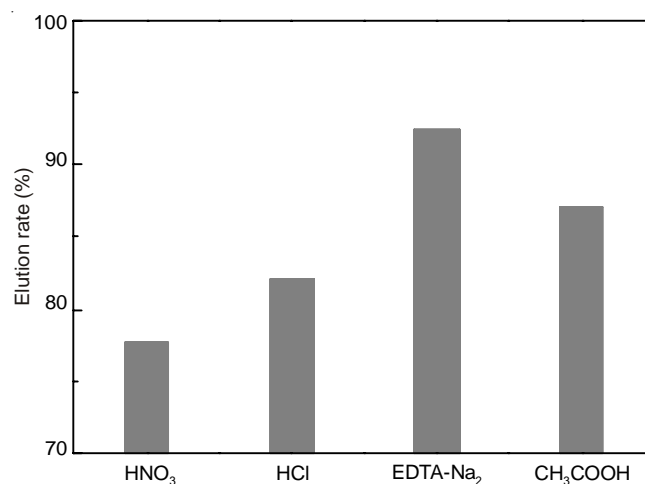
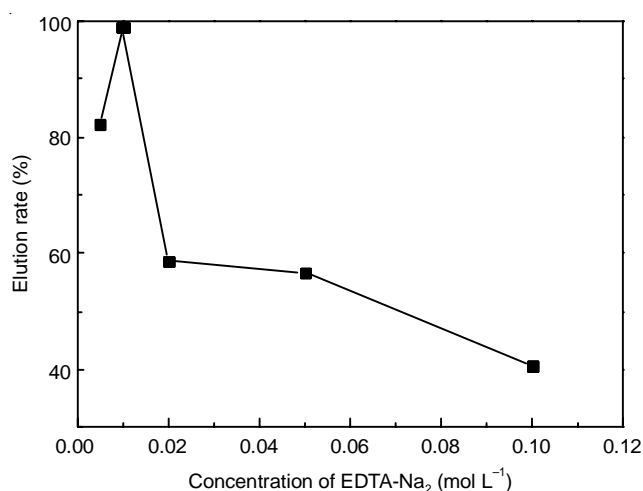


Fig. 10. Effect of different types of eluents

almost metal ions. It could be concluded that reaching equilibrium in a short time is due to the high activity and high efficiency of adsorbent.

Effect of amounts of Fe₃O₄@C particles: The effect of the amounts of adsorbents on the extraction efficiency was investigated. The enrichment experiments of Cd(II) were performed using different amounts (from 10 to 50 mg) of the synthesized materials. As shown in Fig. 9, the results shown that the extraction efficiency increased gradually when more adsorbents were used. However, the extraction equilibriums were achieved at 40 mg of the particles. So, taking all factors into consideration, we selected 40 mg as the optimal amount.

Desorption solvent: Desorption study was performed respectively by using EDTA-Na₂ solution, hydrochloric acid solution, nitric acid and acetic acid solution at the same dose, as shown in Fig. 10. The result showed that EDTA-Na₂ solution were the most efficient elution, then experimental recovery rate was investigated by different concentration of EDTA-Na₂ solution (0.005, 0.01, 0.02, 0.05, 0.1 mol L⁻¹). As it can be seen from Fig. 11, recovery efficiency could achieve more effect by using 4 mL 0.01 mol L⁻¹ EDTA-Na₂ solution.

Fig. 11. Effect of concentration of EDTA-Na₂ on the elution

Reusability of Fe₃O₄@C microspheres: In order to investigate the regeneration ability of Fe₃O₄@C microspheres recycled test was carried out in turn under optimal conditions. In the subsequent recycling, the removal ability decreased gradually as the number of cycles of reuse of Fe₃O₄@C microspheres increases, however. Repeatedly operating for seven

times, the adsorption rate was still more than 90 %. It indicated that Fe₃O₄@C microspheres could be reused.

Interferences: To evaluate the selectivity of the Fe₃O₄@C towards Cd(II), the potential interferences from various coexisting cationic and anionic species in environmental sample matrixes have been investigated. The experimental results indicates that 300 mg L⁻¹ Na⁺, 150 mg L⁻¹ Mg²⁺, 3 mg L⁻¹ Ca²⁺ and Cu²⁺, 1 mg L⁻¹ Pb²⁺, 280 mg L⁻¹ NO₃⁻, 150 mg L⁻¹ SO₄²⁻ pose no interference. Generally, in practice for the detection of Cd(II) in environmental samples, the concentrations of the above mentioned coexisting species in the samples can be well controlled below the tolerant limit by employing appropriate sample pretreatment. Thus, potential interferences from these ionic species or sample matrixes cause no problem for practical applications. There is no need for special treatment of the samples or their digests for Cd(II) determination after adsorption and desorption by the Fe₃O₄@C microspheres.

Detection performance: With the overall optimized procedure, a certain amount of magnetic Fe₃O₄@C magnetic microspheres were put into Cd(II) solution under optimized condition. After repeating of the same operation eleven times, the results showed the detection limit of the method was 0.036 mg mL⁻¹ and the relative standard deviation was 3.65 %.

Determination of sample water: The method was applied to analysis Cd(II) in different environmental water samples, including pure water, tap water, lake water and river water. Environmental water samples were investigated in order to test the method with Fe₃O₄@C magnetic microspheres. No residues of the Cd(II) were detected in these water samples. To determine the recoveries of this method, the water samples were spiked with 10 µg L⁻¹ of each analyte. As it can be seen from Table-1, the results were satisfactory as recovery in the range of 95-101 %.

TABAL-1
DETERMINATION RESULTS OF Cd(II) IN WATER
SAMPLES AND THE RECOVERIES (n = 6)

Sample	Cd(II) added (µg L ⁻¹)	Cd(II) found (µg L ⁻¹)	Recovery (%)
(a) Pure water	0	Not detected	
	10	10.1	101
(b) Tap water	0	Not detected	
	10	9.81	98.1
(c) Jean lake water	0	Not detected	
	10	9.55	95.5
(d) Muddy river water	0	Not detected	
	10	9.50	95

Note: Data in this table averages of six replicates

(a) Pure water bought from the supermarket

(b) Tap water in the laboratory

(c) Jean lake in Shenyang Linggong University

(d) Muddy river in Shenyang, Liaoning Province

Conclusion

In summary, magnetic Fe₃O₄@C nanoparticles were fabricated by hydrothermal method for Cd(II) preconcentration.

The experimental results showed that static adsorption capacity was 35 mg g⁻¹ at pH 7.5 and 35 °C. Adsorbed Cd(II) could be eluted by using 4 mL 0.01 mol L⁻¹ EDTA-Na₂. The detection limit of the method was 0.036 mg mL⁻¹ and the relative standard deviation was 3.65 %. Environmental water samples were determined by using this method and the results were satisfactory as recovery in the range of 95-101 %. This method could be used to analyze cadmium in water samples.

ACKNOWLEDGEMENTS

This paper was supported by Natural Science Foundation of Liaoning Province of China (2013020088), Key Laboratory fund of Shenyang Ligong University (4771004kfs24).

REFERENCES

- P. Bradac, B. Wagner, D. Kistler, J. Traber, R. Behra and L. Sigg, *Environ. Pollut.*, **158**, 641 (2010).
- S. Satarug, J.R. Baker, S. Urbenjapol, M. Haswell-Elkins, P.E.B. Reilly, D.J. Williams and M.R. Moore, *Toxicol. Lett.*, **137**, 65 (2003).
- M. Selvi, A. Gül and M. Yilmaz, *Chemosphere*, **52**, 259 (2003).
- J.A. Ryan, H.R. Pahren and J. LucasLucas, *Environ. Res.*, **28**, 251 (1982).
- H. Matusiewicz, *Spectrochim. Acta B*, **52**, 1711 (1997).
- P. Wu, Y.C. Zhang, Y. Lv and X.D. Hou, *Spectrochim. Acta B*, **61**, 1310 (2006).
- J.R. Meng, J. Bu, C.H. Deng and X.M. Zhang, *J. Chromatogr. A*, **1218**, 1585 (2011).
- C. Huang and B. Hu, *Spectrochim. Acta A*, **63**, 437 (2008).
- K. Shrivastava and D.K. Patel, *Food Chem.*, **122**, 314 (2010).
- C.Y. Hu, J. Guo, Y. Du, H.H. Xu and Y.H. He, *Trans. Nonferrous Met. Soc. China*, **21**, 114 (2011).
- B. Holland, S.R. Yazdi, G.I. Titapiccolo and M. Corredig, *J. Dairy Sci.*, **93**, 893 (2010).
- Q.L. Zhang, Y.C. Lin, X. Chen and N.Y. Gao, *J. Hazard. Mater.*, **148**, 671 (2007).
- R. Rahimi, H. Kerdari, M. Rabbani and M. Shafiee, *Desalination*, **280**, 412 (2011).
- L.H. Reddy, J.L. Arias, J. Nicolas and P. Couvreur, *Chem. Rev.*, **112**, 5818 (2012).
- J.P. Ge, Y.X. Hu, M. Biasini, W.P. Beyermann and Y.D. Yin, *Angew. Chem. Int. Ed.*, **46**, 4342 (2007).
- T. Zhang, X.F. Zhang, X.J. Yan, L. Kong, G. Zhang, H. Liu, J. Qiu and K.L. Yeung, *Chem. Eng. J.*, **228**, 398 (2013).
- B.C. Zhu, J. Zhao, H.Q. Yu, L.G. Yan, Q. Wei and B. Du, *Chem. Eng. J.*, **219**, 411 (2013).
- Y.H. Deng, C.H. Deng, D.W. Qi, C. Liu, J. Liu, X.M. Zhang and D.Y. Zhao, *Adv. Mater.*, **21**, 1377 (2009).
- M. Arruebo, W.Y. Ho, K.F. Lam, X.Q. Chen, J. Arbiol, J. Santamaria and K.L. Yeung, *Chem. Mater.*, **20**, 486 (2008).
- G. Zhao, T. Wen, C. Chen and X. Wang, *RSC Adv.*, **2**, 9286 (2012).
- J. Xu, H. Lv, S.-T. Yang and J. Luo, *Rev. Inorg. Chem.*, **2-3**, 139 (2013).
- M.S. Mauter and M. Elimelech, *Environ. Sci. Technol.*, **42**, 5843 (2008).
- R. Wu, J. Liu, L. Zhao, X. Zhang, J. Xie, B. Yu, X. Ma, S.-T. Yang, H. Wang and Y. Liu, *J. Environ. Chem. Eng.*, **2**, 907 (2014).
- S.-T. Yang, J. Luo, J. Liu, Q. Zhou, J. Wan, C. Ma, R. Liao, H. Wang and Y. Liu, *Nanosci. Nanotechnol. Lett.*, **5**, 372 (2013).
- B. Yu, J. Xu, J. Liu, S.-T. Yang, J. Luo, Q. Zhou, J. Wan, R. Liao, H. Wang and Y. Liu, *J. Environ. Chem. Eng.*, **1**, 1044 (2013).