EDTA-Silane Modified Magnetite Core-Shell Nanoparticles as a Solid Phase Extraction Sorbent for the Determination of Pb and Cd in Environmental Water Samples Coupled With Hydride Generation Atomic Fluorescence Spectrometry

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INTRODUCTION

Toxic heavy metal pollution, such as Pb and Cd, is one of the most serious environmental problems. These metals are non-degradable and tend to accumulate in living organisms, causing various diseases and disorders (1,2). Due to the potential adverse effects of these two elements, their accurate and precise determination in environmental samples at trace and ultra-trace levels is highly important. Several analytical methods, e.g., electrothermal atomic absorption spectrometry (ETAAS) (3,4), flame atomic absorption spectrometry (FAAS) (5), inductively coupled plasma optical emission spectrometry (ICP-OES) (6), inductively coupled plasma mass spectrometry (ICP-MS) (7), and total reflection XRF spectrometry (8), etc., have been reported for the determination of heavy metals determination. But the direct determination of trace metal ions is often limited due to their low concentration and strong interference from the real sample matrices. In order to prevent these limitations, preliminary pre-concentration and separation procedures are essential and have been applied prior to instrumental determination, such as co-precipitation (9), solvent extraction (10), cloud point extraction (CPE) (11), solid-phase extraction (SPE) (12,13), and magnetic solid-phase extraction (MSPE) (14,15).

ABSTRACT

An efficient adsorbent, N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid functionalized magnetic core-shell silica nanoparticles ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$), was synthesized and used as an adsorbent for the simultaneous extraction and pre-concentration of Pb and Cd from water samples through magnetic solid-phase extraction (MSPE). After adsorption, these ions were desorbed with hydrochloric acid, followed by the determination with hydride generation atomic fluorescence spectrometry (HG-AFS). The sorbent was characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Several important parameters influencing the extraction efficiency, such as pH, amount of adsorbent, adsorption and elution time, elution concentration and volume, sample volume, interfering ions and adsorption capacity, were studied and optimized. The detection limits for Pb and Cd of 0.03 and 0.028 ng mL^{-1} , respectively, were obtained. The linear range was 0.12–15.0 ng mL^{-1} for Pb and 0.10–4.0 ng mL^{-1} for Cd and the relative standard deviations were 3.72% and 2.41% ($n=7$), respectively. The pre-concentration factor was 83.3 for Pb and 66.7 and Cd, respectively. The method was applied for the determination of target ions in different samples with high recoveries.

Among these methods, MSPE appears to be one of the most effective selections owing to its ease of automation, high extraction efficiency, and rapid phase separation (16). In MSPE, magnetic nanoparticles (MNPs), generally magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), were usually used as the MSPE sorbents (17). However, naked Fe_3O_4 nanoparticles tend to be oxidized and aggregate, and are not selective and suitable for the extraction of analytes in complex matrices (18). Thus, it is necessary to coat them with an inorganic layer such as silica or alumina (19). Silica shell not only prevents Fe_3O_4 NPs from aggregating in wide pH ranges and improves their chemical stability, but also is often terminated by the silanol groups that can react with silane coupling agents in order to conjugate with a variety of specific ligands (20).

The N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (TMS-EDTA) used in this work is an EDTA derivative in which one of the carboxylate groups is replaced by an alkyl spacer with a reactive trialkoxysilane group for binding to the surface of the magnetic shell (21). It has carboxyl groups and amino groups which are suitable sites for effective coordination with metal ions.

In this research, the synthesis, characterization, and application of N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles is reported as an efficient adsorbent for the separation

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and pre-concentration of Pb and Cd in water samples prior to their determination by hydride generation atomic fluorescence spectrometry (HG-AFS). It is well documented that heavy metal ions can form complex compounds with the carboxyl groups through surface chelation mechanisms. The for the fast separation and pre-concentration of Pb and Cd in water samples. The proposed sorbent was characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy.

EXPERIMENTAL

Instrumentation

The concentrations of Pb and Cd were measured using a model PF6-2 non-dispersive hydride generation atomic fluorescence spectrometer (Beijing Purkinje General Instrument, P.R. China). The optimum instrumental operating parameters are listed in Table I. The samples were weighed using a model Mettler XS-204 electronic balance (Greifensee, Switzerland). A model pH5-3C digital pH meter (Shanghai, P.R. China) was used for pH adjustments. A model S10-3 magnetic mechanical stirrer (Shanghai, P.R. China) and a model DZF-6020 oven (Shanghai, P.R. China) were used to homogenize the samples. To disperse the nanoparticles in the solutions, a model KH-500B ultrasonicator (Suzhou, P.R. China) was used. The FTIR spectra were recorded in the 4000–500 cm^{-1} region on a Varian 640 spectrometer (Varian, USA). Scanning electron microscopy (SEM) images were obtained on a model JSM-7500F (Tokyo, Japan).

Standard Solutions and Reagents

The stock standard solutions (1000 mg L^{-1}) of Pb and Cd were supplied by the National Research Center for Certified Reference

Materials (Beijing, P.R. China). Working solutions were prepared daily by appropriate dilution of the stock solutions, and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, KBH_4 , methanol and ethanol were of analytical grade and purchased from Guangfu Chemical Company (Tianjin, P.R. China), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, KOH and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were of analytical grade and purchased from Kemiou Chemical Company (Tianjin, P.R. China), HCl and acetone were of analytical grade and purchased from Luoyang Chemical Company (Henan, P.R. China). Tetraethyl orthosilicate (TEOS) was obtained from Wuhan University (Hubei, P.R. China). N-[(3-Trimethoxysilyl) propyl]ethylenediamine triacetic acid trisodium salt (TMS-EDTA) (45 wt%) was purchased from J&K Chemical Company (Beijing, P.R. China). Ultrapure water with a resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ was obtained using the Milli-Q® purification system (Millipore Corporation, USA).

Synthesis of Fe_3O_4 Nanoparticles

The nanoparticles were prepared according to the method described by Massart, 1981 (22), but with minor modification. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4.4 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.98 g) were dissolved in 60 mL deionized water by ultrasonic treatment for 10 minutes. An amount of 143 mL of 0.7 mol L^{-1} ammonia was added dropwise into the mixed solution under nitrogen atmosphere via vigorous stirring at 40°C . During the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$, it was noticed that the solution changed color from the original brown to dark brown and then to black. The precipitate was magnetically separated using a permanent magnet, then washed with distilled water and ethanol to neutral pH. Subsequently, the obtained magnetic Fe_3O_4 nanoparticles were dried under vacuum at 40°C for 12 hours.

TABLE I
Operating Parameters of the AFS Instrument

Parameters	Pb	Cd
Negative high voltage of the PTM	280 V	280 V
Atomizer height	8 mm	8 mm
Main lamp current	50 mA	50 mA
Lamp ancillary electrode current	50	50
Flow rate of carrier gas	300 mL min^{-1}	300 mL min^{-1}
Flow rate of shield gas	600 mL min^{-1}	600 mL min^{-1}
Atomizer temperature	200°C	200°C
Read mode	Peak area	Peak area
Carrier solution	$1.0\%(\text{v/v}) \text{ HCl}$	$2.0\%(\text{v/v}) \text{ HCl} + 1.0\%(\text{m/v}) \text{ thiourea} + 1.0 \mu\text{g mL}^{-1} \text{ Co}^{2+}$
Reductant	$1.5\%(\text{m/v}) \text{ KBH}_4 + 1.0\%(\text{m/v}) \text{ KOH} + 1.5\%(\text{m/v}) \text{ K}_3[\text{Fe}(\text{CN})_6]$	$2.5\%(\text{m/v}) \text{ KBH}_4 + 0.5\%(\text{m/v}) \text{ KOH}$

Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ Nanoparticles

To protect the magnetic core by silica film and prepare core-shell magnetic nanoparticles, 1.5 g of prepared Fe_3O_4 nanoparticles was dispersed with 50 mL of anhydrous ethanol, then subjected to 10 minutes of ultrasonic treatment. Thereafter, 5 mL of ammonia, 8 mL of deionized water, and 1 mL of tetraethylorthosilicate (TEOS) were added into the suspension in a 40 °C water bath. The mixed suspension was stirred and allowed to react for 24 hours. Finally, the reaction product was separated by magnetic decantation, washed twice with anhydrous ethanol, and dried at 40 °C for 12 hours under vacuum. Thus, Fe_3O_4 coated with SiO_2 was obtained (23).

Synthesis of Core-Shell $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ Nanoparticles

The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were functionalized with TMS-EDTA. The silanization procedure started by setting the pH at 4.5 with HCl (1 M) and then dispersing 100 mg of nanoparticles in MeOH/ H_2O 85:15 (100 mL). The beaker was placed into an ultrasonic bath for 2 hours. TMS-EDTA

(1 mmol) was then added together with a few drops of glacial acetic acid. The mixture was stirred vigorously for 24 hours. The products were precipitated from the reaction mixture with a small magnet and washed once with water and twice with acetone. Finally, they were dried in vacuum at room temperature for 30 minutes (21).

MSPE Procedure

The adsorption test was carried out in a batch system. First, 5.0 mg of dry synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ nanoparticles were dispersed into a 10-mL sample solution containing 3.0 ng mL^{-1} Pb and 1.0 ng mL^{-1} Cd. Then, the buffer solutions were added to the samples to achieve a pH of 5.5, and the mixture was ultrasonicated for 7 minutes at room temperature. Then the magnetic adsorbents were separated from the solution by using a magnet. In the desorption step, 0.5 mL HCl (0.8 mol L^{-1}) was added as the eluent and ultrasonicated for 7 minutes. Finally, the magnet was used again to collect the nanoparticles, and the eluent was transferred into a test tube for subsequent AFS analysis.

RESULTS AND DISCUSSION

Characterization of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$

The morphology of the samples was observed by SEM (Figure 1). The SEM images showed that the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ nano-adsorbent particles have relatively homogeneous and porous structures which play an important role in the enhancement of the adsorption capacity.

FT-IR Spectral Analysis

The FT-IR spectrum of the Fe_3O_4 nanoparticles shows the absorption peak at 562 cm^{-1} which corresponds to the Fe-O vibration (Figure 2A). The silica shell coated on the surface of the magnetite core can be confirmed by the spectrum in Figure 2B. The bands at 1092 cm^{-1} and 799 cm^{-1} are assigned to the Si-O-Si vibrations (23), the absorption peak of Fe_3O_4 at 573 cm^{-1} indicated that the MNPs were covered by a silica layer throughout the experiment. The surface modification of the MNPs by TMS-EDTA is further confirmed by the FT-IR spectrum (Figure 2C). Compared with $\text{Fe}_3\text{O}_4/\text{SiO}_2$, the characteristic absorption band of the Si-O stretching vibration overlaps with the C-N stretching vibrations (24). Absorp-

Fig. 1. SEM images of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ nano-adsorbent particles.

Fig. 2. FT-IR spectra of (A) Fe_3O_4 , (B) $\text{Fe}_3\text{O}_4/\text{SiO}_2$, and (C) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ nanoparticles.

tion peaks at 1637 cm^{-1} are assigned to the C=O stretching vibrations of the -COO^- . Moreover, the characteristic absorption band appearing at 1399 cm^{-1} can be assigned to the C-O stretching vibration of the -COO^- group (25), which suggests the existence of the carboxyl group of TMS-EDTA modified on MNPs. Also, the surface modification of core-shell nanoparticles can be confirmed, 1082 cm^{-1} and 819 cm^{-1} might be ascribed to Si-O-Si vibrations and 576 cm^{-1} is due to the Fe-O stretching vibrations.

Adsorption Capacity

Adsorption capacity is an important factor to evaluate the performance of a sorbent. In order to determine this factor, the nano-adsorbents were subjected to several loadings with 10 mL sample solutions containing various concentrations of Pb and Cd. At the designed contact time, the metal concentration in the supernatants was analyzed by AFS after the adsorbent was removed with the help of a magnet. The values of the adsorption capacity increased with the increase of initial concentrations of the target ions and then it reached a plateau. The static adsorption capacity (7.52 mg g^{-1} for Pb and 5.61 mg g^{-1} for Cd) of the nano-adsorbent was obtained.

Optimization of Extraction Conditions

Several experimental variables affecting the extraction recovery of Pb and Cd were investigated, including sample pH, the adsorbent amount, ultrasonic time, sample volume, HCl concentration, and elution volume and time.

The pH of the medium has an influence on the sorption process and a convenient pH value can improve the adsorption efficiency. A series of batch equilibrium tests were carried out to confirm the effect of pH upon Pb and Cd

adsorption by $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ in a wide range of pH from 2 to 9. When the other parameters were kept constant, the Pb and Cd concentrations in the eluent were determined by HG-AFS. The data, graphed as a function of pH, are depicted in Figure 3. The recovery percentage increased along with an increasing pH value from 2.0 to 5.0. It was found that the recovery does not change very much with a further increase from 5.0 to 7.0. When the pH was still further enhanced, the recovery percentage decreased minutely because of the precipitation of the hydroxide species. At lower pH values, a decrease in the quantitative recovery of the sorbent could be attributed to the electrostatic repulsion of the protonated active sites on the sorbent with the positively charged Pb and Cd species. In view of the above results, all subsequent experiments were performed at pH 6.0.

In addition, in order to minimize sample processing and desorption time, the ultrasonic time for the extraction process was also optimized in the range from 2–14 minutes. The results from Figure 4 show that 7 minutes was the appropriate adsorption time to obtain excellent recoveries with minimal time required for sample processing.

In the MSPE technique, the amount of magnetic adsorbent is one of the main factors affecting the extraction of the analytes. Hence, this parameter was studied in the range of 2.0–12 mg. The mixture was applied to the MSPE procedures. As shown in Figure 5, 5.0 mg of adsorbent was enough to obtain quantitative recovery. No further increase was observed with an increase in adsorbent. Thus, 5.0 mg of adsorbent solution was selected for further experiments.

It can be seen from Figure 3 that M^{2+} had a lower adsorption percentage at a lower pH, which

indicates that the acid could desorb M^{2+} in the adsorbent. In addition, HCl is a mostly harmless acid to HG-AFS. Therefore, HCl was selected as the eluent and the concentration was investigated in the range of 0.2–1.2 mol L^{-1} . The results in Figure 6 show that the recoveries increased with an increase in HCl concentration. Considering that the instrument could not tolerate a strong acid, 0.8 mol L^{-1} HCl was selected as the eluent for further experiments. An amount of 0.2–1.2 mL of 0.8 mol L^{-1} HCl was used to investigate the effects of elution volume. The results indicated that the recoveries increased along with an increase in elution volume. In order to achieve a high enrichment factor, the volume should be as small as possible. An amount of 0.6 mL of 0.8 mol L^{-1} HCl was sufficient to quantitatively elute the metal ions and was employed as the optimum elution volume.

The effect of sample volume on the recoveries was studied to obtain a higher enrichment factor. Figure 7 shows that quantitative recovery was achieved with 50 mL for Pb and 40 mL for Cd. The pre-concentration factors calculated were 83.3 for Pb and 66.7 for Cd at a final volume of 0.6 mL.

Interferences

Under optimized conditions, the interference of various cations on the recovery of Pb and Cd were investigated. The results obtained showed that $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ is a good candidate for pre-concentration of target analytes without any serious matrix interference in different real samples (see Table II).

Analytical Performance

Under optimized conditions, the analytical characteristics of the method were investigated, i.e., precision, detection limits, and linearity of Pb and Cd determination in aqueous samples based on the

Fig. 3. Effect of pH on the sorption of Pb and Cd. Sample volume: 10 mL; sample weight: 5 mg; adsorption time: 7 min; eluent: 0.6 mL 0.8 mol L⁻¹ HCl.

Fig. 4. Effect of adsorption time on the sorption of Pb and Cd. Sample weight: 5 mg; sample volume: 10 mL; eluent: 0.6 mL 0.8 mol L⁻¹ HCl.

Fig. 5. Effect of amount of sorbent on the sorption of Pb and Cd. Sample volume: 10 mL; adsorption time: 7 min; eluent: 0.6 mL 0.8 mol L⁻¹ HCl.

Fig. 6. Effect of the HCl concentration on the sorption of Pb and Cd. Sample weight: 5 mg; sample volume: 10 mL; adsorption time: 7 min; eluent volume: 0.6 mL HCl.

Fig. 7. Effect of the sample volume on the the sorption of Pb and Cd. Sample weight: 5 mg; adsorption time: 7 min; eluent: 0.6 mL 0.8mol L⁻¹ HCl.

Foreign Ion	Foreign ion/Pb ²⁺ ratio	Foreign ion/Cd ²⁺ ratio	Recovery (%) (mean±S.D., n=3)	
			Pb	Cd
Na ⁺	10,000	10,000	97.0±1.2	95.5±1.1
K ⁺	10,000	10,000	95.1±1.3	100.1±1.9
Mg ²⁺	2500	2000	93.8±0.9	99.8±2.1
Ni ²⁺	1000	800	94.9±1.5	98.4±1.8
Cu ²⁺	200	150	92.2±0.8	94.5±1.1
Zn ²⁺	1000	1000	97.5±0.9	97.3±1.2
Co ²⁺	500	400	91.3±0.8	94.7±1.0
Mn ²⁺	250	500	94.5±0.9	96.1±1.2
Ba ²⁺	2000	1800	92.0±0.3	98.8±1.2
Fe ³⁺	50	50	93.6±1.1	95.7±1.7

adsorption of Pb and Cd on $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ nanosorbent. The obtained linearity was 0.12–15 ng mL^{-1} for Pb and 0.10–4.0 ng mL^{-1} for Cd. The LOD (3σ) was 0.030 ng mL^{-1} and 0.028 ng mL^{-1} for Pb and Cd, respectively. Also, the resultant repeatability expressed as the relative standard deviation (RSD, $n=7$) was calculated as 2.72% and 3.41% for Pb and Cd, respectively.

The efficiency of the developed method was evaluated by comparing the obtained results with those of other similar methods reported in the literature and is given in Table III. As can be seen, the LOD obtained in this work was lower than in reported methods. Besides, compared to these reported methods, the present MSPE method was fast, precise, easy to operate, and had high adsorption capacity.

Analytical Application

The developed procedure has been applied to the determination Pb and Cd in water samples. Tap water and lake water were also analyzed after spiking with different concentrations of Pb and Cd with high recoveries. The samples were collected locally and filtered with a 0.22 μm membrane filter to remove suspended particles such as water-insoluble inorganic, organic, silt, clay, and other microorganisms. The results are shown in Table IV for three replicated analyses of each sample show that the method is suitable for the analysis of real samples.

CONCLUSION

In this study, synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TMS-EDTA}$ was successfully applied as a new sorbent for the magnetic solid phase extraction and convenient, fast, and efficient enrichment of trace Pb and Cd in water samples. It is a very fast extraction method, because the MNPs have generally high surface area and produce fast magnetic sep-

Method	Detection Limit (ng mL^{-1})		Enrichment Factor		References
	Pb	Cd	Pb	Cd	
SPE-FAAS	0.63	0.30	175	63	(26)
SPE-ETAAS	4.4	1.5	100	100	(27)
MSPE-FAAS	0.7	0.01	294	294	(28)
MSPE-ICP-OES	0.08	0.06	236	294	(29)
MSPE-AFS	0.03	0.028	83.3	66.7	This work

Sample	Analyte	Added (ng mL^{-1})	Found ^a (ng mL^{-1})	Recovery (%)
Tap Water	Pb	0	nd ^b	–
		2.0	1.86 $\pm$ 0.06	93.2
		4.0	3.72 $\pm$ 0.16	93.0
	Cd	0	nd ^b	–
		1.5	1.43 $\pm$ 0.11	95.1
		3.0	2.83 $\pm$ 0.19	94.3
Lake Water	Pb	0	0.12 $\pm$ 0.08	–
		2.0	2.03 $\pm$ 0.13	101.5
		4.0	3.70 $\pm$ 0.31	92.5
	Cd	0	0.08 $\pm$ 0.02	–
		1.5	1.53 $\pm$ 0.04	102.2
		3.0	2.87 $\pm$ 0.26	95.6

^a Mean value $\pm$ standard deviation, $n=3$.

^b Not detected.

aration. Ease of operation, high selectivity, and sensitivity are other advantages. In addition, the combination of MSPE with the proposed nano-adsorbent and atomic fluorescence spectrometric analysis results in high analytical performance.

Received April 21, 2016.

REFERENCES

1. A. Duran, M. Soylak and S. A. Tuncel, J. Hazard. Mater. 155, 114 (2008).
2. Y. Tang, S. Liang, J. Wang, S. Yu and Y. Wang, J. Environ. Sci. 25, 830 (2013).
3. D. Bohrer, P. Cícero do Nascimento, M. Guterres, T. Trevisan and E. Seibert, Analyst 124, 1345 (1999).
4. Y. H. Sung and S. D. Huang, Anal. Chim. Acta. 495, 165 (2003).
5. C. Duran, H. B. Senturk, L. Elci, M. Soylak and M. Tufekci, J. Hazard. Mater. 162, 292 (2009).
6. E.L. Silva, P. dos Santos Roldan and M.F. Giné, J. Hazard. Mater. 171, 133 (2009).
7. J. Yin, Z. Jiang, G. Chang and B. Hu, Anal. Chim. Acta. 540, 333 (2005).

8. B. Zawisza and R. Sitko, *Spectrochim. Acta B At. Spectrosc.* 62, 1147 (2007).
9. Z. Bahadir, V.N. Bulut, D. Ozdes, C. Duran, H. Bektas and M. Soylak, *J. Ind. Eng. Chem.* 20, 1030 (2014).
10. X. Jia, Y. Han, X. Liu, T. Duan and H. Chen, *Microchim. Acta* 171, 49 (2010).
11. W.I. Mortada, I.M. Kenavy and M.M. Hassanien, *Anal. Methods.* 72, 114 (2015).
12. R.M. P. Crecente, C.G. Lovera, J. Garcia, J.A. Mendez, S.G. Martin and C.H. Latorre, *Spectrochim. Acta, Part B* 101, 15 (2014).
13. T.T. Shih, I.H. Hsu, S.N. Chen, P.H. Chen, M.J. Deng, Y. Chen, Y.W. Lin and Y.C. Sun, *Analyst* 140, 600 (2015).
14. M. Zhang, Z. Zhang, Y. Liu, X. Yang, L. Luo, J. Chena and S. Yao, *Chem. Eng. J.* 178, 443 (2011).
15. M. Babazadeh, R. Hosseinzadeh-Khanmiri, J. Abolhasani, E. Ghorbani-Kalhor and A. Hassanpour, *RSC Adv.* 5, 19884 (2015).
16. Y. Zhai, S.E. Duan, Q. He, X. Yang and Q. Han, *Microchim. Acta* 169, 353 (2010).
17. E. Ziaei, A. Mehdinia and A. Jabbari, *Anal. Chim. Acta* 850, 49 (2014).
18. A. Tadjarodi, A. Abbaszadeh, M. Taghizadeh and N. Shekari, *Mater. Sci. Eng., C* 49, 416 (2015).
19. X.O. Zhang, H.Y. Niu, Y.Y. Pan, Y. Shi and Y. Cai, *J. Colloid. Interf. Sci.* 362, 107 (2011).
20. M. Helmi, R. Farimani, N. Shahtahmassebi, M.R. Roknabadi and N. Ghows, *Nanomed. J.* 1, 71 (2014).
21. D. Dupont, J. Luyten, M. Bloemen, T. Verbiest and K. Binnemans, *Ind. Eng. Chem. Res.* 53, 15222 (2014).
22. R. Massart, *IEEE Trans. Magn.*, 17, 1247 (1981).
23. M. Naghizadeh, M. A. Taher, M. Behzadi and F. H. Moghaddam, *Chem. Eng. J.* 281, 444 (2015).
24. M. Najafi, Y. Yousefi and A.A. Rafati, *Sep. Purif. Technol.* 85, 193 (2012).
25. R. Qin, F. Li, M. Chen and W. Jiang, *Appl. Surf. Sci.* 256, 27 (2009).
26. B.W. Yang, Q.J. Gong, L.P. Zhao, H. Sun, N.N. Ren, J.X. Qin, J. Xu and H.Y. Yang, *Desalination*, 278, 65 (2011).
27. X.P. Huang, X.J. Chang, Q. He, Y.M. Cui, Y.H. Zhai and N. Jiang, *J. Hazard. Mater.*, 157, 154 (2008).
28. S. Turan, S. Tokalıoğlu, A. Sahan and C. Soykan, *React. Funct. Polym.* 72, 722 (2012).
29. D.H. Chen, B. Hu and C.Z. Huang, *Talanta* 78, 491 (2009).