Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

Electronic Supporting Information

Preparation of dithizone grafted poly(allyl chloride) core-shell-shell magnetic composite microspheres for solid-phase extraction of ultra-trace levels of Pb(II), Cu(II) and Cr(III) ions

Lei Zhang[a], Xiaodi Gao[a], Zhichao Xiong[a], Lingyi Zhang[a*], Bohao Yu[a], Runsheng Zhang[b], Weibing Zhang[a*]

[a] *Shanghai Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, 200237, Shanghai, China.*

[b] *Shanghai Key Laboratory of Crime Scene Evidence, Shanghai Research Institute of Criminal Science and Technology, Shanghai Public Security Bureau, Shanghai, P. R. China*

weibingzhang@ecust.edu.cn

zhanglingyi@ecust.edu.cn

Contents

Optimization of parameters

Effect of pH

When performing MSPE, the pH of the solution played a key role for adsorption of metal ions on the magnetic microspheres. Therefore, the solutions with different pH were prepared in the range of 3 - 9 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. The relationship between the adsorption efficiency and the pH was shown in Fig. S1. The efficiency was calculated by the following expression:

$$\text{Adsorption efficiency}=(C_i-C_f)/C_i$$

where C_i and C_f are the initial and final concentrations of target heavy metal ion in the solution, respectively.

With the increasing pH from 3 to 6, the adsorption efficiency was markedly increased. When pH was further increased from 6 to 9, the adsorption efficiency almost didn't changed. This phenomenon might be explained as follow (Fig. S2.). In the strong acidic solution (pH=2), the active sites on the surface of magnetic microspheres are occupied by proton, which have electrostatic repulsion for target heavy metal ions. With the increasing of pH, the groups of C=S and N=N of dithizone can serve as active sites for combination with target heavy metal ion, forming a stable penta-heterocycles chelating complex. Therefore, weak acidic environment (pH 6) is preferred for the extraction of target metal ions.

Effect of adsorbent amount

The relationship between adsorbent amounts and the adsorption efficiency was studied as shown in Fig. S3. The experimental results indicated that the adsorption efficiency was obviously improved by increasing adsorbent amount in range of 5-10 mg. When the amount of adsorbent was above 10 mg, the adsorption efficiency increased slowly. So 10 mg of adsorbent was selected for further studies.

Adsorption kinetics and adsorption capacity

Adsorption kinetics of Pb(II), Cu(II) and Cr(III) ions by the magnetic microspheres were examined. The adsorption efficiencies of three ions with different extraction time (1-120min) are shown in Fig. S4. The experimental results indicated that the phase extraction process was very fast. When the adsorption time was longer than 5 min, the target metal ions adsorption efficiency reached 95 %. The magnetic microspheres have high specific surface area and more adsorption sites which result in fast adsorption. Thus, adsorption time of 10 min was the best choice.

In order to determine the adsorption capacity, 10 mg of prepared dithizone grafted Fe_3O_4@MPS@poly(allyl chloride) magnetic microspheres were added to solution of heavy metal ions (50 mL, 20 mg L^{-1}, pH=6) followed by shaking 12 h at 25 °C. After removing adsorbent by a magnet, Pb(II), Cu(II) and Cr(III) ions in solution were detected by ICP-OES. The adsorption capacities were found to be 66.9 62.2 62.1 mg g^{-1} for Pb(II), Cu(II) and Cr(III) ions, respectively. Comparing with other adsorbents reported in the literatures shown in Table S1, adsorption capacity obtained by this method for adsorption of Pb, Cu and Cr ions were higher than that of most reported adsorbent [1-5].

Effect of eluent

During the study of pH effect, it was found that low led to poor efficiency, which suggested to use acidic solution for elution of the target metal ions. In this work, hydrochloric acid and nitric acid were evaluated as the desorption solution. The experimental results in Table S1 indicated that 1.5 mL of 1.0 mol L^{-1} HCl was sufficient to simultaneously and quantitatively recover all the metal ions. The effect of desorption time was also evaluated by eluting target metal ions sequentially. It was found that a 10 min extraction resulted in quantitative recovery of target metal ions. Therefore, 1.5 mL of 1.0 mol L^{-1} HCl and 10 min were selected as the best eluent condition.

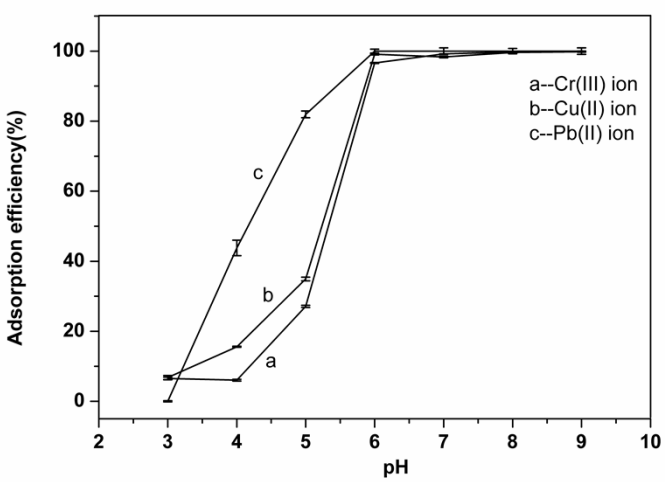

Figure S1. Effect of pH on the adsorption efficiency of heavy metal ions. Condition : initial concentration: 10 mL 1.0 mg L^{-1}, amount of adsorbent: 10 mg, extraction time : 20 min

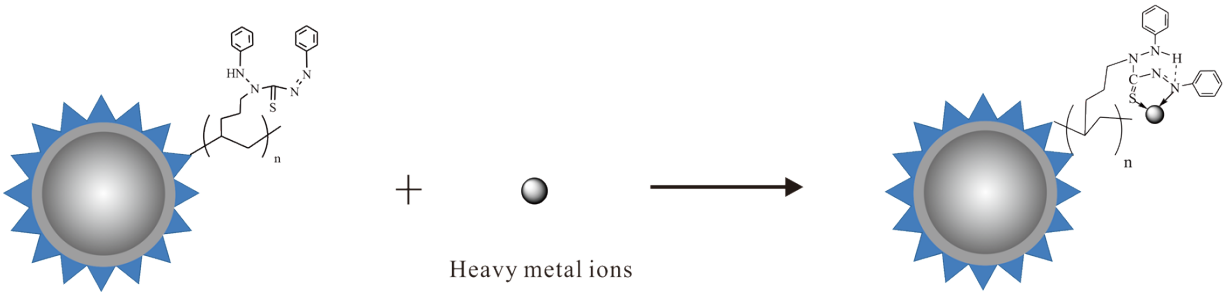

Figure S2. Adsorption mechanism of the heavy metal ions

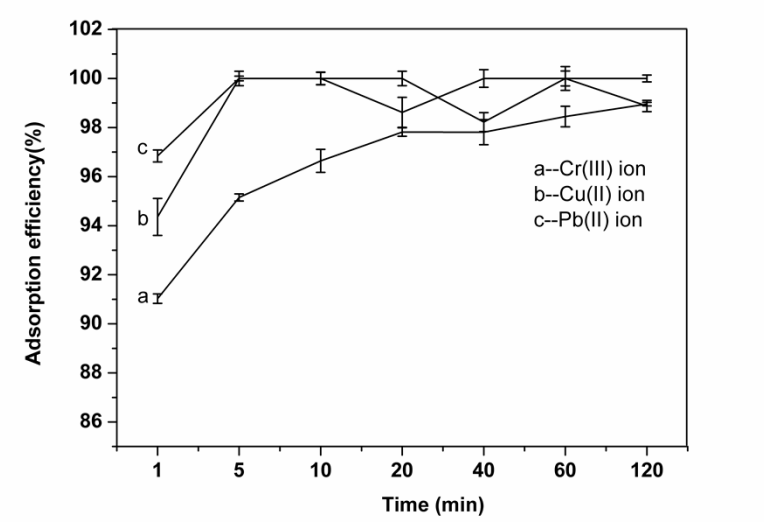

Figure S3. Absorbent amount effect on the adsorption efficiency of heavy metal ions. Condition: initial concentration: 10 mL 1.0 mg L^{-1}, pH=6, extraction time: 20 min

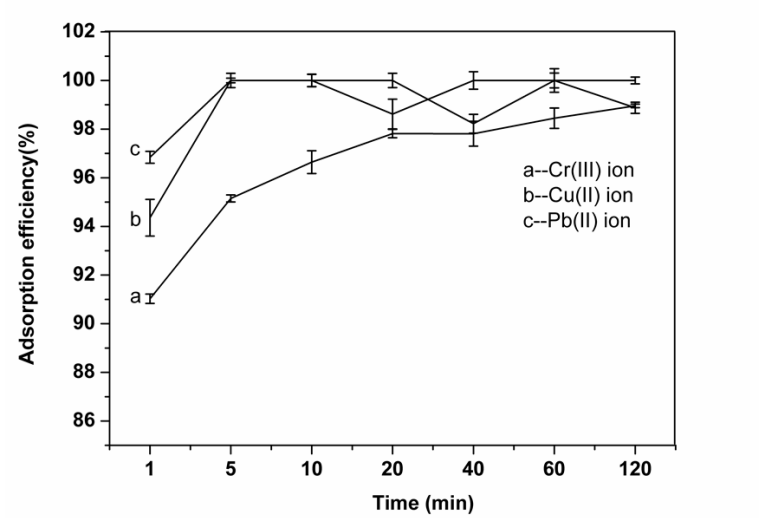

Figure S4. Adsorption time effect on the adsorption efficiency of heavy metal ions. Condition: initial concentration: 10 mL 1.0 mg L^{-1}, pH=6, amount of adsorbent: 10 mg

Table S1. The Recovery of heavy metal ions with eluent condition

	1.0 mL 0.1mol L^{-1} HNO_3	1.0 mL 0.1mol L^{-1} HCl	1.0 mL 1.0 mol L^{-1} HCl	1.5 mL 1.0 mol L^{-1} HCl
Cr	71.7%	82.2%	87.6%	99.1%
Cu	85.7%	84.0%	84.7%	98.4%
Pb	85.9%	85.9%	85.9%	94.3%

Table S2. Comparison between this method and literatures

[a]Dithizone nanoporous fructose

[b]Maximum adsorption capacity

Adsorbent	Detector	Detection limit (μg L^{-1})			MAC[b](mg g^{-1})			Ref	Separation mode
		Cr	Cu	Pb	Cr	Cu	Pb		
Bismuthiol-II-immobilized magnetic nanoparticles	ICP-OES	0.043	0.058	0.085	8.6	5.3	9.4	1	Magnetic separation
Dithizone-np-F[a]	FAAS	-	0.15	1.2	-	81	178	2	SPE column
Dithizone modified magnetic nanoparticles	ICP-OES	0.035	0.011	0.062	20.7	20.5	60.9	3	Magnetic separation
DHMP-activated carbon	FAAS	-	2.9	8.4	-	0.63	0.45	4	SPE column
XAD-2 functionalized with o-aminophenol	FAAS	-	4.0	25.0	-	3.37	3.32	5	SPE column
Dithizone grafted poly(allyl chloride) magnetic microspheres	ICP-OES	0.029	0.079	0.87	62.1	62.2	66.9	This work	Magnetic separation

[1] J. S. Suleiman, B. Hu, H. Y. Peng, C. Z. Huang, *Talanta*, 2009, **77**, 1579-1583.

[2] M. Behbahani, M. Najafi, M. M. Amini, O. Sadeghi, A. Bagheri, M. Salarian, *Microchim Acta*, 2013, **180**, 911-920.

[3] G. H. Cheng, M. He, H. Y. Peng, B. Hu, *Talanta*, 2012, **88**, 507-515.

[4] M. Ghaedi, F. Ahmadi, A. Shokrollahi, *J. Hazard. Mater.*, 2007, **142**, 272-278.

[5] M. K umar, D. P. S. Rathore, A. K. Singh, *Talanta*, 2000, **51**, 1187-1196.

Table S3. The adsorption efficiencies for four cyclic enrichments

	Number 1	Number 2	Number 3	Number 4
Cr	96.7%	96.6%	95.2%	99.3%
Cu	95.1%	99.1%	98.2%	99.5%
Pb	98.7%	100%	100%	97.4%