



Chemically modified activated carbon with 1-acylthiosemicarbazide for selective solid-phase extraction and preconcentration of trace Cu(II), Hg(II) and Pb(II) from water samples

Ru Gao, Zheng Hu, Xijun Chang*, Qun He, Lijun Zhang, Zhifeng Tu, Jianping Shi

Department of Chemistry, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:

Received 12 May 2009

Received in revised form 2 July 2009

Accepted 3 July 2009

Available online 10 July 2009

Keywords:

1-Acylthiosemicarbazide-modified

activated carbon

Solid-phase extraction

Metal ions

ICP-OES

ABSTRACT

A new sorbent 1-acylthiosemicarbazide-modified activated carbon (AC-ATSC) was prepared as a solid-phase extractant and applied for removing of trace Cu(II), Hg(II) and Pb(II) prior to their determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The separation/preconcentration conditions of analytes were investigated, including effects of pH, the shaking time, the sample flow rate and volume, the elution condition and the interfering ions. At pH 3, the maximum static adsorption capacity of Cu(II), Hg(II) and Pb(II) onto the AC-ATSC were 78.20, 67.80 and 48.56 mg g⁻¹, respectively. The adsorbed metal ions were quantitatively eluted by 3.0 mL of 2% CS(NH₂)₂ and 2.0 mol L⁻¹ HCl solution. Common coexisting ions did not interfere with the separation. According to the definition of IUPAC, the detection limits (3σ) of this method for Cu(II), Hg(II) and Pb(II) were 0.20, 0.12 and 0.45 ng mL⁻¹, respectively. The relative standard deviation under optimum conditions is less than 4.0% (n=8). The prepared sorbent was applied for the preconcentration of trace Cu(II), Hg(II) and Pb(II) in certified and water samples with satisfactory results.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, water pollution caused by heavy metals is one of the major economic and environmental problems all over the world. Among heavy metal ions, Cu(II), Hg(II) and Pb(II) are considered to be non-biodegradable like organic pollutants in water, and attracted more attention due to their toxicity, persistent in nature particularly, even at low concentrations [1–3]. Therefore, preconcentration and selective separation of trace Cu(II), Hg(II) and Pb(II) from natural water are very essential and need further study.

The traditional separation/preconcentration methods for removing heavy metals include liquid–liquid extraction [4], ion-exchange [5] and chemical precipitation [6], etc., but these methods are usually time consuming and require relatively large volumes of high purity solvents. Recently solid-phase extraction (SPE) has been widely used for preconcentration of heavy metals due to advantages such as, high enrichment factor, high recovery, rapid phase separation, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [7,8]. The quest for new adsorbents is an important factor in improving analytical parameters such as selectivity, affinity and capacity in SPE techniques [9,10]. An

efficient solid-phase extractant should consist of a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with heavy metal ions. To date, many adsorbents, such as silica gel [11], chelating resins [12], modified ZrO₂ [13], and fullerene [14], have been employed in SPE.

Activated carbon is one of the most extensive adsorbents of the removal of metal ions from aqueous solution due to its large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards [15–17]. However, without any surface treatment, activated carbon does not adsorb metal ions quantitatively at trace and ultratrace levels [18], which prompts us to study the possibility of modifying traditional activated carbons with organics or inorganics to increase their adsorption capacity with respect to metal ions. Activated carbon functionalized with pyrocatechol violet [19], ammonium pyrrolidine dithiocarbamate [20] and 5,5-diphenylimidazolidine-2,4-dione (phenytoin) [21], etc. has been reported as a chelating collector for metal ions, i.e. Cu(II), Co(II), Cd(II), Mn(II), Ni(II) and Pb(II). The modified activated carbon exhibits sorption capacities higher than untreated activated carbon.

It has been observed that weakly acidic functional groups are present in the surface of some activated carbons, obtained by different oxidation procedures [22–25], and found the number of micropores and the surface areas of oxidized activated carbon remarkably enhance [23]. In previous studies [26], the existence of protonable complexing groups in the surface of carbon, such

* Corresponding author. Tel.: +86 931 8912422; fax: +86 931 8912582.
E-mail address: gaoru07@lzu.cn (X. Chang).

as carboxylic, lactonic and phenolic groups has been extensively studied.

In this work, the new extractant was prepared by immobilizing 1-acylthiosemicarbazide (ATSC) chemically on the surface of activated carbon, which has been oxidized advance by nitric acid. The adsorption behavior of analytes on the ATSC modified activated carbon (AC-ATSC) and the experimental conditions for the preconcentration process were investigated in detail. The result showed that the new sorbent has a high adsorption capacity for the solid-phase extraction of Cu(II), Hg(II) and Pb(II) presented in the water samples. Parameters that affect the sorption and elution efficiency of the metal ions were also studied. Then, the method was applied to preconcentrate trace metal ions from natural water samples with satisfactory results.

2. Experimental

2.1. Instruments and apparatus

An IRIS Advantage ER/S inductively coupled plasma optical emission spectrometer (Thermo Jarrel Ash, Franklin, MA, USA) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected were as follows: Cu 324.754, Hg 194.227 and Pb 216.999 nm. A pH-10C digital pH meter (Xiaoshan Instrument Factory, Xiaoshan, ZJ, China) was used for the pH adjustments. An electrothermal atomic absorption spectrometry (ET-AAS) (WFX-1D, China) was used.

Fourier Transform Infrared (FT-IR) spectra ($4000\text{--}200\text{ cm}^{-1}$) in KBr were recorded on a Nicoletb NEXUS 670 FT-IR spectrometer (Nicolet Madison, WI, USA). An YL-110 peristaltic pump (General Research Institute for Non-ferrous Metals Beijing, China) was used in preconcentration process. A self-made glass microcolumn ($50\text{ mm} \times 2.5\text{ mm i.d.}$) was used in this study.

2.2. Chemicals and reagents

Unless otherwise stated, reagents of analytical and spectral purity were used for all experimental and doubly distilled deionized water was used throughout. Standard labware and glassware used were repeatedly cleaned with acid and rinsed with double distilled water. Activated carbon (AC), 100–200 mesh ($0.150\text{--}0.075\text{ mm}$) (Tianjin Fine Chemical Research Institute, Tianjin, China) and thiosemicarbazide (TSC) (Beijing Chemical Industry, Beijing, China) were used for the experiment. N,N'-Dicyclohexylcarbodiimide (DCC) was purchased from Sinop-harm Chemical Reagent Co. Ltd. (Shanghai, China). Standard stock solutions of Cu(II), Hg(II) and Pb(II) (1 mg mL^{-1}) were prepared by dissolving spectral pure grade chemicals $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 and $\text{Pb}(\text{NO}_3)_2$ (The First Reagent Factory, Shanghai, China) in double distilled water with the addition of hydrochloric acid (The First Reagent Factory, Shanghai).

2.3. Sample preparation

The reference materials (GBW 08301, river sediment) were obtained from the National Research Center for Certified Reference Materials (Beijing, China). The water samples were collected from Yellow River and Yantan Park (Lanzhou, China). The polyethylene bottles filled with the samples were cleaned with detergent, water, diluted nitric acid and water in sequence. The water samples were filtered through a $0.45\text{ }\mu\text{m}$ polytetrafluoroethylene (PTFE) millipore filter and acidified to a pH of about 2 with concentrated HCl prior to storage for use. Tap water samples were taken from our research laboratory (Lanzhou University, Lanzhou, China) without pretreatment before determination, the pH value was adjusted to 3 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$ prior to use.

2.4. Preparation of activated carbon modified with thiosemicarbazide

2.4.1. Oxidation process of activated carbon

Activated carbon powder was kept in 10% (v/v) hydrochloric acid solution for 24 h in order to remove adsorbed impurities. Then 10 g of purified activated carbon was immersed in 8 mol L^{-1} HNO_3 under stirring for 5 h at $60\text{ }^\circ\text{C}$ to increase the oxygen functional groups on the surface and improve the uptake process, the mixture was filtered and rinsed with deionized water until to neutral and dried under vacuum at $80\text{ }^\circ\text{C}$ for 8 h. The product was carboxylic derivative of activated carbon (AC-COOH). The numbers of oxygenated surface groups determined by the Boehm titration method [27,28] were summarized as follows: carboxylic 1.17 mmol g^{-1} , lactonic 0.75 mmol g^{-1} , phenolic 0.68 mmol g^{-1} at pH 4.3.

2.4.2. Synthesis of activated carbon modified with thiosemicarbazide (AT-ATSC)

Amount of 5.0 g dried oxidized activated carbon, 3 g of DCC and 2 g of TSC, 100 mL of dimethylformamide (DMF) were added in a flask in sequence, stirred at room temperature for 24 h. The resulting solid phase was filtered, washed with ethanol and water, and then dried at $80\text{ }^\circ\text{C}$ for 8 h.

2.4.3. FT-IR characterization

FT-IR spectra were taken by using KBr to observe the functional groups of AC and AC-ATSC and the spectra were shown in Fig. 1.

According to the literature [24], the FT-IR transmittance spectra bands of HNO_3 -oxidized activated carbon can differentiate into three ranges of spectra: $4000\text{--}2000$ (dehydration and aliphatic units), $2000\text{--}1300$ (oxygen function groups) and $1300\text{--}800\text{ cm}^{-1}$ (various C–O single bond). For the HNO_3 -oxidized activated carbon, the characteristic vibration of unionized and uncoordinated carboxyl is shown as a strong peak of COO^- , stretching at 1705.97 cm^{-1} and a shoulder of OH deformation vibration at 1457.93 cm^{-1} , it is presented the carboxylic derivative of activated carbon was prepared successfully. Compared with that of HNO_3 -oxidized activated carbon, the IR of AC-ATSC showed remarkable spectral changes, notably $1820\text{--}1300\text{ cm}^{-1}$. The new peaks around 1695.50 cm^{-1} were assigned to C=O vibrations, the new bands at 1445.37 cm^{-1} was related to the stretching vibration of C–N, the band appeared at 1099.57 and 894.14 cm^{-1} were assigned to the vibration of C=S [29].

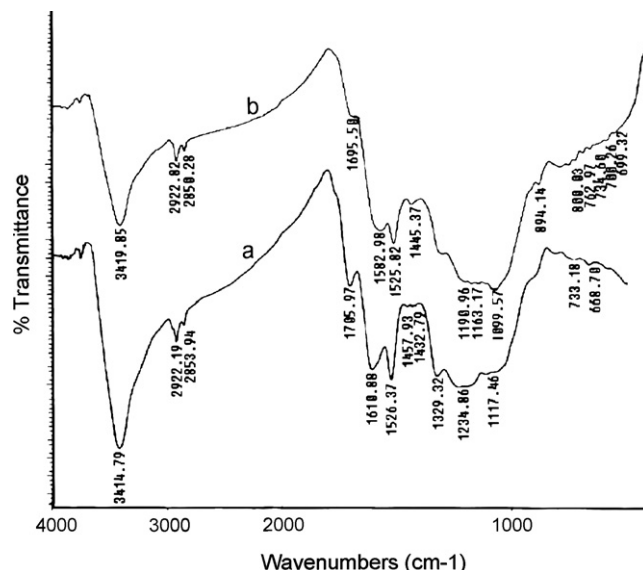


Fig. 1. IR spectra of AC (a) and AC-ATSC (b).

2.5. General procedures

2.5.1. Batch method

A series of standards or sample solutions containing Cu(II), Hg(II) and Pb(II) were transferred into a 10 mL beaker, and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$. Then the volume was adjusted to 10 mL with double distilled water, 50 mg of AC-ATSC was added, and the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ions onto the sorbents. After centrifugation, the concentrations of the desorbed metal ions in the elution were directly measured by ICP-OES.

2.5.2. Column procedure

A total of 50 mg of functionalized AC-ATSC was packed in the PTFE column plugged with a small portion of glass wool at both ends. Before using, 2.0 mol L^{-1} HCl and doubly distilled deionized water were successively passed through the microcolumn in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Cu(II), Hg(II) and Pb(II) were prepared, and the pH value was adjusted to the desired pH value with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} $\text{NH}_3 \cdot \text{H}_2\text{O}$. Each solution was passed through the column at a flow rate of 3.0 mL min^{-1} controlled by a peristaltic pump. Afterwards, the metal ions retained on column were eluted with 2% $\text{CS}(\text{NH}_2)_2$ and 2.0 mol L^{-1} HCl solution. The analytes in the elution were determined by ICP-OES.

3. Results and discussion

3.1. Effect of solution pH

Solution acidity effects the metal ions adsorption: proton in acid solution can protonate binding sites of the chelating molecules, and hydroxide in basic solution may complex and precipitate many metals [30]. In order to evaluate the effect of pH, several metal ions, viz, Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) were tested and determined in different pH value (pH 1–7). Aliquots of 10 mL of the solutions were tested by equilibrating 50 mg sorbents. It could be seen in Fig. 2 that the adsorption percentage increases with the increase of pH and the metal recoveries ($\geq 95\%$) were reached for simultaneous preconcentration of Cu(II), Hg(II) and Pb(II) at $\text{pH} \geq 3$. To avoid hydrolyzing at higher pH and determine these elements simultaneously, pH 3 was selected as the enrichment acidity for further study.

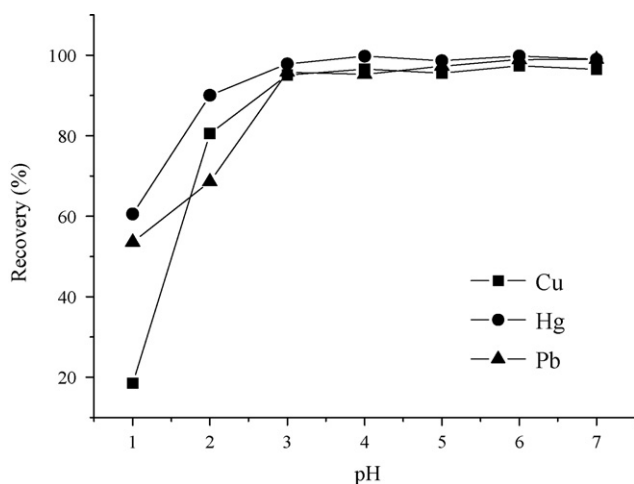


Fig. 2. Effect of pH on adsorption of $1.0 \mu\text{g mL}^{-1}$ Cu(II), Hg(II) and Pb(II); AC-ATSC 50 mg; shaking time 30 min; temperature 25°C .

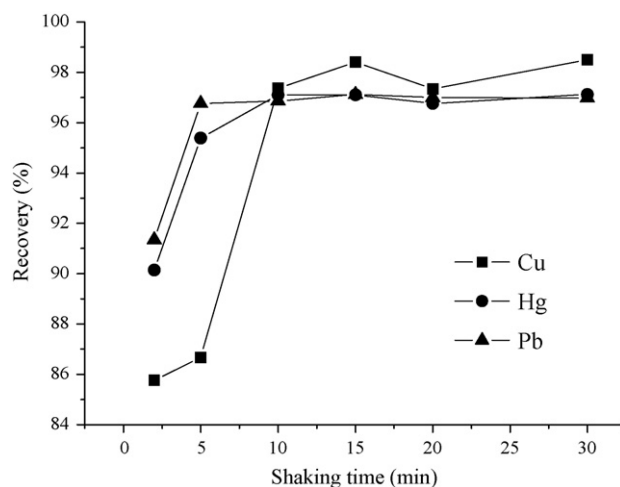


Fig. 3. Effect of shaking time on adsorption of $1.0 \mu\text{g mL}^{-1}$ Cu(II), Hg(II) and Pb(II); AC-ATSC 50 mg; volume 10 mL; pH 3; temperature 25°C .

In addition, Zn(II) and Mn(II) were not adsorbed by AC-ATSC at pH 3, Co(II), Ni(II) and Cd(II) could be adsorbed about 20–30% at pH 3, Cr(III) and Fe(III) could be adsorbed about 50–60% at pH 3, but they do not interfere with enrichment and determination of Cu(II), Hg(II) and Pb(II).

3.2. Effect of shaking time

The effect of shaking time on the percentage extraction of metal ions is considered to be of significant importance to determine the possible discrimination order in the behavior of the new synthesized phases towards the different metal ions. In this work, different shaking time (range from 2 to 30 min) was studied for the percentage extraction of Cu(II), Hg(II) and Pb(II) by AC-ATSC. The result listed in Fig. 3 showed that the 95% uptake of Cu(II), Hg(II) and Pb(II) were achieved within 10 min. It also indicated that AC-ATSC had rapid adsorption kinetics for Cu(II), Hg(II) and Pb(II).

3.3. Effect of flow rate and maximum sample volume

In a SPE system, the flow rate of Cu(II), Hg(II) and Pb(II) solutions through the packed bed column is a very important parameter for controlling the time of adsorption and analysis. Using the column procedure, its effect was studied at the optimum conditions by passing 20 mL of sample solution through the microcolumn with a peristaltic pump. The flow rate was adjusted in range of $0.5\text{--}6.0 \text{ mL min}^{-1}$. The results are presented in Fig. 4. It was found that the retention of the studied ions was practically not changed up to 3.0 mL min^{-1} flow rate. However, the recoveries of the analytes were less than 95% at a flow rate greater than 3.0 mL min^{-1} , as target metal ions could not equilibrate properly with the sorbent beds. So, the flow rate was maintained at 3.0 mL min^{-1} throughout the column experiment.

To determine the maximum volume, 50, 100, 200, 300, 400 and 500 mL of sample solutions containing $1.0 \mu\text{g}$ Cu(II), Hg(II) and Pb(II) were passed through the column with 50 mg sorbent at optimum flow rate. Quantitative recovery ($\geq 95\%$) was obtained for the sample volume of 300 mL for the Cu(II), Hg(II) and Pb(II) and at greater volume percent of recovery decreased. Thus, 300 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. A high enrichment factor of 100 was obtained because 3 mL eluent was used in these experiments.

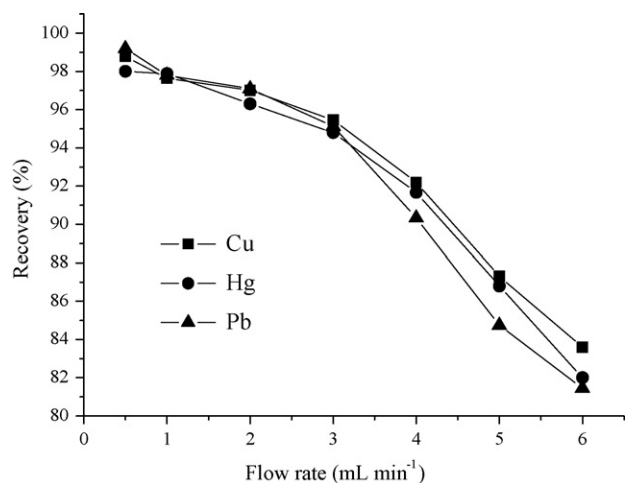


Fig. 4. Effect of flow rate on adsorption of Cu(II), Hg(II) and Pb(II); sample volume 20 mL; pH 3; temperature 25 °C.

3.4. Effect of elution condition on recovery

Since the adsorption of cations at pH < 1 was negligible, one can expect that elution will be favoured in acidic solution. So various concentrations and volumes of thiourea and HCl solution were used for the desorption of retained Cu(II), Hg(II) and Pb(II). The obtained results showed (Table 1) that 3.0 mL of 2% (w/w) CS(NH₂)₂ and 2.0 mol L⁻¹ HCl solution was sufficient for complete elution. When the flow rate for desorption of Cu(II), Hg(II) and Pb(II) was varied from 0.5 to 4.0 mL min⁻¹. The results showed that target ions can be quantitatively eluted at flow rate below 1.0 mL min⁻¹, and 3.0 mL of 2% CS(NH₂)₂ and 2.0 mol L⁻¹ HCl solution was used as eluent in the following experiments.

3.5. Effects of interfering ions

To verify the possibility of analytical applications for the proposed method, the effects of some interfering ions, which interfere with the determination of Cu(II), Hg(II) and Pb(II) and often accompany with them in various real samples, were examined under the optimized conditions. For this purpose, solutions of 1.0 µg mL⁻¹ of Cu(II), Hg(II) and Pb(II) containing the added interfering ions were prepared according to the batch procedure. The recovery data of Cu(II), Hg(II) and Pb(II) were given in Table 2. It is clear that in excess of 1000 µg mL⁻¹ of K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, 400 µg mL⁻¹ of SO₄²⁻, HPO₄²⁻, and 100 µg mL⁻¹ of Zn(II), Cd(II), Mn(II), Ni(II), Co(II), these ions did not significant interfere with the determination of the analytes. The recoveries of Cu(II), Hg(II) and Pb(II) were not less than those in the absence of coexisting ions, indicating that AC-ATSC had a high selectivity towards Cu(II), Hg(II) and Pb(II) and present a potential to apply to analyze real samples.

Table 1
Elution recovery (%) for Cu(II), Hg(II) and Pb(II) adsorbed on AC-ATSC sorbent.

Eluent ^{a,b}	Recovery (%)		
	Cu(II)	Hg(II)	Pb(II)
1.0 M HCl	80.3	50.7	82.1
2.0 M HCl	95.5	70.6	96.1
3.0 M HCl	96.4	75.0	96.3
4.0 M HCl	97.6	78.5	97.0
6.0 M HCl	97.4	80.7	97.8
2.0 M HCl + 1% CS(NH ₂) ₂	96.7	90.3	95.4
2.0 M HCl + 2% CS(NH ₂) ₂	97.6	96.2	99.8

^a Eluent volume 3 mL.

^b Eluent flow rate 1.0 mL min⁻¹.

Table 2

Effect of coexisting ions on percent recovery of 1.0 µg mL⁻¹ Cu(II), Hg(II) and Pb(II) adsorbed on AC-ATSC.

Coexisting ion	Concentration (µg mL ⁻¹)	Recovery of analytes (%)		
		Cu(II)	Hg(II)	Pb(II)
K ⁺	1000	95.4	96.7	96.6
Na ⁺	1000	99.6	100.0	98.8
Ca ²⁺	1000	95.9	95.2	99.8
Mg ²⁺	1000	97.5	96.3	97.2
Cl ⁻	1000	98.6	95.7	96.8
Zn ²⁺	100	99.6	100.1	99.1
Cd ²⁺	100	98.4	97.5	99.3
Mn ²⁺	100	98.2	100.5	98.6
Ni ²⁺	100	97.6	98.2	97.7
Co ²⁺	100	96.9	95.6	99.2
SO ₄ ²⁻	400	95.5	97.3	101.3
HPO ₄ ²⁻	400	96.3	95.8	98.5

3.6. Adsorption capacities

The capacity of the adsorbent is an important factor to determine how much sorbent is required to quantitatively adsorb a specific amount of metal ion from solution [31]. The adsorption capacity was tested following the batch procedure. A series of 10 mL of Cu(II), Hg(II) and Pb(II) ions solutions (10–300 µg mL⁻¹) were adjusted to the appropriate pH 3. The proposed separation and preconcentration

Table 3

Analysis results for the determination of Cu(II), Hg(II) and Pb(II) in certified reference material (GBW08301, river sediment) and water samples.

Ion	Found ^a (µg g ⁻¹)	Certified (µg g ⁻¹)
GBW 08301		
Cu	51.0 ± 0.8	52.0 ± 0.4
Hg	0.2 ± 0.1	0.2 ± 0.1
Pb	78.0 ± 3.4	79.0 ± 6.0
Lake water		
Cu	3.4 ± 0.2	3.4 ± 0.1
Hg	0.2 ± 0.03	0.2 ± 0.02
Pb	5.7 ± 0.5	5.8 ± 0.3

^a The value following "±" is the standard deviation (n = 3).

Table 4

Analytical results for the determination of trace Cu(II), Hg(II) and Pb(II) in natural water samples.

Ion	Added (µg L ⁻¹)	Found ^a (µg L ⁻¹) Concentration	Recovery (%)	R.S.D.(%)
Yellow river water				
Cu	0	4.52 ± 0.3		
	5	9.60 ± 0.08	101.6	3.6
	10	14.46 ± 0.14	99.4	1.6
Hg	0	0.67 ± 0.11		
	5	5.70 ± 0.22	100.6	1.4
	10	10.67 ± 0.23	100.0	1.0
Pb	0	3.65 ± 0.18		
	5	8.64 ± 0.09	99.8	3.4
	10	13.66 ± 0.12	100.1	2.6
Tap water				
Cu	0	0.87 ± 0.20		
	5	5.75 ± 0.10	97.6	3.4
	10	10.61 ± 0.18	97.4	1.8
Hg	0			
	5	4.88 ± 0.15	97.6	1.6
	10	9.94 ± 0.32	99.4	1.3
Pb	0	1.58 ± 0.11		
	5	6.59 ± 0.21	100.1	4.2
	10	11.36 ± 0.10	97.8	2.7

^a The value following "±" is the standard deviation (n = 3).

Table 5

Figures of merit of comparable methods for determination of Cu(II), Hg and Pb(II) by solid-phase extraction.

Methods/reagent(s) used	Analyte	pH	Capacity (mg g ⁻¹)	LOD (ng mL ⁻¹)	Ref.
High surface area ZrO ₂	Cu	7.5–8.0	<5.0	0.033	[13]
	Pb	7.5–8.0	<5.0	0.02	
Bicarbonate-treated peanut hull carbon	Hg	3.5–10	12.38	–	[32]
	Pb	4	26.7	0.65	[33]
Activated carbon/zincon	Cu	4	13.2	0.045	[34]
	Pb	5	17.5	0.027	
EDA-incorporated microbeads	Cu	5	12.8	–	[35]
	Hg	5	38.5	–	
	Pb	5	30.2	–	
Silica gel/8-hydroxyquinoline	Cu	4.0–7.0	28.6	0.86	[36]
	Pb	4.5–7.0	32.7	0.92	
Activated carbon/1-acylthiosemicarbazide	Cu	3	78.2	0.20	Present work
	Hg	3	68.7	0.12	
	Pb	3	48.6	0.45	

LOD: limit of detection.

tration procedures (Static method) described above were applied. A breakthrough curve was gained by plotting the concentration ($\mu\text{g mL}^{-1}$) vs. the micrograms of Cu(II), Hg(II) and Pb(II) adsorbed per gram of AC-ATSC. The sorption capacities of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the ligand immobilized onto matrix. From the experiment data, it was found that the maximum adsorption capacity of AC-ATSC for Cu(II), Hg(II) and Pb(II) up to 78.20, 67.80 and 48.56 mg g⁻¹, respectively. The results showed this is satisfactory for the trace analysis of Cu(II), Hg(II) and Pb(II).

3.7. Analytical precision and detection limits

Under the selected conditions, eight portions of standard solutions were treated and analyzed simultaneously following the column procedure. The relative standard deviations (R.S.D.) of the method was found to be lower 4% (Cu(II) 3.5%, Hg(II) 1.9%, Pb(II) 3.7%), indicating that the method present good precision for the analysis of trace Cu(II), Hg(II) and Pb(II) in solution samples. The detection limit (3σ), defined by IUPAC, was found to be 0.20, 0.12 and 0.45 ng mL⁻¹ for Cu(II), Hg(II) and Pb(II), respectively. The linear range of the method was from 1.85 to 100 ng mL⁻¹ with the correlation coefficient better than 0.999.

3.8. Application of the method

In order to ascertain the accuracy of the proposed procedure, the method has been applied to the determination of trace Cu(II), Hg(II) and Pb(II) in certified reference material (GBW 08301, River Sediment), Yellow River water, lake water and tap water samples. The results were listed in Tables 3 and 4, respectively. Good agreement was obtained between the estimated content by the proposed method and certified values. The analytical results for lake water were in agreement with the electrothermal atomic absorption spectrometry (ET-AAS). For the analysis of Yellow River water and tap water samples, the standard addition method was used. The recoveries of Cu(II), Hg(II) and Pb(II) were in range of 97–101%. Evidently, the obtained results indicated the method is reliable, feasible and satisfactory to analyze water samples.

3.9. Comparison with other methods

Comparative information from some studies on preconcentration of Cu(II), Hg(II) and Pb(II) by various methods for the figure of merits is given in Table 5. As seen from the data in Table 5, the proposed method developed AC-ATSC had a relatively high acidity,

capacity and a low LOD compared to other methods reported in Table 5.

4. Conclusions

In this study, the proposed selective and sensitive method for the determination of trace levels of Cu(II), Hg(II) and Pb(II) was developed by using thiosemicarbazide-modified activated carbon as a solid-phase extractant. The synthesized of AC-ATSC was relatively simple and convenient. The adsorbents showed good characteristics of adsorption and desorption for Cu(II), Hg(II) and Pb(II) in aqueous solution. The results presented the new sorbent has excellent selectivity, short contact time, easy elution and high adsorption capacity. In addition, most of common coexisting anions and cations did not interfere with study ions under the optimum conditions. The credible method was applied to the analysis of trace Cu(II), Hg(II) and Pb(II) in real samples with satisfactory results.

References

- [1] N. Chiron, R. Guilet, E. Deydier, Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherms and kinetic models, *Water Res.* 37 (2003) 3079–3086.
- [2] M. Zabihi, A. Ahmadpour, A. Haghghi Asl, Removal of mercury from water by carbonaceous sorbents derived from walnut shell, *J. Hazard. Mater.*, doi:10.1016/j.jhazmat.2008.12.108.
- [3] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, *J. Colloid Interface Sci.* 333 (2009) 14–26.
- [4] A. Nasu, S. Yamaguchi, T. Sekine, Solvent extraction of copper(I) and (II) as thiocyanate complexes with tetrabutylammonium ions into chloroform and with trioctylphosphine oxide into hexane, *Anal. Sci.* 13 (1997) 903–911.
- [5] G.H. Tao, Z. Fang, Dual stage preconcentration system for flame atomic absorption spectrometry using flow injection on-line ion-exchange followed by solvent extraction, *J. Anal. Chem.* 360 (1998) 156–160.
- [6] M. Soyulak, N.D. Erdogan, Copper(II)-rubeanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* 137 (2006) 1035–1041.
- [7] K. Pyrzynska, Functionalized cellulose sorbents for on-line preconcentration of trace metals for environmental analysis, *Crit. Rev. Anal. Chem.* 29 (1999) 313–321.
- [8] S.A. Ahmed, Alumina physically loaded by thiosemicarbazide for selective preconcentration of mercury(II) ion from natural water samples, *J. Hazard. Mater.* 156 (2008) 521–529.
- [9] C.F. Poole, New trends in solid-phase extraction, *Trends Anal. Chem.* 22 (2003) 362–373.
- [10] J.R. Dean, *Extraction Methods for Environmental Analysis*, Wiley, New York, 1998.
- [11] C.Z. Huang, B. Hu, Silica-coated magnetic nanoparticles modified with γ -mercaptopropyltrimethoxysilane for fast and selective solid phase extraction of trace amounts of Cd, Cu, Hg and Pb in environmental and biological samples prior to their determination by inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 63 (2008) 437–444.

- [12] M. Kumar, D.P.S. Rathore, A.K. Singh, Pyrogallol immobilized amberlite XAD-2: a newly designed collector for enrichment of metal ions prior to their determination by flame atomic absorption spectrometry, *Microchim. Acta* 137 (2001) 127–134.
- [13] E. Vassileva, N. Furuta, Application of high-surface-area ZrO_2 in preconcentration and determination of 18 elements by on-line flow injection with inductively coupled plasma atomic emission spectrometry, *Fresenius J. Anal. Chem.* 370 (2001) 52–59.
- [14] J. Muñoz, J.R. Baena, M. Gallego, M. Valcárcel, Development of a method for the determination of inorganic cadmium and cadmium metallothioneins in fish liver by continuous preconcentration on fullerene and flame atomic absorption spectrometry, *J. Anal. At. Spectrom.* 17 (2002) 716–720.
- [15] A. Seco, P. Marzal, C. Gabaidon, J. Ferrer, Adsorption of heavy metals from aqueous solution on to activated carbon in single Cu and Ni system and in binary Cu–Ni, Cu–Cd and Cu–Zn system, *J. Chem. Technol. Biotechnol.* 68 (1997) 23–30.
- [16] M. Sanchez-polo, J. Rivera-utrilla, Adsorbent-Adsorbate Interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons, *Environ. Sci. Technol.* 36 (2002) 3850–3854.
- [17] R. Qadeer, J. Hanif, M. Saleem, M. Afzal, Adsorption of samarium on activated charcoal from aqueous solution, *J. Chem. Soc. Pak.* 14 (2) (1992) 91–96.
- [18] A.M. Starvin, T. Prasada Rao, Solid phase extractive preconcentration of uranium(VI) onto diarylazobisphenol modified activated carbon, *Talanta* 63 (2004) 225–232.
- [19] I. Narin, M. Soyak, L. Elci, M. Dogan, Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column, *Talanta* 52 (2000) 1041–1046.
- [20] M. Soyak, L. Elci, M. Dogan, Determination of certain trace metal impurities in refined and unrefined salts after preconcentration over activated carbon, *Fresenius Environ. Bull.* 5 (1996) 148–155.
- [21] M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerzohori, A. Khanmohammadi, M. Soyak, Three modified activated carbons by different ligands for the solid phase extraction of copper and lead, *J. Hazard. Mater.* 152 (2008) 1248–1255.
- [22] T. Gan, K.B. Wu, Sorption of Pb(II) using hydrogen peroxide functionalized activated carbon, *Colloids Surf. A: Physicochem. Eng. Aspects* 330 (2008) 91–95.
- [23] H. Teng, T.-S. Yeh, L.-Y. Hsu, Preparation of activated carbon from bituminous coal with phosphoric acid activation, *Carbon* Vol.36 (1998) 1387–1395.
- [24] H.A. Omar, H. Moloukhia, Use of activated carbon in removal of some radioisotopes from their waste solutions, *J. Hazard. Mater.* 157 (2008) 242–246.
- [25] D.J. Malik, V. Strelko Jr., M. Streat, A.M. Puziy, Characterisation of novel modified active carbons and marine algal biomass for the selective adsorption of lead, *Water Res.* 36 (2002) 1527–1538.
- [26] V.L. Snoeyink, W.J. Weber Jr., The surface chemistry of active carbon; a discussion of structure and surface functional groups, *Environ. Sci. Technol.* 1 (1967) 228–234.
- [27] H.P. Boehm, *Advances in Catalysis*, Academic Press, New York, 1966, pp. 179–274.
- [28] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, *Carbon* 32 (1994) 759–769.
- [29] W.S. Qu, Y.H. Zhai, S.M. Meng, Y.Q. Fan, Q. Zhao, Selective solid phase extraction and preconcentration of trace mercury(II) with poly-allylthiourea packed columns, *Microchim. Acta* 163 (2008) 277–282.
- [30] L.J. Zhang, X.J. Chang, Y.H. Zhai, Q. He, X.P. Huang, Z. Hu, N. Jiang, Selective solid phase extraction of trace Sc(III) from environmental samples using silica gel modified with 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl) propyl) benzamide, *Anal. Chim. Acta* 629 (2008) 84–91.
- [31] T. Madrakian, A. Afkhami, M.A. Zolfigol, M. Solgi, Separation, preconcentration and determination of silver ion from water samples using silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin, *J. Hazard. Mater.* 128 (2006) 67–72.
- [32] C. Namasivayam, K. Periasamy, Bicarbonate-treated peanut hull carbon for mercury(II) removal from aqueous solution, *Water Res.* 27 (1993) 1663–1668.
- [33] Z.H. Li, X.J. Chang, Z. Hu, X.P. Huang, X.J. Zou, Q. Wu, R. Nie, Zincon-modified activated carbon for solid-phase extraction and preconcentration of trace lead and chromium from environmental samples, *J. Hazard. Mater.* 166 (2009) 133–137.
- [34] J. Yin, Z.C. Jiang, G. Changm, B. Hu, Simultaneous on-line preconcentration and determination of trace metals in environmental samples by flow injection combined with inductively coupled plasma mass spectrometry using a nanometer-sized alumina packed micro-column, *Anal. Chim. Acta* 540 (2005) 333–339.
- [35] A. Denizli, G. Özkan, M.Y. Arica, Preparation and characterization of magnetic polymethylmethacrylate microbeads carrying ethylene diamine for removal of Cu(II), Cd(II), Pb(II), and Hg(II) from aqueous solutions, *J. Appl. Polym. Sci.* 78 (2000) 81–89.
- [36] A. Goswami, A. Singh, B. Venkataramani, 8-Hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination, *Talanta* 60 (2003) 1141–1154.