

Zincon-modified activated carbon for solid-phase extraction and preconcentration of trace lead and chromium from environmental samples

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ARTICLE INFO

Article history:

Received 27 May 2008

Received in revised form

16 September 2008

Accepted 5 November 2008

Available online 13 November 2008

Keywords:

Lead

Chromium

Modified activated carbon

Solid-phase extraction

ICP-OES

ABSTRACT

A new method that utilizes zincon-modified activated carbon (AC-ZCN) as a solid-phase extractant has been developed for simultaneous preconcentration of trace Cr(III) and Pb(II) prior to the measurement 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 4, the maximum adsorption capacity of Cr(III) and Pb(II) onto the AC-ZCN were 17.9 and 26.7 mg g⁻¹, respectively. The adsorbed metal ions were quantitatively eluted by 1 mL of 0.1 mol L⁻¹ HCl. Common coexisting ions did not interfere with the separation. According to the definition of IUPAC, the detection limits (3σ) of this method for Cr(III) and Pb(II) were 0.91 and 0.65 ng mL⁻¹, respectively. The relative standard deviation under optimum condition is less than 3.5% (n = 8). The method has been applied for the determination of Cr(III) and Pb(II) in biological materials and water samples with satisfactory results.

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1. Introduction

The interest in the determination of trace heavy metal ions, such as lead and chromium in environmental waters has increased immensely during the last few decades because of the environmental problems and public health studies. Therefore, the monitoring of chromium and lead at trace levels in different environment matrices that are directly related with human health has a high importance.

Monitoring environmental pollutants at ultra-trace level needs an effective sample preconcentration step. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [1,2].

In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor. Many sorbents have been used for preconcentration of metal ions, such as C₁₈ [3], Lewatit S 100 [4], XAD resins [5], polyurethane foam [6], microcrystalline naphthalene [7], modified silica gel [8,9], cellulose [10], nanometer titanium dioxide [11] and ion exchange resins [12]. Activated carbon is still by far the most important one in current use

in the environmental pollution control due to its large surface area, high adsorption capacity, porous structure, selective adsorption and high purity standards [13,14]. However, without any surface treatment, activated carbon presents an adsorption capacity for metal ions from fair to as low to none, due to the fact that metal ions often exist in solution either as ions or as hydrous ionic complex [15,16]. For this reason, modification and impregnation techniques have long been used to increase the surface adsorption and so as the removal capacity and to add selectivity to activated carbon.

There are several recent reports on the use of modified activated carbon for metal enrichment. Activated carbon functionalized with pyrocatechol violet [17], 1,2-cyclohexanediondioxime [18], tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) [19], tannic acid [20], bis-salicyl-aldehyde-1,3-propan-diimine (BSPDI) [21], tartrazine [22], 1,10-phenanthroline [23], dithioxamide [24], 4-propyl-2-thiouracil [25], diarylazo-bisphenol [26], ammonium pyrrolidine dithiocarbamate [27] and *N,N*-ethylenebis-(ethane sulfonamide) [28] is reported as a chelating collector for metal ions, i.e. Fe(III), Cu(II), Cr(III), Zn(II), Cd(II), Co(II), Ni(II), Pb(II), Mn(II) and U(VI). The modified activated carbon exhibits sorption capacities higher than untreated activated carbon.

In our work, activated carbon was modified by zincon (ZCN) to improve the surface properties and adsorption capacity. The new adsorbent of AC-ZCN has a high sorption capacity for the solid-phase extraction of Cr(III) and Pb(II) present in the liquid samples by ICP-OES. Parameters that can affect the adsorption and elution efficiency of the metal ions were studied in batch and column modes.

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Then, the method was validated by analyzing the standard reference material (GBW 08301, river sediment) and applied to the analysis of biological and water samples with satisfactory results.

2. Experimental

2.1. Chemicals and reagents

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to the published procedure [29].

Standard stock solutions of Cr(III) and Pb(II) (1 mg mL^{-1}) were prepared by dissolving spectral pure-grade $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ (The First Reagent Factory, Shanghai, China). Activated carbon (AC) (gas chromatographic grade, 40–60 mesh, Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) and zincon (ZCN) (The First Reagent Factory, Shanghai, China) were used in this work. The standard reference material (GBW 08301, river sediment) was provided by the National Research Center for Certified Reference Materials (Beijing, China).

2.2. Instruments and apparatus

An IRIS advantage ER/S inductively coupled plasma 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: Cr 283.563 nm, Pb 216.999 nm. A pHs-3C digital pH meter, Shanghai Lei Ci Device Works (Shanghai, China) was used for the pH adjustments. Infrared spectra ($4000\text{--}400 \text{ cm}^{-1}$) in KBr were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, Nicolet (Madison, WI, USA). A VG-PQEXCEL inductively coupled plasma mass spectrometry, (Thermo Elemental, Waltham, USA) was used for the determination. A reciprocating shaker bath SHZ-88-1, Taicang Laboratorial Equipment Factory (Jiangsu, China) was used for controlling the shaking speed. An YL-110 peristaltic pump, General Research Institute for Non-ferrous Metals, (Beijing, China) was used in the column process. A PTFE (polytetrafluoroethylene) column ($50 \text{ mm} \times 9.0 \text{ mm i.d.}$) was used.

2.3. Sample preparation

Yellow River water was collected from Yellow River, Lanzhou, China. The water samples were filtered through a $0.45 \mu\text{m}$ PTFE millipore filter (Tianjin Jinteng Instrument Factory, Tianjin, China), and acidified to a pH of about 1 with concentrated HCl prior to storage for use.

Pig liver was purchased from Binhe market, Lanzhou, China. Pig liver was dried in an oven at 80°C to constant weighed. 1.0 g pig liver sample was weighted and transferred into a digestion tube, and then 5 mL of concentrated HNO_3 was added into it. The tube was left at room temperature for one night. Then it was placed in a digester block and heated slowly until the temperature was up to 165°C . This temperature was maintained until the evolution of the brown fumes ceased. After the tube was cooled down, 1.3 mL perchloric acid was added into it. Then the temperature was raised to 210°C until evolution of white fumes began. The volume was adjusted to 100 mL with double distilled water when the tube was cooled down [30].

2.4. Preparation of ZCN coated activated carbon (AC-ZCN)

Activated carbon powder was kept in nitric acid (1:1) solution for 24 h so as to remove the metal ions and other impurities sorbed on it. Then it was filtered and rinsed with doubly distilled water until it was free from acid. It was dried in a drying furnace at 110°C .

ZCN coated activated carbon (AC-ZCN) was prepared by dissolving 0.15 g of ZCN in 200 mL of 0.005 mol L^{-1} NaOH under stirring, then 5.00 g of activated carbon was added into the mixture [24]. After 18 h, the product was recovered by filtration, washed with distilled water until the filter out was no longer alkaline. The final product was dried at 70°C overnight.

2.5. Procedures

2.5.1. Batch method

A series of standards or sample solutions containing Cr(III) and Pb(II) were transferred into a 25 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. 25 mg of AC-ZCN was added, and the mixture was shaken vigorously for 15 min to facilitate adsorption of the metal ions onto the sorbents. The concentrations of the metal ions in the solution were directly determined by ICP-OES. The sorbent was then eluted with HCl of optimum concentration and the desorbed metal ions were measured by ICP-OES.

2.5.2. Column SPE procedure

50 mg of functionalized AC-ZCN was packed in the PTFE column plugged with a small portion of glass wool at both ends. Before use, 0.5 mol L^{-1} HCl and doubly distilled deionized water were successively passed through the microcolumn in order to equilibrate, clean and neutralize it. A suitable aliquot of the sample solution containing $1.0 \mu\text{g mL}^{-1}$ of Cr(III) and Pb(II) in a volume of 50 mL was passed through the column after adjusting its pH to 4.0, at a flow rate of 2.0 mL min^{-1} controlled with a peristaltic pump. The bound metal ions were stripped off from the column with 0.1 mol L^{-1} HCl. The concentration of the metal ions in the eluate was determined by ICP-OES.

3. Results and discussion

Due to the existence of a donating nitrogen atom as well as =O (OH) group and NH group, ZCN was expected to increase both the stability and selectivity of its complex toward ions [25].

The purpose of this work is to investigate the feasibility of adsorption of Cr(III) and Pb(II) on activated carbon modified with ZCN. For obtaining maximum signal for evaluation of these ion contents, the effective parameters viz. pH of sample, amount of sorbent, elution and flow rate must be optimized.

3.1. FT-IR characterization

The modified activated carbon was confirmed by IR analysis (Fig. 1). Comparison of the IR spectrum of AC-ZCN with activated carbon, many new peaks appeared in the spectrum. According to the literature [31,32], the new peaks can be assigned as follows: the peak at 1667.05 cm^{-1} is due to C=N stretching vibration. The peak at 1602.43 cm^{-1} is caused by N=N stretching vibration. The bands around 1443.18 and 1516.34 are due to the benzene ring characteristic vibrations in zincon. The peak at 3277.95 cm^{-1} can be assigned to N-H stretching vibration and the bands around 3412.35 cm^{-1} are due to O-H stretching vibration. Consequently, the above experimental results suggest that activated carbon is successfully modified by zincon.

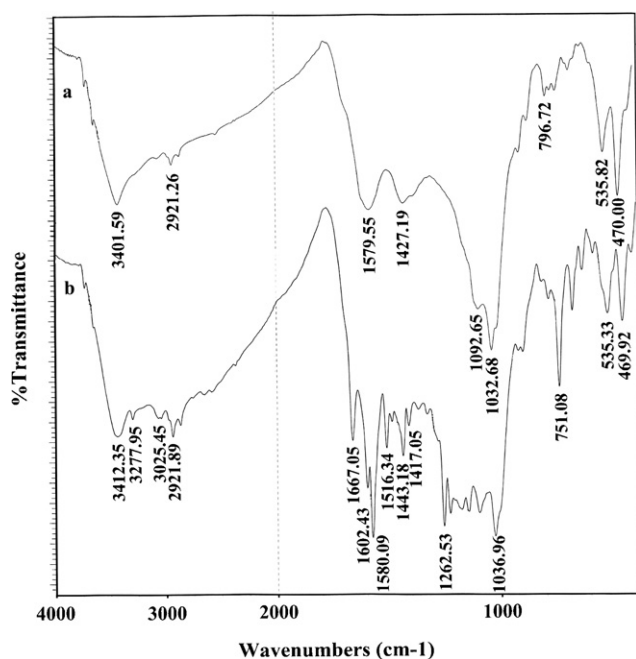


Fig. 1. IR spectra of activated carbon (a) and AC-ZCN (b).

3.2. Effect of pH

The pH value plays an important role with respect to the adsorption of different ions on oxide surfaces. In order to evaluate the effect of pH, ten 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 enriched and determined in different pH value, namely pH 1, 2, 3, 4, 5, 6 and 7. Aliquots of 10 mL of the solutions were tested by equilibrating 25 mg sorbents. The adsorption experiments were in triplicates. The results shown that the highest metal recovery values were found to be of Cr(III) and Pb(II) by AC-ZCN from pH 3–7 than any other ions. As shown in Fig. 2, in order to avoid hydrolyzing at higher pH and determine these elements simultaneously, pH 4 was selected as the enrichment acidity for further study. In addition, Co(II) and Mn(II) were not enriched by AC-ZCN at pH 4; Zn(II), Fe(III), Ni(II), Cu(II), Cd(II), and Hg(II) could be adsorbed by AC-ZCN about 60–80% at pH 4, but they do not interfere with enrichment and determination of Cr(III) and Pb(II).

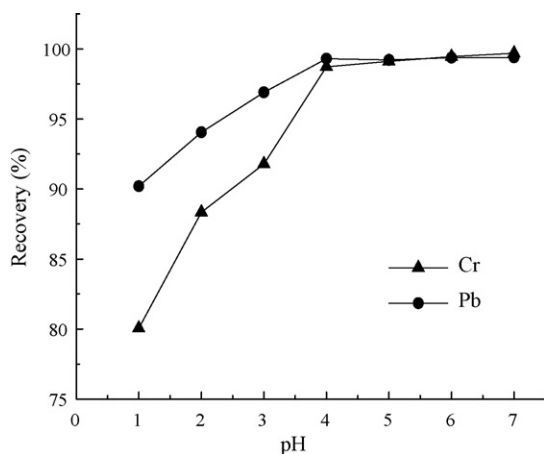


Fig. 2. Effect of pH on adsorption of $1.0 \mu\text{g mL}^{-1}$ Cr(III) and Pb(II) on AC-ZCN. Other conditions: shaking time 15 min, temperature 25°C .

3.3. Effect of the mass of sorbent

The AC-ZCN can retain all of the mentioned metal ions while the untreated activated carbon cannot quantitatively retain Cr(III) and Pb(II). Evidently, the preconcentration of the metals with the untreated activated carbon is not suitable for Cr(III) and Pb(II). Therefore, AC-ZCN seems to be a better sorbent in simultaneous sorption of Cr(III) and Pb(II). The effects of the amount of AC-ZCN on the sorption of metal ions at pH 4 were examined in the range of 5–40 mg. The results showed that quantitative recoveries were obtained in the range of 25–40 mg for Cr(III) and 15–40 mg for Pb(II). We select 25 mg of sorbent for further studies.

3.4. Effect of shaking time

The shaking time is an important factor in determining the possibility of application of AC-ZCN for the selective extraction of metal ions. In this work, different shaking time (range from 2 to 40 min) was studied for the percentage extraction of Cr(III) and Pb(II) by AC-ZCN. The results showed that it took only 5 and 2 min for Cr(III) and Pb(II) to reach maximum recovery (>90%), respectively, which indicated that kinetics of equilibrium is very fast.

3.5. Effect of flow rate

The flow rate of the sample solution affects the retention of cations on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions (pH, eluent, etc.) by passing 50 mL of sample solution through the microcolumn with a peristaltic pump. The flow rates were adjusted in the range of $0.5\text{--}3.0 \text{ mL min}^{-1}$. It was found that the retention of the studied ions was practically not changed up to 2.0 mL min^{-1} flow rate. The recoveries of the analytes decrease slightly when the flow rate is over 2.0 mL min^{-1} . Thus, a flow rate of 2.0 mL min^{-1} is employed in this work.

3.6. Elution condition, maximum sample volume and enrichment factor

The elution condition was studied by using various concentrations and volumes of HCl for the desorption of retained Cr(III) and Pb(II). The obtained results were shown in Table 1. It was found that 1.0 mL of 0.1 mol L^{-1} HCl was sufficient for complete elution for both ions. So, 1.0 mL of 0.1 mol L^{-1} HCl was used as eluent in further experiments.

In order to explore the possibility of enriching low concentrations of analytes from a large volume of solution, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 50, 100, 150, 200, 250 and 300 mL of sample solutions containing $1.0 \mu\text{g mL}^{-1}$ of Cr(III) and Pb(II) were passed through the microcolumn at the optimum flow rate. Quantitative recovery (>95%) of Cr(III) and Pb(II) was obtained for a sample volume of 150 mL and at higher volume percent of recovery decreased. Therefore, 150 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. The adsorbed metal ions could be eluted with 1.0 mL 0.1 mol L^{-1} HCl, so the enrichment factor achieved by this method was 150.

Table 1

Eluent data (%) for Cr(III) and Pb(II) adsorbed on AC-ZCN (Eluent volume 1.0 mL).

Eluent (HCl mol L^{-1})	0.01	0.05	0.1	0.5	1.0	2.0
Cr	83.98	96.85	99.13	99.35	98.64	98.07
Pb	86.06	95.49	99.21	98.78	98.22	102.17

3.7. Adsorption capacities

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 25 mg of sorbent was equilibrated with 50 mL of various concentrations of Cr(III) and Pb(II) for 1 h. In order to reach the "saturation", the initial metal ions concentrations were increased till the plateau values (adsorption capacity values) obtained. The results showed that adsorption capacity of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the adsorbent. The maximum adsorption capacity has been found to be 17.9 and 26.7 mg g⁻¹ for Cr(III) and Pb(II), respectively.

3.8. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Cr(III) and Pb(II) on AC-ZCN were investigated. In these experiments, solutions of 1.0 µg mL⁻¹ of Cr(III) and Pb(II) containing the added interfering ions were treated according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 90%. The results showed that in excess of 2000-fold K(I), Na(I), Ca(II), NH₄⁺, 50-fold Fe(III), Co(II), Cu(II), Cd(II) and 30-fold Mn(II), Ni(II), Zn(II), Hg(II) ions had no significant interferences in the determination of the analytes. This is due to the low adsorbing capacity or rates for interfering ions. It can be seen that the presence of major cations has no obvious influences on the determination of Cr(III) and Pb(II) under the selected conditions.

3.9. Analytical precision and detection limits

Under the selected conditions, eight portions of standard solutions were enriched and analyzed simultaneously following the general procedure. The detection limits (3σ) of the method defined by IUPAC were found to be 0.91 and 0.65 ng mL⁻¹ for Cr(III) and Pb(II), respectively. The relative standard deviation (RSD) of the eight replicate determinations were lower 3.5% (Cr(III): 3.5%; Pb(II): 2.9%), which indicated that the method had good precision for the analysis of trace Cr(III) and Pb(II) in solution samples.

3.10. Application of the method

The proposed method has been applied to the determination of trace Cr(III) and Pb(II) in standard material (GBW 08301, river sediment), pig liver, Yellow River water sample. The results were listed in Tables 2 and 3. The analytical results for the standard material were in good agreement with the certified values. The analytical results for pig liver were in agreement with the electrothermal atomic absorption spectrometry (ET-AAS) method. For the analysis of natural Yellow River water samples, the standard addition

Table 2

Analytical results for the determination of Cr(III) and Pb(II) in biological sample and standard reference material (GBW 08301, river sediment).

Ion	Found by the proposed method ^a (µg g ⁻¹)	Certified value (µg g ⁻¹)
Pig liver		
Cr	2.285 ± 0.11	2.310 ± 0.13
Pb	9.541 ± 0.08	9.710 ± 0.09
GBW08301		
Cr	89 ± 2.3	90 ± 8.0
Pb	80 ± 1.5	79 ± 12.0

^a The value following "±" is the standard deviation (n=5).

Table 3

Analytical results for the determination of Cr(III) and Pb(II) in Yellow River sample.

Ion	Added (µg L ⁻¹)	ICP-OES		ICP-MS	
		Found ^a (µg L ⁻¹)	Recovery (%)	Found ^a (µg L ⁻¹)	Recovery (%)
Cr	0	0.16 ± 0.09		0.19 ± 0.11	
	5	5.07 ± 0.07	98.3	5.15 ± 0.08	99.2
	10	10.13 ± 0.05	99.7	10.09 ± 0.19	99
Pb	0	4.81 ± 0.10		4.74 ± 0.06	
	5	9.80 ± 0.06	99.9	9.78 ± 0.05	100.4
	10	14.78 ± 0.03	99.8	14.60 ± 0.09	99.1

^a The value following "±" is the standard deviation (n=5).

Table 4

Comparison of capacities.

Chelating agent	Adsorbent	Analyte	Capacity (mg g ⁻¹)	Ref.
–	Activated carbon	Pb	13.05	[33]
Alpha-benzoin oxime	Diaion SP-850 resin	Cr	4.16	[34]
–	Nanometer-sized alumina	Pb	4.14	
–	Nanometer-sized alumina	Cr	13.6	[35]
–	–	Pb	17.5	
Maleic acid	XAD resin	Cr	7.25	[36]
8-Hydroxyquinoline	Silica gel	Pb	25.28	[37]
Zincon	Activated carbon	Cr	17.9	
		Pb	26.7	Present work

method was used, the recoveries of Cr(III) and Pb(II) were determined by both ICP-OES and ICP-MS. According to the results shown in Table 3, good agreement was obtained between the estimated content. These results indicated the suitability of AC-ZCN for selective solid-phase extraction and determination of trace Cr(III) and Pb(II) in environmental samples.

3.11. Comparison with other methods

Comparative information from some studies on preconcentration of Cr(III) and Pb(II) by various methods for the figure of merits is given in Table 4. As seen from the data, zincon-modified activated carbon had a relatively high capacity compared to other methods reported in Table 4.

4. Conclusions

In this study, a simple, rapid, accurate, selective and reliable method for the determination of trace levels of Cr(III) and Pb(II) was developed using ZCN coated activated carbon as a solid-phase extractant. The most important characteristic of ZCN coated activated carbon is its faster sorption and desorption for studied ions over other sorbents. ZCN coated activated carbon also had a relatively high capacity compared to other methods. In addition, the preparation of ZCN coated activated carbon is relatively simple and rapid. This new developed method has been successfully applied to analyze of trace Cr(III) and Pb(II) in biological and natural water samples. The precision and accuracy of the method are satisfied.

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