Speciation Analysis of Chromium in Water Samples With Pretreated Orange Peel Solid Phase Extraction and Determination by ICP-MS

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INTRODUCTION

The development of simple, selective, and accurate analytical methods for chromium speciation in environmental water samples is drawing growing attention due to different toxicological and biological properties greatly depending on its chemical form (1). Chromium is generally produced in industrial activities such as electroplating, corrosion control, leather tanning, and the production of paints and pigments. In the environment, chromium exists mainly in two oxidation states, Cr(III) and Cr(VI). Chromium(III) is known as an essential trace nutrient to normal carbohydrate, lipid, and protein metabolism and is not toxic at low concentrations, whereas Cr(VI) is generally more dangerous for humans due to its toxicity and carcinogenic properties (2,3).

The permissible limit of chromium in drinking water as recommended by the Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO) is less than 0.05 mg L⁻¹ (4). The determination of total chromium is not sufficient in evaluating the environmental impact. Therefore, the development of analytical methods for the determination of the redox species [Cr(III)/Cr(VI)] is more important than methods for total Cr. In general, the speciation analysis of chromium requires separation of

ABSTRACT

A novel method was investigated using chemically pretreated orange peel (POP) powder to separate and pre-concentrate Cr(III) in environmental water. In this study, the raw orange peel was pretreated with petroleum ether-NaOH and employed as selective sorbent for the separation of Cr(III) ions in the presence of Cr(VI). The influences of pH, sample flow rate, elution concentration and volume, and breakthrough volume were investigated in detail. Cr(III) was selectively adsorbed on the micro-column packed with POP in the pH range from 3.5 to 5.5, while the unretained Cr(VI) was determined directly in the effluent. The retained Cr(III) was eluted with 2.0 mL of 1.2 mol L⁻¹ HNO₃ followed by determination with ICP-MS.

Under the optimum conditions, the detection limits based on 3 σ criterion were 0.009 ng mL⁻¹ and 0.037 ng mL⁻¹ for Cr(III) and Cr(VI), respectively. The relative standard deviations (RSD) were less than 4.1% (n=11, c=2.0 ng mL⁻¹). The proposed method was successfully applied to the speciation determination of Cr(III) and Cr(VI) in water samples. The recoveries in spiked environmental water samples ranged from 98.5% to 103.8%. A reference water sample GBW(E)080642 was also analyzed and the results were in good agreement with the certified values.

the species prior to measurement using a detection system such as inductively coupled plasma mass spectrometry (ICP-MS). Often, one of the determined species is retained on the sorbent, while the other one remains in the solution.

Solid-phase extraction (SPE) has been developed for the separation and pre-concentration of analytes in environmental samples because of short extraction time, high enrichment factor, low consumption of eluent, easy automation, and the possibility of combining with different detection techniques in on-line or off-line modes (5). In an SPE procedure, the choice of appropriate adsorbent is a critical factor in obtaining high selectivity, full recovery, and a high enrichment factor. Many sorbents have been used for the separation and pre-concentration of chromium species, including chelating resin (6,7), ion imprinted polymer (8-10), ionic liquid (11), modified silica gel (12,13), and nano materials (14-16). However, most of the above-mentioned adsorbents are expensive, require chemical synthesis, and generate secondary waste. In recent years, many natural forms of agricultural byproducts have been explored as an alternative sorbent to replace the synthetic adsorbents listed above due to their environmentally benign nature, low cost, and being easily obtained. From the review of the literature, these eco-friendly biosorbents [e.g., moss (17), eggshell membrane (18-20), animal fiber (21), cellulose (22), fungal biomass (23), and β -cyclodextrin (24), etc.]

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were widely applied in the analytical field for solid-phase extraction and determination of trace metal ions.

Orange peel (OP) is widely available as a byproduct from fruit juice production. It mainly consists of cellulose, pectin (galacturonic acid), hemi-cellulose, chlorophyll pigments and lignin, and flavonoids. There are many carboxylic, hydroxyl, and amide groups in these components, which may interact with some metallic species through electrostatic attraction, ion exchange and/or the chelation mechanism (25). In previous works, orange peel has been used as biomaterial to remove heavy metals pollutants in wastewater treatments (26-29). However, without any surface treatment, orange peel may suffer from poor selectivity and adsorption capacity. For this reason, it needs to be transformed into a water-insoluble matrix, either by pretreatment or modification. To the best of our knowledge, pretreated orange peel as sorbent for solid phase extraction of chromium speciation has never been exploited for analytical purposes.

In the present work, a chemically pretreated orange peel (POP) was prepared in an attempt to improve its physico-chemical properties which exhibit high affinity for Cr(III). It can adsorb trivalent chromium very effectively, but is less effective for Cr(VI). A separation and pre-concentration system consisting of a pretreated orange peel-packed column for Cr(III) retention was developed and coupled to an inductively coupled plasma mass spectrometer (ICP-MS). The results show that POP can be used in SPE for the efficient separation and pre-concentration of trace Cr(III). The proposed method has been applied for the determination of chromium species in tap water and lake water.

EXPERIMENTAL

Instrumentation

An X Series II ICP-MS system (Thermo Elemental Corporation, USA) with a concentric nebulizer was used in this work. For the elimination of matrix effects, the samples and standards were spiked with 2.0 ng mL⁻¹ of ¹¹⁵In internal standard before measurement (30). The optimum ICP-MS operating and measurement parameters are listed in Table I.

A Nicolet AVATAR 330 Fourier transform infrared spectrometer (FT-IR) (Thermo Electron Corporation, USA) was used to identify the functional groups in the adsorbent OP and POP.

An in-house built PTFE micro-column (20 mm × 2.0 mm i.d.) was packed with modified orange peel powder in a manifold for separation/pre-concentration.

The pH values of the solutions were measured with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode.

A certified reference material (CRM) sample, GBW(E)080642

Trace Elements in Water, was purchased from the National Research Center for CRMs, Beijing, P.R. China.

De-ionized water (DW) was used throughout this work wherever required.

The laboratory glassware was cleaned by soaking in 10% nitric acid and rinsed with distilled water prior to use.

Standard Solutions and Reagents

The stock standard solution (1.0 mg mL⁻¹) of Cr(III) was purchased from the National Research Center for Certified Reference Materials, Beijing, P.R. China. Cr(VI) stock standard solution (1.0 mg mL⁻¹) was prepared by dissolving appropriate amounts of potassium dichromate (Shanghai Chemical Reagent Co., Ltd, Shanghai, P.R. China) in high purity water. The working standard solutions were prepared daily by appropriate dilutions of the corresponding stock solution with DW prior to their use. All reagents were of analytical grade unless otherwise stated.

TABLE I
ICP-MS Operating Conditions

Instrument	Thermo Elemental X Series II ICP-MS
Plasma power	1350 W
Cool argon flow rate	14.0 L min ⁻¹
Auxiliary argon flow rate	0.78 L min ⁻¹
Nebulizer argon flow rate	1.00 L min ⁻¹
Sampler/Skimmer cone	Ni
Sampling volume	1.0 L min ⁻¹
Sampling depth	7.8 mm
Sampling pattern	Quantitative
Scanning mode	Peak jumping
Measure point/peak	1
Repeated time	3
Quality resolution	0.65–0.80 amu
Isotope used	m/z: ⁵² Cr and ⁵³ Cr

Preparation of Adsorbent POP

Orange peel (OP) was obtained from a campus fruit shop. It was washed several times with DW and dried at 70 °C for 12 hours. The dried sample was crushed and sieved to 150 mesh particle size. Then 50 g of dried OP was soaked in 250 mL petroleum ether for about 12 hours to remove chlorophyll pigments and low molecular weight polyphenols. The sample was vacuum-filtered, repeatedly washed with ethanol until there was no color in the filtrate, then dried at 70 °C for 24 hours. This sample was mixed with 250 mL 0.2 mol L⁻¹ NaOH and stirred for 3 hours at room temperature. The base/peel slurry was filtered, washed with distilled water until the pH reached neutral, and then dried at 70 °C for 24 hours, thereafter named as POP. With this step, the number of carboxylate ligands in the biomass could be increased and the binding ability of the metal ions enhanced by treating with sodium hydroxide. The POP was stored in desiccators prior to characterization and test use.

Column Preparation

A 60 mg quantity of the POP was packed into a PTFE microcolumn (20 mm × 2.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 2.0 mol L⁻¹ HNO₃ and DW were passed through the column to clean and condition it. The column was then preconditioned to the desired pH value with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃·H₂O before passing the chromium-containing solutions. The desired flow rates (0.5–3.0 mL min⁻¹) were easily obtained.

General Procedure

An aliquot of sample solution containing Cr(III) and Cr(VI) was prepared, and the pH value adjusted to the desired pH with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃·H₂O. The sample solution was

passed through the microcolumn with a peristaltic pump at a flow rate of 2.0 mL min⁻¹. Cr(III) retained by the microcolumn was eluted with 2.0 mL of 1.2 mol L⁻¹ HNO₃, followed by ICP-MS determination in the eluent, whereas Cr(VI) was found to remain in the effluent and measured directly by ICP-MS.

Preparation of Real Samples and Standard Reference Material

Tap water was collected in our laboratory after flowing for about 5 minutes, while lake water was collected locally from East Lake (Wuhan, P.R. China) and stored in polyethylene bottles. Before analysis, all of the real water samples were filtered through a 0.45 µm pore size membrane to remove the suspended matter. The certified reference sample GBW (E)08642 Trace Elements in Water was diluted 5000-fold with DW before measurement. The pH of the samples was adjusted to the desired value with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃·H₂O. Then the procedure given above was applied to the samples. The blanks were prepared in the same way as the sample, but omitting the sample.

RESULTS AND DISCUSSION

FTIR Analysis

The adsorption of chromium ions onto any biomass is due to the functional groups on the components. To confirm the pretreatment of the biomass, FTIR spectra were obtained on the raw and pretreated biomass. The IR spectra of the POP and OP were recorded in the range of 4000–400 cm⁻¹, and are shown in Figure 1. The FTIR spectrum of POP exhibits a broad peak at 3416 cm⁻¹, which corresponds to the O-H stretching vibrations of cellulose, pectin, absorbed water, hemicelluloses, and lignin (32). The peak at 2924 cm⁻¹ could be assigned to the -CH₂- group in the cellulose (33). The peak observed at 1609 cm⁻¹ may be assigned to the carbonyl (-C=O) stretching from the carboxylic acid and carboxylate groups, respectively. The bands observed in 1000–1300 cm⁻¹ were assigned to the C-O stretching vibration of the carboxylic acids and alcohols. These results were similar to the FT-IR results by Feng et al. (29).

Fig.1. FTIR spectra of OP and Pretreated OP.

Effect of pH on Adsorption of Cr(III) and Cr(VI)

The solution pH has been suggested as one of the most important parameters with respect to the selective retention of Cr(III) over Cr(VI) on the POP microcolumn. In this work, the effect of pH on the adsorption rate of chromium species in the microcolumn was evaluated with the solution containing 5 ng mL^{-1} of Cr(III) and Cr(VI) at the pH varying from 2.0 to 8.0, under a flow rate of 2.0 mL min^{-1} . Figure 2 shows that the quantitative recovery (>96%) for Cr(III) was obtained in the pH range of 3.5–5.0, whereas Cr(VI) was less than 2.0%. It can be seen that the Cr(III) adsorption was favorable at pH 4. The adsorption behavior of Cr(III) and Cr(VI) on POP may be attributed to this reason. At pH >3, the number of negatively charged absorbent sites increased, which provides a favorable force of attraction for the positively charged Cr(III) cations [Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, and $\text{Cr}(\text{OH})^{2+}$] (34). However, the negatively charged Cr(VI) species [$\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , and CrO_4^{2-}] may hardly be adsorbed due to electrostatic repulsion. At pH <2.0,

because the surface active sites of the POP were protonated, the competition of H^+ with the Cr(III) cations for the same surface sites resulted in a decrease in the adsorption of Cr(III). This mechanism is in agreement with the findings of previous reports on other biosorbents (35). Various mechanisms such as electrostatic repulsion and attraction, ion exchange, and chelation could be attributed to causing adsorption of Cr(III) on biosorbent surfaces. In the experiment, pH 4.0 proved to be best suited for Cr(III) separation by POP.

Influence of Sample Flow Rate

The flow rate of the sample solution is a very important factor affecting the pre-concentration efficiency of Cr(III), recovery rate, and analysis time. The flow rate ($0.5\text{--}3.0 \text{ mL min}^{-1}$) of the sample solution containing 1.0 ng mL^{-1} Cr(III) was examined at pH 4. It can be seen from Figure 3 that the recovery rates were higher than 95% for a sample solution flow rate of $0.5\text{--}2.5 \text{ mL min}^{-1}$. Above 2.5 mL min^{-1} , the recovery rates decreased with an increase in flow rate of the sample solution. Therefore, a flow rate of 2.0 mL min^{-1} was applied for

the sample solutions in all experiments.

Elution of Cr(III)

The choice of a suitable eluent is also important for pre-concentration and separation. From Figure 2 it can be seen that the adsorption of Cr(III) on POP is negligible at pH 1. In acidic conditions, due to the protonation of all functional groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, etc., in the POP biosorbent and the competition of the H^+ ion with Cr(III) cations for the effective adsorption sites on the sorbent, desorption of the Cr(III) species from the POP surface is possible. For this reason, various concentrations and volumes of HNO_3 were explored for the elution of Cr(III) retained in the microcolumn at a flow rate of 2.0 mL min^{-1} . The desorption efficiency of Cr(III) with $0.1\text{--}1.6 \text{ mol L}^{-1}$ HNO_3 solution and $0.5\text{--}3.0 \text{ mL}$ HNO_3 was investigated. The results indicated that quantitative recoveries for Cr(III) could be obtained with 2.0 mL of 1.2 mol L^{-1} HNO_3 . Thus, the optimum volume of HNO_3 (1.2 mol L^{-1}) solution chosen for this work was 2.0 mL with a recovery of >96%.

Fig. 2. Effect of pH on adsorption of Cr(III) and Cr(VI) on POP. Cr(III) and Cr(VI): 5.0 ng mL^{-1} , respectively. Sample volume: 20 mL

Fig. 3. Effect of flow rate of sample solution on recovery of Cr(III) on POP. pH: 4.0; Cr(III): 1.0 ng mL^{-1} .

Effect of Sample Volume

The influences of sample volume on the recovery of Cr(III) were studied. Sample volume is a main parameter for obtaining a high pre-concentration factor. For this purpose, 10 ng of Cr(III) was dissolved in different DW volumes ranging from 25–250 mL and the recommended procedure according to optimized experimental conditions was followed. Figure 4 shows that quantitative recoveries of Cr(III) (>96%) were found to be stable up to 200 mL. Above 200 mL, the recoveries decreased slightly with an increase in sample volume. In this study, the pre-concentration factor was calculated by the ratio of highest sample volume (200 mL) and final elution volume (2 mL). Thus, the pre-concentration factor was 100-fold in this method.

Adsorption Capacity

The adsorption capacity study as recommended by Kalyan et al. (35) was adopted under the optimized conditions. Accordingly, 20 mL of sample solutions of a series of concentrations (5.0–300 $\mu\text{g mL}^{-1}$) were adjusted to the appropriate pH, and the proposed procedure was followed. The breakthrough curve was determined by plotting the concentration ($\mu\text{g mL}^{-1}$) versus the milligram of Cr(III) adsorbed on per gram of POP. The adsorption capacity calculated from the breakthrough curve was 136.2 mg g^{-1} at pH 4.0.

Effect of Ratio of Cr(III) to Cr(VI)

In aqueous solution, the change in the redox equilibrium state may occur between Cr(III) and Cr(VI), and thus the concentration of the

chromium species may change. To study the recovery and selectivity in standard solutions, the effect of the ratio of Cr(III) to Cr(VI) on the analytical results was evaluated. The results presented in Table II show that quantitative recoveries of Cr(III) and Cr(VI) were obtained with the ratio of Cr(III)/Cr(VI) ranging from 0.5 to 10, and that the two species of chromium are completely separated and relatively stable at pH 4.

Interferences of Coexisting Ions

The separation procedure was applied to the determination of Cr(III) and Cr(VI) species in different concentrations of coexisting ions. The representative potential interference ions were added individually to a 50-mL aqueous solution containing 1.0 ng mL^{-1} of Cr(III) and Cr(VI), respectively. The potential interferences from coexisting ions on the separation and determination of chromium speciation were investigated. In these experiments, the tolerance limit of coexisting ions is defined as the ion concentration causing a relative error of less than $\pm 5\%$ for 1.0 ng mL^{-1} Cr(III) and Cr(VI), respectively. The results in Table III show that the recoveries of Cr(III) and Cr(VI) were almost quantitative in the presence of all coexisting ions and that most of the probable coexisting cations and anions did not interfere. The tolerable levels of some heavy metal ions were suitable for the separation of the Cr(III) species in the water samples examined because the levels of the transition metals in these samples were lower than their interference level.

Column Re-use

To investigate the re-usability and potential regeneration of the adsorbent, several adsorption/desorption operation cycles were carried out in this work. The column could be re-used after regeneration with 10 mL of 1.2 mol L^{-1}

Fig. 4. Effect of sample volume on recovery of Cr(III) on POP. pH: 4.0; Cr(III): 10 ng

TABLE II
Recovery of Chromium Speciation
in Different Concentration Ratios of Cr(III) and Cr(VI) (n=3)

Cr(III)/ Cr(VI) Ratio	Added ($\mu\text{g L}^{-1}$)	Cr (III)		Cr (VI)	
		Found ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
0.5	5	4.93 $\pm$ 0.11	98.6	9.87 $\pm$ 0.08	98.7
1	5	5.00 $\pm$ 0.09	100	4.97 $\pm$ 0.12	99.4
5	20	19.9 $\pm$ 0.21	99.5	3.96 $\pm$ 0.04	99.0
10	20	19.7 $\pm$ 0.14	98.5	2.04 $\pm$ 0.05	102

HNO₃ solution and 50 mL of DW, and is stable up to 20 adsorption-elution cycles without any noticeable decrease in the recovery of Cr(III).

Analytical Performance of the Method

The calibration curve for Cr(III) was linear up to 100 ng mL⁻¹ with a correlation coefficient (r^2) of 0.9993. According to the definition of IUPAC (3σ), the detection limit of this method was 0.009 ng mL⁻¹ for Cr(III) and 0.037 ng mL⁻¹ for Cr(VI) using ICP-MS determination. The relative standard deviations (RSDs), examined by 11 replicate measurements of 2.0 ng mL⁻¹ Cr(III) and Cr(VI) model solutions, were 2.5% for Cr(III) and 4.1% for Cr(VI), respectively. The pre-concentration factor was 100.

A comparison of the proposed method with others in the literature is given in Table IV. As can be seen, the present method using the POP system has a high pre-concentration factor (11, 20, 21, 24, 36), and the detection limit is better than other methods described in the literature (11, 21, 24). Pretreated orange peel is a green sorbent of low cost, requiring only simple preparation in comparison to different sorbents.

Application of Method to Real Samples

The accuracy of the proposed method was validated by the determination of total chromium and its species using a standard reference materials of GBW (E)080642 Trace Elements in Water after 5000-fold dilution with DW. The analytical results were in good agreement with the reported total Cr concentration of 100±5 µg mL⁻¹ (Table V).

By analyzing two real water samples (tap and lake water), followed by the spike addition of standards, the feasibility of determining Cr(III) and Cr(VI) on POP was confirmed. In addition, the recovery experi-

ments of different amounts of Cr(III) and Cr(VI) were carried out using the standard addition method to assess the selectivity and precision. The results in Table V show that good agreement was obtained between the added and measured analysis amounts. These results indicate that the Cr(III) and Cr(VI) species were completely separated and quantitatively recovered, ranging from 98.5–103.8%. Thus, the method was successfully applied

for the separation and speciation of chromium using POP sorbent and the determination of trace Cr(III) and Cr(VI) in environmental water samples.

TABLE III
Influence of Coexisting Ions on Determination Cr(III) and Cr(VI)

Ions	Amount (µg)	Recovery (%) Cr(III)	Recovery (%) Cr(VI)	Ions	Amount (µg)	Recovery (%) Cr(III)	Recovery (%) Cr(VI)
K ⁺	2500	101.2	98.6	Cu ²⁺	25	96.9	95.5
	5000	95.2	94.6		50	95.7	95.1
Na ⁺	2000	99.5	101.3	Zn ²⁺	50	97.3	98.2
	3000	98.7	96.2		100	97.0	96.1
Ca ²⁺	1000	102.4	97.8	Cd ²⁺	50	99.4	96.9
	2500	96.5	95.2		100	101.2	97.3
Mg ²⁺	1000	97.2	98.9	V(V)	25	100.5	98.6
	2500	95.8	96.7		50	95.1	96.4
Al ³⁺	100	96.9	95.8	SO ₄ ²⁻	1000	98.2	98.9
	200	95.2	95.3		1500	96.5	95.7
Fe ³⁺	100	98.1	98.6	PO ₄ ³⁻	1000	95.7	97.2
	150	96.4	95.9		1500	94.1	93.6

TABLE IV
Comparison of Present Method With Other SPE Methods

Adsorbent	Method	Medium	PF ^a	DL ^b (µg L ⁻¹)	Reference
Ion-imprinted polymer	ETAAS	pH 3.5-4.75	10	0.018	(11)
Eggshell membrane	ETAAS	pH 2.0	13.3	0.01	(20)
Animal fiber	FAAS	pH 4.0	32	0.3	(21)
B-cyclodextrin	GFAAS	pH 5.5-6.0	25	0.056	(24)
Carbon nanotubes	ICP-MS	pH 2.0-4.0	63	0.01	(36)
Pretreated orange peel	ICP-MS	pH 3.0-5.5	100	0.009	This work

^a PF = preconcentration factor.

^b DL: = detection limit.

TABLE V
Analytical Results for Chromium Speciation in SRM and Water Samples (n=3)

Sample	Spiked (ng mL ⁻¹)		Found (ng mL ⁻¹)		Total Cr	Recovery(%)	
	Cr (III)	Cr (VI)	Cr (III)	Cr (VI) ^b		Cr(III)	Cr(VI)
GBW(E)080642 ^a	0	0	24.82±0.9	75.56±1.3	100.38±2.0		
Tap Water	0	0	0.63±0.02	< LOD	0.62±0.03		
	2.0	2.0	2.65±0.08	2.01±0.04	4.62±0.12	101.0	100.5
	5.0	5.0	5.61±0.14	4.94±0.19	12.79±0.32	99.6	98.8
Lake Water	0	0	4.26±0.11	1.38±0.05	6.64±0.34		
	2.0	2.0	6.23±0.22	3.43±0.08	10.64±0.31	98.5	102.5
	5.0	5.0	9.45±0.28	6.35±0.17	16.58±0.34	103.8	99.4

^a The GBW(E)080642 sample was detected after 5,000-fold dilution.

^b Certified value of total Cr in GBW(E)080642: 100±5 µg mL⁻¹.

CONCLUSION

In this work, a new and inexpensive method is applied for the speciation of chromium by solid phase extraction (SPE) combined with inductively coupled plasma mass spectrometry (ICP-MS). Cr(III) was selectively retained on the pretreated orange peel (POP) microcolumn in the pH ranging from 3.5 to 5.5, while Cr(VI) was retained in the solution. The results showed that POP possesses good potential for the separation and determination of Cr(III) and Cr(VI) in natural water samples. The proposed method is characterized as simple, selective, and low cost, as well as safe, effective, more rapid, and cleaner. It provides good sensitivity, selectivity, and detection limits, as well as a high pre-concentration factor, and is potentially useful in the speciation analysis of Cr(III) and Cr(VI). It was successfully applied to the separation and determination of chromium species in environmental water samples with satisfactory results.

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