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ORIGINAL PAPER

Fast, green and effective chromium bio-speciation using *Sepia pharaonis* endoskeleton nano-powder

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Abstract The development of a fast, effective, simple and low-cost procedure for chromium speciation is an analytical challenge. In this work, a new and simple method for speciation and determination of chromium species in different matrices was developed. *Sepia pharaonis* endoskeleton nano-powder was used as an adsorbent for the dispersive micro-solid-phase extraction. Finally, the desorbed chromium was determined using a graphite furnace atomic absorption spectrometer. The experimental results showed that Cr(III) could be quantitatively extracted by the adsorbent, while Cr(VI) adsorption was negligible. Concentrated H_2SO_4 and ethanol reduced Cr(VI)–Cr(III), and total chromium content was assessed as Cr(III). Then, the Cr(VI) concentration in the sample was calculated as the difference. The optimum conditions were obtained in terms of pH, adsorbent amount, contact time, and type, concentration and volume of eluent. Under the optimum conditions that involved the speciation of chromium ions from 25 mL of the water samples at pH 7.0 using 0.025 g of the adsorbent with contact time of 5 min, the method was validated in terms of linearity, precision and accuracy. The calibration curve was linear over the concentration range of 0.01–25.00 μg L^{-1} for Cr(III). The obtained limit of detection for the proposed method was 0.003 μg L^{-1}. The maximum adsorption capacity of the adsorbent was found to be 995.57 mg g^{-1}. The proposed method was validated by the speciation of Cr(III) and Cr(VI) in different real water and wastewater samples with satisfactory results.

Keywords Chromium · Speciation · Nano-powder · Cuttlefish endoskeleton · *Sepia pharaonis*

Introduction

It is well known that the toxicity, bioavailability and the other properties of heavy metals depend on their molecular structure and their electronic and oxidation state. The term "speciation" identifies the different oxidation states, and "speciation analysis" describes the analytical methods for determination of one or more individual chemical species (Das et al. 2012). Chromium as a major pollutant occurs frequently in the environment, originating from natural sources and industrial activities such as electroplating, tannery and pigment industries and anticorrosion coatings (Malherbe and Claverie 2013).

Chromium is mainly found in two oxidation states, III and VI, both show different chemical properties and toxicological consequences. Cr(VI) is known as the most toxic, carcinogenic and mutagenic material to living organisms

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due to its strong oxidation potential and its relatively small size. These properties enable Cr(VI) to penetrate through biological cell membranes and damage lungs, liver, kidneys and macromolecules such as proteins and DNA. Also Cr(VI) acts as an inhibitor in the enzymatic sulfur uptake of the cell (Shirkhanloo et al. 2015; Şahan et al. 2014). On the other hand, Cr(III) is considered as essential to mammals in trace amounts and influences the maintenance of the normal glucose tolerance factor, and lipid and protein metabolism (Pagana et al. 2011; Sorouraddin et al. 2013; Sadeghi and Zeraatkar 2012). Therefore, the assessment of chromium toxicity in various liquid and solid matrixes requires effective speciation studies. Commonly, an elemental speciation method is a combination of effective separation with a sensitive detection technique. Due to low levels of chromium in the environmental and biological samples, extraction procedures as well as a suitable preconcentration method are often necessary prior to analysis. This step will also eliminate the matrix effect. Various conventional and recent miniaturized methods such as chemical co-precipitation (Krishna et al. 2004; Uluozlu et al. 2009) membrane extraction (Safari et al. 2013), ion exchanging by resin (Narin et al. 2008; Zou et al. 2008; Sacmacı et al. 2012), cloud point extraction (CPE) (Diniz and Tarley 2015; Wang et al. 2010; Matos et al. 2009), solid-phase extraction (SPE) (Jia et al. 2016; Chen et al. 2014; Wu et al. 2012; Amin and Kassem 2012) and dispersive liquid–liquid micro-extraction (DLLME) (López-García et al. 2013; Wen et al. 2013; Yousefi and Shemirani 2013) have been developed for separation and enrichment of chromium species. Of these methods, SPE is the most widely employed procedure for the study of chromium speciation, particularly in water samples (Das et al. 2012). This is because of advantages such as convenience, time saving, low cost, reduced solvent utilization, high enrichment factor, possible miniaturization, high flexibility in choosing appropriate adsorbent as well as recycling potential for multiple uses (Chen et al. 2014). As some SPE procedures take operator time, use toxic solvents and are not economic, the development of simple, cheap, green efficient techniques for the chromium speciation seems essential.

In previous studies, various solid phases such as organic polymers (Jia et al. 2016), chelating and ion exchanging resins (Şahan et al. 2014), functionalized alumina and silica gel (Mahmoud et al. 2008; Martendal et al. 2009) have been designed, synthesized and employed as the adsorbents. However, tedious and time-consuming procedures for their synthesis of adsorbents as well as the use of toxic reagents and solvents are the main draw backs of these systems. On the other hand, the use of nanoparticles in separation science has drawn attention due to their excellent properties including large surface area, mechanical strength and homogeneous distribution of nanoparticles in the solution. These increase favorable mass transport to the surfaces (Parham and Rahbar 2009). Various synthetic nano-sized materials such as Fe_3O_4@ZrO_2 nanoparticles, amino-functionalized Fe_3O_4/SiO_2 nanoparticles, single-wall carbon nanotubes and titanium dioxide nanotubes have been successfully used for speciation and pre-concentration of Cr(III) and Cr(VI) in different matrices (Wu et al. 2012; Diniz and Tarley 2015; Chen et al. 2010, 2014).

The objective of this work was to develop a new analytical procedure for chromium speciation using *Sepia pharaonis* endoskeleton nano-powder (SPEN) as nontoxic, low cost and environmental friendly adsorbent without any pretreatment or activation. *S. pharaonis* endoskeleton is a bio-mass waste. It also exists naturally in beaches where cuttlefish lives. Cuttlebone is a highly porous hard tissue in *S. pharaonis*. It is a white, oblong oval 10–25 cm long and 4–7.5 cm wide with a hard chitinus coat (Li et al. 2010; Ben Nasr et al. 2011). The proposed method demonstrated the high potential ability of SPEN for speciation of trace concentrations of Cr(III) and Cr(VI) in different matrices. The separated target analytes were successfully determined by graphite furnace atomic absorption spectrometer (GFAAS). This study had been performed from January 2015–January 2016 at faculty of pharmacy, Ahvaz Jundishapur University of Medical Sciences. To the best of our knowledge, the application of raw nano-sized bio-mass has not been reported before for speciation of chromium.

Materials and methods

Apparatus and reagents

AAS-vario6 Analytik Jena graphite furnace atomic absorption spectrometer (Germany) equipped with a chromium hollow cathode lamp (NARVA, Germany) was used to determine the chromium content at 359.4 nm. The phase separation of the sample solution was performed on CLEMENTS laboratory centrifuge (Sydney). The pH values were controlled with a Metrohm pH-meter model 623 (Herisau, Switzerland). Heidolph magnetic stirrer (Germany) was also used.

All reagents were of the highest available purity and at least analytical reagent grade and prepared from Merck (Darmstadt, Germany). The de-ionized water obtained from a Millipore Continental Water System (Bedford, MA,

USA) was used throughout this study. Stock Cr(VI) and Cr(III) solutions (1000 mg L^{-1}) were prepared by dissolving the appropriate amounts of $K_2Cr_2O_7$ and $Cr(NO_3)_3{\cdot}9H_2O$ in 0.1 mol L^{-1} HNO_3, respectively. Diluted standard solutions were prepared daily by appropriate dilution of these stock solutions. *S. pharaonis* endoskeletons were collected from Nakhiloo Island near the North coast of Persian Gulf in Bushehr Province, Iran, in September 2014. Before use, the endoskeleton was brushed to remove any adhering materials. After that, it was rinsed with deionized water and dried at 60 °C for 24 h and allowed to cool. It was crushed in a laboratory mortar. Nano-sized SPEN was obtained in a Nano Shat PBM ball mill (model 210, Iran). These nanoparticles were stored in the desiccator before use.

Characterization techniques

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the SPEN in the scanning range of 400–4000 cm^{-1} was recorded on Vortex 7 FTIR (Bruker, Germany). The experiments were carried out on the powdered samples ground in an agate mortar to produce KBr pellets, and spectra were obtained by sample scan time of 10 s with scanner velocity of 10 kHz. All spectra were corrected for the background noise.

Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX)

FESEM analysis of the SPEN was conducted to show dimension and morphology of this adsorbent. EDX spectroscopy was used for chemical characterization and elemental analysis of the adsorbent. All FESEM and EDX experiments were performed using low vacuum Mira 3-XMU instrument (Tescan, Germany).

X-ray fluorescence spectroscopy (XRF)

XRF analysis was conducted to determine the elemental composition (qualitative and semi-quantitative) of the adsorbent using ED 2000-Oxford instrument (England).

Speciation and determination procedure

A 25 mL portion of the sample solution containing chromium species at pH 7 was mixed with 25 mg of SPEN, and the mixture was stirred for 5 min at 1000 rpm. Then, the suspension was centrifuged at 4000 rpm for 10 min, and SPEN-containing Cr(III) was separated, while Cr(VI) remained in the supernatant.

The SPEN was washed with 2 mL of deionized water; then, Cr(III) was desorbed by stirring the SPEN with 4 mL of 1 mol L^{-1} HNO_3 for 1 min. Afterward, the concentration of Cr(III) in the eluate was determined by GFAAS. To determine total chromium as Cr(III) using the above method, first 0.5 mL concentrated sulfuric acid and 0.5 mL ethanol were added to the solution containing Cr(VI) and Cr(III). The added reagents could rapidly reduce Cr(VI)–Cr(III) (Bag et al. 2000; Tuzen and Soylak 2006; Barrera et al. 2006). The Cr(VI) content was calculated by subtraction of the Cr(III) from the total chromium concentration.

The adsorption efficiency was calculated using Eq. (1), where q_e (mg g^{-1}) is the amount of Cr(III) or Cr(VI) adsorbed on SPEN under equilibrium conditions. C_0 and C_e are the initial and the equilibrium concentrations of the analyte, respectively. V is the volume of solution (L), and W is the amount of adsorbent (g).

$$q_e = (C_0 - C_e) \times V/W \quad (1)$$

A blank solution was prepared using SPEN under the same analytical conditions without adding any chromium species. All reported data were the averages of three determinations.

Results and discussion

Characterization of SPEN

SPEN was characterized by FT-IR, FESEM and XRF. The FT-IR spectra of the SPEN in Fig. 1 shows the major band at 1476 cm^{-1} (C–O), and a sharp band at 863 cm^{-1} (Ca–O) corresponds to the presence of carbonate. These major

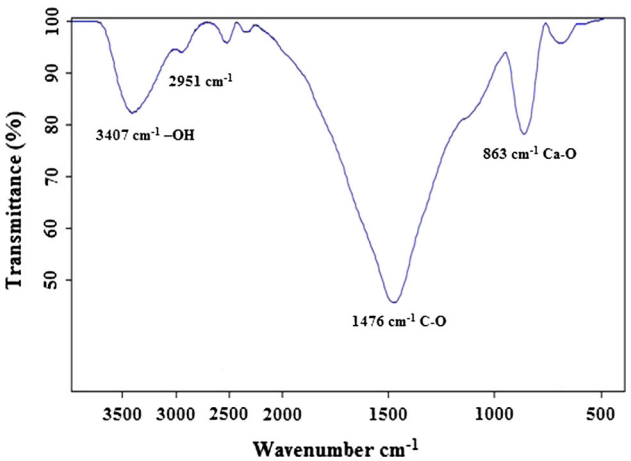

Fig. 1 FT-IR spectra of SPEN

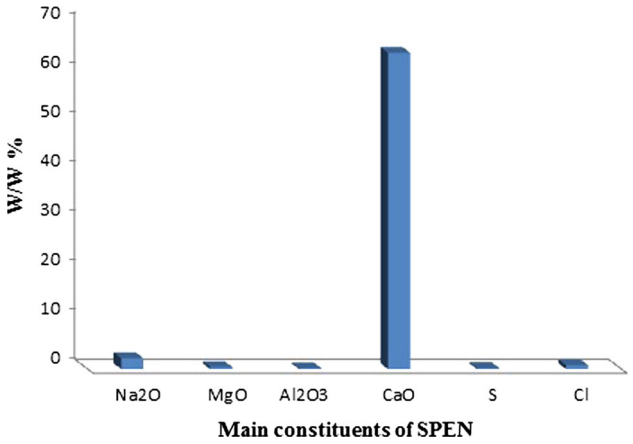

Fig. 2 XRF photograph of SPEN

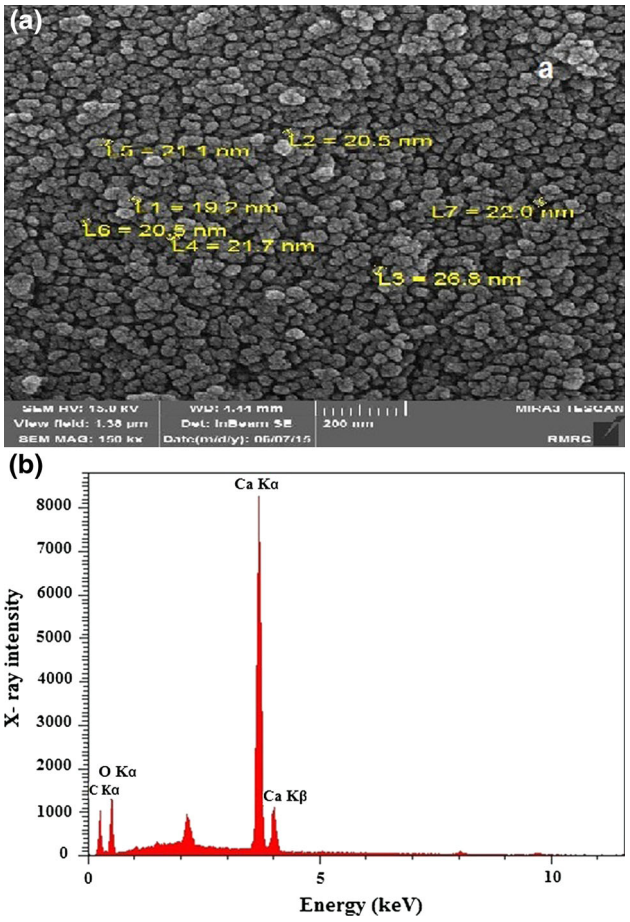

Fig. 3 FESEM micrograph (**a**) and EDX spectra (**b**) of SPEN

and sharp bands show that $CaCO_3$ is the main constituents of this adsorbent. Moreover, the chitin content of SPEN was proven by observing a broad –OH and –NH absorption peak at 3407 cm^{-1} and the reference band of chitin at 2951 cm^{-1}. Lower adsorption bands at 600–700 cm^{-1} may be due to the chitinous content of the SPEN. However, the representative amide bands ascribed to the CONH group (in chitin) vibration modes appeared at 1300–1659 cm^{-1} may suffer interference from broad C–O bands at 1467 cm^{-1} (Li et al. 2010; Ben Nasr et al. 2011; Brugnerotto et al. 2001; Majtan et al. 2007).

XRF analysis of the adsorbent in Fig. 2 indicates that 64 % (w/w) of SPEN is CaO, which related to the $CaCO_3$ content of SPEN. These data confirm that the main constituent of the SPEN is calcium carbonate. Additionally, the existence of chitin and its functional groups is also obvious. A FESEM micrograph for the SPEN as well as EDX spectra is illustrated in Fig. 3. As shown in Fig. 3a, cuttlebone nano-powder has spherical shapes with diameters of <100 nm that present large surface area and therefore provides enough adsorption sites for analyte. This property helps to explain the excellent capability of SPEN for the removal of the investigated ions via the adsorption process. The EDX spectra (Fig. 3b) also confirmed the data obtained from XRF. These constituents can greatly determine the adsorption capacity of SPEN for metal ions which can be associated with adsorption mechanisms such as ion exchange between calcium ion and tested metal ions in solution and complexation of the examined analytes with functional groups of chitinous constituent of adsorbent.

Effect of pH on selective extraction for Cr(III) and Cr(VI)

It is well known that the pH level has significant influence on adsorption process (Saygi et al. 2008). The influence of pH on the retention of Cr(III) and Cr(VI) on 0.1 g SPEN was investigated in the PH range of 2–8 using 25 mL of solutions (containing 1 mg L^{-1} of each chromium species) with separate tests. As can be seen in Fig. 4, Cr(III) retention increases with an increase in pH having shown a maximum adsorption capacity in pH 7 while at this pH the adsorption of Cr(VI) on the nano-powder is at minimum level. It seems that the existence of calcium carbonate as the major component of SPEN may adsorb this metal via the ion exchange mechanism. Ca(II) ion is exchanged by Cr(III) (Li et al. 2010), and Cr(VI) cannot be adsorbed by this mechanism. The reason for the slight decrease in the adsorption efficiency of Cr(III) at pHs below 5 is probably due to the protonation of the adsorbent surface that causes the repulsive forces between the Cr(III) and the adsorption sites. Meanwhile, Cr(VI) which presents as CrO_4^{2-} in acidic solutions shows relatively high adsorption on the protonated surface of SPEN. On the other hand, it can be

assumed that in basic solutions micro-precipitation of Cr(III) hydroxide might be due to the pK_{sp} value of this precipitate (30.2). Based on obtained results, in all further studies, pH 7 was selected as optimum pH for separation of chromium species.

Influence of the amount of SPEN and sample volume

The influence of the amount of SPEN on the bio-speciation of Cr(III) and Cr(IV) was investigated at optimum pH 7. To obtain the experimental data, the amount of SPEN for the maximum adsorption of Cr(III) in 25 mL of sample solution (containing 1 mg L^{-1} of both Cr(III) and Cr(VI) ions) at initial pH 7 was optimized in the range of 0.01–1.00 g. As shown in Fig. 5, the maximum adsorption capacity was achieved for Cr(III) when the amount of SPEN was 0.025 g, while Cr(VI) retention was minimum. However, with higher amounts of SPEN, retention of Cr(VI) was slightly increased while Cr(III) retention remained quantitative that might be due to the more available sites on adsorbent and potential electrostatic forces between Cr(VI) and positive charges on SPEN which attributed to the presence of different cations in its composition.

The maximum applicable sample solution volume was achieved by increasing the volume of sample solution (10–750 mL) while the amount of Cr(III) (25 μg) remained constant. It can be seen in Fig. 6 that the retention of Cr(III) was quantitative up to 500 mL of sample volume and at volumes higher than that the adsorption of Cr(III) slightly decreased. Recovery of the adsorbed Cr(III) to 4 mL HNO_3 solution as eluent makes it possible to obtain an enrichment factor of about 125.

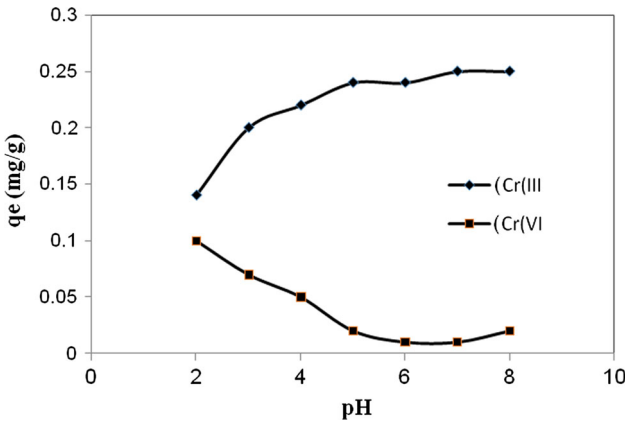

Fig. 4 Effect of the pH on the speciation of the target ions. Conditions: 25 mL of 1 mg L^{-1} of each target ion, 0.1 g SPEN, contact time of 10 min

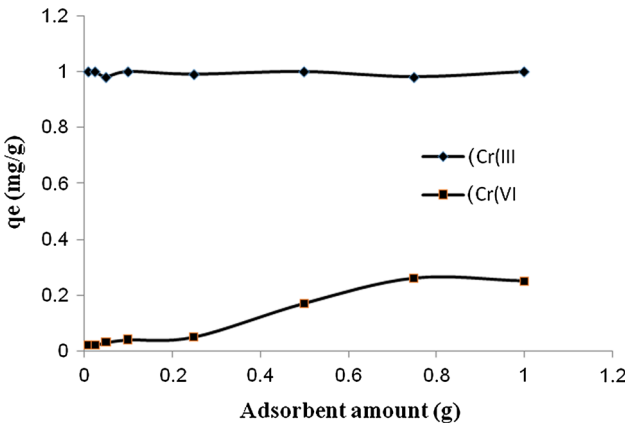

Fig. 5 Effect of the amount of SPEN on the speciation of the target ions. Conditions: 25 mL of 1 mg L^{-1} of each target ion, pH 7, contact time of 10 min

Effect of contact time, temperature and stirring rate of solution

Different contact times ranging from 1 to 120 min were tested for speciation and determination of Cr(III) and Cr(VI) from 25 mL model solutions containing 1 mg L^{-1} of each component at pH 7 with 0.025 g of SPEN. As results illustrated in Fig. 7 show, it was found that the system reached equilibrium at a contact time of 5 min at a stirring rate of 1000 rpm and effective separation of analytes was obtained. Contact times longer than 5 min had no significant effect on speciation efficiency. This short equilibrium time revealed that fast kinetic of adsorption

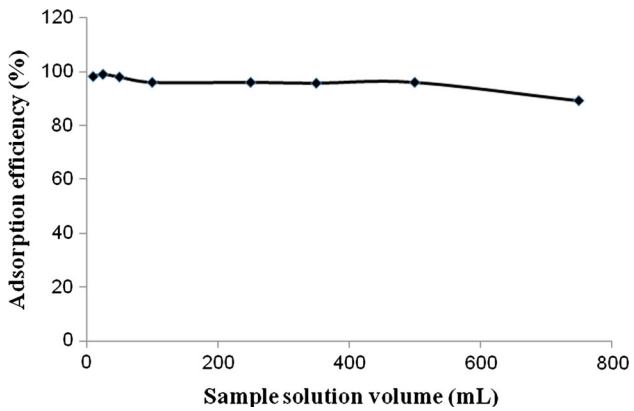

Fig. 6 Effect of the sample volume on the adsorption of Cr(III) ions on SPEN. Conditions: pH 7, 0.025 g SPEN, contact time of 10 min

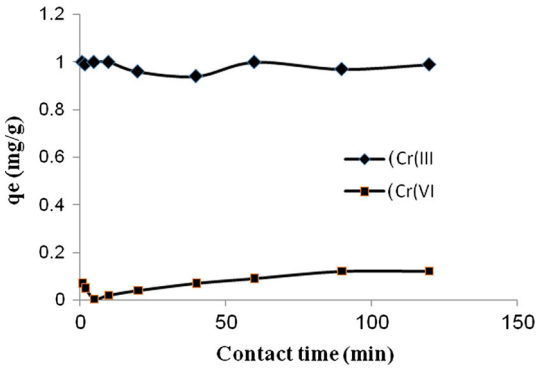

Fig. 7 Effect of contact time on the speciation of the target ions. Conditions: 25 mL of 1 mg L^{-1} of each target ion, pH 7, 0.025 g SPEN

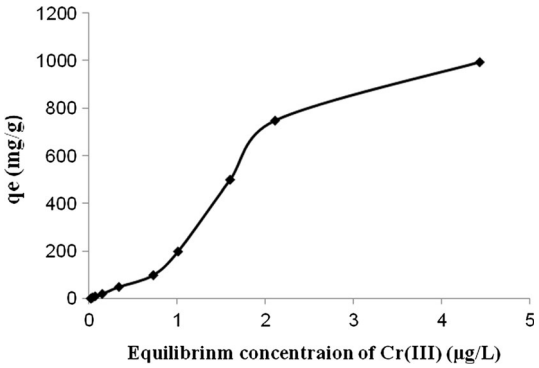

Fig. 8 Equilibrium isotherm of Cr(III) sorption. Conditions: 25 mL of different concentrations of Cr(III), pH 7, 0.025 g SPEN, contact time of 5 min

process of Cr(III) could be attributed to the rapid exchange reaction between the analyte and SPEN as the major suggested sorption mechanism (Peng et al. 2010).

More experiments were designed to evaluate the effects of temperature (20–70 °C) and stirring speed (100–1000 rpm) of sample solution. The results showed (Figs. S1 and S2 in supplementary data) that the sorption capacity remained nearly constant in the examined range of temperature and stirring speeds, and these parameters had no significant effects on speciation efficiencies.

Adsorption isotherm and loading capacity

Adsorption isotherm studies can provide valuable data on the pathway of adsorption reaction. For this reason, 25 mg of adsorbent was added to 25 mL aliquots of Cr(III) solutions containing a series of concentrations in the range of 1–1000 mg L^{-1}, under optimized conditions (pH 7, contact time = 5 min, 30 °C and stirring rate = 1000 rpm) according to the recommended procedure. The amount of the adsorbed Cr(III) per gram of SPEN versus equilibrium concentration of analyte at each concentration level (q_e) was depicted in Fig. 8. As can be seen, the adsorption capacity rises sharply with the increase in equilibrium concentration of Cr(III) and then approaches a maximum value. The maximum adsorption and loading capacity of SPEN obtained from this isotherm curve was 995.57 mg g^{-1} for Cr(III) solution with an initial concentration of 1000 mg L^{-1} (Lazaridis and Charalambous 2005; Chen et al. 2014). In order to model the sorption behavior of Cr(III) by SPEN, Langmuir and Freundlich isotherms were used in this study (Rahbar et al. 2014). The results showed that the Freundlich isotherm ($R^2 = 0.984$) fitted better than Langmuir model ($R^2 = 0.290$) in terms of correlation coefficient values, which suggests the multilayer adsorption of Cr(III) on SPEN. Moreover, the superiority of the Freundlich isotherm potentially provides a logical explanation for the excellent adsorption capacity of this adsorbent.

Optimization of the eluent type, concentration and volume

Different solutions including hydrochloric acid, nitric acid and ethylene diamine tetra acetic acid (EDTA) were examined to choose the best solvent for effective elution of Cr(III) adsorbed on SPEN. Selection of these solvents was made based on the obtained results from "Effect of pH on selective extraction for Cr(III) and Cr(VI)" section (in acidic media Cr(III) was not effectively retained) and capability of complex formation between Cr(III) and EDTA. The results are illustrated in supplementary data (Figs. S3–S5). Based on these results, HNO_3 was the best eluent among tested solvents. The effects of concentration and volume of this eluent were investigated ranging from 0.1 to 2.0 mol L^{-1} and 2–7 mL, respectively. The effective elution of traces of Cr(III) from the pores of the SPEN was carried out by using 4 mL of 0.5 mol L^{-1} HNO_3 solution (78.5 %). It must be mentioned that the process of desorption is very fast with this optimized solvent, and the time taken is only about 1 min.

Effect of diverse ions

The influence of commonly occurring ions in water samples was investigated on the recovery of the Cr(III). 25 mL of sample solutions containing 25 µg of Cr(III) and foreign

Table 1 Determination of chromium species in various water samples by the proposed method

Sample	Added (μg L^{-1})		Found (μg L^{-1})[a]		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Mineral water	0	0	0.035 ± 0.005	0.057 ± 0.003	–	–
	0.050	0.050	0.082 ± 0.003	0.105 ± 0.004	94.0	96.0
	0.200	0.200	0.230 ± 0.002	0.262 ± 0.001	97.5	102.5
Tap water	0	0	ND[b]	0.221 ± 0.002	–	–
	0.050	0.050	0.048 ± 0.004	0.274 ± 0.003	96.0	106.0
	0.200	0.200	0.203 ± 0.001	0.426 ± 0.001	101.5	102.5
River water	0	0	0.025 ± 0.006	0.195 ± 0.003	–	–
	0.050	0.050	0.076 ± 0.002	0.242 ± 0.003	102.0	94.0
	0.200	0.200	0.222 ± 0.002	0.398 ± 0.001	98.5	101.5
Electroplating wastewater	0	0	0.094 ± 0.005	0.056 ± 0.004	–	–
	0.050	0.200	0.142 ± 0.001	0.263 ± 0.002	96.0	103.5
	0.200	0.050	0.284 ± 0.003	0.105 ± 0.002	95.0	98.0

[a] x ± s ($n = 3$)

[b] Not detected

ions in different concentrations were subjected to the optimized extraction procedure. The maximum acceptable error was determined as ±5 %. 200 mg L^{-1} of common cations [Na(I), K(I), Mg(I) and Al(III)] and anions (carbonate, chloride, sulfate and phosphate) had no effect on the extraction recovery. Ca(II) and nitrate ions did not interfere up to 100 mg L^{-1}. The results showed that large numbers of performing ions have no considerable influence on the extraction and determination of chromium species.

Analytical performance

A calibration curve was made by correlating the absorbance of the solution obtained from the elution step and Cr(III) concentration in the spiked standard solutions. The linear calibration graph in the range of 0.01–25 μg L^{-1} was obtained for the determination of Cr(III) with the equation of $y = 0.79x + 0.45$ ($R^2 = 0.9993$). The limit of detection of the method was defined as LOD = $3S_b/m$ (where S_b is standard deviation of the blank values and m is the slope of calibration curve). The LOD of the proposed method was found to be 0.003 μg L^{-1}. The repeatability of the method (relative standard deviation, %RSD) was evaluated for 0.05, 0.50 and 5.00 μg L^{-1} ($n = 6$) of Cr(III) solutions. The obtained %RSD values were in the range of 2.1–8.0 %.

Analysis of the real samples

The presented method for chromium speciation based on the solid-phase extraction was applied to various environmental real samples. The water samples analyzed were obtained locally without further preparation. The mineral water was purchased from local supermarket, and the tap water was collected of our laboratory from the city water, in Ahvaz, Iran. River water from Karoun River (Ahvaz, Iran) was collected in polyethylene bottles. The electroplating wastewater was obtained from a local factory. All water samples were filtered through Whatman 0.45-μm pore size filter, immediately and acidified to 1 % with nitric acid (except electroplating waste water) and then stored at 4.0 °C in polyethylene containers.

To determine the accuracy and applicability of the developed procedure in real samples, the spiking recovery method was used. An appropriate portion of real sample (20 mL of the mineral water, 5 mL of the tap and river water and 2 mL of the wastewater) and a known amount of a standard solution was added into a 25 mL volumetric flask and diluted to the mark with deionized water. Then, the speciation procedure was performed on spiked and un-spiked samples according to the developed method. The concentration of the analyte was determined in both the spiked and un-spiked portions. As can be seen in Table 1, good recoveries indicated that the matrix of real samples had no serious interference on the recovery of the chromium species.

Conclusion

In this work, it was demonstrated that SPEN as an environmental friendly and low-cost solid phase is capable of separating Cr(III) and Cr(VI) in one step without the use of

Table 2 Comparison of the analytical performance of the different reported methods for speciation and determination of chromium species

Method	LDR[a]	LOD (μg L^{-1})	EF[b]	Real sample	References
Coprecipitation	0.5–10	1	50	Tap, sea and hot mineral spring water	Diniz and Tarley (2015)
EME[c]-HPLC	20–500	5.4	21.8–33	Tap, river and mineral water	Jia et al. (2016)
SPE-FAAS	0–0.25	7.7	75	Tap and mineral water–Tannery wastewater	Lazaridis and Charalambous (2005)
SPE-CPE-FAAS	0–200	1.1	12	Water samples	Mahmoud et al. (2008)
CPE-HPLC	50–5000	3.5–7.5	40–45	Sediment	Majtan et al. (2007)
CPE-ETAAS	2.5–80	0.7–2.5	48	River water	Malherbe and Claverie (2013)
SPE-HPLC-ICP-MS	0.01–10	0.0041	4.8	Wastewater	Martendal et al. (2009)
SPE-ICP-MS	0.1–100	0.0075	–	Tea leaves and infusion	Matos et al. (2009)
DLLME-ETAAS	0.005–0.2	0.002	240	Tap, mineral and sea water—toy samples	Pagana et al. (2011)
DLLME-Spect.[d]	0.2–20	0.05	159	Tap, mineral and cooling system water	Peng et al. (2010)
SPE-GFAAS	0.01–25	0.003	125	Tap, mineral and river water—electroplating wastewater	This work

[a] Linear dynamic range

[b] Enrichment factor

[c] Electromembrane extraction

[d] Spectrophotometry

organic solvents or any toxic reagent. This method could separate, extract and determine ultra-trace levels of the chromium species in a short time via the simple procedure. The Cr(III) was adsorbed in solid phase quantitatively while the Cr(VI) remained in solution which provides an opportunity for recovery of this essential element. Further, the outstanding maximum adsorption capacity (995.57 mg g^{-1}) places SPEN as one of the best biomass adsorbents for recovery of Cr(III) from aqueous solutions. This method also showed advantages including: wide linear range (0.01–25.00 μg L^{-1}); much better LOD (0.003 μg L^{-1}); and desirable enrichment factor (125) in comparison with a variety of other methods reported in related literature (Table 2). The proposed method demonstrated good efficiencies in the presence of a variety of possible interferences. Finally, the presented system could separate and determine the chromium species from different water and wastewater samples.

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