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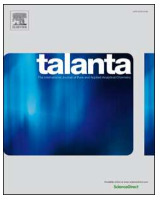

Speciation analysis of chromium by carboxylic group functionalized mesoporous silica with inductively coupled plasma mass spectrometry

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ABSTRACT

Carboxyl-group functionalized mesoporous silica (CFMS) prepared by one-pot co-condensation method was employed for the solid phase extraction (SPE) of chromium species for the first time. A new approach of SPE coupled to inductively coupled plasma mass spectrometry (ICP-MS) was thus established for the speciation of chromium in environmental water samples. The influences of pH, volume of sample, extraction time, amount of adsorbent, elution conditions, co-existing ions and adsorption capacity were investigated on adsorption or elution of chromium species. Cr(VI) was not retained on the CFMS material in the pH range of 1.0–9.0, while Cr(III) was quantitatively adsorbed at pH 5.0–9.0. The captured Cr(III) was enriched by using 1.5 mol L^{-1} HNO_3 as elution solvent and detected by ICP-MS. Under the optimized SPE conditions, the maximum adsorption capacity of the CFMS for Cr(III) was 57.67 mg g^{-1} and the enrichment factor was 25, with the detection limit (LOD) of 0.02 μg L^{-1}. The proposed protocol has been successfully applied to chromium speciation in rain, lake and river water samples, which exhibited a prospect in field separation and enrichment of chromium species in environmental waters.

1. Introduction

It is worth noting that the role and impact of trace heavy metal on the environment and living organisms depend primarily on its chemical form. For example, Cr(III) is considered as an essential trace element for glucose metabolism and maintaining the proper functioning in the human body [1]. By contrast, Cr(VI) can easily react with proteins and other cell molecules, causing skin ulcerations, nasal perforations, and lung cancer, etc. [2,3]. Therefore, it is necessary to carry out elemental speciation analysis in studying the toxicity, biocompatibility and other properties of chromium species.

As the most powerful determination technique for trace element, ICP-MS has been proved to be of high detection power, fast analysis, multi-element capability, etc. However, ICP-MS can not discriminate different species of trace elements. Therefore, high efficient separation procedures are essential to realize selective separation before ICP-MS determination [4–6]. Chromatographic methods, such as high-performance liquid chromatography (HPLC) [7], are directly combined with ICP-MS, making efficient speciation analysis of chromium species. However, high expense limits the application development of these hyphenated techniques. On the other hand, non-chromatographic separation methods which are of low cost and high efficiency are also employed for speciation of chromium. Solid phase extraction (SPE), as one of the most commonly used techniques in preconcentration of many metal ions, enables the concentration and purification of analytes from solution by sorption on a solid matrix. Using SPE as separation approach can reduce solvent demand, disposal costs and extraction time [8]. A variety of adsorbents such as chromosorb resins [9], metal oxides [10,11], multiwalled carbon nanotubes [12,13], and mesoporous silica [14–17], have been extensively exploited for selective extraction of chromium species.

Mesoporous silica has the characteristics of large specific surface area, adjustable pore size and uniform pore structure. The materials are easily modified with organic functional groups, which show unique

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advantages in the separation and enrichment of trace element forms because of its high selectivity and loading capacities [18]. As the most common organic functional groups used for modifying silica surface chemistry [19], amino, thiol and carboxyl have been demonstrated to be the specific ligands for most of metal ions [14,15,20,21]. However, the applications of carboxylic group functionalized mesoporous silicas (CFMSs) were focused mainly on the enzyme immobilization, removal of cationic dyes, and drug delivery [22–26]. To the best of our knowledge, there is no detailed report in the literature on applying CFMSs as adsorbent for speciation of chromium so far.

Two papers by Che's group provided an excellent discussion for synthesis of carboxylic group functionalized mesoporous silicas via co-structure directing method [27,28]. In this present work, we tried to utilized carboxyl group functionalized mesoporous silica as SPE adsorbent for the speciation of inorganic chromium, and ICP-MS was used for determination of chromium. By comparing the morphology, structure and property of two homemade CFMS-1 and CFMS-2 with different reactant composition, we employed CFMS-2 as extraction matrix for chromium speciation based on SPE of mesoporous silica, and the adsorption behavior of Cr(III) and Cr(VI) on CFMS-2 were investigated comprehensively. Because Cr(III) can be retained on the adsorbent in a specific range of pH, while Cr(VI) can not, various parameters influencing SPE of Cr(III) were optimized, including pH, volume of sample, extraction time, amount of adsorbent, elution conditions, co-existing ions and adsorption capacity. Herein, we report the attempt to utilize carboxylic group functionalized mesoporous silica as SPE adsorbent for separation of chromium species. By combing with ICP-MS, we achieved with a high detection power selective chromium speciation in environmental waters.

2. Experimental

2.1. Apparatus

All the measurements of chromium concentration were carried out by a Perkin-Elmer NexION 350D inductively coupled plasma mass spectrometer (Perkin-Elmer SCIEX Instruments, Concord, Canada) with kinetic energy discrimination. The optimal operation conditions for ICP-MS are summarized in Table S1. The pH values of solutions were controlled with a FiveEasy Plus pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). X-Ray powder diffractometer (XRD) patterns of CFMSs were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) using a Cu Kα radiation source. High resolution transmission electron microscopy (HRTEM) was obtained with a JEM-200CX microscope (JEOL, Tokyo, Japan) operating at a 200 kV accelerating voltage. Scanning electron microscopy (SEM) obtained with a Hitachi S-3400N II (Hitachi, Tokyo, Japan) was used for acquiring the morphology images and energy disperse spectroscopy (EDS) spectra of materials. N_2 adsorption-desorption isotherms was carried out on a Micromeritics ASAP 2020 BET surface analyzer system (Micromeritics, Shanghai, China). The surface area was calculated by using the Brunauer-Emmett-Teller (BET) equation, and pore size distribution was obtained by using the Barrett-Joyner-Halenda (BJH) model. Characterization of carboxylic group was investigated by Fourier transform infrared spectroscopy (FT-IR) on a Nicolet-6700 spectrometer (Thermo Nicolet Corporation, WI, USA) in the range of 4000–450 cm^{-1} and confirmed by ^{13}C CP NMR spectrum recorded on a Bruker AVANCE III HD 400 MHz NMR (Bruker, Switzerland). The elemental analysis (EA) of CFMSs was obtained from an Elementar Vario EL II (Elementar, Hanau, Germany). Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were performed on a Perkin-Elmer Pyris 1 DSC (Netzsch, Bavaria, Germany).

2.2. Reagents and samples

Cetyltrimethylammonium bromide (CTAB) was purchased from TCI (Tokyo, Japan). Tetraethylorthosilicate (TEOS) was obtained from Alfa Aesar (Tianjin, China). Carboxyethylsilanetriol sodium salt (CES) was bought from J & K Chemical Technology (Shanghai, China). Hydrochloric acid (HCl) was guaranteed reagent and bought from Merck (Zurich, Switzerland). Other chemicals were of analytical grade and used without further purification. Ultra-pure water provided by a Milli-Q water system (Millipore, Bedford, MA. USA) was used throughout the study.

The stock standard solutions (1000 $mg\,L^{-1}$) of Cr(III) and Cr(VI) were supplied by Chinese Academy of Measurement Sciences (Beijing, China). Working standard solutions were prepared daily by diluting the stock solutions appropriately with ultra-pure water and stored in PTFE bottles at 4 °C.

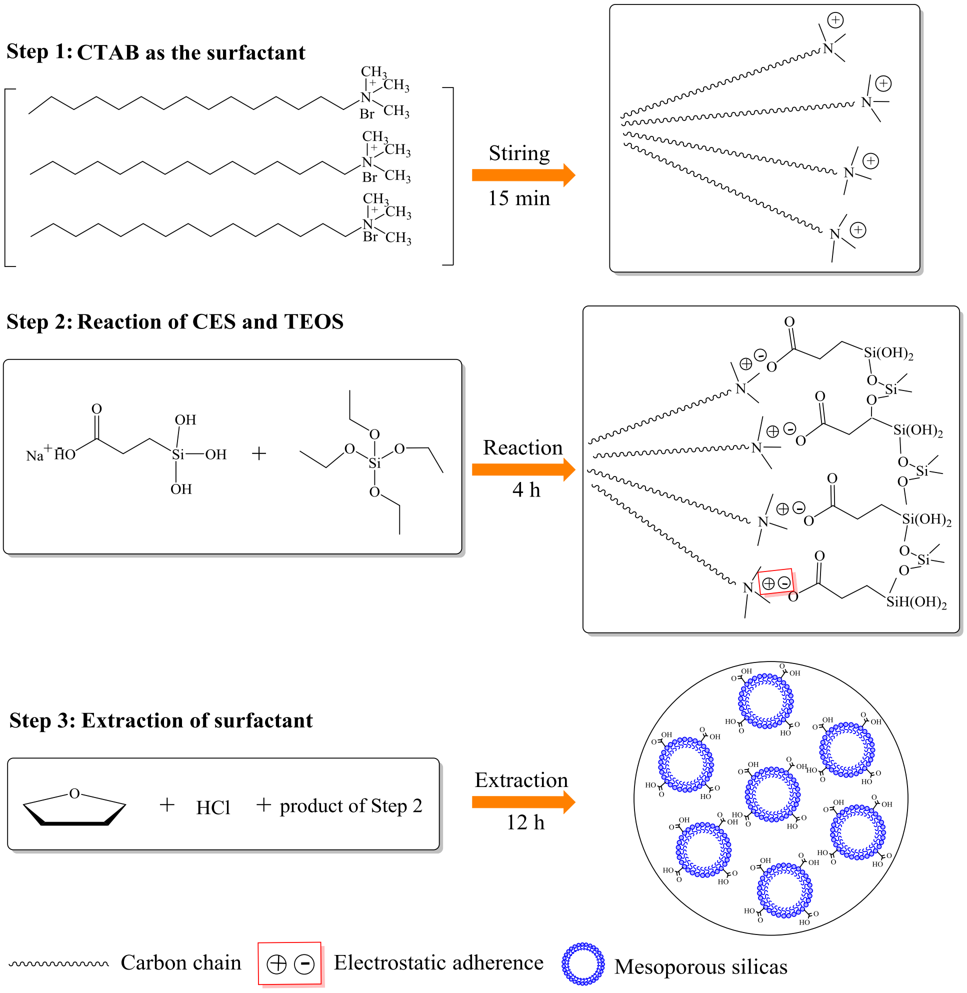
Rain water was collected from the Xianlin Campus of Nanjing University two weeks before experiment. Lake water and river water was sampled from Yangshan Lake and Yangtze River, respectively, in Nanjing one week before experiment. Each environmental water sample was filtered through a 0.45 μm cellulose acetate membrane before use and stored in a PTFE bottle at 4 °C. All glass and plastic bottles were cleaned with 20% (v/v) nitric acid and rinsed with ultra-pure water and then dried at room temperature before use.

2.3. Preparation of carboxylic group functionalized mesoporous silicas (CFMSs)

Carboxyl-group functionalized mesoporous silicas were synthesized by one-pot co-condensation method following the procedure reported by Han et al. [28] with minor modification. Scheme 1 shows the reaction process. Firstly, CTAB and water were mixed in a three-necked flask, which was placed in a water-bath at room temperature. Once the CTAB were dissolved in water, CES and TEOS used as co-structure guide reagent were added with injection syringe, and the dropping speed was controlled by a syringe infusion pump (Baoding Longer, Hebei, China). The reaction system was stirred for 1 h. Subsequently, the mixture was placed in an oil bath at 100 °C under static conditions for 2 h. After the suspension was centrifuged, white particle powders were washed with water and dried in vacuum oven for 24 h. Next, the obtained material, called as-synthesized CFMS, was transferred into a solution of tetrahydrofuran (THF) with hydrochloric acid to extract template CTAB (0.5 g of as-synthesized material in 100 mL THF with 0.5 mL HCl). After soxhlet extraction for 24 h, carboxyl-group functionalized mesoporous silica was collected by washing with water and dried in vacuum oven. The molar ratio of reactants was set to 7 TEOS: x CES: 1 CTAB: 2000 H_2O, and the value of x was adjusted to 1 and 2 to acquire two carboxyl-group functionalized mesoporous silicas, respectively, labeled with CFMS-1 and CFMS-2.

2.4. Procedure for the speciation of Cr(III)

Batch experiment of SPE procedure for the speciation of chromium was carried out by using carboxyl-group functionalized mesoporous silica as extraction matrix. 50 mL of standard Cr(III), Cr(VI) solutions or real water samples, which were adjusted to pH 5.0 by adding 0.1 $mol\,L^{-1}$ HNO_3 or 0.1 $mol\,L^{-1}$ $NH_3{\cdot}H_2O$, were transferred to a centrifuge tube containing adsorbent material of CFMS-2 (10 mg). Then, the centrifuge tube was placed in a rotary mixer (Changzhou Dingxin Experimental Instrument Co. Ltd., Changzhou, China) for 10 min to complete the extraction process. After adsorption, the CFMS-2 adsorbent was separated by centrifugation (Himac CP70NE, Hitachi, Tokyo, Japan) at 8000 rpm for 5 min. Next, 1.5 $mol\,L^{-1}$ HNO_3 was used as eluent for the desorption of Cr(III). Finally, the concentration of Cr (III) in solutions was analyzed by ICP-MS, and the concentration of Cr (VI) was calculated by subtraction from the total chromium.



Scheme 1. Schematic diagram of the preparation of carboxyl-group functionalized mesoporous silica.

3. Results and discussion

3.1. Template removal

FT-IR, EA and TGA were applied for checking the removal of template (CTAB) from as-synthesized CFMSs. Taking as-synthesized CFMS-2 as the example, it displayed two obvious absorption bands at 2853 and 2923 cm^{-1} (Fig. 1A), which can be assigned to the symmetrical and asymmetrical stretching vibrations of the methylene groups of CTAB, respectively [29], while CFMS-2 treated with THF in HCl did not. Furthermore, EA provided evidence for the amount (w%) of nitrogen, hydrogen and carbon. As-synthesized CGFM-2 contained 1.61% nitrogen, 6.49% hydrogen and 31.16% carbon, while CFMS-2 just contained 0.12% nitrogen 2.64% hydrogen and 4.56% carbon. This clearly

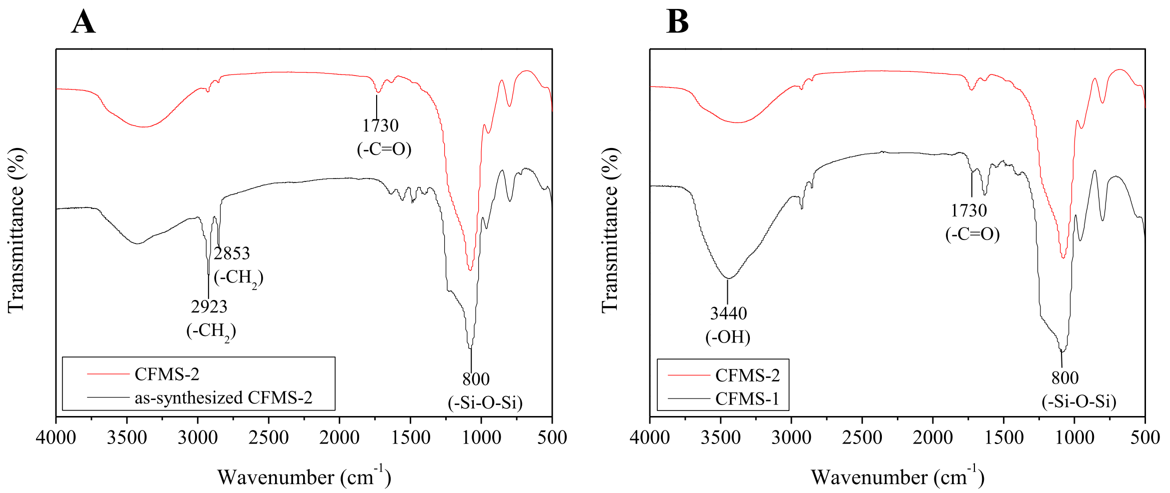


Fig. 1. Comparison of FT-IR spectra of as-synthesized CFMS-2 with CFMS-2 (A), and comparison of FT-IR of CFMS-1 with CFMS-2 (B).

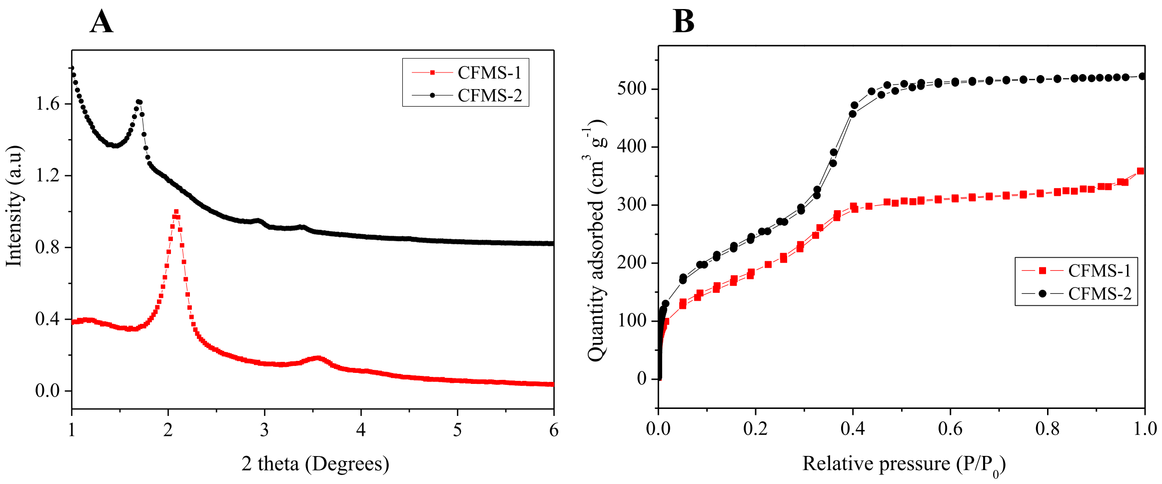


Fig. 2. XRD patterns (A) and N_2 adsorption-desorption isotherms (B) of carboxyl-group functionalized mesoporous silicas.

demonstrated that template has been removed because only CTAB contains nitrogen. Moreover, TGA curves (Fig. S1) of as-synthesized CFMS-2 exhibited a much more weight loss at 200–500 °C than CFMS-2 did. The reason was that as-synthesized CFMS-2 contained more organic functional groups. From the results of FT-IR, EA and TGA, it was confirmed that the template of CTAB has been effectively removed.

3.2. Characterization of morphology and structure of CFMSs

The structure and morphology of CFMSs were characterized by XRD, N_2 adsorption-desorption isotherms, SEM and TEM. The low-angle XRD patterns of CFMS-1 and CFMS-2 are shown in Fig. 2A. A well-resolved peak in the region of $2\theta = 1.5–2.0°$ and two additional weak peaks, confirmed the formation of a typical 2D hexagonal p6mm mesophase in two materials prepared [28]. It could be clearly seen that the peaks of CFMS-1 shifted to lower angles, suggesting an irradiation induced increase of lattice parameter [30]. The N_2 sorption-desorption isotherms of CFMS-1 and CFMS-2 displayed a type IV isotherm (Fig. 2B), indicating typical mesoporous structure. The corresponding pore size distributions calculated by the BJH method for carboxyl-group functionalized mesoporous silicas are shown in Fig. S2. The surface area, mesopore volume and pore size are collected in Table 1. As anticipated, CFMS-2 possessed higher BET specific surface area and pore volume than CFMS-1. The particle morphologies of carboxyl-group functionalized mesoporous silicas were characterized by SEM. The micrograph of CFMS-2 in Fig. 3A revealed that spherical particles have an average size of 500 nm, which was significantly larger than CFMS-1. In addition, TEM was performed to further confirm the arrangement of the mesopores. The magnified image for the CFMS-2 (Fig. 3B) showed ordered 2D hexagonal mesopores obviously in good agreement with the results obtained from XRD and N_2 sorption-desorption isotherm, and the well-ordered mesoporous pore structure can be clearly observed in Fig. S3.

The successful modification of carboxyl groups was proven by FT-IR spectra. Fig. 1B indicates the FT-IR patterns of carboxyl-group functionalized mesoporous silicas in the range of 4000–500 cm^{-1}. A broad band at 3600–3200 cm^{-1} can be corresponded to intra- and intermolecular -OH stretch vibration. One fact is that both CFMS-1 and CFMS-2 contained carboxyl groups, which can be revealed by the absorption bands at 1730 cm^{-1} due to C=O stretching. Additionally, the bands at 800 and 1079 cm^{-1} can be attributed to Si-O-Si symmetrical stretching vibration and asymmetric stretching vibration, respectively. Also in Fig. 4 were the EDS results showing the expected peaks for Si, O and C. Specifically, the atomic percent of Si and O present in CFMS-2 were higher than that in CFMS-1, which implied that CFMS-2 contained more carboxyl groups.

From the characterization results including morphology, structure and composition of two CFMSs, CFMS-2 possessed more ordered mesoporous pore structure and carboxyl groups. In order to obtain more information about carboxyl group, the solid-state ^{13}C MAS NMR of CFMS-2 was measured. As shown in Fig. 5, the signal around 180, 27.5 and 7.5 ppm were associated with C1, C2 and C3 of CES, respectively. Obviously, the results of ^{13}C MAS NMR patterns confirmed that carboxyl-group has been successfully modified in CFMS-2.

Table 1
The physical characteristics of carboxyl-group functionalized mesoporous silicas.

Material	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
CFMS-1	660.32	0.55	2.83
CFMS-2	869.94	0.79	2.71

3.3. Optimization of speciation conditions

3.3.1. Influence of pH

The pH of sample solution plays an important role in the retention of Cr(III) and Cr(VI) on CFMS-2. In this work, the effect of pH was investigated in the pH range from 1.0 to 9.0 by using 5 mL of 20 μg L^{-1} Cr(III) and Cr(VI) as sample solution. As seen in Fig. 6, the adsorption percentage of Cr(III) and Cr(VI) were both negligible in the pH range of 1.0–3.0. In addition, Cr(III) was adsorbed quantitatively when the pH > 3.0. However, almost no adsorption of Cr(VI) on CFMS-2 was observed within pH 1.0–9.0. The adsorption mechanism of Cr(III) on CFMS-2 in the pH range of 4.0–9.0 could be explained by the electrostatic force on the surface and chelation of -COOH towards $Cr(H_2O)_6^{3+}$, $Cr(H_2O)(OH)^{2+}$ and/or $Cr(H_2O)(OH)_2^{+}$ respectively. On the contrary, the reason for no retention of Cr(VI) on CFMS-2 could be attributed to the existence form of Cr(VI) and surface nature of the adsorbent [9]. Cr (VI) exists mainly as anions ($HCrO_4^-$, CrO_4^{2-} and/or $Cr_2O_7^{2-}$) in the tested pH range [31]. In acidic medium, the anions of Cr(VI) were not adsorbed through electrostatic interaction with adsorbent, because carboxyl groups modified in CFMS-2 were not protonated. As the pH increased, the anions of Cr(VI) were not retained on CFMS-2 owing to the electrostatic repulsion between anions and the negatively charged surface of CFMS-2. Therefore, the pH of sample solution was maintained at approximately 5.0 in subsequent investigations.

3.3.2. Influence of sample volume

In order to explore the effect of sample volume on adsorption performance of CFMS-2, the various volumes of sample solutions ranged

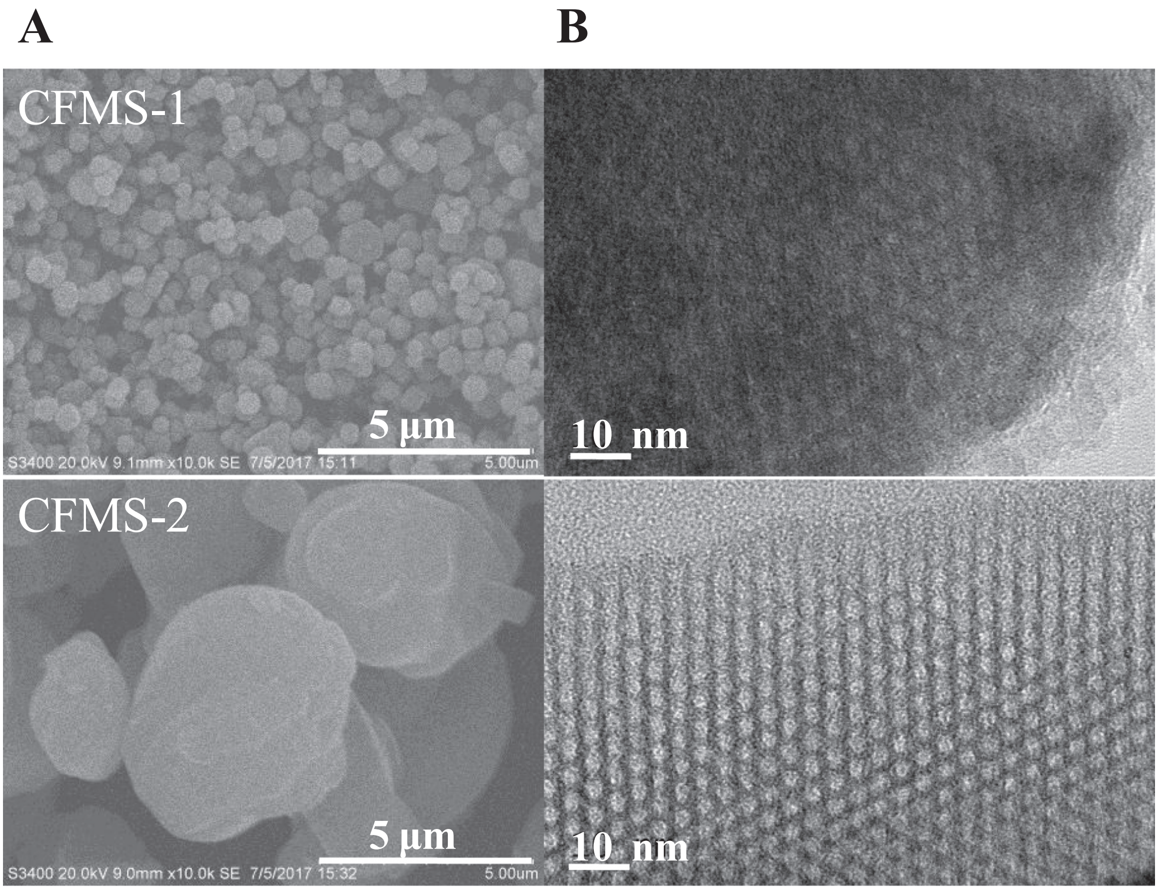
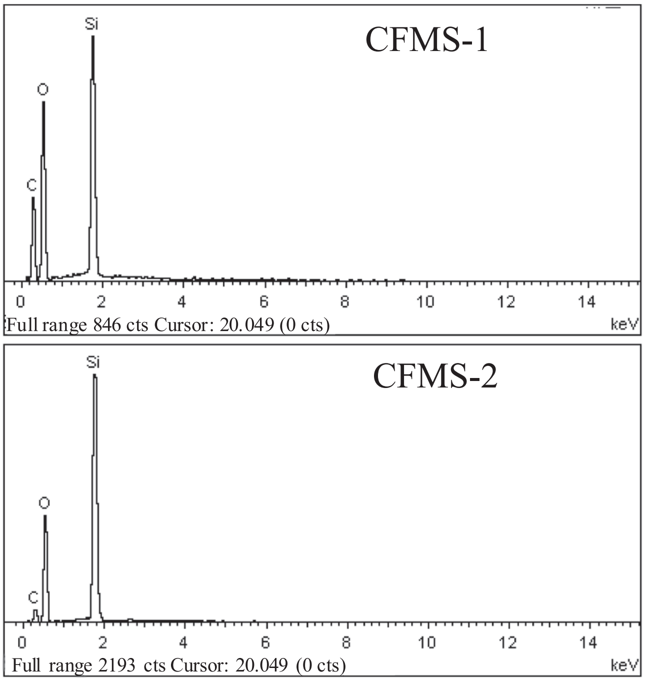


Fig. 3. SEM (A) and TEM images (B) of carboxyl-group functionalized mesoporous silicas.

from 5 to 50 mL containing 0.1 µg of Cr(III). As shown in Fig. S4A, the experimental results indicated that the adsorption percentage of Cr(III) were all above 90%. In order to gain higher enrichment factor, a large volume of sample solution is necessary. Therefore, a sample volume of 50 mL was selected in further experiments.

3.3.3. Influence of extraction time

Extraction time is another important factor because it affects the



Element	Weight (%)	Atomic (%)
C K	35.60	44.81
O K	50.46	47.68
Si K	13.95	7.51
Total	100.00	

Element	Weight (%)	Atomic (%)
C K	19.40	27.45
O K	52.00	55.24
Si K	28.60	17.30
Total	100.00	

Fig. 4. EDS results of carboxyl-group functionalized mesoporous silicas.

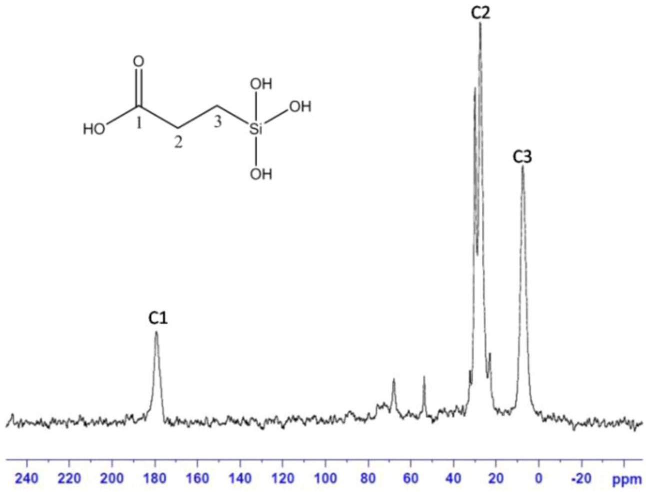


Fig. 5. ^{13}C CP NMR spectrum of the CFMS-2.

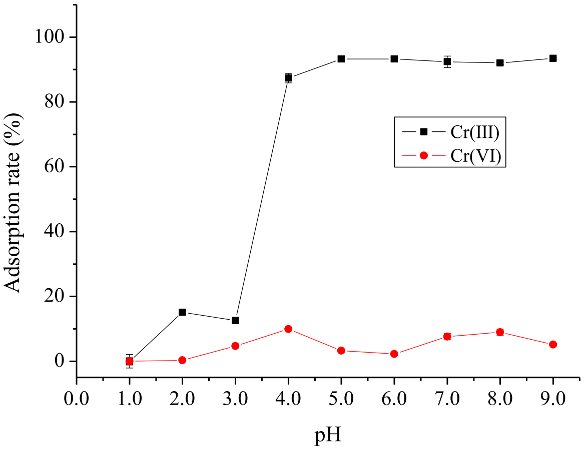


Fig. 6. Influence of solution pH on the adsorption of Cr(III) and Cr(VI) onto CFMS-2.

adsorption performance. The influence of extraction time on the adsorption of Cr(III) was investigated in the range of 2–30 min (Fig. S4B). It was observed that extraction time had no significant effect on the adsorption efficiency and the extraction equilibrium could be established quickly. Therefore, 5 min was chosen as adsorption time in this work.

3.3.4. Influences of amounts of adsorbent

In this study, the effect of adsorbent dosage on the adsorption of Cr (III) was investigated by adding varying amounts of CFMS-2 from 1 to 20 mg. The results were given in Fig. S4C. Quantitative adsorption of Cr (III) was obtained in the range 10–20 mg of adsorbent. Therefore, 10 mg of CFMS-2 was enough for the complete adsorption of Cr(III) in 50 mL solution containing 0.1 μg of Cr(III) and thus adopted in all subsequent experiments.

3.3.5. Influence of elution conditions

The selection of an appropriate elution condition is essential for the desorption of Cr(III). For this purpose, the effect of eluent type, composition and volume, and elution time were investigated under optimum adsorption conditions. High acidity solution was regarded as feasible eluent, because Cr(III) was not adsorbed onto CFMS-2 when the pH of sample solution was less than 4.0 (Fig. 6). As shown in Fig. S5A, the recovery of Cr(III) was obviously increased when the concentration of HCl and HNO_3 increase from 0.1 to 2.0 mol L^{-1}. In comparison, 1.5 mol L^{-1} HNO_3 was a good choice to desorb Cr(III). In order to get a higher enrichment factor, different volumes of 1.5 mol L^{-1} HNO_3 were applied to elute Cr(III) from the CFMS-2. From Fig. S5B, it was found that 2 mL of 1.5 mol L^{-1} HNO_3 was enough to effectively desorb Cr(III) with the recovery higher than 95%. So, the enrichment factor obtained by this method was 25. In addition, the influence of elution time varied from 2 to 30 min was studied (Fig. S5C). The results showed that the elution process was completed within a short period of time. Therefore, 5 min was selected as elution time.

Table 2
Influence of co-existing ions on the SPE of Cr(III).

Coexisting ions	Concentration (mg L^{-1})	Adsorption percentage (%)
Na^+	5	94.3
K^+	5	95.1
Ca^{2+}	5	90.8
Mg^{2+}	1	91.5
Zn^{2+}	1	93.2
Al^{3+}	1	91.7
Ni^{2+}	1	92.6
Fe^{3+}	0.5	95.3
Cu^{2+}	0.1	95.8
Pb^{2+}	5	95.0
NO_3^-	5	93.9
SO_4^{2-}	5	92.5
Cl^-	5	95.6

3.3.6. Influence of co-existing ions

The potential interference of various ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Ni^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, NO_3^-, SO_4^{2-} and Cl^-) were investigated on the determination of Cr(III). Specifically, various ions were added individually to a solution containing 0.1 μg of Cr(III) ions under the optimal conditions described above. The results are summarized in Table 2. According to the data, the retention of Cr(III) on CFMS-2 was not effected by interference of each coexisting ion at a certain level, and the adsorption of Cr(III) was still above 90%.

3.3.7. Adsorption equilibrium isotherm and adsorption capacity

In order to draw the adsorption equilibrium isotherm and evaluate the adsorption capacity of CFMS-2 for Cr(III), a set of adsorption experiments were conducted by changing the initial concentrations of Cr (III) solution in the range of 1–70 mg L^{-1} using 10 mg of CFMS-2 as SPE adsorbent. According to Langmuir adsorption isotherm models, the adsorption capacity was measured via the following formula: $Q_e = [(C_0\text{-}C_e)*V]/m$, where C_0 is the original concentrations and C_e is equilibrium concentrations, m is the weight of adsorbent, and V is the solution volume. As can be seen from Fig. S4D, the maximum adsorption capacity of CFMS-2 for Cr(III) was 57.67 mg g^{-1}, which was superior to the literature reported data (Table 3).

3.3.8. Analytical performance

Under the above optimized conditions, the analytical performance of the proposed method for Cr(III) was evaluated. The linear equation in the concentration range of 0.05–4.0 μg L^{-1} was $y = 23.31x + 0.354$ ($R^2 = 0.998$), which was shown in Fig. S6. Furthermore, the limits of detection (LODs, defined as three times the signal-to-noise ratio) for Cr (III) was 0.02 μg L^{-1} and a precision of 1.0% RSD is obtained at the level of 0.5 μg L^{-1} Cr(III), which indicated good reproducibility for the speciation of Cr(III). In addition, an enrichment factor of 25 was obtained with loading sample volume of 50 mL and elution solvent volume of 2.0 mL.

3.3.9. Application of real water samples

In order to examine the applicability of the proposed method (SPE-ICP-MS), the concentration of Cr(III) in three real samples (rain water, lake water and river water) were analyzed, and the concentration of Cr

Table 3
Comparison of analytical performance obtained in this work with other adsorbents for the determination of Cr(III).

Analytical technique	Adsorbent	Adsorption capacity	Enrichment factor	Contact time	Recovery (%)	Precision (%)	Detection limit (μg L^{-1})	Ref.
MSPE-GFAAS	Zincon-Si-MNPs	9.16	100	3 min	88–109	6.0	0.016	[4]
MSPE-GFAAS	Fe_3O_4@SiO_2@IDA	8.2	100	10 min	83.8–96.6	4.8	0.0091	[6]
CPE-HPLC	Triton X-114	/	45	35 min	96.4–104.0	1.2	7.5	[7]
SPE-ICP-MS	Monolithic capillary columns	2.15*	/	10 min	91–108	3.7	0.9	[31]
Online-SPE-ICP-AES	Chelating resin	/	/	9.4 min	99–103	/	0.08	[32]
SPE-FAAS	Organic polymers	1.42	47.3	10 min	90.5–108.3	2.34	0.84	[33]
SPE-ICP-MS	Chromium(III)-imprinted silica gel	30.5	40	2 mL min^{-1}	/	4.44	0.004	[34]
DMSPE-FAAS	Amino-functionalized Fe_3O_4/SiO_2	/	27	/	94.8–103.5	3.7	10.5	[35]
SPE-ICP-MS	Carboxylic-mesoporous silica	57.67	25	15 min	91.9–103	1.0	0.02	This wok

Unit of adsorption capacity: mg g^{-1}; *μg cm^{-1}.

Table 4
Determination of chromium species in environment water samples (n = 4).

Sample	Spiked (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Rain	0	0	0.042 ± 0.003	0.053 ± 0.007	–	–
	0.3	0.3	0.325 ± 0.006	0.347 ± 0.005	95.0	98.3
	0.6	0.6	0.629 ± 0.005	0.623 ± 0.004	98.0	95.4
Lake	0	0	0.079 ± 0.005	0.069 ± 0.004	–	–
	0.3	0.3	0.353 ± 0.003	0.360 ± 0.008	93.1	97.6
	0.6	0.6	0.684 ± 0.007	0.615 ± 0.003	101	91.9
River	0	0	0.073 ± 0.006	0.065 ± 0.004	–	–
	0.3	0.3	0.368 ± 0.003	0.376 ± 0.006	98.7	103
	0.6	0.6	0.686 ± 0.004	0.671 ± 0.005	102	101

(VI) was calculated by subtraction from the total chromium. The analytical results are given in Table 4. For spiked water samples, the supernatants were collected for detecting Cr(VI) in sample solution by ICP-MS after Cr(III) was adsorbed. As can also be seen in Table 4, the recoveries of chromium by addition-recovery method in the rain, lake and river water samples were between 91.9% and 103%, which demonstrated that the determination of chromium in environmental samples could be achieved by the proposed methods.

4. Conclusion

In this work, homemade carboxyl-group functionalized mesoporous silica by one-pot co-condensation method was firstly utilized as SPE adsorbent for the separation of chromium species. Based on the fact that Cr(III) can be selectively uptaken by sorbent with electrostatic forces and chelation in a wide range of pH, while Cr(VI) can not, the separation between Cr(III) and Cr(VI) was realized without any aggressive pretreatment. In addition, the captured Cr(III) can be eluted by using HNO_3 and detected by ICP-MS, and concentration of Cr(VI) was the difference between the total chromium and Cr(III). This protocol has been successfully applied to detect inorganic chromium species in environmental waters (rain, lake and river waters) with the recoveries between 91.9% and 103%. Therefore, our developed method exhibited good potential for the speciation of chromium in environmental water samples.

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Conflict of interest

The authors declare that they have no conflict of interest.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.11.043.

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