Chromate surface-imprinted silica gel sorbent for speciation of Cr in surface waters

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Abstract: This study is focused on the synthesis of chromate anion imprinted sorbent supported on silica gel for nonchromatographic Cr speciation in surface waters. The preparation procedure is based on grafting of 3-methyl-1-trimethoxysilylpropylimidazolium, preliminarily coordinated to CrO_4^{2-} as a template ion, onto the surface of silica gel. Sorption and desorption characteristics of surface-imprinted sorbent toward Cr(III) and Cr(VI) were examined by batch solid-phase extraction. An excellent separation of Cr(VI), selectively retained on the sorbent, from Cr(III) remained in the solution, was achieved at pH 2–3 for 20 min. A freshly prepared mixture of ascorbic acid and nitric acid was selected as the most efficient eluent for quantitative desorption of the retained Cr(VI). An analytical procedure for Cr speciation in surface waters was developed and validated through analysis of certified reference materials. Detection limits achieved and relative standard deviations for typical concentration levels of Cr(VI) in surface waters matched the requirements of analytical procedures used in monitoring programs.

Key words: Chromate anion surface-imprinted sorbent, chromium speciation, solid-phase extraction, surface waters

1. Introduction

Nowadays, it is commonly accepted that many elements can naturally exist in the environment under various chemical forms with considerably different properties and behaviors in the environment, which results in substantial distinctions in their toxicity, mobility, and bioavailability. Undoubtedly this means that determination of total element concentrations is generally not sufficient for comprehensive clinical and environmental considerations. Therefore, speciation analysis has reasonably become an important topic of present-day analytical research.

During the recent years, one of the most investigated problems is the speciation analysis of chromium, mainly because of the totally contrasting physiological effects of its predominantly existing chemical forms, i.e. Cr(III) and Cr(VI). The former is identified as an essential nutrient for humans, required for glucose and fats metabolism,[1] while the latter and its compounds are definitely recognized as carcinogenic and mutagenic substances.[2]

From a practical point of view, application of expensive and complicated hyphenated methods such as chromatographic separation followed by ICP-MS measurement might be replaced by simple offline quantitative separation of Cr species followed again by instrumental measurement. Solid-phase extraction (SPE) is a widely used separation technique that offers several significant benefits such as low solvent consumption,

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high enrichment factors, fastness, simple operation in batch and column modes, good reproducibility, and relatively low cost compared to other methods.[3] Furthermore, the correct selection of a suitable sorbent is very important because reliable species separation is a crucial stage of each successful SPE procedure. A large variety of materials were proposed as effective sorbents in nonchromatographic speciation analysis of chromium, e.g. nanosized TiO_2[4−6], silver nanoparticles[7], graphene oxide[8], single-walled[9] and multiwalled carbon nanotubes,[10−12] ion-imprinted polymers,[13−17] functionalized polymeric sorbents,[18−25] Fe_3O_4 coated with ZrO_2,[26] Al_2O_3,[27,28] and chitosan.[29] It might be accepted that, from an analytical point of view, sorption and enrichment of more toxic Cr(VI) is a preferable step of SPE procedures for Cr speciation, especially in surface waters.

In the present study, we report on the synthesis of chromate surface-imprinted silica gel sorbent prepared by grafting of 3-methyl-1-trimethoxysilylpropylimidazolium chloride onto the surface of silica gel particles and its further application for chromium speciation analysis. The imprinting process was carried out in the presence of chromate anion as a template, which further ensures high selectivity toward Cr(VI). The optimal chemical conditions for separation and enrichment of Cr(VI) were defined. The analytical procedure for Cr(VI) determination in surface waters was developed and validated through analysis of certified reference materials.

2. Results and discussion

2.1. Synthesis and characterization of chromate surface-imprinted silica gel sorbent

The synthesis of chromate anion surface-imprinted silica gel sorbent (Cr(VI)-SIS) via a multistep procedure is described in Section 3.3 and shown in Figure 1. After successful leaching of Cr(VI) from the surface of the synthesized sorbent, some specific binding sites with functional groups in a predetermined orientation and cavities with special size of CrO_4^{2-} were formed. Nonimprinted sorbent (NIS) is synthesized in the same way as described above, in the absence of template.
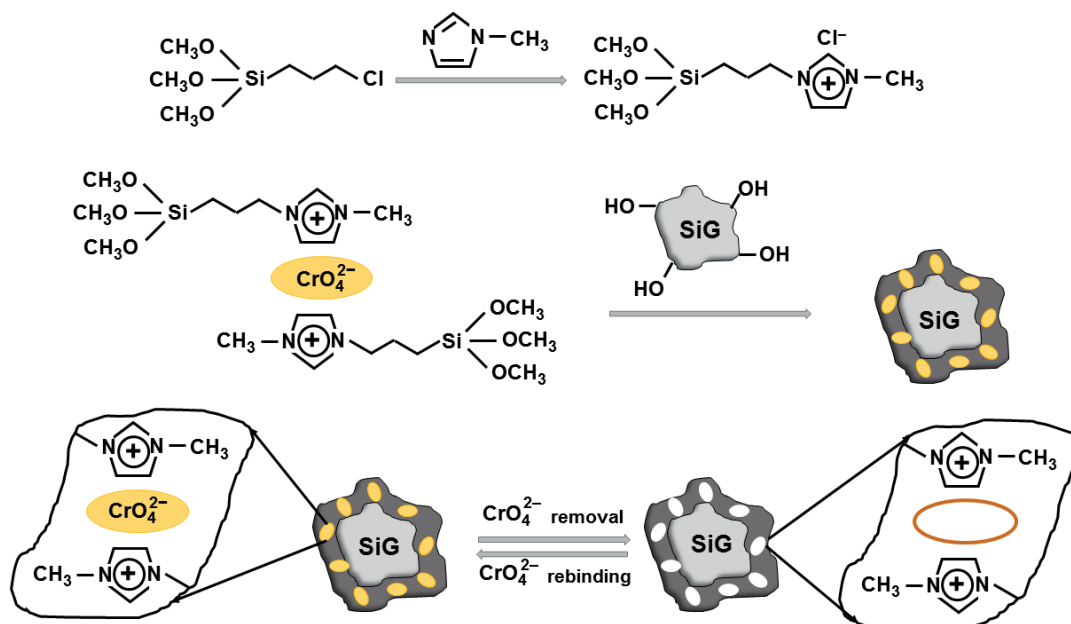

Figure 1. Schematic illustration of preparation process of Cr(VI)-SIS.

To evaluate the degree of 1-methylimidazole incorporation, the elemental analysis of the synthesized Cr(VI)-SIS was performed. The obtained results, 8.32 wt. % C and 2.44 wt. % N (for Cr(VI)-SIS) and 7.27 wt. % C and 1.84 wt. % N (for NIS), suggested that 1-methylimidazole was successfully introduced onto the silica gel surface. The content of 1-methylimidazole units/groups in Cr(VI)-SIS was calculated as 0.87 mmol per gram of the dry sorbent.

2.2. Optimization of Cr(VI) separation procedure

2.2.1. Effect of pH on sorption efficiency of Cr(VI)-SIS

Sorption affinity of Cr(VI)-SIS particles toward Cr(III) and Cr(VI) strongly depends on the pH of the aqueous media first because of their surface properties and second because of the different Cr species' distributions under acidic and basic conditions. The optimal pH value for quantitative separation of Cr species was defined by batch experiments carried out in a pH range between 1 and 8. The results obtained, presented in Figure 2, showed quantitative retention of Cr(VI) on Cr(VI)-SIS particles in nearly the whole investigated pH range (2–6) because both anionic $HCrO_4^-$ and CrO_4^{2-} are electrostatically attracted by the positively charged methylimidazolium groups. The degree of sorption of Cr(III) is below 5% at lower pH values and tends to increase after pH 4. This behavior of Cr(III) might be explained by the presence of free silanol groups on the surface of silica gel, which are deprotonated at pH levels higher than 5 and could retain the positively charged Cr(III) ions, i.e. Cr^{3+}, $Cr(OH)_2^+$, and $Cr(OH)^{2+}$.[30] Accordingly, the range of pH 2–3 was selected as optimal for quantitative separation of Cr(VI) from Cr(III).
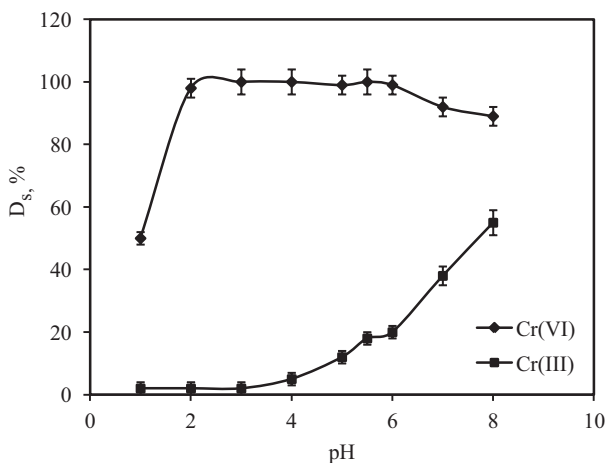

Figure 2. Dependence of the degree of sorption (D_S , %) on pH.

The kinetics of sorption was investigated under optimal conditions (pH 2–3); as the sorbent 50 mg of Cr(VI)-SIS particles was mixed with 10 mL of aqueous solution, containing 2 μg of Cr(VI), and then vigorously shaken for 40 min. Aliquots (0.2 mL) of the supernatant solution were recurrently removed and Cr was measured by electrothermal atomic absorption (ETAAS). Results obtained showed that retention of Cr(VI) is a relatively fast process and 20 min is completely enough to achieve quantitative sorption.

2.2.2. Capacity and adsorption isotherms

The experimental adsorption capacity (Q) of the Cr(VI)-SIS was determined after saturation of the sorbents with chromate anions under optimum conditions at room temperature (Figure 3). For this purpose, increasing amounts (2–30 μg) of Cr(VI) anions were added to 50 mg of sorbent and the equilibrium chromium concentration after adsorption was measured by flame atomic absorption spectrometry (FAAS). The sorption capacity Q was calculated using the following equation:
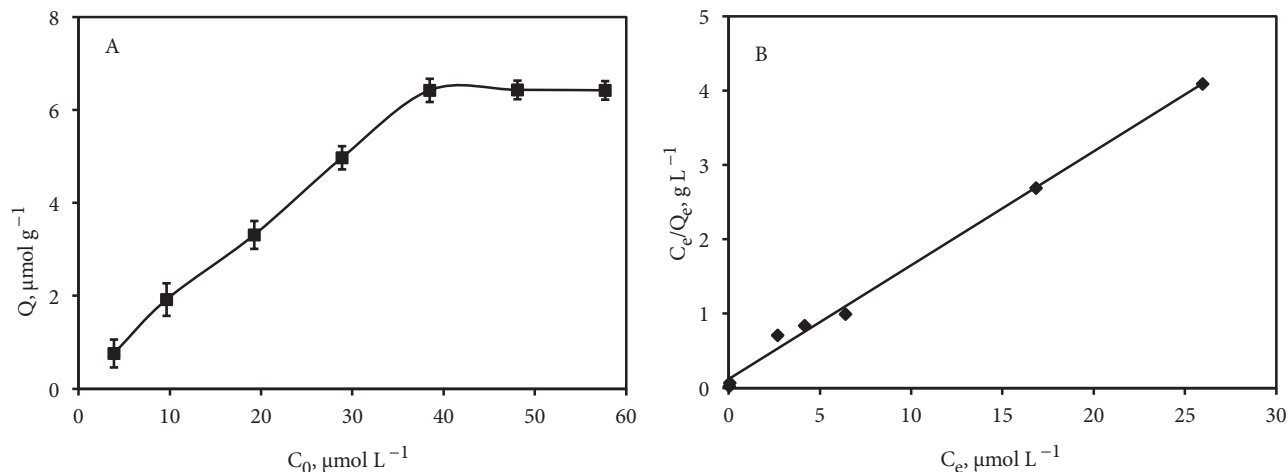

Figure 3. Experimental adsorption capacity of Cr(VI) onto Cr(VI)-SIS (A) and the fitting curve of the Langmuir adsorption isotherm (B). Experimental conditions: pH 3, sorption time 20 min, temperature 25 $^\circ$C.

$$Q = [(C_0 - C_e) \times V]/m, \tag{1}$$

where Q is the mass of chromate anions adsorbed per unit mass of the sorbent, μmol g^{-1}; V is the volume of the solution, L; m is the mass of the sorbent, g; and C_0 and C_e are the initial and equilibrium concentrations after adsorption of the chromium anions in aqueous solution, respectively, μmol L^{-1}.

The results presented in Figure 3A show that the amount of chromate anions adsorbed per unit mass of Cr(VI)-SIS increased with the initial concentration of Cr(VI) and reached plateau values, determining the adsorption capacity values. The experimentally determined Q was 6.42 μmol Cr(VI) per gram of Cr(VI)-SIS.

A Langmuir isotherm model was used for curve-fitting of derived adsorption data. According to the Langmuir isotherm theory the sorption process occurs in a surface monolayer of homogeneous sites, the number of which is fixed.[31] The expression of the linearized Langmuir isotherm (Eq. (2)) is:

$$C_e/Q_e = C_e/Q_{max} + 1/(b \times Q_{max}), \tag{2}$$

where C_e is the equilibrium concentration of chromate anions in the solution, μmol L^{-1}; Q_e is the adsorption capacity of the adsorbed chromium ions onto the sorbents at equilibrium, μmol g^{-1}; Q_{max} is the maximum adsorption capacity, μmol g^{-1}; and b is the Langmuir constant that relates to the affinity of binding sites, L μmol^{-1}. Calculated coefficients of the Langmuir model for the isotherms as presented in Figure 3B were $Q_{max} = 6.54$ μmol g^{-1} and b = 1.18 L μmol^{-1} and the obtained regression coefficient was $R^2 = 0.992$. The high R^2 value achieved for the adsorption of chromium anions onto Cr(VI)-SIS shows that the Langmuir

equation gives a good mathematical fit to the adsorption isotherm. The experimental value of sorption capacity, determined according to the procedure described in Section 3.5, was 6.42 μmol g^{-1} sorbent, very close to the value calculated by the Langmuir model (Eq. (2)). The determined sorption capacity of NIS sorbent was 4.75 μmol g^{-1} sorbent, around 25% lower than that obtained for imprinted particles.
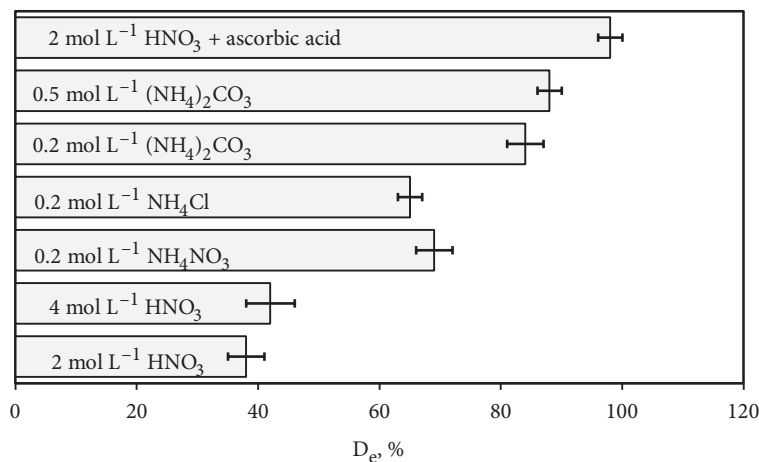

Figure 4. Effect of various eluents on the degree of desorption (D$_e$, %) of Cr(VI).

2.2.3. Elution study

Taking into account that the separation of Cr species is based on electrostatic interactions, various solutions were tested as appropriate eluents for quantitative desorption of Cr(VI). The initial idea was that elution of Cr(VI) could be realized by ion exchange, but the results obtained were unsatisfactory (Figure 4). The highest degree of elution achieved by using $(NH_4)_2CO_3$ as an ion exchanger was a little over 80%. A possible explanation for the superiority of $(NH_4)_2CO_3$ over the other ion exchangers used could be the stronger competitive action of the doubly charged carbonate anions at pH 9–10, even though quantitative elution was not acquired.

A suitable alternative to overcome this obstacle was elution based on reduction of Cr(VI) to Cr(III). For this purpose, ascorbic acid was used as a mild and environmentally friendly reducing agent. It was experimentally verified that Cr(VI) was entirely eluted (D$_e$ > 98%) with a freshly prepared solution of ascorbic acid (3 mmol L^{-1}) in 2 mol L^{-1} HNO$_3$.

Kinetics of the elution process was studied after the loading of the sorbent with 10 μg of Cr(VI) and subsequent elution with 10 mL of 3 mmol L^{-1} ascorbic acid in 2 mol L^{-1} HNO$_3$ for 10–40 min. Aliquot samples (0.2 mL) were taken and measured by ETAAS. The results showed that 20 min of elution time ensured quantitative elution of retained Cr(VI).

2.3. Effects of competitive ions

The separation of Cr species is a result of electrostatic attraction between Cr(VI), i.e. HCrO$_4^-$, and the positively charged methylimidazolium groups. In this regard, the extent of possible interferences of other anions, e.g. SO$_4^{2-}$, HCO$_3^-$, Cl$^-$, PO$_4^{3-}$, or HPO$_4^{2-}$, on the extraction efficiency of Cr(VI)-SIS particles toward Cr(VI) has to be evaluated. Results obtained from interference studies and SPE experiments performed according to the optimized chemical conditions (Section 3.6) are shown in Table 1. As far as examined anions exist at various

concentration levels in surface waters, known amounts of Cr(VI) were also directly spiked in several spring, river, and mineral water samples (previously acidified to pH 2–3 by addition of HNO$_3$) and the SPE procedure was carried out under the optimized chemical conditions. Recoveries obtained for Cr(VI) for all studied samples were in the range 97%–99%, with relative standard deviations (RSDs) of less than 7%, which can be accepted as evidence for the absence of matrix interferences on the extraction efficiency of Cr(VI)-SIS sorbent toward Cr(VI) in real samples with relatively low mineralization. However, the degree of sorption of Cr(VI) in the presence of Black Sea water varied between 55% and 60%, which means that highly mineralized samples should be preliminarily diluted in order to remove matrix interferences from high concentrations of SO$_4^{2-}$ and Cl$^-$ in sea water. The same is valid for mineral waters with very high mineralization.

Table 1. Degree of sorption of Cr(VI) in the presence of different concentrations of anions and real samples (procedure described in Section 3.6).

Anion	Concentration, mg L^{-1}	Degree of sorption, %
Cl$^-$	1000	93 ± 3
	5000	91 ± 3
	10,000	63 ± 7
NO$_3^-$	1000	95 ± 3
	5000	90 ± 3
	10,000	53 ± 8
SO$_4^{2-}$	1000	92 ± 3
	5000	91 ± 4
	10,000	54 ± 6
H$_2$PO$_4^-$	500	92 ± 3
	2500	91 ± 4
	5000	53 ± 7
H$_2$CO$_3$/HCO$_3^-$	1000	94 ± 2
	5000	91 ± 3
	10,000	90 ± 3
Black Sea water	1:2 diluted	90 ± 4
	1:1 diluted	89 ± 4
	Nondiluted	51 ± 8
River Beli Iskar	Nondiluted	93 ± 3
Spring water	Nondiluted	94 ± 3
Tap water (Sofia)	Nondiluted	95 ± 3

The batch-to-batch reproducibility of the synthesis of Cr(VI)-SIS was tested by using sorbents prepared independently from different batches. The relative standard deviation of the degree of sorption of 0.2 μg mL^{-l} Cr(VI) with different sorbents was 4%, which confirms very good reproducibility of the applied synthesis procedure. Experiments performed showed that Cr(VI)-SIS particles can be used for at least 50 sorption/desorption cycles without significant loss of extraction efficiency.

2.4. Analytical figures of merit and applications to real samples

The accuracy and precision of the developed SPE procedure has been evaluated by the analysis of parallel samples of procedural blank (5 parallel blanks, containing 10 mL of Milli-Q water and 50 mg of Cr(VI)-SIS particles) and certified reference material Chromium VI-WS (Fluka) (5 parallel solutions of 10 mL of CRM and 50 mg of Cr(VI)-SIS particles). Results obtained (Table 2) were used for the calculation of the limit of detection

(LOD, 3σ criteria), quantification limits (LOQ, 10σ criteria), and RSD (%) for studied concentration levels. For the validation of the developed procedure, a CRM, Chromium VI-WS in sea water after 100 dilutions, was additionally analyzed. The results obtained (Table 1) were in reasonable agreement with the certified values (Student t-test, 95% confidence limit), which indicates the absence of systematic errors and confirms the validity of the proposed analytical method for selective determination of Cr(VI) in various types of surface waters. The developed SPE procedure was applied for the determination of Cr(VI) in real surface waters. The content of Cr(VI) in Black Sea water is relatively low and varied between 0.1 and 0.3 μg L^{-1}. For the rivers Iskar and Beli Iskar, at unpolluted monitoring sites, levels of Cr(VI) are between 0.2 and 0.5 μg L^{-1}, and for several mineral waters levels of Cr(VI) varied from $<$LOD to 0.2 μg L^{-1}.

Table 2. Analysis results, mean $\pm$ SD, μg L^{-l}.

Sample	Certified value, μg L^{-l}	Found, μg L^{-l}	RSD, %	Recovery, %
CRM Chromium VI-WS	19.5 ± 0.221	19.32 ± 0.57	3	98 ± 2
CRM Chromium VI in sea water	450 ± 13.9	438 ± 0.13	2	97 ± 3

LOD: 0.02 μg L^{-l}; LOQ: 0.06 μg L^{-l}.

2.5. Conclusions

Sorbent based on surface Cr(VI)-imprinted silica gel has been characterized for selective and efficient SPE of Cr(VI) and incorporated into an analytical procedure developed for Cr speciation in surface waters. The synthesis procedure for sorbent preparation and the enrichment procedure for Cr(VI) selective determination are simple and easy to perform. The analytical characteristics (LOD, LOQ, RSD) meet the requirements of European Directive 2009/90/EC, which renders analytical procedures applicable to river basin monitoring programs.

Comparison of the proposed method with some other methods and strategies for Cr speciation (employing also nanomaterials as sorbents) is presented in Table 3. It is worth mentioning that the detection limits achieved depend on the instrumental method used and direct comparison of different procedures with different measurement methods is often misleading. The value of the enrichment factor is typically in relation with the measurement method and sorbent properties; however, sample throughput has also been taken into account. It can be seen from Table 3 that the proposed analytical method for selective determination of Cr(VI) ensures detection limits that are close to those of methods employing ETAAS as measurement method and fit well with environmentally relevant concentrations of Cr in surface waters, even at background levels in unpolluted sites.

3. Experimental

3.1. Reagents

The stock standard solutions for Cr(VI) and Cr(III) (1000 μg mL^{-1}) were Titrisol (Merck, Darmstadt, Germany) in 2% HNO$_3$. Silica gel 60 (Merck), 1-methylimidazole (MIA), (3-chloropropyl)trimethoxysilane (CPTMS) (Sigma-Aldrich, Munich, Germany), and methanol (Labscan, Dublin, Ireland) were used to prepare the Cr(VI)-SIS. Certified reference materials used for method validation were Chromium VI-WS, Fluka, LOT: 01453; and Cromium VI in sea water, Fluka, Lot: LRAA8706. All reagents were of analytical-reagent grade and all aqueous solutions were prepared in high-purity water (Milli-Q, Millipore Corp., Milford, MA, USA).

Table 3. Comparison of analytical procedures for Cr(III)/Cr(VI) speciation.

Species	Sorbent	Instrumental method	Sample	LOD, µg L^{-1} /Enrichment factor	Ref.
Cr(III) Cr(VI)	Nanometer-sized TiO_2 microcolumn	ICP-OES	Water	0.32/50	4
Cr(III) Cr(VI)	Nanometer-sized TiO_2 immobilized on silica gel	ICP-OES	Water	0.22 Cr(III)/50	5
Cr(III) Cr(VI)	Nanometer-sized TiO_2	FI ETAAS	Drinking water	0.01 Cr(VI) 0.006 Cr(III)	6
Cr(III) Total Cr	Ag-NPs CPE by Triton X-114	ETAAS	Water Beer, wine	0.002 Cr(III)	7
Cr(VI) Cr(III)	Graphene oxide, decorated with magnetite modified with triethylenetetramine	FAAS	Tannery waste water River water Industry water	1.4 Cr(VI) 1.6 Cr(III)	8
Cr(III) Cr(VI)	SWCNTs, oxidized	ICP-MS	Natural water Waste waters	0.01 Cr(III) 0.024 Cr(VI)	9
Cr(III)	MWCNTs, oxidized with conc. HNO_3	FAAS	Natural water	1.15 Cr(III)/22	10
Cr(III)	MWCNTs, impregnated with D2EHPA	ICP AES	Tap and well water Industrial waste water	0.05 Cr(III)/60	11
Cr(VI)	MWCNTs, APDC	FAAS	River water Waste and tannery water	0.9 Cr(VI)	12
Cr(III) Cr(VI)	Cr(III)–pyrrolidinedithiocarbamate complex/acrylamide/ethylene glycol dimethacrylate	ETAAS	Tap and river water Municipal sewage	0.018 Cr(III)	13
Cr(III) Cr(VI)	Cr(III)-8-hydroxyquinoline/styrene/divinylbenzene	FAAS	CRM of waste water	7.0 Cr(III)	14
Cr(III) Cr(VI)	Cr(III)/3-(2-aminoethylamino) propyltrimethoxysilane (on silica gel)	ICP-MS	ICP-MS	4.43 ng L^{-1} Cr(III)	15
Cr(III)Cr(VI)	Cr(III)/3-aminopropyl-triethoxysilane/tetraethyl-orthosilicate on silica gel	ICP-AES	Lake water Tap water	0.11 Cr(III)	16
Cr(III) Cr(VI)	Cr(III)/3-aminopropyl-triethoxysilane on SBA-15	ICP-AES and UV-Vis	Plating and leather wastewater	0.53 Cr(III)	17
Cr(III) Cr(VI)	poly-N-(4-bromophenyl)-2-methacryl-mide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzeneP-3 resin	FAAS	Tap water Lake water Spring water Wastewater	1.58 Cr(III)/100	18
Cr(III)	poly(N,N'-dipropionitrile methacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propanesulfonic acid) resin	FAAS	Water Food samples	1.1 Cr(III)	19
Cr(III) Cr(VI)	β-Cyclodextrin cross-linked polymer	ETAAS	Environmental waters	0.056 Cr(III)/25	20
Cr(III) Cr(VI)	poly(1,3-Thiazol-2-yl methacrylamide-co-4-vinyl pyridine-co-divinylbenzene)	FAAS	Stream water Wastewater	2.4 Cr(VI)/30	21
Cr(III) Cr(VI)	Poly(methacrylic acid) and poly(vinylimidazole) cross-linked with ethylene glycol dimethacrylate	FAAS	Tap water Mineral water Lake water	0.84 Cr(III)/47.3 2.81 Cr(VI)/8.6	22

Table 3. Continued.

Species	Sorbent	Instrumental method	Sample	LOD, µg L^{-1} /Enrichment factor	Ref.
Cr(III) Cr(VI)	N,N-bis(2-aminoethyl)ethane-1,2-diamine functionalized poly(chloromethyl styrene-co-styrene) adsorbent	HPLC ICP-MS	Waste water	0.0068 Cr(VI)/105 0.0041 Cr(III)/128	24
Cr(III) Cr(VI)	Fe$_3$O$_4$@ZrO$_2$	FAAS	Environmental samples Biological samples	0.69 Cr(III)/25	26
Cr(III) Cr(VI)	Fe$_3$O$_4$@Al$_2$O$_3$ modified by surfactant Triton X-114	FAAS	Water Soil	1.4-3.6 Cr(III) for waters 5.6 for soil	27
Cr(III) Cr(VI)	Fe$_3$O$_4$@Al$_2$O$_3$	FAAS	Water Waste water	0.083 Cr(III)/140	28
Cr(III) Cr(VI)	Chitosan-modified Fe$_3$O$_4$ nanoparticles	ICP-OES	Waters	0.02 Cr(III)/100 0.03 total Cr	29
Cr(VI)	Chromate surface-imprinted silica gel sorbent	ETAAS	Surface waters	0.02 Cr(VI)	This work

3.2. Apparatus

The FAAS/ETAAS measurements were carried out with a PerkinElmer Model AAnalyst 400 atomic absorption spectrometer equipped with an HGA 900. Instrumental parameters for FAAS measurements, in air/acetylene flame, were optimized according to the instrument manual. For ETAAS measurements pyrolytically coated graphite tubes were used as atomizers and sample solutions (10–20 µL) were introduced into the graphite furnaces using the PerkinElmer AS 800 autosampler. All measurements were carried out with at least three replicates and based on integrated absorbance. Optimal instrumental parameters for ETAAS measurements were defined according to the manufacturer's recommendations for Cr, e.g., pretreatment temperature 1100 °C and atomization temperature 2500 °C.

Elemental analysis was performed using the Euro EA CHNS-O elemental analyzer (EuroVector, Redavalle, Italy).

An EBA 20 centrifuge (DJB Labcare Ltd., Buckinghamshire, UK) was used to separate modified silica and extracted metal solution in batch experiments.

A microprocessor pH-meter (Hanna Instruments, Póvoa de Varzim, Portugal) was used for pH measurements.

3.3. Synthesis of the chromate anion surface-imprinted sorbent

The synthesis scheme of chromate anion surface-imprinted sorbent involves several steps (Figure 1). i) Silica gel (SiG) surfaces were first activated by refluxing 10 g of silica gel with 80 mL of 6 mol L^{-1} hydrochloric acid under stirring for 8 h. Activated silica gel (aSiG) was filtered and washed with deionized water to neutral reaction and then dried under vacuum at 60 °C for 8 h. ii) The synthesis of 1-(trimethoxysilylpropyl)-3-methylimidazolium chloride ([TMSP-MIA]Cl) was adapted from the procedure reported by Valkenberg et al.[32] A mixture of 1-methylimidazole (2.84 g, 34.5 mmol) and 3-(chloropropyl)trimethoxysilane (6.86 g, 34.5 mmol) was stirred and refluxed under nitrogen flow at 70 °C for 48 h. The resulting liquid product was extracted twice with ether

and then dried under vacuum at room temperature. The final compound [TMSP-MIA]Cl was obtained as a yellow viscous liquid. iii) To prepare a chromate anion complex with [TMSP-MIA]Cl, 0.456 g of ammonium chromate was dissolved in 30 mL of methanol containing 0.150 mg NaOH (used to prevent the reduction of Cr(VI) in methanol) and 1.689 g of [TMSP-MIA]Cl was added to this solution. The complex formation was carried out for 1 h at room temperature with continuous stirring. iv) Afterward, to prepare the chromate anion surface-imprinted sorbent, this solution was gradually added to activated silica gel (1.0 g) dispersed in methanol (10 mL) in a flask of total volume of 100 mL. The suspension was refluxed with stirring for 24 h. The obtained product was recovered by filtration and washed with methanol to remove the residual [TMSP-MIA]Cl. Chromium anions were removed from the sorbents by several sequential elution steps using 4 mol L^{-1} nitric acid and 3 mmol L^{-1} ascorbic acid as eluents. This procedure was repeated until the Cr concentration (template ions) in the washing solution was below the LOD as measured by ETAAS. Finally, the prepared material was dried under vacuum at 60 °C for 8 h.

3.4. Sorption/elution studies

Model experiments were carried out using 10.00 mL of aqueous standard solution, containing 2 μg ($A_{initial}$) of Cr(VI) or Cr(III) and 50 mg of Cr(VI)-SIS in polypropylene centrifuge tubes. The pH of these solutions was varied in the range of 1–8, using HNO$_3$ or NH$_4$OH. The mixture was shaken on an electric shaker for 20 min and then centrifuged at 5000 rpm for 20 min. The supernatant, as an effluate, was removed and Cr content (A_{end}, μg) was determined by FAAS. The degree of sorption (D_s) was defined as D_s, $\% = ((A_{initial} - A_{end})/A_{initial}) \times 100$.

The Cr(VI)-SIS after sorption was washed with deionized water and retained Cr was eluted from the sorbent particles for 20 min with 3 mL of various elution solutions. After centrifugation Cr content in the eluate solution (A_{el}, μg) was measured by FAAS. The degree of elution ((D_e) was defined as D_e, $\% = (A_{el}/A_s) \times 100$, where A_s is Cr content retained on the sorbent.

3.5. Sorbent capacity

The total sorption capacity (mg Cr(VI) g^{-1} sorbent) of the synthesized Cr(VI)-SIS was determined by shaking model solutions of Cr(VI) with increasing concentration with 50 mg of sorbent for 20 min at optimal sorption pH level of 3. The amount of Cr in the effluate was determined by ETAAS.

3.6. Analytical procedure for Cr(VI) and Cr(III) determination in surface waters.

The water samples were filtered through 0.45-μm membrane filters on site during sampling and acidified with 1 mL of 1 mol L^{-1} HNO$_3$ per 100 mL of sample, before transportation to the laboratory.

3.6.1. Determination of total Cr

Total Cr content in water sample was determined by ETAAS under optimized instrumental parameters.

3.6.2. Determination of Cr(VI)

The water sample of 20 mL was directly (if acidified during sampling or acidified before analysis to pH 2–3) mixed with 50 mg of sorbent Cr(VI)-SIS and the suspension was shaken for 20 min. After centrifugation for 10 min, the supernatant was discarded, the sorbent was washed with deionized water, and then 1 mL of the eluate

solution (3 mmol L^{-1} ascorbic acid in 2 mol L^{-1} HNO_3) was added. The suspension was shaken for 20 min and after centrifugation Cr(VI) was determined in the eluate solution by ETAAS under optimized instrumental parameters.

3.6.3. Determination of Cr(III)

If necessary, Cr(III) content could be simply calculated as a difference between both measurements for total Cr and Cr(VI).

Acknowledgment

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