

Speciation, selective extraction and preconcentration of chromium ions via alumina-functionalized-isatin-thiosemicarbazone

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Abstract

A method is presented and described for speciation, extraction and preconcentration of Cr(III) and Cr(VI) based on dynamic and static solid phase extraction techniques. Three newly designed alumina phases-physically adsorbed-isatin-thiosemicarbazone (I–III) were synthesized, characterized, tested for stability and applied as inorganic ion exchangers and chelating solid sorbents for various metal ions. The selectivity characteristics incorporated into these alumina phases were studied and evaluated via determination of the distribution coefficients and separation factors of chromium species versus other interacting metal ions. Quantitative recovery of Cr(VI) was accomplished by alumina phases (I–III) in pH 1.0 giving percentage extraction values of ~99.9–100.0%, while Cr(III) was found to be quantitatively recovered by these sorbents in pH 7.0 leading to percentage extraction values ~100.0% with minimal or no interference between these two species under the studied buffering conditions. Selective solid phase speciation and preconcentration of Cr(III) and Cr(VI) in various real water samples were successfully performed and accomplished by newly designed alumina phases (I–III) via a preconcentration micro-column.

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1. Introduction

Toxic heavy metal ions are among the major sources of environmental pollution especially in water resources. Chromium is a typical element characterized by its existence in different oxidation species that show opposite levels of toxicity to the environments as well as humans, animals and plants. Two oxidation states of chromium, Cr(III) or trivalent chromium and Cr(VI) or hexavalent chromium, are known. Hexavalent chromium is a highly toxic species due to its oxidizing power of organic and inorganic species in human body leading to a direct impact on lung, liver and kidney. Hexavalent chromium is designated also as a carcinogenic suspect agent by the U.S. EPA and directly related to some diseases that are ranging from dermatitis to lung and kidney cancer [1,2]. The major hexavalent chromium pollution sources are directly related to the industrial activities including electroplating, steel, and textile industries as

well as cooling towers, tanning and oxidative dyeing industries with hexavalent chromium being transferred to the environments through waste water release [3]. On the other hand, trivalent chromium is known as an essential trace elemental species for stabilization and activation of a number of biologically important compounds including enzymes, proteins and nucleic acids as well as for proper metabolism of carbohydrates, lipids and proteins [4]. Moreover, trivalent chromium in moderate concentrations is an essential nutrient for good human health and the link between chromium (III) and insulin function was significantly reported in metabolic research [5,6]. In addition to its existence in two main oxidation states, chromium occurs in the aquatic environment at the nanogram per milliliter levels or lower.

At present few analytical techniques with sufficient sensitivity and selectivity are available for the direct determination of such nanogram per milliliter levels of total chromium in water samples. However, some forms of preliminary separation and preconcentration are required to determine low levels of individual chromium species by sensitive analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS), flame atomic absorption spectrophotometry (FAAS),

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inductively coupled plasma instrumentations (ICP-OES) [7,8]. Several reports were recently published for determination and speciation of chromium in different samples by applications of various analytical techniques [9–14]. Most of these methods were based on applications of some sorts of solid phase extraction and preconcentration via modified organic phases or resins. These organic solid phase extractors and preconcentrators were experienced with some disadvantages if compared to inorganic modified solid phases such as alumina or silica [15–17].

Solid phase extraction (SPE) and preconcentration are now applied in many fields [18–20]. Several advantages are well known and reported for SPE versus liquid extraction techniques [21,22]. The utilization of SPE is mainly based on either chemical or physical immobilization or adsorption of certain organic compounds on the surface of some solid inorganic or organic solid supports. Selection of the organic compounds and solid supports is usually based on different aimed properties that must be present in the newly designed solid phase extractors and preconcentrators [23–27].

The strong and growing interests in identification of the accurate and real concentration of Cr(III) and Cr(VI) species separately rather than total chromium content are recently aimed and directed the attention of researchers toward chromium speciation. Therefore, it is very important as a starting step to efficiently separate, extract and preconcentrate these two species from their matrices and determine the real concentration of each ion. In this work, we report the immobilization of isatin-thiosemicarbazone as an example of nitrogen, oxygen and sulfur containing chelating compound on the surface of three alumina types for the formation of selective inorganic chelating and ion exchangers for extraction, preconcentration and speciation of chromium ions in various water samples.

2. Experimental

2.1. Instrumentation

IR spectra of the active and modified alumina phases were recorded from KBr pellets by using a Perkin Elmer infrared spectrophotometer, model 1430 and determination of metal ions concentration was performed by a Perkin Elmer flame atomic absorption spectrophotometer, model 2380. The pH-measurement of metal ions and buffer solutions were carried out by an Orion 420A pH-meter calibrated against potassium hydrogenphthalate at pH 4.008. The concentration of chromium (VI) and total chromium was determined by Hach digital UV–vis spectrophotometer, model DR/2010 at $\lambda = 540$ nm.

The electron impact mass spectra of active alumina, isatin-thiosemicarbazone and modified alumina phases (I–III) were carried out by using a Varian MAT 212 mass spectrometer equipped with a direct insertion probe (DIP) in the Institute for Inorganic and Analytical Chemistry, Münster University, Germany. The mass spectra sheets were computerized to give I/Base and its corresponding mass.

2.2. Chemicals and reagents

Three alumina types of analytical grade were used in this work (150 mesh size and 58 Å pore diameter) purchased from Aldrich Chemical Company, USA. The pH values of aqueous suspensions of these three alumina phases were found to have pH 4.0 ± 0.5 , 7.0 ± 0.5 and 9.0 ± 0.5 for acidic, neutral and basic alumina, respectively. Isatin was obtained from Merck-Schuchardt, and purified by recrystallization, mp 203°C , and thiosemicarbazide was purchased from Aldrich Chemical Company, USA. The metal salts are all of analytical grade and purchased from Aldrich Chemical Company, USA and BDH limited, Poole, England.

2.3. Synthesis of alumina phases-physically adsorbed-isatin-thiosemicarbazone (I–III)

Isatin-thiosemicarbazone was synthesized according to the following method. A 0.01-M solution of thiosemicarbazide in 100 ml ethanol/water mixture was prepared under reflux and stirring. A hot solution of 0.01 M-isatin in 100 ml ethanol was then added and the reaction mixture was heated for 5 min to precipitate the product as yellow needles, mp 267°C . Alumina phases-physically adsorbed-isatin-thiosemicarbazone (I–III) were synthesized according to the following procedure. Isatin-thiosemicarbazone (2.2 g, 10.0 mmol) was transferred to a 250 ml flask and dissolved completely in 50 ml of ethyl alcohol. To this solution, a sample of 10.0 ± 0.1 g-alumina, either acidic, neutral or basic, was added and the reaction mixture was further stirred for 6 h. The newly modified alumina phases (I–III) were filtered, washed with 50 ml ethyl alcohol and finally with 50 ml of diethyl ether and allowed to dry in an oven adjusted to 60°C for 8 h. The pH-value of aqueous suspension and color of the modified alumina phases (I–III) are listed in Table 1.

2.4. Stability test of alumina phases (I–III) in different acidic solutions

Alumina phase, 0.5 g, was mixed with 50 ml of different buffer solutions (pH 1–7) in a 100-ml volumetric flask and automatically shaken for 1 h. The solid phase was filtered, washed with a 50 ml portion of the same buffer solution followed by doubly distilled water (DDW) and dried at 70°C . The examined alumina phase, 25.0 ± 1 mg, was then added to a solution containing 9.0 ml of buffer (pH 6.0) and 1.0 ml of 0.1 M-Cu(II) solution and this mixture was then automatically shaken for

Table 1
Physical properties of modified alumina phases (I–III)

pH	Color	Modified alumina phases	Phase
4.7	Yellow	Acidic alumina-physically adsorbed-isatin-thiosemicarbazone	I
5.3	Yellow	Neutral alumina-physically adsorbed-isatin-thiosemicarbazone	II
6.2	Yellow	Basic alumina-physically adsorbed-isatin-thiosemicarbazone	III

30 min by an automatic shaker. The percentage hydrolysis values of alumina phases (I–III) in different buffer solutions were determined from the metal uptake of Cu(II).

2.5. Surface coverage determination

Determination of the surface coverage values of alumina phases (I–III) was performed by thermal desorption method. In this method, 100 ± 1 mg of dry alumina phases (I–III) were ignited in a furnace at 550°C for 1 h and left to cool down at 70°C . The alumina sample was transferred to a desiccators and left to reach the room temperature. The weight loss of isatin-thiosemicarbazone was determined by difference in the sample masses before and after thermal desorption process. Blank samples of alumina phases were also subjected to the same procedure.

2.6. Determination of the distribution coefficient

A concentration of metal ion ($\sim 1.0 \mu\text{g ml}^{-1}$) was prepared and determined by flame atomic absorption spectrophotometry. Alumina phase, 50 mg, was mixed with 50 ml of metal ion in a 100 ml measuring flask. The mixture was shaken for 1 h by an automatic shaker, the solid phase was filtered and the filtrate was subjected to atomic absorption analysis. Standard and blank metal ion solutions were also prepared and measured.

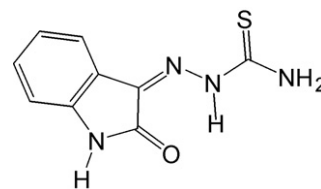
2.7. Determination of the metal sorption capacity

The metal sorption capacity values ($\mu\text{mol g}^{-1}$) of the modified alumina phases for extraction of different metal ions from various buffer solutions were determined in triplicate by the batch equilibrium technique. In this method, 50 ± 1 mg of dry phase was added to a mixture containing 1.0 ml of 0.1-M metal ion solution and 9.0 ml of the selected buffer solution into a 50 ml measuring flask. These flasks were then shaken at room temperature for 30 min by an automatic shaker. The mixture was filtered and washed with 100 ml of DDW. The unbounded metal ion was determined by complexometric EDTA titration and/or flame atomic absorption spectrophotometric analysis.

The effect of shaking time intervals (5, 10, 15, 20, 25 and 30 min) on the values of metal sorption capacity and the percentage extraction was also studied for Cr(III) and Cr(VI) by the batch equilibrium technique according to the following procedure. 50 ± 1 mg of the dry alumina phase was added to a mixture containing 1.0 ml of 0.1 M-metal ion and 9.0 ml of the selected buffer solution. The reaction mixture was then shaken by an automatic shaker for the selected time, filtered, washed with 100 ml-DDW and the unextracted metal ion was determined by flame atomic adsorption analysis.

2.8. Applications of modified alumina phases (I–III) for extraction, preconcentration and speciation of chromium from water samples

Preconcentration of chromium species was performed according to the following procedure. Sample (I) was collected



Scheme 1. Structure of isatin-thiosemicarbazone.

from Alexandria drinking tap water and a 1.0 L sample was spiked with $\sim 5.0 \text{ ng ml}^{-1}$ of Cr(III). The solution was passed over a preconcentration micro-column packed with 100 mg of the modified alumina phases (I–III) with a flow rate of 10 ml min^{-1} under air pressure. The adsorbed Cr(III) on the modified alumina surface was eluted by the flow of 5.0 ml of conc. HNO_3 and determined by flame atomic absorption spectrophotometry. Samples (II) and (III) are dyeing waste water and sea water, respectively. 1.0 L of each sample was used to study the speciation of Cr(III) and Cr(VI) via spiking with $\sim 5.0 \text{ ng ml}^{-1}$ each. The water sample was adjusted to a pH 1.0 and passed over a preconcentration micro-column packed with 100 mg of the modified alumina phases (I–III) with a flow rate of 10 ml min^{-1} under air pressure. The adsorbed Cr(VI) was eluted by 5.0 ml of concentrated HNO_3 as a preconcentration reagent and determined by UV–vis spectrophotometry and flame atomic absorption spectrophotometry.

3. Results and discussion

3.1. Characterization and stability of surface modified alumina phases (I–III)

The 70-eV EI-MS of alumina phases (I–III) were measured by the direct insertion probe as previously reported [24,28]. The structure of isatin-thiosemicarbazone is shown in Scheme 1 and the mass spectrum of this compound was found to exhibit two major peaks at m/z 220 (100%) that are related to the molecular ion peak and m/z 190 (75%) due to a loss of CO^\bullet from the molecular ion. The other detected fragment ion peaks at m/z 177, 160, 145, 119, 117, 104 and 77 can be correlated to simple fragmentation pathways that were generated from the molecular ion. The 70-eV EI-MS of modified alumina phase (I–III) showed few fragment ions at m/z 145, 119, 117, 104 and 77 with low relative abundance ($\leq 3.0\%$). This trend can be correlated to the low percentage of immobilized isatin-thiosemicarbazone on the surface of alumina phases as well as good thermal stability of the modified phases under applied heating conditions by the direct insertion probe [24].

Thermal desorption method [29] was used to determine the surface coverage of modified alumina phases (I–III). In this method, alumina phases were heated in the temperatures range $\sim 500\text{--}600^\circ\text{C}$ and the solid residue corresponds to the stable and dry alumina matrix. The results were then used to calculate the surface coverage values expressed in mmol g^{-1} and percentage as listed in Table 2.

The modified alumina phases (I–III) were tested for their stability in different buffer solutions (pH 1–7) to identify the

Table 2
Stability of modified alumina phases in pH (1–7)

Phase	Thermal desorption mmol g ⁻¹ (%coverage)	Percentage stability (%)						
		pH						
		1.0	2.0	3.0	4.0	5.0	6.0	7.0
I	0.100 (2.2%)	95	84	83	83	86	86	100
II	0.160 (3.5%)	100	87	87	86	88	88	100
III	0.164 (3.6%)	100	97	97	96	96	96	96

possible leaching and/or hydrolysis degree of the organic modifier from the surface. The treated alumina phases were then used to determine the $\mu\text{mol g}^{-1}$ of adsorbed Cu(II). The values of the determined $\mu\text{mol g}^{-1}$ of the hydrolyzed alumina phases were compared with those of the unhydrolyzed phases to calculate the stability percentage for each modified alumina phase in the tested solutions. Table 2 shows the results obtained for the stability towards hydrolysis and/or leaching process of the modified alumina phases (I–III). It is evident that these alumina phases exhibited high stability over the entire pH-range especially modified alumina phase (III).

3.2. Evaluation of the distribution coefficient values

Determination of the distribution coefficient values (K_d) is a direct method for evaluation of the capability of modified alumina phases for extraction of the various metal ions from aqueous and organic solutions and can be used to provide a possible discrimination order between the studied metal ions [30]. This method is successfully applied for very low concentration ranges of metal ion, parts per million ($\mu\text{g ml}^{-1}$) or parts per billion (ng ml^{-1}). Evaluation of the distribution coefficient can lead to a more detailed series of values, which assists in further evaluation of the trends in metal uptake as well as the selectivity properties incorporated in the modified alumina phase. The K_d value is determined from the following equation:

$$K_d (\text{ml g}^{-1}) = \frac{C_{i,\text{ex}} (\mu\text{g g}^{-1})}{C_{i,\text{sol}} (\mu\text{g ml}^{-1})}$$

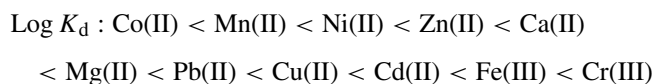
Table 3 compiles $\log K_d$ values for a series of tested metal ions by alumina phases (I–III). It is evident from the values listed

Table 3
 $\log K_d$ -values of metal ions by phases (I–III)

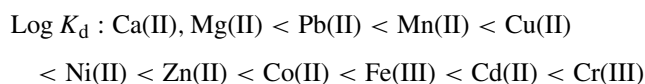
Metal ions	Phase (I)	Phase (II)	Phase (III)
Ca(II)	2.33	2.40	2.27
Mg(II)	2.39	2.40	2.59
Mn(II)	2.12	2.95	2.29
Zn(II)	2.30	3.51	3.57
Ni(II)	2.21	3.40	3.20
Pb(II)	2.82	2.91	3.03
Co(II)	1.08	3.52	3.57
Fe(III)	3.78	3.89	3.29
Cu(II)	3.35	3.33	4.48
Cd(II)	3.51	4.30	4.10
Cr(III)	4.25	5.21	5.22

in Table 3 that Cr(III) is highly extracted by the three newly modified alumina phases providing $\log K_d$ values of 4.25, 5.21 and 5.22 for phases (I), (II) and (III), respectively. The second highest extracted metal ions are Fe(III), Cd(II) and Cu(II) with $\log K_d$ values of 3.78, 4.30 and 4.48 for phases (I), (II) and (III), respectively. Finally, the increasing trends in $\log K_d$ values for tested metal ions by modified alumina phases (I–III) can be outlined in the following orders:

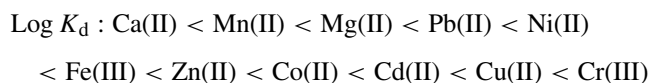
Phase (I)



Phase (II)



Phase (III)



The incorporated selectivity characteristics into newly modified alumina phases (I–III) can be also evaluated and expressed in terms of the separation factor α , which can be derived from the measurements under static or dynamic condition. The separation factor ($\alpha_{A/B}$) [30] of any two species A and B is calculated from the distribution coefficients $K_{d(A)}$ and $K_{d(B)}$, respectively, as given in the following equation:

$$\alpha_{(A/B)} = \frac{K_{d(A)}}{K_{d(B)}}$$

The separation factors of Cr(III) versus other interfering metal ions are calculated and represented in Figs. 1–3 for modified alumina phases (I–III). It is evident from these graphs that excellent separation factors for Cr(III) are attained by the three studied alumina phases.

3.3. The metal sorption capacity values

The process of metal extraction by modified alumina phases is highly dependent on the medium pH. The following series of metal ions were selected to study and evaluate this factor, Mg(II), Ca(II), Mn(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Hg(II), Cu(II), Cr(III), Cr(VI) and Fe(III). This series was examined by alumina phases (I–III) in various solutions of pH 1–7. However, buffer solutions in the basic range were excluded due to precipitation of most metal ions under these buffering conditions. The maximum metal sorption capacity values ($\mu\text{mol g}^{-1}$) under the optimum pH-range are listed in Table 4.

The most highly extracted metal ion is Cr(III) giving sorption capacity values of 760, 760 and 780 $\mu\text{mol g}^{-1}$ by the three newly modified alumina phases (I), (II) and (III), respectively, in buffer solution with pH 7.0. The collected results of this study is consistent and in good agreement with those outlined from

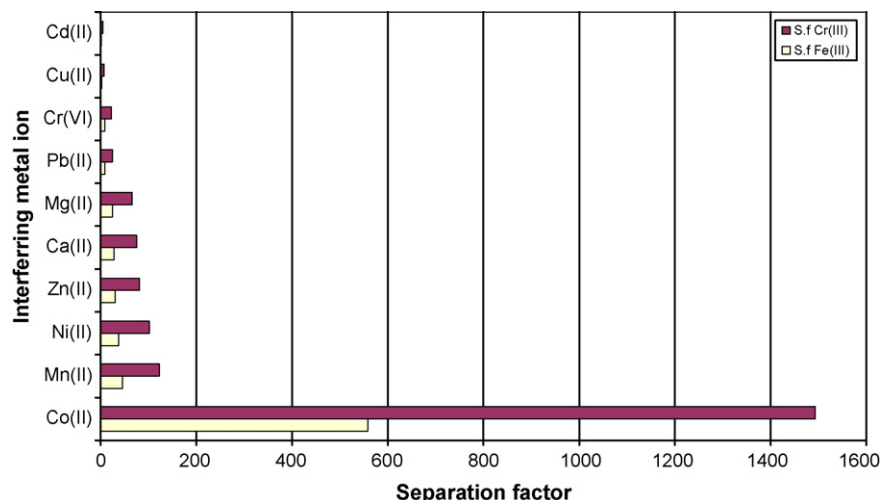


Fig. 1. Separation factors of Cr(III) and Fe(III) versus other interfering metal ions by alumina phase (I).

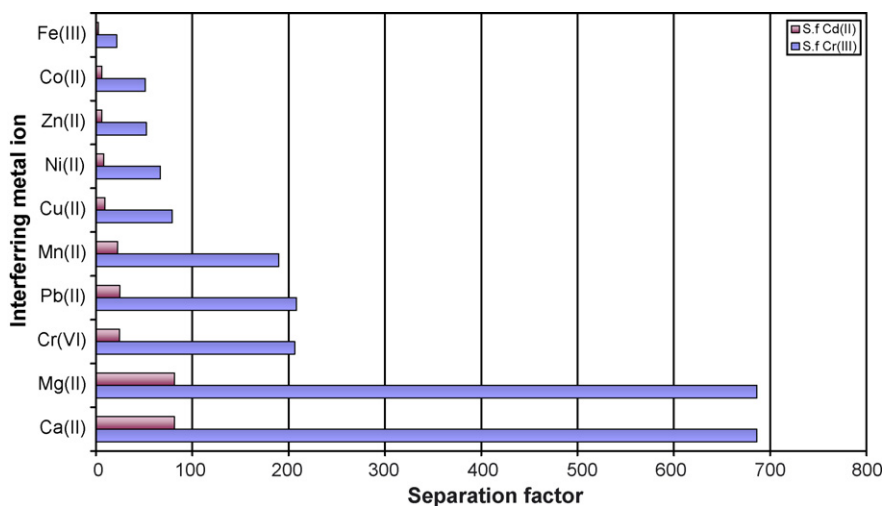


Fig. 2. Separation factors of Cr(III) and Cd(II) versus other interfering metal ions by alumina phase (II).

the distribution coefficient and separation factor determinations and strongly point out to the high affinity of modified alumina phases towards binding and extraction of Cr(III) as compared to other tested metal ions. Most of the tested metal ions along with

Cr(III) are not or minimally extracted by alumina (I–III) at low pH-buffer solutions except Cr(VI) which exhibited its high sorption capacity values as 200–400 $\mu\text{mol g}^{-1}$ under pH 1.0 buffer solution as given in Table 4.

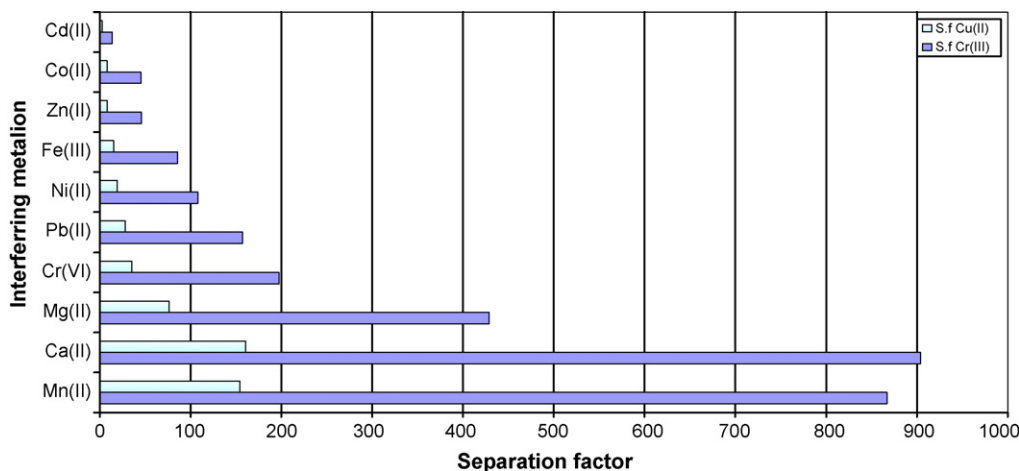


Fig. 3. Separation factors of Cr(III) and Cu(II) versus other interfering metal ions by alumina phase (III).

Table 4
Maximum metal capacity values expressed in $\mu\text{mol g}^{-1}$ under optimum buffering conditions

Metal	Mg(II)	Ca(II)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Pb(II)	Cr(III)	Cr(VI)
Maximum ($\mu\text{mol g}^{-1}$), phase (I)	40 (7)	20 (7)	20 (7)	340 (3, 4)	00 (1–7)	220 (7)	580 (7)	80 (6)	100 (5–7)	300(7)	230 (6)	760 (7)	200 (1)
Maximum ($\mu\text{mol g}^{-1}$), phase (II)	30 (7)	20 (7)	30 (7)	325 (4)	00 (1–7)	180 (6, 7)	570 (7)	80 (6)	100 (7)	360(7)	230 (6)	760 (7)	200 (1)
Maximum ($\mu\text{mol g}^{-1}$), phase (III)	40 (6, 7)	20 (6, 7)	40 (7)	320 (3, 4)	00 (1–7)	180 (7)	570 (7)	100 (6)	100 (7)	360(7)	240 (6)	780 (7)	400 (1)

Numbers in parentheses are the optimum pH-values.

Table 5
Variation of the metal capacity values of Cr(III) and Cr(VI) in buffer solutions

pH	Phase (I)		Phase (II)		Phase (III)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	0	200	0	200	0	400
2	0	100	0	180	0	200
3	0	0	0	100	0	160
4	10	0	20	0	0	100
5	340	0	440	0	370	40
6	470	0	510	0	470	0
7	760	0	760	0	780	0

The study of the variation of pH on the metal sorption capacity can be used to account for the possible separation, extraction and speciation of Cr(VI) and Cr(III) or other interfering metal ions by a direct and simple selection of the contact buffer solution. In addition, a comparison of the metal sorption capacity for a mixture of Cr(III) and Cr(VI) in different solutions of pH 1–7 was performed. Table 5 compiles the collected results of this study and clearly refers to the strong affinity of modified alumina phases (I–III) to selectively bind and extract Cr(VI) in the pH buffer range ~ 1.0 – 3.0 . Maximum $\mu\text{mol g}^{-1}$ metal uptake values of Cr(VI) were obtained for the three studied alumina phases (I–III) in the buffer solution, pH 1.0. On the other hand, Cr(III) was experienced with a reverse order or behavior. Cr(III) was found to be highly extracted at higher pH buffer solutions (pH 5–7) as previously reported in metal capacity section.

The effect of shaking time on the percentage extraction values of Cr(III) and Cr(VI) in buffer solution with pH 1 and pH 7 as the optimum solutions was also studied and evaluated via application of the static technique. Maximum percentage extraction values ($\sim 100\%$) were attained after only 10 min of shaking time. In addition, 5 min of shaking was found to give 88.3 and 91.7% extraction of Cr(III) and Cr(VI), respectively. The results of this study refer to fast equilibration time and kinetics of the extraction processes between chromium species and modified alumina phases (I–III).

3.4. Applications of modified alumina phases (I–III) for selective extraction, removal, preconcentration and speciation of Cr(III) and Cr(VI) from water samples

3.4.1. Selective solid phase preconcentration of Cr(III) from water samples

Table 6 summarizes the results of selective metal extraction and removal of Cr(III) from Alexandria drinking tap water

Table 6
Selective solid phase preconcentration of Cr(III) from Alexandria tap water by modified alumina phases (I–III) at pH 7.0

Percent extraction (%)	Detected ($\mu\text{g ml}^{-1}$)	Spiked (ng ml^{-1})	Phase
99.0 ± 2.0	1.0336	5.22	100 mg (I)
99.0 ± 2.0	1.0336	5.22	100 mg (II)
96.0 ± 3.0	1.0022	5.22	100 mg (III)

Values are based on triplicate analysis.

Table 7

Speciation of Cr(III) and Cr(VI) at pH 1.0 via selective solid phase extraction from real water samples

Extraction Cr(VI) (%)	Extraction Cr(III) (%)	Spiked Cr(VI) (ng ml ⁻¹)	Spiked Cr(III) (ng ml ⁻¹)	Water sample	Phase
100.0 ± 3.0	0.00	5.0	5.0	Waste water	(I)
99.9 ± 4.0	0.10	5.0	5.0	Waste water	(II)
99.9 ± 4.0	0.10	5.0	5.0	Waste water	(III)
106.0 ± 5.0	0.00	5.0	5.0	Sea water	(I)
95.8 ± 5.0	0.10	5.0	5.0	Sea water	(II)
94.8 ± 4.0	0.10	5.0	5.0	Sea water	(III)

Values are based on triplicate analysis.

samples by the modified alumina phases via a micro-column application with a preconcentration factor of 200. Three different concentrations, 1.0, 5.0 M and concentrated nitric acid, were tested for elution of the adsorbed chromium species from the surface of modified alumina phases (I–III). The results of this optimization step indicated that concentrated nitric acid is the optimum desorbing eluent. One can conclude from the results outlined in Table 6 that excellent percentage recovery values (96.0–99.0 ± 2.0–3.0%) were established for preconcentration of Cr(III) by the modified alumina phases (I–III).

3.4.2. Speciation of chromium via selective solid phase extraction

The ability of modified alumina phases (I–III) to selectively extract and preconcentrate Cr(VI) species in presence of interfering Cr(III) ion from a mixture containing equal concentrations of these species was further studied as the final step to explore the potential applications of alumina phases (I–III) for speciation of Cr(VI) in real water samples. The tested water samples were adjusted to a pH 1.0 and passed over a micro-column packed with the examined alumina phase. Concentrated nitric acid was used as the optimum eluent providing a preconcentration factor of 200. The results of atomic absorption analysis showed percentage recovery values of Cr(VI) species from a dyeing waste water sample (II) in the range of 100.0–99.9 ± 3.0–4.0% by modified alumina phases (I–III). However, the percentage recovery values of the Cr(III) species from sample (II) were determined as 0.00, 0.10 and 0.10% by modified alumina phases (I), (II) and (III), respectively. The same trend and behavior were also observed for speciation of both Cr(VI) and Cr(III) species in sea water sample (III) by alumina phases (I), (II) and (III). The percentage recovery values of Cr(VI) in this case were found to be 106.0, 95.8 and 94.8 ± 4.0–5.0% as determined by modified alumina phases (I), (II) and (III), respectively. The interference and contribution of Cr(III) in this respect was minimally identified judging from the percentage recovery values. The results of this speciation study are listed in Table 7.

4. Conclusion

The newly designed chelating alumina phases were characterized by excellent chemical stability during the course of this work and highly experienced by their good stability in the interacting solutions, pH 1.0 and 7.0. These solid phases were successfully applied and employed in chromium speciation, preconcentration and selective extraction procedures by

simply controlling the pH value of the contact solution. Cr(VI) was selectively sorbed at pH 1.0, while Cr(III) was selectively extracted at pH 7.0 via possible chelation with donor atoms containing isatine-thiosemicarbazone as a surface modifier. The presented method is also potentially applicable for the speciation of chromium in real matrices as drinking tap, dyeing waste and sea water samples. The procedure applied for chromium speciation in these three examined water samples as well as the conclusion drawn from the obtained results can be extended as general guide lines for further chromium speciation in any water sample by simple and direct applications of alumina-loaded-isatin-thiosemicarbazone as reported in this work.

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