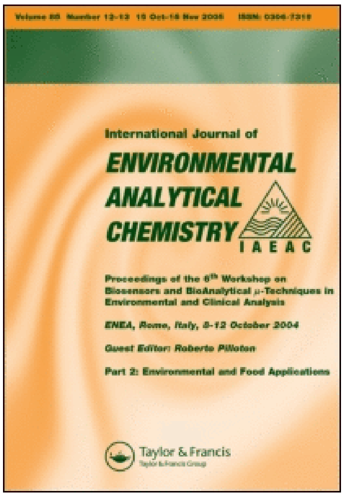

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Chromium speciation, selective extraction and preconcentration by alumina-functionalised 2-pyridenecarboxyladehyde thiosemicarbazone

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A method is proposed and explored for speciation of Cr(III) and Cr(VI), selective extraction and preconcentration in various water samples based on dynamic and static techniques. Three newly designed alumina phases-physically adsorbed-2-pyridenecarboxyladehyde-thiosemicarbazone [Al-2PC-TSC (I–III)] were synthesised and characterised. Stability tests and application of [Al-2PC-TSC (I–III)] as inorganic ion exchangers and chelating solid sorbents for various metal ions were studied and evaluated. The distribution coefficient and separation factors of chromium species versus other interfering metal ions were determined to examine the incorporated selectivity into these alumina phases. Quantitative recovery of Cr(VI) was accomplished by [Al-2PC-TSC (I–III)] at $pH = 1.0$ while Cr(III) was found to be quantitatively recovered on these sorbents at $pH = 7.0$ 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 via a micro-column, with 200 as a preconcentration factor. Selective speciation of Cr(VI) and Cr(III) via preconcentration from seawater and industrial water samples by alumina phases in $pH = 1$ was found to give percentage recovery values of Cr(VI) in the range 93.5–97.3 ± 3.0–5.0% and 94.0–97.5 ± 3.0–4.0%, for seawater and industrial water samples, respectively.

Keywords: speciation; chromium; solid-phase extraction; alumina; 2-pyridenecarboxyladehyde-thiosemicarbazone

1. Introduction

Trace heavy metals are widely known as the major sources of environmental pollution and well recognised for their direct and negative impact on the human health as well as biological organisms and ecological system. The influence of heavy metal is mainly dependent on their chemical forms or species rather than total concentration of the element [1]. Metal speciation studies must be designed and established to identify and determine the actual concentration of each species. For some heavy metals this speciation technique is highly important owing to the fact that certain oxidation states of some metals are highly toxic to humans and associated with severe health problems, while other species are less toxic or even considered as essential trace elements [2].

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Chromium represents a typical element with different oxidation states species that show opposite levels of toxicity. Hexavalent chromium Cr(VI) is a highly toxic species due to its oxidising power of organic and inorganic species. It is also designated as a suspected carcinogenic agent by the US EPA and directly related to some cancer diseases [3,4]. Trivalent chromium is the chemical species of naturally occurring chromium known as an essential trace element [5]. The release of chromium species to numerous sites including drinking water supply systems is mainly a result of its extensive industrial uses and applications [6,7].

Determination of trace nano-gram per millilitre levels or lower of chromium species must be first performed by isolation followed by instrumental analysis. Low chromium levels are usually determined after separation of one specific form and preconcentration via coprecipitation [8], liquid–liquid extraction [9], sorption [10], ion-exchange [11], electro-analytical techniques [12] and chelating sorbents [13–15]. Solid phase extraction techniques-based chelating sorbents are now the methods of choice for speciation, separation and preconcentration of trace constituents from various environmental matrices and natural water systems due to their high separation efficiency, good kinetics, excellent reproducibility and high sensitivity [16–20]. The anchoring of active functional groups to active solid surfaces leads to the incorporation of strong selective capabilities of these designed solids for quantitative separation of various cationic and anionic species from aqueous solutions as well as real matrices [21–23]. Selection of the surface immobilised functional groups is usually aimed and based on different incorporated selectivity characteristics that must be present in the newly designed solid phase extractors and preconcentrators [24–26]. Several reports have been published recently concerning the determination and speciation of chromium in different samples. Most of these methods are based on modified organic phases or resins [27–30]. These organic solid phase extractors and preconcentrators have some disadvantages when compared to inorganic modified solid phases such as alumina or silica [31–33].

Owing to the strong and growing need for accurate and real determinations of Cr(III) and Cr(VI) species in their matrices separately rather than the total chromium content, an efficient separation, extraction and preconcentration technique must be designed and explored. In this work we report the immobilisation of 2-pyridenecarboxyladehyde-thiosemicarbazone as an example of sulphur and nitrogen containing chelating compound on the surface of three alumina types for the formation of selective chelating inorganic solid sorbents. These can be further applied for selective speciation, extraction and preconcentration of chromium species in various water samples.

2. Experimental

2.1 *Instrumentation*

The pH-measurement of metal ions and buffer solutions were carried out by an Orion 420A pH-meter calibrated against potassium hydrogenphthalate at $pH = 4.008$. Infrared spectra of the active alumina and its modified phases were recorded from KBr pellets by using a Perkin-Elmer spectrophotometer, model 1430 and determination of metal ions concentration was performed by a Perkin-Elmer flame spectrophotometer, model 2380. 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, 2-pyridenecarboxyladehyde-thiosemicarbazone and modified alumina phases [Al-2PC-TSC (I–III)] were carried out by using a Varion 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 computerised to give I/Base and its corresponding mass.

2.2 *Materials and reagents*

The metal salts are in chloride, acetate or nitrate form and all of analytical grade and purchased from Aldrich Chemical Company, Milwaukee, WI, USA and BDH Limited, Poole, England. The metal ion solutions were prepared from doubly distilled water (DDW). 2-pyridenecarboxyladehyde and thiosemicarbazide were purchased from Aldrich Chemical Company, Milwaukee, WI, USA and used as received. Three alumina types of analytical grade were used in this work (150 mesh size and 58Å pore diameter) purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Buffer solutions (pH 1.0–7.0) were prepared from 1.0 M-hydrochloric acid solution and 1.0 M-sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 litre. The pH-values of resulting solutions were adjusted and checked with a pH metre. The pH values of aqueous suspensions of these three alumina phases were found to have pH $\sim 6.0 \pm 0.5$, 7.0 ± 0.5 and 9.0 ± 0.5 for acidic, neutral and basic alumina, respectively.

2.3 *Synthesis of alumina phases-physically adsorbed 2-pyridenecarboxyladehyd-thiosemicarbazone*

The following method was used to synthesise 2-pyridenecarboxyladehyde-thiosemicarbazone. A solution of 0.01 M- thiosemicarbazide in a 100 mL ethanol/water mixture was prepared under reflux and stirring. A hot 0.01 M solution of 2-pyridenecarboxyladehyde in 100 mL ethanol was then added and the reaction mixture was heated for 5 minutes to precipitate the product as white needles. Alumina phases-physically adsorbed-2-pyridenecarboxyladehyde-thiosemicarbazone [Al-2PC-TSC (I–III)] were synthesised according to the following procedure. 2-pyridenecarboxyladehyde-thiosemicarbazone (1.8 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 ± 0.1 g alumina, either acidic, neutral or basic, was added and the reaction mixture was further stirred for six hours. The newly modified [Al-2PC-TSC (I–III)] phases 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 eight hours. The pH-values of aqueous suspension and colour of the modified alumina phases are listed in Table 1.

2.4 *Stability of [Al-2PC-TSC (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 one hour. The solid phase was filtered, washed with a 50 mL portion of the same pH solution followed by doubly distilled water (DDW) and dried at 70°C. The buffered alumina phase, 25.0 ± 1 mg, was then added to a solution containing 9.0 mL of buffer solution ($pH = 6.0$) and 1.0 mL of 0.1 M Cu(II) solution and this mixture was then shaken for 30 minutes by an automatic shaker.

Table 1. Physical properties of modified alumina phases.

Phase	Modified alumina phases	Colour	pH
I	Acidic alumina-physically adsorbed-2-pyridinecarboxyadehyde-thiosemicarbazone	White	6.1
II	Neutral alumina-physically adsorbed- 2-pyridinecarboxyadehyde-thiosemicarbazone	White	6.3
III	Basic alumina-physically adsorbed 2-pyridinecarboxyadehyde-thiosemicarbazone	White	6.6

The hydrolysis percentage values of alumina phases [Al-2PC-TSC (I–III)] in different buffer solutions were determined from the metal uptake of Cu(II).

2.5 *Surface coverage determination*

The determination of surface coverage values of alumina phases [Al-2PC-TSC (I–III)] was performed by the thermal desorption method. In this method, 100 ± 1 mg of dry alumina phases were ignited in a furnace at 550°C for one hour and left to cool at 70°C. The sample was transferred to a desiccator and left to reach room temperature. The weight loss of 2-pyridenecarboxyladehyde-thiosemicarbazone was determined by the difference in 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 each tested metal ion ($\sim 1.0\,\mu g\,mL^{-1}$) was prepared and determined by flame atomic absorption spectrophotometry. Alumina phase, 50 mg, was mixed with 50 mL of this metal ion solution in a 100 mL measuring flask. The mixture was shaken for one hour 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 capacity*

The metal capacity values ($\mu mol\,g^{-1}$) of the modified alumina phases for the extraction of different metal ions in 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 were then shaken at room temperature for 30 minutes 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 atomic absorption spectrophotometric analysis.

The effect of shaking time intervals (1, 5, 10, 15, 20, 25 and 30 minutes) on the values of metal capacity and the percentage extraction of Cu(II) was also studied for the same series of metal ions 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 Cr(III) 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 [Al-2PC-TSC (I–III)]*

2.8.1 *Selective extraction and speciation of chromium from drinking tap water samples*

A 1.0 L sample, collected from Alexandria drinking tap water, was adjusted to pH 1.0 and spiked with 1.0 $\mu g\,mL^{-1}$ each of Cr(III) and Cr(VI) in a mixture. The sample solution was passed over a micro-column (length 10.0 cm, i.d. 1.0 cm, and connected to a 500 mL reservoir) packed with 100 mg of the modified alumina phases [Al-2PC-TSC (I–III)] with a flow rate of 10 $mL\,min^{-1}$ under air pressure. The total chromium was determined by flame atomic absorption analysis and the percentage extraction of Cr(VI) species was determined by the UV-Vis spectrophotometric determination at $\lambda = 540$ nm.

2.8.2 *Selective extraction, preconcentration and speciation of chromium from waste and sea water samples*

Selective extraction, preconcentration and speciation of chromium species was performed according to the following procedure. Sample (I) is a dyeing wastewater with organic dyeing materials as the major constituents and chromium species as the minor or trace constituents, while sample (II) is seawater. A 1.0 L of each sample was spiked with $\sim$5.0 $ng\,mL^{-1}$ of Cr(III) and Cr(VI). The aqueous solution was adjusted to pH 1.0 and passed over a preconcentration micro-column packed with 100 mg of the modified alumina phases [Al-2PC-TSC (I–III)] with a flow rate of 10 $mL\,min^{-1}$ under air pressure. The adsorbed chromium species were eluted by 5.0 mL of concentrated HNO_3 as a preconcentration reagent and subjected to analysis by UV–Vis spectrophotometry and atomic absorption spectrophotometry.

3. Results and discussion

3.1 *Characterisation and stability of surface modified alumina phases [Al-2PC-TSC (I–III)]*

The 70-eV EI-MS of alumina phases [Al-2PC-TSC (I–III)] were measured by the direct insertion probe as previously reported [34]. The mass spectrum of 2-pyridenecarboxyladehyde-thiosemicarbazone was found to exhibit the molecular ion peak, $[C_7H_8N_4S]^{+\bullet}$, at *m*/*z* 180 (100%). Three other peaks are located at *m*/*z* 120 (50%), 79 (30%) and 65 (20%) corresponding to the formation of $[C_6H_6N_3]^+$, $[C_5H_5N]^+$ and $[C_5H_5]^+$ fragment ions, respectively. The 70-eV EI–MS–DIP spectrum of [Al-2PC-TSC (I)] is characterised by the presence of these peaks at *m*/*z* 18, 28 and 44 corresponding to H_2O, CO and CO_2, respectively. The 70-eV EI–MS of modified alumina phases [Al-2PC-TSC (II–III)] showed few fragment ions ($\leq$2.0%) at *m*/*z* 120, 79 and 65 that can be correlated to simple fragmentation pathways generated from the molecular ion. This trend can be correlated to the low percentage of immobilised 2-pyridenecarboxyladehyde-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 [34].

The structure of 2-pyridenecarboxyladehyde-thiosemicarbazone is shown in Figure 1. The infrared spectrum of this organic modifier was found to exhibit the following strong characteristic peaks at 3434 cm^{-1} (ν_{NH2}), 3226, 3158 cm^{-1} (ν_{NH}), 1643 cm^{-1}($\nu_{C=N}$), 1535 cm^{-1}($\nu_{C=S}$), 1464–1184 cm^{-1}($\nu_{C=C}$) aromatic. On the other hand, the infrared spectra of [Al-2PC-TSC (I–III)] were found to show these infrared peaks as very weak ones upon immobilisation of 2-pyridenecarboxyladehyde-thiosemicarbazone on the surface of newly modified alumina phases. The most dominant infrared peaks are mainly due to alumina matrix at 3600–3400, 1650 and 1000–400 cm^{-1}. This behaviour may be mainly attributed to the low percentage coverage values as listed in Table 2.

The thermal desorption method [35] was used to determine the surface coverage of modified alumina phases [Al-2PC-TSC (I–III)]. In this method, alumina phases are heated at high temperatures in the range ~500–600°C. The obtained residue corresponds to the stable alumina matrix, which can then be used to calculate the surface coverage values expressed in mmol g^{-1} and percentage as listed in Table 2. The confirmation of surface modification can be also evaluated on the basis of pH determination of aqueous suspensions. The results of this step are compiled in Table 1. The pH values are determined as 6.1, 6.3 and 6.6 for modified acidic, neutral and basic alumina phases, respectively. These pH-values prove a direct change in the physical as well as chemical properties of the three studied alumina upon surface coverage, loading and binding of 2-pyridenecarboxyladehyde-thiosemicarbazone.

The modified alumina phases [Al-2PC-TSC (I–III)] were tested for their stability in different buffer solutions (pH = 1–7) to identify the possible leaching and/or hydrolysis degree of the organic modifier from the surface. The treated alumina phases were then used to determine the μmol g^{-1} of adsorbed Cu(II). The determined μmol g^{-1} values of the hydrolysed alumina phases were compared with those of the unhydrolysed one to calculate the percentage of stability 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 [Al-2PC-TSC (I–III)]. It is evident that [Al-2PC-TSC (II)] and [Al-2PC-TSC (III)] have high stability over the entire pH range.

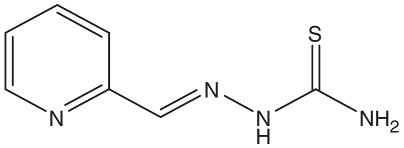

Figure 1. Structure of of 2-pyridenecarboxyladehyde-thiosemicarbazone.

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

	Thermal desorption		Percentage stability p^{H}						
Phase	mmol g^{-1}	(%coverage)	1.0	2.0	3.0	4.0	5.0	6.0	7.0
I	0.116	(2.1)	100	84	85	85	89	89	90
II	0.171	(3.1)	100	96	96.5	95	96	96	100
III	0.171	(3.1)	100	96	96	96.5	95	100	100

3.2 *Evaluation of the distribution coefficient values*

Evaluation of the capability of modified alumina phases for selective extraction of various metal ions from aqueous and organic solutions can be explored on the basis of distribution coefficients (K_d) as a direct method [36]. The obtained results can be then used to provide a possible discrimination order between the studied metal ions. This method is successfully applied for very low concentration ranges of metal ion, part per million (ppm) or part per billion (ppb). Evaluation of the distribution coefficient can lead to a more detailed series of values, which assists in further evaluation of the metal uptake trends as well as the selectivity incorporated into modified alumina phase. The K_d value is determined from the following equation:

$$K_d, \mathrm{mL\,g^{-1}} = \frac{C_{i,\mathrm{ex}}(\mu\mathrm{g\,g^{-1}})}{C_{i,\mathrm{sol}}(\mu\mathrm{g\,mL^{-1}})} \tag{1}$$

Table 3 compiles log K_d values for a series of tested metal ions by [Al-2PC-TSC (I–III)] and compared with those determined for blank acidic, neutral and basic alumina. It is evident from the listed values that Cr(III) is highly extracted by the three newly modified alumina phases providing log K_d values of 5.08, 5.16 and 5.26 for [Al-2PC-TSC (I)], [Al-2PC-TSC (II)] and [Al-2PC-TSC (III)], respectively. These values are higher than those determined from blank alumina phases pointing out the role and selectivity incorporated in modified alumina phases for extraction and binding with Cr(III). In addition, the role of metal binding by alumina surface free hydroxo-groups as weak ion exchangers is negligible compared to the surface reactivity of 2-pyridenecarboxyladehyde-thiosemicarbazone loaded on newly modified alumina phases [Al-2PC-TSC (I–III)] judging from log K_d values as listed in Table 3 for most tested metal ions. Cd(II) and Cu(II) were also found to exhibit the same trend and behaviour as Cr(III) with alumina phases [Al-2PC-TSC (I–III)]. Finally, the increasing orders of log K_d values for tested metal ions by modified alumina phases can be outlined in the following orders:

[Al-2PC-TSC (I)]:
Log K_d:
Ca(II) < Zn(II) < Mg(II) < Pb(II) < Mn(II) < Co(II) < Ni(II) < Fe(III) < Cd(II) < Cu(II) < Cr(III).

Table 3. Log K_d-values of metal ions by modified *vs*. blank alumina phases.

Metal ions	Acidic alumina	Neutral alumina	Basic alumina	Al-2PC-TSC (I)	Al-2PC-TSC (II)	Al-2PC-TSC (III)
Ca(II)	2.15	2.1	2.80	2.39	2.30	2.04
Mg(II)	2.14	2.2	2.76	2.88	2.78	2.62
Mn(II)	2.16	2.2	2.69	2.98	3.73	3.41
Zn(II)	2.56	3.4	4.16	2.61	2.38	3.91
Ni(II)	2.56	3.0	3.78	3.48	2.93	3.10
Pb(II)	3.20	4.0	4.40	2.91	2.98	2.04
Co(II)	2.39	3.0	3.35	3.28	2.45	3.04
Fe(III)	2.67	3.4	4.11	3.56	3.67	3.78
Cu(II)	2.81	3.5	4.33	4.88	3.83	4.14
Cd(II)	2.55	3.4	4.06	4.44	4.40	4.69
Cr(III)	2.94	3.3	4.14	5.08	5.16	5.26

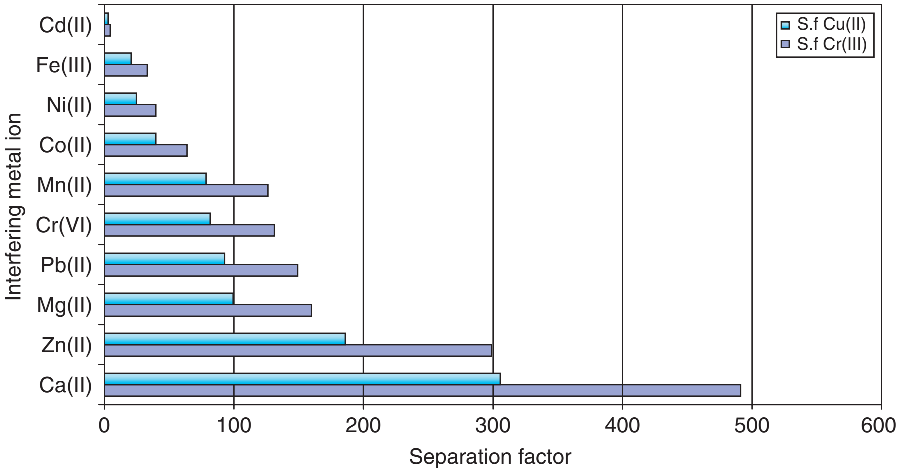

Figure 2. Separation factors of Cr(III) and Cu(II) *vs*. other interfering metal ions by modified acidic alumina phase [Al-2PC-TSC (I)].

[Al-2PC-TSC (II)]:
Log K_d: Ca(II) < Zn(II) < Co(II) < Mg(II) < Ni(II) < Pb(II) < Fe(III) < Mn(II) < Cu(II) < Cd(II) < Cr(III).
[Al-2PC-TSC (III)]:
Log K_d: Ca(II) < Pb(II) < Mg(II) < Co(II) < Ni(II) < Mn(II) < Fe(III) < Zn(II) < Cu(II) < Cd(II) < Cr(III).

The incorporated selectivity into newly modified alumina phases [Al-2PC-TSC (I–III)] may also be evaluated and expressed in terms of the separation factor α, which can be derived from the measurements under static or dynamic conditions. The separation factor ($\alpha_{A/B}$) [36] of any two metal cations A and B is calculated from the distribution coefficients $K_{d(A)}$ and $K_{d(B)}$, respectively, as given in the following equation:

$$\alpha_{(A/B)} = \frac{K_{d(A)}}{K_{d(B)}} \tag{2}$$

The separation factors of Cr(III) versus other interfering metal ions are calculated and represented in Figures 2, 3 and 4 for modified alumina phases [Al-2PC-TSC (I–III)]. It is evident from these graphs that excellent separation factors for Cr(III) are attained by the three studied alumina phases with no or minimum interference of most metal ions except Cu(II) in the case of [Al-2PC-TSC (I)] and Cd(II) in the case of [Al-2PC-TSC (II)] and [Al-2PC-TSC (III)].

3.3 *Metal sorption capacity*

The process of metal extraction by modified alumina phases is highly dependent on the pH of the medium. The following series of metal ions were selected, 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 [Al-2PC-TSC (I–III)] in various solutions of pH 1–7. However, buffer solutions in the basic range were excluded due to possible

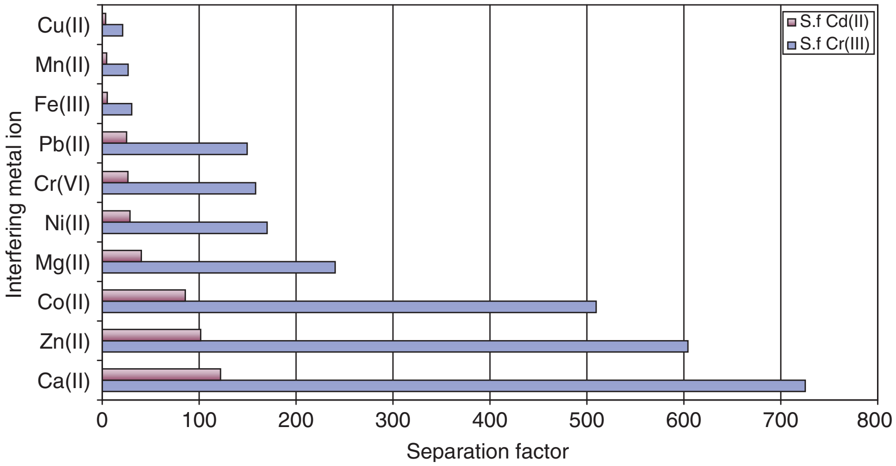

Figure 3. Separation factors of Cr(III) and Cd(II) *vs*. other interfering metal ions by modified neutral alumina phase [Al-2PC-TSC (II)].

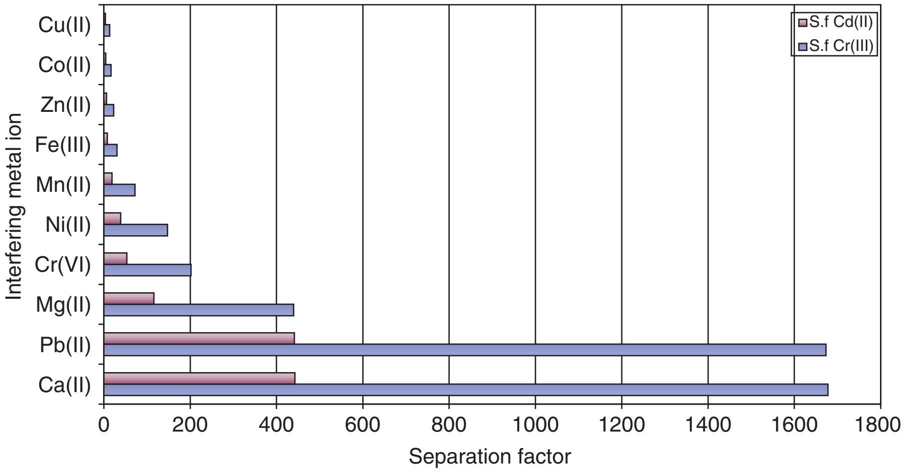

Figure 4. Separation factors of Cr(III) and Cd(II) *vs*. other interfering metal ions by modified basic alumina phase [Al-2PC-TSC (III)].

precipitation of most metal ions under these buffering conditions. The maximum metal capacity values (μmol g^{-1}) at the optimum pH-range are listed in Table 4.

The most highly extracted metal ion is Cr(III) with 770, 750 and 720 μmol g^{-1} by the three newly modified alumina phases [Al-2PC-TSC (I)], [Al-2PC-TSC (II)] and [Al-2PC-TSC (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 the distribution coefficient and separation factor determination 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. At low pH-buffer solutions, most of the tested metal ions along with Cr(III) were not or minimally extracted by alumina [Al-2PC-TSC (I–III)] except

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

	Al-2PC-TSC (I)		Al-2PC-TSC (II)		Al-2PC-TSC (III)	
Metal ion	Max.	$\mu mol\,g^{-1}$	Max.	$\mu mol\,g^{-1}$	Max.	$\mu mol\,g^{-1}$
Mg(II)	40	(7)	50	(7)	30	(7)
Ca(II)	30	(7)	50	(7)	50	(7)
Mn(II)	40	(7)	20	(7)	30	(7)
Fe(III)	250	(4)	260	(4)	230	(3,4)
Co(II)	20	(6,7)	20	(6,7)	30	(6,7)
Ni(II)	200	(6,7)	180	(6,7)	200	(6,7)
Cu(II)	590	(7)	580	(7)	570	(7)
Zn(II)	80	(6,7)	80	(6)	110	(7)
Cd(II)	100	(7)	80	(5)	60	(6,7)
Hg(II)	320	(7)	320	(7)	320	(7)
Pb(II)	220	(6,7)	220	(6,7)	220	(6,7)
Cr(III)	770	(7)	750	(7)	720	(7)
Cr(VI)	500	(1)	540	(1)	600	(1)

Note: 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.

	Al-2PC-TSC (I)		Al-2PC-TSC (II)		Al-2PC-TSC (III)	
pH	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	0	500	0	540	0	600
2	0	360	0	280	0	520
3	0	340	0	200	20	300
4	10	200	20	100	30	280
5	340	100	440	0	450	100
6	470	100	510	0	540	40
7	760	0	760	0	720	0

Cr(VI) which exhibited its high 500–600 $\mu mol\,g^{-1}$ values under pH 1.0 buffer solution as shown in Table 4.

The study of the variation of pH on the metal 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 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 Figure 5 shows a direct representation and these are clearly show the strong affinity of modified alumina phases [Al-2PC-TSC (I–III)] toward selective binding and extraction of Cr(VI) from buffer solutions in the pH range 1.0 to 4.0. Maximum $\mu mol\,g^{-1}$ metal uptake values of Cr(VI) were obtained for the three studied alumina phases [Al-2PC-TSC (I–III)] in the buffer solution, $pH = 1.0$. The reason for this behaviour of [Al-2PC-TSC (I–III)] in a strongly acidic medium is mainly based upon the strong ability of the surface loaded H_2N-group to bind with free protons already present in the medium by HCl

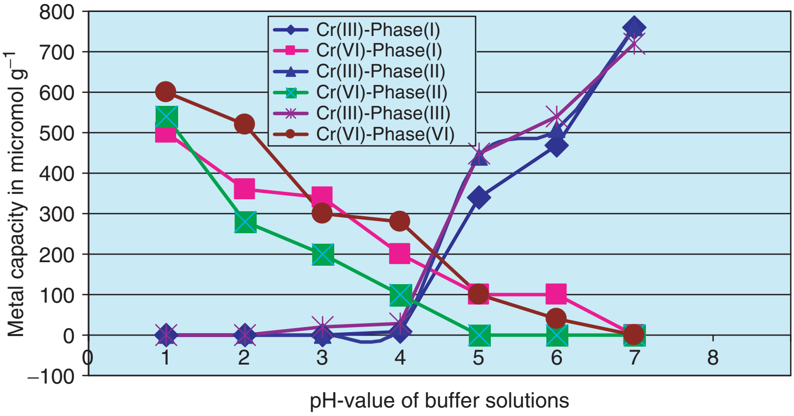

Figure 5. Effect of pH on the metal capacity values of Cr(III) and Cr(VI) by [Al-2PC-TSC (I–III)].

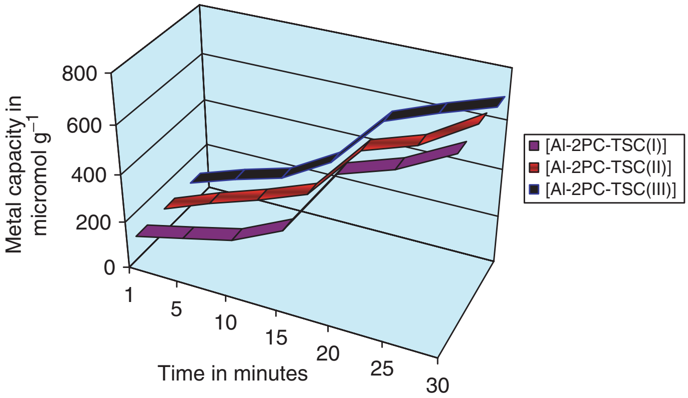

Figure 6. Effect of shaking time on the metal capacity values of Cr(III) by [Al-2PC-TSC (I–III)].

in buffer, pH = 1.0. This reaction is considered as the direct reason for possible formation of positively charged species, [$-NH_3^+$]. This surface H_3N^+group is then directly bound to the negatively charged chromate ion, CrO_4^{2-} for the formation of surface ion-pair adduct. On the other hand, Cr(III) exhibited a reverse order and behaviour. Cr(III) was found to be highly extracted at higher pH buffer solutions (pH 5–7) as previously reported in the metal capacity section. The results of this study indicate that separation and speciation of Cr(III) and Cr(VI) can be accomplished experimentally by selecting the appropriate pH-value of these two species.

The effect of shaking time on the metal capacity values determined for Cr(III) as the highest extracted metal ion by the three alumina phases [Al-2PC-TSC (I–III)] at different shaking times are shown in Figure 6. The effect of shaking time is a very important factor in the evaluation process of the rapidness of binding between the two interacting species, metal ion and modified solid phases. It is evident from Figure 6 that the three newly designed alumina phases [Al-2PC-TSC (I–III)] are highly similar in their binding processes with Cr(III) as well as in their percentage extraction toward Cr(III).

3.4 *Applications of [Al-2PC-TSC (I–III)] for selective extraction, removal, preconcentration and speciation of Cr(III) and Cr(VI) from water samples*

3.4.1 *Selective solid phase extraction of Cr(III) from water samples*

Table 6 summarises the results of micro-column applications for selective extraction, separation and removal of Cr(VI) and Cr(III) in 1.0 L samples of Alexandria drinking tap water containing equal concentrations of both species. Modified alumina phases [Al-2PC-TSC (I)] and [Al-2PC-TSC (II)] were found to provide excellent percentage extraction of Cr(VI) under the applied experimental buffering condition (pH = 1). Minimum interference, 2.9–3.0%, of Cr(III) in the processes of Cr(VI)-speciation was observed and outlined in Table 6. In addition to the results outlined and listed in Table 6 for 1.0 L samples, other volumes of drinking tap water samples were also studied including 500, 100 and 50 mL and the obtained results of this sample volume study were found to be consistent with the given percentage extraction values of Cr(VI) in Table 6.

3.4.2 *Speciation of chromium via selective solid phase extraction*

The ability of modified alumina phases [Al-2PC-TSC (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 exploring the potential applications of alumina phases [Al-2PC-TSC (I–III)] for direct speciation of Cr(VI) from waste and sea 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 with a flow rate of 10.0 mL min^{-1}. This flow rate value was found to be the optimum

Table 6. Selective solid phase extraction of Cr(III) and Cr(VI), 1.0 μg mL^{-1} each, alumina phases [Al-2PC-TSC (I–III)] at pH = 1.0 from drinking tap water.

Phase	Percentage extraction of Cr(III)	Percentage extraction of Cr(VI)
[Al-2PC-TSC (I)]	2.9	97.1
[Al-2PC-TSC (II)]	3.0	97.0
[Al-2PC-TSC (III)]	6.8	93.2

Note: Values are based on triplicate analysis.

Table 7. Speciation of Cr(III) and Cr(VI), 5.0 ng mL^{-1} each, at pH = 1.0 in waste and sea water samples.

Phase	Water sample	Percentage extraction Cr(III)	Percentage extraction Cr(VI)
[Al-2PC-TSC (I)]	Wastewater	2.5	97.5 ± 4.0
[Al-2PC-TSC (II)]	Wastewater	2.8	97.2 ± 3.0
[Al-2PC-TSC (III)]	Wastewater	6.0	94.0 ± 3.0
[Al-2PC-TSC (I)]	Seawater	2.7	97.3 ± 3.0
[Al-2PC-TSC (II)]	Seawater	3.0	97.0 ± 5.0
[Al-2PC-TSC (III)]	Seawater	6.5	93.5 ± 4.0

Note: Values are based on triplicate analysis.

Table 8. Comparison of newly modified alumina phases [Al-2PC-TSC (I–III)] *vs.* other recently published solid phases.

Method and application	[Al-2PC-TSC (I-III)]	Reference [27]	Reference [30]	Reference [37]
Newly synthesised	Yes	No	No	Yes
Solid support and organic chelating modifier	Acidic, basic and neutral alumina 2PC-TSC	Commercial Type Dowex M 4195 bis-Picolylamine	Commercial Type Chromosorb 108 resin. Dithizone	Saccharomyces cerevisiae on sepiolite
Surface coverage value	Determined	No	No	No
Surface characterisation	Identified	No	No	No
Tested metals beside Cr-species	A series of di- and tri-valent ions	Only interfering anions and cations	Only interfering anions and cations	Only interfering anions and cations
Adsorption capacity values	720–770 μmol g^{-1} Cr(III) 500–600 μmol g^{-1} Cr(VI)	29.7 mg g^{-1} Cr(VI)	4.50 mg g^{-1} Cr(III)	228 μmol g^{-1} Cr(III)
Effect of pH	Yes	Yes	Yes	Yes
Effect of contact time	Yes	Studied as flow rate	Studied as flow rate	No
Distribution and separation factors	Determined	No	No	No
Selective extraction	Studied	Yes	Yes	Yes
Real samples	Drinking tap water Dyeing wastewater Seawater	Tap water River water Electroplating water	Tap water River water Seawater	Spiked water River water
Sample volume	1000–50 mL	500–25 mL	750–25mL	1000–100 mL
Detection limits	Not Evaluated	1.94 μg L^{-1}	0.75 g L^{-1}	94 ng mL^{-1} Cr(III)
Concentration of Cr in speciation procedures	Cr (III) and Cr(VI) 5.0 ng mL^{-1} each	5.0–30 μg 100 mL^{-1}	0.0–25.0 μg 100 mL^{-1}	5–50 μg 100 mL^{-1}
Volume of eluent	5.0 mL concenterated nitric acid	10.0 mL of 4 M-NH_3.	8–10 mL of 2M HNO_3 in acetone	10 mL of 1M HCl
Preconcentration factor	200	10	10	10
Percent recovery	93.2–97.5% ± 3.0–5.0%	≥95.0% ± ≤5.0%	≥95.0% ± ≤5.0%	96.3% ± ≤0.2%

experimental condition in this step. Less than 10.0 mL min^{-1} as a flow rate was found to be too time consuming and application of >10.0 mL min^{-1} proved insufficient to force maximum extraction of Cr(VI) by the studied alumina phases [Al-2PC-TSC (I–III)]. The highest percentage extraction values of either Cr(III) or Cr(VI) were obtained with concentrated nitric acid when compared with other 1.0 and 5.0 molar solutions. The optimised volume of nitric acid in this step is 5.0 mL. Therefore, concentrated nitric acid was used as an eluent with a preconcentration factor of 200.

The results of atomic absorption analysis and UV-Vis spectrophotometric determination showed percentage recovery values of 94.0–97.5 ± 3.0–4.0% for Cr(VI) species from wastewater sample by modified alumina phases [Al-2PC-TSC (I–III)]. However, the percentage recovery values of the Cr(III) species from the wastewater sample were determined as 2.5, 2.8 and 6.0% by modified alumina phases (I), (II) and (III), respectively. The same trend and behaviour were also observed for speciation of both Cr(VI) and Cr(III) species in seawater sample by alumina phases [Al-2PC-TSC (I–III)] in pH = 1. The percentage recovery values of Cr(VI) in this case were found to be 97.3, 97.0 and 93.5 ± 3.0–5.0% as determined by modified alumina phases (I), (II) and (III), respectively. Minimum interference and contribution of Cr(III) was also identified judging from the percentage recovery values. The results of this speciation study are listed in Table 7. A comparative evaluation of alumina phases [Al-2PC-TSC (I-III)] as solid phase extractors and preconcentrators of chromium species *versus* other recently published solid phases are compiled in Table 8.

4. Conclusion

The newly designed chelating alumina phases were highly characterised by good stability in the interacting solutions, pH 1.0 and 7.0 and successfully applied for chromium speciation, preconcentration and selective extraction by simply controlling and tuning the pH value of the contact solution. Cr(VI) is quantitatively sorbed at pH 1.0, while Cr(III) is selectively extracted at pH 7.0. The presented method is also potentially applicable for the speciation of chromium in real water samples. The reported results in this study as well as our recently published work [38, 39] on chromium speciation reveals that N and S donor atoms containing chelating compounds such as 2-pyridenecarboxylade-hyde-thiosemicarbazone can be successfully used as surface modifiers for chelation, extraction, preconcentration and speciation of chromium from different real matrices.

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