

Use of 6-Mercapto Purinylazo Resin in Chromium Speciation

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The present work describes a procedure of preconcentration, separation and determination of the two forms of chromium, viz. Cr(III) and Cr(VI), in waste water by using 6-mercaptopurine anchored by azo function to a polymeric styrene divinylbenzene (8%) matrix as solid phase extractor. The maximum exchange capacity for Cr(III) at pH 6.5 is 0.44 mmol g^{-1} and that for Cr(VI) at pH 1.0 is 1.06 mmol g^{-1}. In the column operation, the recoveries of both Cr(III) and Cr(VI) in the presence of various foreign ions which are generally present in waste water were examined; it was observed that no such interferences occur in the sorption step. Flow rate optimization studies show that the column is efficient for the separation of both forms of chromium at a flow rate of 1.2 mL min^{-1}. The metal ion concentration was measured by flame atomic absorption spectrometry. The method has been applied for the separation and speciation of chromium in waste water samples.

The toxicity of chromium in the environment is dependent on the species in which it exists. The hexavalent form of the chromium is considered a more toxic species than innocuous and less mobile Cr(III) compounds.[1] It is well established that the reduction of Cr(VI) to Cr(III) by enzymes results in the formation of reactive intermediates that contribute to the cytotoxicity, genotoxicity and carcinogenicity of Cr(VI)-containing compounds.[2,3] Various authors have focused the toxic effect of hexavalent chromium on microorganisms, plants and health.[4,5] Cr(III) compounds play an important role in the metabolism of glucose and in certain lipids,[6] whereas Cr(VI) interferes with the enzymatic sulfur uptake of the cell[7] and also affects lungs, liver and kidney.[8] Insoluble Cr(VI) compounds retained in the lungs over extended period of time cause lung cancer.[9]

In natural water, chromium species mainly occur as chromate and cationic hydroxo complexes.[10,11] So it is important to know the individual species of chromium in natural water, waste water or drinking water. Chromium speciation depends mainly on the redox potential and pH of the media: e.g. above pH 7 Cr(III) predominates and below pH 6 Cr(VI) is the major species.[12] But low chromium levels are usually determined by separation of one specific form by sorption,[13] liquid-liquid extraction,[14,15] coprecipitation[11,16,17] or electrodeposition[18] followed by instrumental analysis. The second form is then determined after it has been reduced or oxidized, as the residual chromium content in the solution.[19,20]

Solid phase extraction is now entering a challenging area for the preconcentration and separation of trace metal ions. Anchoring the active site to a solid support in a polymer matrix provides an immobilized active surface capable of forming coordinate bonds with the metal ions. In recent years, separation and preconcentration of chromium species have been carried out by using polyimine Detata sorbent,[21] anionic solid exchanger,[22] solid phase resin[23,24] and by biosorption.[25,26] Nevertheless, few reports have been published on the use of solid phase resin for pH-dependent speciation following selective elution of different forms of chromium viz. Cr(III) and Cr(VI).[21,24] We have reported earlier that the syntheses of resins containing imidazole,[27] benzimidazole,[28] naphthol 3,6-disulfonic acid[24] and 6-mercaptopurine[29] in a polystyrene bed have been used for the preconcentration and separation of heavy metal ions.

The present work describes the preconcentration and separation of the two forms of chromium, viz. Cr(III) and Cr(VI), by using a chelating resin containing 6-mercaptopurine as a functional group anchored by azo function (–N=N–) to the polymeric styrene-divinylbenzene and finally determination of these two species by using dinitrogen oxide–acetylene flame.

Experimental

Apparatus. A GBC Avanta Atomic Absorption Spectrometer was used for absorbance measurement with the following conditions for chromium: hollow cathode lamp current 6 mA, wavelength 357.9 nm. A 0.45 μm pore size Millipore membrane filter was used for the filtration of natural water samples.

Materials. Potassium dichromate (BDH, Bombay), chromium(III) nitrate (BDH, Bombay) were reagent grade and were used as provided. The standard solution of Cr(III) for AAS measurement was obtained from E. Merck (Germany). All other chemicals used were reagent grade. The diverse metal ion solutions were prepared from analytical grade reagents.

Synthesis of the Resin. The polystyrene crosslinked with 8% divinylbenzene (5 g, 30–60 mesh) was first nitrated by a mixture of 14 M HNO_3 and 18 M H_2SO_4 (1:1) followed by reduction to amino group by excess $SnCl_2$ and 12 M HCl. The amino compound thus obtained was diazotized by 1 M $NaNO_2$ and 1 M HCl, followed by coupling with a basic solution of 6-mercaptopurine (3.5 g) at (0–5) °C to obtain 6-mercaptopurinylazo resin (Fig. 1). It was vacuum dried and preserved at room temperature.[29]

Metal Ion Capacity as a Function of pH. A batch technique was used. Taking metal ion in excess to the 6-mercaptopurinylazo resin capacities were determined in the pH range 1.0–9.0. 100 mg of the resin was taken in a beaker and metal ion solution

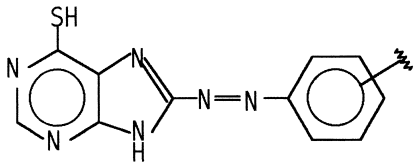

Fig. 1. Structure of 6-mercaptopurinylazo resin.

(excess) was added. In order to adjust the acidic pH, 0.1 M HCl was used, whereas for adjustment of basic pH, 2 M aqueous sodium acetate solution was used. The concentration of the metal ion was determined as described earlier.

Desorption of Metal Ions. In order to obtain the best solution for desorption, the resin containing maximum sorbed metal ions was shaken with 30 mL of various eluting agents viz 0.01–2 M HCl or HNO_3 for 24 h. After filtration the concentration of each metal ion was determined as usual.

Column Operation. A glass column (130 mm length and 10 mm i.d.) with a glass wool plug over its stopcock was used. 6-mercaptopurinylazo resin (1.0 g) was immersed in doubly distilled water and we allowed the swollen beads to flow through the top of the column so that large particles would settle at the bottom in order to avoid the choking problem. Before use, the column was washed thoroughly with doubly distilled water and then conditioned at appropriate pH.

The sorption and recovery characteristics for Cr(III) and Cr(VI) in the presence of various metal ions were thoroughly studied. A 100 mL portion of the mixture of the test metal ion was allowed to flow through the resin column at a flow rate of 1.2 mL min^{-1}. The metal ion not sorbed was completely washed out using sodium acetate buffer of appropriate pH. The sorbed Cr(III) and Cr(VI) were completely eluted at the flow rate of 1.2 mL min^{-1} with 4 M HCl and the concentration was measured.

Results and Discussion

Sorption and Desoprtion of Metal Ions. The sorption behavior of Cr(III) and Cr(VI) of the resin was carried out by batch method at different pH values which are shown in Fig. 2. The sorption of Cr(III) on this resin shows that, with increasing pH, the exchange capacity increases with a limiting value of 0.44 mmol g^{-1} at pH 6.5, whereas for Cr(VI) it is reversed. The exchange capacity decreases with increasing pH and shows a maximum of 1.06 mmol g^{-1} at pH 1.0. At lower pH, the nitrogen atom of azo group is protonated[30,31] and subsequently binds Cr(VI). The sorption of Cr(III) at higher pH may be due to chelation by azo group and N-7 of purine moiety.[32] Hence complete separation of the two forms of chromium is possible by adjusting the pH at appropriate levels. The effect of different eluents on the desorption of metal ion is given in Table 1. Complete desoprtion of both the species took place with 10 mL 4 M HCl.

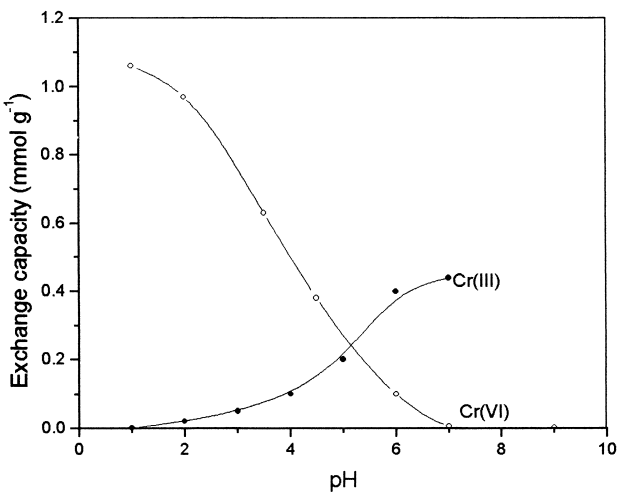

Fig. 2. Exchange capacities of Cr(III) and Cr(VI) on the resin versus pH.

Table 1. Desorption of Cr(III) and Cr(VI) by Different Eluents

Eluents	Recovery/%	
	Cr(III)	Cr(VI)
0.01 M HCl	23.9	6.2
0.1 M HCl	24.2	10.1
1 M HCl	35.2	38.7
2 M HCl	62.0	71.4
4 M HCl	97.8	98.3
0.01 M HNO_3	27.3	6.2
0.1 M HNO_3	36.4	17.6
1 M HNO_3	63.4	42.8
2 M HNO_3	98.3	88.5

Effect of Diverse Ions. The effect of foreign metal ions on the retention of both Cr(III) and Cr(VI) were investigated by mixing 2 μg mL^{-1} each of Cr(III) and Cr(VI) with 20-fold excess of foreign ions after following the recommended procedure (Table 2). The presence of macro amounts of diverse metal ions like those in the first transition series did not interfere. Desorption of Cr(III) and Cr(VI) was done to the extent of almost 100% using suitable eluent as already described. Hence, attempts were made to separate Cr(III) and Cr(VI) from synthetic mixtures by simply varying the pH of the solution.

Effect of Flow Rate. The flow rate of the sample solution affects the retention of Cr(III) and Cr(VI) on the resin. Therefore, the effect of the flow rate of sample solution was exam-

Table 2. Separation of 2 μg mL^{-1} Each of Cr(III) and Cr(VI) from Several Binary Mixtures in a Sample Volume of 50 mL at pH 6.5 and 1.0, Respectively

Foreign ion[a)]	Recovery/%	
	Cr(III)	Cr(VI)
Al(III)	89.1	—
Fe(III)	93.2	—
V(IV)	92.0	—
Cd(II)	101.2	—
Ni(II)	99.4	—
Co(II)	96.3	—
Zn(II)	97.0	—
Vanadate	—	89.0
Phosphate	—	89.0
Arsenite	—	97.1
Molybdate	—	99.0
Arsenate	—	96.7

a) In each case, the amount of foreign ion added was 2000 μg.

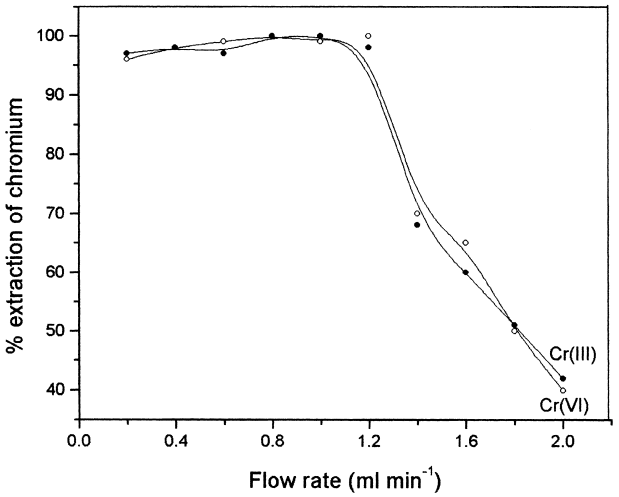

Fig. 3. Optimization of flow rate for the sorption of both Cr(III) and Cr(VI).

ined under optimum conditions of pH and eluent. The flow rate of the sample solution was adjusted in the range of 0.2–2 mL min^{-1}. It can be observed from Fig. 3 that the sorption of both Cr(III) and Cr(VI) are quantitative at a flow rate of 1.2 mL min^{-1}.

Reuse of the Resin. To test the long term stability of the column, the column containing 6-mercaptopurinylazo resin was subjected to successive binding and stripping cycle by passing 100 mL 1 μg mL^{-1} solution of both Cr(III) and Cr(VI) and then eluted by 4 M HCl. The column is equally efficient after 50 times regeneration. Thus multiple use of the resin column is feasible.

Applications

Separation of Cr(III) and Cr(VI) from the Binary Synthetic Mixtures. For the optimization of column separation, different amounts of each of Cr(III) and Cr(VI) were mixed so as to have a total volume of 100 mL. The pH of the solution was adjusted to 1.0, at which the recovery of Cr(VI) is the highest while that of Cr(III) is the lowest. The solution was drawn through the column at a flow rate of 1.2 mL min^{-1}. In another set of experiments pH was adjusted to 6.5, at which Cr(III) was retained whereas Cr(VI) is not. Both the retained species were eluted by 10 mL 4 M HCl maintaining the same flow rate. The concentration of both the species thus eluted was measured by flame AAS. The results are shown in Table 3.

Analysis of Actual Water Samples. In order to validate the methodology proposed for chromium speciation, it was applied for quantitative determination of Cr(III) and Cr(VI) in the waste water samples, collected at three different points of Fertilizer Corporation of India (FCI), Durgapur, India. This concern manufactures different nitrogenous fertilizers. While doing so, in a process for conversion of nitrogen and hydrogen into ammonia, it uses Cr_2O_3 as supporting catalyst. The waste water was filtered through a 0.45 μm Milipore membrane filter. After 200 mL of the filtrate was taken, the pH was maintained at 1.0 and the solution was fed into the resin column. In another portion of the filtrate (200 mL), the pH was adjusted to 6.5 and fed into the column. After elution (10 mL eluent was used in each case) the concentration was measured by AAS using dinitrogen oxide–acetylene flame. Results of the different species present in different natural water samples are presented in Table 4 and are compared with those of our earlier method.[24]

Table 3. Separation of Cr(III) and Cr(VI) in Binary Synthetic Mixtures

No. of obsd	Amounts taken/μg	Amounts found/μg[a)]	Error/%
1	Cr(III):100	Cr(III):101.2 ± 0.2	1.2
	Cr(VI):100	Cr(VI):104.3 ± 0.4	4.3
2	Cr(III):100	Cr(III):104.6 ± 0.2	4.6
	Cr(VI): 50	Cr(VI): 51.3 ± 0.5	2.6
3	Cr(III): 50	Cr(III): 48.7 ± 0.4	2.6
	Cr(VI):100	Cr(VI):104.2 ± 0.1	4.2
4	Cr(III): 10	Cr(III): 9.2 ± 0.3	8.0
	Cr(VI):100	Cr(VI):101.2 ± 0.2	1.2
5	Cr(III):100	Cr(III):103.5 ± 0.6	3.5
	Cr(VI): 10	Cr(VI): 11.2 ± 0.5	12.0

a) Average of five determinations.

Table 4. Determination of Different Species of Chromium in Natural Water

Sampling station	Chromium species found/ng mL^{-1} a)	
	Reference method (24)	Proposed method
1	Cr(III):115.9 ± 0.3	Cr(III):117.3 ± 0.2
	Cr(VI): 68.4 ± 0.1	Cr(VI): 69.4 ± 0.1
2	Cr(III): 79.6 ± 0.5	Cr(III): 81.2 ± 0.3
	Cr(VI): 45.4 ± 0.3	Cr(VI): 46.5 ± 0.2
3	Cr(III): 92.4 ± 0.3	Cr(III): 94.3 ± 0.2
	Cr(VI): 53.2 ± 0.5	Cr(VI): 55.3 ± 0.1

a) Average of five determinations.

Conclusions

Chromium speciation study in waste water can be carried out very effectively as a function of pH using 6-mercaptopurinylazo chelating resin. At pH 1.0 Cr(VI) is selectively sorbed, whereas at pH 6.5 Cr(III) is sorbed by the resin. The method could be applied successfully for the speciation of chromium in natural water samples.

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