



Sorption Study of Chromium(III) in Glycine Medium Using Poly[dibenzo-18 crown-6] and Column Chromatography

Pratibha S Patil*, Nitin D Nikam and Baburao S Mohite

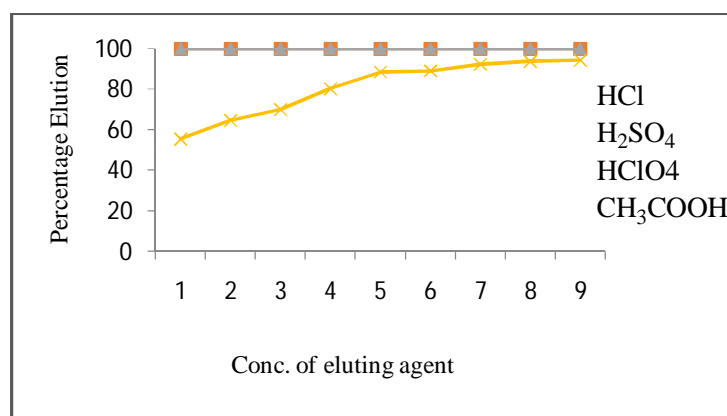
Analytical and Environmental Research Lab, Department of Chemistry,
Shivaji University, Kolhapur, 416004 M.S. **INDIA**
Email: psp.2303@gmail.com

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ABSTRACT

A simple chromatographic separation method has been developed for quantitative sorption of chromium(III) from an aqueous solution of 1×10^{-5} M Glycine using poly [dibenzo-18-crown-6] as stationary phase. The sorption of chromium(III) was quantitative 1×10^{-3} M to 1×10^{-6} M Glycine. The elution of chromium(III) was quantitative with 0.5–8.0 M HCl, 0.5–8M HClO₄ and 0.5–8.0 M H₂SO₄. The capacity of poly [dibenzo-18-crown-6] for chromium(III) was found to be 1.54 ± 0.01 mmol/g of crown polymer. The effects of concentrations of glycine, chromium(III), foreign ions and eluents have been studied. Chromium(III) was separated from a number of cations in Multi component mixtures. The applicability of the proposed method was ascertained for the determination of chromium(III) in real samples. The reliability of method was checked by comparison of the results with those obtained using flame photometer. The method is very simple, rapid and selective with good reproducibility (approximately $\pm 2\%$).

Graphical Abstract



Elution of chromium(III) with various eluting agents

Keywords: Sorption, Separation, Chromium(III), Chromatography, poly [dibenzo-18-crown-6], Glycine.

INTRODUCTION

Chromium and its compounds are very useful in everyday life. It is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation, chromium chemicals production, and pulp and paper production. The recovery and removal of such species are important not only from environment protection view point, but also for the importance as the secondary resource recycling and economical purposes [1]. Chromium and its compounds are known as strategic minerals widely used in various industrial plants such as electroplating, leather tanning, painting, pigment production and metallurgy [1, 2]. Chromium metal (Cr) occurs naturally in the environment and has both beneficial and potential human risks. Cr exists in many oxidation states with Cr(III) and Cr(VI) being the primary existing oxidation states in the environment. Cr(III) is an essential nutrient for maintaining lipid, insulin, and glucose metabolism and its deficiency may lead to diabetes [3], of the many Cr species, hexavalent chromium (Cr(VI)) is one of the most toxic, especially when compared to trivalent chromium [4]. Chromium oxidation states ranges from +2 to +6. Among them trivalent and hexavalent ions are two relatively stable valance states in the natural samples [5]. Although Cr(III) is an essential component for some biological activities, Cr(VI) is categorized as one of the most toxic chemical species, being an agent for various cancers [2, 6]. Thus, there moving of hexavalent chromium from industrial wastewater before discharging to the environment is a crucial concern as well as a challenging problem in industries from economical view point. Liquid-liquid extraction [7-10], facilitated transport through liquid membrane [11-14], adsorption by activated carbon [15-18] and ion exchange [19-22] are among the techniques frequently used for recovering of chromium ions. Nowadays, membrane technologies have gained an important role in a variety of industries such as water desalination, food processing and medical applications [14, 23, 24].

Many methods have been reported for the quantitative determination of chromium. The analytical technique varies from inductively coupled plasma-atomic emission spectroscopy [25], atomic absorption spectroscopy [26], neutron activation analysis [27], X-ray absorption spectroscopy [28], complexometric [29], catalytic kinetic [30], sequential injection [31] to flow injection methods [32-35], for the separation of chromium various methods were used [36-38].

According to literature survey reveals that there are no reports on the use of poly[dibenzo-18-crown-6] for the chromatographic separation of chromium(III) in glycine medium. The aim of the present study is to optimize conditions on a laboratory scale for the chromatographic separation and recovery of chromium(III) from other associated metal ions employing poly[dibenzo-18-crown-6] as the sorbent in glycine as counter ion.

MATERIALS AND METHODS

Apparatus and reagents: A Ziess (German) Spectrophotometer, a digital pH meter (Model LI-120, ELICO, India) with glass and calomel electrodes and a digital Flame photometer (PI, Model No. 041, India) were used.

All chemicals were of analytical reagent grade or chemically pure grade and distilled water was used throughout the study. Chromium sulphate [$\text{Cr}_2(\text{SO}_4)_3$] (E Merck grade) was used for preparing chromium(III) stock solution (1M) and standardized gravimetrically [39]. A solution containing $100 \mu\text{g mL}^{-1}$ of chromium(III) was prepared by appropriate dilution of standard stock solution. Glycine solution (1×10^{-1} M) was prepared by dissolving 1.875 g of glycine in distilled demonized water and diluted to 250 mL. Poly[dibenzo-18-crown-6] (E Merck Darmstadt, Germany) was used after screening to 100-200 mesh. A total of 0.5 g of polymer was slurred with distilled deionized water and poured into a Pyrex glass chromatographic column (20×0.8 cm i.d.). The column was used after preconditioning with glycine solution.

General procedure: 50 μg of chromium(III) was mixed with glycine in the concentration range of 1×10^{-1} M to 1×10^{-9} M in a total volume of 10 mL. The solution was then passed through poly[dibenzo-18-crown-6] column, preconditioning with same concentration of glycine as that of the sample solution at flow rate of 0.5 mL min^{-1} . The column was then washed with the same concentration of glycine. The sorbed chromium(III) was then eluted with different eluting agents (described later) at the flow rate of 0.5 mL min^{-1} . 5.0 mL fraction were collected and chromium(III) in the aqueous phase was determined spectrophotometrically. Takao *et al.*, described a extraction-spectrophotometric determination of with 4-(2-pyridylazo)-resorcinol (PAR) at 540 nm [40]. The concentration of chromium(III) was calculated from a calibration graph.

RESULTS AND DISCUSSION

Sorption of chromium(III) on poly[dibenzo-18-crown-6] as a function of glycine concentration:

Sorption studies of chromium(III) were carried out from glycine medium. The concentration of glycine was varied from 1×10^{-1} M to 1×10^{-9} M (Table 1). After sorption, the elution of chromium(III) was carried out with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) sorption of chromium(VI) from 1×10^{-3} M to 1×10^{-6} M glycine. The results are shown in (Figure 1). The subsequent sorption studies of chromium(III) were carried out with 1×10^{-3} M glycine.

Table 1. Sorption of chromium(III) as a function of glycine concentration
Cr(III) = $50 \mu\text{g mL}^{-1}$, Eluent = 4.0 M HCl

Glycine concentration (M)	Sorption of Cr(VI) (%)
1×10^{-1}	88.20
1×10^{-2}	97.34
1×10^{-3}	100
1×10^{-4}	100
1×10^{-5}	100
1×10^{-6}	100
1×10^{-7}	94.25
1×10^{-8}	88.55
1×10^{-9}	76.20

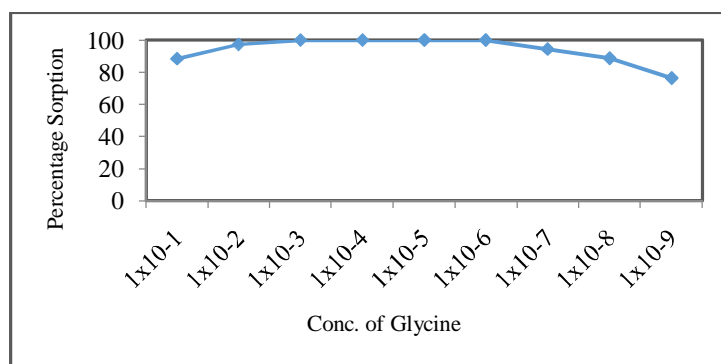


Figure 1. Sorption of chromium(III) as a function of glycine concentration

Elution study of chromium(III) with various eluting agents: 50 $\mu\text{g mL}^{-1}$ of chromium(III) was sorbed on the poly[dibenzo-18-crown-6] column at 1×10^{-5} M glycine concentration. After sorption, elution of chromium(III) was carried out using hydrochloric acid, sulphuric acid, perchloric acid and acetic acid (Table 2). The concentration of eluting agents varied from 0.5 M to 8.0 M. The elution profile of chromium(III) with various eluting agents is shown in (Figure 2). Showed that chromium(III) was quantitatively eluted with 0.5 M to 8.0 M hydrochloric acid and Sulphuric acid,

0.5 M to 8.0 M perchloric acid. Further elution studies of chromium(III) in this work was carried out with 4.0 M hydrochloric acid.

Table 2. Elution of chromium(III) with different eluting agents Cr(III) = 50 $\mu\text{g mL}^{-1}$, glycine $1 \times 10^{-5}\text{M}$

Conc. Acid	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
	Percentage Elution								
HCl	100	100	100	100	100	100	100	100	100
H ₂ SO ₄	100	100	100	100	100	100	100	100	100
HClO ₄	100	100	100	100	100	100	100	100	100
CH ₃ COOH	55.60	64.82	70.12	80.45	88.60	89.18	92.45	93.86	94.45

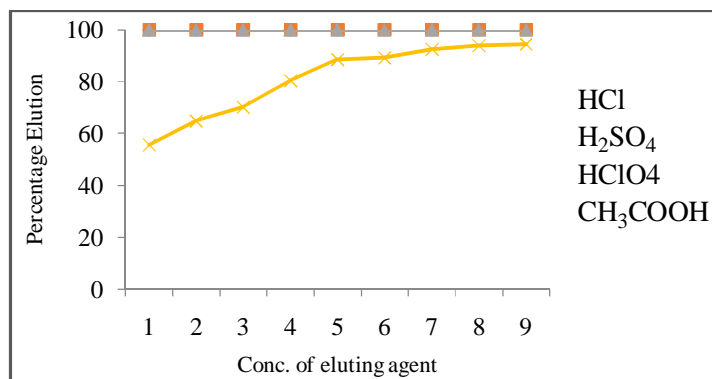


Figure 2. Elution of chromium(III) with various eluting agents.

Effect of varying concentration of chromium(III): In order to find out the capacity of poly[dibenzo-18-crown-6] for the chromium(III), the concentration of chromium(III) was varied from 50-600 $\mu\text{g 10mL}^{-1}$ in glycine and 4.0 M hydrochloric acid as eluent. The results (Table 3) showed that the sorption of chromium(III) was quantitative (100%) up to 400 μg . With increase in concentration of chromium(III) there was decrease in the percentage sorption of chromium(III) and is shown in the (Figure 3). From this study it was found that the capacity of poly[dibenzo-18-crown-6] for chromium(III) was found to be $1.54 \pm 0.01 \text{ mmol g}^{-1}$ of crown polymer.

Table 3. Effect of varying concentration of chromium (III) glycine $1 \times 10^{-5}\text{M}$, eluent 1.0 M HCl

Chromium(III) (μg)	Percentage sorption (%)
50	100
100	100
150	100
200	100
250	100
300	100
350	100
400	100
450	97.30
500	95.45
550	84.46
600	77.51

Separation of chromium(III) from binary mixtures: An aliquot of solution containing 50 μg of chromium(III) was mixed with foreign ions and glycine was added so that its concentration was $1 \times 10^{-5}\text{M}$ in total volume of 10 mL. The tolerance limit was set as the amount of foreign ions required to cause $\pm 2\%$ deviation in the recovery of chromium(III). The solution was passed through a poly[dibenzo-18-crown-6] column, preconditioned with $1 \times 10^{-5}\text{M}$ glycine at a flow rate of 0.5 mL

min⁻¹. Subsequently the column was washed with 15 mL of 1×10^{-5} M glycine to remove unsorbed metal ions. Various foreign ions were not sorbed and hence passed through the column. The effluent was collected and analyzed for foreign ion content. The tolerance limit of various foreign ions is shown in table 4. The most of the alkali metals show high tolerance limit. In case of alkaline metal lithium(I), sodium(I), potassium (I), rubidium(I) and cesium(I) are strongly tolerates. Most of the p-block and d-block elements were sorbed and shows low tolerance limit. Amongst the inner transition elements, as compared lanthanum(III), cerium(III), thallium(III) show low tolerance limit. The anion of inorganic and organic acids showed high tolerance limit (Table 4).

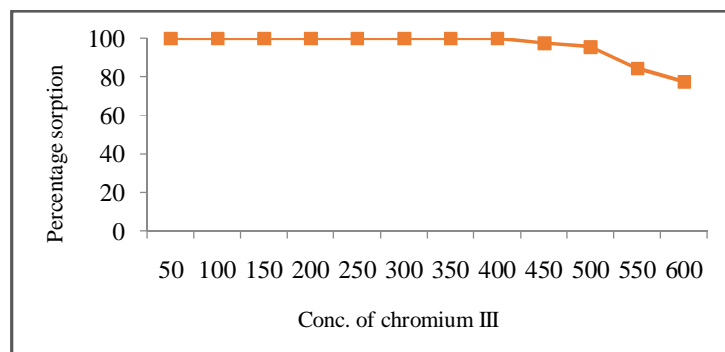


Figure 3. Effect of varying concentration of chromium(III).

Table 4. Separation of chromium(III) from binary mixtures Cr(III)- 50 µg, sorption- 1×10^{-5} M glycine, eluent- 2.0 M HCl

Ion	Added as	Tol. Limit (mg)	Ion	Added as	Tol. Limit
Li ⁺	LiCl	15	Tl ³⁺	Tl(NO ₃) ₃ .3H ₂ O	0.1
Na ⁺	NaCl	12	La ³⁺	La(NO ₃) ₃ .6H ₂ O	0.03
K ⁺	KCl	18	Ce ³⁺	CeCl ₃ .6H ₂ O	0.8
Rb ⁺	RbCl	16	V ⁴⁺	VOSO ₄ .4H ₂ O	0.7
Cs ⁺	CsCl	8	Th ⁴⁺	Th(NO ₃) ₄	0.8
NH ₄ ⁺	NH ₄ Cl	14	Cr ⁶⁺	K ₂ Cr ₂ O ₇	1.3
Be ²⁺	BeSO ₄ .4H ₂ O	1.5	Mo ⁶⁺	(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	9
Mg ²⁺	MgCl ₂ .6H ₂ O	0.5	W ⁶⁺	Na ₂ WO ₄ O.4H ₂ O	7
Ca ²⁺	CaCl ₂	1.5	Cl ⁻	HCl	2
Sr ²⁺	Sr(NO ₃) ₂	0.1	Br ⁻	HBr	7
Ba ²⁺	Ba(NO ₃) ₂	0.8	SCN ⁻	NaSCN	3
Co ²⁺	CoCl ₂ .6H ₂ O	Co-extran	ClO ₄ ⁻	HClO ₄	3
Ni ²⁺	NiCl ₂ .6H ₂ O	Co-extran	CH ₃ COO ⁻	CH ₃ COOH	4
Zn ²⁺	ZnCl ₂	0.5	SO ₄ ²⁻	H ₂ SO ₄	2
U ⁶⁺	UO ₂ (NO ₃) ₂ .6H ₂ O	2	BO ₃ ³⁻	H ₃ BO ₃	6
Pb ²⁺	Pb(NO ₃) ₂	4	Tartrate	Tartaric acid	11
Fe ³⁺	FeCl ₃ .6H ₂ O	1.2	EDTA	EDTA	6
Al ³⁺	Al(NO ₃) ₃ .9H ₂ O	0.5	Ascorbate	Ascorbic acid	3

Separation of chromium(III) from Multicomponent mixtures: Separation of chromium(III) was carried out from number of associated elements in multi component mixture. The mixture containing lithium(I), uranium(VI), chromium(III), cobalt(II), mercury(II), potassium(I), sodium(I), nickel (II), manganese(II), cadmium(II) and lead(II) was passed through the poly[dibenzo-18-crown-6] column at 1×10^{-5} M glycine concentration, lithium(I), potassium (I), sodium(I) was not sorbed and hence passed through the column. The uranium(VI), chromium(III), cobalt(II) mercury(II), potassium(I), nickel (II), manganese(II), cadmium(II) and lead(II) were sorbed. The sorbed uranium(VI) was first eluted with 25 mL of 0.2 M ammonium carbonate. After that chromium(III) were eluted with 4 M hydrochloric acid and effluents are analyzed spectrophotometrically. Using this method, separation of cobalt(II),

chromium(III), mercury(II), potassium(I), manganese(II), nickel (II), lithium(I), potassium (I), sodium(I), cadmium(II) and lead(II) mixtures was achieved. The results are shown in table 5.

Table 5. Separation of chromium(III) from Multicomponent mixtures

No	Mixture	Taken μg	Found μg	Recovery* %	Sorption Condition	Eluent
1	Li(I)	100	100	100	$1 \times 10^{-3} \text{M}$	NSPC**
	U(VI)	100	100	100	Glycine	0.2 A.C.
	Cr(III)	50	49	98		4 M HCl
2	K(I)	100	99	99	$1 \times 10^{-3} \text{M}$	NSPC**
	Cr(III)	50	50	100	Glycine	4 M HCl
	Co(II)	50	48	96		0.5 M HBr
3	Na(I)	100	100	100	$1 \times 10^{-3} \text{M}$	NSPC**
	Cr(III)	50	49.5	99	Glycine	4 M HCl
	Hg(II)	100	98	98		0.5 M HBr
4	Li(I)	100	100	100	$1 \times 10^{-3} \text{M}$	NSPC**
	Pb(II)	25	24	96	Glycine	3 M HBr
	Cr(III)	50	49	98		3.0 M HCl
5	Li(I)	100	100	100	$1 \times 10^{-3} \text{M}$	NSPC**
	Mn (II)	50	49	98	Glycine	0.5 M HBr
	Cr(III)	50	50	100		3.0M HCl
6	K(I)	100	99	99	$1 \times 10^{-3} \text{M}$	NSPC**
	Cd(II)	50	49	98	Glycine	0.5 M HBr
	Cr(III)	50	49.5	99		3.0M HCl
7	Li(I)	100	100	100	$1 \times 10^{-3} \text{M}$	NSPC**
	Ni(II)	50	49	98	Glycine	0.5 M HBr
	Cr(III)	50	49.5	99		3.0M HCl

* Average of triplicate analysis, ** NSPC = No Sorption Passing through the Column
A.C.- Ammonium Carbonate

APPLICATION

Determination of chromium in pharmaceuticals samples: The sample of tablet was dissolved in 10 mL 0.1 M HCl. The solution was evaporated almost to dryness it was lixiviated with water and solution was made up to 500 mL aliquot of solution was taken from which chromium(III) was extracted and analyzed as per general procedure (Table 6).

Table 6. Determination of chromium in pharmaceuticals samples

Sample	Present Mcg tablet^{-1}	Found Mcg tablet^{-1}
Chromoplex	0.200	0.199
Fourts B	0.150	0.149
Optisulin	0.500	0.498

CONCLUSION

The important feature of this method is that using column chromatographic method and poly[dibenzo-18-crown-6] the separation of chromium(III) from associated element in glycine medium has been achieved. The capacity of poly [dibenzo-18-crown-6] for chromium(III) was found to be 1.54 ± 0.01 mmol/g of crown polymer. Chromium(III) was separated from number of cations in binary as well as multi component mixtures. The method was extended to the determination of chromium(III) in real sample. The aim of present investigation is to demonstrate a simple, selective and cheap method and has good reproducibility (approximately $\pm 2\%$).

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