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Sorption study of Cadmium(II) in glycine medium using poly [dibenzo-18 crown-6] and Column chromatography

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Abstract

A simple chromatographic separation method has been developed for quantitative sorption of Cadmium(II) from an aqueous solution of 1×10^{-3} M Glycine using poly [dibenzo-18-crown-6] as stationary phase. The sorption of Cadmium(II) was quantitative 1×10^{-2}M to 1×10^{-4}M Glycine. The elution of Cadmium(II) was quantitative with 1.0–8.0 M HCl, 1.0-8.0M $HClO_4$, 2.0-8.0 M H2SO4 and 1.0-8.0M CH3COOH The capacity of poly [dibenzo-18-crown-6] for Cadmium(II) was found to be 0.533 ± 0.01 mmol/g of crown polymer. The effects of concentrations of Glycine, Cadmium (II), foreign ions and eluents have been studied. Cadmium(II) was separated from a number of cations in multicomponent mixtures. The applicability of the proposed method was ascertained for the determination of Cadmium(II) 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±2%).

Keywords: sorption, separation, Cadmium(II), Glycine, poly [dibenzo-18- crown-6], Chromatography

1. Introduction

Cadmium makes up about 0.1 ppm of Earth's crust. Compared with the more abundant 65 ppm zinc, cadmium is rare [1]. No significant deposits of cadmium-containing ores are known Greenockite (CdS), the only cadmium mineral of importance, is nearly always associated with sphalerite (ZnS). This association is caused by the geochemical similarity between zinc and cadmium which makes geological separation unlikely. As a consequence, cadmium is produced mainly as a byproduct from mining, smelting, and refining sulfidic ores of zinc, and, to a lesser degree, lead and copper. Small amounts of cadmium, about 10% of consumption, are produced from secondary sources, mainly from dust generated by recycling iron and steel scrap. Production in the United States began in 1907 [2] but it was not until after World War I that cadmium came into wide use [3, 4]. One place where metallic cadmium can be found is the Vilyuy River basin in Siberia [5].

A considerable amount of work has been done in recent years on the ion exchange separation of cadmium from various other elements [6, 17]. While Kallmann's [11] anion exchange method has successfully separated a considerable number of cations from cadmium, published methods on cation exchange have been applied to separate cadmium from only a small number of other cations, and are therefore of a limited application.

The discovery of crown ether opened a new era in supramolecular chemistry used in various fields in chemistry. As most of crown ether are useful as stationary phase in chromatographic method [18]. Polymeric crown ethers exhibit special features such as high resistance to chemicals, radiolysis, temperature and also polar solvents. By using poly [dibenzo-18-crown-6] we have reported the sorption behavior and selective separation of metal cation [19, 23]. According to literature survey reveals that there are no reports on the use of poly [dibenzo-18-rown-6] for the chromatographic separation of Cadmium(II) in glycine medium. The aim of the present study is to optimize conditions on a laboratory scale for the chromatographic separation and recovery of Cadmium(II) from other associated metal ions employing poly [dibenzo-18-crown-6] as the sorbent in glycine as counter ion.

2 Experimental

2.1 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. A stock solution of Cadmium(II) was prepared by dissolving 1.207 g of cadmium nitrate (Sigma-Aldrich Chemicals Pvt Limited Plot No 12 Bommasandra - Jigani Link Road 560100 Bangalore India) in 100 mL of distilled deionized water and standardized gravimetrically [24]. A solution containing 100 µg/mL of Cadmium(II) 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 deionized 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 deionised water and poured into a Pyrex glass chromatographic column (20×0.8 cm i.d.). The column was used after preconditioning with glycine solution.

2.2 General procedure

50 µg of Cadmium(II) was mixed with glycine in the concentration range of 1×10^{-7} M to 1×10^{-1}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. The column was then washed with the same concentration of glycine. The sorbed Cadmium(II) was then eluted with different eluting agents (described later) at the flow rate of 0.5 mL/min. 5.0 mL fraction were collected and Cadmium(II) in the aqueous phase was determined spectrophotometric ally with PAR at 520 nm [25]. The concentration of Cadmium(II) was calculated from a calibration graph.

3. Results and Discussion

3.1. Sorption of Cadmium(II) on poly [dibenzo-18-crown-6] as a function of glycine concentration.

Sorption studies of Cadmium(II) were carried out from glycine medium. The concentration of glycine was varied from 1×10^{-7} M to 1×10^{-1}M. After sorption, the elution of Cadmium(II) was carried out with 4.0 M hydrochloric acid. It was found that there was quantitative (100%) sorption of Cadmium(II) from 1×10^{-4} M to 1×10^{-2} M L- glycine. The results are shown in (Figure: 1). the subsequent sorption studies of Cadmium(II) were carried out with 5×10^{-3} M glycine.

Table 1: Sorption of Cadmium(II) as a function of glycine concentration Cd (II) = 50 µg, Eluent = 4.0 M HCl

Glycine concentration (M)	Sorption of Cd (II) (%)
$1\text{x}10^{-1}$	85.4
$1\text{x}10^{-2}$	100
$1\text{x}10^{-3}$	100
$1\text{x}10^{-4}$	100
$1\text{x}10^{-5}$	88
$1\text{x}10^{-6}$	86
$1\text{x}10^{-7}$	65

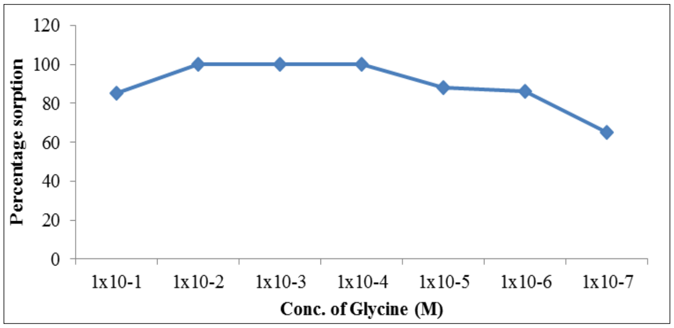

Fig 1: Sorption of Cadmium(II) as a function of glycine concentration.

3.2. Elution study of Cadmium(II) with various eluting agents

50 µg/mL of Cadmium(II) was sorbed on the poly [dibenzo-18-crown-6] column at 5×10^{-4} M glycine concentration. After sorption, elution of Cadmium(II) was carried out using hydrochloric acid, sulphuric acid, perchloric acid and acetic acid. The concentration of eluting agents varied from 0.5 M to 8.0 M. The elution profile of Cadmium(II) with various eluting agents is shown in (Fig 2). It showed that Cadmium(II) was quantitatively eluted with 1.0 M to 8.0 M hydrochloric acid, 2.0M to 8.0 M sulphuric acid, 1.0M to 8.0 M per chloric acid and 1.0M to 8.0 M acetic acid. Further elution studies of Cadmium(II) in this work was carried out with 4.0 M hydrochloric acid.

Table 2: Elution of Cadmium(II) with different eluting agents Cd (II) = 50 µg, glycine 0.001 M

Conc.	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0
Acid	Percentage Elution (%)								
HCl	96	100	100	100	100	100	100	100	100
H_2SO_4	90	94	100	100	100	100	100	100	100
$HClO_4$	96	100	100	100	100	100	100	100	100
CH_3COOH	98	100	100	100	100	100	100	100	100

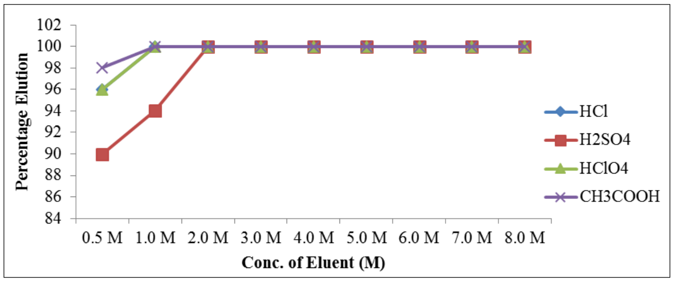

Fig 2: Elution of Cadmium(II) with different eluting agents.

3.3. Effect of varying concentration of Cadmium (II)

In order to find out the capacity of poly [dibenzo-18-crown-6] for the cadmium (II), the concentration of Cadmium(II) was varied from 100-1000 µg/10 mL in glycine and 4.0 M hydrochloric acid as eluent. The results (Table 3.3) showed that the sorption of Cadmium(II) was quantitative (100%) up to 300 µg. With increase in concentration of Cadmium(II) there was decrease in the percentage sorption of Cadmium(II) and is shown in the Fig 3. From this study it was found that the capacity of poly [dibenzo-18-crown-6] for Cadmium(II) was found to be 0.944 ± 0.01 mmol/g of crown polymer.

Table 3: Effect of varying concentration of Cadmium(II) glycine 1×10^{-3} M, eluent 1.0 M HCl

Cadmium(II) (µg)	Percentage sorption (%)
25	100
50	100
75	100
100	100
125	100
150	100
175	100
200	100
225	100
250	100
275	100
300	100
325	93
350	86
375	72
400	68
450	63
475	60

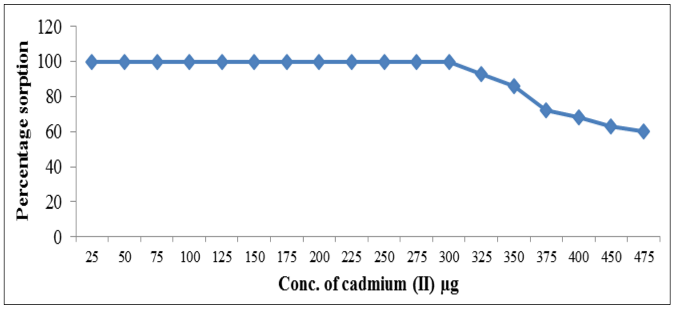

Fig 3: Effect of varying concentration of cadmium (II).

3.4 Separation of Cadmium(II) from binary mixtures

An aliquot of solution containing 50 µg of Cadmium(II) was mixed with foreign ions and glycine was added so that its concentration was 1×10^{-3} M in total volume of 10 mL. The tolerance limit was set as the amount of foreign ions required to cause ±2% deviation in the recovery of cadmium (II). The solution was passed through a poly [dibenzo-18-crown-6] column, preconditioned with 1×10^{-3}M glycine at a flow rate of 0.5 mL/min. Subsequently the column was washed with 15 mL of 1×10^{-3}M glycine to remove un sorbed 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), cesium(I) and alkaline earth metals magnesium(II), calcium(II), strontium(II) tolerate strongly. 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), thallium (IV), cerium (III), shows low tolerance limit. The anion of inorganic and organic acids showed high tolerance limit.

Table 4: Separation of Cadmium(II) from binary mixtures Cd(II) = 50 µg, sorption- 1×10^{-3} M glycine, eluent- 4.0 M HCl

Ion	Added as	Tol. Limit (mg)	Ion	Added as	Tol. Limit
Li^+	LiCl	10	Tl3+	$Tl(NO_3)_3.3H_2O$	0.8
Na^+	NaCl	9	La3+	$La(NO_3)_3.6H_2O$	0.5
K^+	KCl	7	Ce^{3+}	$CeCl_3.6H_2O$	0.5
Rb^+	RbCl	6	V^{4+}	$VOSO_4.4H_2O$	0.5
Cs^+	CsCl	7	Th^{4+}	$Th(NO_3)_4$	Co-Extrn
NH_4^+	NH_4Cl	15	Cr^{6+}	$K_2Cr_2O_7$	0.4
Be^{2+}	$BeSO_4.4H_2O$	Co-Extrn	Mo^{6+}	$(NH_4)_6Mo_7O_{24}.4H_2O$	2.5
Mg^{2+}	$MgCl_2.6H_2O$	5	W6+	$Na_2WO_4O.4H_2O$	6
Ca^{2+}	$CaCl_2$	5	Cl^-	HCl	5
Sr^{2+}	$Sr(NO_3)_2$	2	Br-	HBr	3
Ba^{2+}	$Ba(NO_3)_2$	0.8	SCN^-	NaSCN	4
Co^{2+}	$CoCl_2.6H_2O$	Co-Extrn	ClO_4^-	$HClO_4$	1
Ni^{2+}	$NiCl_2.6H_2O$	Co-Extrn	CH_3COO^-	CH_3COOH	5
Zn^{2+}	$ZnCl_2$	Co-Extrn	$SO4\ _2^-$	H_2SO_4	1.5
U^{6+}	$UO_2(NO_3)_2.6H_2O$	Co-Extrn	BO_3^{3-}	H_3BO_3	2.5
Pb^{2+}	$Pb(NO_3)_2$	3	Tartrate	Tartaric acid	4
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	0.3	EDTA	EDTA	1.5
Fe^{3+}	$FeCl_3.6H_2O$	1.5	Ascorbate	Ascorbic acid	2
Al^{3+}	$Al(NO_3)_3.9H_2O$	0.1			

3.5 Separation of Cadmium(II) from Multi component mixtures

Separation of Cadmium(II) was carried out from number of associated elements in multi component mixture. The mixture containing lithium(I), cadmium (II),Nickel(II), lead(II), sodium(I), potassium (I), iron(III) was passed through the poly[dibenzo-18-crown-6] column at 1×10^{-3} M glycine concentration. The lithium (I), sodium (I), potassium (I) and iron (III) was not sorbed and hence passed through the column. The cadmium (II), Nickel (II), lead (II) were sorbed. The sorbed nickel (II) was first eluted with 25 mL of 0.1 M acetic acid. After that lead (II) were eluted with 4.5 M hydrotropic acid and finally the cadium (II) was eluted with 1.0 M hydrochloric acid and effluents are analyzed spectrophotometric ally. Using this method, separation of cadmium (II), Nickel (II), lead (II) mixtures was achieved. The results are shown in the Table 5.

Table 5: Separation of Cadmium(II) from Multi component Mixtures

No	Mixture	Taken µg	Found µg	Recovery%	Sorption Condition	Eluent
1	Li(I)	50	50	100	$1x10^{-3}$M Glycine	NSPC
	Ni(II)	50	49	98		$0.1MCH_3COOH$
	Cd(II)	50	50	100		1.0 M HCl
	Pb (II)	50	50	100		4.5 M HBr
2	Na(I)	50	50	100	$1x10^{-3}$ M Glycine	NSPC
	Ni(II)	50	50	100		$0.1MCH_3COOH$
	Cd(II)	50	50	100		1.0 M HCl
	Pb (II)	50	50	100		4.5 M HBr

3	K(I)	50	50	100	1x10^{-3}M Glycine	NSPC
	Ni(II)	50	49.5	99		0.1MCH_3COOH
	Cd(II)	50	50	100		1.0 M HCl
	Pb(II)	50	50	100		4.5 M HBr
4	Fe(III)	50	50	100	1x10^{-3}M Glycine	NSPC
	Ni(II)	50	49	98		0.1MCH_3COOH
	Cd(II)	50	50	100		1.0 M HCl
	Pb(II)	50	50	100		4.5 M HBr

*NSPC = No sorption and hence passes through the column

3.6. Determination of cadmium in wood's metal

1.0 g woods metal was dissolved in aqua regia and evaporated almost to dryness, it was then treated with 5 ml hydrochloric acid and evaporated almost to dryness and was extracted with water and diluted to 250 ml. An aliquot of sample solution was subjected as per the above method. The results of triplicate analysis are shown below.

Table 6: Determination of cadmium in Wood's Metal

Alloy	Percentage of cadmium (II)	
Wood 's Metal	Present	Found
	10	9.98

4. Conclusion

The important feature of this method is that using column chromatographic method and poly [dibenzo-18-crown-6].The separation of Cadmium(II) from associated element in glycine medium has been achieved. The capacity of poly [dibenzo-18-crown-6] for Cadmium(II) was found to be 0.944 ± 0.01 mmol/g of crown polymer. Cadmium(II) was separated from number of cations in binary as well as multi component mixtures. The method was extended to the determination of Cadmium(II) in real sample Wood's metal. The aim of present investigation is to demonstrate a simple, selective and cheap method and has good reproducibility (approximately ± 2%).

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