

A Study on the Adsorption Behavior of Some Heavy Metals on Duolite GT-73 Chelating Resin

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Received February 11, 2000

Preconcentration and separation of trace elements are of widespread interest in ultra-trace analysis, and the chelating ion exchange method often affords simple and rapid separation techniques when determination is made by atomic absorption and atomic emission spectrometry. Chelating resins are distinguished from ordinary types of ion exchange resins by the selectivities and firmness with which they bind elements. The selective properties of chelating ion exchanger for particular metal ions are mainly based on the nature of the functional group, minor extend on the size, charge, and other physical properties of the resin.¹

Conforming with the hard and soft acids theory, the functional group containing S donor atoms interacts strongly with the soft acid, like heavy metals. Among these groups, thiols,²⁻⁵ dithiocarbamate,⁶ dithiozone,⁷ and thiosemicarbazide⁸ are of particular interest. Much has been reported on this topic and recently reviewed by Qu.⁹ Duolite GT-73 and Spheron Thiol 1000 bearing thiol(-SH) groups are commercially available resins employed in the separation of heavy metals.

Duolite GT-73 is a macro porous resin based on a cross linked polystyrene matrix. The functionality of the resin is provided mainly by the thiol group, with minor quantities of the sulfonic acid group. It was developed for the removal of mercury from waste water by Alczo Chemicals (Netherlands), and recently Iglesias et al. used it to separate precious metals of gold and palladium from diluted liquors.¹⁰ The manufacturer claims it has a high affinity for Ag, Cu, Pb, Cd, that have a low solubility product of metal sulfide.

In the present paper, we have studied the relationship between the affinity for Duolite GT-73 chelating resin and the solubility products of metal sulfide. Nine of the elements [Al(III), Ag(I), Cd(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II)] were chosen, and the pH effect of the eluent on the affinities for the ions investigated. A breakthrough curve of the ions is also studied to understand the relative affinity of the ions for Duolite GT-73 chelating resin.

Experimental Section

An inductively coupled plasma-atomic emission spectrometer (ICP-AES) from Baird ICP 2070 (Franklin, U.S.A.) was used for the determination of the elements. The operating conditions and spectral lines are shown in Table 1.

Water of 18 M Ω was used throughout the experiment. It was prepared by distillation followed by further purification using a mixed bed ion exchange resin and activated carbon columns. All single element stock solutions (1000 ppm)

were purchased from Junsei Chemical Co. (Tokyo, Japan), and the pH was adjusted to 3-8 by 1.0 M of NaOH and HNO₃ solutions.

The Duolite GT-73 chelating resin in 16-50 mesh, which was purchased from Sigma Chem, Co. (St. Louis, U.S.A.), has ground to 150 mesh. The original resin had a capacity of 1.4 meq/mL (3.9 meq/g), and the pK_a of the thiol was about 8. Solution of 50 mL of 1 ppm was loaded at a flow rate of 0.36 mL/min into a 150 mm(*l*) \times 7 mm (*i.d*) column containing 100 mg of dry resin. The concentration of the ions in the eluate was measured by ICP-AES, and the amount of ions adsorbed was obtained by difference with the initial concentration. A breakthrough curve was plotted to compare the relative affinities of the ions. It was measured by introducing a mixed solution [5 ppm of Al(III), Cd(II), Cu(II), Mn(II), Ni(II), Pb(II), and Zn(II)] into the column containing 100 mg of resin, and successive aliquots of 5 mL eluate were taken for analysis.

Results and Discussion

Since the adsorption of ions on the resin depends mainly on the flow rate of the eluent and the amount of resin, adsorption percents of ions as a function of flow rates were investigated. Table 2 shows the adsorption percents of ions with flow rates on 100 mg resin at pH 6. There is more than 95% adsorption at a flow rate of 0.36 mL/min. Therefore,

Table 1. Specification and operating conditions of ICP-AES

Spectrometer	750 mm focal length 1800 grooves/mm 0.2 nm/mm (2nd order)
RF generator	40.68 MHz
RF power	800 W
Flow rate (L/min)	Carrier 0.64 Coolant 8.5 Auxiliary 1.0
Nebulizer	Concentric type
Observation height	10 mm above induction coil
Spectral line (nm)	Al(III) 396.152 Ag(I) 328.068 Cd(II) 214.438 Cu(II) 324.754 Fe(III) 259.740 Mn(II) 257.610 Ni(II) 231.604 Pb(II) 220.053 Zn(II) 213.856

subsequent studies were carried out at the flow rate of 0.36 mL/min.

Table 3 shows the solubility products¹¹ of the metal sulfides and the adsorption percents at several pH levels. For each metal ion investigated, the adsorption percent increases with increasing pH, reaching a maximum at neutral pH. Ag(I), Cu(II), and Pb(II), which have a low solubility product, are adsorbed completely at pH 4-8. Therefore, their relative affinities to the ions can not be compared. Cd(II), which has a solubility product of $10^{-26.1}$, is completely adsorbed at pH 6-8.

On the other hand, Zn(II), Fe(III), Mn(II) and Al(III), which have a larger solubility product of metal sulfide compared with Ag(I), Cu(II), Pb(II) and Cd(II), show lower adsorption percents (50-63%) at pH 3. The adsorption percents of Zn(II), Fe(III), Mn(II) and Al(III) are also smaller at pH 6, although more than 90% of each is adsorbed. In this case, adsorption percents are not proportional to solubility products, and affinities to Zn(II) and Al(III) do not show large differences, although their $-\log K_{sp}$ values differ by 15. It seems that minor functional group (sulfonic acid) also plays an important role in the affinity of the resin, when the solubility product of metal sulfide become large ($>10^{-21}$). Titration of the resin with NaOH solution showed that the relative amount of sulfonic acid group to thiol is less than 20%. The trivalent ion of Al(III) shows higher affinity than divalent Mn(II) although Al(III) has a larger solubility product, because the trivalent ion of Al(III) has a higher affinity to sulfonic acid group than divalent Mn(II) ion.

At pH 7-8, some of the ions [Fe(III), Mn(II), and Al(III)] precipitated as metal hydroxides and the adsorption percents

Table 2. Adsorption percents of metal ions with variation of flow rate on 100 mg resin at pH 6

Element	flow rate (mL/min)					
	0.24	0.36	0.50	0.70	0.85	1.0
Cu(II)	100	100	100	100	98	97
Pb(II)	100	100	100	100	98	96
Cd(II)	100	100	96	95	94	91
Zn(II)	97	95	81	75	70	66
Mn(II)	97	96	79	72	66	59

Table 3. K_{sp} values of metal sulfide and adsorption percent of metal ions at pH 3-8

Element -log K_{sp}	adsorption percent at pH						
	3	4	5	6	7	8	
Ag(I)	50.1	98	100	100	100	100	100
Cu(II)	35.2	97	100	100	100	100	100
Pb(II)	27.9	97	100	100	100	100	100
Cd(II)	26.1	91	94	97	100	100	100
Zn(II)	21.6	60	69	84	95	97	96
Fe(III)	18.5	61	70	82	94	-	-
Mn(II)	12.6	50	58	69	96	-	-
Al(III)	6.7	63	70	84	92	-	-

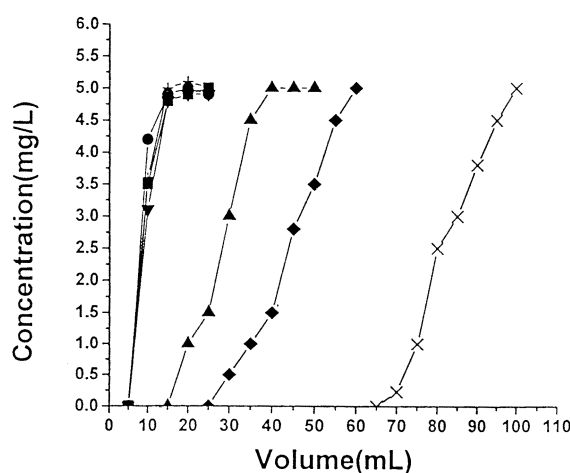


Figure 1. Breakthrough curve of metal ion at pH 4. Cu(x), Pb(◆), Cd(▲), Zn(▼), Ni(+), Mn(■), Al(●). 5 ppm solution was loaded with a flow rate of 0.36 mL/min on 100 mg of resin.

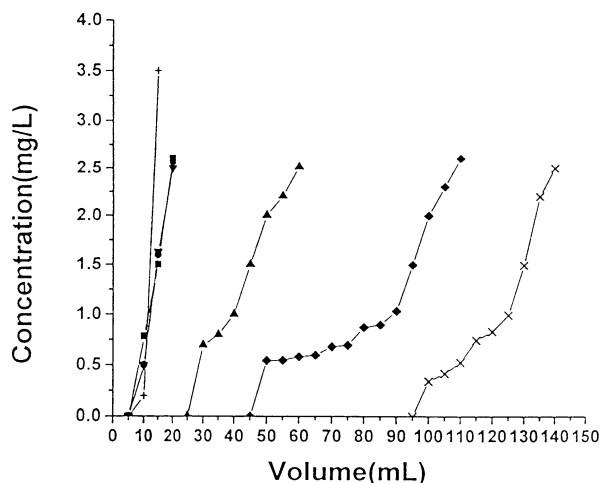


Figure 2. Breakthrough curve of metal ion at pH 6. Cu(x), Pb(◆), Cd(▲), Zn(▼), Ni(+), Mn(■), Al(●). 5 ppm solution was loaded with a flow rate of 0.36 mL/min on 100 mg of resin.

decreased sharply. These values are not shown in Table 3. The $-\log K_{sp}$ values of metal hydroxide for Fe, Mn and Al are 37.4, 12.7 and 32.9, respectively. The solubilities of metal hydroxides are comparable to or much smaller than those of the metal sulfides.

The most reliable method for comparing the relative affinities of the ions is to conduct column breakthrough studies. 5 ppm of mixed solution of seven ions were introduced to the column containing 100 mg of resin, and successive aliquots of 5 mL eluate were taken for the determination of the ions.

Figure 1 shows breakthrough curves of seven ions at pH 4. Cu(II) has the largest breakthrough capacity (the initial volume at which the ion begins to appear) among the seven ions investigated. The respective breakthrough capacities of Cu(II), Pb(II), Cd(II), and Zn(II) are 65, 25, 15, and 5 mL, and the values are inversely proportional to the solubility products of the metal sulfides. The smaller the solubility product, the larger the breakthrough capacity. On the other hand, the breakthrough capacities of Zn(II), Ni(II), Mn(II),

and Al(III) do not show any differences although the solubility product of Zn and Al differ by 10^{15} . This tendency is similar with the adsorption percent studies shown in Table 3. In this case, a minor functional group (sulfonic acid) also plays a role in the affinity for the resin, and the affinity to the sulfonic acid decreases in the order of Al(III), Ni(II), Zn(II). However, Ni(II), Mn(II) and Zn(II), which have the same charge and roughly same effective ionic radius (600 pm) show similar breakthrough curves. Also, trivalent Al(III) shows a similar breakthrough curve although it has the smallest K_{sp} value.

Figure 2 shows the breakthrough curve at pH 6. The curve shows similar behavior with Figure 1 except the breakthrough capacities of the ions are increased. Cu(II) has the largest breakthrough capacity, an increase from 65 to 95 mL. Breakthrough capacities for Pb, Cd and Zn are also increased about 50%. Ni(II), Mn(II), Zn(II) and Al(III) have same the breakthrough capacities. Therefore, it can be concluded that the affinity for the ions of Duolite GT-73 chelating resin depends mainly on the solubility product of metal sulfides when the values are small ($<10^{-26}$). Also, this study suggests that the ions of low solubility products of metal sulfides, including In(III) ($pK_{sp} = 73.2$), Bi(III) ($pK_{sp} = 79.0$), Cu(I) ($pK_{sp} = 47.6$), Hg(I) ($pK_{sp} = 47.0$), Hg(II) ($pK_{sp} = 52.4$) and others, will have high affinity to the ions. On the other hand, when the solubility product of metal sulfide becomes

as large as 10^{-21} , the affinity to the ions decreases, and the minor functional group of sulfonic acid become more important in the affinity phenomenon.

Acknowledgment. The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998 (015-D00171).

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