Cation Exchange Studies on Hydrous Chromium Oxide

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Summary: The exchange behaviour and the pH dependence on adsorption of first transition series metal ions have been studied over hydrous chromium oxide (HCO). The metal ions Mn(II), Fe(II), Cu(II), Co(II) and Zn(II) were separated from one another over HCO column using buffers of pH 3, 4.5, 5 and 6.

Introduction

Many elements form insoluble hydrous oxides which adsorb ions from solutions specially when they are freshly prepared. This has been attributed partly due to ion-exchange process [1-3]. Our earlier reports on the ion-exchange studies on hydrous zirconium oxide (HZO) indicate its amphoteric nature [4,5]. Other workers have also reported the useful separation of numerous cations by column chromatography [2,6] and thin layer chromatography [7]. The present work describes the adsorption and separation of transition metal ions, viz. Mn(II), Fe(II), Cu(II), Co(II) and Zn(II) on HCO.

Experimental

Hydrous chromium oxide was prepared by making 0.2M solution of $CrCl_3.6H_2O$ in 1000 ml of deionized water followed by dropwise addition of 6% NH_4OH with constant stirring untill precipitation was complete (the final pH was adjusted to 6). The precipitate was allowed to stand overnight at room temperature and was then washed several times with demineralized water until the supernatant was free from ammonium and chloride ions. The precipitate was filtered and dried at 50°. After immersion in water, the granular material was then divided into three portions and dried separately at

$50°$, $100°$ and $250°$. The dried samples were sieved to give a 100-200 mesh fraction. The water contents (determined on the basis of formation of Cr_2O_3 at $600°$) were 29.5%, 24.0% and 18.0% and the molar ratios of Cr_2O_3 and H_2O were 1:3.56, 1:2.66 and 1:1.88 in the materials dried at 50, 100 and $250°$ respectively.

Distribution Coefficients and Separation Factors

The distribution coefficient (Kd) of the metal ions was determined by batch equilibrium technique described earlier [4,5]. The amount of metal ions adsorbed was determined from the difference between initial and final concentration in clear supernatant solutions using standard spectrophotometric methods.

Column Operation

A column (8.0 cm x 0.8 cm) was set in vertical position and a pad of glass wool was placed in its porous bed to support the resin. A thick slurry of the ion-exchanger in water was prepared and poured into the column followed by washing with 6M HCl and then treating with distilled water to remove last traces of undesirable ions.

Results and Discussion

The first transition series elements are being increasingly important in catalytic and other industrial purposes. Their general behaviour resembles very closely and the quick separation of their trace amount is difficult. The present studies are aimed to separate micro amounts of Mn(II), Fe(II), Cu(II), Co(II) and Zn(II) and their elution in a mixture by ion-exchange chromatography. The Kd values of the metal ions with respect to their relative equilibrium towards HCO at different pH values were determined. In the acidic solution, the cations were rapidly and reversibly exchanged, with HCO. The Kd values and the separation factor, α, are given in Table 1. The selectivity for all samples of hydrous chromium oxide decreases in the order Fe(II) >Cr(II) >Zn (II) >Co(II) > Mn(II). A similar selectivity order of these ions has been observed on HZO. A comparative study of the separation factors for transition metal ions shows its lower values for transition metal ions for HZO and relatively higher values for Dowax 50W-X8 [8].

Table 1: Kd values (mg/g) and separation factor (α) for transition metal ions on HCO at final pH-6.

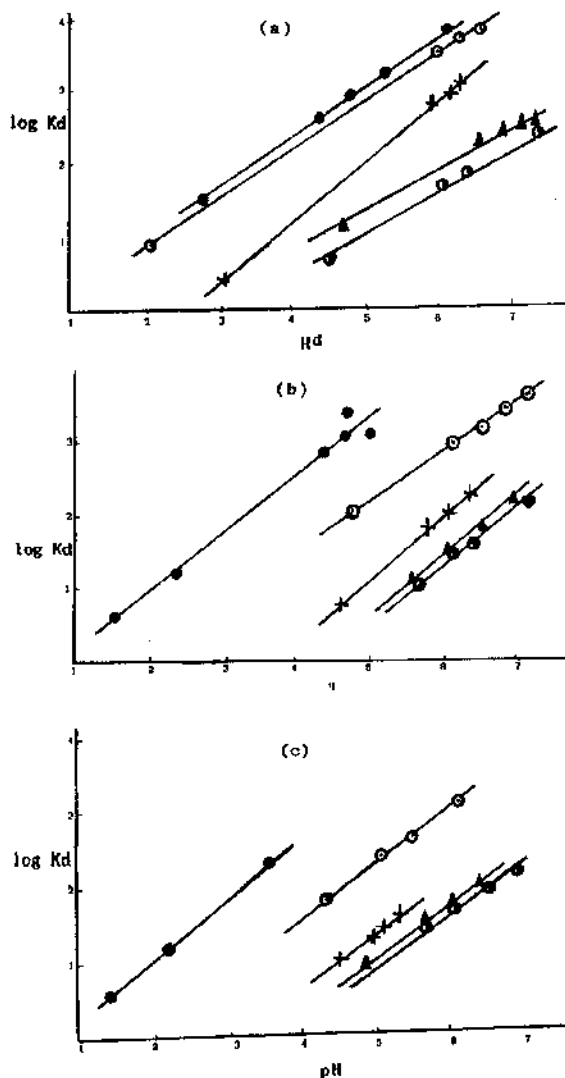| Temp. (°C)	Parameter	Mn^{2+}	Co^{2+}	Zn^{2+}	Cu^{2+}	Fe^{2+}
50	Kd	28.18	50.1	4.5×10^2	2.0×10^3	3.1×10^3
	α	1.8	9.0	4.4	1.5	
100	Kd	22.39	31.62	1×10^2	7.9×10^2	$1.8 \times 10^{3*}$
	α	1.4	3.2	7.9	22.8	
250	Kd	39.8	50.12	1.1×10^2	1×10^3	$2.0 \times 10^{4*}$
	α	1.3	2.2	9.1	20.0	

*Extrapolated values from figure 1.

Fig. 1: Log Kd of transition metal ions against final pH (a) Exchanger dried at $50°$. (b) Exchanger dried at $100°$; (c) Exchanger dried at $250°$. Cu^{2+} (⊙), Fe^{2+}, (●), Zn^{2+} (+), Co^{2+}(▲) Mn^{2+} (⊚).

A slight increase in Kd values for Mn(II), Co(II) and Zn(II) has been observed for HCO dried at 100° and 250°, while at the same pH, the sample gave a higher Kd values for Cu on HCO dried at 50°. The increased Kd values may be due to a large John-Teller deformation from an octahedral configuration of $[Cu(H_2O)_6]^{2+}$. Increased Kd for Cu(II) has also been observed by Sakellanide and Nobelis on HZO [9].

The drying of the resin, usually caused a decrease in adsorptive capacity (Table-2). This may be due to loss of water from the material causing a growth in the size of crystallite and consequently the effective surface area is decreased. The crystal growth has already been confirmed by the sharpness of the diffraction lines observed in X-ray crystallographic studies on HZO resin [2].

The exchanger holds more cations in the neutral medium than in the acidic medium and hence the adsorptive capacity increases with increase in pH. However, since in alkaline media some of the cations precipitated out as their hydroxide, therefore, the present studies could not be extended in alkaline media.

Table 2:Effect of drying temperature on transition metal ions uptake by hydrous chromium oxide (solid 0.25g/25 ml solution).

Temp. ($^\circ$C)	Ions	Adsorption Capacity* (ppm)		
		pH 5	pH 6	pH 7
50		0.25	0.60	1.59
100	Mn^{2+}	-	0.56	1.57
250		0.24	0.85	1.84
50		0.41	1.00	1.84
100	Co^{2+}	-	0.82	2.00
250		0.33	0.82	2.00
50		1.33	2.39	-
100	Zn^{2+}	0.33	1.5	2.6
250		0.55	1.5	-
50		2.50	2.80	-
100	Cu^{2+}	1.90	2.78	2.28
250		1.90	-	-
50		2.6	2.28	-
100	Fe^{2+}	2.85	-	-
250		2.85	2.98	-

* Initial concentration of metal ions = 3 ppm.

Elution Curves for Transition Metals

The mixed solution of iron(II), manganese (II), copper(II), Zn(II) and cobalt(II) having concentration 0.1mg/1 was passed through the column

and the adsorbed ions were eluted with buffers at pH varying from 1 to 8. The mixed solution was pretreated with small amount of sodium hexanediote (sodium adipate) for reduction of the oxidized manganese. Small amount of hydroxylamine was added to the eluent in order to prevent the oxidation of Mn(II) during elution. The order of elution of the metal ions agrees with the affinity sequence of the batch equilibrium. The affinity sequence is Fe(II) >Cu(II) >Zn(II) >Co(II) >Mn(II). A similar affinity sequence is observed on HZO: Fe(II) > Cu(II) > Zn(II) > Cd (II) > Co (II) >Ni(II) > Ca (II) [8]. A slight different affinity sequence has been reported on hydrous tin (IV) oxide: Cu(II) >Zn (II) >Co(II) >Fe (II) >Ni(II) >Mn (II) [10].

From the values obtained for α (Table 1), the following effective separation were expected under suitable conditions. Mn-Co, Zn, Cu-Fe on HCO dried at 50° and Mn-Co, Zn, Cu and Fe on HCO dried at 100° and 250°. On the basis of the α-values, the HCO dried at 100° is suggested to be excellent.
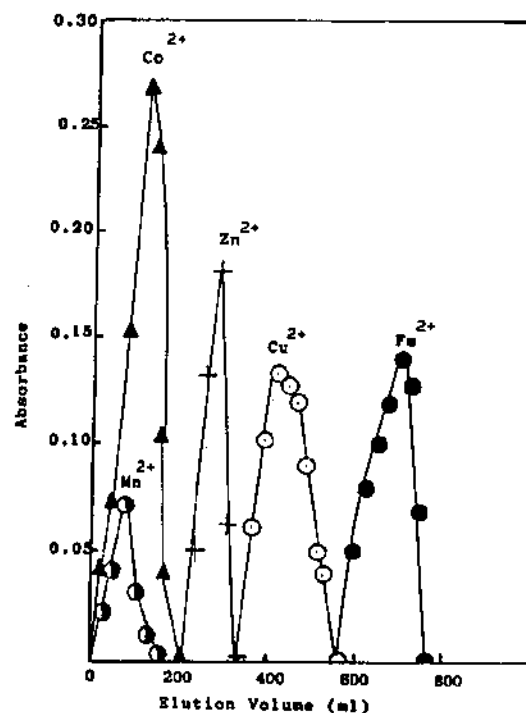

Fig. 2: Elution of transition metal ions on HCO dried at 100°. Flow rate 0.8 ml/min; Concentration of metal ions, 0.1 mg each.

Figure 2 shows that the transition metals Mn-Co, Mn, Cu, and Fe can be separated at pH 6,5. 4.5 and 3 respectively with their recoveries upto 90%, 94%, 85%, 90% and 93% respectively. The exchanger, HCO can therefore, be successfully used for recovery and determination of trace amounts of first row transition elements in the commercial ores.

References

1. C.B. Amphlet, L.A. McDonold and M.J. Redman, *Chem. Ind.*, 365 (1957).
2. K.A. Kraus, H.O. Phillips, T.A. Carlson and J.S. Johnson, Proc. 2nd Inter. Conf. on Peaceful uses of Atomic Energy, Gencrva, 1957, Vo. 28, United Nations, Geneva 1958, p.3
3. M.J. Fuller, *Chromatogr. Rev.*, 14, 45 (1971).
4. J. Iqbal, H. Nawaz, M.L. Mirza and B.A. Nasir, *J.Sci.Res.* (in press).
5. B.A. Nasir, J. Iqbal, S. Anjum, U. Noreen, *J.Chem.Soc.Pak.*, 12, 111 (1990).
6. K.A. Kraus and H.O. Phillips, *J.Am.Chem.Soc.*, 78, 694 (1956).
7. J.P. Adloff, *J.Chromatogr.*, 5, 366 (1961).
8. M. Abe, B.A. Nasir and T. Yoshida, *J.Chromatogr.*, 153, 295 (1978).
9. P.V. Sakellaridis and F.Z. Nobelis, *J.Inorg.Nucl.Chem.*, 36, 2599 (1974).
10. J.D. Doxaldson, M.J. Fuller and J.W. Price, *J.Inorg.Nucl.Chem.*, 30, 1083 (1968), 30, 2841 (1968).