

An Analytical Approach for Removal of Heavy Metals from Aqueous Solutions by Inorganic Basic Lead Molybdate Ion Exchanger 8-Hydroxyquinoline

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Abstract: The present paper deals with the synthesis, ion exchange properties and analytical applications of basic lead molybdate as a new inorganic ion-exchanger. A simplified synthesis and physicochemical properties which show that the chelating resin HQCR₄ in H⁺ behaves as a weak cation exchanger. The results of rate of sorption experiments reveal that the rate of sorption is high during the initial period of contact time and time required for maximum sorption capacity is 50 min. The sorption capacities determined for six metal ions in three pH systems resulted the following order. Hg²⁺ > Co²⁺ > Cd²⁺ > Zn²⁺ > Ni²⁺ > Cu²⁺. The results of distribution coefficients determined for thirteen metal ions in different pH system indicate that Hg²⁺, Cu²⁺ and Fe³⁺ are strongly adsorbed on HQCR₄ resin Th⁴⁺, Zn²⁺, Co²⁺ and Ni²⁺ only partially while Cd²⁺, Mn²⁺ and Zr.

Keywords: Catechol - formaldehyde copolymer, 8-Hydroxyquinoline, Separation, Metal ions

Introduction

8-Hydroxyquinoline (8-HQ) forms chelate compounds with a number of metal ions. Chromatography on 8-hydroxyquinoline with metal ions can permit differentiation of various ions by stability and colour of the metal complex formed. Its incorporation in a resin matrix was therefore, deemed of interest in connection with separation and extraction of metal ions. Chelating resins have many practical applications in separation, preconcentration, water treatment, environmental protection *etc.*

The synthesis and application of chelating resins have been reviewed recently¹⁻¹⁴. The chelating resins are assumed to form chelate rings in the sorbent phase during the sorption of metals¹⁵. The possibility of forming chelate ring in the sorbent phase is affected by different factors such as the nature of the chemically active group capable of complexation, the physical nature of the polymeric matrix, steric factors, sorption conditions *etc.* This chapter deals with the synthesis of catechol formaldehyde based resin containing 8-hydroxyquinoline as functional groups.

The sorption behavior of resin towards various metal ions, distribution coefficients, the sorption and influence of pH on metal uptake has been investigated.

Experimental

Catechol, formaldehyde and 8-hydroxyquinoline (BDH, India) were used. All other reagents were of AR grade and prepared in double distilled water.

Apparatus

An electric rotary shaking machine were used for shaking and UV-Visible spectrophotometer (Carry 100, Conc Varian) and Shimadzu 8201PC spectrophotometric measurements and IR analysis was carried out on Chemito IR spectrophotometer. The pH change during the experiments was observed by pH meter(WTW 540 GLP). Brunauer-Emmett-Teller surface area (BET) measurement was conducted using Micro metrics adsorption equipment (ASAP 2010) determining the nitrogen (99.99% purity) as the analysis gas. The powdered catalyst samples were overnight placed in the oven at 110 °C in order to remove the moisture, degasified the sample followed by the analysis of surface area by heating to 350 °C for 4 hours under Nitrogen atmosphere.

Preparation of 8-hydroxyquinoline chelating resin (HQCR₄)

The 8-hydroxyquinoline chelating resins were prepared by mixing catechol, formaldehyde and 8-hydroxyquinoline in the presence of hydrochloric acid as a catalyst. The details of the conditions of synthesis of chelating resins are given in the Table 1. The reaction mixture was refluxed for 12 h in a round bottom flask and the separated resinous product was washed with demineralized water (DMW) to remove the unreacted reagents. The resin was dried at 60±2 °C in vacuum oven. The 60-100 mesh fraction of the resin was used for the metal sorption studies.

Rate of sorption

The rate of sorption was studies by shaking 0.1 g of the chelating resin, (HQCR₄) with 20 mL of 5×10⁻³ mol dm⁻³ solution of metal ion. After different time intervals the contents of the flask were filtered used Whatman No.4 filter paper and the amount of unadsorbed metal ion was determined in the filtrate by EDTA titration.

Sorption of metal ions by batch operation

Sorption of metal ions was determined by batch operation unless other wise stated, the following method was applied. To a glass stoppered conical flask containing 100 mg of resin and 18 mL of 1 mol L⁻¹ acetate buffer (pH 3-7) or hydrochloric acid (pH 1,2) were added. When this mixture had been equilibrated 2 mL of metal ions solutions (0.1 mol L⁻¹) was added to the conical flask, then the mixture was shaken at room temperature for 6 h. The resin was filtered off on a glass wool and the amount of metal ions remaining in the filtrate was determined complex-metrically using EDTA.

Breakthrough capacity

The column technique permits a continuous operation which is much superior to batch process in respect of time and space. The breakthrough behavior of Co²⁺, Zn²⁺ and Hg²⁺ was investigated by passing 1×10⁻³ mol dm⁻³ solution of metal ion (pH ~7) through a glass column (*i.d.* 4 mm) packed with 1 g of HQCR₄. The flow rate was maintained ~0.5 mL min⁻¹.

Distribution studies

The relative affinities of the chelating resin (HQCR₄) for 13 metal ions were studied by batch equilibrium method as mentioned above. The distribution coefficients (K_d values) were calculated from the following equation

$$K_d (\text{mL g}^{-1}) = \frac{\text{Amount of metal ion in the resin phase g}^{-1}}{\text{Amount of metal ion in the solution phase mL}^{-1}}$$

Infrared Studies

The FTIR spectrum of the 8-hydroxyquinoline chelating resin sample HQCR₄ was studied using KBr disc technique.

Chromatographic separations

The chelating resin HQCR₄ in H⁺ form was packed into a chromatographic glass tube (*i.d.* 0.5 cm) to form a bed 10 cm in height. The sample solutions containing the desired metal ions having large difference in K_d values were introduced into the column and eluted at flow rate 0.5 mL min⁻¹ with suitable eluent.

Results and Discussion

The experimental conditions for the preparation of chelating resin samples by mixing catechol, formaldehyde and 8-hydroxyquinoline, yield of the products and sorption capacities are summarized in Table 1. The physicochemical properties of 8-hydroxyquinoline chelating resin sample HQCR₄ are given Table 2. In order to know the appropriate time required for the maximum adsorption of the metal ion on HQCR₄ resin, the sorption capacity was determined by shaking the resin with the metal ion solution for different time intervals. The results of these experiments are plotted in Figure 1. The results of sorption capacities of Zn²⁺, Cd²⁺, Hg²⁺, Cu²⁺, Ni²⁺ and Co²⁺ on HQCR₄ at different pH (2-6) are presented in Table 3. The distribution coefficients (K_d values) of 13 metal ions were determined by batch experiments in the pH range (1 -7). The observed K_d values are presented in Table 4. The results of infrared spectrum of the chelating resin sample HQCR₄ are plotted in Figure 2.

Table 1. Preparation of 8-hydroxyquinoline chelating resins (HQCR₄)

Resin Sample	Mixing amounts			2N HCl mL	Yield, g	Sorption capacity for Cu ²⁺ mg
	C ₆ H ₄ (OH) ₂ mol	HCHO mol	8-HQ mol			
HQCR ₀	0.10	0.10	0.00	10	1.20	18.4
HQCR ₁	0.10	0.10	0.05	10	1.90	28.5
HQCR ₂	0.1	0.10	0.10	10	2.60	35.6
HQCR ₃	0.1	0.20	0.05	10	2.00	28.9
HQCR ₄	0.1	0.20	0.10	10	2.78	36.4

Table 2. Physicochemical properties of Resin (HQCR₄)

Properties	Result
Moisture content, %	5.64
Solid, %	94.36
Void space fraction	0.56
True density, g mL ⁻¹	1.10
Ion exchange capacity for H ⁺ / Na ⁺ exchange (m mol g ⁻¹) dry resin	0.20

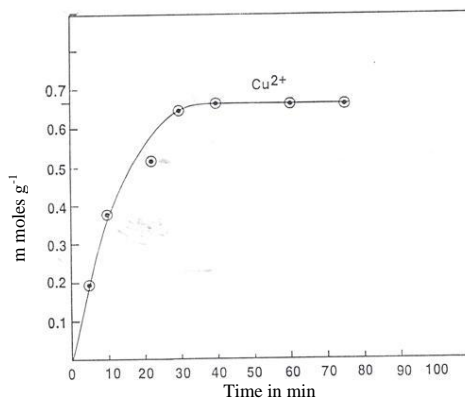


Figure 1. Rate of sorption of Cu^{2+}

Table 3. Sorption capacity (mg g^{-1}) of hydroxyquinoline chelating resin sample (HQCR_4) for different metal ions

Metal ion	pH2	pH4	pH6
Zn^{2+}	24.80	33.80	39.80
Hg^{2+}	75.40	120.60	148.80
Cu^{2+}	19.05	28.00	35.60
Cd^{2+}	27.00	40.10	59.80
Ni^{2+}	22.03	37.80	50.00
Co^{2+}	29.50	48.50	68.70

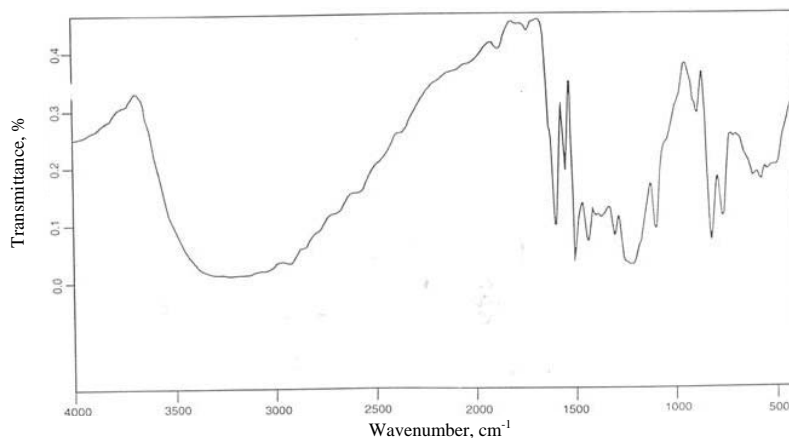


Figure 2. FTIR spectrum of chelating resin sample (HQCR_4)

The result of break through experience investigated for Co^{2+} , Zn^{2+} and Hg^{2+} are plotted in Figure 3. The quantitative separation of metal ions in their synthetic mixtures were tried on the column of HQCR_4 , based on the differences in K_d values. Those, achieved experimentally are summarized in Table 5. The percent error observed during these experiments is also given. The elution curves for the separations of Pb^{2+} - Zn^{2+} , Pb^{2+} - Th^{4+} , Ni^{2+} - Cu^{2+} , Zr^{4+} , Hg^{2+} Al^{3+} - Fe^{3+} , Ni^{2+} - Co^{2+} - Hg^{2+} and Cd^{2+} - Zn^{2+} Hg^{2+} are plotted in Figure (4-10). Ion exchange capacity was determined by passing 1 mol dm^{-3} NaCl solution through a column of HQCR_4 in H^+ form and titrating the eluted H^+ against a standard NaOH solution.

Table 4. K_d values of metal ions on (HQCR₄) at different pH

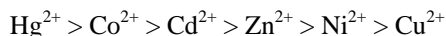
Ion	Metal				K_d values mL g ⁻¹		
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7
Hg ²⁺	200.8	220.3	310.0	380.0	400.2	445.7	590.5
Cu ²⁺	155.2	208.0	280.1	344.1	392.3	410.8	427.3
Th ⁴⁺	68.0	100.0	104.2	115.0	182.4	200.4	261.1
Zn ²⁺	63.2	89.4	95.0	101.3	165.1	199.0	240.0
Co ²⁺	78.6	103.3	140.0	206.7	218.0	256.5	388.1
Ni ²⁺	20.2	35.8	59.6	70.4	73.6	88.8	100.1
Cd ²⁺	16.4	28.2	31.0	35.4	42.0	62.5	102.0
Mn ²⁺	13.0	20.8	24.3	29.4	34.0	38.6	48.6
Zr ⁴⁺	2.0	8.3	10.6	15.6	19.6	27.9	39.0
La ³⁺	13.0	20.0	34.0	47.6	56.5	68.9	80.0
Pb ²⁺	1.9	2.2	4.6	10.6	23.1	30.1	42.0
Fe ³⁺	80.5	100.0	140.0	220.0	333.0	400.2	450.0
Al ³⁺	12.3	23.0	44.5	60.1	75.6	92.0	99.7

Table 5. Separations of metal ions achieved on the column of (HQCR₄)

Mix No.	Metal ions	Eluents mL	Eluate mL	Amount Loaded μ g	Amount found μ g	Error %
1.	Pb ²⁺	0.1 M HNO ₃	30	410	412	+0.49
	Zn ²⁺	0.2 M HNO ₃	30	327	325	-0.61
2.	Pb ²⁺	0.1 M HNO ₃	30	410	412	+0.49
	Th ⁴⁺	1 M HNO ₃	40	464	460	-0.86
3.	Ni ²⁺	0.01M HNO ₃	30	240	245	+2.08
	Cu ²⁺	0.1 M HNO ₃	30	318	312	-1.87
4.	Zr ⁴⁺	0.2 M HNO ₃	30	364	365	+0.27
	Hg ²⁺	1 M HNO ₃	40	400	396	-1.00
5.	Al ³⁺	0.01 M HNO ₃	30	270	270	0.00
	Fe ³⁺	0.2 M HNO ₃	50	558	552	-1.08
6.	Ni ²⁺	0.01 M HNO ₃	30	240	245	+2.08
	Co ²⁺	0.2 M HNO ₃	40	236	237	+0.42
7.	Hg ²⁺	1 M HNO ₃	40	400	396	-1.00
	Cd ²⁺	0.1 NaNO ₃	30	340	342	+0.59
	Zn ²⁺	0.02 M HNO ₃	30	327	325	-0.61
	Cu ²⁺	0.1 M HNO ₃	40	400	396	-1.00

The sorption capacity of various samples of 8-hydroxyquinoline chelating resins (HQCR₄) given in Table 3 reveal that in the syntheses of HQCR₄ increased amount of 8-hydroxyquinoline results increase sorption capacity as well as yield of the resin. Sample HQCR₄ was chosen for further studies owing to its highest sorption capacity maximum yield and good appearance. The physicochemical properties given in Table 2 show that the chelating resin HQCR₄ in H⁺ for also behaves as a weak cation exchanger. The results of rate of sorption experiments plotted in Figure 1 reveal that the rate of sorption is high during the initial period of contract time and time required for maximum sorption capacity is 50 min. The fast uptake of metal ions by HQCR₄ in the aqueous solutions may be explained on the basis of present 8-hydroxyquinoline a chelating reagent¹¹⁻¹⁶.

The sorption capacities determined for six metal ions in three pH systems (Table 4) resulted the following order.



The sorption was found to increase with the increase in pH, however, the capacity order for the investigated metal ions remained unchanged. The variation in sorption capacities for different metal ions may be explained on the basis of difference in stability of metal 8-HQ complexes under experimental conditions. The results of distribution coefficients determined for thirteen metal ions in different pH system indicate that Hg^{2+} , Cu^{2+} and Fe^{3+} are strongly adsorbed on HQCR₄ resin. Th^{4+} , Zn^{2+} , Co^{2+} and Ni^{2+} only partially while Cd^{2+} , Mn^{2+} , Zr^{4+} , La^{3+} , Pb^{2+} and Al^{3+} are scarcely adsorbed. The reason for selective sorption of certain types of metal ions can be attributed to the large difference in the stability constants of metal-8 HQ complexes.

In the FTIR spectrum of HCQR₄ (Figure 2), a broad absorption band in the region 3100 - 3400 cm^{-1} is evident due to O-H stretching in polymeric association. The peak at 2930 cm^{-1} belongs to O-H stretching in chelate compound. The absorption band at 1602 cm^{-1} seems due to the presence of C = N group stretching vibration in the ring. In the spectrum the bonds at 1553, 1503 and 1436 cm^{-1} , are due to aromatic rings. The peaks of 1218 cm^{-1} seems due to stretching vibration of phenols¹⁷⁻²². The results of breakthrough curve (Figure 3) revealed that as many as 58 bed volumes of Hg^{2+} (corresponding to 116.34 mg retention) can be passed through the chelating resin HQCR₄ column without any trace being detected in the effluent. On the other hand in case of resin sample HQCR₄ only 20 bed volumes (corresponding to 40.12 mg) were required to elute Hg^{2+} . The higher breakthrough capacity of HQCR₄ may be attributed due (metal-8-HACR₄) complex formation. Similarly for HQCR₄ breakthrough for Co^{2+} and Zn^{2+} occurs after 55 and 40 bed volumes (corresponding to 32.41 and 26.16 mg) respectively.

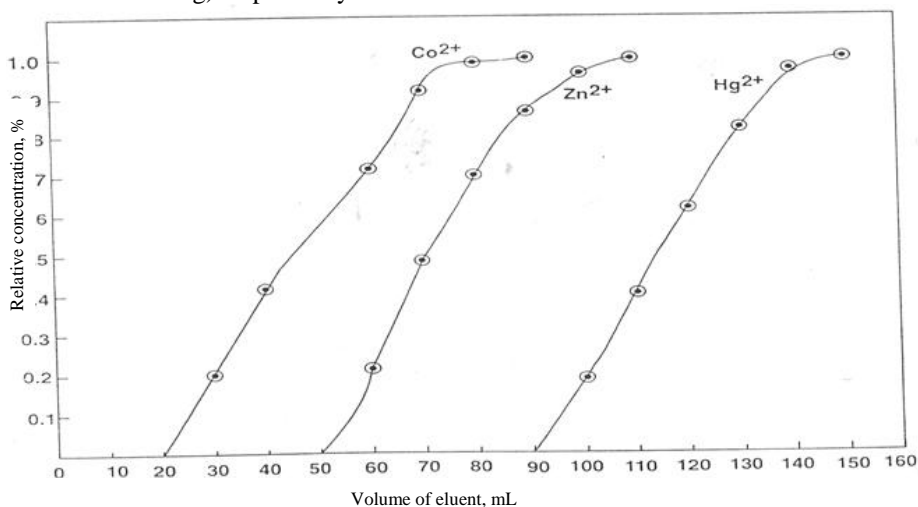
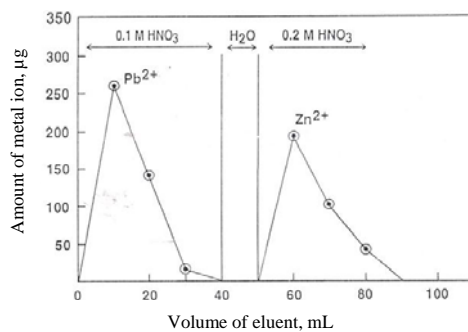
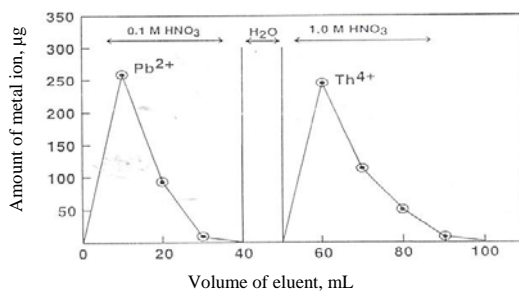
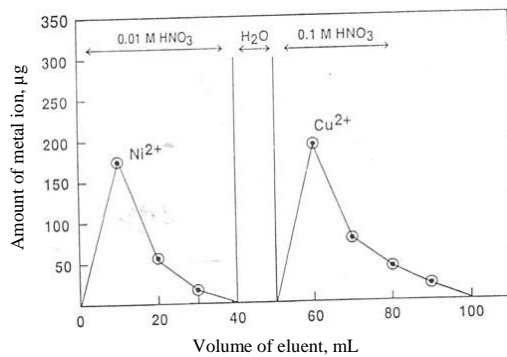
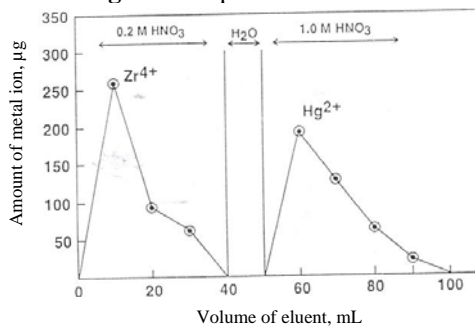


Figure 3. Breakthrough curves of different metal ions

On the basis of large difference in K_d values, separations were tried and experimentally successful results are reported in Table 5. It is interesting to note that no significant tailing was obtained during the elution various metal ions and only small volume of eluent were required to give compact chromatograms Figure (4- 10).

**Figure 4.** Separation of Pb^{2+} - Zn^{2+} **Figure 5.** Separation of Pb^{2+} - Th^{4+} **Figure 6.** Separation of Ni^{2+} - Cu^{2+} **Figure 7.** Separation of Zr^{4+} - Hg^{2+}

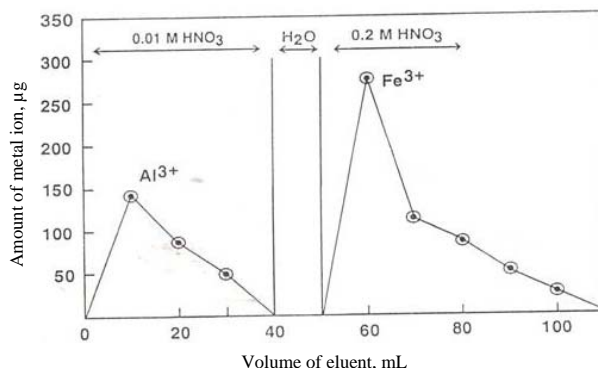


Figure 8. Separation of Al^{3+} - Fe^{3+}

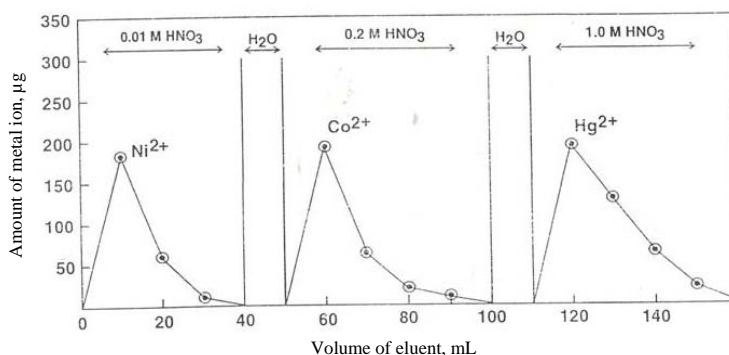


Figure 9. Separation of Ni^{2+} - Co^{2+} - Hg^{2+}

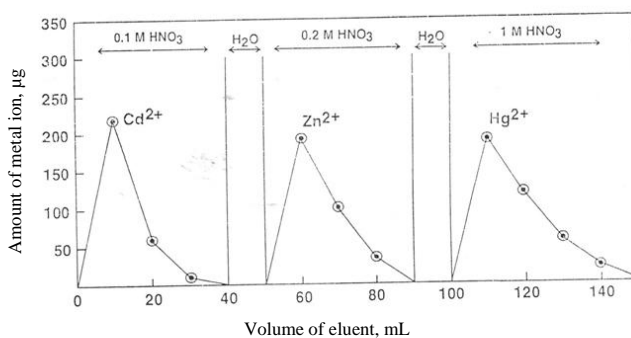


Figure 10. Separation of Cd^{2+} - Zn^{2+} - Hg^{2+}

Conclusion

The single-step attachment of 8-hydroxyquinoline as ion exchange resin represents a significant improvement over the previously published method, and will be of benefit to the many marine chemists utilizing this sort of resin for concentrating trace transitional metals from seawater in various applications.

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