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Heavy metal ion uptake properties of polystyrene-supported chelating polymer resins

A RAVIKUMAR REDDY and K HUSSAIN REDDY*
Department of Chemistry, Sri Krishnadevaraya University,
Anantapur 515 003, India
e-mail: ravichem1@rediffmail.com

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Abstract. Metal ion uptake properties of polystyrene-supported chelating polymer resins functionalized with (i) glycine, (ii) hydroxy benzoic acid, (iii) Schiff base and (iv) diethanol amine have been investigated. The effects of pH, time and initial concentration on the uptake of metal ions have been studied. The uptake of metal ion depends on pH. The resins are more selective at pH 10 for Pb(II) and Hg(II), whereas at pH 6 they are found to be Cd(II) and Cr(VI) selective. Metal ion uptake properties of resins follow Freundlich's equation. The resins are recyclable and are therefore employed for the removal of heavy metal pollutants from industrial waste water.

Keywords. Uptake properties; heavy metal ion; selectivity; recyclability.

1. Introduction

Chelating polymer resins are found to be more selective by nature[1,2] as compared to other conventional techniques[3–9] in the removal of metal ions. In the light of the above, several polystyrene-supported chelating polymer resins have been synthesized[10] recently. In continuation, we report here the metal ion uptake properties of these resins.

2. Experimental

Stock solutions of Pb(II), Hg(II), Cd(II) and Cr(VI) were prepared from AR grade, lead nitrate, mercuric chloride, cadmium nitrate and potassium dichromate salts. Metal uptake by the resin was determined using a UNICAM model 839 atomic absorption spectrophotometer [for Pb(II), Cd(II) and Cr(VI)] and a Shimadzu UV-160A spectrophotometer [for Hg(II)].

2.1 *Recommended procedure for the removal of metal ions*

The effect of pH on metal ion uptake was studied by stirring 2·5 ml of 1×10^{-2} M metal [Pb(II), Hg(II), Cd(II) or Cr(VI)] solution, 7·5 ml buffer (pH 2–10) solution and resin 0·2 g in a 100-ml beaker for 1 h. The effect of time was studied by repeating the above procedure at pH 10 at different time intervals (15, 30, 45, 60, 120 min). The selectivity of the metal ion was determined by stirring an aliquot containing 0·1 M Pb(II) (0·5 ml),

*For correspondence

Hg(II) (0·5 ml), Cd(II) (1 ml) and Cr(VI) (2 ml) in a 100 ml beaker along with 1 g of the resin and 7·5 ml of buffer (pH 10) solution. The maximum uptake capacities of each polymer resin was determined by reacting 50, 100, 150, 200, 250 and 300 ppm of metal solutions with polymeric resin under suitable pH conditions [pH 10 for Pb(II) and Hg(II) and pH 6 for Cd(II) and Cr(VI)] for about 1 h. In all cases the metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively, and quantity of the metal ion present in the filtrate estimated using atomic absorption spectroscopy and spectrophotometric methods using 1,10-phenanthroline.[11] The amount of metal ion was deduced from the predetermined calibration curve.

3. Results and discussion

Polystyrene-supported chelating resins are shown in figure 1. The resins are stable and show maximum decomposition temperature in the range 450–550°C. Metal ion-uptake properties of these resins are studied at room temperature (25–30°C).

3.1 *Effect of pH and time on uptake of metal ion*

At lower pH values (< pH 6) protonation of chelating groups takes place, complexation with available ligands is reduced and hence the percentage uptake decreases. At higher pH values (> pH 6) deprotonation takes place and hence the percentage uptake increases through the formation of stable polymer–metal complexes. The uptake of Pb(II) and Hg(II) increases with increase in pH and reaches a plateau value at pH 10. In case of Cd(II) and Cr(VI) the plateau value is observed at pH 6. As the uptake of Pb(II) and Hg(II) from basic medium is either high or fairly significant, NH_4Cl–NH_4OH buffer solution of pH 10 is selected for further studies. In case of Cd(II) and Cr(VI), the maximum adsorption is observed at pH 6. Therefore CH_3COOH–CH_3COONa buffer of pH 6 is recommended for further studies. The selectivity patterns of the metal ions by the resins are as follows.

pH 2: Hg(II) > Cd(II) > Cr(VI) > Pb(II) (CMPS-GL); Pb(II) > Cd(II) > Cr(VI) > Hg(II) (CMPS-HB); Hg(II) > Cr(VI) > Cd(II) > Pb(II) (CMPS-AH); Pb(II) > Cd(II) > Hg(II) > Cr(VI) (CMPS-DE).

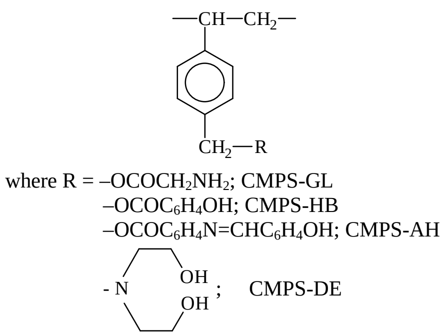

Figure 1. Polystyrene-supported chelating polymer resins.

pH 6: Pb(II) > Cd(II) > Hg(II) > Cr(VI) (CMPS-GL); Cr(VI) > Pb(II) > Hg(II) > Cd(II) (CMPS-HB); Cd(II) > Hg(II) > Cr(VI) > Pb(I) (CMPS-AH); Cr(VI) > Cd(II) > Hg(II) > Pb(II) (CMPS-DE).

pH 10: Pb(II) > Hg(II) > Cd(II) > Cr(VI) (CMPS-GL & CMPS-DE); Pb(II) > Hg(II) > Cr(VI) > Cd(II) (CMPS-HB and CMPS-AH). The data (see also figure 2) suggest that the resins are more selective for Pb(II) at higher pH (pH 10). The removal of metal ions at different time intervals suggest that an hours time is sufficient for maximum and constant uptake.

3.2 *Selectivity studies*

Figure 2 suggests that the results obtained under competitive conditions (selectivity studies) are in good agreement with those obtained under non-competitive conditions (at different pH conditions for different metal ions). Metal ion uptake decreases in

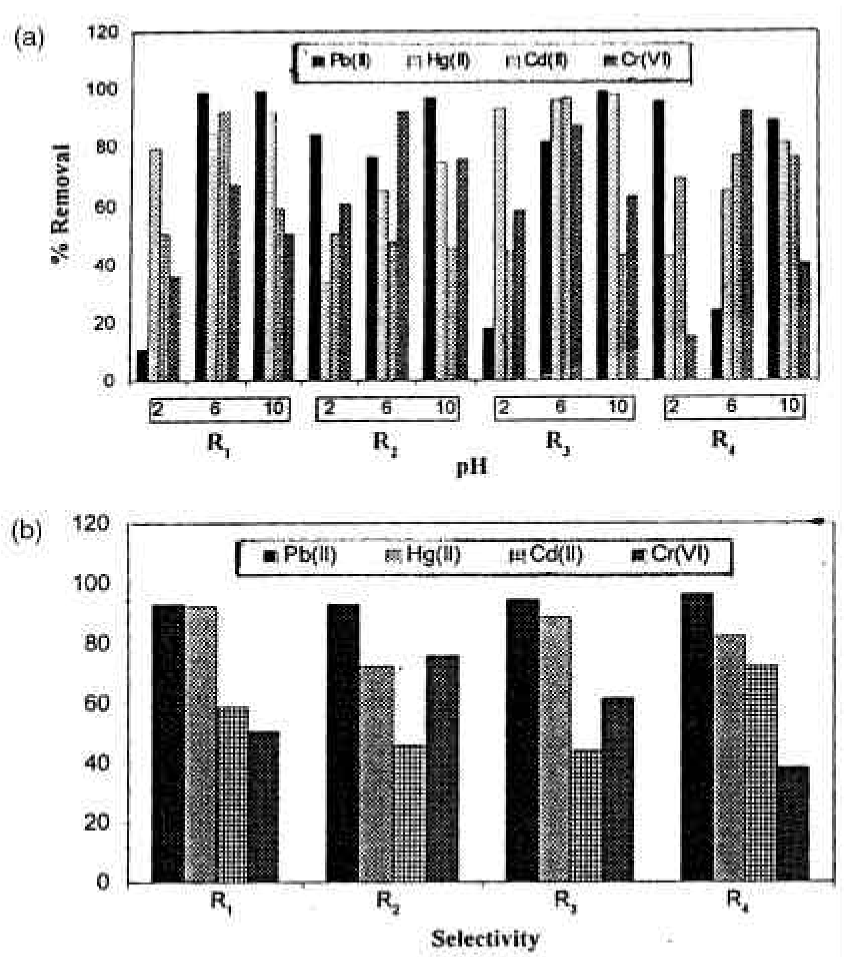

Figure 2. (**a**) Effect of pH. (**b**) Selectivity in the uptake of metal ions by the resins R_1 = [CMPS-gl], R_2 = [CMPS-hb], R_3 = CMPS-ah], R_4 = [CMPS-de].

the order: CMPS-AH > CMPS-GL > CMPS-DE > CMPS-HB. The affinity of the given resins for metal ion is in the order: Pb(II) > Hg(II) > Cd(II) > Cr(VI) (CMPS-GL and CMPS-DE); Pb(II) > Hg(II) > Cr(VI) > Cd(II) (CMPS-HB and CMPS-AH). The azomethine grouping in CMPS-AH is responsible for its efficiency and is highly selective in the removal of metal ions.

3.3 *Effect of initial concentration of metal ions on its uptake by different chelating polymer resins*

Effect of initial concentration of heavy metal ions is an important variable, which determines the maximum up take capacity of the polymer. Figure 3 shows the uptake capacities of the CMPS-GL, GMPS-HB, CMPS-AH and CMPS-DE for the ions from the single metal aqueous solutions under study. The maximum uptake capacities of the resins are – CMPS-GL: Pb(II), 10·970 mg/g; Hg(II), 11·020 mg/g; Cd(II), 4·735 mg/g; Cr(VI), 12·085 mg/g. CMPS-HB: Pb(II), 10·570 mg/g; Hg(II), 7·970 mg/g; Cd(II), 2·445 mg/g; Cr(VI), 11·715 mg/g. CMPS-AH: Pb(II), 12·965 mg/g; Hg(II), 12·305 mg/g; Cd(II) 5·035 mg/g; Cr(VI), 11·755 mg/g. CMPS-DE: Pb(II), 13·705 mg/g; Hg(II), 10·465 mg/g; Cd(II), 4·105 mg/g; Cr(VI), 11·210 mg/g. The affinity order: CMPS-GL: Cr(VI) > Hg(II) > Pb(II) > Cd(II). CMPS-HB: Cr(VI) > Pb(II) > Hg(II) > Cd(II). CMPS-AH: Pb(II) > Hg(II) > Cr(VI) > Cd(II). CMPS-DE: Pb(II) > Cr(VI) > Hg(II) > Cd(II). Thus, the metal uptake capacities of the present resins are quite comparable to those of resins employed earlier.[12–14]

The uptake of metal ion by the resin increases with increase in initial metal ion concentration and reaches a plateau at higher concentration. The uptake of metal ions by the resins involves either chelation or adsorption or both. This behaviour is approximately described by adsorption isotherms. Longmuir adsorption isotherms show

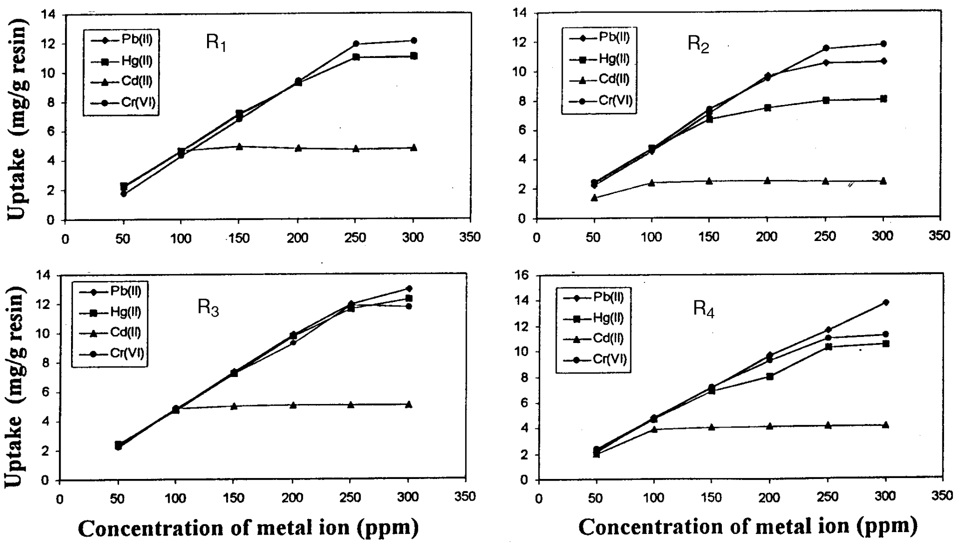

Figure 3. Effect of initial concentration on the removal of metal ion by R_1 = [CMPS-gl], R_2 = [CMPS-hb], R_3 = [CMPS-ah], R_4 = [CMPS-de].

Table 1. The values of empirical constants for the adsorption of heavy metal ions on various chelating resins obtained from Freundlich's equation.

	1/*n*				*k*			
Resin	Pb(II)	Hg(II)	Cd(II)	Cr(VI)	Pb(II)	Hg(II)	Cd(II)	Cr(VI)
CMPS-GL	1·0	1·1	0·2	1·3	7·94	17·78	0·003	10
CMPS-HB	1·0	0·6	0·18	1·0	2·24	0·50	0·025	3·16
CMPS-AH	1·0	1·0	0·25	1·1	10·00	7·94	0·004	3·16
CMPS-DE	1·0	0·9	0·08	1·0	12·60	15·85	0·008	2·82

deviation from the straight line. In case of Freundlich's adsorption, straight lines are observed for the adsorption of the same metal ions on the resins. Freundlich's equation,

$$Y = KC^{1/n} \text{ i.e. } \log_{10}Y = \log_{10}K + (1/n)\log_{10}C,$$

where, Y = grams of metal ion adsorbed per gram resin, C = initial concentration (moles per litre), n and K = emperical constants.

Straight lines were obtained on plotting $\log_{10}Y$ versus $\log_{10}C$. These are called Freundlich's adsorption isotherms. The slope of the line is equal to $1/n$ and the intercept is equal to $\log_{10}K$. K and n values for the adsorption of metal ions on various resins are presented in table 1. The table suggest that the higher the '$1/n$' and 'K' values, the maximum is the adsorption and vice versa.

3.4 *Effect of recyclability on adsorption of metal ions*

The metallated resin used can be brought back to its original state by desorbing the metal ions using 6 M HCl in tetrahydrofuran. The metal-free polymers can be reused after neutralization. For every cycle the metal ion uptake and percentage desorption was studied. The metal ion uptake efficiency is found to be almost the same, even after four cycles using different resins.

4. Conclusions

The presence of heavy metal ions, viz. Pb(II), Hg(II) and Cd(II), in aquatic systems pose heavy risks to human health. Therefore, removal of such metal ions from water bodies may be considered an interesting and important research activity. Chelating resins are stable, and can be used for the removal of metal ions at room temperature. Their metal uptake efficiency increases with pH and reaches a plateau at pH 10 for Pb(II) and Hg(II), and pH 6 for Cd(II) and Cr(VI). The favourable characteristic of the present chelating polymers is the time required for maximum and constant uptake of metal ion from aqueous media. Just an hour's time is sufficient in the present methods, while other recently reported methods[15–17] required longer periods of time. Metal ion selectivity is different for different resins, i.e. Pb(II) > Hg(II) > Cd(II) > Cr(VI) for CMPS-GL and CMPS-DE, Pb(II) > Hg(II) > Cr (VI) > Cd(II) for CMPS-HB and CMPS-AH. Metal ion uptake efficiencies of the polymer resins are not altered much even after four cycles, and are in the order CMPS-AH > CMPS-GL > CMPS-DE > CMPS-HB. Thus polymers containing the azomethine grouping are found to be most efficient in the removal of metal ions.

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