Uptake of Pb(II) and Cd(II) by a New Phenolformaldehyde Polymer Resin Derived by the Insertion of Sulfur Ligands in the Form of Xanthate

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ABSTRACT: A new phenolformaldehyde polymer resin containing potential soft-type donor atoms (sulfur atoms) was synthesized by the reaction of sodium salt of 2,4-dihydroxyacetophenone formaldehyde resin with carbon disulfide. The resin was characterized by elemental analysis, IR, and ^{1}H-NMR spectral studies. Because of its insolubility in aqueous media, the resin was successfully used in the removal of Pb(II) and Cd(II). Parameters such as the effect of pH, the effect of time, competitive studies, the effect of initial metal-ion concentration, and the recyclability of the polymer resin were studied. The amount of metal removed by the resin was determined with atomic absorption spectrophotometry. The retention properties were strongly dependent on pH. The elution of metal ions was investigated in acid media. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1932–1936, 2004

Key words: resins; synthesis; recycling; selectivity

INTRODUCTION

The separation and removal of heavy metal ions from industrial waste water has been studied continuously for many decades. The pathways of contamination and toxic effects of heavy metal ions are well known. Many techniques have been developed to remove such metal ions from industrial wastewater, such as adsorption techniques employing activated carbon,[1] starch xanthate,[2] fly ash,[3] and surpentine minerals.[4] Alkaline precipitation[5] and ion-exchange[6] methods have also been used for the removal of toxic metals. Recently, bioprecipitation of some toxic metal ions by sewage bacteria was reported.[7] However, conventional methods are generally nonselective and less efficient. The use of complexing agents for the separations of metal ions are well established. An alternative mode of application of complex formation is, however, the use of functionalized polymers in which various chelating groups have been incorporated and are attached to the polymer matrix. The syntheses of such functionalized polymers have been accomplished with either polymerization or simple functionalization principles.[8] The former involves the polymerization of monomers containing the desired ligands. Recently, this type of polymer was found to have wide spread applications in the removal of heavy metal ions from a variety of matrices.[9,10] The selective removal of these metal ions continues to be a problem. In continuation of our research,[11–13] we attempted to synthesize a selective resin for the removal of Pb(II) and Cd(II).

EXPERIMENTAL

Materials and methods

2,4-Dihydroxyacetophenone was prepared according to a literature procedure.[14] It was recrystallized from distilled water. Formalin (37%), oxalic acid, and carbon disulfide Merck were used without further purification. Stock solutions of Pb(II) and Cd(II) were prepared from AR-grade lead nitrate and cadmium nitrate salts.

Physical measurements

Elemental analyses were performed microanalytically by CDRI, Lucknow. IR spectra were recorded with KBr pellets with a Beckmann IR-20 spectrophotometer. NMR spectral analyses were carried out in dimethylsulfoxide-d_6-with a Bruker DRX 400-MHz instrument. Metal uptake by the resin was determined with a Unicam UK model 839 atomic absorption spectrophotometer [for Pb(II) and Cd(II)]

Synthesis of 2,4-dixanthateacetophenone formaldehyde (DXPF) resin

A mixture of 2,4-dihydroxyacetophenone and formalin solution (1 : 1.1) and 3% (w/w) oxalic acid was
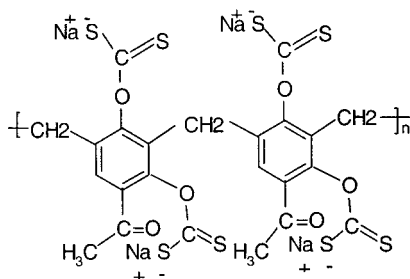
Figure 1 DXPF resin.

placed in a reaction tube, sealed, and placed in an oil bath at 100°C for 24 h. The tube was then cooled to room temperature and desealed, and water was removed by decantation. The solid remaining in the tube was dissolved in dimethylformamide and the solution was added dropwise to a large excess of 10% aqueous sodium chloride solution with constant stirring. The resin that separated out was collected by filtration, washed several times with distilled water, till free from chloride ions. The resin was dried at 60°C for about 1 h.

2,4-Dihydroxyacetophenone formaldehyde (DAPF) resin (0.0184 mol) was dissolved in 1,4-dioxane; to this mixture, freshly cut dry sodium (0.0368 mol) was added. The contents were stirred until the reaction was complete. The yellow product, sodium salt of DAPF, was filtered and washed with an excess of dioxane and dried by washing with ether. The sodium salt of DAPF (1 mol) and CS_2 (1.5 mol) were placed in a round-bottomed flask and stirred for about 12 h. The intense yellow product, DXPF resin, was filtered, washed with water and ether, and dried *in vacuo* for about 6 h.

RESULTS AND DISCUSSION

2,4-Dihydroxyacetophenone derivatives are promising analytical reagents. In the light of this, it was of interest to investigate functionalized resins containing the resacetophenone moiety and xanthate grouping. The structure of the functionalized polymer is given in Figure 1. Analytical data and the yields of the resins are given.

DAPF yield = 92%.

ANAL. Calcd for DAPF: C, 65.9%; H, 4.9%. Found: C, 65.4%, H, 4.9%.

DXPF yield = 70%.

ANAL. Calcd for DXPF: C, 38.5%; H, 2.1%. Found: C, 37.4%, H, 2.3%.

The data suggest that the yields of the resins were sufficiently high. The resins were insoluble in common organic solvents and soluble in dimethylformamide and dimethylsulfoxide. ^{1}H-NMR spectra of the resins were recorded in DMSO-d_6.

^{1}H-NMR (δ, DAPF): 9.5 (OH), 7.2–7.8 (Ar—H), 3.4 (—CH_2—), 1.8 (—CH_3).

^{1}H-NMR (δ, DXPF): 7.2–7.7 (Ar—H), 3.6 (—CH_2—), 2.1 (—CH_3).

IR spectra of the resins were recorded in the range $4000–400$ cm^{-1} with KBr discs. A comparison of IR spectra of DAPF with that of DXPF showed the absence of νOH (3400 cm^{-1}) and the presence of νC=S (1584 cm^{-1}).

IR (DAPF, cm^{-1}): ν 3400 (O—H), 2885 (C—H), 1665 (C=O).

IR (DXPF, cm^{-1}) 2984 (CH), 1673 (C=O), 1584 (C=S).

Thus, these data support the formation of the functionalized polymer.

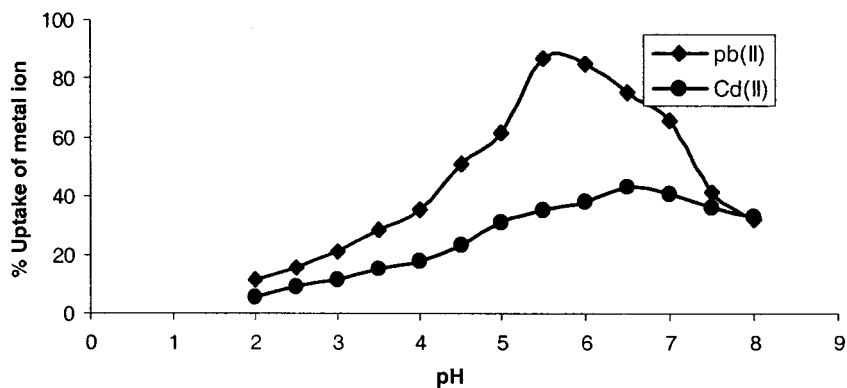### Effect of pH on the uptake of metal ions

The effect of pH on metal-ion uptake was studied at different pH values. Metal-ion [Pb(II) or Cd(II)] solution (2.5 mL of 1×10^{-2} M), buffer solution (7.5 mL, pH = 2–8), and resin (0.2 g) were combined in a 100-mL beaker and maintained under stirring for 2 h. The metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively. The amount of metal ion present in the filtrate was estimated with atomic absorption spectroscopy (AAS). Figure 2(a) indicates that the uptake of metal ion by the resin depended on pH. The overall uptake of metal ions by the resin from pH 2 to 8 was in the order Pb(II) > Cd(II). The uptake of Pb(II) and Cd(II) increased with increasing pH and reached a plateau value around pH 5.5 and 6.5, respectively. The resin was more efficient in the uptake of Pb(II) than of Cd(II).
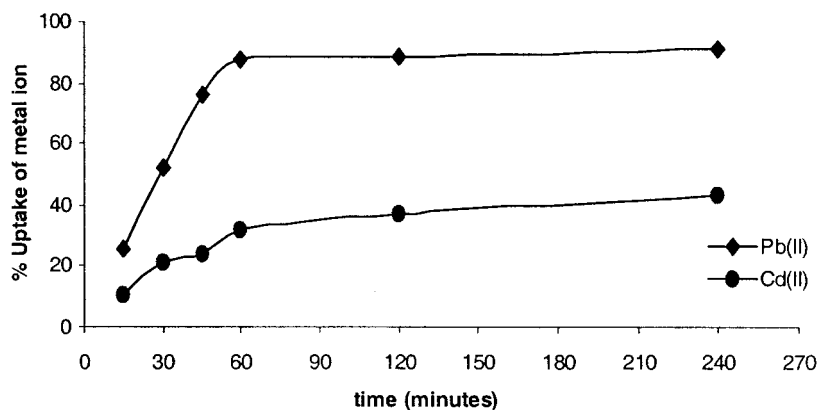
Effect of time on metal-ion uptake

The effect of time on metal-ion uptake was studied at pH 5.5 [for Pb(II)] and 6.5 [(for Cd(II)]. Metal solution (2.5 mL of 1×10^{-2} M solution), buffer solution, and resin (0.2 g) were mixed in a 100-mL beaker; the mixture was maintained under stirring for different periods of time (15, 30, 45, 60, 120, and 240 min). The metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively. The amount of metal ion present in the filtrate was estimated with AAS. From Figure 2(b), it is evident that 1 h was sufficient for a maximum and constant uptake of Pb(II), but more time was needed for Cd(II).
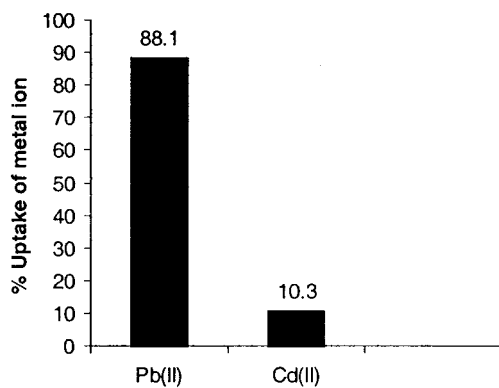
Selectivity studies

In this case, 100 ppm of each metal ion in the solution were allowed to react with the polymer at pH 6.0. An aliquot [containing 0.1M Pb(II) (0.5 mL) and Cd(II) (1

(a)

(b)

(c)

Figure 2 (a) Effect of pH on the uptake of metal ions. (b) Effect of time on the uptake of metal ions. (c) Selectivity of the metal ions by DXPF resin.

mL)] was taken in a 100-mL beaker containing 1 g of the resin and 7.5 mL of the buffer solution. The mixture was maintained under stirring for 2 h. The metallated resin was filtered and washed thoroughly with distilled water. The filtrate was collected quantitatively in a 100-mL standard flask and diluted to volume. The amount of each metal ion left in the filtrate

was determined by AAS. The overall competitive conditions were in good agreement with the results obtained in the noncompetitive conditions. From Figure 2(c), it is evident that Pb(II) was more selective than Cd(II). The high uptake capacity of Pb(II) by the DXPF resin was probably due to the faster complexation of the resin with Pb(II). Thus, DXPF was more selective

for the removal of Pb(II). As shown in Figure 2(a), the time required for Pb(II) maximum uptake was just 1 h, but it was much longer for Cd(II). Because of this, Pb(II) complexed with the resin much faster than Cd(II). This complextaion rate of Pb(II) was greater when it was in competition with Cd(II). Due to these reasons, the resin was more selective for Pb(II).

Effect of the initial concentration of metal ions

An important variable in the uptake of heavy metal ions is the metal-ion concentration. The amount of metal-ion uptake increased with increasing initial metal-ion concentration and reached a plateau value at a higher concentration. In this case, 50, 100, 150, 200, 250, 300, 350, and 400 ppm of metal solution were allowed to react with the polymeric resin under suitable pH conditions [pH 5.5 for Pb(II) and pH 6.5 for Cd(II)]. Metal ion (2.5 mL) of suitable concentration, buffer (7.5 mL), and resin (2.0 g) were mixed in a 100-mL beaker. The contents were stirred for 2 h and filtered, and the filtrate was collected quantitatively. The procedure was repeated for all metal ions [Pb(II) and Cd(II)] at different concentrations. The metal-ion uptake at different concentrations by the resin was determined.

The maximum uptake capacities of DXPF were 11.69 and 4.53 mg/g of Pb(II) and Cd(II), respectively. Different functionalized polymers with wide-range uptake capacities for heavy metal ions have been reported. Kimiaki et al.[15] removed 10.3 mg of Pb(II)/g of resin with a chloromethylated polystyrene containing a $-P(OEt)_2$ group. Denzili et al.[16] showed the uptake of 4.2 mg of Cd(II)/g, with procion Red MX-3B-immobilized poly(hydroxyethylmethacrylate ethylene glycol dimethacrylate). Zhengyu[17] found that the Hg(II) equilibrium uptake capacities of HCHO–thiourea–urea copolymer, HCHO–PhOH–urea copolymer, and benzoic acid-modified HCHO–thiourea copolymer were 31.5, 30.2, and 28.8 mg/g of resin, respectively Chattopadhyay et al.[18] used a chelating resin containing an imidazolylazo group for the removal of Pb(II), Ag(II), and Hg(II). Thus, the metal uptake capacities of our polymer were quite comparable to those used earlier, and our polymer was more selective.

Effect of recyclability on the adsorption of metal ions

The most important advantage of the functionalized polymer was its reusability after a particular process. The polymer could be brought into its original state by desorption of the metal ions from metallated resins with 2*M* HCl in tetrahydrofuran. The metal-free polymer could be reused after neutralization. In an acidic medium, the metallated polymers were protonated and released the metal ion into solution. For every

TABLE I
Effect of Recyclability on the Uptake of Metal Ions by DXPF Resin

Number of cycles	Pb(II)		Cd(II)	
	Uptake (ppm)	Desorption (%)	Uptake (ppm)	Desorption (%)
1	180.4	97.1	50.6	98.2
2	175.4	98.3	48.7	98.5
3	171.8	95.6	45.4	95.3
4	160.1	97.8	43.2	96.1
5	162.3	94.5	43.1	95.7

cycle, the metal-ion uptake and percentage desorption were studied. The data are given in Table I. The metal-ion uptake was almost the same even after five cycles.

CONCLUSIONS

A functionalized polymer was synthesized with a condensation polymerization technique and subsequent modification. Characterization was done by elemental analyses, IR, and ^{1}H-NMR spectra. The metal uptake efficiency increased with pH and reached a plateau value around pH 5.5 [for Pb(II)] and pH 6.5 [for Cd(II)] and decreased with increasing pH. The favorable characteristic of this polymer was the time required for the maximum and constant uptake of metal ions from aqueous media. Just 1 h was sufficient for the removal of metal ion in these methods, whereas recently reported methods[19–21] have required longer periods of time. As observed, the uptake increased with concentration and reached a plateau value. This was because at higher concentrations, no more free sites were available on the chelating polymeric surface for either adsorption or chelation. The metal-ion selectivity of this functionalized polymer was in the order Pb(II) > Cd(II). The metal-ion uptake efficiency of the polymer was not altered much, even after five cycles. Thus, the polymer with its xanthate moiety was more efficient in the removal of heavy metal ions.

References

1. Huang, C. P.; Bstarz, F. B. J Environ Eng 1971, 104, 863.
2. Wing, R. E.; Doone, W. H.; Russel, C. R. J Appl Polym Sci 1975, 19, 847.
3. Netzer, A.; Wilkinson, P.; Beszedits, S. Water Res 1974, 8, 813.
4. Sundersen, B. B.; Bulusis, K. R.; Kulkarni, D. M. Ind J Environ Health 1978, 20, 413.
5. Patterson, J. W.; Allen, H. F.; Scala, J. J. J—Water Pollut Control Fed 1977, 9, 2397.
6. Lindstdt, K. K.; Hanch, C. P.; Connor, J. J. J—Water Pollut Control Fed 1971, 43, 1507.
7. Shukla, M.; Pandeya, G. S. Ind J Chem Technol 1994, 1, 308.

8. Prabhakar, L. D.; Marysaral, A. Polym Int 1997, 42, 149.

9. George, B.; Pillai, V. N. R.; Mathew, B. J Appl Polym Sci 1999, 74, 3432.

10. Beatty, S. T.; Fischer, R. J.; Hegers, D. L.; Rosenberg, E. Ind Eng Chem Res 1999, 38, 4402.

11. Reddy, K. H.; Reddy, A. R. J Appl Polym Sci, to appear.

12. Reddy, K. H.; Reddy, A. R. Ind J Chem A 2002, 41, 934.

13. Reddy, A. R.; Reddy, K. H. Ind J Chem Technol 2002, 9, 97.

14. Cooper, S. R. Org Synth 1941, 21, 103.

15. Kimiaki, M.; Masahiro, A. Chem Abstr 109, 134491.

16. Denzili, A.; Buyuktuncel, E.; Genc; Piskin, E. Anal Letts 1998, 31, 2791.

17. Zhengyu, Z. Huaxueshijie 1987, 28, 252.

18. Chattopadhyay, P.; Sinha, C.; Pal, D. K. J Anal Chem 1997, 357, 368.

19. Roozemond, D. A.; Hond, F. D.; Veldhuis, J. B.; Strasdeit, H.; Driessen, W. L. Eur Polym J 1988, 24, 867.

20. Ebraheem, K. A.; Hamdi, S. T. React Funct Polym 1997, 34, 5.

21. Latha, A. G.; George, B. K.; Kannon, K. G.; Ninan, K. N. J Appl Polym Sci 1991, 43, 1159.