



REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS USING GUARANTETRAETHYLENEPENTAMINE (GTEPA) RESIN

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ABSTRACT

Guarantetraethylenepentamine (GTEPA) resin is synthesized by incorporating tetraethylenepentamine group onto guaran by a modified Porath's method of functionalization of polysaccharides. The distribution coefficient of Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} on GTEPA resin at different pHs have been systematically studied. Finally the heavy metal ions were eluted quantitatively with different strength of acids.

Key words : Guarantetraethylenepentamine (GTEPA) resin, Polysaccharides, Distribution coefficient.

INTRODUCTION

The removal of metal ions from sewage and industries waste is attracting the attention of researchers due to limitations of conventional waste treatment processes. Ion exchangers find tremendous applications in waste water treatment because of greater selectivity and higher exchange properties.

Applications of chelating cellulose ion exchanger with the functional group of diethylenetriamine acetic acid have been reported for the determination of lead and cadmium in soils, plants and fertilizers¹. Sulphoxime cellulose (8-hydroxyquinoline-5-sulphonic acid cellulose) prepared by Mannich reaction from aminoethyl cellulose or via chlorodeoxy and ethylene diamine cellulose was used in FI-GFAAS system for the preconcentration of trace metals like Cd, Co, Ni, Pb and V from water and mineralized water².

Lewatit OC-1026 ion exchange resin was used for the recovery of zinc, in a

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relatively pure form, from a zinc rich industrial waste liquor and from model zinc rich solution. The chelating resin Puzolit S-930, metal fix chelamine and metal fix chelosolve showed greater selectivity for Cu, Cd, Pb ions from zinc rich waste liquors³. Amongst all the natural polymers, cellulose and guaran is of special interest due to its easy availability and wide applications both in natural as well as modified form. Biswas et al.⁴ have reported specific application of such easily available polysaccharides for the removal of pollutants from the waste water.

The styrene – DVB based chelating resin containing 4-(2-thiazoylazo) resorcinol (TAR) functional group have been investigated for the sorption behaviour of thirteen metal ions including U (VI) by batch and column experiments⁵. This chelating resin is highly selective for Cu (II) and U (VI) in the pH range of 1-2. Vinyl graft copolymers of some important carbohydrates including cellulose have been reported earlier for the removal of metal ions from aqueous solution by Khalil et al.⁶ Grebonyak et al.⁷ also reported the adsorption of heavy metal ions i. e. Ni, Cu, Zn, Cd by aminocarboxyl ion exchanger ANKB-35 and parameters of ion adsorption from highly concentrated solution were established in order to determine regeneration condition of the resins.

The guaran sulphonic acid cation exchanger is used for removal of toxic metal ions from underground mine water of Rajpura Dariba Mines, Udaipur, India⁸. The resin has also been used for removal of trace heavy metal ions from aqueous solutions.

EXPERIMENTAL

Guarantetraethylenepentamine resin (GTEPA) was synthesized by the method of functionalisation of polysaccharides described by Porath⁹, in which guaran was treated with epoxychloropropane followed by tetraethylenepentamine in strongly alkaline medium.

All other reagents and chemicals used were of high purity and commercial products were used as such.

Perkin-Elmer Model – 460 Atomic Absorption Spectrophotometer was used for quantitative determination of trace metals. For different metals, standard wavelengths of main resonance line and an air – acetylene flame were used.

Anion-exchange capacity determination

GTEPA resin (10.0 g) was completely converted into chloride form by treatment

with liberal excess of 0.1 N hydrochloric acid. Then the resin was washed with distilled water. Washings were collected in the same volumetric flask, the contents were neutralized with dilute nitric acid and the volume made up to 250 mL. Aliquots (25 mL) of the effluent was titrated against 0.11 N silver nitrate solution using potassium chromate (10% aqueous solution) as indicator. Moisture content was also determined by drying known amount of the resin in the oven. Scientific weight capacity (Q_{weight})¹⁰ was calculated using the formula:

$$Q_{\text{weight}} = \frac{\text{Effluent volume} \times \text{Milliequivalents of titrant used}}{\text{Volume of aliquot} \times \text{Weight of dried resin}} \quad \dots(1)$$

It was found to be 2.05 meq/g of the dry GTEPA resin and the moisture content was 16.4%.

Chelation chromatography on GTEPA resin

Standard stock solution of Cu^{2+} of the strength 0.1 M and those of Co^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} and Pb^{2+} of the strength 0.01 M were prepared by dissolving the appropriate salts into solutions. These were diluted so as to give 0.60 mg/mL of Ni^{2+} , 0.10 mg/mL of Cd^{2+} , 0.65 mg/mL of Zn^{2+} , 0.10 mg/mL of Pb^{2+} and 6.30 mg/mL of Cu^{2+} in individual solutions.

The molal distribution coefficient (K_d) of metals showing pronounced adsorption on chelating resin were determined by the batch equilibrium method. Portions of GTEPA resin (1.0 g) in the chloride form were placed in glass stoppered conical flasks containing a known volume of an appropriate buffer and 1 mL portion of a metal solution was added. The mixtures were shaken mechanically for 24 hr at 25°C. After equilibrium, the two phases were separated by filtration and aliquot of the filtrate was analysed for the metal concerned using the atomic absorption spectrometer. For this determination, standard solutions of metals were analysed atomic absorption spectrometrically. For different metals, standard wavelengths of main resonance line and an air acetylene flame were used. The corresponding calibration curves were plotted for different metals. The concentration of the filtrates of metals were determined with the help of calibration curves and the distribution coefficients (K_d) were calculated.

RESULTS AND DISCUSSION

The resins prepared with DVB - styrene backbone are hydrophobic and this affects their efficiency in metal ion separation and concentration from solution. Also these resins

are prepared from petrochemicals, which are very costly. The scarce supply and cost limit their use.

The naturally occurring polysaccharides give hydrophilic backbone for preparation of chelating resins. The naturally occurring polysaccharide guaran imparts the ease of accessibility of ion to the functional group in the macromolecules from the surrounding solution. A new range of chelating ion-exchangers having polyamine groups and based on guaran matrix can be used as hydrophilic, renewable and selective ion exchangers. Cellulose dihydroximate has been reported earlier for the separation of Cu^{2+} , Ni^{2+} , Co^{2+} , Ca^{2+} and Fe^{2+} by Maekawa et al.¹¹ The GTEPA resin is more selective than cation exchangers and finds applications in preconcentration, isolation and separation of free metal ions (aquo or solvated) due to binding dissociation equilibria. The relative preference for various metal ions in GTEPA is pH dependent. The distribution coefficients of various metal ions are given in Table 1.

Table 1. Distribution coefficients of various metal ions at different pH

pH	K_d						
	Fe^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}
4	282.4	470.0	870.5	230.4	332.1	142.0	108.1
5	320.3	550.8	948.0	344.8	412.4	208.2	296.0
6	391.5	891.2	1510.2	494.1	680.5	380.0	398.5
7	1015.9	423.6	1114.4	568.2	799.2	590.4	693.1
8	880.4	396.1	886.6	649.2	1109.4	817.6	766.0
9	620.0	330.2	714.4	866.0	1694.6	1105.1	1223.4
10	309.8	278.4	687.2	720.2	548.9	872.7	694.6

The perusal of the results shows that the distribution coefficient value first increases and then decreases with increasing pH. The order of the K_d values for metal ions at the pH of their maximum adsorption follows the sequence : $\text{Cu} > \text{Ni} > \text{Pb} > \text{Fe} > \text{Cd} > \text{Zn} > \text{Co}$. Pb, Cd, Cu and Zn show strong adsorption in high pH range, i. e. 9. Fe shows maximum adsorption at pH 7, whereas Co and Ni show an appreciably high adsorption at pH 6. Difference in distribution coefficients at the same pH for different metal ions suggests possible strategy for separation of these ions from their mixtures.

The metal ions were eluted quantitatively with different strength of acids. Zn^{2+} was eluted with 0.05N HCl; Fe^{2+} with 0.5N HCl; Cu^{2+} with 2.5N HCl; Cd^{2+} with 0.5N HNO_3 and Pb^{2+} was eluted with 1N HNO_3 . Co^{2+} and Ni^{2+} were eluted with 0.5N HCl and 1.0N HCl, respectively. Then the resin column was washed thoroughly with demineralized water. It could be reused upto five cycles with recovery better than 96%. After elution the resin can be finally disposed off either by burning it or by incineration as it is based on biopolymer.

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