



USE OF GUAR DERIVED CHELATING ION-EXCHANGE RESIN IN SEPARATION OF METALS

S. Loonker, S. Vijavargiya and J.K. Sethia

Department of Chemistry, Jai Narain Vyas University, Jodhpur-342 001, Rajasthan

ABSTRACT

Guar derived chelating ion-exchange resin, functionalized with 5-bromo anthranilic acid (GTBAA), was synthesized by the reaction of 5-bromo anthranilic acid with the guar triazine. The resin characterization *viz.*, bulk density, moisture content, specific bulk volume, degree of substitution, IR spectra, nitrogen content, pH titration and ion-exchange capacity was determined. Metal analysis was done by using atomic absorption spectrophotometry. The effect of pH was considered in a batch equilibrium study on the chelation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Mn(II) metal ions. The metal capacity of resin at different pH was evaluated. The quantitative separation of copper and manganese was achieved using column separation through batch equilibrium method. At the maximum pH of adsorption, the resin capacity follows the order : Cu(II) > Zn(II) > Co(II) > Ni(II) > Mn(II) > Cd(II).

INTRODUCTION

Guar (*Cyamopsis tetragonoloba*) is a drought-tolerant summer annual legume, which is cultivated in sandy soils. India is the largest producer of guar seed and most of guar production activity is carried out in Rajasthan, especially in Jodhpur, due to the favourable weather conditions. Under the suitable weather conditions India and Pakistan are the leading guar cultivating countries. Highly refined guar gum is used as a stiffener in soft-ice cream; a stabilizer for cheese, instant puddings and whipped cream substitutes; and as a meat binder. Lower grade guar is used in cloth and paper manufacture, oil well drilling muds, explosives, ore flotation and a host of other industrial applications. It has also been utilized as matrix in ion-exchanger resins, which are extensively used in water treatment, trace metal-separation, desalination and other industrial processes, especially in textile, paper, explosives, pharmaceutical, cosmetics and mining industries.

The whole world is forced to diminish down to acceptable level contents of heavy metal in water and industrial wastewaters. Compared with other usual methods, ion exchange provides advantages. Removal of trace amounts of heavy metals can be achieved by means of selective ion-exchange processes. By ion exchange either all ions can be removed from a solution or substances are separated. Therefore, selective removal of ionic contamination and complete deionization can be distinguished. The choice between both depends mainly on the composition of the solution and on the extent of decontamination required.

Ion-exchange is the process by which an ion in solution exchanges with another type of ion from a molecule. The ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign, when the ion-exchanger is in contact with an electrolyte solution. Two factors influence the effectiveness of ion-exchange with a resin, the first is favourably of a given ion and second, the number of active sites available on the resin (Myasoedova & Sarrin 1982).

Resins are used for the separation of multivalent ions from univalent ions by selective sorption even when the concentration of univalent ions is high; chelating resins have been applied for separation of traces of calcium and magnesium from concentrated solution of sodium chloride, lithium

chloride and sodium hydroxide and for the determination of traces of copper in soda, sodium hydroxide and ammonium chloride.

In last three decades a great interest has been shown in synthesis and investigation of chelating resins. In many cases these resins exhibit very high selectivity to some ions or groups of ions. The first application of these sorbents was in analytical chemistry. In connection with the aim, increasing selectivity of these chelating resins finds their applications in separation and concentration processes (Bohra et al. 1993). Chelating agents find applications in chromatographic separation of chemically similar ions at a high pH.

A number of chelating ion-exchange resin have been produced by resin manufactures to encourage the application of ion-exchange to a broader range of processes occurring in solutions. Guar poly ions have been used in the ion-exchange chromatography of many biological materials and metal ions (Guthrie 1971).

Amongst all the natural polymers, guar is of special interest due its easy availability and wide application both in natural as well as modified form. Chemical modification of guar can be used to study the sorption of Cu^{+2} ions from its aqueous solution.

The preferential complexing tendency of a chelating agent anchored on a polymer is used for separation of transition metals. This paper deals with separation of copper-nickel, copper-manganese and copper-zinc by guar gum polymers anchored with 5-bromo anthranilic acid using column chromatography.

MATERIALS AND METHODS

Guar together with triazine of reagent grade was used. Solvent like dioxane and methanol of A.R. grade were procured from E. Merk and Sarabhai M. Chemicals respectively.

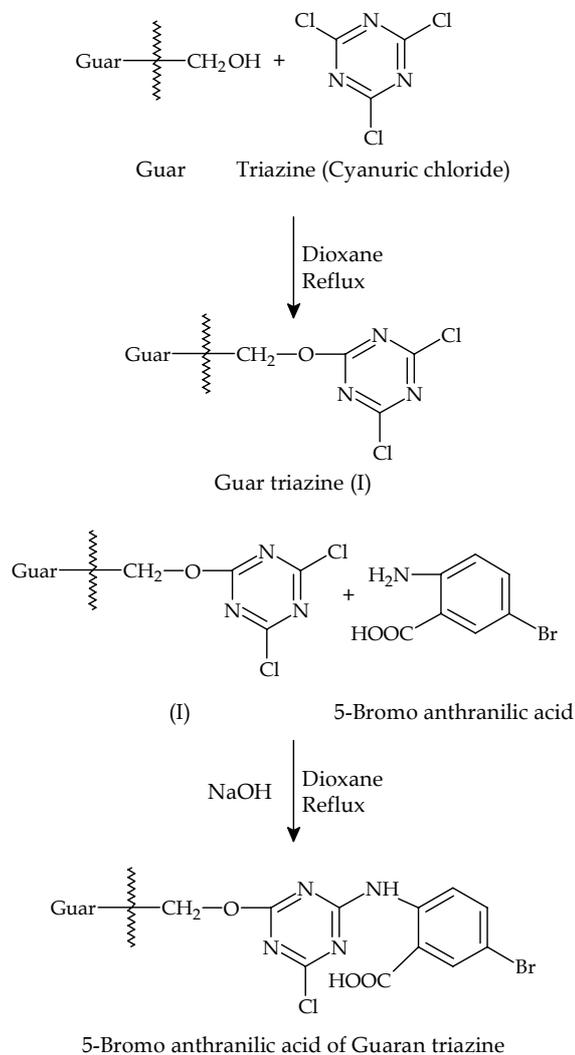
Physical measurement: Metal analysis was accomplished on a Perkin-Elmer 2380 atomic absorption spectrophotometer. I.R. Spectra of the synthesized resin was recorded on a Shimadzu IR 400 spectrophotometer using KBr pellets. Nitrogen analysis was done by the Kjeldahl method.

Synthesis of resin: For the synthesis of 5-bromo anthranilic acid derivative of guar (GTBAA), guar was first cross-linked with triazine to form guar triazine which was then reacted with 5-bromo anthranilic acid for derivatization of GTBAA.

Preparation of guar triazine: For the synthesis of triazine of guar 1 mol (486 g) of guar powder was taken and slurried in maximum quantity of dioxane maintained at about 5°C while external cooling and stirring was continued. 18.3 g of cyanuric chloride was added to this reaction mixture and pH was maintained at 7-8 by adding NaHCO_3 . The whole mixture was spontaneous stirred for half an hour.

Synthesis of 5-bromo anthranilic acid derivative of guar (GTBAA): 0.05 mol of triazine of guar was slurried with dioxane in a round bottom flask. 10 mL of 50% (w/v) aqueous sodium hydroxide was added to it at 50°C with constant stirring.

0.1 mol (21.6 g) of recrystalline 5-bromo anthranilic acid was added to the slurry and dissolved in dioxane. The pH was maintained at 9-10 by adding concentrated solution of NaOH. The reaction mixture was then constantly stirred for 2-3 hrs at $25\text{-}30^{\circ}\text{C}$. The product so obtained was filtered on a Buchner funnel under vacuum. The product was washed with distilled water and finally dried at 110°C .



Analysis of metal uptake: A batch equilibrium technique was employed for the investigation of metal uptake by the resin. The method involved equilibrating H⁺ from the resin with 1 mL of 1000 ppm metal ion solution and a known volume of sodium acetate-acetic acid buffer of pH range 3.5-7. Two phases were separated after equilibrium and an aliquot of filtrate was analysed for the metal using atomic absorption spectrophotometer. The calibration curves for different metals were plotted using standard metal solutions and the unknown concentration of metal ion was determined from these curves. The distribution coefficient (K_A) and metal capacity were calculated.

Column separation: The dynamic ion-exchange was carried out in an ion-exchange column, which is a 20 cm long burette, containing glass wool plug and packed with slurry of guar triazine 5-bromo anthranilic acid resin (GTBAA), 1 mg in dioxane to a column height of 8-10 cm. The resin was then washed with the buffer of pH 5.0 at which the adsorption of mixture was carried out. 20 mL aliquot of solution containing 100 ppm of Cu(II) and another with Mn(II) metal ions, each was passed

through the column at a flow rate 1 ± 0.2 mL/min. The loaded metal were eluted using sodium acetate-acetic acid buffer of pH 5.5 (for Mn^{2+}), and 0.1 N HCl (for Cu^{2+}) metal concentration in the elutes was determined using the atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

In the IR spectra of guar triazine anthranilic acid (GTBAA) a band near 3400 cm^{-1} was assigned for ν (N-H), while another broad band at $3000\text{--}2840\text{ cm}^{-1}$ was ascribed to ν (O-H). The C = O stretching vibration of carboxylic acid appeared at 1670 cm^{-1} . The moisture constant, bulk density, specific bulk volume and nitrogen content of the resin are given in Table 1 and pH titrations are represented in Fig. 1.

Uptake of metals by the resin: The theoretical H^+ ion-exchange capacity of GTBAA resin was calculated and found to be 0.572 meq/g. The metal capacity Vs. pH counter of GTBAA resin with Fe(II), Co(II), Ni(II), Cd(II) and U(VI) metal ion are represented in Fig. 2.

The result shows that the metal uptake by the resin first increases, but later decreases with increasing pH. The resin exhibited maximum capacity for Cu(II), Cd(II) at pH 5.0, Zn(II) at pH 6.5, for Co(II) and Mn(II) at pH 6.0 and Ni(II) at pH 5.5. At the pH of maximum adsorption, the capacity follows the order :



This order also represents the order of increasing adsorption of metal ion on GTBAA resin and the stability of their chelates with the resin. The distribution coefficient of metal ions with resin also followed the above order. At the pH of maximum adsorption the distribution coefficient values of Cu(II), Zn(II), Cd(II), Ni(II), Co(II) and Mn(II) were 1098, 1089, 368, 901, 926 and 368 respectively. It can be deduced from these data that the resin is highly selective for copper at pH 5.0 and for Mn(II) at pH 6.0. These metals can be easily separated from others using this resin.

Separation of metals by resin: A study on the data of distribution coefficient values of various metal ions of GTBAA resin reveals that the resin can achieve separation of a mixture of metal ions. The K_{AE} values for copper (1098) and manganese (115) indicate that a mixture of Cu(II) – Mn(II) can be separated at pH 5.0.

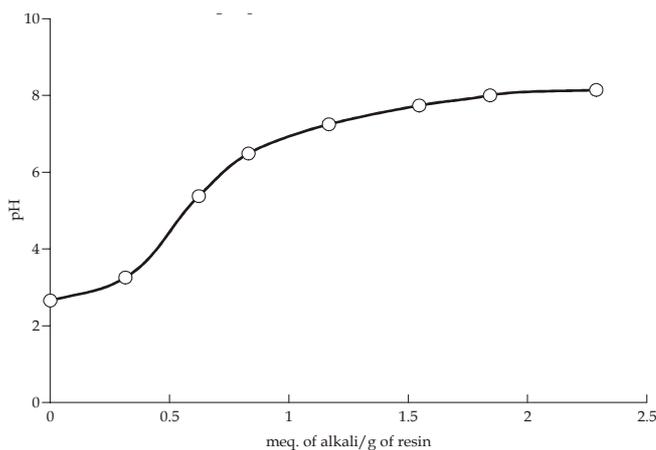


Fig. 1: pH titration curve for CEAA resin.

Therefore, Cu-Mn separation was carried out by column chromatography. Manganese ions being less strongly held by the resin, moved down the column more rapidly and were collected before copper. Thus, mixture of Cu and Mn can be separated easily.

ACKNOWLEDGEMENT

The authors are thankful to the Dean and Head, Deptt. of Chemistry, Faculty of Science, J.N.V. University for providing the necessary laboratory facilities.

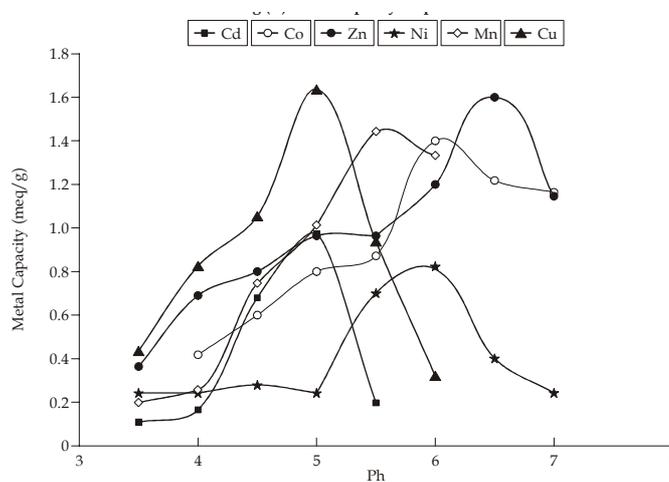


Fig. 2: Metal capacity Vs. pH counters.

Table 1: Resin characteristics.

Resin	Moisture content (%)	Bulk density (g/cm ³)	Specific bulk volume (cm ³ /g)	Nitrogen content (%)
Guar triazine anthranilic acid (GTBAA)	2.7	0.689	1.48	5.32

Table 2: Distribution coefficients of metal ions on different pH values.

pH	K _A Values					
	Zn(II)	Co(II)	Ni(II)	Cu(II)	Cd(II)	Mn(II)
3.5	141	-	70	145	32	103
4.0	267	182	132	270	49	-
4.5	-	238	298	450	230	125
5.0	362	351	490	1098	368	115
5.5	451	481	901	395	91	226
6.0	-	926	630	132	-	368
6.5	1089	-	-	-	-	-
7.0	486	496	-	-	-	109

REFERENCES

Bohra, S., Kanungo, N. and Mathur, P.N. 1993. Asian J. Chem., 5: 60.
 Guthrie, J.D. 1971. Ion Exchange guar in high polymers', Guar and Guar derivatives, (N.M. Bikalee and J. Segal eds.), Willey Interscience, New York, Part V, 1277-1291.
 Myasoedova, G.V. and Sarrin, S.B. 1982. Russ. J. Anal. Chem., 37(3): 383.