SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATION OF NEW POLYSACCHARIDE CATION EXCHANGER RESIN CONTAINING METHACRYLIC ACID FOR INDUSTRIAL WASTE WATER TREATMENT

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ABSTRACT: TMAA (Tamarind methacrylic acid) cation exchanger resin was synthesized, based on locally available polysaccharide Tamarind Kernel powder. The resin was characterized by FTIR and elemental analysis. The resin was found to be stable in acidic as well as in basic medium. Physicochemical properties of the resin were examined. The total cation exchange capacity was measured and effect of pH and metal ion concentration on ion exchange capacity were studied. The distribution coefficients at different pH were also studied using batch equilibration method. The developed column technique has been used for the binary separation of Cu^{+2}/Zn^{+2}, Cu^{+2}/Pb^{+2}, Cu^{+2}/Cd^{+2} and waste water treatment.

Key Words: Polysaccharide based resins, distribution coefficient, pH effect, column technique, binary separation

INTRODUCTION

Generation of wastewater can result from domestic and industrial activities, which contains organic and inorganic pollutants, having direct impact on environment and human beings. It is therefore mandatory to treat wastewater either of domestic or industrial origin, prior to its disposal or release in to environment. Ion-exchange resins comprises of one of the most important scientific developments of the 20th century. Various applications towards water softening, environmental remediation, wastewater treatment[1], hydrometallurgy, chromatography, biomolecular separations, and catalysis were recognized in numerous publications and are in public domain[2-3]. In analytical chemistry inorganic ion exchanger had established their place due to their differential selectivity for metal ions[4-7]. The distribution coefficient of Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, and Pb^{+2} on cellulosetetraethylenepentamine (TEPA) resin at different pH have been reported[8]. In recent years, the cation exchanger resins have been of interest to chemists due to their application in the field of metal ion separation[9-10], wastewater treatment[11], mine water treatment[12] and pollution control[13]. Similar experiment were carried out by Lobosova L et al which synthesized Lewatit TP 214 Chelating resin[14], and Gawale R & Marathe K.V also synthesized Indion 225H Cation exchanger resin[15] .

The objective of present research is to promote synthesis of TMAA cation exchanger resin. The exchanger has been found to be very selective for binary separation of Cu^{+2}, Zn^{+2}, Cd^{+2} and Pb^{+2} as well as for its use in metal, waste water treatment.
The paper also discusses the synthesis and Characterization of TMAA resin and its applications for removal and recovery of toxic metal ions from reference solution and effluent of R.K. Textile, Basani, Jodhpur, India.

MATERIALS & METHODS

Reagent and chemicals

All the reagent and chemicals used were of high purity commercial grades and used as such. The functionalisation of polysaccharide tamarind with methacrylic acid group via epichlorohydrin had been described in an Ease German patent[16]. However, we have employed Porath's method[17] of functionalisation of polysaccharides.
Perkin-Elmer model 460 Atomic absorption spectrophotometer was used for quantitative determination of trace metals. For different metal ions standard wavelengths of main resonance line and air acetylene flame were used.

Procedure

Synthesis of Tamarind Methacrylic acid (TMAA) cation exchanger resin

32 g tamarind kernel powder (0.2 mole anhydrous glucose unit (AGU) was suspended in 60 ml dioxane. While stirring the reaction mixture on a magnetic stirrer, 5ml of 20% aqueous NaOH solution were added followed by 9.25 g (0.1mol) of epoxychloropropane and the mixture was stirred for 5 hrs at 60 °C. After keeping it over night, compound was filtered and washed with dioxane and ether. This form of functionalized tamarind can be stored at 25 °C for a long period. It can be activated by reaction with sodium hydroxide by converting the chlorohydrin functional group into an epoxide group, when it is required to be loaded with a ligand.
Since the functionalisation was to be done immediately, a drop of phenolphthalein was added to the dioxane suspension of tamarind chlorohydrin, followed by drop wise addition of 20% aqueous sodium hydroxide with stirring at 50 °C till the appearance of the pink colour. The 0.2 mole of methacrylic acid (MAA) was added drop wise, stirring for 4 hrs, and left overnight. Tamarind incorporating MAA group was filtered, washed with HCl-methanol, and finally with ether and dried (Scheme presented in figure.1).

Characterization of the resin

The physicochemical properties like moisture content, Density, ion exchange capacity and thermal stability were studied according to the literature methods[18] and the results are presented in Table-1

Table 1: Properties of Resin

S. No.	Properties	Inference
1.	Color	Light brown
2.	Moisture content	2.2%
3.	Density	0.89 gm cm^{-3}
4.	Total ion exchange capacity	3.92 Meq/g
5.	Thermal stability	278°C
6.	Cation exchange capacity	4.225 $mmol.cm^{-3}$

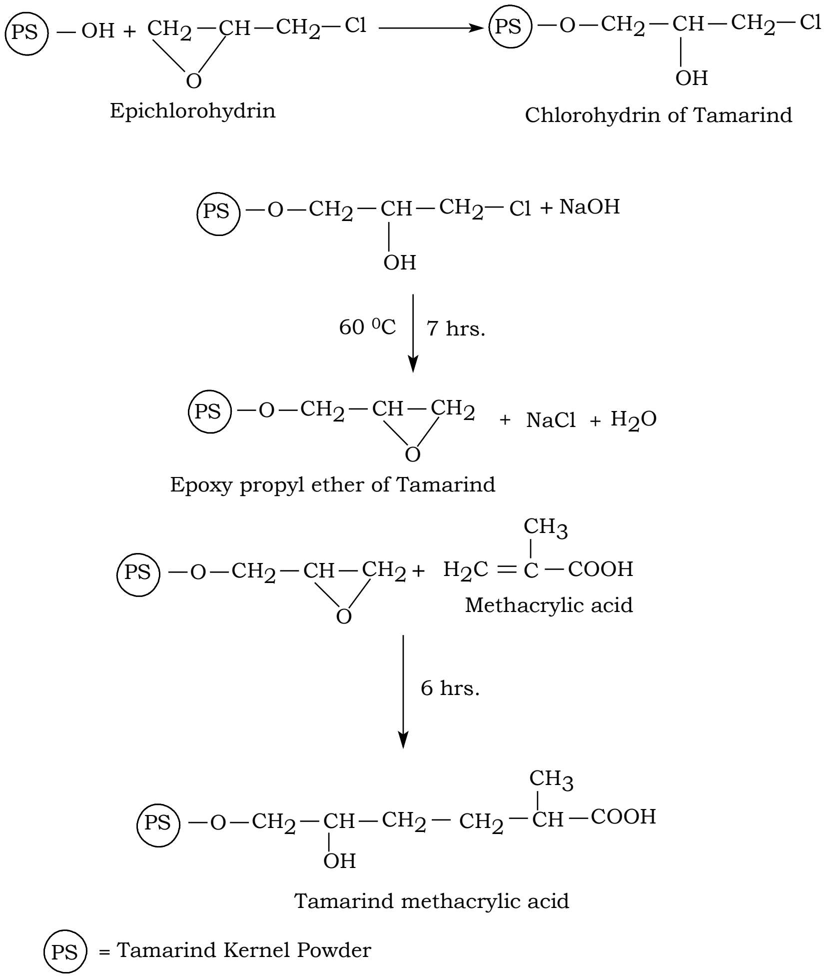

Figure. 1 Synthesis of Tamarind Methacrylic acid resin (TMAA)

Kd Values for Metal Ions

Adopted Method for removal of heavy toxic metal ions
A 50 ml aliquot of effluent was taken in a clean beaker. The pH was adjusted by traditional method of using sodium bicarbonate and hydrochloric acid. 20 mg of tamarind methacrylic acid (TMAA) resin were added to the solution and stirred on a magnetic stirrer for one hour. The solution was filtered through whatman filter paper no. 40. The residue on the filter paper was equilibrated with 4N HCl, and the solution was filtered through whatman filter paper no. 42; the volume was made up to 250 ml with distilled water.

Measurement of distribution coefficient of metal ions over a wide range of condition is a good way to avoid choosing eluting conditions for column separations by a strictly trial and error method.

The heavy metal ion concentration in the filtrate was estimated using atomic adsorption spectrophotometer. The distribution coefficient (K_d) were calculated using the formula –

$$K_d = \frac{\text{Amount of metal ion in resin phase/gm of resin}}{\text{Amount of metal ion in solution phase/ml of solution}}$$

Binary separation

For separation studies 2 gm of swollen resin was taken in glass column (10 x 1.1cm).The rate of flow in all separation was maintained at 2ml/min. The absorbed metal ions were eluted using suitable eluents. 5ml fractions was collected and analyzed by AAS.

RESULTS AND DISCUSSION

IR data[19]: -

The FTIR spectrum of Methacrylic acid were characterized by –COOH & >C=O stretching vibration. 3433.1cm^{-1} broad –OH stretching of –COOH, 1654 cm^{-1} (s) for >C=O of carbonyl group, 1543 cm^{-1} (s) for C=C , 1408 cm^{-1} (m) for C-H of -CH_3 group and 945 cm^{-1} out of plain C-H bend for olefinic region rustically (Figure-3).
s=strong m =medium

Effect of pH on distribution coefficient

The distribution coefficients of various metal ions are given in table-2
Estimation of Cu^{+2}, Zn^{+2}, Cd^{+2}, and Pb^{+2} removal capacity of TMAA resin at different pH was analyzed and removal Capacity after 120h was determined at various pH value from acidic to alkaline range. The relative preference for various metal ions in TMAA resin is pH dependent.
The analysis of the data shows that the distribution coefficient value (Table-2) first increases and then decreases with increasing pH. Due to principle of selectivity the order of distribution ratio of divalent ions measured in the range pH 2-8 were found to be Cu > Zn > Cd > Pb. It has been found that the percentage removal of Cu, Zn, Cd and Pb are maximum at pH 6, 6, 7 and 7 and shown in figure 2.

Table 2: Distribution coefficients of various metal ions at different pH

pH	Cu^{+2}	Zn^{+2}	Cd^{+2}	Pb^{+2}
2	5437	4647	2319	1968
3	5596	4834	4502	2318
4	5832	5146	4676	3051
5	6699	7081	5930	4765
6	**8159**	**8129**	7264	6129
7	6898	6913	**7647**	**7163**
8	6809	6677	6677	6307

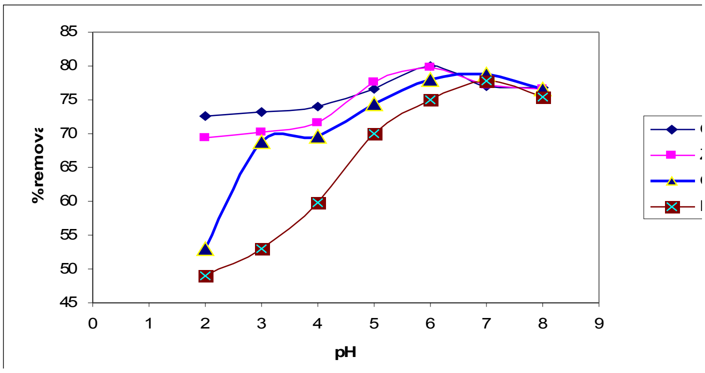

Figure. 2 %Removal curve for Cu, Zn, Cd and Pb

Binary separations (Table-3) were carried out using the exchanger column. Separations were carried out for Cu^{+2}/Zn^{+2}, Cu^{+2}/Zn^{+2}, Cu^{+2}/Cd^{+} .The recovery range from 98-100% with a variation ±1% for the repetitive determinate.

Table 3: Binary separation of metal ions on TMAA cation exchanger resin

Metal ion Amount taken(μg)	Eluents	Amount (μg)	%Error
Cu^{+2}:10	1MCH_3COONa + 1MHCl	9.85 ± 0.5	1.5
Zn^{+2}:10	1MHNO_3	9.90 ± 0.3	1.0
Cu^{+2}:10	1MCH_3COONa + 1MHCl	10.2 ± 0.3	2.1
Cd^{+2}:10	1MHNO_3	9 .96 ± 0.7	4.0
Cu^{+2}:10	1MCH_3COONa + 1MHCl	9.80 ± 0.5	2.0
Pb^{+2}:10	1MHNO_3	10.1 ± 0.2	1.0

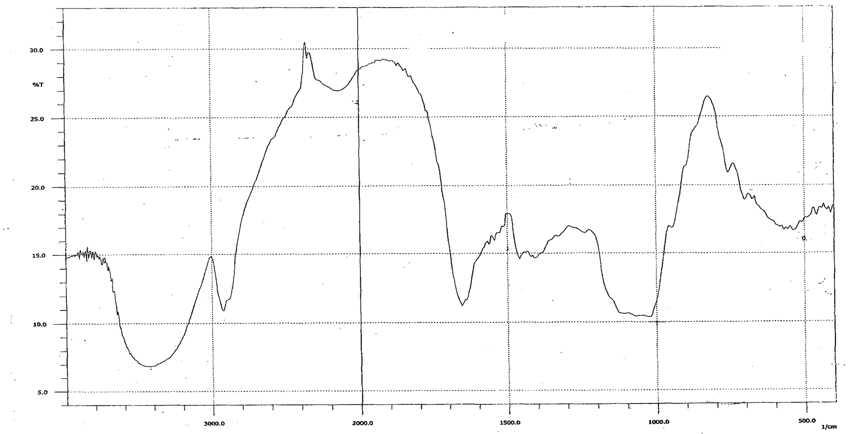

Figure.3 IR Data of TMMA Resin

Conclusion

The synthesized resin shows lower moisture content indicating the high degree of cross-linking in this resin. The K_d determinations revealed that there is a considerable difference between the distribution coefficients of metal ions at optimum condition, which can be used in the successful separation of heavy metal ions which in turn helpful for the disposal of various pollutants and dangerous metals from environment, waste water and from food chain for human beings. The exchanger may be suitable for the removal of Cu, Zn, Cd and Pb from wastewater and may be quite helpful for the environmentalists.

The synthesized resin is applicable for removal and recovery of trace metal ions from effluent of R.K. Textile, Basani, Jodhpur. It would be interesting to use the TMMA resin for the economic treatment of effluent containing the aforementioned metal ions.

Acknowledgement

The Authors are thankful to Head, Department of Chemistry, J.N.V. University Jodhpur, Rajasthan (India) for providing all necessary facilities.

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