

Synthesis and Application of Tamarind Hydroxypropane Sulphonic Acid Resin for Removal of Heavy Metal Ions from Industrial Wastewater

Aresh Vikram Singh, Sarika Nagar

Abstract—The tamarind based resin containing hydroxypropane sulphonic acid groups has been synthesized and their adsorption behavior for heavy metal ions has been investigated using batch and column experiments. The hydroxypropane sulphonic acid group has been incorporated onto tamarind by a modified Porath's method of functionalisation of polysaccharides. The tamarind hydroxypropane sulphonic acid (THPSA) resin can selectively remove of heavy metal ions, which are contained in industrial wastewater. The THPSA resin was characterized by FTIR and thermogravimetric analysis. The effects of various adsorption conditions, such as pH, treatment time and adsorbent dose were also investigated. The optimum adsorption condition was found at pH 6, 120 minutes of equilibrium time and 0.1 gram of resin dose. The orders of distribution coefficient values were determined.

Keywords—Distribution coefficient, industrial wastewater, polysaccharides, tamarind hydroxypropane sulphonic acid resin, thermogravimetric analysis.

I. INTRODUCTION

THE wastewater from mining operations, tanneries, electroplating, battery and steel industries are contained heavy metal ions such as, ferrous, copper, zinc, lead etc. These heavy metal ions show adverse effect for human and animal physiology when they exist beyond the tolerance levels. Therefore, it is necessary to develop viable and relevant technologies for removal of heavy metal ions from industrial wastewater. The removal of heavy metal ions from wastewater can be achieved by several processes, such as precipitation [1], solvent extraction [2], [3], chemical and electrochemical technique [4] and advanced oxidation process [5], [6]. These methods are extremely expensive, ineffective, or generate secondary pollution. The modified polymer PAA with dihydroxybenzene has been studied for adsorption of metal and chromium VI in aqueous solution by Vetriselvi [7]. In recent years, the adsorption of metal ion by ion exchange method [8]-[12] has received much attention and become one of the most popular methods for the removal of heavy metals from the industrial wastewater.

An effective adsorbing material should consist of a stable and insoluble matrix and recent developed polysaccharide materials have been demonstrated to be such kind of material

Aresh Vikram Singh is Professor with Department of Chemistry, Jai Narain Vyas University, Jodhpur-342001, India (phone: 912912720840, 919461286995, e-mail-areshvikram04@rediffmail.com).

Sarika Nagar is Research Scholar at Department of Chemistry, Jai Narain Vyas University, Jodhpur-342001 (e-mail-nagarsarika2615@gmail.com).

[13]. The functionalization of a polysaccharide matrix with different chelating functionalities have shown the removal of metal ions from aqueous solution [14], [15]. The adsorption of metal ions using chelating ion exchange resins is a green analytical method since it does not involve the use of heavy chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction technique or other methods [16], [17]. The main aim of research work on cation and anion exchange resin has been done on polysaccharides, which are insoluble functionalized polymers. These resins provide flexible working conditions and good stability for metal ions. The interest of polysaccharide based resins is due to the fast adsorption of metal ions, higher selectivity in comparison with other polymers. [18].

The present work was undertaken to synthesize and characterization of new tamarind THPSA resin, which selectively remove heavy metal ions from industrial effluent.

II. MATERIALS AND METHOD

A. Sample

The effluent of Sunshine steel industry, Jodhpur, Rajasthan (India) has the characteristics features as summarized in Table I.

B. Synthesis of Tamarind THPSA Resin

The THPSA resin has been synthesized by modified Porath's method [19]. 32.4 g (0.2 mol) of tamarind powder was taken in round bottom flask and slurred in dioxane. 50% of aqueous solution of sodium hydroxide was added in the flask to make it alkaline, till pH reached to 9.5. The solution was stirred for one hour. 9.25 g (0.1mol) epichlorohydrin was added drop wise and stirring was continued for 5 h at 60 °C. The product epoxypropyl ether of tamarind was formed and it was used for next reaction.

Epoxy propyl ether of tamarind was allowed to react with 14.02 g (0.1 mol) of THPSA in the alkaline medium and the stirring was continued for another 4 h at 60 °C. The product was filtered under vacuum and washed with 90% methanol, containing few drops of hydrochloric acid to remove inorganic impurities. Finally it was washed with pure methanol. The product tamarind THPSA resin was free flowing light white powder. The yield was 49.65 g.

TABLE I
 THE CHARACTERISTICS OF SUNSHINE STEEL INDUSTRY, JODHPUR

| | | | | | | | | | | |
|---------------------|----------------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| pH | 2.48 | | | | | | | | | |
| Appearance | Turbid | | | | | | | | | |
| Total Hardness | 846 | | | | | | | | | |
| Metal ion | Cu ²⁺ | Zn ²⁺ | Pb ²⁺ | Cd ²⁺ | Ni ²⁺ | Mg ²⁺ | Cr ²⁺ | Ca ²⁺ | Fe ²⁺ | Co ²⁺ |
| Concentration (ppm) | 2.58 | 4.25 | 0.85 | 0.58 | 0.46 | 21.3 | 0.94 | 82.6 | 2.49 | 0.78 |
| Others anions (ppm) | Fluoride=0.32; Sulphate=715.48; Cyanide=0.06 | | | | | | | | | |

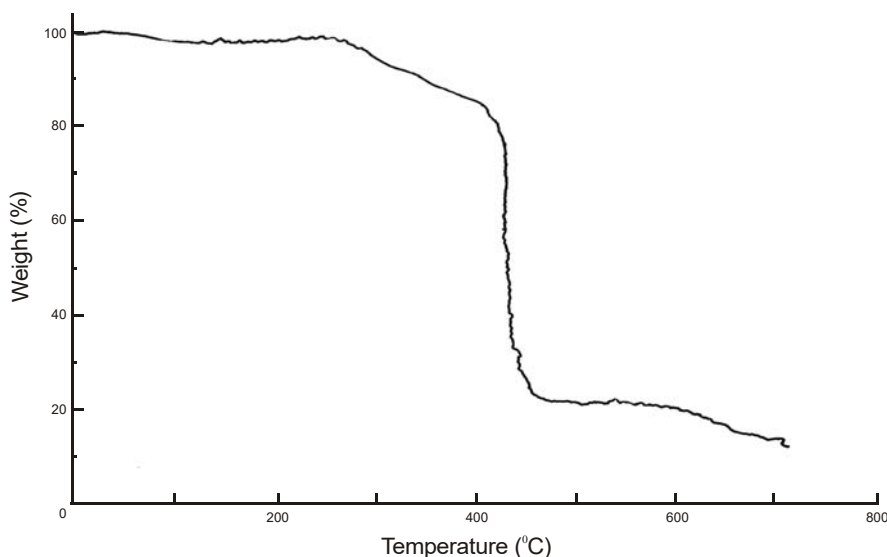


Fig. 1 TGA curve of THPSA resin (20 °C/min)

C. Determination of Removal Percentage of Metal Ions

The concentration of metal ions in solution as well as filtrates was determined using Atomic Absorption Spectrophotometer and percentage removal of metal ions by THPSA resin was calculated using (1)

$$\% R = [(I-F / I) \times 100] \quad (1)$$

where % R is percentage removal, I and F are initial and final equilibrium concentrations of metal ion in solution respectively.

D. Determination of Distribution Coefficient (K_d) of Metal Ions in Solution

The distribution coefficient (K_d) of metal ions was determined by batch method [20]. The pH of the solution was adjusted to the desired value using acetate buffer and the resin was equilibrated for 2 h. A sample solution (100 ml) containing a known concentration of the studied metal ions were transferred to an Erlenmeyer flask and after adjusting its pH values, 0.1g of the modified THPSA resin was added to the solution and the mixture was shaken continuously in a temperature controlled shaker at 25 °C. The amounts of metal ions in the solution before and after equilibration were determined by using AAS. The distribution coefficient (K_d) of metal ions was calculated by (2):

$$K_d = (R_p/S_p) \times (V/W) \text{ mg/g}^{-1} \quad (2)$$

where R_p and S_p are amount of metal in resin and solution phase. V and W are volume of solution in ml and weight of dry resin in grams.

E. Column Operation

The column operation was prepared for recovery of metal ions. In the column experiment, a glass tube with 1.6 cm internal diameter and 20 cm height, packed with 8 cm of resin (7.5 g) was used. Separation of metal ions by selective elution on column was carried out for binary mixture. The flow rate was controlled by a peristaltic pump. The column followed by treating with distilled water to remove the last traces of unadsorbed ions. The solution mixture was passed through the column at a flow rate of 1 ml/min. Elution was carried out at different concentration of hydrochloric acid solutions.

III. RESULTS AND DISCUSSION

A. IR Characterization

Perkin Elmer FTIR (model 5000, USA) Instrument was employed for FTIR spectra analysis of functionalized THPSA resin. The FTIR spectra show broad band -OH stretching frequency in the region of 3600-3200 cm^{-1} . The peak at 2929 cm^{-1} is attributed to C-H stretching vibrations. Another strong and sharp peak at 1650 cm^{-1} may be due to -OH bending. Another variable peak at 1480-1350 cm^{-1} is attributed to C-H bending. A strong peak at 1300-1000 cm^{-1} denotes C-O stretching vibration. The sulphonate group displays asymmetric and symmetric S=O stretching frequencies in the region 1350-1342 cm^{-1} and 1165-1150 cm^{-1} . The frequency of

S=O absorption is increased by the electronegative substitution.

B. Thermogravimetric Analysis

Thermogravimetric analyzer (Dupont 951, USA) was used. The sample was dried and powdered to the average mesh size in the vacuum desiccator. The sample was packed for analysis and the constant heating rate 20 °C per minute was maintained in air atmosphere. The THPSA resin is found to stable up to 401 °C and then the degradation was found to be rapid. The obtained TGA curve of THPSA resin is shown in Fig. 1.

TABLE II
PERCENTAGE REMOVAL OF METAL IONS FROM THE INDUSTRIAL WASTEWATER BY THPSA RESIN

| pH | Pb(II) | Cd(II) | Zn(II) | Cu(II) | Fe(II) |
|----|--------|--------|--------|--------|--------|
| 2 | 49.22 | 59.48 | 65.97 | 69.83 | 77.48 |
| 3 | 55.63 | 67.75 | 73.36 | 71.49 | 81.46 |
| 4 | 67.23 | 76.43 | 78.24 | 84.73 | 86.13 |
| 5 | 69.45 | 81.19 | 85.67 | 91.27 | 95.15 |
| 6 | 89.14 | 92.34 | 94.12 | 96.23 | 97.74 |
| 7 | 53.67 | 73.34 | 75.36 | 78.48 | 81.67 |
| 8 | 49.32 | 52.78 | 57.53 | 59.92 | 65.90 |

C. Ion Exchange Capacity (IEC) of THPSA Resin

It was found to be 2.94 meq/g of the dry THPSA resin [21].

D. Removal of Metal Ions from Effluent of Sunshine Steel Industry, Jodhpur, India

The results of percentage removal of metal ions from effluent of Sunshine Steel Industry by THPSA resin are given in Table II. It is clear from the table that the percentage removal of metal ions first increases and then decreases with increasing pH, the optimum results obtained at pH 6.0.

E. Distribution Coefficient (K_d) of Metal Ions

The pH has a strong effect on the distribution coefficient (K_d) of metal ions. The results of distribution coefficient (K_d) of metal ions from effluent of Sunshine steel industry, Jodhpur are given in Table III. The perusal of the results shows that the distribution coefficient value first increases and then decreases with increasing pH, the optimum results were obtained at pH 6.0. The capacity reaches the maximum value and all ion exchange sites take part in the reaction and form complex with the metal ions, therefore metal adsorption starts in the suitable pH range [22].

TABLE III
DISTRIBUTION COEFFICIENT (KD) OF METAL IONS OF THPSA RESIN (KD X 10²)

| pH | Pb(II) | Cd(II) | Zn(II) | Cu(II) | Fe(II) |
|----|--------|--------|--------|--------|--------|
| 2 | 10.14 | 17.78 | 20.34 | 24.28 | 26.38 |
| 3 | 12.89 | 26.26 | 27.13 | 33.3 | 43.73 |
| 4 | 17.25 | 32.86 | 36.26 | 28.14 | 59.82 |
| 5 | 24.97 | 52.58 | 56.82 | 95.88 | 169.34 |
| 6 | 80.18 | 110.27 | 154.12 | 240.72 | 859.95 |
| 7 | 15.76 | 27.87 | 30.02 | 40.27 | 47.43 |
| 8 | 10.45 | 12.49 | 13.39 | 16.35 | 20.48 |

F. Effect of pH

The pH plays an important role for adsorption of metal ions on polysaccharide resins. The pH affects the solubility of metal ion, concentration and formation of complex with metal ions. The metal ions compete with H⁺ ions at the adsorption sites of resin in the low pH range [23]. The uptake of free metal ions depends on pH, where optimum adsorption of metal ions occurs at pH 6 and then declining at higher pH. Adsorption of metal ions on THPSA resin increased over pH range from 2.0 to 6.0.

G. Quantitative Separation of Metal Ions from Binary Mixtures

Based on the difference in the value of distribution coefficient of studies metal ions on THPSA resin from aqueous solution, separation experiments for these metal ions were carried out by column chromatography. An ideal situation would be such that one K_d value of metal ion is greater than the K_d value of the other metal ion.

In the case of separation of Cd (II) from chelated Cu (II), Cd (II) was eluted with 0.5 N HCl. First fractions contained only Cd (II), later Cu (II) was eluted with 1.5 N HCl. Recovery of Cd (II) was found to be 92.14% while for Zn (II) it was 94.34%.

IV. CONCLUSION

The experimental results reported here validate that THPSA resin is a promising adsorbent for removal of heavy metal ions from industrial effluents due to its cost effectiveness, eco-friendliness, and rapidness.

REFERENCES

- [1] T. R. Harper and N. W. Kingham, "Removal of arsenic from wastewater using chemical precipitation methods," *Water Environ. Res.*, vol. 64, No. 3, pp. 200-203, 1992.
- [2] P. R. Kiezyk and D. Mackay, "Waste water treatment by solvent extraction", *The Cana. J. of Chem. Eng.* vol. 49, no. 6, pp. 747–752, Dec. 1997.
- [3] A.P.De. Los, F.J. Hernandez, L.J. Lozano, S. Sacher, J.I. Moreno and C. Gaoline, "Removal of metal ions from aqueous solution by extraction with ionic liquids", *J.Chem.Eng.Data.* vol.55, pp.605-608, 2010.
- [4] Carlos Barrera-Díaz, Ivonne Linares-Hernández, Gabriela Roa-Morales, Bryan Bilyeu and Patricia Balderas-Hernández, "Removal of biorefractory compounds in industrial wastewater by chemical and electrochemical pretreatments", *Ind. Eng.Chem.Res.*, vol.48, pp. 1253–1258, Aug. 2008.
- [5] U. Kepa, E. Stanczyk-Mazanek and L. Stepniak, "The use of the advanced oxidation process in the ozone + hydrogen peroxide system for the removal of cyanide from water", *Desalination*, vol.233, no.1-3, pp.187-193, 2008.
- [6] Ei-Diwani G, Ei-Rafie SH, Hawash S. "Use of sonication advanced oxidation process for purification of energetic wastewater", *J. Agric. Environ Sci*, vol.6, pp.119-128, 2009.
- [7] V. Vetriselvi, R. Jaya Santhi, "Redox polymer as an adsorbent for the removal of chromium (VI) and lead (II) from the tannery effluents", *Water Res. and Ind.*, vol. 10, pp. 39–52, 2015.
- [8] C.C. Wang, C.Y. Chen, C.Y. Chang, "Synthesis of chelating resins with iminodiacetic and its wastewater treatment application", *J. Appl. Polym. Sci.*, vol 10, pp. 1353-1357, 2002.
- [9] Joanna Kluczkan, Teofil Korolewicz, Maria Zołotajkin, Jakub Adamek, "Boron removal from water and wastewater using new polystyrene-based resin grafted with glycidol", *Water Res. and Indus.*, vol. 11, pp. 46-57, 2015.

- [10] A. Singh and S. K. Saraf, "Synthesis, Characterization and ion-exchanging properties of a novel ion-exchange resin, Part II.", *Int. J. Polym. Mater.*, vol. 58, pp. 499-508, July 2009.
- [11] D. Das, A. K. Das and C. Sinha, "A new resin containing benzimidazolylazo group and its use in the separation of heavy metals", *Talanta*, vol. 48, no.5, pp.1013-1022, May 1999.
- [12] A.G. Lata, K.G. George, and K.N. Ninan, "Synthesis of a polysaccharide chelating resin and application in metal ions extraction", *J. Appl. Polym. Sci.*, vol. 43, pp.1159-1169, 2003.
- [13] G. Crini, Prog, "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment", *Poly. Sci.*, vol. 30, pp. 38-70, 2005.
- [14] D.A. Fadel, S.M.El. Bahy and Y.A. Abdelaziz, "Heavy metals removal using iminodiacetate chelating resin by batch and column techniques", *Desalination and Water Treatment*, vol. 57, issue 53, pp 25718-25728, Feb. 2016.
- [15] A.V. Singh and I.K. Kumawat, "Preparation and characterization of tamarind 4-hydroxybenzoic acid (THBA) resin and its use in extraction of heavy metal ions from industrial wastewater", *WaterSA*, vol. 38, no. 4, pp. 529-536, July 2012.
- [16] R. K. Sharma, "Design, synthesis, and application of chelating polymers for separation and determination of trace and toxic metal ions. A green analytical method", *Pure Appli. Chemi.* vol.73, no.1, pp.181-186, 2001.
- [17] A.V. Singh, D.K. Soni and I.K. Kumawat, "Synthesis, characterisation and application of new tamarind triethylamine (TTEA) resin for removal of toxic metal ions from the effluent of Puneet Steel Industry, Jodhpur, Rajasthan", *Water and Environ. J.*, vol.26, pp.371-380, Sept. 2012.
- [18] P. K Roy, A. S Rawat and V. Choudhary, "Synthesis and analytical application of a chelating resin based on a crosslinked styrene/maleic acid copolymer for the extraction of trace-metal ions" *J. Appl. Polym. Sci.*, vol.94, pp.1771-1779, 2004.
- [19] I. Porath and N. Fornstedt, "Group fractionation of plasma protein on dipolar ion exchangers", *J. Chromatog A*, vol.51, pp.479-489, 1970.
- [20] Ali Pourmand, Nicolas Dauphas, "Distribution coefficients of 60 elements on TODGA resin: Application to Ca, Lu,Hf, U and Th isotope geochemistry", *Talanta*, vol., 81,pp 741-753 Jan. 2010
- [21] I. Vogel, "Vogel's Textbook of quantitative chemical analysis," 5th edition. Longman Group UK Ltd, England 1989, pp 207-208.
- [22] V. Nenov and B. Bonev, "sorption of heavy metals by modified chelating ion exchange", *Int. J. Environ. Tech. Manag.*, vol.12, no.2-4, pp. 345-358, 2010.
- [23] S.S. Kalaivani, T. Vidhyadevi, A. Murugesan, K. V. Thiruvengadaravi, D. Anuradha, S. Sivanesan, L. Ravikumar, "The use of new modified poly(acrylamide) chelating resin with pendent benzothiazole groups containing donor atoms in the removal of heavy metal ions from aqueous solutions", *Water Res. and Ind.*, vol. 5, pp 21-35, Apr. 2014.