Synthesis, Characterization and Application Of New Cation Exchanger Guar Gum Phenol -2, 4-Disulphonic Acid [GPDSA] Resin for Removal of Toxic Metal Ions from the Effluent of Laxmi Steel Industry, Jodhpur, Rajasthan

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ABSTRACT: New ion exchange guar gum phenol -2, 4-disulphonic acid (GPDSA) resin was chemically synthesized. The prepared resin was characterized on the basis of ion exchange capacity, elemental analysis, pH titration, FT-IR spectra and thermogravimetric analysis (TGA). Chemical resistivity of GPDSA resin was assessed in several acidic and basic media. The present method is simple and rapidly applicable for the removal and recovery of metal ions from effluent of industries. The distribution coefficient (K_d) values of metal ions have been determined by batch method. Owing to the large differences in K_d values of heavy metal ions at different pH, the removal and recovery of metal ions from their aqueous solutions and effluent of Laxmi Steel Industry, Jodhpur has been studied systematically. The adsorption of different metal ions on GPDSA resin follows the order viz $Fe^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+} > Pb^{2+}$.

Key Words: - Distribution coefficients; ion exchange capacity; ion exchanger; toxic metal ions; wastewater; GPDSA resin.

1. INTRODUCTION:

Economical progress and increase in population result in an increase of sewage and wastewaters containing heavy metal ions. In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, separation of these metal ions in natural water at trace level is of paramount importance both for water purification and analysis. For such purpose, various methods have been developed for the removal of these metal ions from aqueous systems such as solvent extraction [1], electrochemical reduction [2], chemical and bio sorption [3], preconcentration [4], reverse osmosis [5] and ion exchange [6]. In recent years, the ion exchange method is applied for removal of toxic metal ions and organic pollutants from drinking, underground and surface waters and also from industrial waste waters produced from different technological processes. Ion exchange method is treated as an emerging technology effective in removing even very low levels of toxic metal ions from industrial effluent. Ion-exchangers of polyvalent metals often exhibit much better ion-exchange behavior and are always of interest because of their high selectivity, resistance to high temperature and to some extent higher chemical stability than commercial ion-exchange resins [7-9].

Ion exchange materials have been proved more suitable tool to various environmental problems [10,11]. Ion-exchange equilibrium on synthetic organic resins has been studied by several authors [12,13]. Removal of heavy metal ions by functionalized polymer has become an important option in the integrated approach to wastewater treatment. The increasing number of publications on adsorption of toxic compounds by modified polysaccharides shows that there is a recent increasing interest in the synthesis of new low-cost adsorbents used in wastewater treatment [14]. The recent developments in the synthesis of adsorbents containing polysaccharides, in particular modified biopolymers derived from chitin [15-16], chitosan [17], starch [18], cellulose [19-23] and cyclodextrin [24] which are not only eco-friendly and cost-effective but are effective also in remediation of common effluents present in the wastewater. The chelating resin containing mercapto and amino groups for the collection of Au (II), Pd (II), Hg (II), along with some transition metals was reported by [25]. Even such polysaccharide cellulose based cellulose imido di acetic acid [CIDAA] resin had been used for the removal of radioisotopes from aqueous solution [26]. Nabi and Naushad studied the synthesis, characterization and analytical applications of a new composite cation exchange cellulose acetate – Zr (1V) molybdophosphate [27].

Guar gum is a galactomannan biopolymeric material isolated from the endosperms of *Cyamopsis tetragonalobus*, which is native to northwestern parts of India [28]. A polysaccharide consisting of linear chains of mannose with 1β→4 linkages to which galactose units are attached with 1α→6 linkages. The ratio of mannose to galactose is 2:1. The guar gum may be potentially used as an adsorbent; however, its water solubility does not permit this under aqueous condition. Its stability [29] and solubility as well as its sorption capacity can be altered through functionalisation by organic group [30] and chelating agent [31]. Chauhan et al studied the synthesis and characterization of novel guar gum hydrogels and their use as Cu (II) sorbent [32]. A hydrophilic polysaccharide matrix of guaran has been used for the preparation of some new chelating resins, i.e. glycine hydroxamate in guaran (GH-G), acetic acid hydroxamate in guaran (AAH-G) and iminodiacetic acid dihydroxamate in guaran (IDAAH-G) after its crosslinking with epichlorohydrin [33]. Water insoluble copolymer of guar gum such as poly (methacrylate) grafted guar gum [34] may be potentially used as adsorbent in the aqueous medium successfully.

The ion exchangers based on guar gum powder are hydrophilic and biodegradable, whereas ion exchangers prepared from petrochemical products are hydrophobic and not biodegradable. Due to rising prices of petroleum products the guar gum powder has been selected for development of guar gum phenol-2, 4-disulphonic acid (GPDSA) resin. Its cost is low, it is locally available in large quantities from agricultural resources, and such biopolymers are also environment friendly.

In this work, we describe the synthesis and characterization of GPDSA resin and its applications for removal and recovery of toxic metal ions from effluent of Laxmi Steel Industry, Jodhpur, India. Various factors affecting adsorption conditions, pH, agitation speed, temperature and treatment time on the removal of metal ions have been studied.

2. MATERIAL AND METHOD:

2.1 Chemicals:

Guar gum powder (Ases Chemical Works, Jodhpur, India), epichlorohydrin (Aldrich, USA), phenol-2,4-disulphonic acid (LOBA Chemic Pvt. Ltd.,Mumbai,India), sodium hydroxide (Sarabhai M. Chemicals, Baroda, India), dioxane (E Merk, Mumbai, India). Standard metal ion solutions were prepared by dissolving appropriate amount of metal salt in double distilled water.

2.2. Apparatus:

2.2.1. Atomic absorption spectrometry

Perkin - Elemer model 2380 atomic absorption spectrometer was used for quantitative determination of trace metals.

2.2.2. FTIR spectrometer

Varian FTIR instrument was used for determination of IR spectra.

2.2.3. PH- meter

Beckman model 335 digital pH meter was used for determination of pH of each solution.

2.2.4. Thermogravimetric analyzer

Thermogravimetric analyzer model 951 was used for determination of thermal stability of synthesized resin.

2.2.5. Elemental analyzer

Carlo Erba model 1160 elemental analyzer was used for determination of C, H and N in the synthesized resin.

2.2.6. Magnetic stirrer

Magnetic stirrer Sisco, Delhi, India was used for synthesis of resin.

2.3 Sample

The effluent of Laxmi Steel Industry, Jodhpur has following characteristics features are given in Table 1.

Table 1 The characteristics features of effluent of Laxmi Steel Industry, Jodhpur, India

Appearance: Turbid pH: 5.8 Colour: Dirty brown Total hardness: 881

Metal ions	Concentration (in ppm)
Fe (II)	1.07
Cu (II)	0.67
Zn (II)	7.16
Pb (II)	0.68
Cd (II)	0.13
Cr (II)	0.74
Ni (II)	0.18
Co (II)	0.78
Mg (II)	102
Ca (II)	184

Other anions (ppm): Fluoride = 0.92; Sulphate =874.12; Cyanide = 0.03

2.4 Method - synthesis of guar gum phenol-2, 4-disulphonic acid (GPDSA) resin

Synthesis of guar gum phenol-2, 4-disulphonic acid resin accomplished in the following two steps.

(A) Preparation of epoxypropyl ether of guar gum

An amount of 32.4 g of guar gum powder (0.2 mol) was taken in a round bottom flask and suspended in 65 ml dioxin. Subsequently, 5 ml of 20 % (w/v) sodium hydroxide was added to make it alkaline, till pH reached 8.5. The solution was stirred at 60°C. Then 9.25 g (0.1 mole) epoxychloropropane (epichlorohydrin) was added with constant stirring. The stirring was further continued for 5 hrs, at 60°C. The product epoxypropyl ether of guar gum was filtered under vacuum and washed with methanol to remove impurities and then dried.

(B) Preparation of phenol -2, 4-disulphonic acid derivative of guar gum

Epoxypropyl ether of guar gum was then allowed to react with 0.1 mol of phenol -2, 4-disulphonic acid and the stirring was continued for another 5 hrs at 60°C. The product formed was filtered under vacuum and washed with aqueous methanol, containing few drops of HCl to remove inorganic impurities and to neutralize excess of NaOH and finally washed with methanol and dried. The yield of the GPDSA resin is 52.92 g. The reaction scheme for the synthesis of GPDSA resin is shown in Figure 1**.**

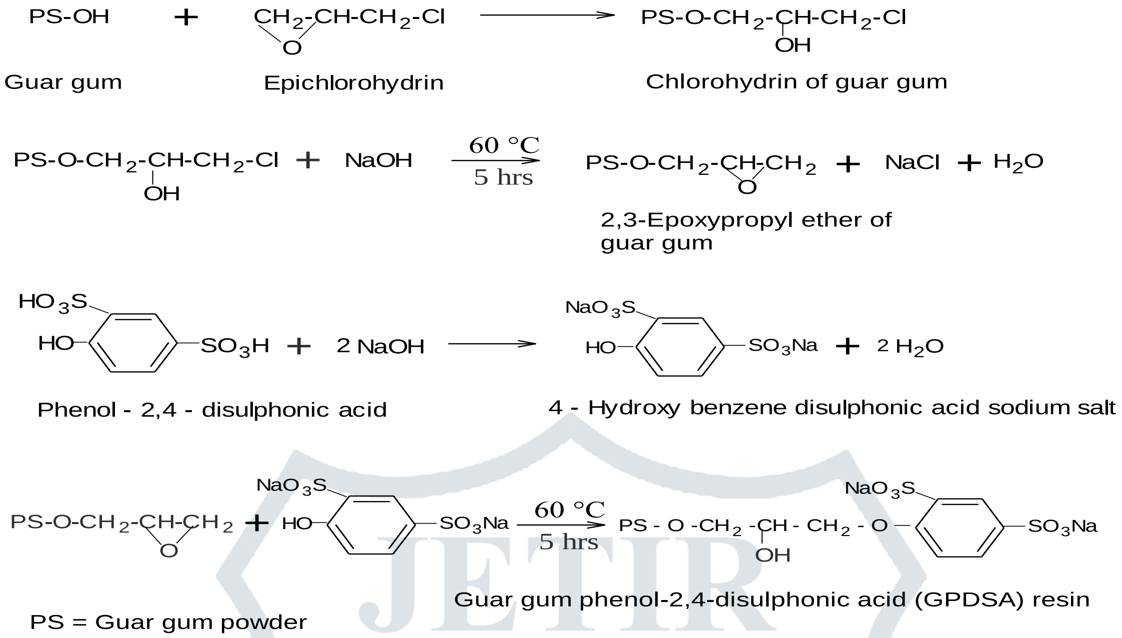

Figure : 1 Synthesis of guar gum phenol -2, 4-disulphonic acid (GPDSA) resin

2.5 Resin durability

It was observed that the absorbancy of different metal ion on the GPDSA resin after 10 cycles (adsorption and desorption) and ion exchange capacities of reported resin were almost constant. The adsorbed metal ions were easily desorbed by treatment with different strength of acids at room temperature. Table 2 shows the absorbency of different metal ions on the GPDSA resin after 10 cycles (adsorption and desorption).

Table 2 The adsorption percentage of different metal ions on GPDSA resin (adsorption and desorption)

Metal ions	Adsorption % of different metal ions onto GPDSA resin after				
	0 Cycle	2 Cycles	4 Cycles	8 Cycles	10 Cycles
Pb (II)	92.64	89.33	87.14	87.14	87.14
Cd (II)	93.84	90.14	87.98	87.98	87.98
Cu (II)	94.02	91.11	89.03	89.03	89.03
Zn (II)	94.13	91.02	88.89	88.89	88.89
Fe (II)	95.32	92.38	90.14	90.14	90.14

2.6 Swelling studies

The H^+ form of dry resin (0.4 g) was equilibrated with 50 ml of distilled water for 4 days. The swollen resin was collected by filtration, adhering traces of water were removed by pressing with filter and sample was weighed. The swollen resin was dried in vacuum for 24 hours and weighed. The equilibrium water content (EWC) of resin was calculated using the following equation.

$$\text{EWC} = \frac{\text{Weight of wet resin} - \text{weight of dry resin}}{\text{weight of wet resin}}$$

2.7 Column experiment

In the column experiment, a glass tube with 1.6 cm internal diameter and 20 cm height, packed with 9.0 cm of resin (8.5g) was used. 50 ml of the metal ion sample solution were passed through the column at a flow rate of 2.0 ml per minute. The flow rate was controlled by a peristaltic pump. The column was washed with 20 ml of deionized water and the washing was rejected. The metal ions were eluted quantitatively with different strength of acids.

2.8 Determination of distribution coefficient

The distribution coefficient (K_d) of metal ions on resins were determined by batch method. In all cases for the determination of $K_{d,}$ 50 ml reference solution was taken in a conical flask and the pH was adjusted by ammonium hydroxide and ammonium chloride. 50 mg of GPDSA resin was added to the solution and stirred on a magnetic stirrer for 2 hours and the contents were equilibrated. The solution was filtered through whatman filter paper no. 40. The residue on the filter paper was equilibrated with 4 N HCl and the solution was filtered through whatman filter paper no. 42.

The heavy metal ion concentrations in the filtrate as well as in the residue were estimated using atomic absorption spectrophotometer. The calibration curves for different metal ions were plotted by analyzing a series of standard solutions of metal ions using AAS. The different wavelength of main resonance line and air acetylene flame was used for the estimation of various metals. The concentration of metal ion in filtrate was determined by the calibration curves and the percentage removal of the metal ions & their distribution coefficient (K_d) on GPDSA resin were calculated using the formula:

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

i.e. $$Kd = \frac{\left(I - \frac{F}{F}\right)XV}{M}\ \frac{ml}{g}$$

Where I is the initial amount of the metal ion in solution, F is the final amount of metal ion after equilibrium with resin, V is the volume of metal ion solution (ml) and M is the weight of the resin taken (g).

2.9 Ion exchange capacity (IEC) determination

Resin capacity is usually expressed in terms of mol per liter (mol/L) of resin or millimol per gram of dry resin. 10 g of the GPDSA resin was completely converted into chloride form by treatment with liberal excess of 0.1 N HCl. Then the resin was washed with distilled water. Washing were also collected in the same volumetric flasks and the contents were neutralized with dil. HNO_3 and volume made up to 250 ml. 25 ml aliquot of the effluent were titrated against 0.11 N silver nitrate solution using potassium chromate as indicator (10 % solution). The scientific weight capacity (Q weight) was calculated using the formula:

$$Q\ weight = \frac{Effluent\ volume\quad X\ \ ml\ mole\ of\ titrant\ used}{volume\ of\ aliquot\quad X\ \ weight\ of\ dried\ resin}$$

2.10 Determination of percentage removal of metal ions concentration

The initial metal ion concentration in solution and filtrate after equilibrium with resin were estimated using atomic adsorption spectrophotometer. The percentage removal of metal ions was calculated using this formula.

Percentage removal of metal ions = $\left[\frac{Ce}{Co} X\, 100\right]$

Co = Initial concentration of metal ion in solution
Ce = Concentration of metal ions in resin at equilibrium

3. RESULT AND DISCUSSION:

It was found that the synthetic GPDSA resin employed to remove toxic metal ions i.e. Fe^{+2}, Zn^{+2}, Cu^{+2}, Pb^{+2} and Cd^{+2} from the solution and effluent of Laxmi Steel Industry, Jodhpur showed almost 95% removal efficiency. The researchers found that the equilibrium exchange of metal was dependent on the solution pH and the molar concentration ratio of resin to the total metals. As stated previously, ion exchangers possess specific properties. They are more and more widely applied in purification of water and industrial wastewater. In the studies the initial pH of complex ions Fe^{+2}, Zn^{+2}, Cu^{+2}, Pb^{+2} and Cd^{+2} was maintained because, as follows from literature data [35] at lower and higher pH values, formed complexes are probably not stable.

The polymeric chelating ion-exchangers have found extensive applications in recovery and removal of transition metal ions from process solutions due to their selectivity particularly against alkali and alkaline earth metal cations. Although many synthetic inorganic ion exchangers have been object of considerable study in recent years because of their selectivity and intercalation [36]. The guaran sulphonic acid cation exchanger is used for the removal of toxic metal ions from underground mine water of the Rajpura Dariba Mines, Udaipur, Rajasthan [37]. The chemical modification of cellulose [38] can be used for the sorption of Cu^{2+} ions from its aqueous solution.

2.3 FTIR characterization of guar gum phenol-2, 4-disulphonic acid (GPDSA) resin

FTIR spectral analysis of guar gum phenol-2, 4-disulphonic acid (GPDSA) resin was employed by Perkin Elmer FTIR instrument using KBr pellets. FTIR spectrum of GPDSA resin shows broad band in the region 3600 -3200 cm^{-1} characteristic –OH stretching. The peak at 2950 cm^{-1} is attributed to C-H stretching vibration and the peak at 1480-1350 cm^{-1} is denotes to C-H bending. A strong peak in the region 1250 – 1070 cm^{-1} denotes C-O stretching vibrations. The GPDSA resin displays asymmetric and symmetric S=O stretching frequency in the region 1350 -1340 cm^{-1} and 1165 – 1150 cm^{-1}[39]. The IR spectrum of GPDSA resin is given in Figure 2.

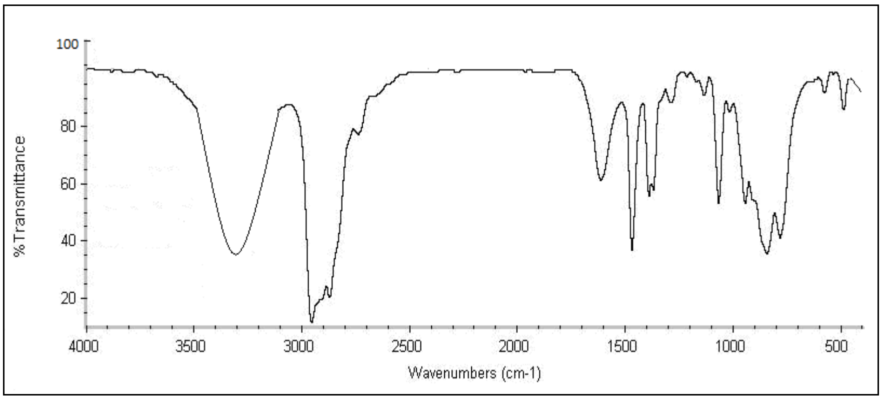

Figure : 2 FTIR of guar gum phenol -2, 4-disulphonic acid (GPDSA) resin

3.2 Thermogravimetric analysis

Thermogravimetric analysis was done on Du Pont 9000 system. The polymer sample was powdered to the same average mesh size and dried carefully in vacuum desicator. The boat was packed uniformly for analysis. For the dynamic measurement, the system was heated at a constant heating rate of 20^0C per minute under static air atmosphere till the complete decomposition. The weight loss between 300-390°C is due to breaking of CH_2–CH_2 bond. The thermo gram is shown in Figure 3.

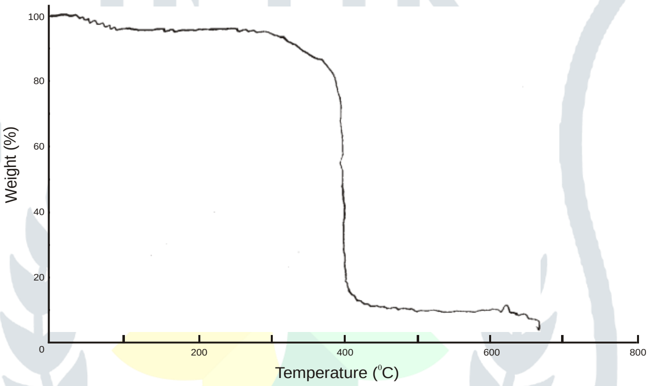

Figure : 3 TGA curve of GPDSA resin.

3.3 Elemental analysis

The results of the elemental analysis were in good agreement with calculated value .The elemental analysis results were in support of the proposed structure of the resin presented in scheme-1. The results of elemental analysis are given in Table 3.

Table 3 Elemental analysis

Elements	C	H	O	S
Calculated Values (%)	38.13	4.23	44.06	13.56
Found Values (%)	37.94	4.16	43.86	13.34

3.4 Swelling studies

The equilibrium water content (EWC) of resin was **8.5 %.**

3.5 Removal of metal ions from effluent of Laxmi Steel Industry, Jodhpur by GPDSA resin

The results of percentage removal of effluent of Laxmi Steel Industry, Jodhpur by GPDSA resin is given in Table 4. It is clear from the reported Table that the percentage removal of metal ions first increases and then deceases with increasing pH and the optimum results obtained at pH 6.0. It has been found that the maximum percentage removal of Fe^{2+}, Zn^{2+}, Cu^{2+} , Cd^{2+} and Pb^{2+} are 95.32%, 94.13%, 94.02%, 93.84% and 92.64% respectively**.** Sankar and Kesavulu investigated the removal of transition metal ion from aqueous solution by poly (MMBP)-DVB resin. Removal percentage of metal ion such as Cu^{+2} and Ni^{+2} were about 60-70% at pH 4.5 [40]. Demirbas et al studied the adsorption of Cu^{+2}, Zn^{+2}, Ni^{+2}, Pb^{+2} and Cd^{+2} on Amberlite IR-120 synthetic sulfonated resin at different pH and temperatures by batch process. The maximum recovery (>99%) has been obtained at about pH 9.0 [41].

Table 4 Percentage removal of metal ions of effluent of Laxmi Steel Industry, Jodhpur, India on GPDSA resin

pH	Zn (II)	Cd (II)	Fe (II)	Pb (II)	Cu (II)
2	58.37	54.61	57.94	61.76	56.71
3	69.69	64.61	68.22	76.47	67.16
4	89.52	75.38	82.24	85.29	86.56
5	92.87	90.76	91.58	89.70	91.04
6	94.13	93.84	95.32	92.64	94.02
7	87.15	73.84	79.43	82.35	83.58

3.6 Distribution coefficient (K_d) of metal ions in effluent of Laxmi Steel Industry, Jodhpur

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 the effluent of Laxmi Steel Industry, Jodhpur are given in Table 5. The results show that the distribution coefficient value first increases and then decreases with increasing pH, and that optimum result were obtained at pH 6.0. Due to principal of selectivity the order of distribution ratio of divalent ions measured in the range pH 2-8 were found to be $Fe^{2+} > Zn^{2+} > Cu^{2+} > Cd^{2+} > Pb^{2+}$ **.** The difference in distribution coefficients at the different pH for different metal ions suggests possible strategy for separation of these ions from their mixtures.

It is clear from the Table 5 that the optimum results for the distribution coefficient (K_d) on the GPDSA resin are obtained at pH 6. The accuracy and precision data has been given in **Table 6**. The results of this investigation shows that the GPDSA resin is more selective and finds applications in preconcentration, isolation and separation of free metal ions (aqua or solvated) due to binding dissociation equilibrium. The resin can be used on a large scale in batch operation. The pore size in the resin can be controlled by adjusting the degree of cross linking, and the resin with proper cross linking can be used as column material.

Table 5 Distribution coefficient of metal ions from the effluent of Laxmi Steel Industry, Jodhpur on GPDSA resin (K_d X 10^2)

pH	Zn (II)	Cd (II)	Fe (II)	Pb (II)	Cu (II)
2	14.12	12.03	13.77	16.15	13.10
3	22.99	18.26	21.47	32.50	20.45
4	85.46	30.62	46.31	58.00	64.44
5	130.39	98.33	108.88	87.14	101.66
6	160.47	152.5	204.00	126.00	157.50
7	67.82	28.33	38.63	46.66	50.90
8	25.44	17.08	18.91	24.00	16.8

Table 6 Optimum results for the removal of metal ions from the effluent of Laxmi Steel Industry, Jodhpur on GPDSA resin

Metal Ions	Amount of Metal ion in effluent (mg)	Amount loaded on GNSA resin (mg)	Removal %	RSD %
Pb (II)	0.68	0.63	92.64	3.33
Fe (II)	1.07	1.02	95.32	2.66
Cu (II)	0.67	0.63	94.02	3.2
Cd (II)	0.13	0.122	93.84	1.6
Zn (II)	7.16	6.74	94.13	3.5

3.7 Ion exchange capacity (IEC) determination

The ion exchange capacity was found to be 3.14 mmol/g of the dry GPDSA resin. The ion exchange capacity of Indion 225H, Duolite C467, ANKB-35 and KU-23 resins are 1.8, 1.0, 1.05 and 1.85, respectively [42-43].

3.8 Statistical analysis

The relative standard deviation values (RSD) of optimum removal percentage of metal ions are shown in **Table 6**. All data represent the mean of three independent experiments.

3.9 Recovery of metal ions

The column experiments used for analyzed the recovery of metal ions. According to the column experiment the metal ions were eluted quantitatively with different strength of acids. Zn^{2+} was eluted with 1.0 N HCl; Cd^{2+} with 1.0 N HCl; Fe^{2+} was eluted with 1.0 N HNO_3; Pb^{2+} with 1.0 N HNO_3; Cu^{2+} was eluted with 1.0 N HNO_3 Then the resin column was washed thoroughly with demineralized water. Data obtained in Table 7 indicated that, different quantity and different strength of hydrochloric acid and nitric acid solution could afford quantitative elution of different metal ions from the resin. Dev and Rao modified amberlite XAD-4 with bis-(N,N- Salicylidene)-1,3-propanediamine for the separation of Cu(II), Fe(II), Ni(II), Co(II), Zn(II), Hg(II), Pb(II) and sorbed metals were eluted by 1 M HCl with a recovery of 98-100 % [44].

Table 7 Quantitative separations of metal ions on a column of GPDSA resin

Metal Ions	Amount Loaded (mg)	Amount recovery (mg)	Recovery of metal ions %	Eluent used	Amount of eluent
Pb (II)	0.63	0.62	98.41	1 N HNO_3	60
Fe (II)	1.02	1.02	100.0	1 N HCl	50
Cu (II)	0.63	0.61	96.82	1 N HCl	60
Cd (II)	0.122	0.120	98.36	1 N HNO_3	70
Zn (II)	6.74	6.58	97.62	1 N HCl	65

3.10 Moisture contents

A physical property of the ion exchange resin that changes with changes in cross linkage is the moisture content of the resin. The amount of cross linking depends on the proportions of different monomers used in the polymerization step. So it is important to determine the moisture contents of the synthesized resins. 1.0 g of the resin in hydrogen form was taken and dried to a constant weight in vacuum desicator at 80°C overnight and the resin was weighed. The moisture percentage was16.1 %.

3.11 Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbent during reaction. To examine the adsorption percentage of metal ions with pH, the pH was varied from 2.0 to 8.0. The uptake of free metal ions depends on pH, where optimum adsorption of metal ions occurs at definite pH and then declining at higher pH. Adsorption of metal ions on GPDSA resin increased at pH 6.0 than decreased. At higher pH, the presence of oxygen containing functional groups makes the adsorbent surface negatively charged and hence there is repulsive electrostatic interaction between the adsorbent and the anions [45, 46]. After pH 9.0, the insoluble metal ions starts precipitating from the solution, making true sorption studies impossible.

3.12 Effect of agitation speed

The effect of agitation speed on adsorption of metal ions was studied by varying the speed of agitation from 0 (without shaking) to 200 rpm, while keeping the optimum temperature (25^0C) and optimum pH as constant. It is clear from Figure 4 that the adsorption of metal ions on ion–exchange resin generally increased with increasing agitation speed. The adsorption of metal ions on GPDSA resin increased when agitation speed increased from 50 to 100 rpm. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of metal ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 100-200 rpm is sufficient to assure that all the surface binding sites are made readily available for metal ions uptake. Then, the effect of external film diffusion on adsorption rate can be assumed as not significant. For convenience, agitation speed of 150 rpm was selected as the optimum speed for GPDSA resin for removal of metal ions from effluent of Laxmi Steel Industry. These results are in close agreement with the reports by Jeon et al [47].

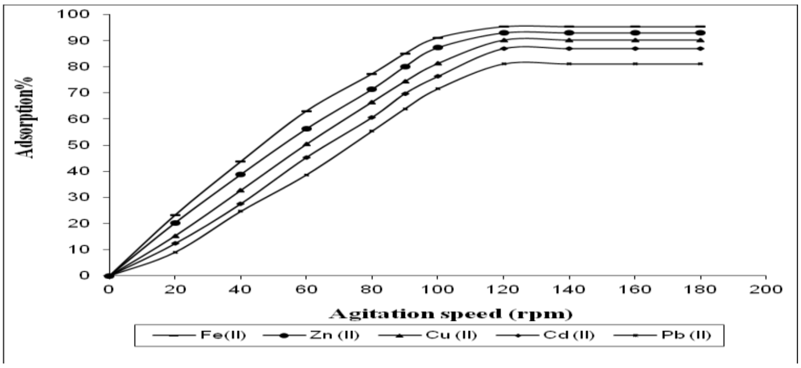

Figure: 4 Effect of agitation speed on adsorption of metal ions on GPDSA resin.

3.13 Effect of treatment time

The results of treatment time indicate that adsorption percentage of metal ions increased with an increase in contact time before equilibrium is reached. The adsorption of metal ions on GPDSA resin increased when contact time was increased from 30 to 240 minutes, optimum contact time for GPDSA adsorbent was found to be 240 min. Hence the GPDSA resin require a longer contact time. Other parameters such as pH of solution and agitation speed were kept optimum, while temperature was kept at 25^0C. Greater availability of sulphonic acid functional groups on the surface of PS which are required for interaction with metal ions, significantly improved the binding capacity and the process proceeded rapidly. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

3.14 Effect of treatment temperature

Figure 5 shows the effect of treatment temperature on the adsorption percentage of the metal ions on GPDSA resin. The adsorption percentage of metal ion decreases by increasing the treatment temperature from 25^0C to 50^0C and then 75^0C at optimum treatment time of 4 h. This observation is in full agreement with the published results. [48].

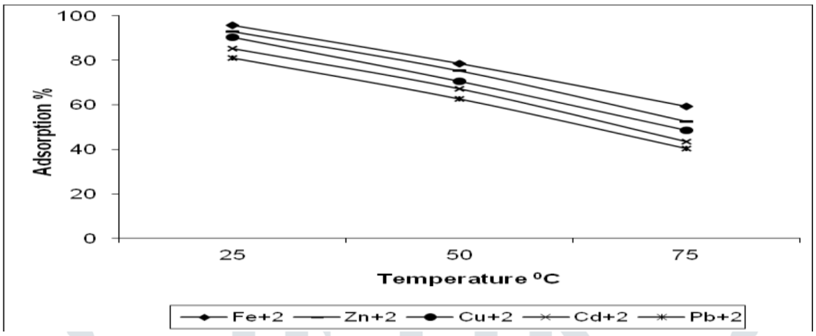

Figure 5 Effect of changing treatment temperature on the adsorption percentage of different metal ions on GPDSA resin.

4. CONCLUSION:

It has been found that the present paper was to examine the GPDSA cation exchange resin for removal of toxic metal ions Fe^{+2}, Zn^{+2}, Cu^{+2}, Pb^{+2} and Cd^{+2}. The resin removed almost 96% toxic metal ions from aqueous solutions and effluent of Laxmi Steel Industry, Jodhpur. The optimum conditions for removal of Fe^{+2}, Zn^{+2}, Cu^{+2}, Pb^{+2} and Cd^{+2} ions using GPDSA exchange resin were found to be pH 6.0 and stirring time ~25 min. The relative standard deviations (RSD) of the repeatability and the reproducibility were < 4.0 %. The GPDSA resin is locally available in large quantities from agricultural resources, and such biopolymers are also environment friendly. It would be interesting to use the GPDSA resin for the economic treatment of effluent containing the aforementioned metal ions.

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REFERENCES:

[1] SHUKLA R and RAO G, 2002, Solvent extraction of metals with potassium-dihydro bispyrazolyl-borate. Talanta, 57, 633–639.

[2] BASHA CA, BHADARINARAYAN NS, ANANTHARAMAN NS, MEERA A, BEGUM KM, 2008, Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor. Journal of Hazardious Material, 152, 71−78.

[3] CHANG X, SU Q, LIANG D WEI X, WANG B, 2002, Efficiency and application poly (acryldinitrophenylamidrazone dinitroacrylphenylhydrazine) chelating fiber for pre-concentrating and separating trace Au(III), Ru(III), In(III), Bi(III), Zr(IV), V(V), Ga(III) and Ti(IV) from solution samples. Talanta, 57, 253–261.

[4] EKIC S D, FILIK H, APAK R, 2004, Use of an o-aminobenzoic acid-functionalized XAD-4 Copolymer Resin for the separation and preconcentration of heavy metal (II) ions. Analytica Chimica Acta, 505, 15–24.

[5] GIBERT O, VALDERRAMA C, PETERKOVA M J, CORTINA L, 2010, Evaluation of selective sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis rejected brine. Solvent Extraction and Ion Exchange, 28, 543–562.

[6] NABI SA, NAUSHAD M, 2008, New and novel organic–inorganic type crystalline 'polypyrrolel/polyantimonic acid composite system: characterization and analytical applications as a cation-exchange material and Hg (II) ion-selective membrane electrode. Colloids and Surfaces A: Physicochemical and Engineering Aspect, 316, 217-225.

[7] SALAZAR E, ORTIZ MI, URTIAGA A, MAND IRABIENM JA, 1992, Kinetics of the separation concentration of chromium (VI) with emulsion liquid membranes.Industrial & Engineering Chemistry Research, 31, 1523-1529.

[8] KABAY MM, SAHA A, STREAT BM, 2003, Removal of Cr (VI) by solvent impregnated resins (SIR) containing aliquat 336.Reactive Functional Polymers, 5**,** 103-115.

[9] SAHA B, IGLESIAS M, CUMMING IW, STREAT M, 2000, Sorption of trace heavy metals by thiol containing chelating resins, 18, 133-167.

[10] GUPTA AP, VERMA GL, IKRAM S, 2000, Studies on a new heteropolyacid-base inorganic ion exchanger; zirconium (IV) selenomolybdate. Reactive Functional Polymers, 43, 33-41.

[11] NABI SA, NAUSHAD M, INAMUDDIN, 2007, Studies on a new heteropoly acid-based inorganic ion exchanger; zirconium (IV) selenomolybdate. Journal of Hazardious Material, 142**,** 404-411.

[12] INAMUDDIN SA, SIDDIQUI WA, KHAN AA, 2007, Synthesis, characterization and ion-exchange properties of a new and novel ‘organic–inorganic’ hybrid cation-exchanger: Nylon-6, 6, Zr (IV) phosphate. Talanta, 71, 841-847.

[13] KHAN AA, ALAM MM, 2004, New and novel organic–inorganictype crystalline ‘polypyrrolel/polyantimonic acid’ composite system: preparation,characterization and analytical applications as a cation-exchange material and Hg(II) ion-selective membrane electrode. Analytica Chimica Acta, 504, 253-264.

[14] CRINI G, 2005, Recent developments in polysaccharide based materials used as adsorbents in waste water treatment. Progress in Polymer Science, 30, 38-70.

[15] SANTOSA J, SISWANTA D, SUDIONO S and SEHOL M, 2007, Synthesis, utilization of chitin–humic acid hybrid as sorbent for Cr (III). Surface Science, 601**,** 5148-5154.

[16] WONG KS, WONG KH, NG S, CHUNG WK, WONG P.K, 2007, Adsorption of copper ion on magnetite immobilized chitin. Water Science Technology, 56, 135–143.

[17] WAN NAGH S, ENDUD CS, MAYANAR R, 2002, Removal of copper (II) ions from aqueous solution onto chitosan and cross-linked chitosan beads. Reactive Functional Polymers, 50, 181-190.

[18] DELVAL F, CRINI G, BERTINI S, FILIATRE *C*, TORRI G, 2005, Preparation, characterization and sorption properties of crosslinked starch-based exchangers. Carbohydrate Polymer, 60, 67-75.

[19] El-MENSNAWY M, SALAMA A, El – ASMY AA, 2008, new modified cellulose for separation and determination of mercury in environment water sample. Canadian Journal of Analytical Science and Spectroscopy, 53, 206 -213.

[20] GERENTE C, MENSIL PC, ANDRES Y, THIBAULT J, CLOIREC PL, 2000, Removal of metal ions from aqueous solution on low cost natural polysaccharides:sorption mechanism approach. Reactive Functional Polymers, 46**,** 135-144.

[21] ZHOU D, ZHANG L, ZHOU J and GOU S, 2004, Cellulose/chitin beads for adsorption of heavy metals in aqueous solution. Water Research, 38, 2643-2650.

[22] GUCLU G, GURDA G, OZGUMUS S, 2003, Competitive removal of heavy metal ions by cellulose graft copolymers. Journal Applied Polymer Science, 90, 2034-2039.

[23] BEKAR UG, GUNER FS, DIZMAN M, ERCIYES, 1999, Heavy metal removal by ion exchanger based on hydroxyethyl cellulose. Journal of Applied Polymer science, 4**,** 3501-3506.

[24] CHAUHAN K, CHAUHAN GS, AHN JH, 2009, Studied the synthesis and characterization of novel guar gum hydrogeals and their use as Cu (II) sorbent. Biosourption Technology, 100, 3599-3603.

[25] ZHANG C, LI X, PANG J, 2001, Synthesis and adsorption properties of magnetic resin micro beads with amine and mercaptan as chelating groups. Journal Applied Polymer Science, 82, 1587-1592.

[26] GUPTA SC, DASS P, SHARMA P, SING AV, 2002, Removal of 58Co, 134Cs, and 95Zr radioisotopes from aqueous solutions using cellulose iminodiacetic acid chelating cum cation-exchanger. Desalination, 143, 141-145.

[27] SUNGUR S, BABAO S, 2005, Synthesis of a new cellulose ion exchanger and use for the separation of heavy metal in aqueous solution. Separation Science andTechnology, 40, 2067-2078.

[28] WHISTLER RL, 2005, Industrial gumes from plants: guar and chia. Economic Botany, 36, 746-751.

[29] CHOUDHARY P, SAMUL S, KUNDU T, NANDI MM, 2001, Graft polymerization of methyl methacrylate onto guar gum with ceric ammonium sulfate/ dextrose redox pair. Journal Applied Polymer Science, 82, 3520-3525.

[30] GUPTA SC, TAK BB, MATHUR NK, NARANG CK, 1993, Removal of ^{185}W, ^{99}Mo and ^{125}Sb radioisotopes from aqueous solutions using polyamine incorporated polysaccharides. Journal of Radioanalysis and Nuclear Chemistry, 70**,** 3-8.

[31] HEGAZY EH, KAMAL H, KHALIFA NA, MAHMOUD GA, 2001, Separation and extraction of some some heavy and toxic metal ions from their waste by grafted membranes.Journal Applied Polymer Science, 81, 849-860.

[32] CHAUHAN K, CHAUHAN GS, AHN JH, 2009, Studied the synthesis and characterization of novel guar gum hydrogeals and their use as Cu (II) sorbent. Biosourption Technology, 100, 3599-3603.

[33] AHUJA M, RAI AK, 1997, Adsorption studies with some chelating ion exchange resins derived from guaran. Carbohydrat Polymer, 33, 57-62.

[34] SINGH V, TIWARI A, SHUKLA P, SINGH SP, SANGHI R, 2006, Grafting of methylmethacrylat on to the plant seed galactomannans using potassium persulphate/ ascorbic acid redox pair. Reactive Functional Polymers, 66, 1303–1308.

[35] REINECKE F, GROTH T, HEISE KP, JEONTGEN W, MULLER N, STEINBUCHE A, 2000, Isolation and characterization of an Achromobacter xylosoxidans strain B3 and other bacteria capable to degrade the synthetic chelating agent iminodisuccinate. FEMS Microbiology Letters, 188, 41–46.

[36] SIDDIQUI WA, KHAN SA, 2007, Synthesis, characterization and ion exchange properties of zirconium (IV) tungstoiodophosphate, a new cation exchanger. Bulletin of Material Science, 30, 43-49.

[37] SINGH AV, GUPTA S, GUPTA SC, 1996, Synthesis of a guaran-sulphonic acid cation-exchanger and its application in metal ion removal from underground mine water of the Rajpura Dariba Mines. Udaipur, India. Desalination, 104, 235-238.

[38] CHAUHAN GS, MAHAJAN S, GULERIA, 2000, LK. Polymers from renewable resources: sorption of Cu^{2+} ions by cellulose graft copolymers. Desalination, 130, 85-88.

[39] RAO CNR, 1963, Chemical applications of infrared spectroscopy. Acadmic Press, New York.

[40] SANKAR TR, KESAVULU K, RAMANA PV, 2007, Synthesis, characterization and thermal studies of polymer–metal complexes derived from poly(2-methacryloxy-5-methyl benzophenone)-divinylbenzene isonicotinoyl hydrazone resins. Journal of Material Science, 42, 8571–8580

[41] DEMIRBAS A, PEHLIVAN E, GODE F, ALTUN T, ARSLAN G, 2004, Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. Journal Colloid and Interface Science, 282, 20-25.

[42] GAWALE R, MARATHE KV, 2007, Removal of metal ions from micellar solution. Indian Journal of Chemical Technology, 14, 362-370.

[43] ATAMANENKO D, VERBICH SV, KRYVORUCHKO Dr. Aditya Prakash, 2001, Sorption of nickel ions from aqueous solutions by ion exchangers. Colloid Journal, 63, 532–539

[44] DEV K, ROA GN, 1996, Synthesis and analytical properties of a chelating resin functionalized with bis-(*N, N'*-salicylidene) 1, 3-propanediamine ligands**.** Talanta, 43, 451-457.

[45] RADOVIC LR, SILVA IF, UME JI, MENENDEZ JA, LEON CA, LEON Y, SCARONI AW, 1997, An experimental and theoretical study of the adsorption of aromatics possessing electron withdrawing and electron-donating functional groups by chemically modified activated carbons. Carbon, 35, 1339–1348.

[46] FARIA PCC, ORFAO JJM, PEREIRA MFR, 2004, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Research, 38, 2043-2052.

[47] JEON C, PARK KH, 2003, Adsorption and desorption characteristics of mercury (II) ion using aminated chitosan bead. Water Research, 39, 3938-3944.

[48] KHALIL MI, FARAG S, 1998, Utilization of some starch derivatives in heavy metal ions removal. Journal of Applied Polymer Science.69, 45-50.