A new Guar gum-based resin containing 4,5–Dihydroxy-1,3-Benzene disulphonic acid group and its use in the separation of Ni(II) and Cd(II) as toxic metal ions from aqueous solution

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Abstract
The Porath's method was used for preparation of Guar gum 4,5-dihydroxy-1,3-Benzene disulphonic acid (GDHBDSA) resin. The parent polymer guar gum was extracted from the seeds of Leguminosae plant Cyamopsis tetragonolobus which is a galactomannan. The GDHBDSA resin was characterized by FT-IR spectra, elemental analysis, pH titration, density, moisture contents, ion exchange capacity and Scanning electron microscopy.

The distribution coefficients (Kd) values of various toxic metal ions i.e. Ni(II) and Cd(II) were estimated by Atomic absorption spectrophotometer. The batch method was used for separation of toxic metal ions from aqueous solution.

Keywords: Nickel, Cadmium, Guar gum, 4-5 dihydroxy 1,3, benzene disulphonic acid group.

Introduction

The characteristics of newly produced guar gum and cellulose resins were researched and analysed. Various analyses and determinations were used to investigate the characteristics of these resins. Fei et al[5] studied on antibacterial action of chitosan and carboxymethylated chitosan. Diverse methods, such as IR spectra, pH titration and sulphur and nitrogen content measurement, were used to validate the synthesis of various derivatives.

Singh and Sharma[13] studied on characterisation and applications of synthesized cation exchanger guar gum sulphonic acid (GSA) resin for removal and recovery of toxic metal ions from industrial wastewater.

Saha et al[10] worked on sorption of trace heavy metals by thiol containing chelating resins, solvent extraction and ion exchange. Wang et al[15] reported on synthesis of chelating resins with iminodiacetic acid and its wastewater treatment application. Toxic metal ions have been removed from effluents containing high concentrations of alkali and alkaline earth metal ions using ion selective exchanger and inorganic as well as organic specific precipitants. Singh and Saraf[11] observed the way to synthesis, characterization and ion-exchanging properties of a novel ion-exchange resin. Das et al[2] reported on new resin containing benzimidazolylazo group and its use in the separation of heavy metals.

Urszula et al[14] studied on use of the advanced oxidation process in the ozone and hydrogen peroxide system for the removal of cyanide from water. Metal and mineral processing industries are producing the majority of wastewater. The wastewater can be recycled if it has undergone appropriate treatment. These findings point to the need for more advanced methods to scavenge toxic metal ions to lower concentration. El-Diwani et al[4] reported on protection of biodiesel and oil from degradation by natural antioxidants of Egyptian Jatropha. Carlos et al[1] worked on removal of bio refractory compounds in industrial wastewater by chemical and electrochemical Pretreatments.

Singh and Kumawat[12] worked on synthesis and characterization of a new guar gum 4-hydroxybenzoic acid resin and its use for the separation of heavy metal ions in industrial effluents whereas Rathore and Singh[8] also worked on development and application of newly synthesized Guar gum Diamino Benzoic Acid (GDABA) resin for elimination of hazardous waste metal ions from industrial effluents. Heavy metal ion-containing effluent samples were taken from the industry in Jodhpur. Jiao et al[6] reported on chemical structures and bioactivities of sulfated polysaccharides from marine algae, de Jesus et al[3] reported on marine polysaccharides from algae with potential biomedical applications. Lata et al[7] reported on synthesis of polyacrylamide chelating resin and its applications in metal ion extractions.

Recently, Rathore and Singh[9] reported on synthesis and characterization of a new ion exchange cellulose -1- butane sulphonic acid (CBSA) resin and its application for removal of hazardous metal ion (Pb^{2+}) from industrial waste water by batch method. Many transition and post-transition metals were separated using cationic and anionic exchange resins.

Material and Methods

Synthesis of GDHBDSA Resin: A weight of 15.70 gm of 4,5 – dihydroxy-1,3 benzene di sulphonic acid disodium salt (monohydrate) (0.05 mole) was taken in a round bottom flask and minimum amount of water was added to dissolve it completely. To this 4.65 ml of epichlorohydrin (0.05 mole) was added and allowed to mix perfectly by continuous stirring on a magnetic stirrer for approximately 6 hours.

Table 1
Chemical Specifications used in Synthesis of Resins

S.N.	Chemicals	Specification
1	Guar gum	Ases Chemical Works, Jodhpur, INDIA
2	Dioxane (AR)	S.D Fine Chem Pvt. Ltd., Boisar, INDIA
3	Sodium Hydroxide (AR)	Sarabhai M. Chemicals, Baroda, INDIA
4	Epichlorohydrin (AR)	Loba Chemic Pvt. Ltd., Mumbai, INDIA
5	4,5-Dihydroxy 1,3-benzene	Loba Chemic Pvt. Ltd., Mumbai, INDIA
6	1- Butane sulphonic Acid (Sodium salt)	Sarabhai M. Chemicals, Baroda, INDIA
7	Diamino benzoic Acid	Sarabhai M. Chemicals, Baroda, INDIA

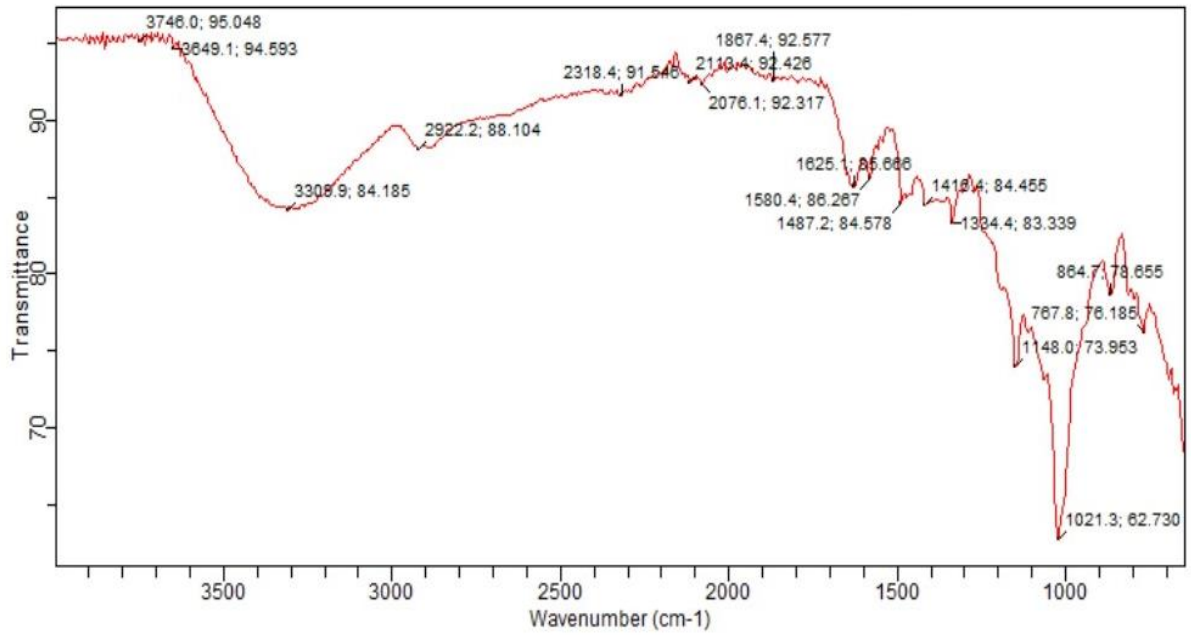

Fig. 1: FTIR spectrum of GDHBDSA resin

Further 4 gm (0.1mole) of NaOH in minimum amount of water was added to convert it into epoxide. In another round bottom flask, 81 gm of guar gum (0.5 mole) was taken and slurried in 60 ml of dioxane.

The mixture was allowed to mix with constant stirring followed by the addition of 5ml of 20 % aq. solution of NaOH on a magnetic stirrer for another 6 hours at a temperature 60˚ C. After keeping it undisturbed overnight, this functionalized form guar gum was allowed to react with the prepared epoxy propyl ether of 4,5 – dihydroxy-1,3 benzene di sulphonic acid disodium salt (monohydrate) with continuous stirring for 6 hours and kept undisturbed for a night. This guar gum incorporated 4,5 – dihydroxy-1,3 benzene di sulphonic acid disodium salt (monohydrate) resin was finally washed with HCl-methanol to eliminate impurities and to neutralized excess of NaOH and then it was dried. The yield of GDHBDSA (Guar gum 4,5-dihydroxy-1,3-Benzenedisulphonic Acid) resin was 103.8 gram. The chemical used are specified in table 1.

FTIR characterisation of GDHBDSA resin: The FTIR spectra of GDHBDSA resin shows a peak at 2922.2 cm^{-1} attributed to C-O stretching vibrations at 1148 cm^{-1} and another variable peak at 1580.4 cm^{-1} for C=0 stretching (Fig. 1). A strong peak in the resin 1250 - 1000 cm^{-1} (1021.3 cm^{-1}) denotes C-O-C stretching vibrations. The GDHBDSA resin shows symmetric O-H stretching in the resin at 3308.9 cm^{-1}. The spectra of polysaccharides are generally observed in the region 4000 to 3500 cm^{-1} which denotes -OH stretching frequencies. The IR spectral study of GDHBDSA resin is shown in fig. 1.

Estimation of S content: Sulphur in the form of barium sulphate was estimated using Messenger's approach. 0.2g of resin was placed in a 250 ml beaker. This was mixed with 1 g of potassium hydroxide, a pinch of potassium permanganate and 25 ml of distilled water. The reaction mixture was heated for 4-5 hours, then cooled and 25 ml of concentrated hydrochloric acid was added to the chilled liquid. This mixture was cooked until it turned colourless. It was then filtered and 1 ml of concentrated HCl was added to the filtrate. After that, a 2 percent $BaCl_2$ solution was added to the filtrate until all of the $BaSO_4$ had precipitated. The $BaSO_4$ was then filtered, washed and dried in the oven. A weigh balance was used to determine the weight of $BaSO_4$. All details are shown in table 2.

Table 2
Calculation for Sulphur content in GDHBDSA resin

1. Weight of resin taken	= 0.200 g
2. Weight of $BaSO_4$ formed	= 0.0324 g
3. 233 g of $BaSO_4$ contains	= 32 g of S
4. 0.1922 g of $BaSO_4$	$= \frac{32}{233}$ x 0.0324 = 0.0044 g of S
5. 0.2 g of resin contains	= 0.0044g of S
6. 1 g of resin contains	$= \frac{0.0044}{0.2}$g of S
7. 100 g of resin contains	$= \frac{0.0044}{0.2}$ x 100= 2.22% of S

GDHBDSA resin contains 2.22 % of sulphur as estimated by messenger's method.

pH titration of polysaccharide derivatives (Batch method): The influence of an ionic polymer's structure on its chemical behaviour could be investigated using an equilibrium pH titration curve (Table 3, fig. 2). A series of samples with varied amounts of resin, NaCl and NaOH were used in this approach. First, the derivatives were changed to their hydrogen ion form to remove the excess acid from the resin which was then washed in water and dried overnight at 50 ^{0}C. 8-9 different flasks were collected and each flask received 0.1 of resin. 1 N NaCl was added to each flask in decreasing amounts and 1N NaOH was added in increasing amounts to each flask.

To keep the proportion of solution volume to resin weight consistent (25 ml per 0.1 g of resin), deionised water was added to the contents of each flask. To achieve a consistent final pH of solution, these flasks were firmly closed and equilibrated on a magnetic stirrer. The pH values obtained were recorded in a table, while pH titration curves for each resin were displayed.

Table 3
pH titration of GDHBDSA resin

Flask No.	Volume of 0.1 N NaOH (ml)	Volume of IN NaCI (ml)	Volume of deionized water (ml)	Final pH
1	0.0	1.4	23.6	3.3
2	0.3	1.2	23.5	5.0
3	0.6	1.0	23.4	6.3
4	0.9	0.8	23.3	6.8
5	1.2	0.6	23.3	7.6
6	1.5	0.4	23.1	8.1
7	1.8	0.2	23.0	8.4
8	2.1	0.0	22.9	8.8

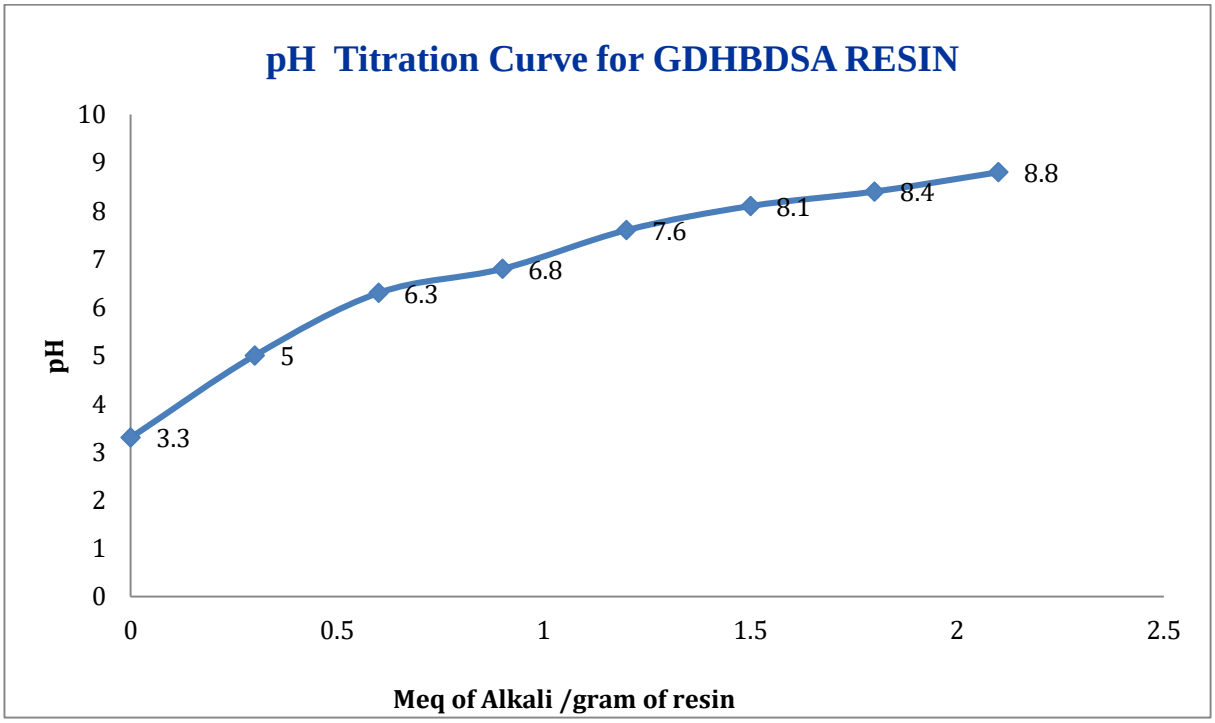

Fig. 2: pH titration curve for GDHBDSA Resin

Ion exchange capacity: The capability of a resin to exchange chemical equivalents (ions) per unit resin volume or weight, which can participate in the ion exchange process, is characterised as its ion exchange capacity. This capability manifests itself in two ways. When the resin is dry, it is measured in milli equivalents per gramme and when it is wet, it is measured in milliequivalents per millilitre. As the degree of cross linking in resin grows, so does the difficulty of introducing additional functional groups. The sulphonation process, which occurs after the crosslinking process, can introduce sulphonic acid groups to the resin's surface or inside the resin.

Similarly, the quaternary ammonium group is inserted after the polymerisation is complete and it can be placed both on the surface and inside the resin. When a resin is strongly crosslinked, few functional groups being integrated into the resin, result in a modest reduction in ion exchange capacity on a dry resin. In contrast to dry resin, the degree of exchange capacity on wet resin rises as cross linking increases. Though some functional groups can be integrated in a more crosslinked resin, they will be positioned closer together in wet resin since cross linking reduces the quantity of water. In the method of water softening, the ion exchange technology has been widely used.

As a result, capacities are typically given in kilogrammes of calcium carbonate per cubic foot of ion exchange resin. By multiplying this figure by 0.0458, it may be converted to equivalent per litre. The quantity of base or acid being used renew the resin has a significant impact on its capacity.

Determination of moisture content: 5 g of properly washed and dried resin in its chloride form was allowed to completely dry in oven at 80 ^{0}C for a day. After complete drying, the weight of dry resin was taken. The moisture content of resin was 6 %.

Method for the determination of total ion exchange capacity: Guar gum's 4,5-dihydroxy-1,3-benzene disulphonic acid derivative is a powerful acid cation exchanger. To begin, 10g of resin was extracted and processed with 10 N HCl to change it to chloride form in order to estimate the capacity. After that, it was rinsed with a lot of ethanol to make it methyl orange-neutral. It was dried in the air once it reached perfect neutrality. Next, 5 g of dry resin was leached in a column with 250 ml of 1 percent (wt/vol) aqueous ammonia supplied dropwise through a funnel. The filtrate was collected in a flask that had been totally dried. The resin was washed with distilled water and put to the same dry flask, which was then neutralised with weak nitric acid. 25 ml amount of effluent was mixed with 0.11N silver nitrate solution and a 10% aqueous potassium chromate solution was utilised as an indicator.

The scientific weight capacity (Q weight)

$$= \frac{\text{Effluent volume X milliequivalents of titrant used}}{\text{Volume of aliquot X Weight of dried resin}}$$

$$= \frac{250 \times 7.2 \times 0.11}{25 \times 4.7}$$

= 1.68 Meq per g of the resin

Determination of bulk density of the dry resin: 10 g of resin was cured to achieve a consistent weight before being placed in a 100 cm^3 graduated cylinder. This cylinder was carefully emptied onto a stiff rubber filter until the resin volume remained unchanged. The findings of reading the unsettled apparent volume are summarized in the table 5.

Scanning electron microscopy: The Scanning electron microscopy (SEM) images were taken to investigate the morphological properties of all the samples. Scanning electron microscope uses electrons to form the image by applying kinetic energy to the electron to produce signals on the interaction of electrons.

Table 4
Determination of moisture content

S.N.	Description	Scale
1	The weight of dry resin	4.7 g
2	Therefore moisture	0.3 g
3	Moisture content	0.3/5 g of the resin or 6%
4	Total effluent volume	250 ml
5	Volume of aliquot	25 ml
6	Strength of $AgNO_3$ Solution	0.11 N
7	Volume of titrant used	7.2 ml

Table 5
Resin

S.N.	Resin	Bulk density (g/cm^3)
1.	Cellulose 1- butane sulphonic acid resin	0.92
2.	Guar gum Diamino benzoic acid resin	0.97
3.	Guar gum 4,5-dihydroxy -1,3- benzene disulphonic acid (GDHBDSA) resin	1.03

As a result, it was concluded that the increase in processing temperature and size reduction process caused a decrease in resistance of hydrocolloid solutions subjected to the deformation, which is a very important factor affecting the physical and chemical properties of different resins (i.e. GDHBDSA). The study reports SEM datasets of native and quaternized guar gum as a tool for their characterization.

The $^1H_1$ spectroscopy was acquired to understand structural changes by quaternization. This conductive sample was put onto the SEM sample area for obtaining its images at different levels of magnification. SEM analysis of native and quaternized sample was recorded using SEM-ZEISS EVO-50 EP instrument with specific magnification i.e. 435X magnification and 100 µm resolution, 1.45KX magnification and 20 µm resolution, 73X magnification and 300 µm resolution for fig. 3 and 73X magnification and 300 µm resolution for GDHBDSA resin. The powdered native and quaternized samples were coated and images were acquired in the magnification range of 1–5K. The images of different resins are shown in the fig. 3.

Calculation of distribution coefficient by batch method: Different amounts of 0.2M acetic acid and 0.2M sodium acetate were taken in a glass stopper conical flask to obtain solutions of desired pH i.e., 2-7. Similarly, to obtain the pH of 8, suitable amount of 0.2M NH_4OH and 0.2M NH_4Cl were mixed. In each flask containing different pH solutions, 0.080gm of dry resin (GDHBDSA) and 1ml of 1000 ppm metal solution were added. These contents were allowed to mix completely on a magnetic stirrer and then filtered. The resulting filtrates were examined for analysis. The results obtained were summarised in tables 6 and 7.

The molar distribution coefficient 'Kd' values of metal ions were calculated by using batch method with the help of atomic absorption spectrophotometer. Air acetylene flame and different wavelengths of main resonance line were used for the estimation of various metals. The following formula was used to calculate Kd values:

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

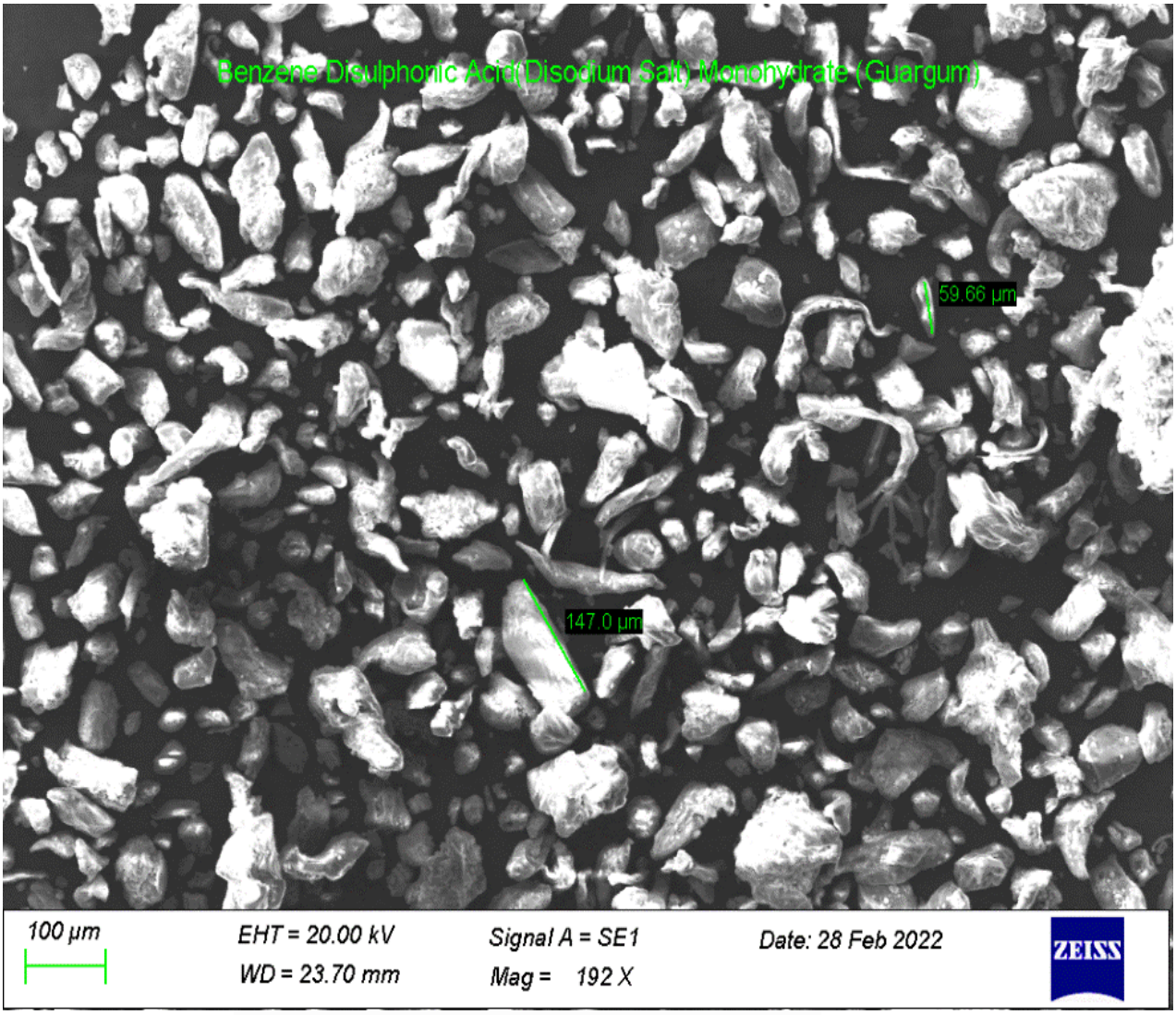

Fig. 3: The Scanning Electron Microscopy (SEM) image for GDHBDSA) resin.

Table 6
Distribution coefficient 'Kd' for on GDHBDSA resin

pH	Absorbance	Concentration of Ni (II) in filtrate (ppm)	Amount of Ni(II) in solution (mg)	Amount of Ni(II) in resin (mg)	'K_d'	% Adsorption of Ni (II) by resin	Metal exchange capacity mg/g
2	0.235	10.3	0.4239	0.5761	699.15	57.61	7.201
3	0.217	9.5	0.3926	0.6074	799.21	60.74	7.592
4	0.197	8.6	0.3553	0.6447	937.06	64.47	8.058
5	0.096	4.2	0.1742	0.8258	2457.73	82.58	10.322
6	**0.059**	**2.6**	**0.1075**	**0.8925**	**4290.86**	**89.25**	**11.156**
7	0.165	7.2	0.2966	0.7034	1221.18	70.34	8.792
8	0.190	8.3	0.3397	0.6603	994.42	66.03	8.253

Inference: It can be inferred that the value of distribution coefficient for Ni(II) on GDHBDSA resin was maximum at pH 6. Ni (II) can be eluted by HCl having pH 2.0 from the resin. The maximum Kd value of Ni (II) metal ion has been obtained at pH 6 which is 4290.86.

Table 7
Chelation of cadmium, Cd(II) on GDHBDSA resin

pH	Absorbance	Conc. of Cd (II) in filtrate (ppm)	Amount of Cd(II) in solution (mg)	Amount of Cd(II) in resin (mg)	'K_d'	% Adsorption of Cd (II) by resin	Metal exchange capacity mg/g
2	0.823	10.5	0.4321	0.5679	676.07	56.79	7.098
3	0.713	9.1	0.3726	0.6274	861.81	62.74	7.842
4	0.474	6.05	0.2482	0.7518	1553.30	75.18	9.397
5	**0.180**	**2.3**	**0.0953**	**0.9047**	**4916.84**	**90.47**	**11.308**
6	0.274	3.5	0.1467	0.8533	3047.50	85.33	10.666
7	0.384	4.9	0.2024	0.7976	2034.69	79.76	9.969
8	0.447	5.7	0.2335	0.7665	1680.92	76.65	9.581

Inference: It can be inferred that the value of distribution coefficient for Cd(II) on GDHBDSA resin was maximum at pH 5. Cd (II) can be eluted by HCl having pH 2.0 from the resin. It is clear from table 7 that max Kd value of Cd ion obtained at pH 5 is 4916.84.

Table 8
Characteristics of effluents contaminated with heavy metal ions

S.N.	Characteristics	Effluent of steel Industry
1	Colour	Brownish
2	pH	4.8
3	Total hardness (ppm)	940
4	Iron	52
5	Copper	1.02
6	Lead	.042
7	Cadmium	0.14
8	Chromium	--
9	Zinc	0.32

Note: The name of industry is not given due to legal aspects.

The characteristics of effluents of steel industry have been reported in table 8. The separation of harmful metal ions is possible from effluents of steel industry for the environment protection. The separation of toxic metal ions from aqueous solution is reported in respective tables. The heavy metal ions from effluent of steel industry show high affinity at pH 8.0 with GDHBDSA resin. At pH 7.0, GDHBDSA resin decreased the concentration of heavy metal ions in effluents. The metal ions were then quantitatively eluted with various strengths of acid solutions. Ni (II) was eluted using 0.05N HCI, with 0.5N HCI and 1.0N HCI respectively. After that, the resin column was carefully rinsed with de-mineralized water. It can be repeated up to 5 times with a 95 % recovery

rate. Because the resin is made of biopolymer, it may be disposed off either by burning.

Conclusion

Among all natural polymers, cellulose, guar gum and tamarind are of particular interest because of their widespread availability and extensive range of applications in both natural and modified forms. For separation and concentration of metal ions in solution, recovering of metal ions from industrial waste water and hydrometallurgical processes, polysaccharide based chelating resins are more efficient and compatible. We synthesized GDHBDSA from guar gum and cellulose derivatives using epichlorohydrin as a cross-linking agent, with potential uses in mineral processing, metal separation, concentration and waste water treatment.

The IR spectra, pH titrations, nitrogen content and sulphur content of the newly synthesized chelating resins were all used to describe them. These novel chelating resins' characteristics such as moisture content, bulk density and scientific weight capacity, have been determined. With the newly synthesized chelate resin GDHBDSA, ion exchange is a good instrument for separating mixtures of diverse counter ions for separation studies of different metal ions. Polysaccharide-based resins are presented in this study. These resins can be used as commercial scale for removal of toxic metal ions from effluents of metal industries.

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