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***Research Article***

# STUDIES OF NEWLY SYNTHESIZED GT–AAH RESIN DERIVED FROM GUAR

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## ABSTRACT

A hydrophilic polysaccharide matrix of guaran has been used for the preparation of some new chelating resins. The objective of this study is to evaluate the removal of toxic and valuable metals using GT–AAH resin via selective ion exchange process. This resin was prepared from cross linked guar containing aspartic acid. The structure of the newly synthesized resin was confirmed by IR–spectra, NMR and elemental analysis. This newly synthesized resin is very efficient for separation of iron and nickel mixture, using column chromatography. The physico–chemical characteristics of this resin like bulk density, moisture content, specific bulk volume and ion–exchange capacity etc. were also determined. The amount of metal ion retained by this resin at equilibrium is determined in terms of distribution coefficient values. The metal exchange capacity of the resin at different pH values was also evaluated. The separation of mixture of Nickel and Iron ions by GT–AAH resin on the basis of their distribution coefficient at various pH was also achieved using column chromatography. This also confirms the usefulness and effectiveness of this resin for the removal of metal ions.

***Key Word:*** *Guar, Triazine, Aspartic Acid, Fe(II), Ni (II) ion separation*

## INTRODUCTION

Guar gum or guaran, derived from the seeds of the Guaran plant (Cyamposis tetragondalobas) is a naturally occurring hydrophilic polysaccharide consisting of linear chain of β–(1, 4)–D–mannosepyranose units with α–D–galactopyranosyl units attached by a (1, 6) linkage. (fig–1). This guargum is used as a stiffener in soft ice creams, a stablizer for cheese, instant pudding and whipped cream substituents. It has been utilized as matrix in ion exchanger which are extensively used in hydrometallurgy, pharmaceutics, food industry, antibiotic, purification, wastes treatment and trace metal separation. This areas receives more attention since many metals are recovered from secondary sources like drainage and sewage water. Resins are particularly useful in metal recovery. When the concentration of targeted ion in the solution is low, the treatment of large volume of solution is low, the treatment of large volume of solution is inevitable. Heavy metal ions were simultaneously determined at μg/L levels by Carddicchio et al(1999) Santoyo et al(2000) determined lead, chromium, copper, cobalt, zince and nickel ion in 22 minutes in ground water using three ionic separation colum system including HPIC–CS2 of Dionex as an anionic column and lonpac CS5 of Dionex as a
bifunctional ion–exchange column. It finds extensive applications in paper industries, waste water treatment and mineral processing industries as a flocculant and a depressant (Mazor, 1956 Bhatnagar and Mathur 1977; Meneria et al. 1986, 1989; Mathur et al, 1988 Mackenzie 1980). The most commonly used chelating resins like chelax–100 (Termillion, 1968 Lee,C.,Kim,N.B.,Lee,I.C.&Chung,k.s
1977; Reley and Taylor, 1968). Dowex -1 (Leyden and underwood, 1964) and other (Moyer and fritz, 1977); Orf and based on DVBS (a petro–chemical product) which is costly and scarce, therefore, in the continuation of our work on chelating resins. (Loonker, S(2007); VijayVargiya S(2007); Sethia, J. K(2009.) also studies adsorption of Newly synthesised resin and separated toxic metal ions. We have put in to an attempt to separate the mixture of Fe and Ni on GT–AAH resin, synthesized in our laboratory. We have used the Guar based resin because of its abundance in the region, Low cost, hydrophilic nature and flocculant action. The resin can also be used to separate other metal ions on the basis of their distribution coefficient values. This paper focuses on the separation of Fe and Ni only.

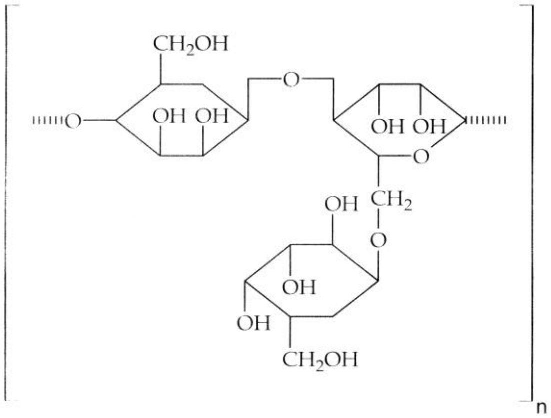


**Figure 1: Structure of Guaran**

## 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.merck and Sarabhai M chemicals respectively.

### *Physical Measurement*

Metals analysis was accomplished on a Perkin–Elmer–380 absorption spectrophotometer. IR spectra of the newly synthesized resin were recorded on a spectrum RXI instrument using KBr pellets. NMR specrtra of the newly synthesized resin was recorded on a spectrum JEOL instrument.

*Synthesis of Resin:* Synthesis of aspartic acid of guar (GT–AAH). Guar was first cross–linked with triazine to form guar which was then reacted with aspartic acid.

*Preparation of Guar Triazine:* In 500ml round bottom flask, 4.90g of guar was taken and stirred in minimum quantity of dioxane maintained at temp. of about $5^0$C by external cooling and stirring was continued. Then 3.90g of cyanuric chloride was added to this reaction mixture and pH was maintained at 7–8 by adding $NaHCO_3$. The whole mixture was spontaneously stirred for half an hour.

*Preparation of guar triazine asparitc hydroximate resin:* 14g of triazine was added with 3g of aspartic acid in maximum quantity of dioxane for three hours with constant stirring on magnetic stirrer. Aspartic acid derivative of guar triazine so formed was taken in round bottom flask. Excess methanol was added and contents were then cooled at $5^0$C to $10^0$C. 3ml of thionyl chloride was then added and the temperature was raised to $40^0$C on a rotavapoure for two hours. Now methanolic solution of 3g hydroxyl amine hydrochloride was added to get the hydroxamate of the ester with pH maintained at 9 to 9.5 by $NaHCO_3$ solution. The derivated guar thus produced was filtered off and washed with double distilled water and finally dried.

### *Characterization of newly synthesized chelating resin*

Characterization of newly synthesized resin was carried out by nitrogen estimation using kjeldahl method. The ion exchange capacity of resin was determined by back titration methods. Bulk density, moisture content and bulk volume were also determined using standard method and data are summarized in table-1. The pH titration were carried out for determination of ion- exchange capacity which are summarized in table-2, in $H^+$ form of dry resin as shown in figure 3.

*Determination of distribution coefficients:* Batch equilibrium technique was applied for measuring the metal uptake by the resin. A set of 8 glass stoppered flasks were taken into each of which 0.082g dried resin and 40ml buffer (prepared by mixing different volume of 0.2M acetic acid and 0.2M sodium acetate) were added adjusting the pH values at 3.5, 4.0, 4.5, 5.0, 5.6, 6.0, 6.5 and 7.0 respectively. A metal ion solution of 1ml of 1000ppm was added to each flask and the contents were agitated for an hour. The two phases so obtained at equilibrium were separated using batch method and the metal content was determined in the aliquot of the filtrate by atomic absorption spectroscopy.

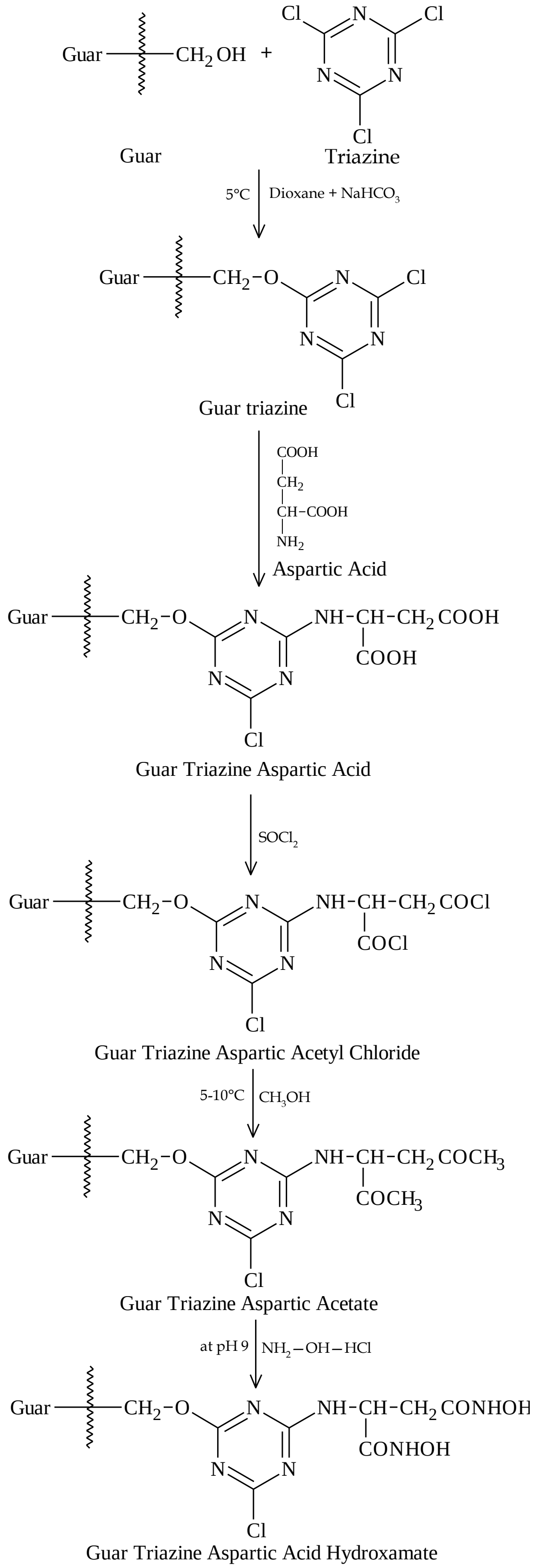


**Figure 2: Guar Triazine Aspartic Acid Hydroxamate**

$$\text{Dg} = \frac{\text{Amount of metal ion resin phase/g dry resin}}{\text{amount of metal ion in 1 ml of aliquote}}$$

**Procedure for column separation of Ni(ii) ions and Fe(ii).**

A long glass column of 20 cm in height and of uniform diameter was used for the separation of metal ions. GT–AAH resin was slurried with dioxan and poured into the column upto the height of 8–10 cm. The resin was washed with the buffer of 6.0 pH at which the absorption of mixture was to be carried out. Two aliquots of 20 ml each containing 100 ppm of Ni (II) and Fe (II) metals ions were passed through the column at a flow rate of 1–2 ml/min. The loaded metal was eluted using 0.1N HCI.

The concentration of Iron and Nickel in elutes was determined using atomic absorption spectrophotometer.

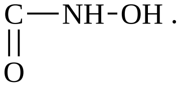
## RESULTS AND DISCUSSION

The FT–IR spectrum of GT–AAH gave a distinct stretening vibration at 3449 $\text{cm}^{-1}$ shows N–H stretching vibration in NH-OH group. Two new vibrations at 1627 $\text{cm}^{-1}$ and 2367 $\text{cm}^{-1}$ in GT–AAH IR–Spectra indicated the presence of carbonyl group and primary amino group.

A new stretching vibration 644.78$\text{cm}^{-1}$ in GT–AAH FT-IR. Spectra showed the presence of C–Cl group.

The $\text{N}^1$NMR spectrum of GT–AAH gave singlet in the downfield region of 10.35 ppm(δ) is attributed to proton of alcoholic group involved in hydroxamate of the resion.

The downfield doublet signal arises in the range of 1.5–3.2 ppm (δ) may be due to amine proton of



$\underset{\underset{O}{||}}{C}\text{—NH-OH}$ .

The downfield signal obtained at 2.03 ppm (δ) may be due to the $CH_2$ - OR

The characteristics of resin viz. moisture content, bulk density, nitrogen content, ion exchange capacity are given in Table (1).

**Table 1: Resin Characterization**

| S. No. | Sample | GT–AAH |
|---|---|---|
| 1. | Moisture Content % | 1.20 |
| 2. | Bulk Density g/$\text{cm}^3$ | 0.45 |
| 3. | Specific bulk Volume | 2.70 |
| 4. | Nitrogen content | 1.50 |
| 5. | Ion exchange capacity | 2.46 |

**Table 2: pH Titration**

| S. No. | Meq of alkali per gram of resin | pH |
|---|---|---|
| 1. | 0.0 | 4.27 |
| 2. | 0.3 | 9.89 |
| 3. | 0.6 | 10.20 |
| 4. | 0.9 | 10.51 |
| 5. | 1.2 | 10.92 |
| 6. | 1.5 | 11.11 |
| 7. | 1.8 | 11.17 |
| 8. | 2.1 | 11.26 |

**Table 3: Distribution coefficient**

| S. No. | pH | Distribution coefficient (Dg)mL/g | |
|---|---|---|---|
| | | Ni | Fe |
| 1. | 3.5 | 310 | 629 |
| 2. | 4.0 | 313 | 663 |
| 3. | 4.5 | 327 | 810 |
| 4. | 5.0 | 347 | 856 |
| 5. | 5.5 | 368 | 856 |
| 6. | 6.0 | 406 | 1008 |
| 7. | 6.5 | 512 | 855 |
| 8. | 7.0 | 388 | 817 |

**Table 4: Separation of Ni(II) ions and Fe(II).**

| Sample | Amount of Ni (II) and Fe (II) in the mixture | | Amount of Ni (II) and Fe (II) in elute (mg) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ni(II) | Fe(II) | Ni(II) | SD | RSD | Fe(II) | SD | RSD% |
| 1 | 5.0 | 4.3 | 4.98 | 0.02 | 0.4 | 4.25 | 0.04 | 0.93 |
| 2 | 6.0 | 5.5 | 5.97 | 0.03 | 0.5 | 5.44 | 0.006 | 1.09 |

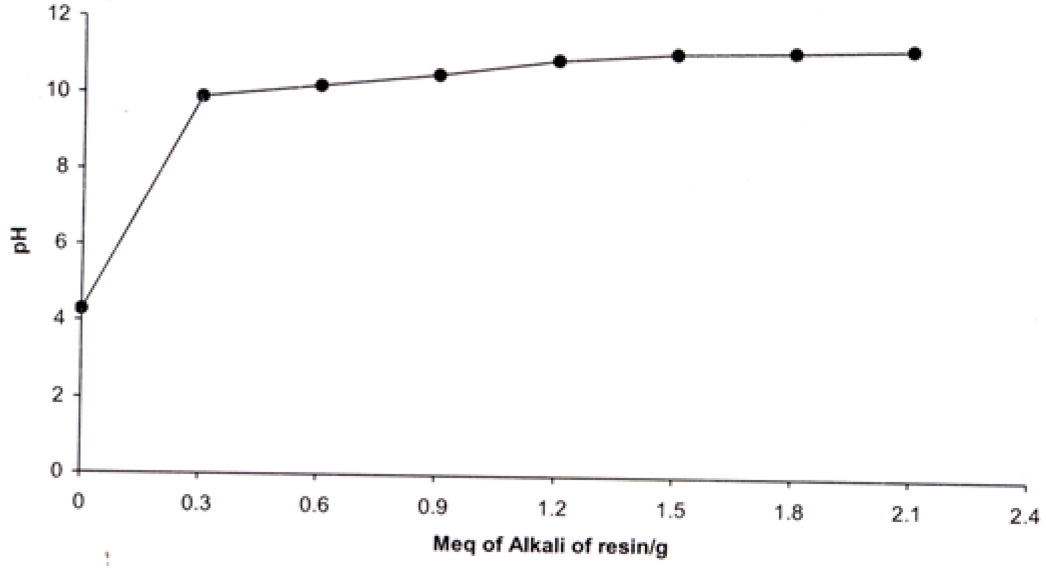


**Figure 3: pH Titration Curve**

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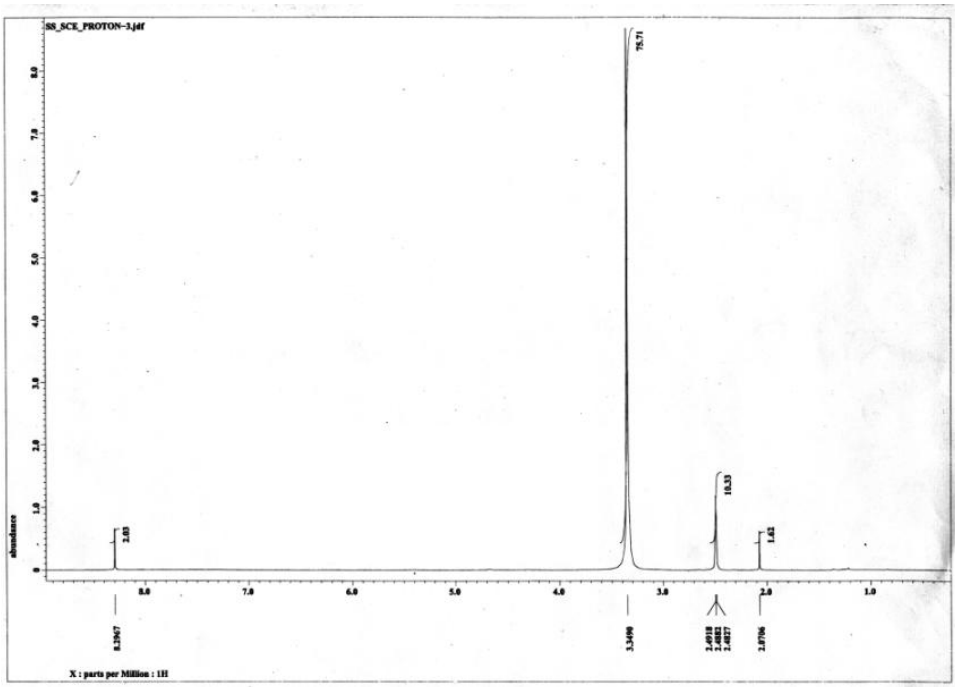
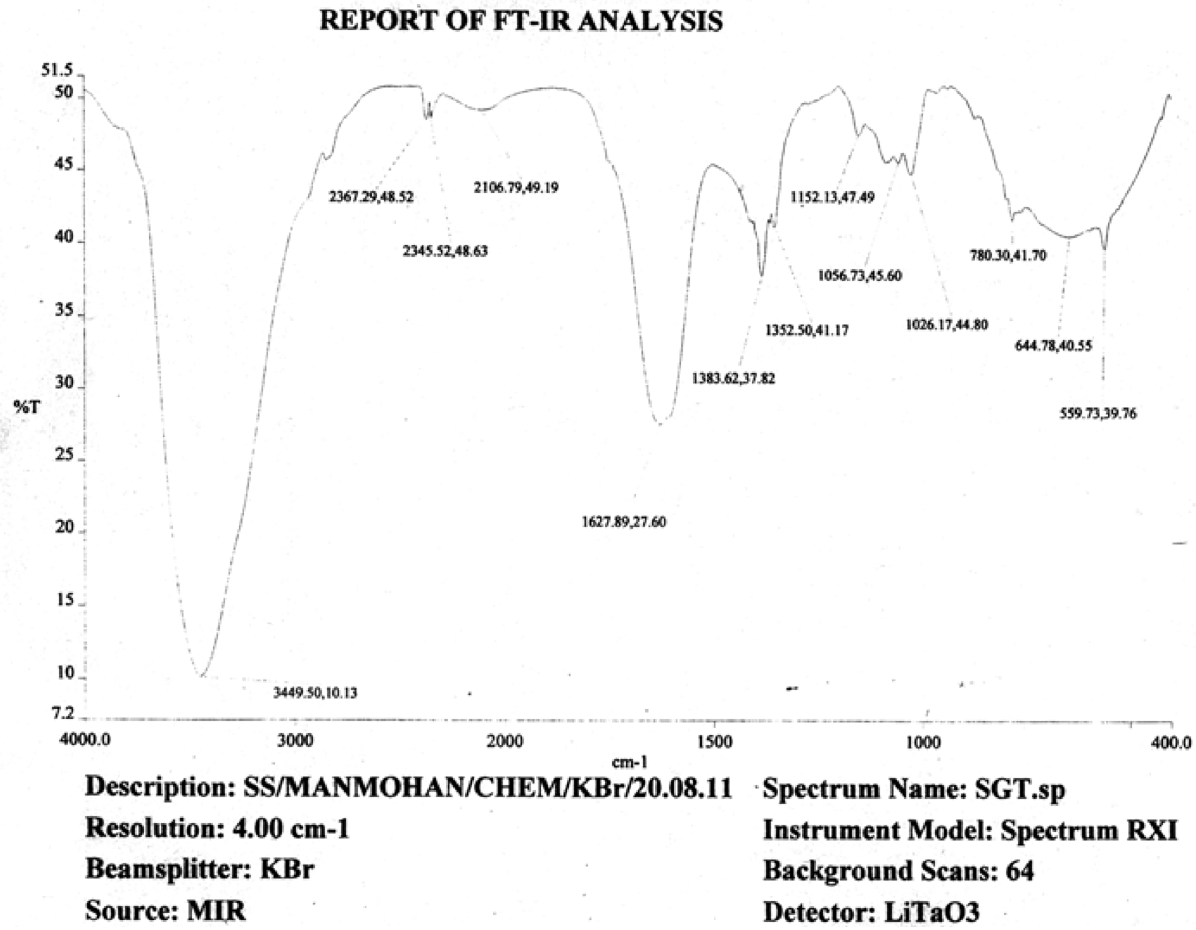


**Figure 4: NMR spectrum of GT–AAH resin**


**REPORT OF FT-IR ANALYSIS**

**Description: SS/MANMOHAN/CHEM/KBr/20.08.11**
**Resolution: 4.00 cm-1**
**Beamsplitter: KBr**
**Source: MIR**

**Spectrum Name: SGT.sp**
**Instrument Model: Spectrum RXI**
**Background Scans: 64**
**Detector: LiTaO3**

**Figure 5: IR spectrum of GT–AAH resin**

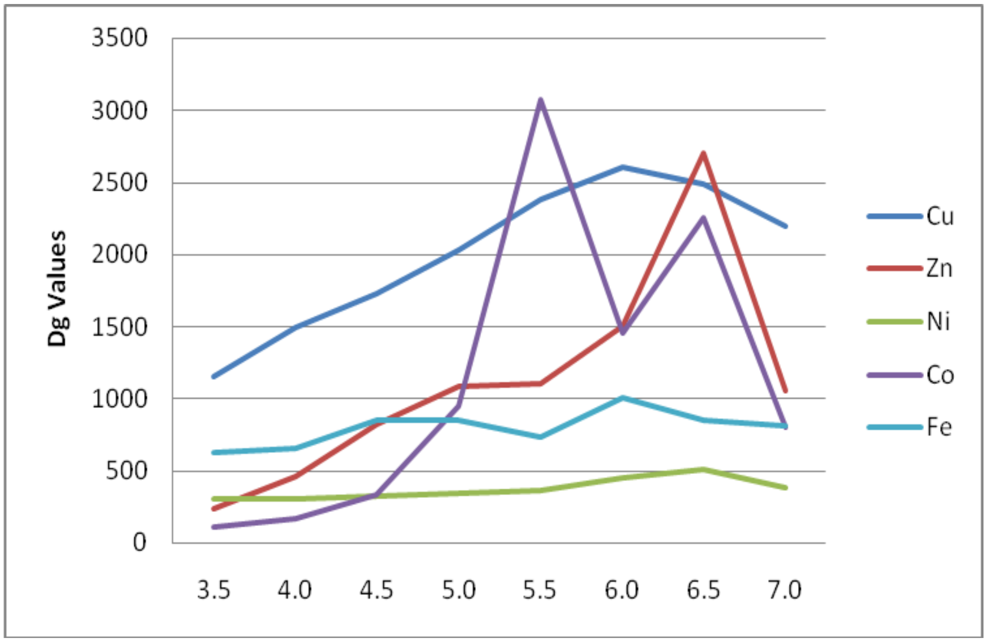


**Figure 6: Dg vs pH of GT-AAH Resin with various metal ions**

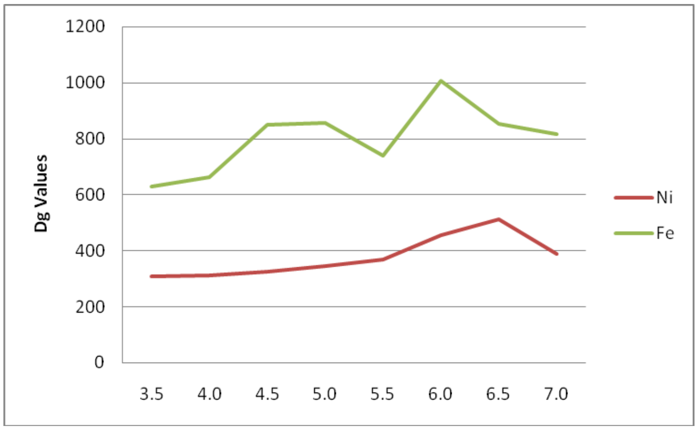


**Figure 7: Dg vs pH of GT-AAH Resin with Ni & Fe metal ions**

### *Uptake of metals by the resin*

The Dg values v/s pH contours of GT-AA resin with various metal ions are represented in fig: (2). The selectivity sequence of various metal ions on GT-AAH resin is as follows. Cu(II) (2605) > Zn (II) (1248) > Fe (II) (1008) > Co (II) (858) > Ni (11) (512). The results show that the metal uptake by the resin increases with increase in pH, then attains a maximum value and then decreases with further increase in pH. The metal uptake by the resin was maximum in the pH range 6.0-6.5.The order of selectivity of resin for various ions is in consistent with the selectivity sequence given by Bogdanov (1977) for hydroxamate acids of the two tautomeric forms exhibited by hydroximic acids, meal complexes are formed through the hydroxamide functional group. Thus, there is considerable covalency in the bonds formed and this contributes to the high selectivity in the hydroxamate interaction with metal ions. The synthesized resin can be utilized for the separation of transition and highly charged metal ions from alkaline earth metals which is the disadvantage of the most widely used resin.

The disadvantage of Chelaxe-100 which high cost and same affinity for transition as well as alkaline earth metals can be overcome to a great extent, by utilizing the synthesized guar gum resins which are cheap, easily available, selective and biodegradable.

### Separation of metal ions by the resin

In our work we also study distribution coefficient values of various metal ions. In this case we separated metal ions using our synthesized resins. The differences in the distribution coefficients values between metal ions are large enough to permit good separation on columns. We have utilized GT–AAH resin for the separation of Nickel–Iron mixture.

## ACKNOWLEDGEMENT

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