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### PREPARATION AND CHARACTERIZATION OF GUARGUM 5-AMINO-1-NAPHTHOL-3-SULPHONIC ACID (GANSA) RESIN AND ITS USE FOR SEPARATION OF HEAVY METAL IONS FROM INDUSTRIAL WASTEWATER

Jyoti Tripathi<sup>\*1</sup>, Deepika Pareek<sup>2</sup>, Dinesh Vaishnav<sup>3</sup> and Aresh Vikram Singh<sup>4</sup>

<sup>\*1,2,3&4</sup>Department of Chemistry, J.N.V.University, JODHPUR-342005,(Raj.)INDIA

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#### ABSTRACT

A new guargum based resin containing 5-amino-1-naphthol-3-sulphonic acid has been synthesized and adsorption behavior for heavy metal ions has been investigated by batch and column experiment. The guargum 5- amino-1-naphthol-3-sulphonic acid resin can selectively separate heavy metal ions from industrial waste water. The GANSA resin was characterization the basis of ion exchange capacity IR spectra and thermogravimetric analysis.The GANSA resin has been used for removal of heavy metal ions  $Cd^{+2}$ ,  $Pb^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  in aqueous solution and effluents of Prince Steel Industry, Jodhpur

#### INTRODUCTION

Ion exchange processes are reversible chemical reactions for removing heavy metal ions from solution and replacing them with other similarly charged ions. In water treatment, it is primarily used for softening where calcium and magnesium ions are removed from water, however, ion exchange processes is being used more frequently for removal of other dissolved ionic species. Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the aquatic and terrestrial environments. The contamination of the aquatic systems with toxic heavy metal ions is a problem of global concern. The pollution of heavy metal ions has become a serious problem with the rapid increase of global industrial. Among the heavy metals, lead causes encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia and toxicity to the reproductive system [1]. The excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract [2]. The Number of methods have been used to remove heavy metal ions from waste waters which principally include chemical precipitation, ion-exchange, reverse osmosis, coagulation and flocculation, membrane separation, biosorption, and adsorption . In recent years, increasing costs and environmental considerations associated with the use of commercial adsorbents, have led to a significant body of research work aimed at developing new low-cost adsorbents derived from renewable resources. In this context, the advantages of using cellulose as the basis for new adsorbent design lie primarily in its high abundance, low cost and the relative ease with which it can be modified chemically [3]. Approaches to cellulose modification have been based on either direct chemical modification approaches [4-7] or the grafting of suitable polymer exchange to the cellulose back bone followed by fictionalizations [8-11]. The adsorption of heavy metal ions on conventional adsorbents such as activated carbon have been used widely in waste water treatment of applications[12]. Chemically, guar gum is a polysaccharide composed of the galactose and mannose. The backbone is a linear chain of  $\beta$  1, 4-linked mannose residues to which galactose residues are 1, 6-linked at every second mannose, forming short side-branches. The present work has been reported the synthesis and application of 5 amino 1 naphthol 3 sulphonic acid derivatives of guargum and it has been employed for removal of toxic metal ions such as lead , copper , zinc from the effluents of Prince Steel Industries .

#### MATERIALS AND METHOD

**Chemicals** – Guar Gum Powder, HCL supplied by ( Sarabhai M. Chemicals Baroda India), Anthranilic acid was supplied by (Ranbaxy Laboratories Ltd. Punjab). All other compounds used in the synthesis were commercial high purity grade, and used without further purification.

#### Apparatus:

##### pH meter

Digital pH meter model 5651, supplied by Electronics Corporation of India (ECI) was used in the determination of pH values.

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### Atomic absorption spectroscopy(AAS)

The concentration of studies metal ions were measured by Perkin Elmer 2380 spectrometer. Atomic Absorption Spectrophotometer was used in the quantitative determination of metals ion concentration in traces.

**Magnetic Stirrer :** Magnetic stirrer manufactured by Metrex Scientific Pvt. Ltd. was used the sample shaken with a DSHZ-300A temperature constant shaking machin

### FTIR spectrometer

The structure of GANSA resin was characterized by Perken Elmer model 5000 FTIR spectrometer.It was employed for all the FTIR spectral analysis of the synthesized resin.

A. **Sample – The effluent of Prince Steel Industries,Jodhpur, Rajasthan has the characteristics features as summarized in table-1**

*TABLE I The characteristics of prince steel industry, jodhpur*

pH	2.48
Appearance	Turbid
Total Hardness	846
Metal ion	Cu <sup>+2</sup> Zn <sup>+2</sup> Pb <sup>+2</sup> Cd <sup>+2</sup> Ni <sup>+2</sup> Mg <sup>+2</sup> Cr <sup>+2</sup> Ca <sup>+2</sup> Fe <sup>+2</sup> Co <sup>+2</sup>
Concentration(ppm)	1.55, 3.25, 0.75, 0.54, 0.54, 23.3 ,0.74 72.6 1.77,.80
Others anions (ppm)	Fluoride=0.35; Sulphate=717.46;Cyanide=0.0

### B. **Synthesis of Guar gum 5 amino 1 naphthol 3 Sulphonic Acid (GANSA) Resin -**

32 gm.(,2mole) guar gum powder was taken in round bottom flask and slurried in dioxane. While stirring the reaction mixture on a magnetic stirrer, 15 ml. of 40% aqueous NaOH solution wer added followed by 9.25g (0.1 mole) of epoxychloropropane and the mixture was stirred for 5 hrs at 60°C. After keeping it overnight, compound was filtered and washed with dioxane and ether. This form of functionalized guargum can be stored at 25°C for long time. It can be activated by reaction with sodium hydroxide (NaOH) by converting the chlorohydrin into an epoxide group. The dioxane suspension of guargum solution chlorohydrin followed by dropwise addition of 20% aqueous sodium hydroxide with stirring at 60°C. It was followed by addition of 23.92g (0.1 mole) of 5-amino-1 naphthol - 3 - sulphonic acid and stirring for 4 hrs and left over night guargum incorporating 5-amino-1-naphthol-3-sulphonic acid group was filtered washed with HCl - methanol and finally with ether and dried. The GANSA resin was free flowing yellow powder and yield was 51.32 gm.

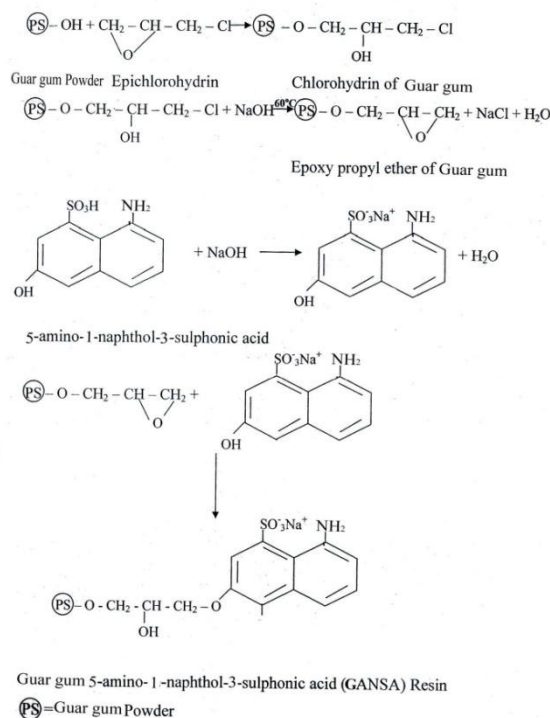


Fig.1: Synthesis of GANSA resin

### C. Batch method

Batch method were conducted using 100mg of GANSA resin of sample solution containing known concentration of heavy metal ions. 100 ml sample solution was taken in a conical flask and the pH was adjusted by appropriate buffer. Twenty milligrams of resin were 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 metal ion concentration in the filtrate as as in the residue was 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 concentration of metal ion in filtrate were determined by the calibration curves and distribution coefficient  $K_d$  were calculated using the formula:

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

### D. Column Preparation

10 cm long glass column of uniform diameter i.e. one centimeter was used. GANSA resin was swelled in DMF. The swollen resin was poured down the column wall and the resin was allowed to settle in order to form a homogenous layers. The height of the resin in the column was about 2 cm. the resin was washed with the buffer of pH at which the adsorption of mixture is to be carried out. The loaded metal ions were eluted using suitable eluants. The quantity of individual metal ions was determined in the eluate by AAS

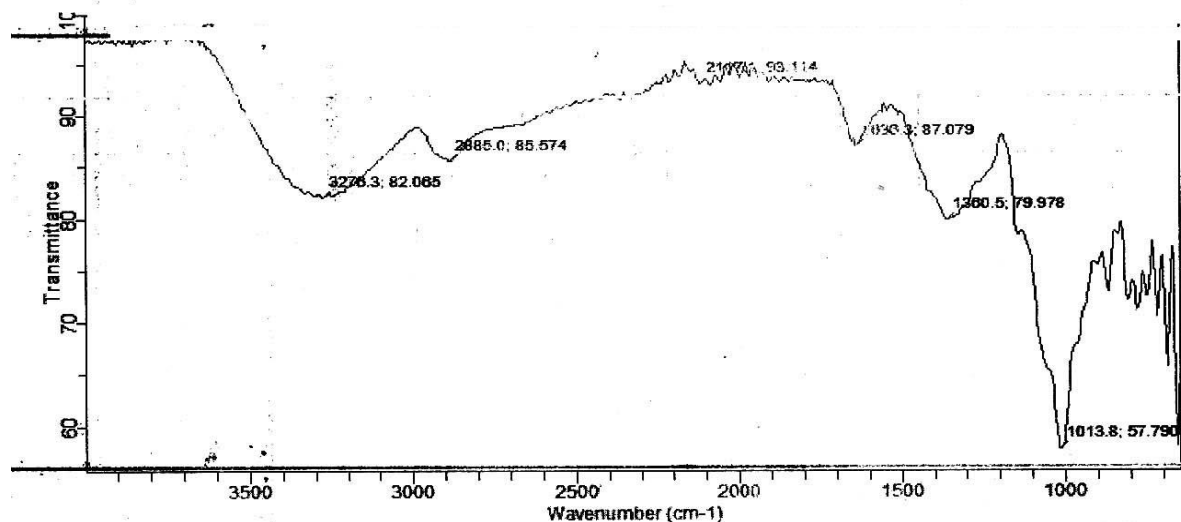
## RESULTS AND DISCUSSION

### A. IR Characterization

Perkin Elmer FTIR (model 5000, USA) Instrument was employed for FTIR spectra analysis of functionalized GANSA resin. The FTIR spectrum of GANSA resin has been characterized -OH and NH group stretching frequency in the region of 3600-3200  $\text{cm}^{-1}$  which the peak at 2900-3050  $\text{cm}^{-1}$  is attributed to C-H stretching vibrations for bicyclic aromatic system. Another strong and sharp peak at 1650  $\text{cm}^{-1}$  may be due to -OH bending. Another variable peak at 1480-1350  $\text{cm}^{-1}$  is attributed to C-H bending. A strong peak at 1300-1000  $\text{cm}^{-1}$

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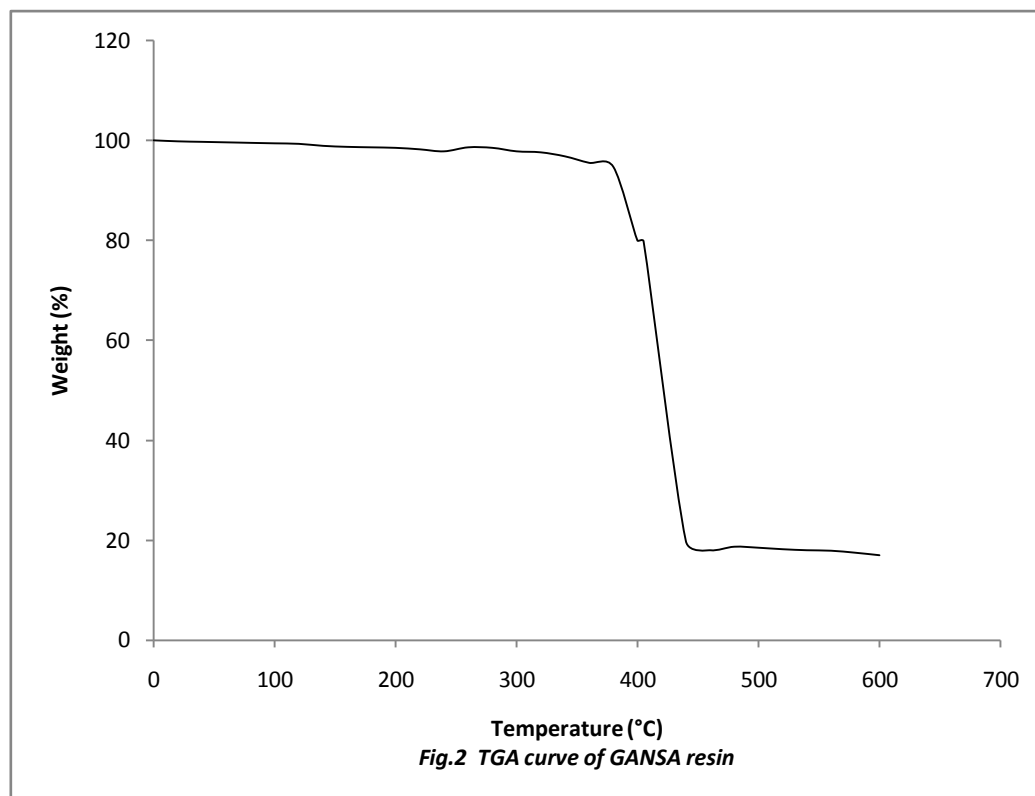
denotes C-O stretching vibration. The sulphonate group displays asymmetric and symmetric S=O stretching frequencies in the region  $1350\text{-}1342\text{ cm}^{-1}$  and  $1165\text{-}1150\text{ cm}^{-1}$ .



*Fig.1. FTIR spectra of Gaurgum-5-Amino-1-Naphthol-3-Sulphonic Acid*

### 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  $20\text{ }^{\circ}\text{C}$  per minute was maintained in air atmosphere. The GANSA resin is found to stable up to  $395\text{ }^{\circ}\text{C}$  and then the degradation was found to be rapid. The obtained TGA curve of GANSA resin is shown in Fig. 2.



*Fig.2 TGA curve of GANSA resin*

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### 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 GANSA resin was calculated using (1)

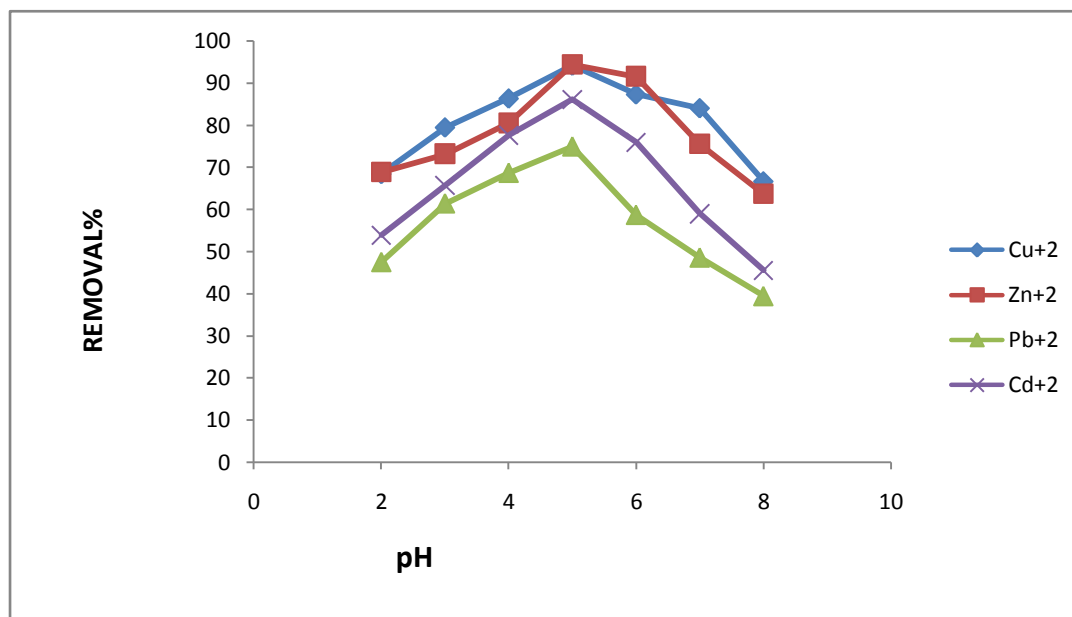
$$\% R = [(I-F / I) \times 100] \quad (1)$$

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

**Table 2: percentage removal of metal ions from the industrial wastewater by gansa resin**

PH	Cu <sup>+2</sup>	Zn <sup>+2</sup>	Pb <sup>+2</sup>	Cd <sup>+2</sup>
2	68.44	68.85	47.48	53.88
3	79.48	73.15	61.40	65.67
4	86.35	80.45	68.65	77.56
5	94.15	94.34	74.90	86.07
6	87.32	91.53	58.67	75.89
7	84.05	75.55	48.55	58.98
8	66.68	63.66	39.40	45.54

The results of percentage removal of metal ions from effluent of prince steel industry, jodhpur by GANSA resin are given in table II. It reveals that maximum removal percentage for Zn(II), Pb(II),Cd(II),Cu(II) were obtained 94.34%,74.90%,86.07%,94.15% at pH 5 respectively



**Fig.3 Percentage removal of metal ions on GANSA resin**

### D. Distribution Coefficient (K<sub>d</sub>) of metal ions

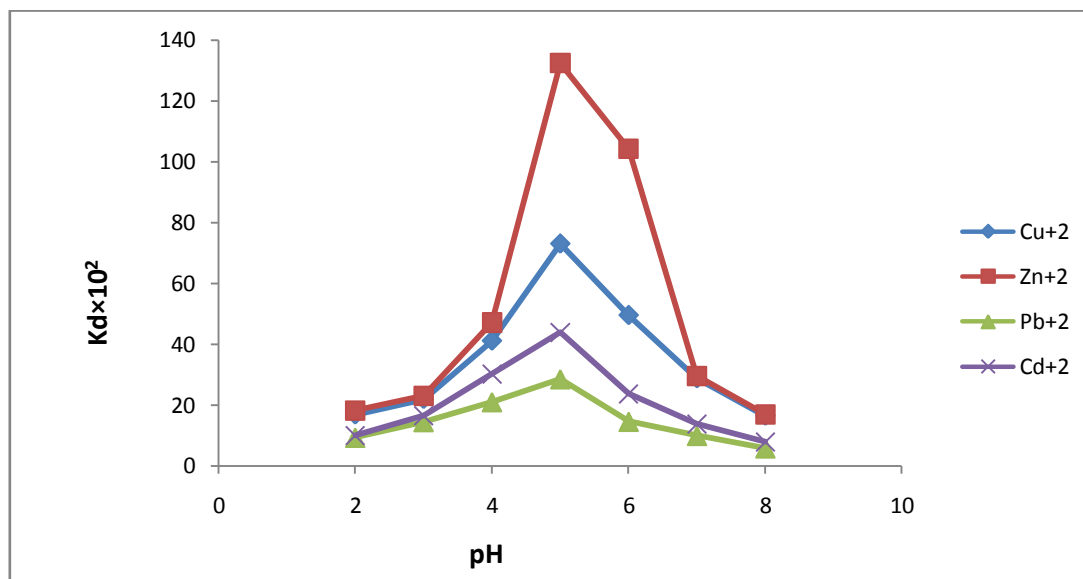
The distribution coefficient K<sub>d</sub> of metal ions on resins were determined by Batch method. In all cases for the determination of K<sub>d</sub> 100 ml sample solution was taken in a conical flask and the pH was adjusted by appropriate buffer. Twenty milligrams of resin were added to the solution 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 metal ion concentration in the filtrate as as in the residue was 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 concentration of metal ion in filtrate were determined by the calibration curves and distribution coefficient K<sub>d</sub> were calculated.

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**TABLE III** distribution coefficient ( $k_d$ ) of metal ions of prince steel industry of jodhpur on gansa resin  $k_d \times 10^2$

PH	Cu <sup>+2</sup>	Zn <sup>+2</sup>	Pb <sup>+2</sup>	Cd <sup>+2</sup>
2	16.86	18.25	9.28	10.11
3	21.97	23.07	14.44	16.63
4	41.13	47.16	21.03	30.19
5	73.06	132.44	28.58	43.88
6	49.55	104.19	14.55	23.67
7	28.77	29.67	9.89	13.77
8	16.45	16.99	5.77	7.99

Metal sorption starts when the pH rises to the range where most acidic ion exchange hydronium ion for metal ions and the capacity reaches the maximum value in the pH range where all the ion exchange sites take part in the reaction and the functional group is able to form complex with the metal cation (13-14). The adsorption capacity of the GANSA resin for Zn(II), Pb(II), Cd(II), Cu(II) was also evaluated. It has been observed that the maximum  $k_d$  value of the resin 132.44, 28.58, 43.88, 73.06 at pH 5 respectively.



**Fig.3** distribution coefficient  $K_d$  of metal ions on GANSA resin

### E. ION exchange capacity of gansa resin

The total capacity of an ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milli equivalents per dry gram of resin or in terms of milli equivalents per milliliter of wet resin. Method for the determination of total ion exchange capacity of the synthesized resin. Back titration procedure was followed for the determination of capacity of resin. One gram resin was taken in an Erlenmeyer flask and 200 ml of standardized NaOH (0.05N) containing 5 ml of 5% NaCl solution was added and was allowed to stand overnight. 25 ml aliquot of supernatant solution was back titrated with standard solution of 0.05 N HCl using phenolphthalein as indicator. Finally total ion exchange capacity [Q(Meq/g)] was calculated using the formula:

$$Q \text{ (Meq/g)} = \frac{(0.05N \times V_1) - 8(0.05N \times V_2)}{M}$$

- $V_1$  = Volume of 0.05 N NaOH solution
- $V_2$  = Volume of 0.05 N HCl consumed
- $M$  = Weight of dry resin in grams

#### GANSA

$$Q \text{ (Meq/g)} = \frac{(0.05 \times 200) - 8(0.05 \text{ N} \times 16.7) / 0.95}{[10 - 8(0.835)] / 0.88}$$

$$\begin{aligned} &= \frac{10 - 8 \times 0.675}{0.88} \\ &= \frac{10 - 5.4}{0.88} = \frac{4.6}{0.88} = 5.2 \text{ Meq/g} \end{aligned}$$

#### F. Separation of binary mixture of Copper and Zinc in GANSA Resin :

Glass column was packed with two grams of swollen resin. the column was equilibrated with  $\text{NH}_4\text{OH}-\text{NH}_4\text{Cl}$  buffer at pH 9.0. Twenty milliliter of mixture containing ten milliliter each of copper and zinc were loaded on the column. The rate of flow was controlled at 2 ml/min., the column was washed with same buffer solution and the sorbed metal were eluted with 0.1 N HCl. Five milliliter of fractions were collected and were analysed for concentration of copper and zinc by AAS. The results are Based on the difference in the value of distribution coefficient of studies metal ions on GANSA resin from aqueous solution. 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.

#### CONCLUSION

GANSA resin are highly selective for the removal of selective toxic heavy metal ion from their aqueous solutions as well as effluent of steel industries . on the basis of  $k_d$  values, the metal ions have been eluted  $K_d$  values order

$$\begin{array}{ccccccc} \text{Zn}^{+2} & > & \text{Cu}^{+2} & > & \text{Cd}^{+2} & > & \text{Pb}^{+2} \\ 132.44 & & 73.06 & & 43.88 & & 28.58 \end{array}$$

The removal of heavy metal ions by GANSA resin is a promising adsorbent for removal of heavy metal ions from industrial effluents due to its cost effectiveness, ecofriendliness, and rapidness.

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