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SYNTHESIS AND CHARACTERIZATION OF CELLULOSE ASCORBIC ACID RESIN AND ITS APPLICATION FOR REMOVAL OF HEAVY METAL IONS FROM EFFLUENT OF STEEL INDUSTRIES

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Keywords: *Polysaccharides, distribution coefficient, heavy metal ions, thermogravimetric analysis, cellulose ascorbic acid resin.*

ABSTRACT
A new cellulose based resin containing ascorbic acid group has been synthesized by Porath's method of functionalization of polysaccharide. The resin was characterize by ion exchange capacity, thermogravimetric analysis and infra red spectroscopy. The distribution coefficient(Kd) of metal ions at different pH was studied using Batch equilibrium method. The resin has been found suitable for removal of heavy metal ions from steel industries

INTRODUCTION
Heavy metal pollution has become a serious problem with the rapid increase of global industrial activities ,mining operations, tanneries and metal industries .Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments.Heavy metals for example mercury , chromium , lead and cadmium have lethal effects on all forms of life even at low concentrations.Among the heavy metals, lead causes encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia and toxicity to the reproductive system [1].The removal of heavy metal ions in various methods including chemical precipitation[2], nano filtration[3], solvent extraction[4] , ion exchange[5] , reverse osmosis[6] and adsorption[7-9],preconcentration[10]. All of these methods adsorption is high efficiency, low cost, easy handling and high availability of different adsorbents . Several research studies have been conducted globally on natural polymers for the removal of toxic metal ions, such as Chitosan[11], alginate[12], cellulose[13] ,lignin[14] , guaran[15],cyclodextrin[16] and activated carbon[17]. They are low cost , eco-friendly and easy available biomaterials .

Cellulose $(C_6H_{10}O_5)_n$ is a natural Polysaccharide which consists β-D-glucopyranose repeat units . Molecular structure of cellulose gives a characteristic property of hydrophilicity, chirality and degradability .The past few years, several research studies has been shown the functionalization of a natural polysaccharide matrix have different chelating functional groups for removal of heavy metal ions from industrial effluents[18-19] .In present work, we have studied the synthesis and characterization of cellulose ascorbic acid (CAA) resin and its application for removal and recovery of toxic metal ions from effluent of Arihant Industries , Jodhpur , India.

MATERIALS AND METHOD
Chemical
All reagent for synthesis and analysis were of analytic grade. Cellulose powder (Ases chemical works, Jodhpur, India), dioxane (S.D. Fine Chem. Pvt. Ltd. Boisar), sodium hydroxide (Sarabhai M. Chemicals, Baroda, India), epoxy chloropropane (Loba Chemie Pvt. Ltd., Mumbai), methanol (E-Merk Bombay, India), hydrochloric acid (Sarabhai M. Chemcials, Baroda, India), ascorbic acid (Siscochem Industries, Mumbai) were used in all experiment.

Apparatus
Atomic absorption spectrometry
Perkin-Elmer model 2380 atomic absorption spectrophotometer (AAS) operating with an air-acetylene was used to analysis the concentration of metal ions in solution.

FTIR spectrometer
Agilent Cary 630 FTIR instrument was employed for the FTIR spectral analysis of cellulose ascorbic acid resin.

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pH- meter

The pH measurement of metal ions and buffer solution were carried out by Beckman digital pH meter model 335.

Sample

The effluent of Arihant Industry,Jodhpur , Rajasthan (India) has the characteristics features as summarized in Table 1 .

Table 1. The characteristics features of effluent of Arihant industry, Jodhpur ,India

Appearance: Turbid pH: 4.6 Total Hardness : 825

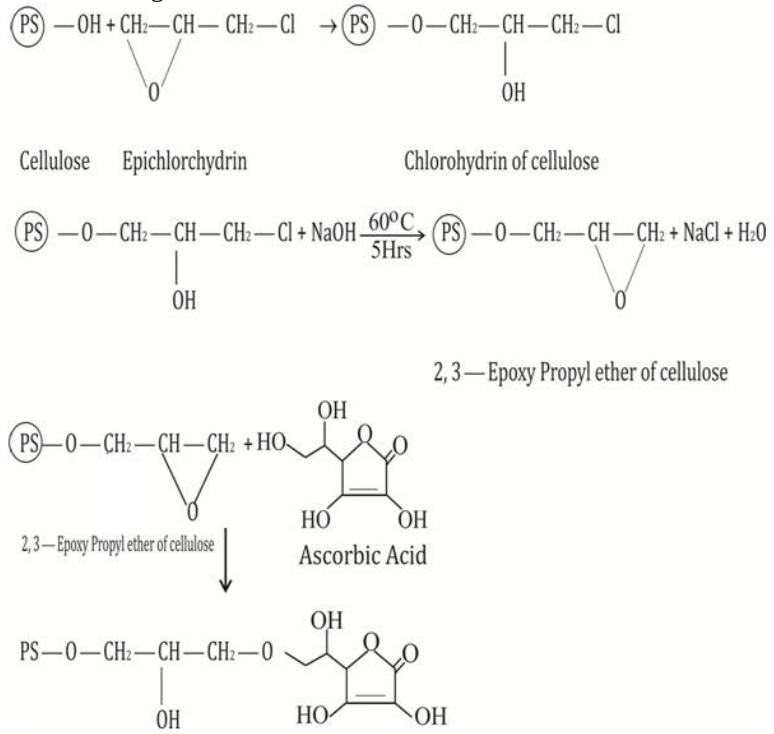
Metal ions	Concentration (in ppm)
Fe(II)	0.65
Zn(II)	6.07
Cd(II)	1.48
Pb(II)	0.62
Cu(II)	3.04
Ca(II)	185.8
Mg(II)	101.5

Other anions (ppm): Fluoride= 0.87; Sulphate=498.5;Cyanide=0.02

Synthesis of Cellulose Ascorbic Acid (CAA) resin

The CAA resin has been synthesized by modified Porath's method .An amount of 41gm (0.5 mol) of cellulose powder was taken in round bottom flask and it was slurriedwithdioxane. After 15ml of 40% sodium hydroxide was added to make it alkaline till pH reached 9-10. The solution was stirred at 60°C for 3hr. Then 9.25 gm (0.1mol) epichlorohydrine was added with constant stirring. The reaction was further continued for 5hr at 60°C. The product epoxypropyl ether of cellulose powder was filtered under vacuum and washed with methanol to remove impurities and dried.

Epoxypropyl ether of cellulose was then allowed to react with an amount of 8.8 gm (0.1mol) of ascorbic acid was added and stirring for 5hr at 60°C and left overnight. The product was filter 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 cellulose ascrobic acid (CAA) resin was free flowing light yellow powder and yield was 54.2 g .



CelluoseAscorbic Acid (CAA) resin

Fig 1 : Synthesis of cellulose ascorbic acid resin

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Batch studies

The distribution coefficient K_d of metal ions on resins were determined by Batch method. In all cases for the determination of K_d 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 well 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:

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

ION EXCHANGE CAPACITY DETERMINATION

The total capacity of an ion exchange resin in define as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. Method for the determining of total ion exchange capacity of the synthesized resin. Back titration procedure was followed for the determination of capacity of resin. 1 gram resin was taken in an Erlenmayer flask and 200 ml of standardized NaOH (0.05 N) 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 HCI using phenolphthalein as indicator. The hydrogen ions released were then calculated. It was found to be 2.84 meq/g of the dry CAA resin[20].

RESULTS AND DISCUSSION

FTIR characterization

Agilent Cary 630 FTIR instrument was employed for the FTIR spectral analysis of cellulose ascorbic acid resin. The FTIR spectra of cellulose ascorbic acid resin shows peak at 2970 cm^{-1} is due to C–H stretching vibration. The CAA resin show stretching vibration at 2500–2900 cm^{-1} due to –OH group. The peak at 1625–1400 cm^{-1} are attributed to C=C stretching in aromatic nuclei. A strong peak in the region 1260–990 cm^{-1} is due to C–O stretching vibration. Another peak at 1600–1450 cm^{-1} is attributed to C–H bending.

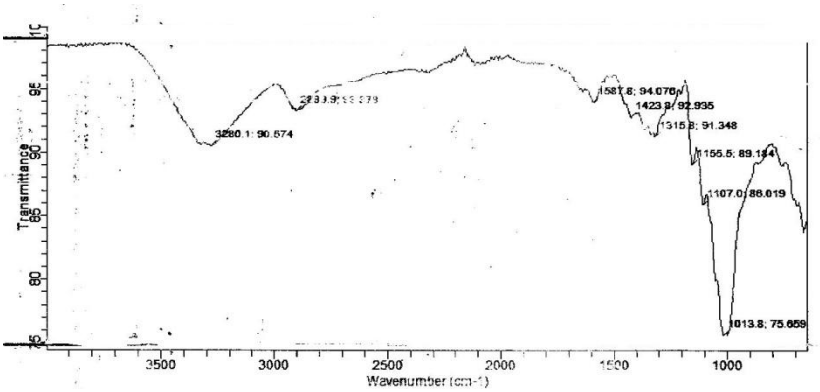

Fig 2 : FTIR spectrum of cellulose ascorbic acid (CAA) resin

Thermogravimetric Analysis

Thermogravimetric analyzer **(**Dupont 951, USA**)** was employed. The sample was powdered and dried to the same average mesh size in the vacuum desiccator. The sample was packed for the analysis. Dynamic measurement ,the system was constant heating rate 20°C per minute under static air atmosphere till the complete decomposition. The CAA resin is found to stable up to 385°C and then the degradation was found to be rapid. The obtained TGA curve of CAA resin is shown in Fig. 3.

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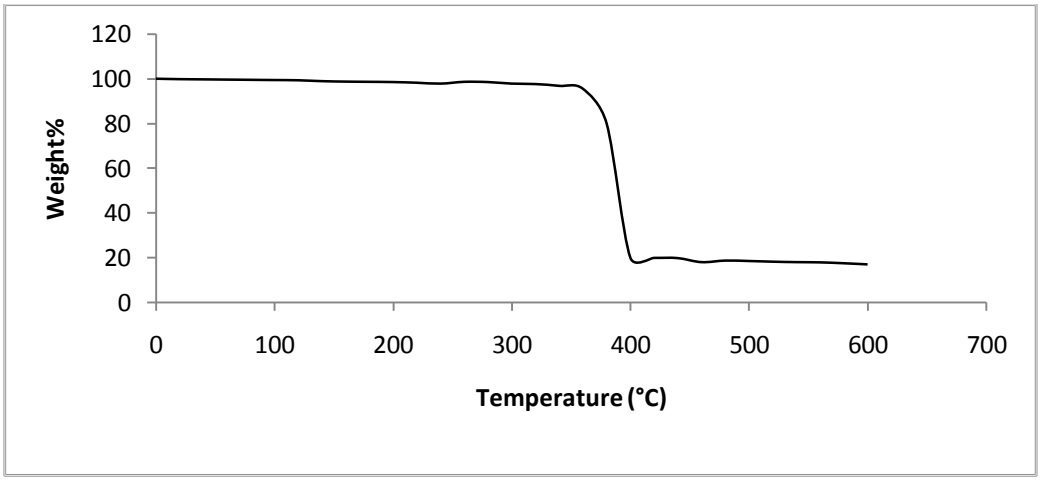

Fig 3 : TGA curve for CAA resin

Distribution coefficient (K_d) of metal ions

The pH has a strong effect on the distribution coefficient (K_d) of metal ions. The perusal of the results shows that the K_d value first increases and then decreases with increasing pH and the optimum result are obtained at pH 6. Metal ion adsorption on CAA resin starts when the pH rises to the range where most acidic ion exchange sites start to exchange hydronium ion for metal 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[21]. The results of K_d of metal ions from effluents of Arihant industry , Jodhpur, India are given in Table. 2 .

Table. 2 Distribution coefficient (K_d) of metal ions from effluent of Arihant industry, Jodhpur

$K_d \times 10^2$

pH	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Fe(II)
2.0	9.62	18.59	15.32	17.65	21.08
3.0	12.73	21.09	19.56	23.42	28.27
4.0	29.67	26.75	39.78	46.87	53.65
5.0	22.41	31.05	46.89	106.53	136.56
6.0	48.53	59.18	76.43	132.02	245.76
7.0	9.76	23.35	25.33	24.08	31.29
8.0	4.11	11.25	14.32	14.56	17.54

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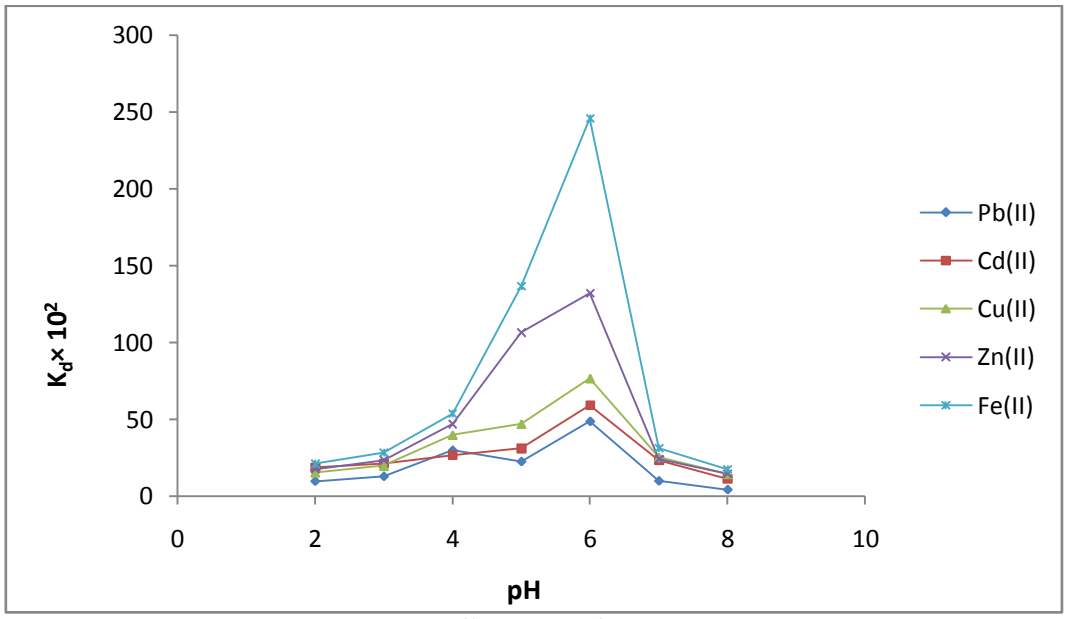

Fig 4 : Distribution coefficient (K_d) of metal ions on CAA resin

Determination of removal percentage of metal ions

The initial metal ion concentration in solution filtrate after equilibrium with resin were estimated using Atomic Absorption Spectrophotometer. The % removal of metal ions was calculated using this formula:

Percentage removal of metal ions = $(C_i - C_f / I)$) x 100

C_i=Initial concentration of metal ion in solution.

C_f = Final concentration of metal ion in solution.

Table 3: Percentage removal of metal ions of on effluents of Arihant Industry, Jodhpur

pH	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Fe(II)
2.0	47.76	56.02	61.07	64.44	69.03
3.0	54.34	68.25	68.42	72.43	74.67
4.0	62.56	70.02	79.81	71.43	81.34
5.0	65.45	74.14	81.65	82.75	84.34
6.0	75.43	82.67	87.14	95.43	94.87
7.0	45.05	56.98	65.75	72.64	76.65
8.0	37.92	41.24	55.42	59.01	65.23

The results of percentage removal of metal ions from effluent of Arihant Industry by CAA resin are given in Table. 3 It is clear from the table that the percentage removal of metal ions first increases and then decrease with increasing pH.The maximum removal % for metal ions at pH 6 respectively. It reveals that maximum removal percentage for Pb(II), Cd(II), Cu(II), Zn(II) and Fe(II) were obtained 75.43%, 82.67%, 87.14%, 95.43%, and 94.87% at pH 6 respectively.

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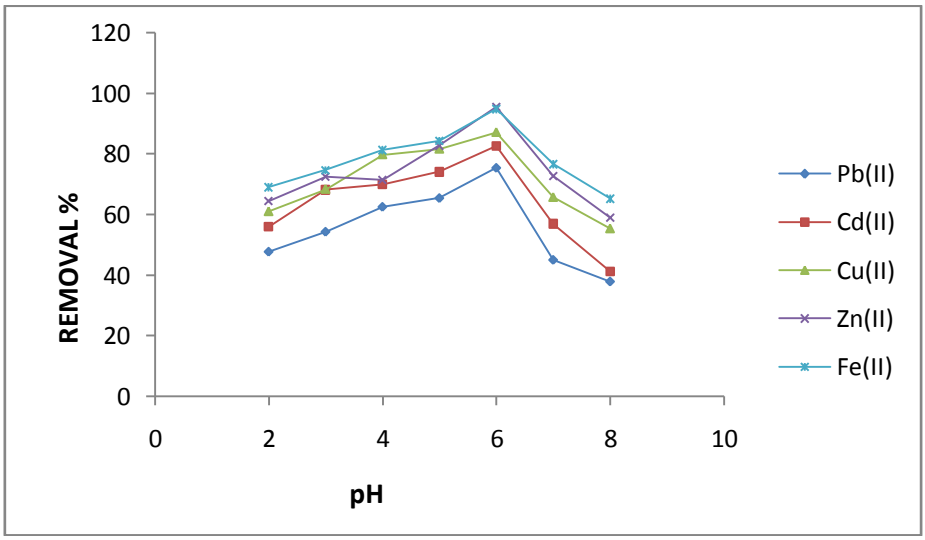

Fig 5: Percentage removal of metal ions by CAA resin.

Fig.5 shows that the percentage removal of metal ions first increase and then decrease with increasing pH. It suggest that selectivity of metal ion is dependent on pH.

Recovery of metal ions

The recovery of metal ions were obtained by column experiment. In the column experiment the metal ions were eluted quantitatively with different strength of acids. The Pb (II)was eluted with .1N HCL, Cu(II) with .05 N HCL , Cd (II) with 1.0 N HCL , Fe(II) with 1.5 N HCL and Zn(II) was eluted with 2.0 N HCL. then the resin column was washed thoroughly with demineralized water. the amounts of metal ions in the filtrate solution were analyzed by using AAS. recovery of Pb (II), Cu (II), Fe(II), Zn(II) were obtained95.55%, 98.88% , 98.47%, 96.61% and 99.13% respectively. The elution of metal ions were carried out with hydrochloric acid solution taken the advantage that, chloride ion is an acceptable matrix for both AAS and spectrophotometric determination of metal ion. Data obtained in table 4 indicated that, different quantity and different strength of hydrochloric acid solution could afford quantitative elution of different metal ions from the resin.

Table : 4 Quantitative separation of metal ions on CAA resin

Metal ion	Amount loaded (mg)	Amount Found (mg)	% Recovery	Eluent use	Eluent (ml)
Pb(II)	0.45	0.43	95.55	0.1 N HCl	50
Cu(II)	1.78	1.76	98.88	0.5 N HCl	55
Cd(II)	1.31	1.29	98.47	1.0 N HCl	45
Fe(II)	0.59	0.57	96.61	1.5 N HCl	50
Zn(II)	5.76	5.71	99.13	2.0 N HCl	60

CONCLUSION

The experimental results validate that CAAresin is a promising adsorbent for removal of heavy metal ions from industrial effluents of Arithant Industry, Jodhpur . The removal of Zn(II),Cu(II), Fe(II), Pb(II) and Cd(II) ions by CAA resin is one of the most promising techniquedue to its cost effectiveness, eco-friendliness and rapidness.The selectivity of metals ions on CAA resin have obtained as follows: Zn(II) >Cu(II) >Cd(II) >Fe(II) >Pb(II).

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