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Synthesis, Characterization and Ion Exchange Property of New Cellulose Dihydroxybenzoic Acid (CDHBA) Resin

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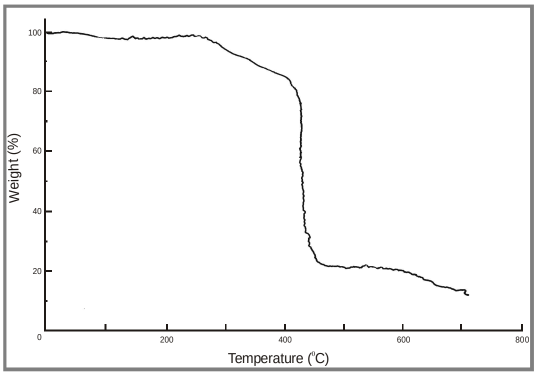
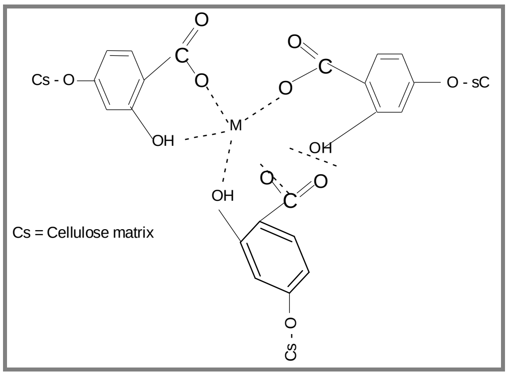
ABSTRACT

A new cellulose based resin containing dihydroxybenzoic acid groups has been synthesized and their adsorption behavior for heavy metal ions has been investigated using batch and column experiments. The dihydroxybenzoic acid group has been incorporated into cellulose by a modified Porath's method of functionalisation of polysaccharides. The cellulose dihydroxybenzoic acid (CDHBA) resin can selectively remove of heavy metal ions, which are contained in industrial wastewater. The CDHBA resin was characterized by FTIR, Thermogravimetric analysis. The effects of various adsorption conditions, such as pH, treatment time, agitation speed, temperature, flow rate and adsorbent dose were also investigated. The orders of distribution coefficient values were determined.

Graphical Abstract





Keywords: Cellulose dihydroxybenzoic acid (CDHBA) resin, Polysaccharides, Distribution coefficient, Thermogravimetric analysis, Industrial wastewater.

INTRODUCTION

Ion exchange method during the last decade has become increasingly important in various analyses in inorganic and organic chemistry. Now days, attention has been paid for the removal of heavy metals from industrial wastewater. Heavy metals such as, ferrous , copper, zinc, lead, etc are detected in waste streams from mining operations, tanneries, electroplating, battery and steel industries. It has a harmful effect on human physiology and other biological systems when they exceed the tolerance levels. In view of this, there is a need of developing viable and relevant technologies that can not only cleanup but also recover valuable components from industrial wastewater. The removal of heavy metal ions from wastewater can be achieved by several processes, such as precipitation[**1**], solvent extraction[**2, 3**], chemical and electrochemical technique[**4**] and advanced oxidation process[**5, 6**]. Most of these processes may be ineffective, extremely expensive, or generate secondary pollution. In recent years, the adsorption of metal ion by ion exchange method[**7-14**],by batch and fixed bed column[**15**] and modified polymer[**16**] ' has received much attention and becomes one of the most popular methods for the removal of heavy metals from the industrial wastewater because of its competitive and effective process for the above purpose.

An effective adsorbing material should consist of a stable and insoluble matrix and recent developed polysaccharide materials have been demonstrated to be such kind of material [**15**]. Many studies have shown the functionalization of a polysaccharide matrix with different chelating functionalities for metal ions removal [**16- 25**]. The adsorption of metal ions using chelating ion exchange resins is a green analytical method since it does not involve the use of heavy chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction technique or other methods [**26**]. The main objective of the most of the research works on chelating resins is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions. The interest in this type of chelating resins are due to the rapid adsorption of metal ions, higher selectivity and less swelling, in comparison with the analogous organic polymers [**27**].

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several D-glucose units [**28**]. The structure of cellulose is given in figure 1. The present work was undertaken to synthesize and characterizations of new cellulose dihydroxybenzoic acid [CDHBA] resin, which selectively remove heavy metal ions from industrial effluent in the form of batch and column processes.

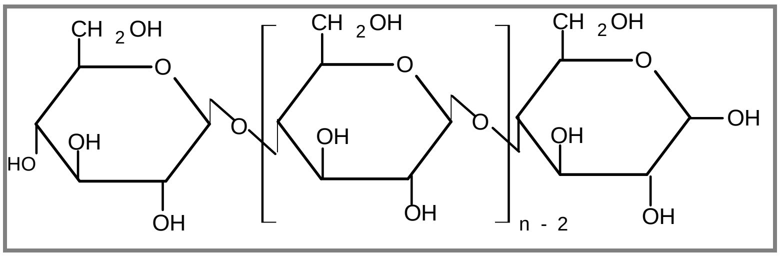


Figure 1. Structure of cellulose

MATERIALS AND METHODS

Materials: Cellulose powder (Ases Chemical Works, Jodhpur, India), Epichlorohydrin (Sisco-Chem Industries, Mumbai, India) Dihydroxybenzoic acid (Loba Chemic Pvt Ltd, Mumbai, India), Sodium Hydroxide (Sarabhai M. Chemicals, Baroda, India), Dioxane (E Merk, Mumbai, India).

Sample: The effluent of Apex steel industry, Jodhpur, Rajasthan (India) has the following characteristics features as summarized in table 1. For column operation, stock solutions (1000 mg L^{-1}) of different metal ions were prepared by dissolving appropriate metal salt in 1000 mL deionized water The stock solution was diluted to obtain standard solutions contain 10 mg l^{-1} of Fe (II), Pb (II), Cd (II) and Pb (II).

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

Metal ions	Concentration (in ppm)
Fe (II)	1.67
Cu (II)	2.02
Zn (II)	3.27
Pb (II)	0.86
Cd (II)	0.26
Cr (II)	0.72
Ni (II)	0.14
Co (II)	0.68
Mg (II)	19.20
Ca (II)	80.00

Appearance: Turbid , pH: 4.4, Colour: Dirty brown, Total hardness: 965
Other anions (ppm): Fluoride = 0.237, Sulphate = 840.12, Cyanide = 0.04

Synthesis of cellulose dihydroxybenzoic acid [CDHBA] resin: The synthesis of cellulose dihydroxybenzoic acid [CDHBA] resin accomplished in the following two steps [A]and [B].

[A] Preparation of epoxypropyl ether of cellulose: 32.4 g (0.2 mole) of cellulose powder was taken in round bottom flask and slurred in dioxane. 50 % of aqueous solution of sodium hydroxide was added in the flask to make it alkaline, till pH reached to 9.5. The solution was stirred for one hour. 9.25 g (0.1 mol) epichlorohydrin was added drop wise and stirring was continued for 5 h at 60°C. The product epoxypropyl ether of cellulose was formed and it was used as such for further reaction.

[B] Preparation of cellulose dihydroxybenzoic acid resin: Epoxy propyl ether of cellulose was allowed to react with 15.4 g (0.1 mol) of dihydroxybenzoic acid in the alkaline medium and the stirring was continued for another 4 h at 60°C. The product was filtered 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 dihydroxybenzoic acid resin was free flowing light white powder. The yield was 56.03 g. The reaction scheme for the synthesis of CDHBA resin is shown in figure 2.

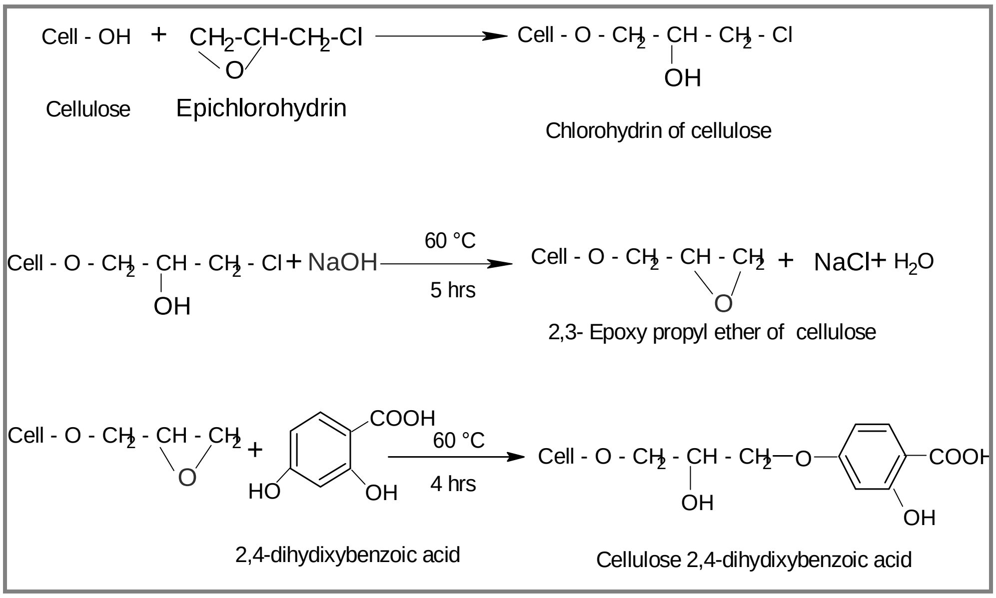


Figure 2. Reaction scheme for synthesis of Cellulose dihydroxybenzoic acid (CDHBA) resin

Physical property of CDHBA resin: The physico –chemical properties like percentage moisture content, percentage solid, true density, apparent density, void volume fraction, swelling studies and volume capacity were studied according to standard methods [29, 30]. These results are shown in table 2.

Table 2. Physical property of CDHBA resin

Properties	Value (SD)
% Moisture	7.6±0.5
% Solid	92.40.5
True Density (dres) g cm^{3-1}	1.160.02
Apparent Density (dcol) g mL^{-1}	0.63580.0053
Void Volume fraction	0.35240.1114
Volume Capacity, mmol cm^{3-1}	2.670.05

Determination of ion exchange capacity: Resin capacity is usually expressed in terms of equivalents per liter of resin or mill equivalents per dry gram of resin. The ion exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation exchanger was determined by standard column process. 0.1 g (dry mass) of the composite ion exchange material in H^+ form was placed in a glass column with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained on the particles. The hydrogen ions eluted with 0.1M solution of different alkali and alkaline earth salts. The flow rate was kept 1 mL min^{-1}. The collected effluent was titrated against a standard solution of sodium hydroxide using phenolphthalein as an indicator. The hydrogen ions released were then calculated.

Determination of removal percentage of metal ions: The calibration curves for different metals were plotted, by analyzing a series of standard solution of metal ions using atomic adsorption spectrophotometer different wavelength of main resonance line and air acetylene flame was used for the estimation of various metals. The wavelengths are given in table 3. The concentration of metal ions in solution as well as filtrates was determined using calibration curves (The curves are not given) finally, the percent removal of metal ions by CDHBA resin was calculated using this formula.

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

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

Table 3. Working range and wavelength of main resonance line for different metals

Element	Wavelength of main resonance line	Working range mg L^{-1}
Copper (Cu)	324.7	1-18
Iron (Fe)	248.3	1-15
Zinc (Zn)	213.9	0.3-3.9
Cadmium (Cd)	228.8	2- 2.5
Lead (Pb)	217.0	1-20

Determination of distribution coefficient (K_d) of metal ions in presence of electrolyte solution (Tartaric acid): The distribution coefficient (K_d) of metal ions was determined by batch method. The pH of the solution was adjusted to the desired value using acetate buffer and the resin was equilibrated for 4 h. A sample solution (100 mL) containing a known concentration of the studied metal ions were transferred to a Erlenmeyer flask and after adjusting its pH values, 0.1g of the modified CDHBA resin was added to the solution and the mixture was shaken continuously in a temperature controlled shaker at 25 ±2°C. The amounts of metal ions in the solution before and after equilibration were determined by using AAS. The distribution coefficient (K_d) of metal ions was calculated by the following equation.

$$K_d = \frac{\text{Amount of metal ion in resin phase}}{\text{Amount of metal ion in solution phase}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry resin}} \quad \text{mL g}^{-1}$$

$$\text{i.e. } K_d = [(I - F / F) \text{ X } V/ M] \quad \text{mL g}^{-1}$$

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).

Column operation: The column operation used for analyzed the recovery of metal ion. In the column experiment, a glass tube with 1.6 cm internal diameter and 20 cm height, packed with 9 cm of resin (8.5 g) was used. Separation of metal ions by selective elution on column was carried out for binary mixture. The flow rate was controlled by a peristaltic pump. The column followed by treating with distilled water to remove the last traces of unadsorbed ions. The solution mixture was passed through the column at a flow rate of 1mL min^{-1}. Elution was carried out at different concentration of hydrochloric acid solutions.

RESULTS AND DISCUSSION

IR characterization: Perkin Elmer FTIR (model 5000, USA) Instrument was employed for FTIR spectra analysis of cellulose powder and functionalized cellulose derivative (CDHBA resin). The FTIR spectra of cellulose powder shows broad band in the region 3600-3200 cm^{-1} characteristic -OH stretching frequency. The peak at 2929 cm^{-1} is attributed to C-H stretching vibrations. Another strong and sharp peak at 1650 cm^{-1} may be due to - OH bending. Another variable peak at 1480 -1350 cm^{-1} is attributed to C-H bending. A strong peak at 1300-1000 cm^{-1} denotes C-O stretching vibration. The spectra of cellulose is shown in figure 3.

A strong peak in the region 3000-2500 cm^{-1} denotes O-H stretching in -COOH group. The peak at 1725-1700 cm^{-1} characteristic C=O stretching vibrations in acidic group. A strong peak in the region 1250-1070 cm^{-1} denotes C-O stretching vibrations.. The peak in the region 1620-1450 cm^{-1} denotes C=C stretching and multiple bond observed due to aromatic compound. The spectra of CDHBA resin is shown in figure 4.

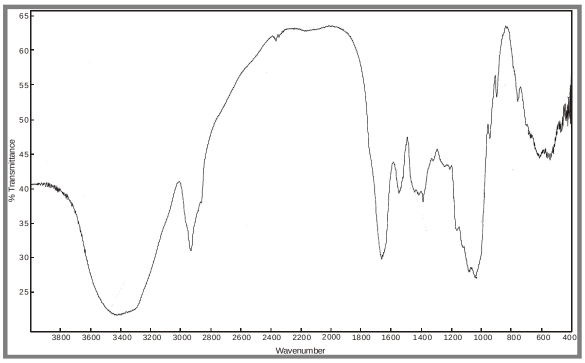


Figure 3. FTIR spectra of cellulose powder.

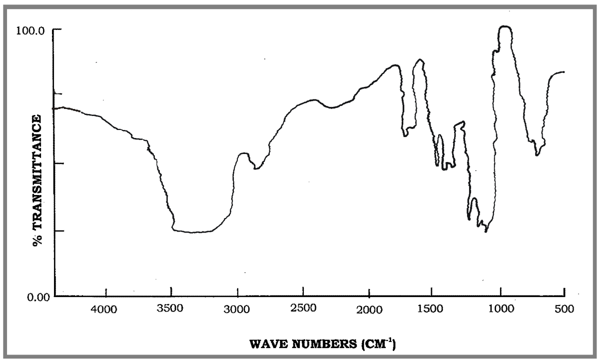


Figure 4. FTIR spectra of CDHBA resin.

Thermogravimetric analysis: For this purpose Thermogravimetric analyzer **(**Dupont 951, USA**)** was employed. 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°C per minute under static air atmosphere till the complete decomposition. The CDHBA resin is found to stable up to 401°C and then the degradation was found to be rapid. The obtained TGA curve of CDHBA resin is shown in figure 5.

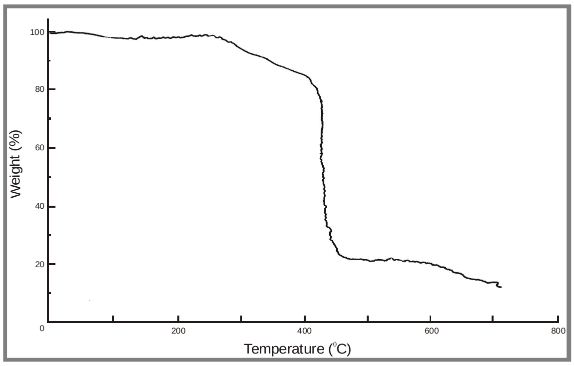


Figure 5. TGA curve of CDHBA resin (20°C min^{-1}).

Ion exchange capacity (IEC) of CDHBA resin: It was found to be 2.87 meq g^{-1} of the dry CDHBA resin.

Removal of metal ions from effluent of Apex steel industry, Jodhpur, India: The results of percentage removal of metal ions from effluent of Apex Steel Industry by CDHBA resin are 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, the optimum results obtained at pH 6.0.

Table 4. Percentage removal of metal ions from the industrial waste water by CDHBA resin

pH	Pb (II)	Cd (II)	Zn (II)	Cu (II)	Fe (II)
2.0	48.09	62.34	64.42	70.12	76.48
3.0	53.64	70.37	72.73	70.12	80.96
4.0	62.45	75.81	77.82	83.09	85.76
5.0	70.30	82.56	84.65	90.62	94.45
6.0	88.65	91.69	93.96	95.97	98.86
7.0	53.83	72.53	74.53	79.58	82.42
8.0	42.32	50.12	56.02	61.32	66.07

Distribution coefficient (K_d) of metal ions: 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 effluent of Apex steel industry, Jodhpur are given in table 5. The perusal of the results shown that the distribution coefficient value first increases and then decreases with increasing pH, the optimum results were obtained at pH 6.0. Metal sorption 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 cations [31].

Table 5. Distribution coefficient (K_d) of metal ions in presence of electrolyte solution (Tartaric acid)) K_d X 10^2

pH	Pb (II)	Cd (II)	Zn (II)	Cu (II)	Fe (II)
2.0	9.26	16.53	18.10	23.46	25.56
3.0	11.57	25.58	26.66	32.50	42.51
4.0	16.62	31.33	35.08	27.80	60.15
5.0	23.65	51.46	55.13	96.59	170.15
6.0	78.02	109.81	155.48	238.46	864.36
7.0	11.65	26.36	29.26	38.96	46.88
8.0	7.33	10.04	12.73	15.25	19.46

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. The results revealed that the relative standard deviation (R.S.D) of the method was lower than 3.0%, which indicated that the method had good precision for the analysis of trace metal ions in solution samples.

Table 6. Optimum results for the removal of metal ions from the industrial wastewater by CDHBA resin at pH 6.0.

Metal Ions	Amount of Metal ion in effluent (mg)	Amount loaded on CDBHA resin (mg)	Removal %	RSD %
Pb (II)	0.86	0.76	88.65	1.18
Cd (II)	0.26	0.23	91.69	1.68
Zn (II)	3.27	3.07	93.96	2.37
Cu (II)	2.02	1.93	95.98	2.52
Fe (II)	1.67	1.65	98.86	2.68

Resin durability: The durability of the metal ions on the CDHBA resin was subjected to several loading and elution operations. It was observed that the absorbency of different metal ion on the CDHBA resin after 10 cycles for all the five metal ions varied by less than 5 to 10 %. The adsorbed metal ions were easily desorbed by treatment of different strength of acids, at room temperature. These results are shown in table 7.

Table 7. The adsorption percentage of different metal ions on CDHBA resin (adsorption and desorption)

Metal ions	Adsorption % of different metal ions onto CDHBA resin after				
	0 Cycle	2 Cycles	4 Cycles	8 Cycles	10 Cycles
Fe (II)	98.86	95.87	92.38	90.54	88.38
Cu (II)	95.97	91.76	92.38	88.32	86.32
Zn (II)	93.96	87.38	87.38	87.18	87.18
Cd (II)	91.69	84.51	84.51	84.51	84.51
Pb (II)	88.65	81.36	81.36	81.36	81.36

Chelating complexes formation by CDHBA resin: CDHBA resin contains dihydroxybenzoic acid functional group, which possesses not only protons that can exchange with cations, but also oxygen atoms that can coordinate directly with metal ions. Therefore, the adsorption ability of CDHBA resin for enriching metal ion may be very strong. The bonds formed in this kind of metal sorption have both covalent and ionic characteristics. The structure of Chelating complex of CDHBA resin with metal ions is given in figure 6.

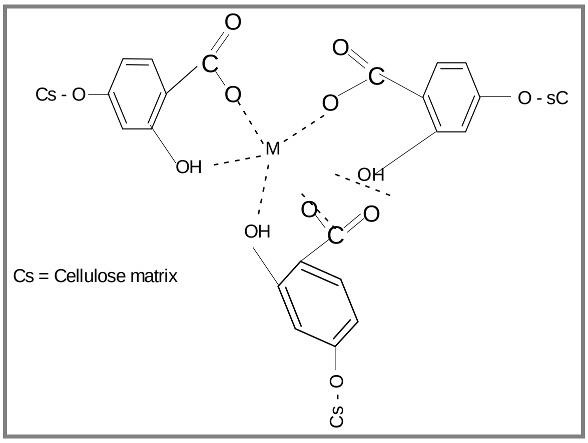


Figure 6. Chelating complex of CDHBA resin with metal ions.

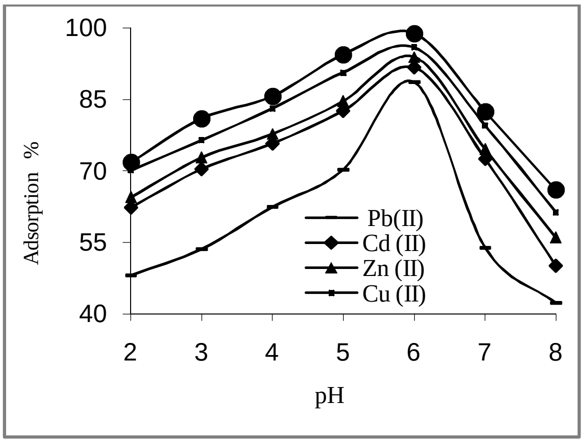


Figure 7. Effect of pH on adsorption of metal ions on CDHBA resin.

Effect of pH: The 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 % of metal ions with pH, the pH was varied from 2.0 to 7.0 as shown in figure 7. The uptake of free metal ions depends on pH, where optical adsorption of metal ions occurs at pH 6 and then declining at higher pH. Adsorption of metal ions on CDHBA resin increased over pH range from 2.0 to 6.0.

Effect of treatment time: The results (Figure 8) of treatment time indicate that adsorption % of metal ions increased with an increase in contact time before equilibrium is reached. It can be seen that adsorption of metal ions on CDHBA resin increased when contact time was increased from 30 to 240 min, hence optimum contact time for CDHBA resin was found to be 240 min. Other parameters such as pH of solution and agitation speed were kept optimum, while temperature was kept at 25^{0}C. Greater availability of dihydroxybenzoic functional groups on the surface of cellulose 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.

Effect of treatment temperature: Figure 9 shown the effect of treatment temperature on the adsorption % of the metal ion on CDHBA resin. The adsorption percentage of metal ion decreases by increasing the treatment temperature from 25°C to 75°C. This observation is in full agreement with the published results by Khalil *et al* in [32].

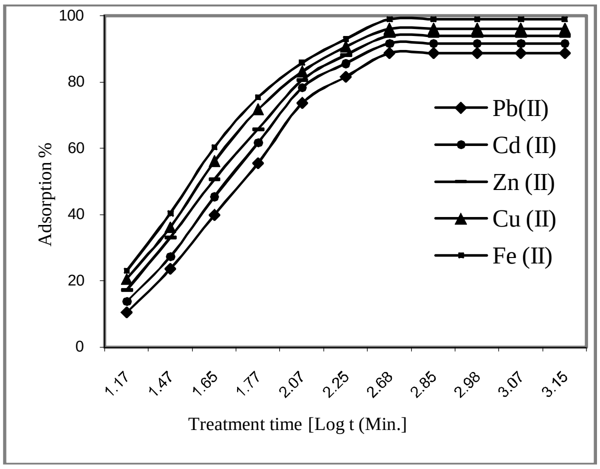


Figure 8. Effect of changing treatment time on the adsorption of metal ions on CDHBA resin.

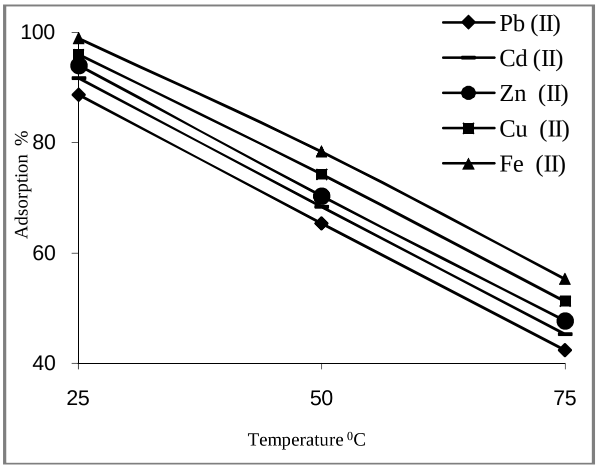


Figure 9. Effect of changing treatment temperature on the adsorption metal ions on CDHBA resin.

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 other parameters keeping optimum. As can be seen from figure 10, the adsorption of metal ions on ion exchange resin generally increased with increasing agitation speed. The adsorption of metal ions on CDHBA resin increased when agitation speed increased from 0 to 120 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 100-120 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 not significant. For convenience, agitation speed of 120 rpm was selected as the optimum speed for CDHBA resin for removal of metal ions from effluent of Apex Steel Industry. These results are in close agreement with the reports by Jeon and Park [33].

Effect of CDHBA dose on adsorption of metal ions: The adsorption of metal ions is significantly influenced by the amount of the CDHBA resin added. The amount of CDHBA resin added into the solution determined the number of binding sites available for the adsorption. The effect of the adsorbent dose on the amount of metal ions removed was studied by the application of varying CDHBA doses. The maximum adsorption by CDHBA resin was achieved with an adsorbent dose of 0.1 g and then constant up to 0.1 g. The initial increase adsorption percentage of metal ions was due to the availability of more adsorption sites. On increasing the CDHBA resin concentration further, the binding of metal ions constant. This effect might be attributed to overlapping or aggregation of adsorption sites of resin resulting in constant the total surface area of the adsorbent. The results are shown in figure 11.

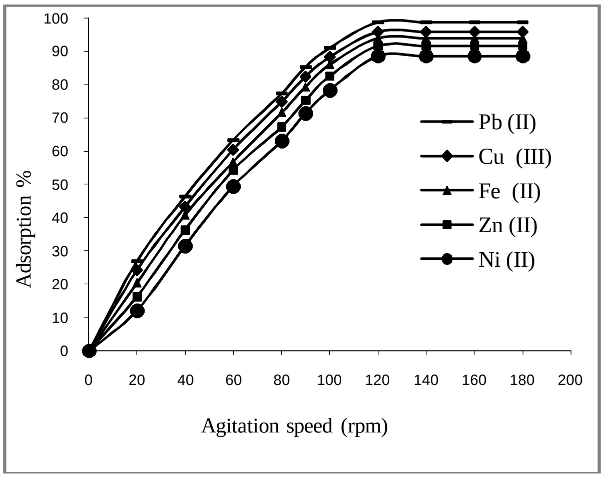


Figure 10. Effect of agitation speed on adsorption of metal ions on CDHBA resin.

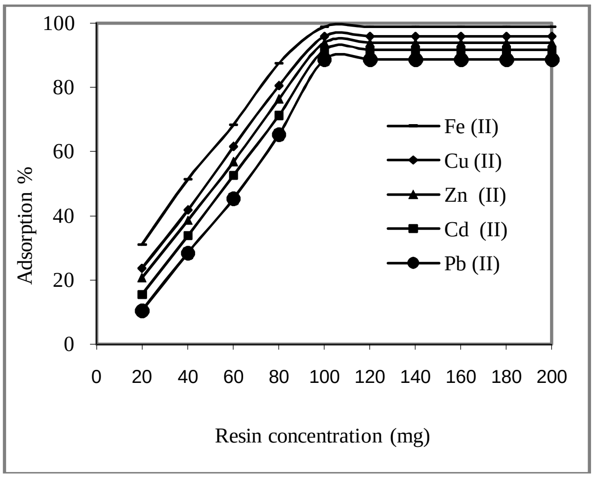


Figure 11. Effect of adsorbent dose on adsorption of metal ions on CDHBA resin.

Effect of flow rate: In the column experiment, the flow rate of the sample solution was an important parameter not only affecting the recovery of metal ions, but also controlling the time of analysis. Therefore, the effect of flow rate on adsorption of metal ions were investigated under the optimum conditions (pH, eluent, etc.) by passing 100 mL of sample solution through the micro column. The flow rates were adjusted in range of 1 to 3 mL min^{-1} controlled by a peristaltic pump. It was found that the optimum flow rate for these metal ions was 1 to 2 mL min^{-1} for maximum loading of metal ions on the chelating resin. Flow rates slower than 1 mL min^{-1}were not studied to avoid long analysis times. However, at a flow rate greater than 1 mL min^{-1}, there was a decrease in the percentage of metal ion recover, as the metal ions probably could not equilibrate properly with the resin bed. Thus, a flow rate of 1.0 mL min^{-1} was selected throughout the column experiment.

Quantitative separation of metal ions from binary mixtures: Based on the difference in the value of distribution coefficient of studies metal ions on CDHBA resin from aqueous solution, separation experiments for these metal ions were carried out by column chromatography. To achieve more clear separation of heavy metal ions in short time, maximum K_d value difference was selected for optimizing the condition of chromatography. The considerable difference in distribution coefficient of the divalent cations implies that separation of metal ion from their mixtures would be possible. An ideal situation would be such that one K_d values is greater than the K_d value for other metal ions.

The Pb (II) was separated from chelated Fe (II) using hydrochloric acid solution as an eluting agent. The Pb (II) was eluted with 0.05 N HCl solution, because at the same condition Fe (II) showed highest k_d value. Therefore, first few fractions contained only Pb (II), because Pb (II) was eluted subsequently due to low k_d value at that condition. The Fe (II) was eluted quantitatively with 2.0 N HCl solution. Recovery of Pb (II) was found 92.16 % while for Fe (II) it was 96.24 %. No cross contamination was observed from this separation. The results are shown in figure 12. Similarly, other binary mixtures were separated.

In the case of separation of Cd (II) from chelated Cu (II), Cd (II) was eluted with 0.5 N HCl. First fractions contained only Cd (II), later Cu (II) was eluted with 1.5 N HCl. Recovery of Cd (II) was found to be 92.14 % while for Zn (II) it was 94.34 %. The results are shown in figure 13.

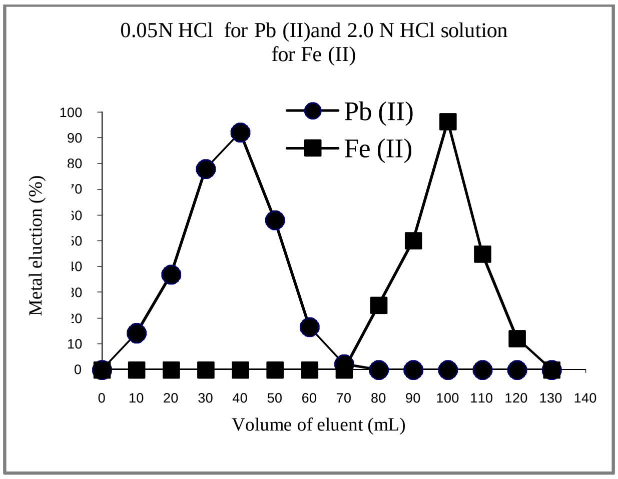


Figure 12. Separation of Pb (II) and Fe (II) by CDHBA resin.

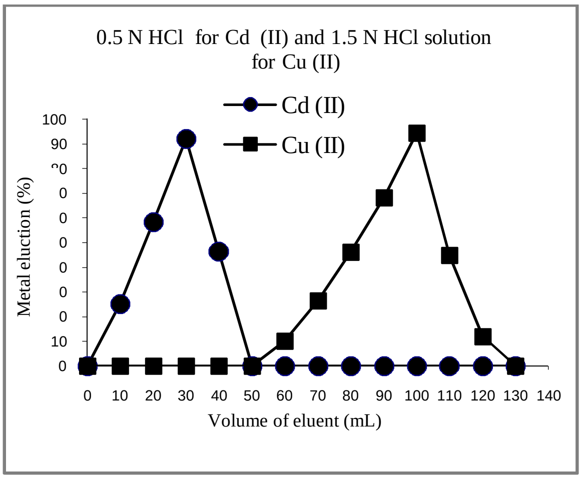


Figure 13. Separation of Cd (II) and Cu (II) by CDHBA resin.

APPLICATION

Ion exchange of cellulose is used for both analytical and preparative purposes in the laboratory, the analytical uses being the more common. An important use of ion-exchange chromatography is in the routine analysis of amino acid mixtures. Columns of cation-exchange resin are used, and the solutions are maintained sufficiently acid so that the amino acids are at least partly in their cationic forms

CONCLUSION

The experimental results reported here in validate that CDHBA resin is a promising adsorbent for removal of heavy metal ions from industrial effluents. The removal of heavy metal ions by CDHBA resin is now considered one of the most promising techniques due to its cost effectiveness, eco-friendliness, and rapidness. The selectivity and ion-exchange capacity of these materials towards metals ions can be controlled by pH of the medium, contact time, temperature, adsorbent dose, agitation speed, etc. Therefore the CDHBA resin is applicable for the removal and recovery of heavy metal ions from industrial effluent. Because the alkali and alkaline earth metals occur in relatively high concentrations in industrial effluent, a desirable property of CDHBA resin having useful environmental or commercial application is their ability to bind heavier elements selectively. It would be interesting to use the CDHBA resin for the economic treatment of industrial wastewater containing the heavy metal ions.

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