

# Heavy Metal Removal by Ion Exchanger Based on Hydroxyethyl Cellulose

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**ABSTRACT:** In the present work, ion exchange resin based on hydroxyethyl cellulose has been synthesized to remove the heavy metals, such as iron, cobalt, copper, and zinc from their aqueous solutions. The conditions in the column and batch modes were investigated for this purpose. The resin, having an average swelling percentage of 75.94 and an exchange capacity of 2.57 meq g<sup>-1</sup> resin, is being introduced as a new ion exchange resin in the heavy metal removal process. An investigation of the column operations using aqueous solutions of heavy metal ions indicated that the resin prepared has some advantages, including high total exchange capacity and good chemical stability. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3501–3506, 1999

**Key words:** ion exchange resin; cellulose; heavy metal; esterification; wastewater

## INTRODUCTION

The removal and recovery of heavy metals from industrial wastewater are gaining wide importance in all industrial branches due to a combination of economic and environmental factors. The need has been increasing for the removal of extremely low concentrations of heavy metals in various solutions because it accumulates in living tissues, causing many harmful effects. Attempts to solve problems of heavy metals removal and recovery from wastewater have led to the development and application of several techniques.<sup>1,2</sup> Methods of heavy metal removal can be grouped into the following four categories: (1) precipitation, (2) adsorption, (3) extraction, and (4) sorption or ion exchange.

The methods cited in (1) are based on precipitating the heavy metals as their hydroxides by using conventional precipitants such as lime or soda. This method is not efficient and economic

because it requires numbers of stages in order to decrease the heavy metal concentration under 1 mg mL<sup>-1</sup>. Although the efficiency of active carbon is high in the removal of heavy metals from wastewater, the high cost of active carbon has restricted its use; and active carbon adsorption process is only used as a final step in the treatment of wastewater.<sup>3</sup> With respect to the low concentrations and handling of large volumes of aqueous solutions, extraction procedures are uneconomic, and precipitation procedures require addition of relatively large amounts of chemicals; whereas application of sorption or exchange on solids is preferable.<sup>4</sup> This makes the use of exchangers for selective separation of heavy metals very attractive. Mounting regulations to ensure environmental protection coupled with efforts and initiatives in the parts of various industries to minimize pollution at the source have resulted in new opportunities in recent years for application of ion exchange technology. Recently, cellulose based ion exchangers have been proposed as potential heavy metal scavengers.

General features of ion exchanger resins have been described in the literature. Cellulose exchangers have some favorable properties.<sup>5</sup> As a

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result of a small number of carboxyl groups in its constitution, natural cellulose has ion exchange properties. Within and between the cellulose chains holes or pores are located, ranging widely in size. When ionizable groups are introduced into such a matrix, the natural polymer cellulose becomes an ion exchange material.<sup>6</sup>

Among all heavy metal removal methods, ion exchange using cellulose based ion exchanger is considered attractive because it is an effective and relatively simple method for the removal of heavy metal ions. Cellulose was chosen as matrix because of its favorable properties. Cellulose is very hydrophilic, various anchor groups can be fixed on cellulose by chemical bonds, and the rate of exchange is relatively high due to the fibrous structure of cellulose.<sup>5–15</sup> As a result of the fiber properties of cellulose, that is, its loose network crosslinked by hydrogen bridges, the majority of active exchange groups located at distances of about 50 Å can become active for the exchange of large molecules, which cannot normally penetrate the pores of a synthetic ion exchange resin. This leads to rapid exchange and to a higher capacity for large molecules, in spite of the smaller absolute exchange capacity of cellulose exchangers compared with synthetic ion exchange resins.<sup>12</sup>

In this study, an ion exchange resin based on a cellulose derivative was synthesized and characterized to remove heavy metals, such as Fe(III), Co(II), Cu(II), and Zn(II) ions from their aqueous solutions. Hydroxyethyl cellulose was chosen as a cellulose derivative and esterified with phthalyl chloride to obtain semi-ester, which would be used as an ion exchanger. Swelling percentage, chemical stability, and ion exchange capacities in the both column and batch modes were determined.

## EXPERIMENTAL

### Materials

Technical-grade hydroxyethyl cellulose was purchased from local industry. Viscosity and hydroxyl values were 1700 cP and 610.94, respectively. Other chemicals used are of reagent grade.

Phthalyl chloride used in esterification of hydroxyethyl cellulose was prepared by reaction of phthalic anhydride with phosphorus pentachloride.<sup>16</sup>

### Esterification of Hydroxyethyl Cellulose with Phthalyl Chloride

In the present study, resin preparation was performed through the esterification reaction between hydroxyethyl cellulose and phthalyl chloride. For this purpose, 27 g of hydroxyethyl cellulose, 80 mL of chloroform, and 20 mL of pyridine were placed into a three-necked flask and then stirred for 30 min at room temperature. While cooling with an ice–salt mixture, 27 g of phthalyl chloride was added dropwise. After adding the phthalyl chloride, the reaction was continued at 50°C for 5 h. The reaction product was filtered and washed with alcohol and water and dried at 30°C *in vacuo*. The yield of the portion obtained by this way was determined as 75% based on total amount of reactants. No doubt that this isolated fraction is the crosslinked structure and was used as ion exchanger (100–355 mesh) in the study.

### Procedures for Determining Structural and Ion Exchanger Characteristics

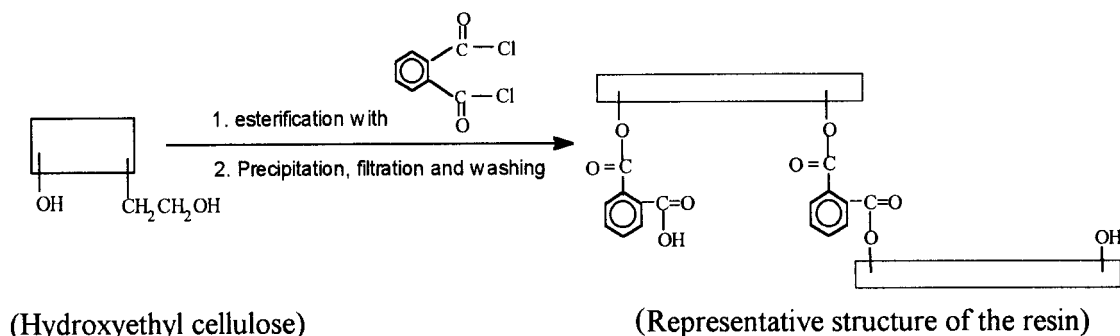
In order to determine the chemical structure of the obtained resin, acid, saponification, and hydroxyl values were determined.<sup>17</sup> The ester value was calculated by means of acid and saponification values.

The swelling percentage measurement was made by allowing the sample of the resin to equilibrate in distilled water overnight under static conditions. The wet weight samples were taken as  $M_w$ , and the corresponding dry weight as  $M_d$ , which was obtained after drying the samples at 100°C, until a constant weight. The gravimetric percentage ( $\alpha$ ) of swelling<sup>4,6</sup> was calculated using eq. (1), as follows:

$$\alpha = [(M_w - M_d)/M_d] \times 100 \quad (1)$$

The total batch capacity of the ion exchange resin was performed according to the ASTM D 2187-82 method.<sup>18</sup> The resin was first converted to H<sup>+</sup> form by treating it with excess 0.2M HCl, and its capacity determined as described in the mentioned ASTM method.

The heavy metal capacity of the resin was also determined by both batch and column operations using metal chloride solutions of Fe(III), Co(II), Cu(II), and Zn(II). For this purpose, the metal chlorides of given metals were dissolved in water in the concentration of 100 mg mL<sup>-1</sup> and used in the experiments.



Scheme 1.

For the determination of the batch capacity, 3.5 g of the wet ion exchange resin was taken in a glass-stoppered flask, and a 100 mL of solution of metal salt was added. Prepared samples in the flask were shaken for 4 h. Solutions were filtered through a dry sintered glass filter. The amount of metal ions adsorbed on the ion exchange resin was determined by the decrease of the concentration of the metal ion in the solution. Metal analysis was performed with Perkin-Elmer model 1130 Atomic absorption spectrophotometer (AAS).

Metal capacity in column was determined in an experimental setup consists of a glass column (30 mm i.d.  $\times$  400 mm high) with a glass filter plug of high porosity. The column was filled with 3.5 g of wet resin. The solution of metal salt containing 100 mg mL<sup>-1</sup> metal ion was passed downstream through a bed of resin at the selected specific flow rate of 1.3 mL min<sup>-1</sup> per mL of the resin. The selected flow rates of the regenerant and rinsing water were controlled by means of a flow meter. Two separator funnels to the rinsing water and heavy metal solution delivery tanks were provided to act as a Mariotte flask in order to ensure a constant flow rate. Solution of metal salt effluents was collected from the resin column in 100 mL of volume fraction. The amount of metal ions adsorbed on the ion exchange resin was determined by a decrease of the metal ion concentration in the solution.

The exhausted ion exchanger was regenerated by washing the ion exchanger in the glass column with 0.2M HCl in amounts of 25 mL of the acid per mL of ion exchanger and by subsequent washing with distilled water to a neutral reaction. The specific flow rate during the regeneration and rinsing with five bed volumes of distilled water is 0.133 mL per milliliter of resin. The regenerated

resin was then exhausted with solutions containing 100 mg mL<sup>-1</sup> metal ion.

The effect of pH on the exchange capacity of ion exchanger was examined for solutions including Fe(III), Co(II), Cu(II), and Zn(II) ions. The experiment was carried out in the same way as explained for batch type capacity determination at different pH values. The adjustment of pH was done by using hydrochloride acid or sodium hydroxide solutions. The corresponding metal chlorides were dissolved in distilled water in a concentration of 100 mg L<sup>-1</sup> metal. Then, 3.5 g of the wet ion exchange resin was taken in a glass-stoppered flask, and 100 mL of metal, including synthetic solution, was added, and the desired pH was adjusted with hydrochloride acid or sodium hydroxide solutions. Prepared samples in the flask were shaken for 4 h. Solutions were filtered through dry-sintered, glass-filtered, and heavy metal concentrations were determined by AAS. The amount of metal ions adsorbed on the sample was determined by the decrease of the concentration of the metal in the solution.

## RESULTS AND DISCUSSION

In the literature, several chemically modified cellulose have been prepared, which exhibit ion-exchange properties similar to those of the well-known commercial ion exchangers.<sup>19-27</sup> Ion exchange celluloses are made by attaching substituent groups with basic or acidic properties to the cellulose molecule, usually by etherification or esterification reactions.<sup>25,28-29</sup> By introducing only partial esterification of the cellulose under conditions that minimize changes in mechanical structure, one can obtain products with physical

**Table I** Some Properties of Ion Exchange Resin and Initial Mixture of Esterification

Properties	Initial Mixture	Ion Exchange Resin
Hydroxyl value	305.47	145.00
Saponification value	—	213.09
Acid value	338 <sup>a</sup>	73.00
Ester value	—	140.09
Water swelling (%)		75.94
Total cation exchange capacity (dry) (meq/g <sub>Resin</sub> )		10.68
Total cation exchange capacity (wet) (meq/g <sub>Resin</sub> )		2.57

<sup>a</sup> Calculated as phthalic acid.

properties that are desirable for many cation exchange procedures.<sup>28,29</sup>

As mentioned previously, in the presented study hydroxyethyl cellulose was esterified with phthalyl chloride to obtain a resin containing free carboxylic acid groups. The formation and representative structure of the prepared resin is given in Scheme 1.

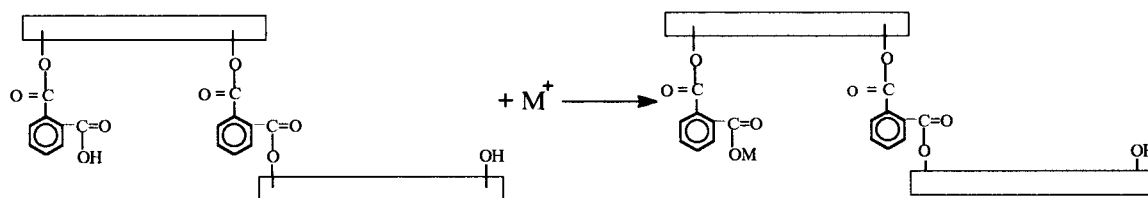
In order to verify this type of structure some chemical analyses were applied. For this purpose, acid, saponification, and hydroxyl values of the resin were determined. The results are given in Table I. As can be seen, the decrease in acid and hydroxyl values and accompanied increase in ester value show that esterification reaction was occurred under the applied conditions. No doubt that the ester product contains free carboxylic acid groups.

It is obvious that the resin is in the crosslinked structure since the precipitated portion of the reaction medium was separated as the main product. Due to this fact, the swelling percentage value was determined and found to be 75.94%.

In the application of prepared resin, the principle reaction occurring between ion exchanger and heavy metal ions can be represented by the reaction in Scheme 2.

The total ion exchange capacity on the basis of wet resin was found as 2.57 meq g<sup>-1</sup>. As mentioned, cellulose based ion exchangers were investigated previously for the same purposes, and the capacities in the range of 0.7–2.7 meq g<sup>-1</sup> were reported, depending on the functional groups inserted to the cellulose molecule. In the present study, hydroxyethyl cellulose was chosen as a cellulose derivative, and carboxylic acid groups were attached to this molecule. It is thought that this new structure should effect the capacity due to the difference in the structure of hydroxyethyl cellulose compared to that of cellulose. The total capacity of the obtained resin is good enough compared to literature values.

Because the ion exchange resin is to be used in aqueous media at various pH values, water resistance, acid resistance, and alkaline resistance were tested. For this purpose, ion exchanger samples were retained in water and in HCl and NaOH solutions. As seen in Table II, no appreciable changes occurred in acid and ester values of the resin retained in water and acid solution. It is clear from these results that the resin obtained was firm enough for use in aqueous and acidic solutions. Thus, the ion exchanger cellulose can be loaded in a series of cycles with solutions of

**Scheme 2**

**Table II** Some Properties of Ion Exchange Resin after Retaining in Water, HCl, and NaOH Solutions

Resin Retention	Saponification Value	Acid Value	Ester Value
Retained in distilled water <sup>a</sup>	215.40	73.00	142.90
Retained in acid solution (pH 2) <sup>a</sup>	214.67	73.00	141.67
Retained in NaOH solutions at pH 8 <sup>b</sup>	215.2	73.00	142.2
Retained in NaOH solutions at pH 9 <sup>b</sup>	198.3	65.7	132.6

<sup>a</sup> Test was conducted for 28 days.

<sup>b</sup> Test was conducted for 168 h.

heavy metals and unloaded again with HCl solution without any noticeable loss of capacity. Additional tests at pH 8 and 9 were also performed in order to understand the upper limit value of pH, which causes cleavage on the resin molecule. As seen in Table II, in the case of NaOH solution at pH 9, the ester value decreased to 132.6 from the original value of 142.2. On the other hand, at pH 8, no remarkable change occurred in the resin molecule. These result showed that the resin prepared in the present study can be used at pH values lower than 9. This type of test was also performed in previous works,<sup>15,30</sup> for the cellulose-based resins modified with melamine formaldehyde and phenol formaldehyde. These reports explained that the durability of the above-mentioned resins were good. Although the ion exchange resin obtained in the present study is not further modified with a synthetic resin, it showed a good durability against water and acid solution, as well as alkaline solution up to pH 9, due to sufficient crosslinking.

The effect of pH on the ion exchange capacity is summarized in Table III. As seen, the exchange capacity reaches a maximum value at pH 6. At low pH values, the capture is becoming lower, and this fact is very important in view of regeneration

of the resin with acidic solution. On the other hand, at higher pH values alkali metal becomes competitive to heavy metal ions and prevents the binding of heavy metal to resin matrix as expected. By evaluating the adsorption capacities of resin at pH 6, the selectivity can be ordered as  $\text{Fe}^{3+} \approx \text{Cu}^{2+} \approx \text{Co}^{2+} > \text{Zn}^{2+}$ .

The ability of the resin to capture the different heavy metal under the column operation is summarized in Figure 1. As seen,  $\text{Zn}^{2+}$  showed the weakest binding characteristic among the metals studied.  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Co}^{2+}$  metal ions appeared in solution after passing of 700 mL effluent. By evaluating the amount of the metals at this point, the selectivity order can be given as  $\text{Fe}^{3+} \approx \text{Cu}^{2+} \approx \text{Co}^{2+} > \text{Zn}^{2+}$ . This behavior is in agreement with the batch capacity result.

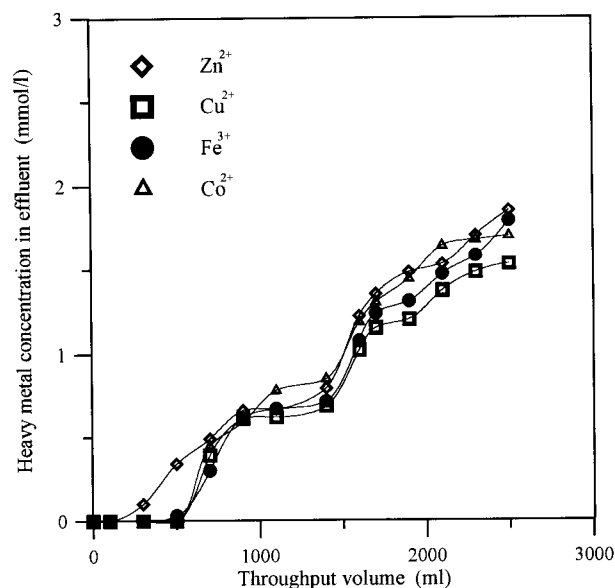
During the course of adsorption of metal ions on ion exchange resin, changes in color are observed. The process of loading and unloading can be observed by the color change of the exchanger material. The colors of metal ion containing resins are similar to those of the starting metal ion. Chromatographic determination of heavy metals is also possible by means of columns filled with obtained ion exchanger because colored, metal-

**Table III** Dependence of Ion Exchange Capacity on pH

Metal Ions	Effluent Concentrations (mmol 100 mL <sup>-1</sup> ) after 24 h at Different pH Values						
	2	4	6	8	10	12	14
$\text{Fe}^{3+}$	1.35	1.36	0.68	0.77	0.80	1.39	1.529
	(0.179)	(0.169)	(0.849)	(0.759)	(0.729)	(0.139)	(—)
$\text{Co}^{2+}$	1.68	1.57	0.86	0.90	0.94	1.48	1.696
	(0.016)	(0.126)	(0.836)	(0.796)	(0.756)	(0.216)	(—)
$\text{Cu}^{2+}$	1.57	1.54	0.79	0.88	0.90	1.45	1.573
	(0.003)	(0.03)	(0.783)	(0.693)	(0.673)	(0.123)	(—)
$\text{Zn}^{2+}$	1.78	1.65	0.91	0.99	1.20	1.53	1.79
	(0.01)	(0.14)	(0.88)	(0.8)	(0.59)	(0.26)	(—)

Values given in parenthesis represent the amount of metal captured by resin.





**Figure 1** Exhaustion curves for test solutions containing metal chlorides.

specific layers develop, and these can be helpful for qualitative evaluation.

## CONCLUSION

This study showed that half ester of hydroxyethyl cellulose with phthalyl chloride can be used as ion exchange resin to remove heavy metals from the aqueous solutions. It should be emphasized that the pH of the solution was found to be 6 for efficient metal capture. The capacity of the prepared resin was determined as  $2.57 \text{ meq g}^{-1}$  resin, and this value is good compared to those given in the literature. The resin capacity is not effected in water and acidic medium; thus, the resin can be used for a number of cycles period.

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