

## Preconcentration and Removal of Cu(II) Ions using Diisocyanate Derivatized Ethylene-Vinyl Alcohol Copolymer Ion Exchange Resin

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### ABSTRACT

In this study, diisocyanate derivatized ethylene-vinyl alcohol copolymer, having polymeric chain instead of network structure, was synthesized by the reaction of isophorondiisocyanate with a product gained as a result of the reaction between EVOH and maleic anhydride at 70 °C. Isocyanate groups of last product were converted to  $-NH_2$  groups by hydrolysis and FTIR spectrum was proved this group with the peak at  $3318\text{ cm}^{-1}$ . Synthesis of this resin is easier than polystyrene-divinyl benzene based resin. Analytical study of this resin as an ion exchanger showed that maximum Cu(II) uptake capacity of resin is 0.15 mmol Cu(II) ion/g sorbent, and maximum 93.8% of retained Cu(II) ions can be recovered with 1 M HCl solutions.

**Keywords:** preconcentration; copper(II); EVOH; chelating resin

### INTRODUCTION

Environmental heavy metal contamination is a serious problem that threatens living organism. These pollutions are drifted everywhere with circulation and joined the food chain. As being a heavy metal, copper is an important industrial material which is abundant in electroplating, steel or metal finishing industrial wastewaters. Many processes such as precipitation, ion exchange, reverse osmosis or adsorption have been used to remove heavy metal ions from wastewater<sup>1,2</sup>. Because of their abundance, low cost, feasible and high adsorption capacity, ion exchange and adsorption processes are preferred than the other methods<sup>3</sup>. Ion exchangers are frequently used for separation rather than preconcentration<sup>4</sup>. But especially chelating resins have been used for the preconcentration of heavy metal because of high stability of metal-chelates<sup>5</sup>. Ion exchange resins such as derivatized polystyrene-divinyl benzene or phenol-formaldehyde are crosslinked polymeric networks having S, N, O donor atoms. Because Copper(II) ions give stable complexes with  $-NH_2$  groups in accordance with Irwing-

Williams Order, the resins having N atoms have been widely used for copper(II) separation or preconcentration<sup>1</sup>.

EVOH copolymer is a well known thermoplastic with advanced barrier properties against gases, flavors and aromas in food, medical, cosmetic, packaging applications etc. Since EVOH copolymer is the hydrolyzation product of ethylene-vinyl acetate copolymer (EVA) the content of hydroxyl functionalities on the polymer backbone of EVOH can be adjusted. Thus, the  $T_g$  of the copolymer gets higher as the hydroxyl content increases due to the increased hydrogen bonding between the polymer chains and this issue makes EVOH superior than polyvinyl alcohol (PVA).

There has been vast amount of studies about the modification of poly vinyl alcohol<sup>6-8</sup>. Thus EVOH is also suitable for polymer modification through the hydroxyl functionalities. There has been a few studies concerning the modification of EVOH with anhydrides. Fedtke performed the reaction of EVOH and maleic anhydride and cured the product with a

commercial epoxy resin within a series of reactions concerning the production of a thermoset polymer network<sup>9</sup>. Bruzaud reacted EVOH with phthalic anhydride and further modified the product with several reagents for other polymeric reactions<sup>10</sup>.

The aim of this study is to obtain an amine functionalized ion exchange resin which separates Cu(II) cation from media and preconcentrates trace amount of copper ions. This resin can be purified with liquid and/or solids via reprecipitation.

## EXPERIMENTAL

### Materials

EVOH copolymer (44 mol % ethylene), maleic anhydride, and isophorone diisocyanate (IPDI) were obtained from Sigma-Aldrich and used as received. Dimethyl amino pyridine (DMAP) was received from Fluka.

The chemicals CuCl<sub>2</sub>·2H<sub>2</sub>O, NH<sub>4</sub>CH<sub>3</sub>COO, NaOH, NaCl, HCl (concd.) were of Merck, analytical reagent grade. DMF and DMSO were of Sigma-Aldrich

### Synthesis of EVOM

6 g of EVOH (0.09 mol hydroxyl group content<sup>10</sup>) was dissolved by heating up to 60 °C in 20 mL of dimethyl formamide and 3 g of maleic anhydride was added and left for overnight. The resulting viscous light yellow solution was then precipitated into methanol, collected, redissolved in DMF and reprecipitated into methanol once more. The white solid was collected dried in vacuum and dark at 40 °C.

### Synthesis of EVOMIS

1 g of EVOM was dissolved in predried DMF and sealed with rubber septum and purged with nitrogen. 1.6 g (7.2 mmol) IPDI was injected to medium followed by the addition of reaction catalyst 0.026 g DMAP dissolved in 3 mL dried DMF. Solution was stirred at room temperature for 24 hours and precipitated in to methanol. White solid was redissolved in DMF and reprecipitated in to methanol, dried under vacuum.

The resin was characterized by using FT-IR (Perkin Elmer, Spectrum 100), DSC (Seiko DSC 7020 with a 10 C/min heating rate) and TGA (Seiko, TG/DTA 6300).

### Column Experiments

2.1768 g resin was filled to glass column of  $\phi$  9.5 mm and 25 cm<sup>3</sup>. Volume of swelled sorbent is 5 cm<sup>3</sup>. pH of solutions were adjusted by the use of a Orion 5 Star pH-meter.

Cu(II) working solutions were prepared from 1000 ppm stock Cu(II) solution which was initially prepared by dissolving 2.6850 g CuCl<sub>2</sub>·2H<sub>2</sub>O in 1 L distilled water. 250 mL of 200 ppm Cu(II) solution was passed through the column, and column was eluted with 25 mL of 1 M HCl solution. All experiments were performed at room temperature.

At the second step, 120 ppm Cu(II) solution was prepared in 0.1 M NH<sub>4</sub>CH<sub>3</sub>COO. 250 mL of this solution was passed through the column at pH 5.44, then column was eluted with 25 mL of 1 M HCl.

In all experiments flow rate was adjusted at 1.06 mL/min and Cu(II) analysis was performed using Varian 220AA-Spectrometer. The pHs of Cu(II) solutions were adjusted under the limiting pH of Cu(II) solubility for working concentrations using Eq. 1<sup>14</sup>.

$$pM_t = 1.999 \text{ pH}^* - 8.29 \quad (1)$$

### Preconcentration Experiments

7 L of 2 ppm Cu(II) solution was passed through the column including 2.1768 g resin. The pH of the solution was adjusted at pH 6 using 0.1 M NH<sub>4</sub>Ac solution. Retained Cu(II) was eluted with 20 mL of 1 M HCl solution and measured using FAAS.

## RESULTS AND DISCUSSION

### Result of Synthesis Reactions

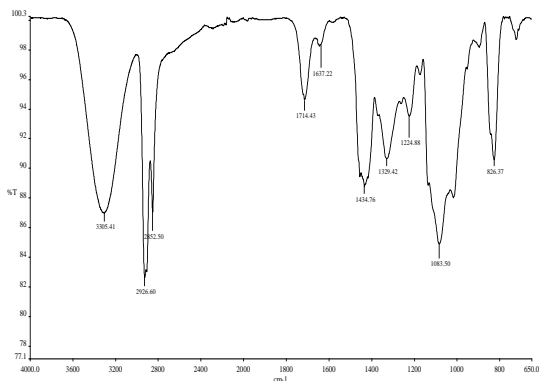
Hydroxyl functionalities of EVOH were reacted with maleic anhydride to obtain EVOM. Since the reaction of hydroxyl group and acid anhydrides is quite feasible and well known<sup>11</sup> no further catalyst was utilized.

Some EVOM was dissolved in DMSO and titrated with standardized NaOH and was found to have 63% of the hydroxyl groups were reacted with maleic anhydride according to the calculation method declared in reference 5.

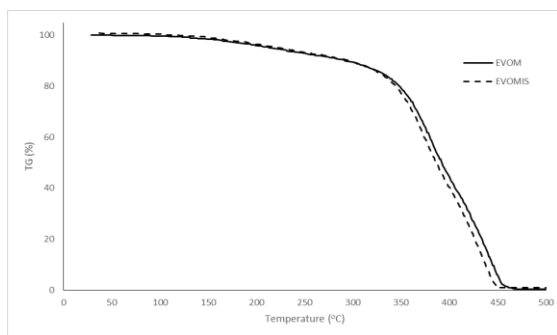
The FT-IR spectrum of last product was given in Figure 1. The formation of classical carboxylic acid band at 1714 cm<sup>-1</sup> and unsaturation band at 1637 cm<sup>-1</sup> of maleic anhydride confirm the addition of maleic anhydride to the EVOH copolymer. The glass transition temperature, T<sub>g</sub>, was also increased from 53 °C to 62 °C. This increase is probably due to the blocking of free rotation of polymer chains with the incorporation of maleic ester groups. Thermogravimetric analysis of the EVOM adduct revealed two decomposition profiles (Figure 2). First profile shows a 8% weight loss at 250 °C that corresponds to the

maleic group titration result if the 0.09 mol of hydroxyl was taken as a starting reference. The second profile is the total decomposition that occurred at around 400 °C.

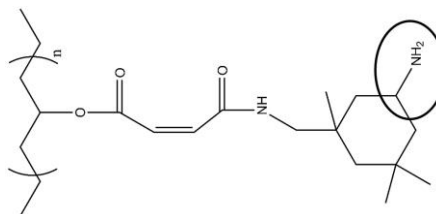
Isophorone diisocyanate was incorporated to the EVOH adduct via the DMAP catalyzed reaction of carboxylic acid and isocyanate group to form an amide linkage without the interference of hydroxyl groups<sup>12</sup> and designated as EVOMIS. Secondary isocyanate structures are much less reactive in the case of aliphatic isocyanate at room temperature<sup>13</sup>. Amine groups were generated by treating the secondary isocyanate groups with water just after the formation of amide group. The FT-IR spectrum (Figure 1) revealed the formation of amide carbonyl band at 1651 cm<sup>-1</sup>, N-H stretching at 1560 cm<sup>-1</sup> and 1220 cm<sup>-1</sup>. TGA curve of EVOMIS displayed similar decomposition profile as shown in Figure 2. Considering all data, authors suggest the structural formula for resin showed in Figure 3.



**Figure 1** The FT-IR spectrum of amine functionalized EVOH copolymer



**Figure 2** TGA curves of both intermediate EVOM and final product EVOMIS



**Figure 3** The suggested structural formula of amine functionalized EVOH copolymer

**Results of Column Experiments**

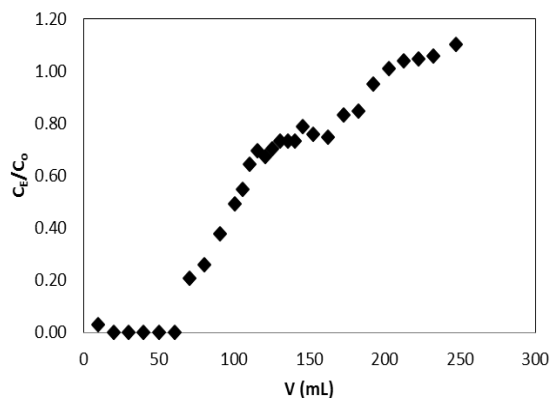
As seen from Table I, all pHs of working solutions are under the limiting pH of solubility of Cu(II). So, surface precipitation is not taken place simultaneously with the ion exchange reaction.

**Table I** Limiting pH of solubility values of working Cu(II) solutions

C <sub>0</sub> (ppm)	pH*	Working pHs
2	6.40	6.00
120	5.51	5.44
200	5.40	5.08

As seen from Figures 4-5, early breakthrough curves were observed during the ion exchange process with amine functionalized EVOH copolymer. Half of the maximum uptake capacity was achieved during the first 100 mL-portion of solution passed. Higher values than 100% in Figure 4 are probably sourced from experimental error.

**Figure 4** Breakthrough curves of 200 ppm Cu(II) solution on functionalized EVOH copolymer



(pH=5.08, 2.1768 g resin, flow rate=1.06 mL/min)

The resin capacities which were determined after eluting the retained Cu(II) with 1 M HCl were shown in Table II. The uptake capacity(Q<sub>e</sub>, mg) was calculated using Eq. 2<sup>15</sup>.

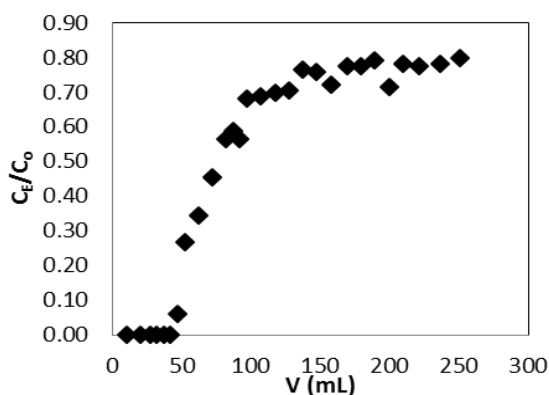
$$Q_e = Q_t / m \quad (2)$$

where  $Q_t$  is the total quantity(mg) of adsorbed Cu(II) cation, and  $m$  is the mass of resin(g).

As seen from Table II, the resin performed well. The experimental conditions are optimal for both Cu(II) detention and elution. Surface amine groups of resin are partly in protonated form at working pH(5.0-5.5)<sup>16</sup>. When the Cu(II) amount achieves critical concentration through column, Cu(II) ions are switched with  $H^+$  ions because of stronger bonding between Cu(II) and N atoms. Thus, increasing curve on the graph(Figure 4) appears after 50 mL of Cu(II) solution passed through from the column. The reason of lower recovery of Cu(II) for 200 ppm initial concentration can be explained by the fact that irreversible retention on resin increases in the absence of buffer solution.

**Table II** The resin capacity for Cu(II)ion and recovery values obtained from 1 M HCl elution

[Cu <sup>2+</sup> ] (ppm)	pH	Q(mmol Cu(II)/g ads.)	Recovery %
120	5.44	0.10	93.85
200	5.08	0.15	59.08



**Figure 5** Breakthrough curves of 120 ppm Cu(II) solution on functionalized EVOH copolymer(pH=6.01, 2.1768 g resin, flow rate=1.06 mL/min, in the presence of 0.1 M NH<sub>4</sub>Ac)

Depending on solution pH, amine-based molecules can act as both cation and anion chelators<sup>16</sup>. Although having variable uptake capacity, the resin cannot release the retained Cu(II) ions because of irreversible reactions occurred on the surface.

#### Result of Preconcentration Experiments

After eluting Cu(II) ions with 20 mL of 1 M HCl solution, it was observed that 47.22% of retained Cu(II) recovered. Low recovery values enhanced the thoughts of irreversible reactions possibility between surface and copper ions.

#### CONCLUSIONS

In this study, aminated resin was obtained via cheaper and easier synthesis method than polystyren-divinyl benzene based resin.

This resin has been behaved as chelating resin. Because Cu(II) gives the most stable complexes with N-donor ligands, it is possible to form coordinative covalent bonds with N atoms of amine group of resin. So, it leads early breakthrough and irreversible adsorption.

Consequently, this amine functionalized resin which is obtained simpler and cheaper way can be used for Cu(II) removal and preconcentration of trace amounts of copper ions.

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#### REFERENCES

- [1] Yalçın S., Apak R., Hizal J., Afşar H., *Separation Sci. and Technology* **2001**, 36(10), 2181-2196.
- [2] Chen C.Y., Chiang C.L., Chen C.R., *Separation and Purification Technology* **2007**, 54, 396-403.
- [3] Shukla S.R., Pai R.S., Shendarkar A.R., *Separation and Purification Technology* **2006**, 47, 141-147.
- [4] Jal P.K., Patel S., Mishra B.K., *Talanta* **2004**, 62, 1005-1028.
- [5] Su Z.X., Chang X.J., Xu K.L., Luo X.Y., Zhan G.Y., *Anal. Chim. Acta* **1992**, 268, 323-329.
- [6] Levesque G., Chiron G., *Ind. Eng. Chem. Res.* **1987**, 26, 899-902.
- [7] Arranz F., Bejerano E.M., Sanches-chaves M., *Macromolecular Chemistry and Physics* **1994**, 195, 3789-3798.
- [8] Baudrion F., Perichaud A., Coen S., *Journal of Applied Polymer Science* **1998**, 70, 2657-2666.
- [9] Fedtke M., Henning K., *Macromolecular Symposia* **1989**, 28, 203-216.
- [10] Bruzard S., Levesque G., *Macromolecular Chemistry and Physics* **2000**, 201, 1758-1764.
- [11] Esen H., Küsefoğlu S., Wool R., *Journal of Applied Polymer Science* **2007**, 103, 626-633.
- [12] Sasaki K., Crich D., *Organic Letters* **2011**, 13, 2256-2259.
- [13] Schuemacher A.C., Hoffmann R.W., *Synthesis* **2001**, 74, 7383-7388.
- [14] Apak R., Hizal J., Ustaer C., *J. Colloid and Interface Science* **1999**, 211, 185-192.
- [15] Ramirez C.M., Silva M.P., Ferreira S.G.L., Vasco O.E., *J. Hazardous Materials* **2007**, 146, 86-90.
- [16] Bryantsev V.S., Diallo M.S., Goddard W.A., *J. Phys. Chem. A* **2007**, 111, 4422-4430.