

Application of α , β and γ cyclodextrin polyurethanes in the removal of size specific copper derivatives

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Abstract

Copper can be found in many wastewater sources including, printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations. Typical concentrations vary from several thousand ppm from plating bath waste to less than 1 ppm from copper cleaning operations. Copper can be removed from wastewater by precipitation as an insoluble hydroxide salt or by ion exchange. In this study, single batch adsorption experiment of copper derivatives, e.g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from aqueous solutions with epichlorohydrin linked α , β and γ cyclodextrin polyurethanes (CDPs) have been investigated for a wide range of experimental conditions: pH, metal concentration and CDP amounts. The aim of this study was to specify highly effective derivatives of copper to fit on the CDP backbone as the size of the copper molecules is different to each other. Recent studies have shown that α , β and γ CDPs are capable of removing copper ions of all derivatives from water to desirable levels with enhanced sorption capabilities. The adsorption efficiencies of CDPs were surprisingly similar and found to be independent for each type of copper derivatives. The phosphate buffer with pH 6.5-7.5 was found the best alkaline environment to remove the ions. Current technologies have been



removed 95% copper ions from solution and unit gram of β -CDP was capable to remove 118 mg of copper ions. These polymers already established as the good carries of organic substances and by combining the inorganic compounds removal, it may be possible to develop a simultaneous system to confiscate both organic and inorganic compounds from waste water.

Keywords: cyclodextrin polymer, heavy metal, remediation, water pollution, adsorption.

1 Introduction

Organic and inorganic water pollutants pose threat to human health even at low concentrations. For instance, because organic pollutants persist in the environment for long periods of time, they can be absorbed by plants thereby finding their way to poisoning the food chains of living organisms [1]. Heavy metal pollution in industrial wastewater has attracted global attention because of its adverse effects on the environment and human health. It is, therefore, crucial to remove these heavy metals from wastewaters effectively before their discharge into the environment.

One of the primary sources of heavy metal pollution in developing countries is industrial discharge. Taking into consideration the toxicity and the bioaccumulation of organic and inorganic pollutants, a dual separation technique to remove both inorganic and organics from water needs to be developed. Currently heavy metal removal methods include chemical precipitation, ion exchange, liquid–liquid extraction, membrane filtration, adsorption and biosorption have widely been used. Among these methods, adsorption is simple and cost effective [2]. In this paper, we utilized modified cyclodextrin polyurethanes for the extinguishing of copper from the copper derivatives containing waste water.

Cyclodextrins (CDs), first discovered by Villiers in 1891, are cyclic oligosaccharides consisting of six cyclodextrin, seven cyclodextrin, eight cyclodextrin or more glucopyranose units linked by (1,4) bonds (fig. 1). They are also known as cycloamyloses, cyclomaltoses and Schardinger dextrins. They are produced as a result of intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase (CGTase) enzyme. CDs have a non-polar cavity which provides a micro-environment for the encapsulation of non-polar, low molecular weight compounds. However, the water solubility of CDs is the main obstacle for water treatment purposes. So, it was highly needed to make them water insoluble by developing effective surface area and enhancing functionality to adsorb metal ions [3].

The α , β and γ CDPs used in this study have been prepared and modified by reacting cyclodextrin and epichlorohydrin (a highly volatile liquid with a chloroformlike odor, C_3H_5ClO : used as a solvent for resins) in aqueous alkaline medium. In the reaction, the cyclodextrin is reacted with 10 to 20 moles of an alkali hydroxide, 10 to 20 moles of epichlorohydrin and 2 to 8 moles of an alcohol additive (n-octanol, glycol derivative or glycerol) calculated on 1 mole of cyclodextrin optionally in the presence of 10 to 15 moles of an organic solvent

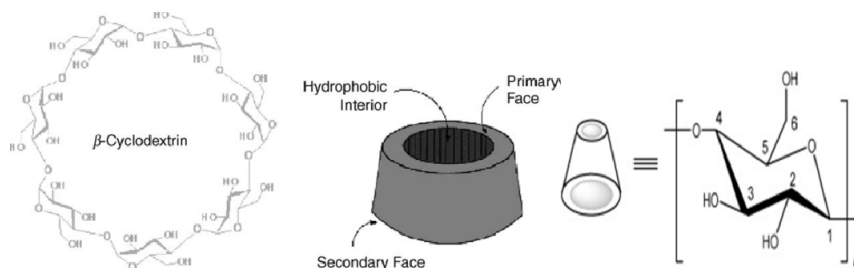


Figure 1: Chemical structure of β -cyclodextrin, representative of other cyclodextrin polymers [5].

that vaporizing at the reaction temperature or 8 to 12 moles of a high boiling organic solvent assuring heterogeneous phase [4].

Copper derivatives like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ have different molecular mass, size and ionic environment in the solution. Expecting the differences in rate to absorb the derivatives of copper into the polymer, this experiment has been conducted to specify the one which better suits on the backbone of cyclodextrin polymers especially on β -CDP.

2 Experimental details

2.1 Materials

The CDPs were provided by the Environmental Engineering Company Limited (Cyclochem Co. Ltd.) of Japan. pH were maintained at 6.5 by preparing phosphate buffer and measured with a pH meter (Model HM-25R, DKK-TOA Corporation, Tokyo, Japan). Stock solutions were prepared by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in double distilled water. Other chemicals were purchased from 'Wako pure chemicals industries, Ltd. (Kyoto, Japan). All reagents were of AR grade chemicals. The pH of the test solutions was adjusted using reagent grade dilute sulfuric acid and sodium hydroxide. The CDPs used in this study were the derivatives of dioxins usually adsorb low molecular weight organic compounds. After adsorption, they can release the particles easily in organic compounds but slowly in water [4].

2.2 Methods

2.2.1 The adsorption experiments

The experiment were performed using model pollutants of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Generally, 30 ml of each pollutant containing 10 ppm of metals was passed through the solution of polymers (50 to 500 mg) at pH 6.5. The mixture was gently stirred under room temperature ($25 \pm 3^\circ\text{C}$) from 0 to 48 hrs followed by centrifugation at 2,500 rpm for 5 min. The obtained supernatant was filtered by 0.45 μm pore size Millipore Membrane filters (OmniporeTM, Ireland) to remove the insoluble materials. The contents of copper

in the solution were measured with a Hitachi flame absorption spectrophotometer, model 180-30 (Tokyo, Japan). A calibration curve was plotted in order to determine the amount of the spiked pollutants absorbed by the polymers.

The accumulate amount of metal on the polymer and the metal removal efficiency were calculated by

$$M = \frac{(C_i - C)}{W} \cdot V \quad (1)$$

where, M refers the adsorbed copper on the polymer in mg; C_i and C are the initial and equilibrium concentrations (mg/L) of metal ion in the solution; V is the volume (L) and W is the weight (g) of the adsorbent. To describe the efficiency of metal ion removal from the solution, the recovery factor (RF) was calculated:

$$RF (\%) = \frac{C_i - C}{C_i} \cdot 100 \quad (2)$$

where, C is the metal ion concentration at some given time in the solution and C_i the initial concentration of metal ion.

2.2.2 Adsorption kinetics

For the kinetics experiments, the initial copper ion concentrations were 10, 50, 100 and 200 ppm and pH were maintained at 6.5 (pH was not controlled during experiments). The temperature range used in this experiment was $25 \pm 3^\circ\text{C}$. Then the copper solutions containing the polymer were agitated for a contact time of 1-24 hours and followed the procedure mentioned in the above adsorption experiment. Triplicate experiments were carried out in each case and the reproducibility was found to be fairly good.

2.2.3 Morphological observation by Scanning Electron Microscope (SEM)

All micrographs of the polymers were taken with a Hitachi S-4000 scanning electron microscope (Ibaraki, Japan). Samples were mounted on aluminum stubs with carbon tape on a graphite support unit. They were then coated with gold to make the surface conductive and to also improve visibility. The samples were finally subjected to an electron beam of energy under vacuum to obtain the micrographs with acceleration voltage of 10 KV. For transmission electron microscopy (TEM), the graphite nano sheets were homogenously dispersed in 2-propanol under ultrasonication for 30 min. A few drops of the suspension were deposited on the TEM grid covered with the membrane dried and evacuated before the analysis. The preparations were observed using Hitachi H-800 transmission electron microscope (Ibaraki, Japan). The acceleration voltage was 75 KV.

2.2.4 Brunauer-Emmet-Teller (BET) analysis of the CDPs

For Brunauer-Emmet-Teller (BET) analysis, an automated gas adsorption analyzer BEL SORP 28SA (Bel-Japan-Inc, Japan) was used. Samples were

degassed with N_2 using the Micrometrics Degassing System at 120 °C prior to measurement of pore volume and surface area. Degassing was carried out under liquid nitrogen for 12 h at a constant N_2 flow rate of 60 mL/min.

2.2.5 Statistical analysis

Each experiment has been carried out at least five times and the mean \pm SD (standard deviation) has been considered for data analysis to confirm representative. Data on metal concentration in the samples were analyzed for statistical significance by one-way ANOVA followed by student's t-test and values of P less than 0.05 were considered to indicate statistically significant differences. Instat 3 for Macintosh, Ver. 30 a (Graphpad Software, Inc. CA USA) were used to perform all statistical analysis.

3 Results and discussion

3.1 Characterization of the polymers

SEM was utilized in order to understand and compare the surface morphology, texture and level of porosity in the material under study. The SEM micrographs of α , β and γ CDPs are shown in fig. 2. The surface of these polymers were round shaped, irregular bead size, smooth texture, sometimes exhibit amorphous and spongy surface and sometimes with no openings.

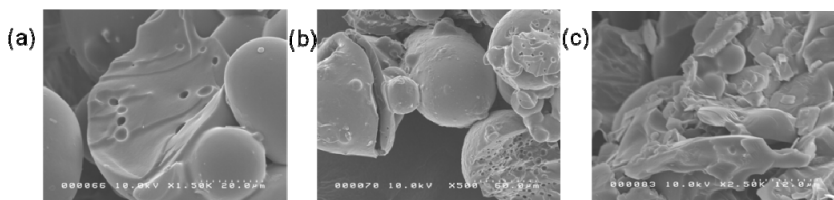


Figure 2: SEM images of the α -CDP (a), β -CDP (b) and γ -CDP (c).

To understand the physical properties and their relation to the adsorption efficiencies of CDPs, we measured the BET surface area, pore size distribution, total pore volume, pH, vapor pressure and solubility. The BET results showed that there is no correlation between the surface area or the pore size and the adsorption efficiencies of the polymers. These polymers ranged 60-300 μ m in size, insoluble in water and organic solvent, non digestible, granular bead texture, white color, neutral in water (pH 6.5) and low surface area.

3.2 Adsorption of Cu^{2+} ions onto CDPs

3.2.1 Effects of pH

The pH is the key parameter in the adsorption process [6]. The effects of initial solution pH on Cu^{2+} adsorption onto CDPs were investigated only at pH 6.5, 25°C, and an initial Cu^{2+} ion concentration of 10 mg/L. Keeping in mind that the

Cu^{2+} adsorption capacity increases with the increase of pH in solution due to less insignificant competitive adsorption of hydrogen ions [7]. At a lower initial Cu^{2+} concentration (10 mg/L), the adsorption capacity increases with increasing the solution pH and then remains almost unchanged at concentration up to 200 mg/L at pH 6.5. This might be due to the fact that almost all Cu^{2+} ions are adsorbed. Cu(II) species can be avail in aqueous solution in the forms of Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})^{3-}$ and $\text{Cu}(\text{OH})_4^{2-}$ and the predominant copper species at $\text{pH} < 6.0$ is Cu^{2+} [8]. Copper derivatives $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ used to give the above mentioned ions in solution and this whole adsorption study was performed at pH level 6.5. So, it was expected that pH level above and below the level, maintained in this experiment will be lead to drop the adsorption efficiency of CDPs to hold the Cu^{2+} ions.

3.2.2 Kinetics experiment

Single batch adsorption experiment was executed to know the kinetics of Cu^{2+} adsorption onto the β -CDPs backbone. The Cu^{2+} concentration ranging from 10 to 200 mg/L and at $25 \pm 3^\circ\text{C}$ were considered for the batch experiment. High sorption occurred with the increasing trend of layer formation around the surface of β -CDP backbone. And the adsorption efficiency increases with the increase of metal ion concentration. To investigate the high contact time to reach optimum equilibrium, agitating of the solution was strictly constrained into 24 hrs. Two kinetic models named Freundlich isotherm and BET isotherms (figs. 3 and 4) were considered to describe the adsorption kinetics of β -CDP.

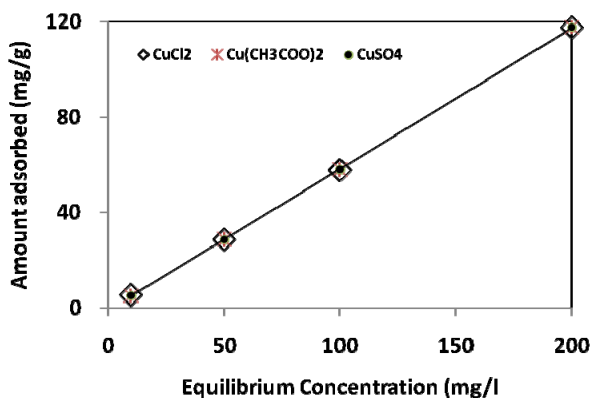


Figure 3: Adsorption isothermal curve of Cu^{2+} on β -CDP. Adsorption condition: adsorbent dose= 1.66 g/L, pH 6.5; temperature= $25 \pm 3^\circ\text{C}$. The solid lines represent the fitting of data by Freundlich isotherms (linear form).

The results obtained for β -CDP did not support by fitting to the Langmuir type adsorption isotherm but fitted well in Freundlich isotherm and BET isotherm (as the polymers possess low surface area). The Freundlich equation may be written as

$$q_e = K_F C_e^{1/n} \quad (\text{Non-linear form}) \quad (3)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (\text{Linear form}) \quad (4)$$

where q_e refers the adsorbed amount of ions per unit weight of adsorbent (mg/g), C_e refers equilibrium concentration of solute in the bulk solution (mg/L), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant indicative of the intensity of the adsorption [9]. Considering $1/n = 0$ as the adsorption study was performed at atmospheric temperature and pressure.

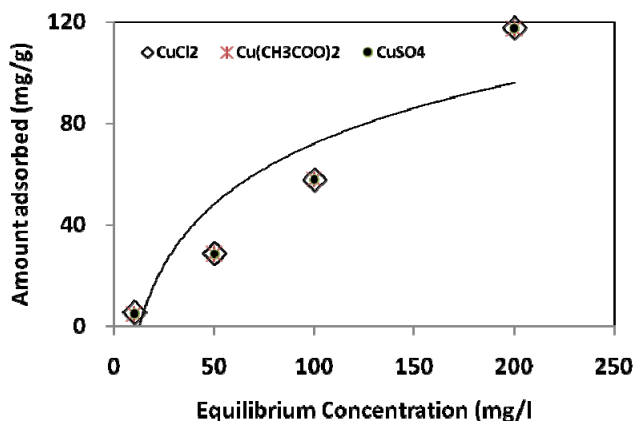


Figure 4: Adsorption isothermal curve of Cu^{2+} on β -CDP. Adsorption condition: adsorbent dose = 1.66 g/L, pH 6.5; temperature = $25 \pm 3^\circ\text{C}$. The solid lines represent the fitting of data by Freundlich isotherms (non-linear form).

3.2.3 Effects of adsorbent and adsorbate concentration

CDPs favor the adsorption of high concentration of heavy metal ions in the solution. On the contrary, it was interesting that the low concentration of heavy metal ions were markedly reduced to adsorb into CDPs.

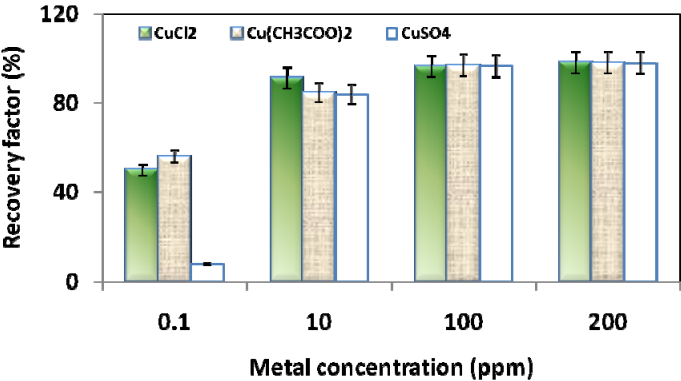


Figure 5: Effects of adsorbate concentration on the rate of adsorption of Cu^{2+} derivatives by CDPs at pH 6.5. Adsorbent dose was 1.66 g/L.

For example, the adsorption ratio gradually increases to 95% from 10 ppm to 200 ppm of Cu^{2+} ions, whereas significantly decreases below 10 ppm of Cu^{2+} ions in the solution. Lower concentrations of Cu^{2+} were not enough to provide the energy required in replacing the hydronium ion from the binding site of the CDPs (fig. 5). On the other hands, the uptake is higher at low adsorbate concentrations and increases when the adsorbate concentrations are higher (fig. 6). But, no significant differences were recorded for the adsorption of Cu^{2+} adsorbed by different amount of adsorbate. It was also observed a balance

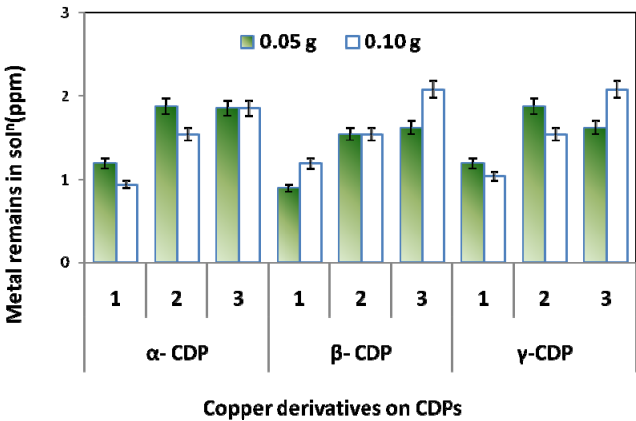


Figure 6: Effects of adsorbent amount on the adsorption efficiency of α , β and γ CDPs. Adsorption condition: adsorbent amount 0.05 g and 0.1 g, initial Cu^{2+} derivatives concentration 10 mg/L (1 = CuCl_2 , 2 = $\text{Cu}(\text{CH}_3\text{COO})_2$ and 3 = CuSO_4), pH 6.5; temperature = $25 \pm 3^\circ\text{C}$.



between hydronium ions and metal ions in contrast with CDPs in solution. So, CDPs cannot remove 100% Cu^{2+} in solution and similar amount of ions always remains after adsorption in same volume of solution. Moreover, this study also revealed that unit gram of β -CDP have high potential to separate large quantity of Cu^{2+} ions (118 mg/g) in compare with other conventional sorption methodology [10].

Besides, it was expected that the derivatives of copper $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ will have different grade of interaction with β -CDP. But, the adsorption behavior on the backbone of β -CDP was found quite similar with each other. So, it may be suggested that the CDPs were not specific to any copper derivatives and will act on the copper pollutants with the same strength to remove from the water solution.

Furthermore, water insoluble cyclodextrin can be easily separated such as centrifugation and filtration. It was found that these polymers could be recycled at least 18 times while still maintaining their high sorption efficiency [11].

4 Conclusion

Water insoluble CDPs especially β -CDP can remove copper ions efficiently with high concentration. The copper derivatives haven't significant adsorption differences with the CDPs. However, the competitive sorption shows the preferential selectivity order: $\text{Cu}(\text{CH}_3\text{COO})_2 > \text{CuCl}_2 \cdot 2\text{H}_2\text{O} > \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Unit gram of β -CDP was capable to remove 118 mg of copper ions. These polymers have already been established as an excellent remover of organic pollutants from contaminated sites. By combining these dual separation techniques, it may be possible to develop a novel treatment procedure, suitable for simultaneous removal of both organic and inorganic pollutants from water treatment system.

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