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# Removal of cadmium and chromium ions using modified α, β, and γ-cyclodextrin polymers

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# Removal of cadmium and chromium ions using modified α, β, and γ-cyclodextrin polymers


## ABSTRACT

The adsorption of cadmium and chromium from aqueous solutions with epichlorohydrin cross-linked α, β, and γ-cyclodextrin polymers (CDPs) was investigated under a wide range of experimental conditions including pH values, metal concentration, and CDP amounts. Recent studies have shown that α, β, and γ CDPs follow the Freundlich, Langmuir, and Brunauer–Emmett–Teller models and are capable of reducing heavy metal ion concentrations in water to desirable levels with enhanced sorption capabilities. The removal of cadmium and chromium achieved equilibrium in 4 h. The pH of effective cadmium removal was 6.5 to 7.5, and phosphate buffer favored the removal of cadmium in the presence of potassium ion. Chromium removal was optimal at pH 3.6 to 6.5. Current technologies can remove 99% cadmium ions from solution, yet this process is not very efficient. Furthermore, a small amount of CDPs can remove large quantities of heavy metal ions and can then be regenerated with acid for reuse. The present results are promising for using inexpensive CDPs as a low-cost material that is effective in remediating waters contaminated with heavy metal species. The sorption kinetics of CDPs along with the conditions to adsorb cadmium and chromium are reported here for the first time.



**Keywords:** Cyclodextrin Polymer, Epichlorohydrin, Heavy Metal, Remediation, Adsorption

## INTRODUCTION

Water-insoluble epichlorohydrin cross-linked cyclodextrin polymers (α, β, and γ-CDPs) are introduced in this study as an alternative to the conventional remediation technology for metal ion uptake from solution. In recent years, water contamination with organic and inorganic pollutants, especially heavy metals, has been a significant concern. These elements eventually reach humans through the food chain by accumulating themselves in plants and animals (1). Heavy metals such as lead, cadmium, and mercury have affinity to sulfur, and hence, they attack the sulfur bonds of enzymes causing them to denature (2, 3). Due to this toxicity and bioaccumulation, a technique is needed to concurrently remove both inorganic and organic contaminants from water.

Cyclodextrins (CDs) are glucose-based macromolecules that can form complexes with organic contaminants and sometimes metals (4). The three most common CDs are their α, β, and γ forms consisting of six, seven, and eight glucose units, respectively (5-7). In our study, we assumed that the hydrophilic peripheral of CDs possess association potential to bind with certain inorganic ions, especially heavy metals, by the alcoholic hydroxyl groups. However, the parental CDs are soluble in water and thus their environmental application was limited and many research have been conducted so far to produce water insoluble CDs by polymerization with a bi-functional linker or others. Other work has shown that functionalization improves both their physical and chemical properties (5, 8).

Functionalization can alter the physical properties of CDs and also make them suitable for a wide range of applications. For example, the addition of specific functional groups can decrease their solubility; increase their stability in the presence of light, heat, and oxidizing

conditions; or decrease their volatility (9, 10). Cyclodextrin polymers purchased for this study was synthesized with epichlorohydrin, and the modified products have a high affinity for organic compounds at low (mg/L) concentrations (11, 12). Furthermore, the epichlorohydrin cross-linked CD polymers have been mainly used in pharmaceutical and food industries. Nevertheless, the interactions of CDs with inorganic ions, especially the heavy metals, have not been extensively investigated, and still remain unknown. To remove cadmium and other metal ions from wastewater, researchers have investigated different materials such as bone char (13), fly ash (14), lignite (15), peat (16), Scarp rubber (17), agricultural wastes (18), zeolites (19), and red mud (20). Some researchers have been trying to absorb heavy metals by combining the characteristics of CDs with ionic liquids (CD–IL polyurethanes) (21). Kozlowski et al. (22) studied the separation of metal ions by plasticized membranes with the application of hydrophobic β-CD polymers (CDPs). However, these adsorbents are limited by poor capacity for regeneration and recovery of the useful materials. This makes them unattractive for broad commercial applications. It is surprising that many studies have been conducted only with β CDP as the parental β-CD because it suffers from poor solubility (at 25°C in water 18 mg/cm$^3$). However, no comprehensive report is available on heavy metal removal using α and γ-CDPs.

This motivates research efforts to develop an industrially viable, economically feasible, environmentally compatible, and chemically recyclable material with quantitative recovery of the material in the removal of metal ions from wastewater. Because of the small amount of research detailing the separation of $Cd^{2+}$ and $Cr^{6+}$ by CDPs, we have studied the metal

sorption capabilities of α, β, and γ-CDPs. These polymers have already been reported to possess high efficiencies to encapsulate organic compounds such as organo-tin (triphenyltin) to suppress their toxicity, and are also used in recovering estrogenic substances from wastewater (23, 24). The heavy metal sorption efficiencies of these CDPs have been studied using model pollutants with the aim to develop a technology for simultaneous removal of both organic and inorganic compounds from wastewater. This paper describes the characterization and functionality assessment of the sorption capabilities of insoluble CDPs.

## MATERIALS AND METHODS

### Materials

α, β, and γ-CDPs were obtained from the Environmental Engineering Company Limited (Kankyo Kogaku Co. Ltd.) of Japan. β-CDP used in this study was prepared and modified by reacting β-CDs and epichlorohydrin in aqueous alkaline medium according to the methodology described by Szejtli, 1998. Epichlorohydrin ($C_3H_5ClO$) is a highly volatile liquid with a chloroform-like odor and is used as a solvent for resin (5). The buffer solutions for maintaining the desired pH were prepared to be 3.6, 5, 6.5–7.5, 8.1, and 9. The pH measurements were made using a pH meter (Model HM-25R, DKK-TOA Corporation, Tokyo, Japan). Stock solutions of the test reagents were prepared by dissolving cadmium and chromium salts (cadmium chloride and potassium dichromate) in double distilled water. In some cases, cadmium standard solution (1000 ppm) from $Cd(NO_3)_2$ in 0.1 mol/L $HNO_3$ and chromium standard solution (1000 ppm) from $K_2Cr_2O_7$ in 0.02 N HCl were purchased

from Wako Pure Chemicals Industries, Ltd. (Kyoto, Japan). All reagents were AR grade chemicals. The pH of the test solutions was adjusted using reagent-grade dilute sulfuric acid and sodium hydroxide.

**Adsorption experiments**

A 0.05 to 0.5 g sample of α, β, or γ CDP was added to 30 ml buffer solution (400 mM borate buffer, pH 9.0; 400 mM Tris-HCl buffer, pH 8.1; 100 mM phosphate buffer, pH 7 or 400 mM acetate buffer, pH 5.0 or 3.6) containing a single standard solution of 0.1, 1, 10, 20, 40, 60, 80, 100, 200, or 500 mg/L of cadmium, or 0.1, 1, 10, 100, or 200 mg/L of chromium. This sample was gently stirred under room temperature from 0 to 72 h followed by centrifugation at 2,500 rpm for 5 min. The obtained supernatant was filtered using 0.45 µm pore size Millipore Membrane filters (Omnipore™, Ireland) to remove the insoluble materials. After filtration, the solution was diluted 10-fold with deionized water. The cadmium or chromium concentration in the solution was measured with a Hitachi flame absorption spectrophotometer (model 180-30 (Tokyo, Japan)). The lower limit of sensitivity was 0.01 µg/ml. Parameters such as shaking time, retention time or adsorption duration, metal concentration in the solution, amount of CD, and pH on metal adsorption were investigated.

The metal concentration retained in the adsorbent phase (mg/g) was calculated by using the following formula:

$$M = \frac{(C_i - C)}{W} . V \qquad (1)$$

Here, $C_i$ and $C$ are the initial and equilibrium concentrations (mg/L) of metal ion in the

solution, and $V$ and $W$ are the volume (L) and weight (g) of the adsorbent, respectively. To describe the efficiency of metal ion removal from the solution, the recovery factor (RF) was calculated as follows:

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

Here, $C$ is the metal ion concentration at a given time in the solution and $C_i$ is the initial concentration of the metal ion.

**Morphological observation by scanning electron microscopy**

All micrographs of the polymers were obtained with a Hitachi S-4000 scanning electron microscope (SEM; 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 improve visibility. The samples were finally subjected to an electron beam under vacuum to obtain the micrographs with an acceleration voltage of 10 kV.

**Brunauer–Emmet–Teller (BET) analysis of the CDPs**

For a 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 a Micrometrics degassing system at 120°C prior to measuring the 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.

**Fourier transform infrared (FTIR) spectroscopy**

Fourier transform infrared (FTIR) spectroscopy measurements were performed to determine the presence of functional groups in the sorbents at room temperature using KBr as the background at a range of 4000–400 $cm^{-1}$ (FT210, HORIBA).

### Statistical analysis

Each experiment was performed at least five times, and mean ± standard deviation (SD) was used for data analysis. Data about metal concentration in the samples were analyzed for statistical significance by a one-way analysis of variance (ANOVA) followed by a 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) was used to perform all statistical analyses.

## RESULTS AND DISCUSSION

### Sorption studies

Novel macrocycles are currently being developed and evaluated for use as selective, recyclable carriers for polymeric transport of heavy metals from contaminated water. The most important factor influencing the transport of metal ions through CDPs is the nature of the ion carrier, especially its hydrophilic properties. α, β, and γ-CDPs can include organic compounds such as benzene derivatives and naphthalene derivatives to form inclusion complexes. If the inclusion complexes are very stable, the organic molecules will not be released easily in water or in other solvents (25). The results obtained here suggest that α, β, and γ-CDPs adsorbed heavy metal ions from water (Fig. 1). The adsorption ratio or

recovery factor was calculated by dividing the concentration of metal ions adsorbed on CDPs by the initial concentration of metal ions in the solution. As indicated in Fig. 1, the CDPs reached adsorption equilibrium within around 4 h. Their adsorption efficiencies were high and reciprocal to each other. The $Cd^{2+}$ binding ability to CDPs increased with time at room temperature. The polymers generally have higher adsorption efficiencies for $Cd^{2+}$. It is nearly 99% between 12 to 48 h, which is higher than the adsorption with β-CDP–IL polyurethanes described by Malefetse et al., 2009 (26). In this study, up to 99% adsorption of $Cd^{2+}$ was recorded for α, β, and γ-CDPs, whereas only 33% adsorption of $Cd^{2+}$ for β-CDP was observed by Malefetse et al., 2009. The adsorption percentage of $Cd^{2+}$ by the parental β-CD was only 18% (26). The use of tosylate and iodide anion as an IL provides an ionic environment unsuitable for interaction between $Cd^{2+}$ and CD–IL polymers. Unpolymerized, water-soluble CDs lack the appropriate binding sites to interact with the metal ions (26). However, water-insoluble CDPs do have the appropriate binding surface loci and interacting interior to bind with the metal ions. The native CDs certainly form complexes with many heavy metal ions, which was also reported by Cardas et al. (27) and Brusseau et al. (28). Adsorption within 24 to 48 h was stable and 24 h of contact time was considered for the adsorption isotherm experiment in our study. No significant differences in adsorption were observed 4 h of contact time.

In the case of $Cr^{6+}$, the CDPs showed a low affinity of 37% (Fig. 1b) and adsorption efficiency as compared with the β CDP described by Malefetse et al. (26). In their study, 100% of $Cr^{6+}$ adsorption to β CDP was reported. This observation suggested that $Cr^{6+}$ requires high electron or ionic concentration on the backbone of CDPs for extraction from

water. Moreover, borate, phosphate, and acetate buffer contains negative ions similar to $Cr^{6+}$ and may influence the adsorption of chromium and even influence the adsorption of $Cd^{2+}$ if they lead to precipitate. In addition to β CDP, both α and γ CDPs have identical adsorption potential for both $Cd^{2+}$ and $Cr^{6+}$ in the solution.

The reaction of epichlorohydrin ($C_3H_5ClO$) with CD monomers yields products used as plasticizers for polymers. During this modification, epichlorohydrin, a highly reactive organic anion, was attached on the backbone of these CDs, thereby providing a hydrophobic environment in the polymers. This hydrophobicity increases chelation of the divalent cadmium ion with the epichlorohydrin-bound CDPs by repelling the water molecules from the binding site of the CDPs. The chromium ion typically requires hexavalent dentition to form a successful complex on the backbone of CDPs. Hence, CDPs have low adsorption efficiencies for chromium, which motivates us to investigate functionalization with appropriate functional groups as a future work. This observation is similar to the work of Welton, (29) and Malfetse et al. (26), who reported high adsorption efficiencies of heavy metal ions when anions on the hydrophobic structure were used. Apparently, this criterion supports the statement that the ideal CD derivative does not exist yet. A CDP with high stability and affinity will be needed to remove or separate the heavy metal ions in solutions (5).

**Kinetic studies and adsorption isotherm**

To determine the relationship of each polymer, the effects of different amounts of polymer on the adsorption efficiency of $Cd^{2+}$ and $Cr^{6+}$ were investigated. Statistically

significant differences were observed in the sorption kinetics of cadmium and chromium. For these experiments, 2.5 gm, 1.0 gm, 0.5 gm, and 0.1 gm of α, β, and γ CDPs were used to concurrently adsorb $Cd^{2+}$ and $Cr^{6+}$ from the solution. Importantly, the amount of CDPs and the $Cd^{2+}$ adsorption efficiencies were correlated. The $Cd^{2+}$ adsorption was higher with lower amounts of α, β, and γ CDPs and decreased with an increase in the amount of the adsorbent material (Fig. 2). For example, 0.1–0.5 gm of CDPs adsorbed 80% to 85% of $Cd^{2+}$ ions in the solution. Further, 1 gm CDPs adsorbed around 80% $Cd^{2+}$. However, 2.5 gm CDPs have slightly lower adsorption efficiency. Increasing the adsorbent concentration did not result in a higher adsorption rate because of selectivity reduction (22). In contrast, the $Cr^{6+}$ ions showed an opposite trend for a different amount of adsorbent (Fig. 2).

For kinetic experiments, the $Cd^{2+}$ and $Cr^{6+}$ concentrations ranging from 50 to 200 mg/L at pH 6 were used with only β CDP as a representative material. An increased adsorption capacity was observed with an increased initial metal ion concentration due to its active surface and interior as well as the absence of internal diffusion resistance. To achieve complete equilibrium, the samples were agitated for 5 h and the adsorption kinetics of β CDP were calculated using the popular Lagergren pseudo-second-order model. The pseudo-second-order kinetic rate equation is formulated as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} t \qquad (3)$$

Here, $k_2$ (g mg$^{-1}$ min$^{-1}$) is the rate constant of the pseudo-second-order adsorption. The slope and intercept of the plot of $t/q_t$ versus $t$ were used to calculate the value for $k_2$ and $q_e$, (Fig. 3). The values of $R^2$ for the pseudo-second-order kinetic model of $Cd^{2+}$ and $Cr^{6+}$ were equal to 1.00 and 0.90, respectively, indicating a good fit to the pseudo-second order as well as a good agreement with the experimental data. The values of $q_e$ for 50, 100, and 200 mg/L of metal ions of $Cd^{2+}$ and $Cr^{6+}$ were calculated as 12.04, 24.57, and 49.50 mg/g and 1.85, 3.02, and 4.16 mg/g, respectively. Thus, adsorption occurred with pseudo-second-order kinetics and the sorption process appeared to be controlled by the chemical process via ion exchange or a complexation process (30).

Adsorption isotherms are used to measure the adsorption capacity of any adsorbent, quantify the adsorbed amount onto the adsorbent, and determine the solute–solution interaction and the degree of accumulation of adsorbate onto the adsorbent. Two commonly used isotherm models, the Langmuir and Freundlich isotherm models, were used in this study (Figs. 4 and 5).

The Langmuir equation is given as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (4)$$

Whereas, the Freundlich equation is expressed as

$$q_e = K_F\, C_e^{\,1/n} \qquad \text{(Non-linear form)} \qquad (5)$$

$$\log q_e = \log K_F + 1/n \log C_e \qquad \text{(Linear form)} \qquad (6)$$

Here, $q_e$ and $q_m$ refer to the adsorbed amount of ions per unit weight of adsorbent (mg/g) and the maximum capacity of adsorbent (mg/g), respectively. $C_e$ denotes the equilibrium concentration of solute in the bulk solution (mg/L), $K_L$ is the "affinity parameter" or Langmuir constant (L/mg), $K_F$ is the constant that indicates the relative adsorption capacity of the adsorbent (mg/g), and $1/n$ is the constant that indicates the intensity of the adsorption (31). The correlation coefficients (α: 0.869, β: 0.8912, and γ: 0.887) showed the applicability of the Langmuir isotherm model to the adsorption of $Cd^{2+}$. On the other hand, the correlation coefficients (α: 0.540, β: 0.940, and γ: 0.611) for the Freundlich model explained the utility of the model with respect to $Cd^{2+}$. The adsorption isotherms of $Cr^{6+}$ give similar results as $Cd^{2+}$ (Fig. 5). A unit gram each of α, β, and γ CDPs can uptake 24.24, 21.00, and 18.6 mg/g of chromium ions in solution, respectively. These results are highly supported by the adsorption/desorption isotherm generated from the BET analysis of the sample (Fig. 6). In Fig. 6, the solid lines represent the fitting of data from the multilayer adsorption and desorption isotherm against the pore volume. The Freundlich model fitted the data particularly better with β CDP when a change in the mechanism of adsorption with concentration was considered. Furthermore, multilayer physisorption may be concluded because adsorptions were highly fitted with the BET isotherm, because the CDPs possessed an extremely low surface area. Weak Van der Waals forces of attraction were responsible for the interaction between the adsorbent and adsorbate involving low enthalpy and temperature. With acid treatment and subsequent

temperature increase, the adsorption rate sharply decreased along with substantial desorption.

Significant adsorption differences were recorded in each case for both $Cd^{2+}$ and $Cr^{6+}$ in adsorbate concentrations below 10 mg/L. As shown in Fig. 7, CDPs favor the adsorption of a high concentration of heavy metal ions from the solution. On the contrary, low concentrations of heavy metal ions were not remarkably adsorbed into CDPs. For example, the adsorption ratio gradually increased to 99% from 10 ppm to 100 ppm of $Cd^{2+}$ ions, whereas it significantly decreased below 10 ppm of $Cd^{2+}$ ions in the solution. Lower concentrations of $Cd^{2+}$ were not sufficient for providing the required energy for replacing the hydronium ion from the binding site of the CDPs (Fig. 7a). For $Cr^{6+}$ however, the uptake was higher at low adsorbate concentrations and it decreased when the adsorbate concentrations were high (Fig. 7b). A balance between hydronium ions and metal ions was observed in contrast with CDPs in solution. Thus, CDPs could not remove 100% $Cd^{2+}$ in solution and a similar amount of ions always remained after adsorption in the same volume of solution. This study also revealed that a unit gram each of α, β, and γ-CDPs have high potential for separating large quantities of heavy metal ions, especially cadmium, in comparison with other conventional sorption methodologies (Table 1). The polymers showed similar affinity towards both the cadmium and chromium ions, and are equally important in water remediation. The sorption affinity of the CDPs towards $Cd^{2+}$ and $Cr^{6+}$ is comparable or superior to the other available adsorbents. However, these results suggest

that these particular polymers may be highly suitable for water recycling at industrial levels in high-performance effluent treatment plants.

**Effects of pH on sorption**

The pH of the CD solution was almost neutral and the presence of CD did not considerably affect the ionic strength of the solution (4). Extraction of $Cd^{2+}$ and $Cr^{6+}$ using CDPs at different pH values gave significantly different results. Removal of the metal ions as a function of pH is shown in Fig. 8. These studies were carried out at the initial concentration of 10 mg/L for $Cd^{2+}$ and $Cr^{6+}$. The sorption of $Cd^{2+}$ and $Cr^{6+}$ on the CDPs increased with an increase in pH. In both acidic and basic environments, the CDPs were inactive to bind metal ions. The highest adsorption was at pH 6.5 to 7.5 in solution and any increase or decrease of pH gave a low adsorption for every CDP. For example, the adsorption of $Cd^{2+}$ and $Cr^{6+}$ was around 10%–12% for all CDPs at pH 3.6 and 9, whereas pH 6.5 gave the highest adsorption at 90%. This was expounded upon by Davis and Leckie (32). They stated that metal adsorption reduced in a manner that suggested competition between the adsorbent and oxide surface for complexation of the metal ion, and metal adsorption reduced considerably by the presence of a complexing ligand in the system at appropriate concentrations. The ionic mobility of $[H_3O]^+$ in water is abnormally higher than most other ions. This has been ascribed to a proton switch and reorientation mechanism involving the ions and chains of H-bonded solvent molecules (33). Thus, by virtue of both high concentration and high mobility in the adsorptive aqueous solution, the proton would favorably compete with metallic ions such as $Cd^{2+}$ and $Cr^{6+}$ for surface

active sites of the adsorbent (34). Hence, at a relatively high pH, the competition provided by $[H_3O]^+$ should enable the ions to be adsorbed. On the contrary, a pH value greater than 8 also creates a basic environment in the solution to precipitate metal such as metal oxides or hydroxides. Moreover, when the solution is acidic or basic, most of the metal ions are in an "ionic form." When neutral, more metal ions are in a "molecular form" that is more hydrophobic and easier to be adsorbed by CDPs. Thus, the sorption ability of CDPs strongly depends on the ionic strength in the range of most natural water (31, 35-37). Thus, for future studies, the ideal pH for $Cd^{2+}$ and $Cr^{6+}$ is chosen as 6.5. Statistically significant differences were observed between the adsorption in the neutral pH range and the adsorption in both acidic and basic environments. Nevertheless, there were no differences between the adsorption in both acidic and basic solutions.

$KH_2PO_4$ was used to prepare the phosphate buffer with a carefully maintained pH value of 6.5 to 7.5. Cadmium adsorption was intensified by the form and dose of potassium salts, probably due to the influence on solubility. $KH_2PO_4$ increased the Cd accumulation rate in the binding sites of CDPs. Further, Wisniowska–Kielian and Ryant have reported greater adsorption of Cd from contaminated soil after a high K dose application (38).

Cadmium species have some common forms in deionized water, such as $Cd^{2+}$, $CdOH^+$, $Cd(OH)_2^0$, and $Cd(OH)_2(s)$. The solubility of $Cd(OH)_2(s)$ is about $10^{3.45}$ M, and is maximal at pH 5.5–7.5. Solubility is approximately $2.56 \times 10^{-4}$ M at pH 9, and hence, $Cd^{2+}$ is the key species at this point. The solubility decreases further and reaches $3.23 \times 10^{-5}$ at pH 12, and the key species in the solution now becomes $Cd(OH)_2(s)$ (39). It is evident from Fig. 8

that the adsorption of $Cd^{2+}$ is higher at a neutral range of pH. At a high pH, precipitation of $Cd(OH)_2(s)$ plays a vital role in removing $Cd^{2+}$ ions from the solution. In this experiment, the above discussion is supported by the fact that a low adsorption capacity of the CDPs under acidic conditions increases sharply in the basic region and further decrease in highly basic regions. The $Cd^{2+}$ adsorption capacities of surface-oxidized carbon nanotubes conducted by Li et al. have shown similar results (39).

**Characterization of the polymers**

SEM was conducted to understand and compare the surface morphology, texture, and level of porosity in the studied material. The SEM micrographs of α, β, and γ-CDPs are shown in Fig. 9. It was evident that the surface of these polymers was round with irregular bead size, smooth texture, and with either amorphous or spongy surface, with or without pores. From these SEM micrographs, it appears that the morphology of α, β, and γ-CDPs are not very different. The same properties have been obtained for cadmium- and chromium-binding CDPs (data not shown). The surface functional groups of the CDPs that are responsible for interactions with the metal ions were determined by FTIR. A spectrum for CDP with the cadmium ions is representative (Fig. 10). Identical FTIR spectra of CDPs show similar structure including analogous functional groups. Typically, the functional moieties include C=O (carboxylic) at 1750–1630 $cm^{-1}$; C=C at 1600–1450 $cm^{-1}$; C–O stretching and O–H bending (ether, phenol, etc.) at 1440–1000 $cm^{-1}$; CH (900–600 $cm^{-1}$) and OH, NH, and CH stretching in alkyl or aryl at 3488–3100 $cm^{-1}$ (40). In the CDP spectra, bands were identified for O–H and C–H at 3356 $cm^{-1}$; $CH_2$ at 2881 $cm^{-1}$; COO– (carboxylic) at 1635

$cm^{-1}$, and C–O at 1403 $cm^{-1}$. The expected peak at 1635 $cm^{-1}$ shifted to 1628 $cm^{-1}$ for the CDPs after adsorption of $Cd^{2+}$. This peak shifting indicates that the carboxylic and hydroxyl functional groups were largely responsible for interactions with the metal ions with the dominance of oxygen atoms as the active binding sites for $Cd^{2+}$ attachment.

Epichlorohydrin cross-linked α, β, and γ-CDPs possess significantly low surface areas (<0.1 $m^2/g$) along with a pore volume and diameter. These polymers range from 60–300 µm in size, are insoluble in water and organic solvent, have a granular bead texture, white in color, are neutral in water (pH 6.5), and have a low saturated vapor pressure (103.40 kPa). It was evident from the $N_2$ adsorption–desorption isotherm (BET isotherm) that the adsorbed volume of $N_2$ slightly increased with increasing $P/P_0$, indicating a small pore size distribution. High correlation was expected between the surface area or the pore size and the adsorption efficiencies of the polymers; however, the BET results did not show this correlation. One reason for this may be that the BET test was done on dry polymer, but the polymer swelled in water during adsorption, and the pores may have changed. In addition, binding cadmium contents per square meter of surface area for α, β, and γ-CDPs were calculated to be $2.4 \times 10^3$ $mg/m^2$, respectively. However, α CDP ($9.8 \times 10^{-3}$ $cm^3/g$) and γ-CDP ($9.2 \times 10^{-3}$ $cm^3/g$) exhibited larger pore volumes as compared to β-CDP ($1.2 \times 10^{-3}$ $cm^3/g$). Thus, no relationship was observed between pore size and binding efficiency.

**Environmental implication of CDPs**

Water-soluble CD capturing the target substances could not be retrieved easily from the solution. However, insoluble in water or organic solvents, “polymer,” could be easily separated, and the target substance was easily concentrated by centrifugation and filtration (25). In most cases, the mechanism of controlled degradation of the CD–pollutants complexes is based on changes in the pH of water solutions, leading to the cleavage of hydrogen or ionic bonds between the host and the guest molecules. Alternative means for the disruption of the complexes take advantage of heating or action of enzymes that are able to cleave α–1, four linkages between glucose monomers. These polymers could be recycled at least 18 times while still maintaining their high sorption efficiency (42). However, the structural integrity of these polymers was found to be somewhat compromised after prolonged recycling. The BET results also give the adsorption/desorption isotherm that showed another prospective trend of α, β, and γ-CDPs (Fig. 6). The adsorption and desorption criteria of these polymers are reasonably similar to each other in solution for potential use in water treatment systems. α, β, and γ-CDPs are naturally occurring CDs and non-food additives. However, the ADI (average daily intake) has been determined only for β CD by WHO (World Health Organization), FAO (UN Food and Agriculture Organization), and JECFA (Joint Expert Committee Food Additives); this value is 5 mg/kg/day. This indicates the non-toxic effects of CDs in the environment [http://www.cyclochem.com/faq/index.html].

## CONCLUSION

This study demonstrated that epichlorohydrin CDPs have the potential to adsorb heavy metal ions in water systems. These polymers were notably insoluble in water, which is an important property for their use in water treatment systems. They have identical adsorption potential for both $Cd^{2+}$ and $Cr^{6+}$. After passing the model pollutants through the polymers, a high percentage removal of these polymers was observed (99% for cadmium and 40% for chromium). A unit gram each of α, β, and γ-CDPs removed 240.9, 239.2, and 244.9 mg of cadmium ions, and 24.2, 21.0, and 18.6 mg of chromium ions, respectively. The sorption characteristics of these polymers are suitable for water treatment in industrial sites and drinking water distribution systems because these polymers have already been established as excellent materials to remove 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 organic and inorganic pollutants from water treatment systems. The negligible cytotoxic effects of CDPs are an important additional attribute in applications such as environmental protection as well as an attractive choice for subsurface remediation.

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**Figure Legends**

FIG. 1. Effect of reaction time on the adsorption rate of $Cd^{2+}$ (a) and $Cr^{6+}$ (b) by α, β, and γ-CDPs. Adsorption condition: initial $Cd^{2+}$ and $Cr^{6+}$ concentration 100 mg/L and 10 mg/L respectively, adsorbent dose 1.66 g/L for $Cd^{2+}$ and 16.66 g/l for $Cr^{6+}$, pH 6.5, temperature 25 ± 3°C.

FIG. 2. Effects of adsorbent amount on the adsorption efficiency of α, β, and γ-CDPs. Adsorption condition: initial $Cd^{2+}$ and $Cr^{6+}$ concentration 10 mg/L, pH 6.5; temperature 25 ± 3°C.

FIG. 3. Pseudo-second-order kinetics for adsorption of $Cd^{2+}$ (a) and $Cr^{6+}$ (b) ions by β-CDP. Adsorption condition: adsorbent dose 4 g/L; pH 6.

FIG. 4. Adsorption isotherm of $Cd^{2+}$. (a), (b), and (c) are Langmuir fits for α, β, and γ-CDP, respectively. (d), (e), and (f) are Freundlich fits for α, β, and γ CDP, respectively. Adsorption condition: adsorbent dose 1.66 g/L, pH 6.5, temperature 25 ± 3°C.

FIG. 5. Adsorption isothermal curve of $Cr^{6+}$ on α, β, and γ-CDPs. Adsorption condition: adsorbent dose 1.66 g/L, pH 6.5, temperature 25 ± 3°C. The solid lines represent the data fit by Langmuir isotherms.

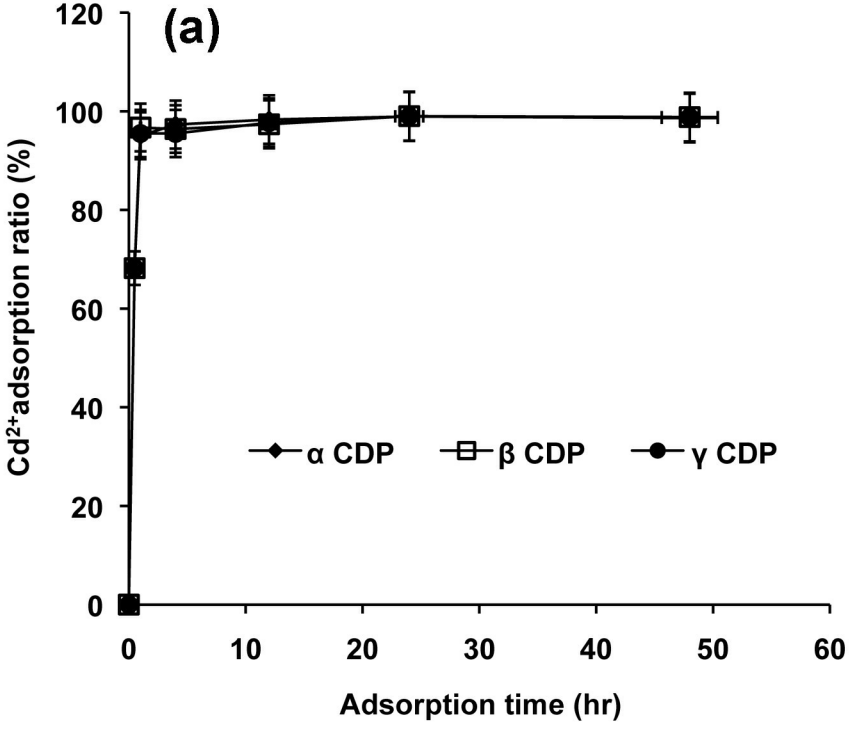
FIG. 6. Adsorption (ADS) and desorption (DES) isothermal curve of $Cd^{2+}$ on α-CDP (a), β-CDP (b), and γ-CDP (c) derived from BET. $p/p_0$ represents the relative pressure in $cm^3\ g^{-1}$.

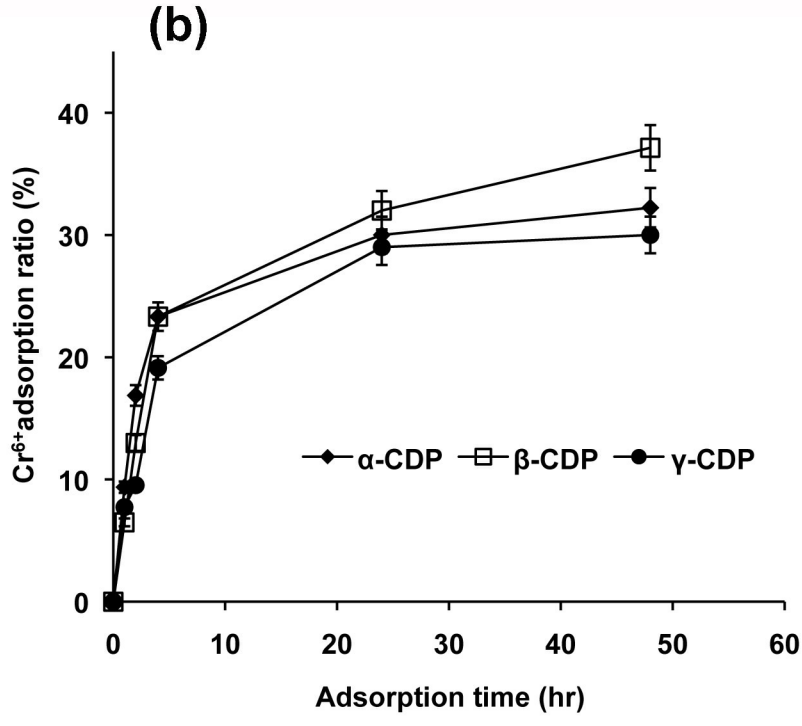
FIG. 7. Effects of adsorbate concentration on the rate of adsorption of $Cd^{2+}$ (a) and $Cr^{6+}$ (b) by CDPs at pH 6.5. The adsorbent dose was 16.66 g/L.

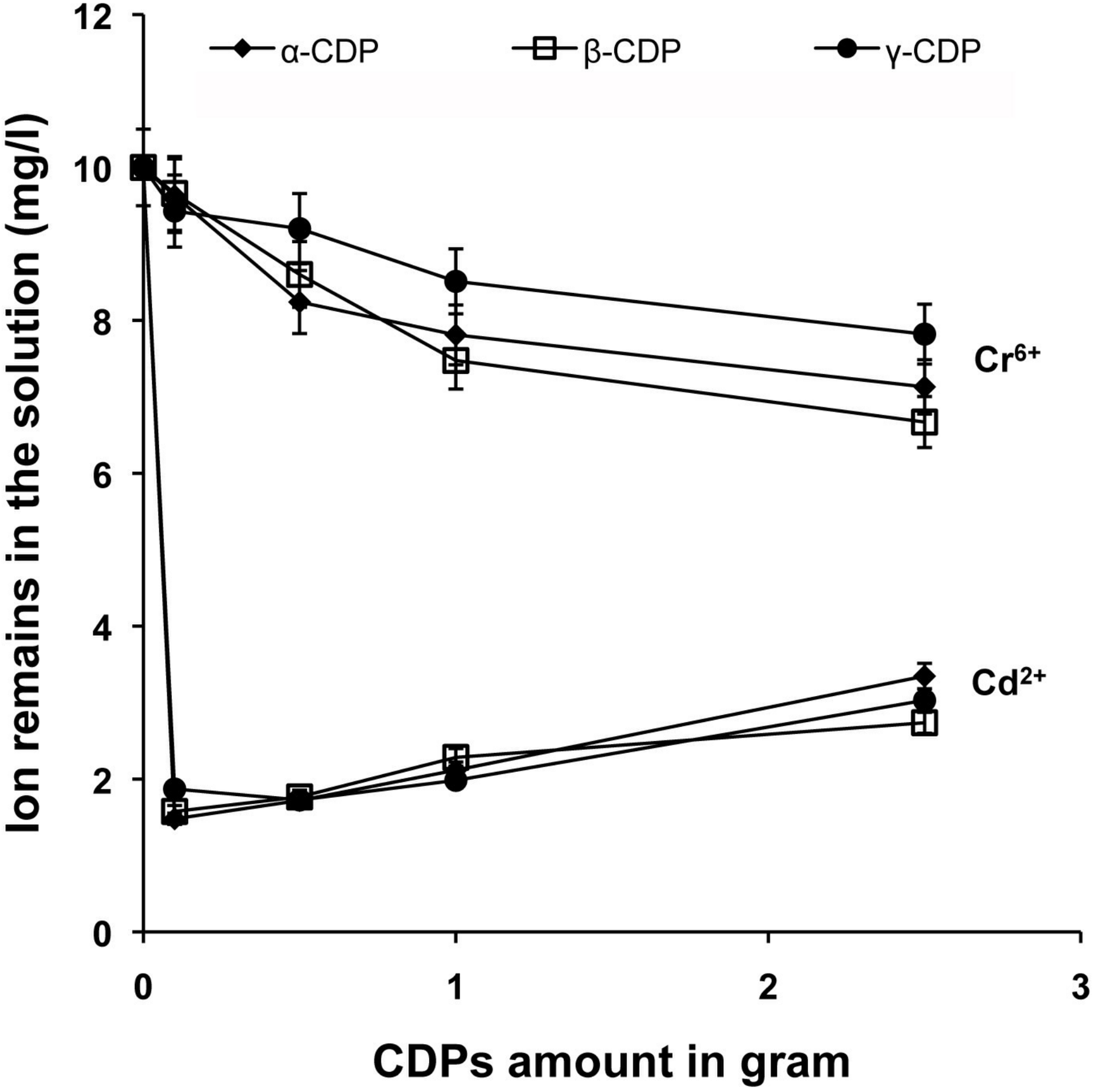
FIG. 8. Effects of pH on the adsorption of $Cd^{2+}$ (a) and $Cr^{6+}$ (b) by α, β, and γ-CDPs at 25 ± 3°C and adsorbate concentration of 10 mg/L.

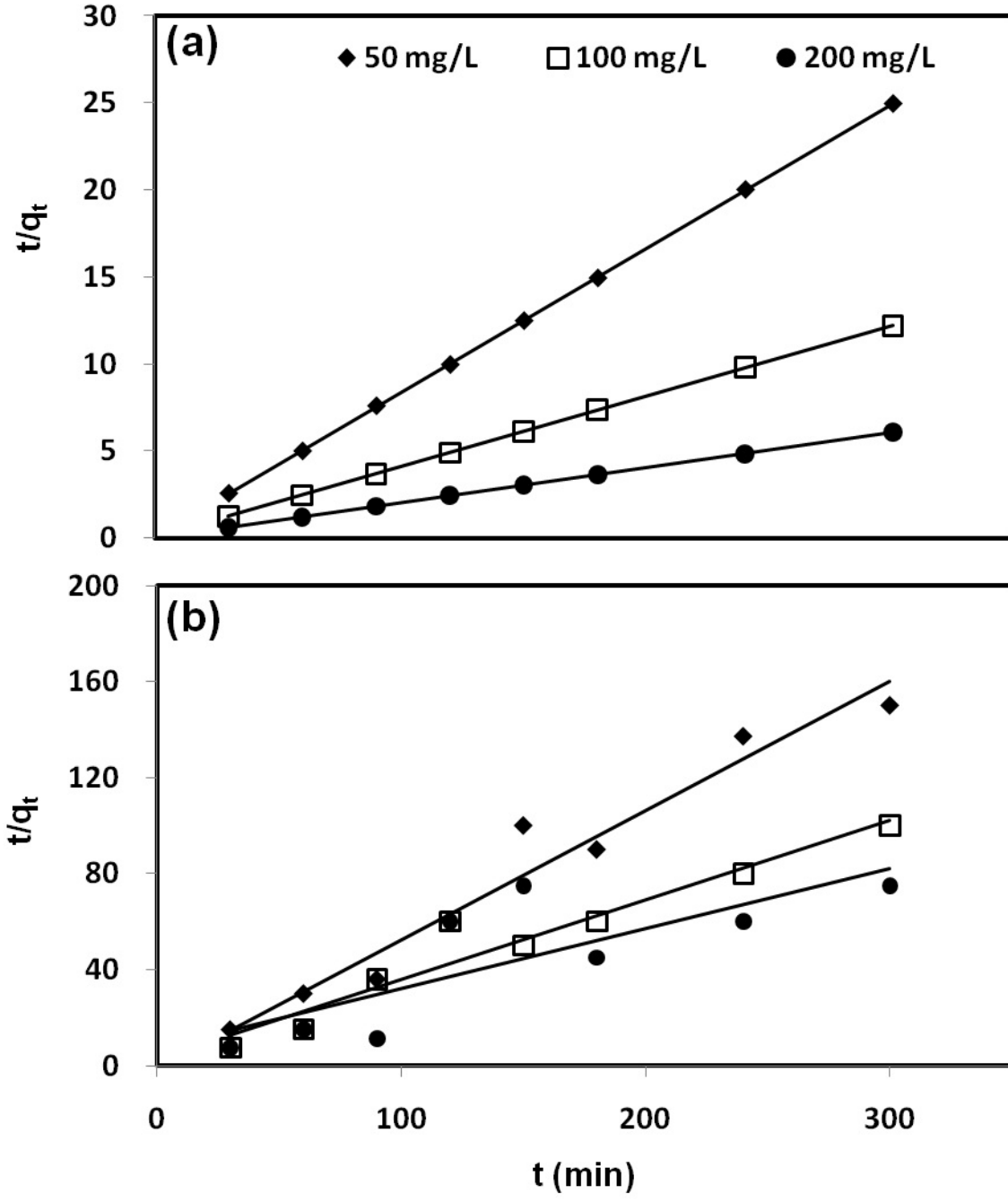
FIG. 9. SEM images of α-CDP (a), β-CDP (b), and γ-CDP (c).

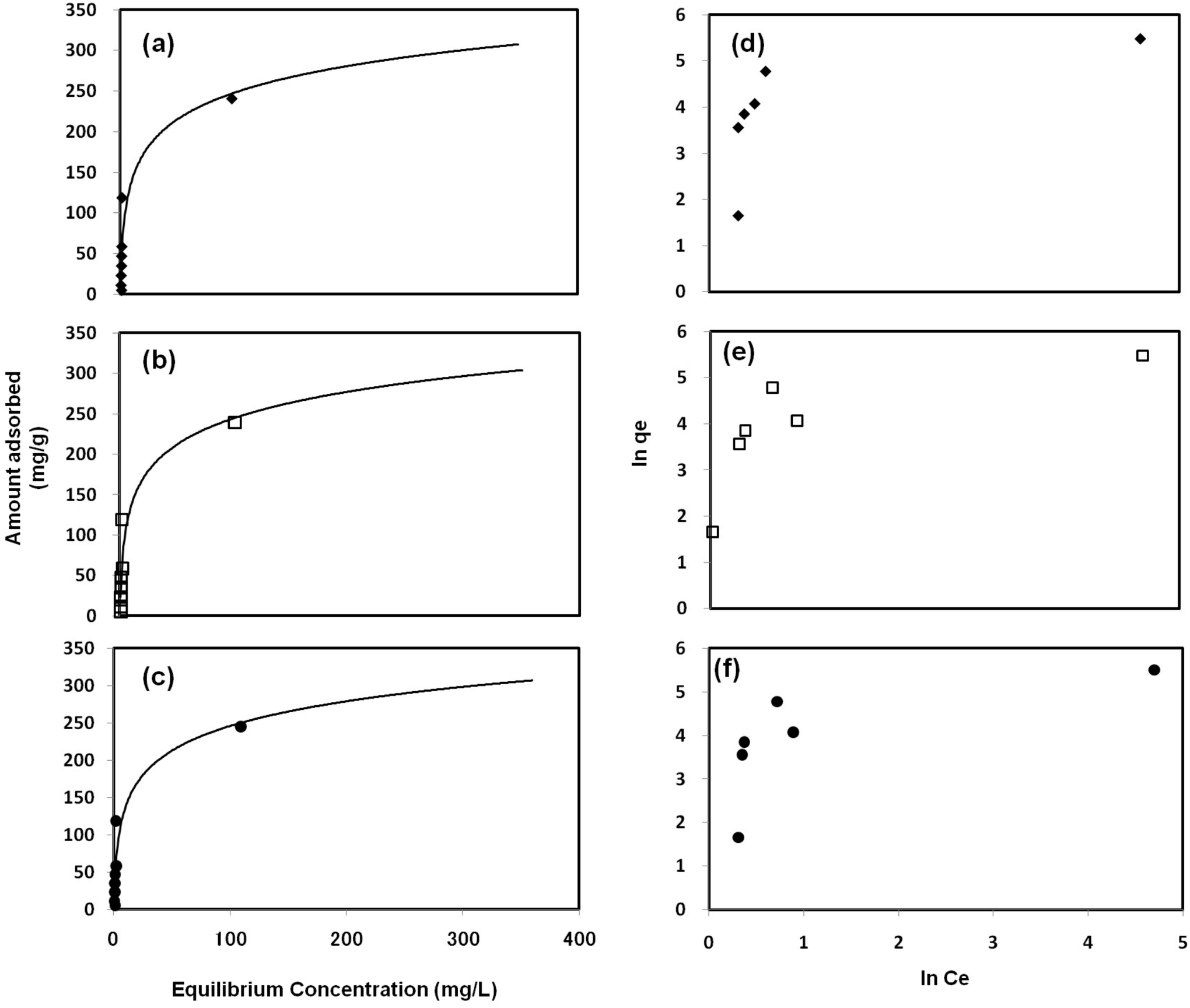
FIG. 10. FTIR spectra of α-CDP (a) β-CDP (b), and γ-CDP (c) before and after adsorption of cadmium.

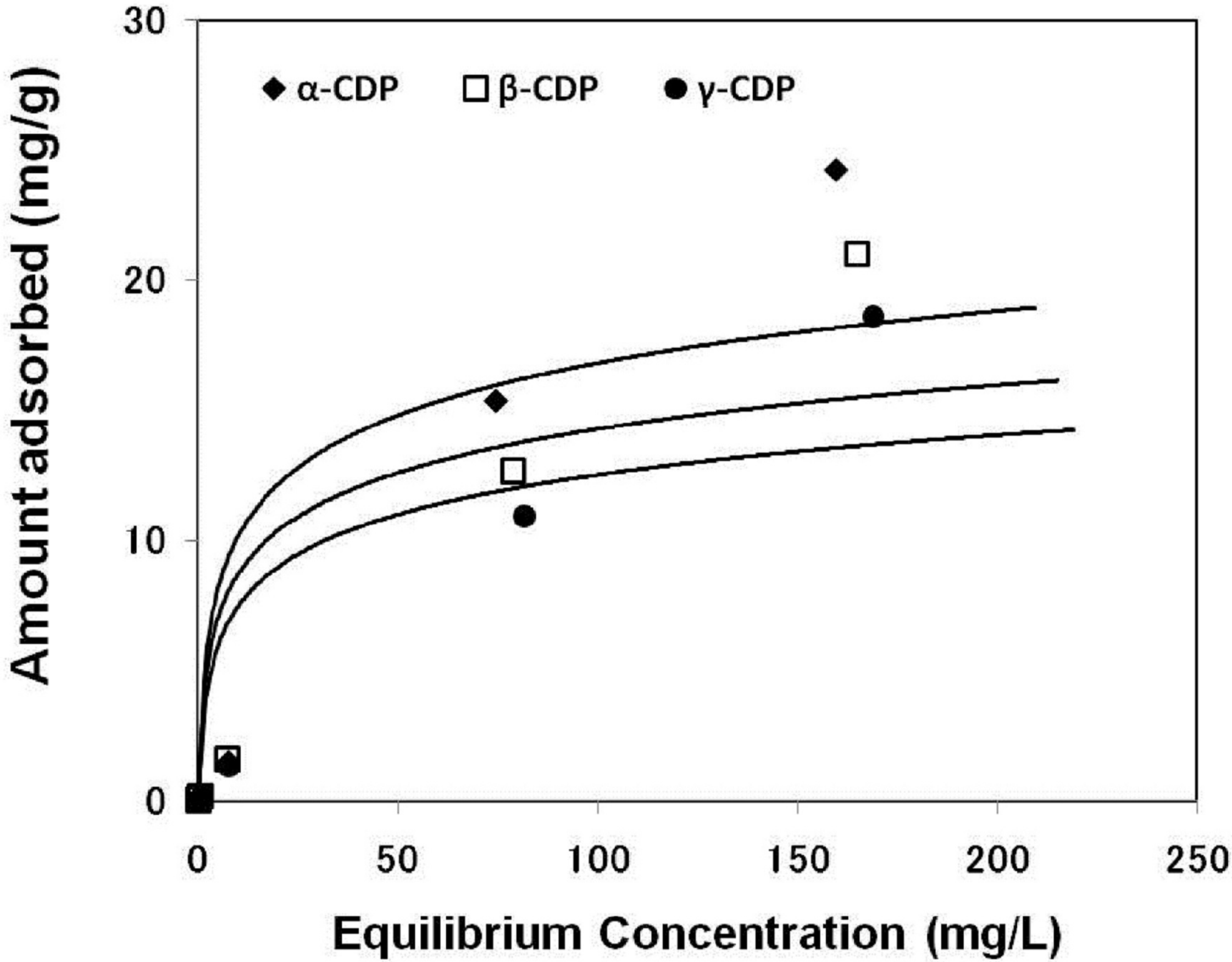

(a)
120
100
80
60
40
20
0
Cd2+adsorption ratio (%)
α CDP
β CDP
γ CDP
0
10
20
30
40
50
60
Adsorption time (hr)

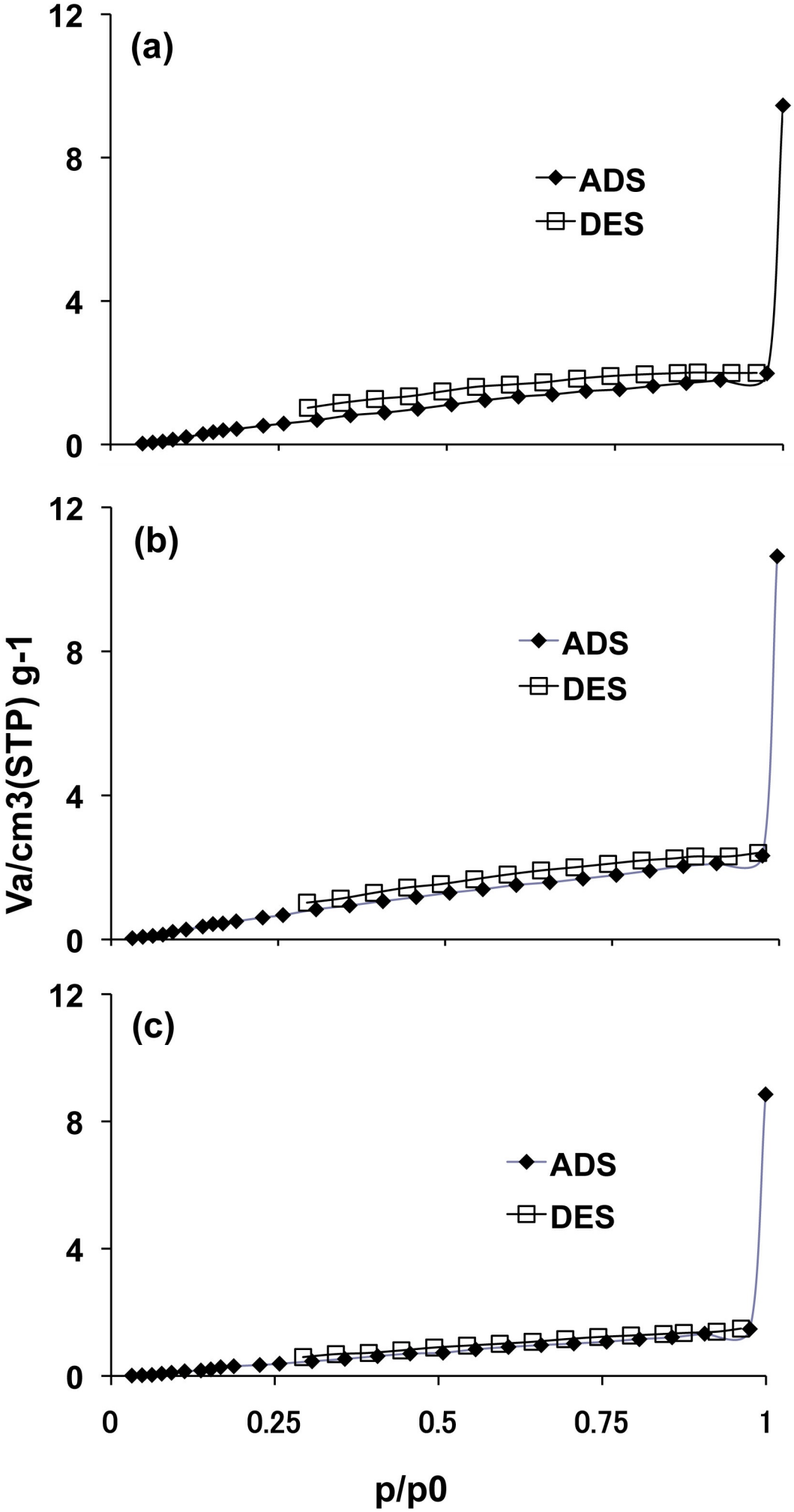

(b)
40
30
20
10
0
Cr6+adsorption ratio (%)
α-CDP
β-CDP
γ-CDP
0
10
20
30
40
50
60
Adsorption time (hr)

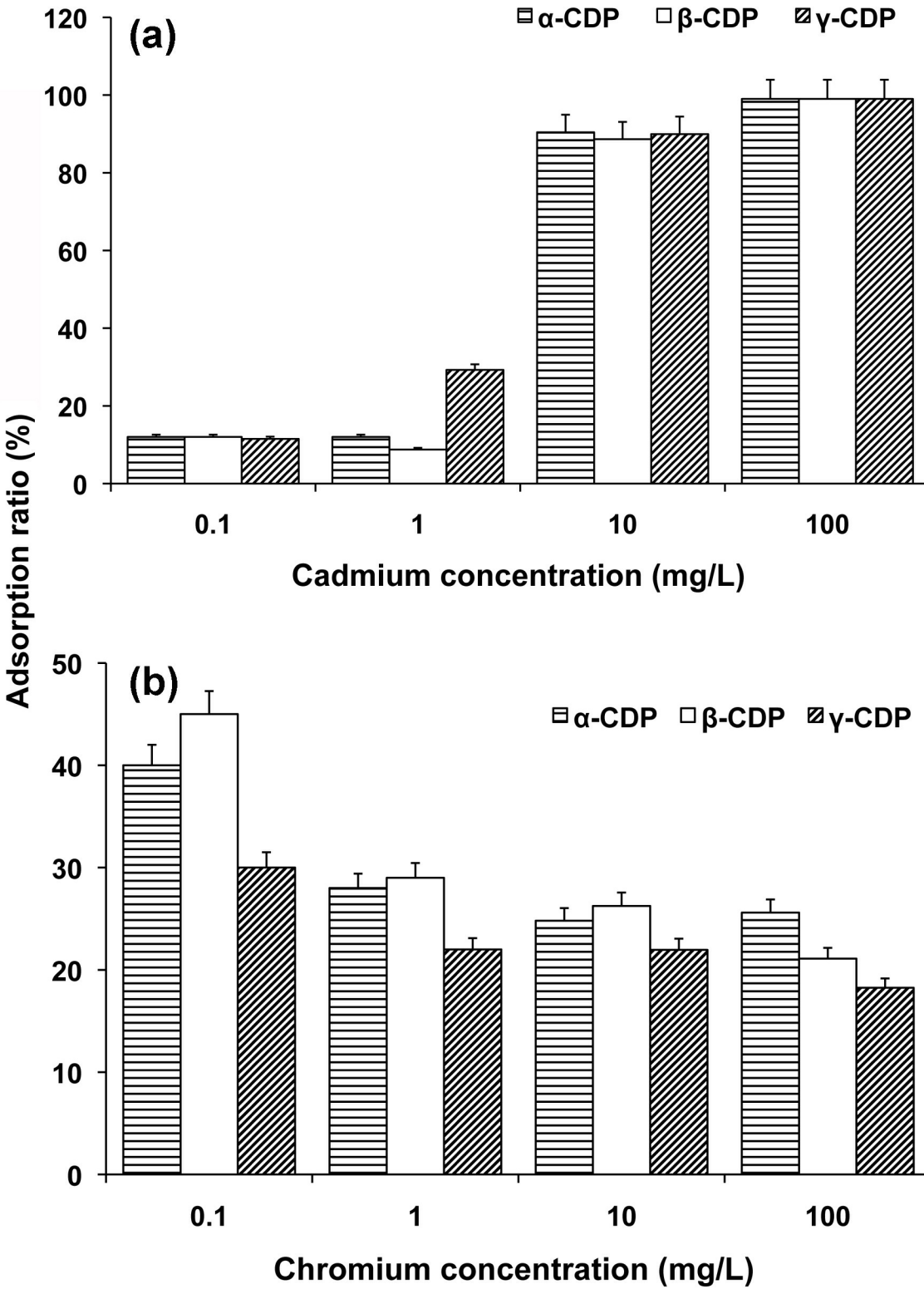

α-CDP
β-CDP
γ-CDP
Ion remains in the solution (mg/l)
12
10
8
6
4
2
0
0
1
2
3
CDPs amount in gram
Cr6+
Cd2+

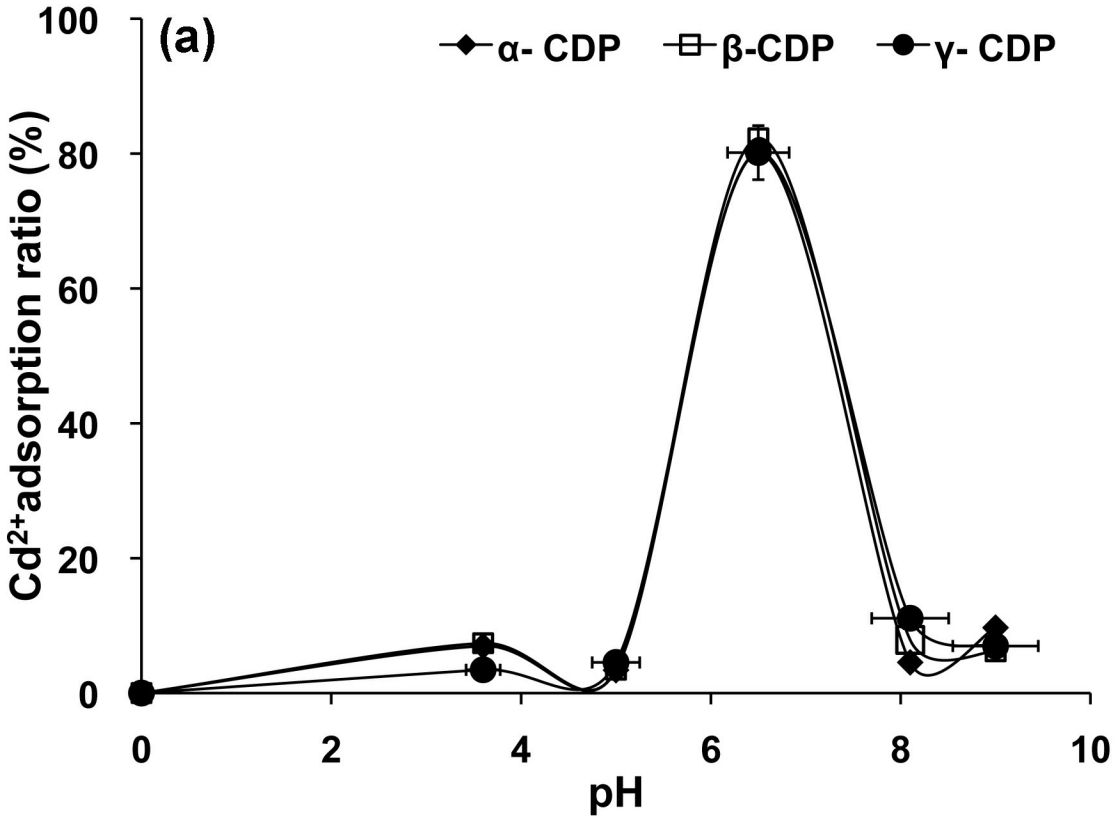

(a)
50 mg/L
100 mg/L
200 mg/L
t/qt
30
25
20
15
10
5
0
(b)
t/qt
200
160
120
80
40
0
0
100
200
300
t (min)

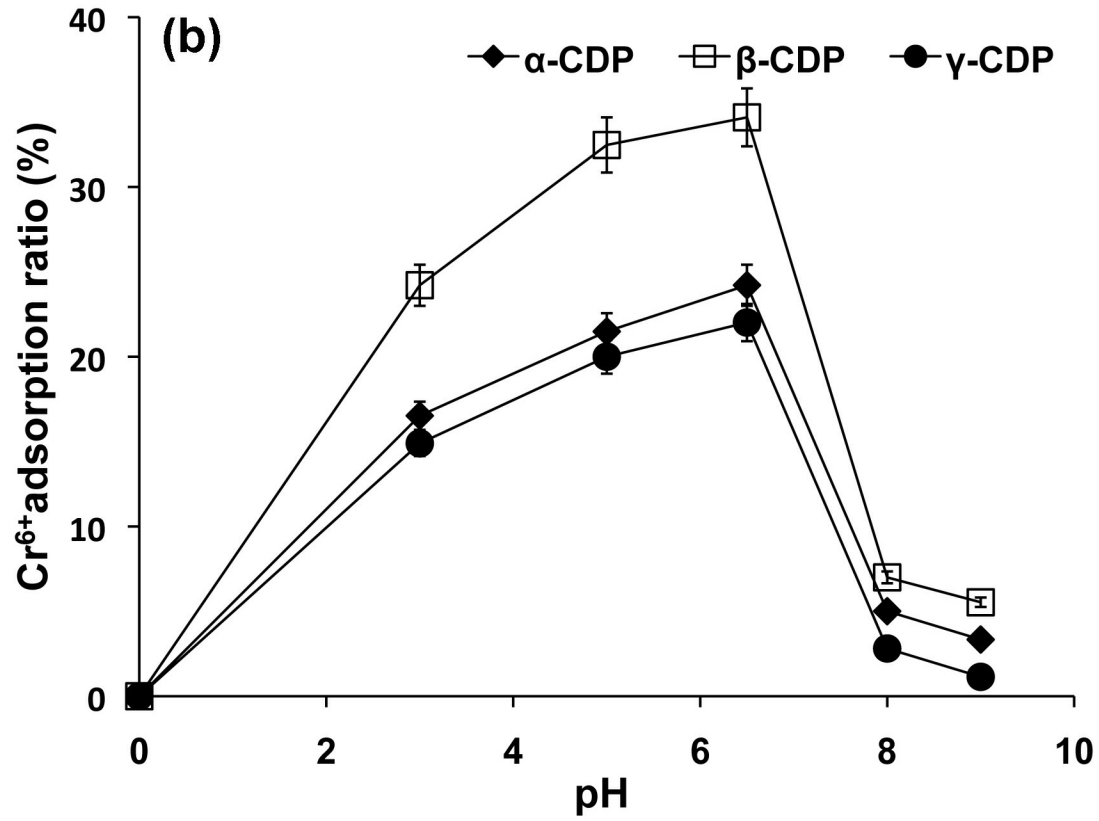

(a)
(b)
(c)
(d)
(e)
(f)
Amount adsorbed (mg/g)
Equilibrium Concentration (mg/L)
ln qe
ln Ce
0
50
100
150
200
250
300
350
400
1
2
3
4
5
6

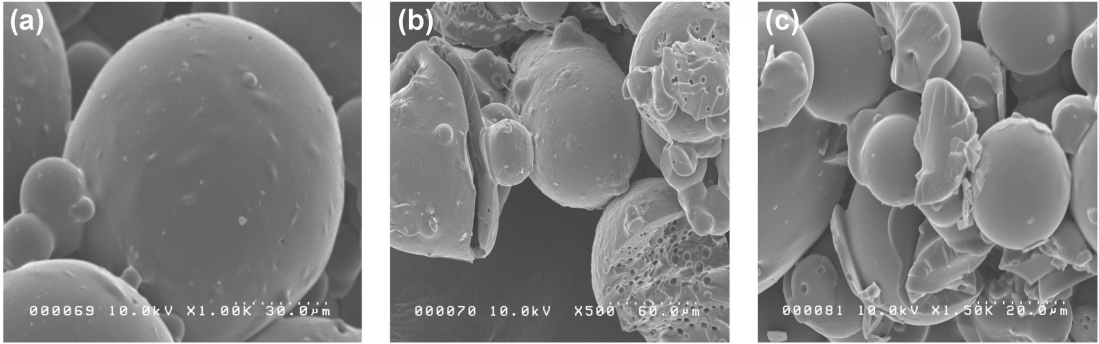

α-CDP
β-CDP
γ-CDP
Amount adsorbed (mg/g)
30
20
10
0
0
50
100
150
200
250
Equilibrium Concentration (mg/L)


(a)
(b)
(c)
ADS
DES
Va/cm3(STP) g-1
p/p0
0
4
8
12
0.25
0.5
0.75
1


(a)
α-CDP
β-CDP
γ-CDP
120
100
80
60
40
20
0
0.1
1
10
100
Cadmium concentration (mg/L)
Adsorption ratio (%)
(b)
α-CDP
β-CDP
γ-CDP
50
40
30
20
10
0
0.1
1
10
100
Chromium concentration (mg/L)


(a)
α- CDP
β-CDP
γ- CDP
Cd2+adsorption ratio (%)
pH
0
20
40
60
80
100
0
2
4
6
8
10


(b)
α-CDP
β-CDP
γ-CDP
Cr6+adsorption ratio (%)
pH
0
10
20
30
40
0
2
4
6
8
10


(a)
000069 10.0kV X1.00K 30.0µm
(b)
000070 10.0kV X500 60.0µm
(c)
000081 10.0kV X1.50K 20.0µm

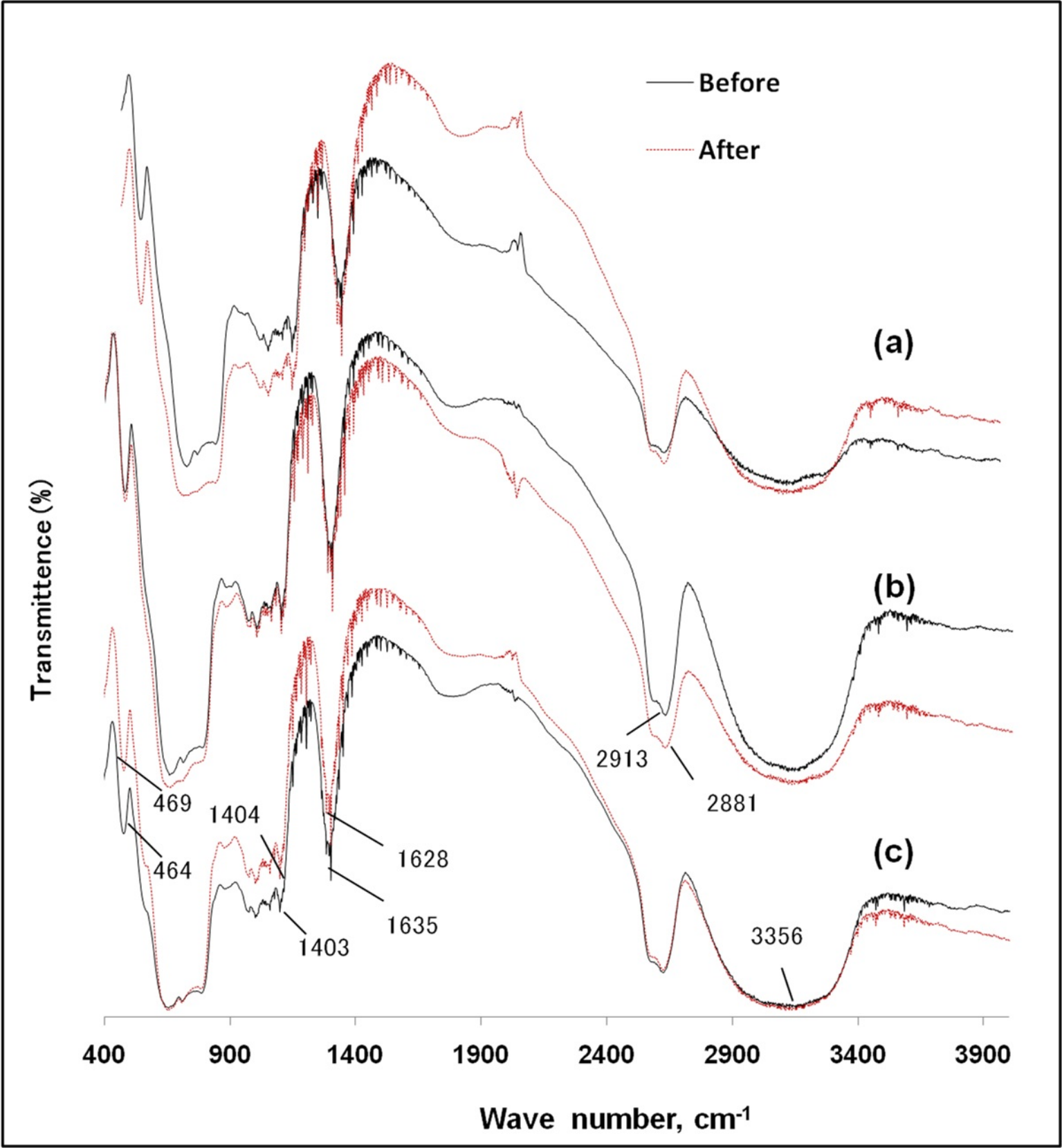

Before
After
(a)
(b)
(c)
Transmittence (%)
469
464
1404
1403
1628
1635
2913
2881
3356
400
900
1400
1900
2400
2900
3400
3900
Wave number, cm-1

TABLE 1 Cadmium and chromium adsorption efficiencies of different adsorbents.

| Adsorbents | Cadmium (mg/g) | Reference | Adsorbents | Chromium (mg/g) | Reference |
|---|---|---|---|---|---|
| Fly ash | 198.2 | 14 | CD–IL | 100(%) | 25 |
| Lignite | 40.25 | 15 | Chitosan | 85.59 | 42 |
| Peat | 21.13 | 16 | Hydrotalcite | 17 | 43 |
| Scarp rubber | 130 | 17 | Chitin | 104 | 44 |
| Red mud | 106.44 | 20 | Sawdust | 16 | 45 |
| CD–IL | 33(%) | 25 | Almond | 11 | 45 |
| Activated carbon (bagasse) | 38.03 | 30 | Activated carbon | 147 | 46 |
| α CDP | 240.9 | Present study | α CDP | 24.24 | Present study |
| β CDP | 239.2 | | β CDP | 21.00 | |
| γ CDP | 244.9 | | γ CDP | 18.6 | |