Removal of phthalate esters by α-cyclodextrin-linked chitosan bead

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Abstract

Removal of phthalate esters (PAEs) by α-cyclodextrin (CD)-linked chitosan bead in aqueous solution was studied. Results of kinetic experiments indicated that diheptyl phthalate (DHpP) was adsorbed most efficiently (3.21 mg/g) among the six PAEs. DHpP recovery was 94.6% from α-CD-linked chitosan bead by shaking both with a mixture of methanol and water (v/v = 8/2). The recovered α-CD chitosan bead was reusable as an adsorbent 20 times in the batch tests. The adsorbed PAE by α-CD-linked chitosan bead decreased as temperature increased. However, coexisting pH, NaCl, and Ca2+ did not affect adsorption efficiency. It was concluded that the application of low cost α-CD-linked chitosan bead could have the potential to effectively remove PAEs from different aquatic environments.

Keywords: Phthalate esters; α-CD-linked chitosan bead; Adsorption; Recovery; Desorption

1. Introduction

Phthalate esters (PAEs) are widely used plasticizers in polyvinyl chloride plastics. Moreover, they are also used as solvents, plastics softeners, and additives in paper coatings (Petrovic et al., 2001). Since phthalate esters are not chemically bound to the PVC polymer, they may leach from solid products during use, or after disposal (Staples et al., 1997a). As a result of the large quantities produced, phthalate esters have become environmental pollutants. Some phthalate esters are suspected carcinogens (Chang et al., 2004) that may affect the male reproductive system (Foster et al., 2000). There are some reports on phthalate ester pollution on aquatic environments adjacent to industrial sites. Some studies have also reported that phthalate esters exercise acute, or chronic toxicity toward aquatic organisms (Jonsson and Baun, 2003; Staples et al., 1997b). Generally, the toxicity of phthalate esters to aquatic organisms increases with increasing alkyl chain length (Adams et al., 1995). Therefore, it is very important to establish a method to remove various phthalate esters from waters. In aquatic and terrestrial systems, microbial interaction is the principal mechanism for phthalate ester degradation (Fang et al., 2007). However, the degradation process is time-consuming, and phthalate esters with long chains degrade poorly (Ejlertsson et al., 1997). Some microorganisms can hardly degrade them from aqueous solution. Furthermore, some studies advocate chemical methods (such as membrane techniques, ultrasound, and photocatalysis) to remove phthalate esters, but the results are inconsistent and still preliminary (Marttinen et al., 2003; Psillakis et al., 2004). Adsorptive removal by β-cyclodextrin and activated carbon is effective (Adhoum and Monser, 2004), but the materials involved are expensive. Therefore, a high speed process that employs relatively cheap materials to remove PAEs from aqueous solution is the focus of our research.

Chitosan is a kind of polysaccharide prepared by the de-N-acetylation of chitin, which makes up the shells of crustaceans such as crabs and shrimps (Tojima et al., 1999). Chitosan’s properties—nontoxicity, biodegradability, and
flocculating regeneration ability—lead to lots of applications. As chitosan is a biopolymer, it has been regarded as a useful material to remove inorganic (Ngah et al., 2005) and organic substances (such as chlorophenol and nitrophenol) from wastewater (Zheng et al., 2004; Crini, 2006). Furthermore, some studies of chemical modification of chitosan have also been carried out to introduce novel functions into this biopolymer (Chung et al., 2005).

Cyclodextrins (CDs), cyclic oligosaccharides consisting of 6, 7, and 8 α-glucopyranose units, have received much attention due to their unique property to form host–guest complexes with various organic compounds (Tojima et al., 1999). Glucopyranose units of 6, 7, and 8 CDs are called α-, β-, and γ-CD, respectively. It was found that these CD polymers (CD-P) were soluble in water and that the inclusion ability of the original CDs was maintained after the coupling reaction (i.e. chitosan bead). Due to the hydrophobic character of PAEs, one would expect them to be included in the cavities of cyclodextrins. Therefore, some researchers have reported on the synthesis of the polymers having the CD moiety and the potential they have to remove toxic compounds from water (Nishiki et al., 2000; Tojima et al., 1999). On the other hand, the preparations of CD-P were reported based on an interest in the synthesis of artificial receptors (Asanuma et al., 2001) or the removal of undesirable compounds from food (Asanuma et al., 1997).

Chitosan has been used for the syntheses of functional polymers having pendant CD moieties (Auzely-Velty and Rinaudo, 2001; Furusaki et al., 1996). In studies obtaining insoluble CD–chitosan by preceding crosslinking, the CD contents were relatively low. The limited CD content can be assumed to lower the cost compared to activated carbon.

The aim of this work was to study the removal of phthalate esters using α-CD-linked chitosan beads in batch and column experiments. Effects of pH value, temperature, NaCl, and Ca2+ on the adsorption of phthalate esters by α-CD-linked chitosan beads were also investigated. Furthermore, the feasibility of PAE recovery using a methanol–water mixture was evaluated.

2. Methods

2.1. Materials

Analytical grade dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPP), dibutyl phthalate (DBP), diheptyl phthalate (DHpP), and di-(2-ethylhexyl) phthalate (DEHP) were purchased from Sigma Chemical Company. Chitosan from shrimp shells with a deacetylation degree of 90% was obtained from the Application Chemistry Company (Kaohsiung, Taiwan).

2.2. Preparation of α-CD-linked chitosan bead

The preparation of α-CD-linked chitosan bead was modified from Tojima et al. (1999). Chitosan (1.5 g, degree of deacetylation 0.75, average molecular weight 40,000 K) was dissolved in a 3% aqueous acetic acid solution (73 mL), and diluted with deionized water to 100 mL. This solution was dripped into an NaOH solution (NaOH 38 g, 95% alcohol 200 mL, and deionized water 750 mL) by hypodermic needle (i.d. = 0.7 mm). The white chitosan beads were stirred overnight in the solution, and the solvent was then replaced by DMF (N,N-dimethylformamide) by decantation. After that 2.5 mL hexamethylene diisocyanate was added and stirred overnight. Then DMF was removed, and the white chitosan beads were transferred to 0.2 M acetic solution (1 L, pH 4.4), which contained 1.42 g NaNH4CN (sodium cyanoborohydride). To this solution, 20 g 2-O-formylmethyl-α-cyclodextrin was added and the mixture was stirred at room temperature for 96 h. Thereafter, the modified chitosan was washed several times with deionized water and subsequently dried to give α-CD-linked chitosan beads.

2.3. Kinetic adsorption and adsorption isotherm tests

Batch experiments for the adsorption of various PAEs on α-CD-linked chitosan beads at 25 °C, pH 7.0 were performed in 300-mL flasks with 100 mL of aqueous solutions containing 100 mg/L of each PAE and α-CD-linked chitosan beads. The solutions and chitosan bead were placed in flasks and shaken at 100 rpm in a shaker for 12 h; the residual concentration of the PAEs in the flasks was then monitored every 1 h. Adsorption isotherm tests for PAEs (10–50 mg/L) on α-CD-linked chitosan bead (1.5 g) were conducted. The temperature and pH were 25 °C and 7.0, respectively. The residual concentrations of various PAEs were measured after 12 h. The Freundlich isotherm, Langmuir isotherm, and BET isotherm were evaluated to understand the adsorption characteristics of α-CD-linked chitosan beads for PAE pollutants. All the analyses were performed at least twice.

2.4. Recovery of PAEs and reuse of α-CD-linked chitosan bead

α-CD-linked chitosan beads (1.5 g) previously saturated with adsorbed PAEs were dried at 60°C and then shaken at 100 rpm for 4 h with a 100-fold volume of solvent mixed with water and methanol to recover the PAEs. The mixture ratio of methanol and water was varied over the range of 9:1–3:7. Every 0.5 h the concentrations of PAEs were analyzed to obtain recovery efficiency. The α-CD-linked chitosan beads were washed with deionized water and dried at 60°C for reuse.

2.5. Effect of temperature, pH, Ca2+ and NaCl on PAE adsorption

The experiments were performed in 300-mL flasks with 100 mL of each PAE (100 mg/L) and 1.5 g of chitosan bead. The reaction time and pH were 12 h and 7, unless stated otherwise. The temperature ranged from 15 to 60°C. The effect of pH on PAE adsorption was studied in the pH range of 2.5–7.0.
range of 6–9. To investigate the effect of $Ca^{2+}$ on adsorption, solutions containing different concentrations of $Ca^{2+}$ (4, 40, 400 mg/L as CaCO$_3$) were used to simulate the possible groundwater environment. The effect of NaCl on adsorption was also studied, with NaCl concentrations in a range from 17 to 1700 mg/L simulating a possible seawater environment.

2.6. Column tests

The continuous column treatment test was done using a Pyrex tube 1.5 cm in diameter and 30 cm long with a water jacket. Twenty grams of $\alpha$-CD-linked chitosan beads was loaded on the column, and the packing volume was 21 mL. An aqueous solution containing 100 mg/L PAEs were fed at the flow rate from 0.6 to 3.9 mL/min into the column. The effluent from the column was sampled every 0.5 h until 100% breakthrough occurred. The column was maintained at 25 °C by circulating water in the column jacket.

PAE removal from the effluent of a plastics plant (Tainan County, southern Taiwan) by an $\alpha$-CD-linked chitosan bead packed column was carried out at 1.2 mL/min. The pilot-scaled reactor contained ID = 20 cm and a packing depth of 280 cm. In the sewage of the plant, the average DEHP concentration was 98 ± 6 mg/L, and the concentrations of all the other phthalates were less than 10 μg/L. The temperature ranged from 24 to 26 °C, and the pH from 7.6 to 8.0. No pre-treatment was conducted before the sewage was continuously introduced to the column system. Additionally, an on-line desorption by an equal parts methanol/water mixture was conducted at 0.6 mL/min for 6 h when the $\alpha$-CD-linked chitosan bead had become saturated. The $\alpha$-CD-linked chitosan bead was recycled at least 20 times by cycling the adsorption and desorption of DEHP.

2.7. Analytical methods for PAEs

Phthalate esters were analyzed by GC-MS. The method of phthalate ester analysis was modified from previous studies (Chen, 2004). GC-MS analysis was conducted using an HP 5890 series II GC and HP 5971 MSD. The GC-MS column was Ultra-2 fused silica capillary column (25 m x 0.2 i.d.). The column temperature range was programmed from 160 to 240 °C. The flow rate of the carrier gas (Helium) was 31 cm/s, and the injector and detector temperatures were 250 and 280 °C, respectively.

3. Results and discussion

3.1. Kinetic adsorption tests

Fig. 1 shows the residual concentration of each phthalate ester in the flask with a shaking time of 12 h. The results indicated that the order of adsorption efficiency was DHpP > DBP > DEHP > DPP > DEP > DMP. PAEs achieved adsorption balance in 6 h, and the maximal adsorbed ratio for DHpP was 96%. The adsorption capacity of PAEs was (mg/g) DHpP (3.21) > DBP (3.16) > DEHP (3.09) > DPP (2.87) > DEP (2.82) > DMP (2.76). The chitosan bead with $\alpha$-cyclodextrin favored the adsorption of DHpP, but not of DMP. The adsorption capacity increased with increased hydrophobicity. The adsorption capacity of $\alpha$-CD-linked chitosan bead pure was more than chitosan bead (Chen and Chung, 2006). The adsorption capacity of activated carbon was higher than $\alpha$-CD-linked chitosan bead (Adhoum and Monser, 2004), but much more expensive.

3.2. Adsorption isotherm

Graphic presentations of the adsorption isotherm results are given in Fig. 2. The adsorption capacity appeared to increase with increasing logarithm equilibrium concentration ($r^2 = 0.987–0.998$), and it fit the Freundlich isotherm.
well compared to the Langmuir isotherm and the BET isotherm (data not shown). The Freundlich equation can be generally described as \( q = KC^{1/n} \) where \( q \) is the adsorption capacity (mg/g) and \( C \) is the equilibrium concentration (mg/L). By plotting \( \log q \) as the \( y \) axis and \( \log C \) as the \( x \) axis, \( K \) and \( 1/n \) were calculated as Freundlich constants. The results and the correlation coefficients are listed in Table 1. In these parameters, \( K \) generally indicates the adsorption capacity of the adsorbent for various pollutants. The adsorption capacity tendency of \( \alpha \)-CD-linked chitosan beads for PAEs was similar to the results of Fig. 1. Freundlich isotherm predicted that the equilibrium capacity would increase steadily with equilibrium concentration in the aqueous solutions. The isotherms of PAEs were linear with that of each equilibrium concentration. However, the coefficients were different for each PAE in the case of \( \alpha \)-CD-linked chitosan bead.

### 3.3. Recovery of PAEs and recycling of \( \alpha \)-CD-linked chitosan beads

For the purpose of reducing costs and waste, a practical method of both recovering PAEs and recycling chitosan beads was developed. The \( \alpha \)-CD-linked chitosan bead, previously saturated with DHpP, was immersed for 4 h with 100 mL of solvent using an aqueous methanol to de-absorb DHpP. The mixture ratio of the solvent varied from 90% to 30% methanol, and calculations of recovery efficiency for each solvent were based on the ratio of the amount of recovered DHpP to the amount of DHpP previously adsorbed on \( \alpha \)-CD-linked chitosan bead. The recovery efficiency depended on the methanol/water ratio and the most efficient mixing ratio of the solvent was 80% methanol to 20% water. Under these conditions, a 94.6% recovery efficiency was attained. DHpP tended not to be released from chitosan bead in the methanol-rich solvent although it could be dissolved in it. The balance between the tendency of DHpP to be adsorbed on \( \alpha \)-CD-linked chitosan bead and to be dissolved into the solvent appeared important. This suggested that \( \alpha \)-CD-linked chitosan bead adsorbed DHpP and could be advantageously reused. Similar results were found in five other phthalate esters as well: DBP (92.7%), DEHP (91.5%), DPP (89.6%), DEP (87.5%), DMP (86.2%), methanol/water (v/v) = 8/2.

The \( \alpha \)-CD-linked chitosan bead was recycled 20 times by cycling the adsorption and desorption of DHpP. The desorption solution contained a mixture of 80% methanol and 20% distilled water. \( \alpha \)-CD-linked chitosan beads (1.5 g) and 100 mL of the solvents were used for the recycling test. Results showed that even after 20 test cycles, desorption efficiency was still maintained at 91.5%. Thus, repeated cycling of \( \alpha \)-CD-linked chitosan bead should be possible.

### 3.4. Effect of temperature and pH on PAE adsorption

The results showed that PAE adsorption amounts decreased as temperature increased (Fig. 3). The peak adsorption occurred at 15°C. This indicated that PAE adsorption on \( \alpha \)-CD-linked chitosan bead was an exothermic reaction: higher temperatures resulted in lower amounts of saturated adsorption. The temperature of Taiwanese rivers generally remains below 40°C throughout the year (Liou et al., 2004). Thus, \( \alpha \)-CD-linked chitosan beads could be applied in a Taiwanese aqueous environment.

Since pH value may affect the charge properties of PAEs, chitosan, and cyclodextrin, and it may further affect the adsorption efficiency of \( \alpha \)-CD-linked chitosan bead for various PAEs, it is necessary to evaluate the impact. The experiments showed that pH changes did not affect adsorption efficiency (\( p > 0.05 \)) (data not shown). Cyclodextrin is water-soluble (Crini, 2005), but PAEs and chitosan are difficult to dissolve in water solutions (Staples et al., 1997a). Hence, pH value more easily affected the charge properties of cyclodextrin than those of PAEs and chitosan. In present

![Fig. 3. Effect of temperature on efficiency of adsorption by \( \alpha \)-CD-linked chitosan bead. Each PAE (100 mg/L) was performed on 1.5 g of \( \alpha \)-CD-linked chitosan bead in aqueous solution at pH 7.0 for 12 h.](image-url)
study, the cyclodextrin was reacted with chitosan to form \(\alpha\)-CD-linked chitosan bead, and the molecules were hard to dissolve into the water solution. Hence, the \(\alpha\)-CD-linked bead became more resistant to pH compared to cyclodextrin (Crini, 2005), and pH changes did not affect the adsorption efficiency of \(\alpha\)-CD-linked bead. The general pH value for freshwater aquaculture ranges from 7.0 to 9.0, hence, it could be suitable to use \(\alpha\)-CD-linked chitosan bead as an adsorbent in PAE-polluted freshwater aquaculture systems.

### 3.5. Effect of \(Ca^{2+}\) and \(NaCl\) on PAE adsorption

In Taiwan, groundwater is an important source for the agriculture industry. Groundwater is harder than surface water, so we used \(Ca^{2+}\) (the main component of hardness) as an indicator to evaluate the effect of \(Ca^{2+}\) coexistence on PAE adsorption. The results showed that the adsorption efficiency of each PAE on \(\alpha\)-CD-linked chitosan bead was not affected at any of three different \(Ca^{2+}\) concentrations \((p > 0.05)\) (data not shown). The average value of hardness in the groundwater in Taiwan was 70 mg/L as \(CaCO_3\) (Lin et al., 2002), hence, using \(\alpha\)-CD-linked chitosan bead as an adsorbent in a groundwater or freshwater aquaculture system could be suitable.

To evaluate the feasibility of using \(\alpha\)-CD-linked chitosan bead to remove PAEs from a seawater system, the effect of \(NaCl\) (representative of salinity) on PAE removal was conducted. Results showed that salinity (\(NaCl\) concentration) would not reduce the adsorption efficiency of \(\alpha\)-CD-linked chitosan bead for phthalate esters (data not shown). The average salinity in the Taiwanese aquaculture system was 1500 mg/L (Chu et al., 1999), suggesting that \(\alpha\)-CD-linked chitosan bead as an adsorbent might be applied in a seawater aquaculture system as well.

### 3.6. Column adsorption test

To test the practical application of \(\alpha\)-CD-linked chitosan bead to the continuous removal of PAEs from raw water, the column adsorption test was conducted. The results indicated that breakthrough time (i.e.: \(C/C_o = 0.2\), with \(C\) and \(C_o\) the effluent and influent concentrations of PAE, respectively) decreased as flow rate increased (data not shown). The six PAEs could be divided into two groups according to their breakthrough times (flow rate at 0.6 ml/min): (1) DHP, DBP, DEHP and (2) DMP, DEP, DPP. The breakthrough times of the more hydrophobic PAEs (group1) were longer than those of the less hydrophobic PAEs (group2) (Fig. 4). Furthermore, other flow rates also showed similar results (data not shown). We suggest that breakthrough time could be related to adsorption capacity. Hence, low adsorption capacity (less hydrophobic) compounds like DMP, DEP and DPP should be treated over a longer contact time with \(\alpha\)-CD-linked chitosan bead or at a low flow rate. Furthermore, it was also found the order of PAE breakthrough times corresponded to their adsorption capacity in the batch test. DHP and DMP had the highest and the lowest adsorption capacity among the six phthalate esters, respectively. For DHP, 100% breakthrough time was at 8 h when the flow rate was 0.6 ml/min, and it fell to 6 h when the flow rate was adjusted to 3.9 ml/min (data not shown). These results suggest that flow rate has a crucial effect on \(\alpha\)-CD-linked chitosan bead adsorption.

From the results of the plastics plant sewage treatment, DEHP breakthrough time and 100% breakthrough time were about at 4.5 and 7 h, respectively (Fig. 5), in line with the results of the laboratory continuous column test. Hence, \(\alpha\)-CD-linked chitosan bead could effectively remove DEHP or its derivatives in a complicated substrate, even from the
discharge of a plastics plant. Furthermore, the continuous column system of α-CD-linked chitosan bead was renewed by cycling the adsorption and desorption of DEHP. After 15 recycling rounds, the adsorption curve of α-CD-linked chitosan bead for DEHP was similar to the curve before recycling, and the final desorption efficiency reached 90.2%. However, after 20 cycles, efficiency dropped to 72.4%. Compared with laboratory results, the desorption efficiency of plant sewage treatment was low. Some coexisting pollutants might accumulate or adsorbed in the packed column, resulting in decreasing adsorption efficiency for DEHP. Moreover, the breakthrough time at 3 h was significantly shorter ($p < 0.05$). The results indicated a continuous adsorption–desorption system was potentially applicable to the treatment of wastewater.

4. Conclusions

Overall, α-CD-linked chitosan bead exhibited efficient removal of various phthalate esters from aqueous solution both in batch and continuous column tests. Furthermore, α-CD-linked chitosan bead could be reused 15 times in the real wastewater at least. The adsorption of phthalate esters by α-CD-linked chitosan bead is dependent upon temperature, but not pH, Ca$^{2+}$, or NaCl. The α-CD-linked chitosan bead exhibits a good capacity to adsorb phthalate esters in the low temperature range. From these results, we suggest that α-CD-linked chitosan bead could be used as a good phthalate ester adsorbent, even in diverse water environments. It also is feasible to apply the continuous adsorption–desorption system in treating wastewater containing PAEs.

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References


