

Adsorption of 4-nonylphenol ethoxylates onto insoluble chitosan beads bearing cyclodextrin moieties

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Abstract In order to develop a treatment method for industrial wastewater, the adsorption of 4-nonylphenol ethoxylates (NPEs), non-ionic surfactants used in the industry, onto chitosan beads having cyclodextrin (CDC beads) was investigated. Three kinds of CDC beads containing different cyclodextrin (CD) moieties were prepared from poly-carboxymethylated α -, β - and γ -CDs. Among α -, β - and γ -CD cavities, β -CD was the most suitable for the adsorption of the phenol derivatives. The amount of adsorption was greater for the NPEs having shorter ethoxylates. Most of the NPE adsorbed on the β -CDC beads were successfully released by the treatment of the CDC beads with various aqueous alcohol solutions. After 20 cycles of the adsorption–desorption were completed, no significant decline in the adsorption amount was observed. Continuous adsorption tests were carried out using the CDC beads filled in a glass column. At the appropriate flow rate, the NPE can be adsorbed with a reasonable saturation amount.

Keywords Adsorbent · Chitosan · Cyclodextrin · Non-ionic surfactant

Introduction

Cyclodextrins (CDs) are cyclomalto-oligosaccharides consisting 6, 7 and 8 anhydroglucopyranose units and form inclusion complexes with various organic hydrophobic substances. As in a recent review written by Prabakaran and Mano [1], chitosan bearing CD moieties have often been investigated because of the interest as a selective adsorbent for wastewater treatment [2–7], removal of unfavorable food contents [8, 9] or as a matrix for the slow-release of drugs in the medical field [10]. We recently revealed that insoluble CDC beads can be easily obtained by the condensation between poly-carboxymethylated β -CD and unmodified chitosan beads (Scheme 1) [4]. We also reported the CDC beads can adsorb hydrophobic phenol derivatives, such as 4-nonylphenol (4-NP) and bisphenol A (BPA) from their aqueous solutions. An important merit of our method is that cross-linking is not necessary before or after immobilization of the CD moieties on chitosan because poly-carboxymethylated CD itself works not only as adsorption sites, but also as a cross-linker.

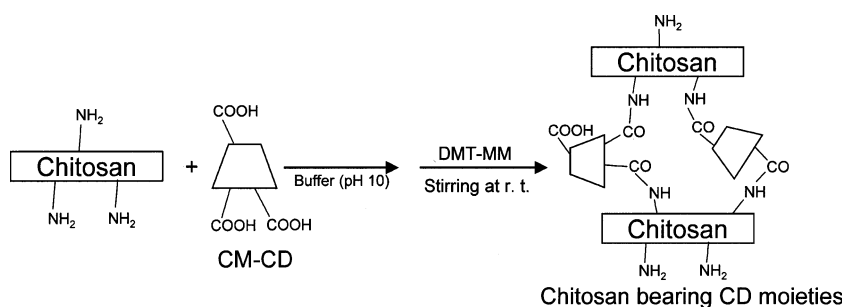
We now describe the adsorption of 4-nonylphenol ethoxylates (NPEs) onto CDC beads. It was reported that NPEs are dumped into industrial effluents and biodegraded to 4-NP in rivers or underground water [11]. Considering that the degradation products of NPEs have an endocrine disrupting activity [12], it was important to remove the NPEs from the wastewater.

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Scheme 1 Preparation of insoluble chitosan beads using poly-carboxymethylated CD and DMT-MM [4]



Experimental

Material

Poly-carboxymethylated CDs (CM-CDs) were prepared from β -CD (Wako Pure Chemicals Industries, Ltd.), α -, or γ -CD (kind gifts from Cyclochem Co., Ltd.). The spherical chitosan beads (Chitopearl AL-10, 1.0 mm ϕ) were purchased from Fuji Spinning Co., Ltd. Water content of the original and the modified chitosan beads were calculated from the difference between weights of the chitosan beads samples before and after drying. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methyl morpholinium chloride (DMT-MM), an water-soluble condensing agent, was synthesized by the reported method [13]. NPEs (Tokyo Chemical Ind., Co., Ltd.) are a mixture of NPEs having different ethoxy chain lengths, and the average number of ethoxy repeating units, n , are indicated in this paper.

Synthesis

Insoluble CDC beads were obtained by a previously reported method [4]. Chitosan beads and poly-carboxymethylated α -, β -, or γ -CDs (prepared by the reported method [14]) were stirred with DMT-MM in a buffer solution (pH 10) at room temperature. The products were washed with water for several days. The CD contents of the products were determined by the phenol–sulfuric acid method [15].

Adsorption and desorption tests

An aqueous 30 ml solution of the NPE or BPA was shaken with 0.3 g of wet CDC beads at 25 °C. The concentration of the phenolic compounds was determined spectrophotometrically. The continuous adsorption tests were done using 3.0 g of β -CDC beads filled in a glass column (5.0 mm ϕ). A solution of NPE ($n = 10$) or BPA (1.0×10^{-4} M) was passed through the column at 0.71 ml/min (space velocity = 21 h $^{-1}$).

Results and discussion

Preparation of CDC beads

The average number of carboxymethyl groups in a CM-CD molecule was estimated by the $^1\text{H-NMR}$ spectrum to 1.9, 3.2 and 3.2 for CM- α -, β - or γ -CDs, respectively. Furthermore, the TOF-MS analyses revealed that each CM-CD was a mixture of the corresponding CM-CD having different number of carboxymethyl groups (0–5, α - and γ -CD, 0–6, β -CD). The CM-CDs were used as the mixture for the preparation of the CDC beads.

In our previous study [4], we used the chitosan beads (2.8 mm ϕ) prepared in our laboratory. The chitosan beads were relatively fragile because they had significantly swelled (water content, 97 wt%). In this study, we used commercial spherical chitosan beads (1.0 mm ϕ , water content, 92 wt%) to improve the toughness of the beads. Table 1 summarizes the results of the condensation between the three kinds of CM-CD and chitosan beads. The CDC beads containing more than 30 wt% of the corresponding CD moieties were successfully obtained under the appropriate condition.

Adsorption of NPE on CDC

As an evaluation of the CDC beads as an adsorbent for nonionic surfactants, simple batch adsorption tests were carried out using β -CDC beads and NPE ($n = 10$), BPA and 4-NP (Fig. 1). The CDC beads adsorbed all the phenols, but the adsorption rate and

Table 1 Preparation of CDC beads

CM-CD	Chitosan beads (g)	DMT-MM (g)	Time (h)	CD (%)
CM- α -CD	6.22 (g)	10.0	3.44	18
CM- β -CD	18.6 (g)	32.0	10.3	24
CM- γ -CD	18.6 (g)	30.0	10.3	16

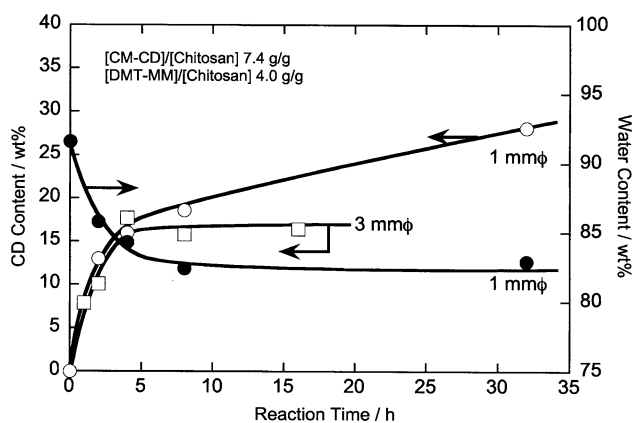


Fig. 1 Adsorption of NPE ($n = 10$), BPA, and 4-NP on β -CDC-beads (CD wt% 20.5%, 0.30 g). C: concentration of phenol derivatives, C_0 : initial concentration of phenol derivatives. C_0 was adjusted to 1.0×10^{-5} mol/l

amount of adsorption at equilibrium were dependent on the adsorbates. We reported that chitosan does not adsorb BPA in a batch systems [2] and we also confirmed the chitosan beads does not adsorb NPEs by preliminary experiments. Therefore, the adsorption of the phenols was assigned to the CD moieties attached to chitosan beads.

NPE showed a lower adsorption rate and lower adsorption amount than 4-NP and BPA. As reported in our previous study, the hydrophobic property of the phenols affects the adsorption onto the chitosan bearing CD. Therefore, the difference was considered to be due to the more hydrophilic property of the NPE than 4-NP and BPA. This was confirmed by adsorption tests using NPEs having various ethoxy chain lengths (Fig. 2). The isotherm for each adsorbate showed a good correlation. The saturation amounts of the adsorption (q_e) and equilibrium constants (K) from the Langmuir plots in Fig. 2 and the corresponding value of K estimated from Fig. 1 by kinetic approximation [4] are summarized in Table 2. It was found that K decreased as the length of the ethoxy chain increased. Based on the fact that NPE became more hydrophilic with the longer ethoxy chain, this also showed that the adsorption occurred more smoothly with more hydrophobic compounds. In contrast to K value, the difference in value of q_e for the various adsorbates was relatively small.

The effect of CD cavity size on the adsorption behavior was also investigated using CDC beads prepared from CM- α -, β -, and γ -CD. The adsorption experiments were summarized by the K values obtained from the Langmuir adsorption isotherm (Table 3). The β -CDC beads showed the largest K with

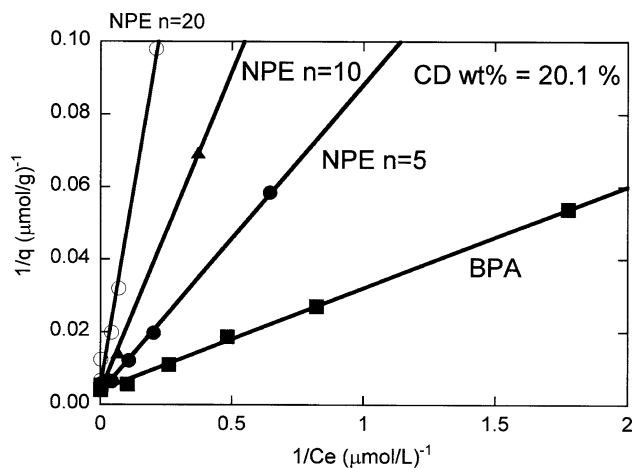


Fig. 2 Adsorption isotherm for Langmuir plots. C_e and q are concentration and adsorption amount of phenols at equilibrium, respectively

both BPA and NPE. However, the order of α , β , and γ was different between BPA and NPE: $\beta > \gamma > \alpha$ for BPA and $\beta > \alpha > \gamma$ for NPE. The relatively large K of α -CD for NPE was probably due to the fact that the ethoxy chain in NPE was included in the α -CD cavity [16] while only the phenol groups in BPA are available for the inclusion.

Regeneration of CDC beads and repeated use

An important merit of a polymer bearing CD moieties as an adsorbent is its reuse for selective adsorption. The CDC can be recycled by treatment with an aqueous alcohol, such as methanol and ethanol [2–4]. In this study, the adsorption of NPE and subsequent desorption using 50 vol% ethanol were repeated 20 times (Fig. 3). The absorbance at 276 nm of the solutions

Table 2 Equilibrium constants from Figs. 1–2

Guest	Langmuir plots		Figure 1 K (M^{-1})
	q_e (M^{-1})	K (M^{-1})	
BPA	251	1.56×10^5	1.07×10^5
NPE $n = 5$	281	4.21×10^4	
NPE $n = 10$	250	2.28×10^4	
NPE $n = 20$	272	8.29×10^3	

Table 3 Equilibrium constants K

Guest	K (M^{-1})		
	α	β	γ
BPA	321	1.56×10^5	953
NPE $n = 10$	6720	2.28×10^4	3100

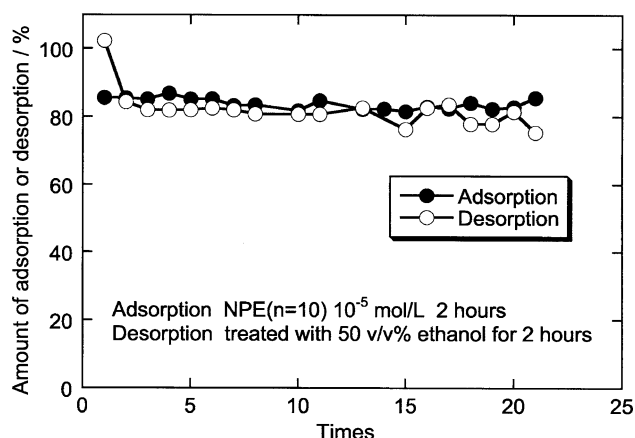


Fig. 3 Results of adsorption–desorption repetition tests

after each adsorption or desorption treatment were plotted as the ratios to that of the NPE 10^{-5} M solution. During the 20 adsorption-desorption cycles, the amount of the adsorption and desorption were almost constant and no significant decrease in the adsorption was observed.

Adsorption of NPE in flow system

The results of the continuous treatment of the solution of NPE ($n = 10$) or BPA using β -CDC beads packed in a glass column are shown in Fig. 4 as the ratio of the UV absorbance of the solution before and after treatment. The β -CDC beads adsorbed both BPA and NPE while the chitosan beads without CD adsorbed only a negligible amount of BPA. In the case of BPA, a sharp rise in the BPA concentration of the eluent was clearly observed and the amount of saturation (570 ml), indicated by the arrow in Fig. 4, was very close to the value calculated from the amount of the CD moieties (560 ml).

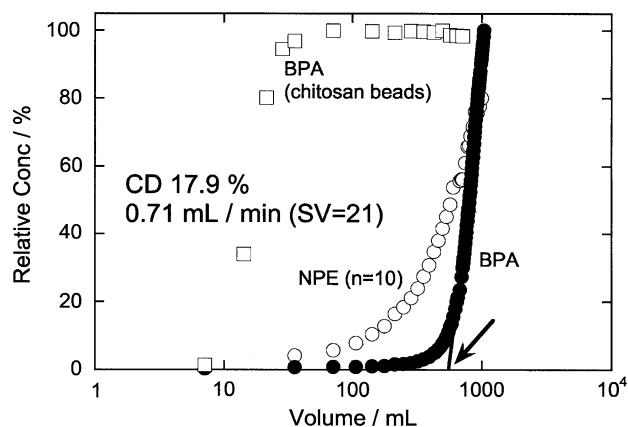


Fig. 4 Breakthrough curves of BPA and NPE ($n = 10$) in aqueous solution

On the other hand, the NPE concentration gradually increased before the expected saturation amount. This was caused by the relatively slow adsorption of NPE and the leaking of NPE can be decreased by a slower flow rate.

Conclusion

The CDC-beads with CD content above 30 wt% were prepared by the condensation between the carboxymethylated α -, β -, or γ -CD and chitosan beads. Among the different sizes of the CD cavities, β -CD was the best for the adsorption of BPA and NPE. The adsorption of NPE depended on the ethoxy chain in the NPE molecules. The used β -CDC beads were recovered by ethanol treatment. The NPE and BPA could be continuously removed from a water solution using the β -CDC beads packed in a glass column.

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