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Comparative study of the adsorption on chitosan beads of phthalate esters and their degradation products

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ABSTRACT

The adsorption behavior of phthalate esters (PAEs) and their degraded products such as phthalate monoesters (MPEs) and phthalic acid (PA) in aqueous solution on chitosan beads was studied. The results of kinetic experiments showed that dibutyl phthalate (DBP) was adsorbed more than di-(2-ethylhexyl) phthalate (DEHP) and dimethyl phthalate (DMP). MPEs exhibited less adsorption than PAEs. Monobutyl phthalate (MBP) had higher adsorption capacity than monomethyl phthalate (MMP) and monoethylhexyl phthalate (MEHP). PA showed the highest adsorption capacity compared to MPEs and PAEs. Fourier transform infrared spectroscopy (FT-IR) was used to characterise the interaction between chitosan and PAEs, MPEs, and PA molecules. Results showed that chitosan adsorbed PAEs mainly due to hydrophobic interactions, and interacted with PA mainly due to interactions between polar active groups. For the monoesters, especially MMP and MEHP, lower hydrophobicity than PAEs and higher hydrophilicity than PA made them less adsorbable.

1. Introduction

Phthalate esters (PAEs) are a class of widely used industrial compounds known technically as dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acid. They are plasticisers widely used to impart flexibility to plastics particularly polyvinyl chloride (Staples, Peterson, Parkerton, & Adams, 1997). Worldwide production of PAEs is approximately 6 million tones per year (Mackintosh, Maldonado, Ikonomou, & Gobas, 2006).

Different types of phthalate esters are produced depending on intended use. The commonly used phthalates are those with commercial advantages. Plasticisers are used to make different products including floor tiles, various types of household furnishing, food packaging, industrial and medical tubing, catheters, blood containers, and numerous other products (Tanaka, 2002).

Regarding the wide production and use of PAEs, these chemicals are regularly released into the environment through production, manufacturing, use and disposal (Staples, Parkerton, & Peterson, 2000). PAEs are considered to be endocrine disruptor chemicals and toxic environmental priority pollutants. They are not chemically bound to the plastic polymer, and therefore can eventually migrate from the plastics to the environment. At the present time, PAEs are detected in different areas of the environment such as in sediments (Huang, Tien, Sun, Hsieh, & Lee, 2008), air (David, Sandra, Tienpont, Vanwalleghem, & Ikonomou, 2003), surface water (Furtmann, 1994; Staples et al., 2000), and in marine and aquatic organisms.

Although most PAEs have very low acute toxicity, chronic exposure to PAEs could result in serious toxic effects to animals especially rodents; as a result concerns were raised regarding the toxicity of these compounds with respect to human health. PAEs have been reported to exert hepatotoxic, cytotoxic, teratogenic and mutagenic effects (Seth, 1982). DEHP has been associated with respiratory symptoms and lung diseases. Through respiratory therapy, PAEs which can be consumed by patients are mainly diethyl phthalate (DEP) and di-(2-ethylhexyl) phthalate (DEHP) (Hill, Shaw, & Wu, 2001). They are also reported to interfere with reproductive systems and the development of different organisms (Cabana, Jones, & Agathos, 2007). DBP can impair fertility of both sexes in rodents, decrease testis weight and sperm production and cause reproductive tract malformations in male rats (Ashby & Lefevre, 2000; Lamb, Chapin, Teague, Lawton, & Reel, 1987). Liver carcinogenicity was observed in rodents following long term exposure to di-(2-ethylhexyl) phthalate (DEHP) and di-iso-nonyl phthalate (DINP) (Peters, Cattley, & Gonzalez, 1997).

PAEs can be removed from the environment through different methods such as hydrolysis (Jonsson, Vavilin, & Svensson, 2006), photo degradation (Zhao, Yang, Wang, & Gao, 2004), microbial

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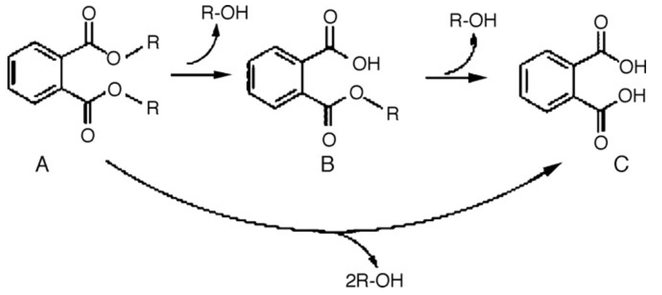

Fig. 1. Metabolic pathway for phthalate ester: (A) phthalate ester, (B) monoester and (C) phthalic acid (Jonsson et al., 2003).

degradation (Jonsson, Ejlertsson, & Svensson, 2003), and adsorption (Ayranci & Bayram, 2005; Chen, Chen, & Chung, 2007). The most applicable removal method of phthalate esters is microbial degradation. The pathway of microbial degradation of PAEs in the environment includes ester hydrolysis to the corresponding monoester which can undergo further enzymatic ester hydrolysis to form phthalic acid. Phthalic acid can be further broken down to benzoic acid, and finally to carbon dioxide (Staples et al., 1997). However microbial degradation is reported to be time consuming and phthalates with long chains are poorly degraded (Ejlertsson, Alnervik, Jonsson, & Svensson, 1997). Adsorption using activated carbon has been shown to be non-selective and expensive, its performance depending on the type of carbon used; the higher the quality the greater the cost (Crini, 2005). The hydrolysis of phthalate esters is shown in Fig. 1.

MPEs are primary metabolic products of PAEs (Niino et al., 2001), they are of no commercial value, and they exist as intermediates during PAE synthesis. They can be formed through biotransformation by higher organisms, microbial processes or through abiotic degradation (Scholz, 2003). Various types of technology are available for removing PAEs from water, however, only few methods are known for removal of PAE metabolites (MPEs and PA). MPEs are valuable biomarkers for exposure to PAEs. Studies show that MPEs have been detected in human saliva (Niino et al., 2001), human urine and faeces (Silva et al., 2003), and in human milk (Mortensen, Main, Andersson, Leffers, & Skakkebæk, 2005), and they have been suggested to be responsible for the toxicological properties of their corresponding PAEs. Monobutyl phthalate (MBP) is reported to decrease rat's maternal weight gain and food consumption (Ema, Kurosaka, Harazono, Amano, & Ogawa, 1996) and monoethylhexyl phthalate (MEHP) exhibits genotoxic effects in human lymphocytes (Kleinsasser et al., 2004). Phthalic acid (PA) induces maternal toxicity in rats (Ema, Miyawaki, Harazono, & Kawashima, 1997) and it is a germ-cell mutagen which can cause an increasing frequency of abnormal sperm in male rats (Jha, Singh, & Bharti, 1998). In view of the toxicity effects of MPEs and PA as presented, it is important to find a method to remove not only PAEs but also their metabolites (MPEs and PA).

Chitosan, the partially deacetylated derivative of chitin, is a nontoxic copolymer consisting of (1 → 4)-2-acetamido-2-deoxy-β-D-glucopyranosyl and (1 → 4)-2-amino-2-deoxy-D-glucopyranosyl units. Chitosan is biodegradable and has a good adsorption capability. It has been used to adsorb heavy metals (Guibal, 2004), and different natural organic compounds (Ngah & Mussa, 1998). It has been proven that chitosan beads can efficiently remove various phthalate esters from aqueous solution (Chen & Chung, 2006, 2007; Chen et al., 2007). The influences of temperature, pH, calcium ions (Ca^{2+}), and sodium chloride on PAE adsorption has been evaluated to determine performance in different water environments such as groundwater, surface water, and sea water. However, there are no reports about removal of MPEs and PA by chitosan beads.

The main goal of this paper was to study the adsorption of PAEs and their degraded products on chitosan beads, with the hypothesis that the amino group in chitosan molecules might be effective in removing monoesters and acids from aqueous solution by interacting with the carbonyl group in MPEs and PA. Hence, chitosan should be more efficient in removing MPEs and PA than PAEs. The adsorption behavior of PAEs and their degraded products (MPEs and PA) was therefore evaluated and compared. Sorbents were characterised by FT-IR spectroscopic analysis to determine the interaction between chitosan and PAEs and their degraded products.

2. Materials and methods

2.1. Reagents and chemicals

Phthalate esters containing di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), and dimethyl phthalate (DMP) and monoesters containing monobutyl phthalate (MBP), monoethylhexyl phthalate (MEHP) and mono-methyl phthalate (MMP), were purchased from Dr. Ehrenstorfer GmbH (Germany) and phthalic acid (PA) was bought from Tianjin Guangfu Fine Chemical Industry Institute. Powdered chitosan, from shrimp shell, with a molecular weight of 78 kDa and degree of deacetylation of 85.5% was purchased from Yuhuan Ocean Biochemical (Zhejiang, China). All other reagents were of suitable analytical grade and deionised water was used to prepare solutions and for washing apparatus. The physicochemical properties of PAEs, MPEs and PA used in these studies are provided in Table 1.

To avoid contamination, plastic equipment was not used in any sampling or experimental processes and all glass apparatus was soaked in chromic acid solution for at least 12 h, washed with deionised water and baked at 180 °C for not less than 4 h.

2.2. Preparation of chitosan beads

Chitosan solution was prepared by dissolving chitosan powder (3 g) in acetic acid solution (1%, v/v, 100 mL). The viscous solution was left overnight before adding drop wise into magnetically stirred sodium hydroxide solution (1 M, 500 mL) forming spherical uniform beads with a relatively uniform size distribution of ~4 mm diameter. The resultant chitosan beads were gently filtered and repeatedly rinsed with deionised water, to remove any residual sodium hydroxide. The chitosan beads were stored in deionised water at 4 °C until required.

2.3. Adsorption study

Adsorption experiments for each PAE (DMP, DEHP and DMP), and each MPE (MMP, MEHP and MBP) and PA on chitosan beads were conducted at room temperature at pH 7.0 (neutral pH). Chitosan beads (3 g) were separately added to an aqueous solutions (10 mL) containing a PAE, MPE or PA (15 mg/L) in a flask (50 mL). The flasks were shaken in a shaker for 12 h at 200 rpm until the adsorption equilibrium was established. The temperature and pH were maintained at 25 °C and 7.0, respectively throughout the experiment. The residual solution concentrations of PAE, MPE or PA were monitored at hourly intervals (as subsequently detailed).

2.4. Instrumental analysis

Determination of phthalates in water was performed using an Agilent 1100 HPLC system equipped with a variable wavelength detector (VWD) and an injection loop manual injector. The analytes was separated using a Kromasil C_{18} column (250 mm × 8 mm, i.d. 5 mm). A personal computer equipped with Agilent Chemstation software for LC was used to process all generated chromatographic

Table 1
Physico-chemical properties of the studied PAEs, MPEs and PA (Peterson & Parkerton, 1999; Staples et al., 1997).

Compound	Formula	Molecular weight (g/mol)	Water solubility (mg/L)	Acid dissociation (pKa)
Dimethyl phthalate (DMP)	$C_{10}H_{10}O_4$	192.2	5220	–
Dibutyl phthalate (DBP)	$C_{16}H_{22}O_4$	278.4	9.9	–
Di-2-ethylhexyl phthalate (DEHP)	$C_{24}H_{38}O_4$	390.6	0.0025	–
Monomethyl phthalate (MMP)	$C_9H_8O_4$	180.2	3721	3.18
Monobutyl phthalate (MBP)	$C_{12}H_{14}O_4$	222.2	409	4.2
Monoethylhexyl phthalate (MEHP)	$C_{16}H_{22}O_4$	278.3	1.85	4.2
Phthalic acid (PA)	$C_8H_6O_4$	166.14	–	2.9

data. Chromatographic parameters were: 20 μL sample injection volume, 1 mL/min flow rate, methanol:water (80:20, v/v) mobile phase, at 35 °C, using a detection wavelength of 224 nm.

2.5. Adsorption capacity

The amount of PAE, MPE or PA adsorbed at equilibrium was calculated using the following equation:

$$\text{adsorption capacity}\,(q_e) = \frac{(C_i - C_e)V}{W}$$

where q_e was the amount adsorbed per unit mass of adsorbent (mg/g), C_i and C_e were the initial and equilibrium concentrations of phthalate ester (mg/L), respectively, W was the weight of chitosan beads (g), and V was the volume of phthalate solution (L).

2.6. FT-IR spectroscopic analysis

FT-IR spectroscopic analysis (using a Nicolet FT-IR 5700) was used to determine the interaction between chitosan and PAE, MPE and PA molecules. Spectra were measured using KBr pellets by pressing mixtures of powdered chitosan bead samples with spectroscopic grade KBr. The FT-IR spectra of chitosan and PAEs, MPEs and PA before and after adsorption were recorded from 4000 to 100 cm^{-1}.

3. Results and discussion

3.1. Adsorption of phthalate esters

The residual solution concentrations of PAEs over the investigated 12 h period are shown in Fig. 2. The results show a rapid initial uptake during the first hour of adsorption for DMP and DBP and 2 h for DEHP, followed by a gradual approach to equilibrium. The adsorption capacity of PAEs and their degraded products were calculated and the order of adsorption capacity for PAEs was DBP (0.022 mg/g) > DEHP (0.01 mg/g) > DMP (0.009 mg/g). A similar trend was found by other investigations into adsorption on chitosan beads (Chen & Chung, 2006), α-cyclodextrin-linked chitosan beads (Chen et al., 2007) and molybdate impregnated chitosan beads (Chen & Chung, 2007).

The sorption of phthalate esters by soil, sediment, or suspended solids is partially governed by the relative compound hydrophobicity. Such hydrophobic compounds adsorb principally to the organic matter associated with the solid. A number of authors have published soil or sediment and water partition coefficients (Staples et al., 1997). The organic carbon-normalised partition coefficients (K_{oc}s) of DMP are from 55 to 360. K_{oc}s of DBP and DEHP are 1375–14,900 and 87,420–5,10,000, respectively. Therefore, theoretically, DEHP should show the higher adsorption capacity followed by DBP and DMP. However, in this study, DEHP showed slower adsorption and lower adsorption capacity than DBP. This indicates that the adsorption of phthalate esters also depends on the structure of the sorbent. Chitosan has a long chain structure and there are hydrophilic groups such as amino and hydroxyl groups outside the carbon chain. The high hydrophobic characteristics of DEHP make it more difficult to contact with the chitosan carbon chain. The higher adsorption capacity for DBP than that of DEHP can also be explained by molecular size, DBP entering more easily into the inner parts of the chitosan beads than DEHP. On the other hand, the larger molecular size of DEHP exhibits a steric hindrance effect, with respect to adsorption on the limited chitosan surface.

3.2. Adsorption of phthalate monoesters

Fig. 3 shows the residual solution concentrations of MPEs after adsorption on chitosan beads over the 12-h period of investigation. MBP was adsorbed rapidly during the first hour followed by no adsorption, while MEHP and MMP showed only a little

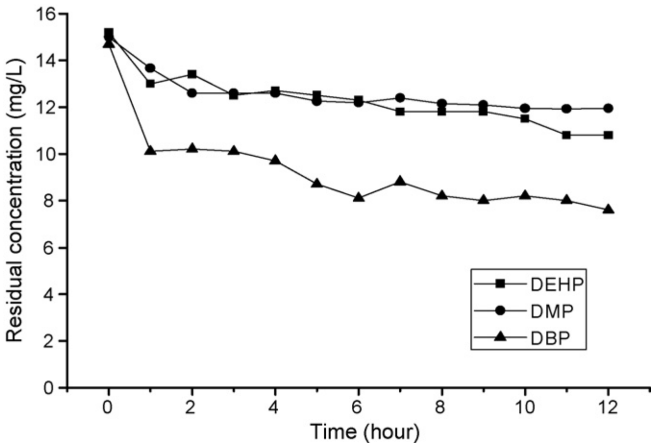

Fig. 2. Adsorption of PAEs on chitosan beads in solution at 25 °C, pH 7, over a 12 h period.

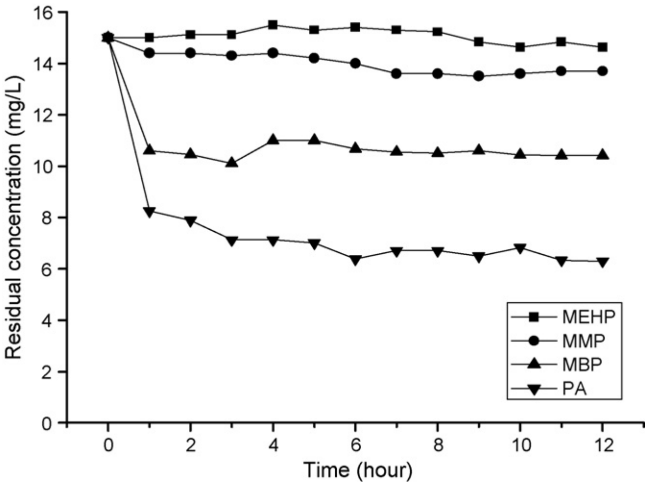

Fig. 3. Adsorption of MPEs and PA on chitosan beads in solution at 25 °C, pH 7, over a 12 h period.

adsorption. The order of adsorption capacity for MPEs was MBP (0.015 mg/g) > MMP (0.003 mg/g) > MEHP (0.001 mg/g). Unexpectedly, the adsorption capacities of all the MPEs were lower than those of the relative PAEs.

MPEs are weak acids and weak electrolytes, they are ionisable compounds in aqueous solution and are more water soluble compared to PAEs. The pKa value for MMP is 3.18 and 4.2 for MBP and MEHP, which are estimated basing on their solubility. MEHP can be 50% ionised at pH $\leq$ 4 and more than 90% ionised at neutral pH (6–7). Adsorbing properties of MPEs decrease with increasing water sample pH (Suzuki, Yaguchi, Suzuki, & Suga, 2001). Jonsson and Boren (2002) suggested that water samples are to be acidified to pH 0.9 during analysis of PA and MPEs to prevent ionisation. MPEs are mostly expected to be in ionic form at a neutral pH. The carboxylate anions ($-COO^-$) of the monoesters were expected to interact with the 'free' amino groups of the chitosan. However, this interaction did not seem to happen, maybe due to the hydrophobicity of the MPEs.

3.3. Adsorption of phthalic acid

Phthalic acid residual solution concentrations after adsorption on chitosan beads over the 12-h period of investigation are also shown in Fig. 3. A rapid initial uptake of PA was observed during the first hour of adsorption. The adsorption capacity of PA was (0.029 mg/g). This may be caused by interaction between the two carboxylate anions in PA and the amino groups in chitosan. In other studies, PA was adsorbed effectively on different types of soils with high contents of iron oxides (Li & Xu, 2007), on carbon surfaces (Ayranci & Bayram, 2005), and on mercury electrodes. However, the mechanism of the adsorption is unknown.

3.4. Adsorption mechanisms

According to the above results, the mechanisms of the adsorption of PAEs, MPEs and PA on chitosan beads may be different. FT-IR spectra are very useful for determining the interaction between molecules, and they also provide information on functional groups. The FT-IR spectra of PAEs, MPEs, and PA before adsorption are shown in Fig. 4. According to the literature (Das & Mahiuddin, 2005), the bands at 1725 cm^{-1} in PAEs and MPEs and 1692 cm^{-1} in MPEs and PA are assigned for ν(C=O). The two equivalent carboxylate groups are identified by ν_{as}(COO–) bands at 1597 and 1584 cm^{-1} and ν_s(COO–) bands at 1400–1463 cm^{-1}.

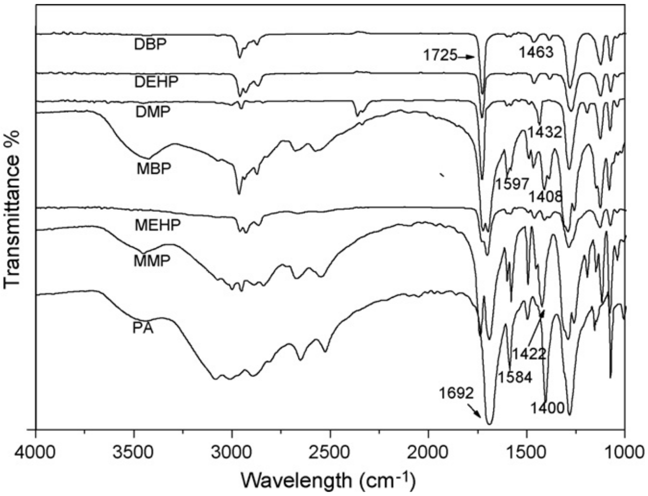

Fig. 4. FT-IR spectra of individual PAEs, MPEs, and PA.

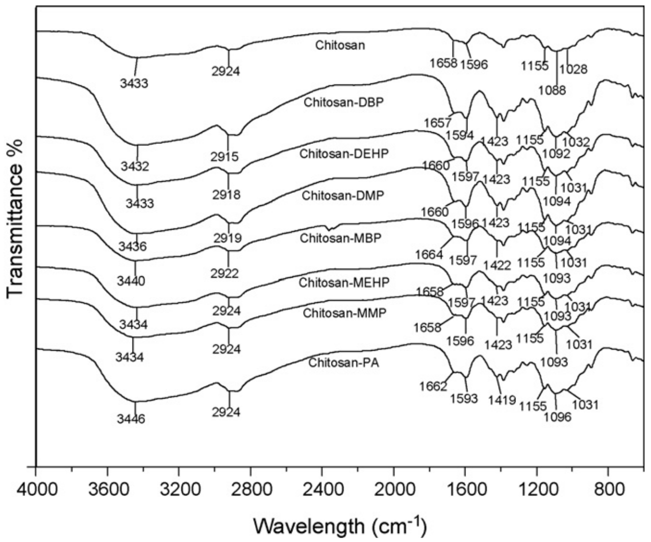

Fig. 5. FT-IR spectra of chitosan before (A) and after adsorption of PAEs, MPEs, and PA.

The FT-IR spectra of chitosan before and after adsorption of PAEs, MPEs, and PA are shown in Fig. 5. The wide peak at 3433 cm^{-1} corresponding to the stretching vibration of $-NH_2$ and –OH groups of chitosan (Wang, Du, Fan, Liu, & Hu, 2005) shifted to 3440 and 3446 cm^{-1} in chitosan-MBP and chitosan-PA, respectively, indicating $-NH_2$ and –OH groups took part in the adsorption. Absorption bands at 1658 cm^{-1} assigned to acetamide groups (Wang et al., 2005) of chitosan tended to have a higher frequency for chitosan-MBP and chitosan-PA, and the band at 1596 cm^{-1} assigned to "free" amino groups of chitosan (Wang et al., 2005) shifted to 1593 cm^{-1} for chitosan-PA. The absorption bands between 1000 and 1200 cm^{-1} came from free hydroxyl groups (Liu, Du, Wang, Hu, & Kennedy, 2004). The peak at 1088 cm^{-1} shifted to a higher frequency in all the samples. Therefore, –OH groups in chitosan participated in the adsorption of PA and MBP, and $-NH_2$ groups were also involved in the adsorption of PA. The band at 2924 cm^{-1} in the chitosan spectrum representing C-H stretching vibrations (Viswanathan, Sundaram, & Meenakshia, 2009) shifted to a lower frequency in chitosan-PAEs, suggesting that the adsorption of PAEs on chitosan was mainly due to hydrophobic interactions. On the other hand, the new obvious peaks at 1423 cm^{-1} for chitosan samples treated with PAE, MPEs, and the band at 1419 cm^{-1} in chitosan-PA are attributed to ν_s(COO–) bands. They are very different from that in the individual PAEs, MPEs, and PA. The ν_{as}(COO–) bands at 1597 and 1584 cm^{-1} in PAEs, MPEs, and PA overlapped with the absorption bands of "free" amino group of chitosan. These results indicated that the carboxylate groups in PAEs, MPEs, and PA participated in the interaction.

In summary, chitosan adsorbed PAEs mainly by hydrophobic interaction and chitosan interacted with PA mainly by interaction between polar active groups. For the MPEs especially MMP and MEHP, lower hydrophobicity than PAEs and higher hydrophilicity than PA made them less adsorbable.

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