Removal of phthalic acid esters from aqueous solution by the biological activated carbon process
Qiuli Chen, Chaosheng Zhang, Meihua Zhao, Hongying Liu, Hongwei Rong and Kefang Zhang

ABSTRACT
This study investigated the removal of phthalic acid esters (PAEs) from aqueous solution by the biological activated carbon (BAC) process. PAEs, such as dimethyl phthalate, diethyl phthalate, dibutyl phthalate, and di(2-ethylhexyl) phthalate, were effectively removed at a 40 mg/L activated carbon dosage by emergency activated carbon treatment for excessive amounts of PAEs. The optimal BAC process parameters were an initial PAE concentration of 10 μg/L and an empty bed contact time of 10 min. Results further showed that with higher summer temperatures, mature biofilms were formed, and CODMn, NH3-N and PAE removal efficiency tended to stabilize for approximately 1 month. During stable BAC operation, biodegradation was the primary mechanism.

Key words | biological activated carbon, phthalate esters, water treatment

INTRODUCTION
Phthalic acid esters (PAEs), used as plasticizers in plastic products, are not chemically bound to vinyl polymers, making migration of PAEs in significant amounts possible (Keresztes et al. 2013). Research has shown that PAEs are sex-hormone-like chemicals that can interfere with the human endocrine system (Ejlerstsson & Svensson 1993). With worldwide production and common application, PAEs are widespread in the environment, and their potential risks to human health have received extensive attention globally. Several PAEs such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate, butyl benzyl phthalate, and di(2-ethylhexyl) phthalate (DEHP) have been identified as priority pollutants by the European Union, the United States Environmental Protection Agency, and other international organizations (USEPA 2012).

PAEs have been detected in rivers and lakes, such as in the Yangtze River (Wang et al. 2008), the Yellow River (Sha et al. 2007), the Pearl River (Liu et al. 2014), the Qiantang River (Sun et al. 2013), urban lakes in Guangzhou (Zeng et al. 2008), and lakes in the Beijing area (Zheng et al. 2014), China, as well as the Ogun River in Nigeria (Adeniyi et al. 2011), the Gomti River in India (Srivastava et al. 2010), the rivers and lakes around Berlin, Germany (Fromme et al. 2002), and the lakes in North Holland, The Netherlands (Zhang et al. 2011a). Furthermore, PAEs were found not only in surface water but also in underground water (Zhang et al. 2011b). Since PAEs are mostly refractory water pollutants and cannot be removed effectively by conventional treatment processes, alternative removal processes are needed.

The most common methods for removing PAEs are biological treatments, photo-catalytic techniques, and activated carbon adsorption processes. Biological treatment is time-consuming, as it requires several days to months for microorganism cultivation (Chi & Cai 2012), and the degradation
of photo-catalytic processes is seldom complete (Singh & Rastogi 2004). The activated carbon adsorption process is widely used for removing organic pollutants from aqueous solution, and it has been proven to be an effective and reliable treatment for PAEs (Gao et al. 2013). However, one drawback of this process is its high cost, and researching cost-reduction is therefore critical. The biological activated carbon (BAC) process, which has the removal mechanisms of adsorption and biodegradation, can prolong the use time of activated carbon to solve this problem. However, only a small number of studies on the BAC process for PAE removal from aqueous solution have been reported (Bodzek et al. 2004).

This study therefore investigated the removal of DMP, DEP, DBP, and DEHP from aqueous solution by the BAC process. The effects of various parameters, including empty bed contact time (EBCT) and initial PAE concentration, were investigated. Furthermore, hanging film and operational stability tests of the BAC process were conducted. Considering that many water plants still use conventional treatment processes, the addition of activated carbon to the water inlet as an emergency treatment for excessive PAEs was also performed, and the effects of activated carbon dosage were studied.

MATERIALS AND METHODS

Chemicals

DMP, DEP, DBP, and DEHP were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) (purity >99.5%, 0.5 g). Methanol, dichloromethane, ethyl acetate, and n-hexane were of chromatographic purity (Dikma Technologies Inc., Beijing, China). All other chemicals were of analytical reagent grade.

Granular activated carbon (GAC) manufactured by Calgon Carbon Co. (Tianjin, China) was used in this study, and the physical characteristics of the GAC are listed in Table 1.

All aqueous solutions were prepared with Milli-Q water (resistivity 18.2 MΩ cm) from a Millipore water purification unit (Millipore, Watford, UK).

<table>
<thead>
<tr>
<th>Material</th>
<th>Iodine number</th>
<th>Effective size</th>
<th>Moisture</th>
<th>Methylene blue value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous coal</td>
<td>1,023 mg/g</td>
<td>2–3 mm</td>
<td>&lt;2%</td>
<td>180 mg/g</td>
</tr>
</tbody>
</table>

Experiments

Figure 1 shows the experimental schematic diagram for the BAC filter, which had a diameter of 150 mm and a height of 2,000 mm. Experiments were designed to detect PAE removal rate by BAC. First, the optimum carbon dosage (10–50 mg/L) was determined for emergency treatment of excessive amounts of PAEs, for cases where there were no deep treatment technologies. Second, BAC was used as a deep technology to treat PAE pollution. The microbial cultivation was started with water obtained from the sand filter of a water treatment plant. GAC was used as an attachment during the cultivation. The concentration of PAEs, CODMn and NH3-N in the outlet of the BAC filter was monitored during the cultivation period. The integrated formation of biofilms on activated carbon, the effects of EBCT (5–20 min), initial PAE concentration (10–50 μg/L), and BAC stability (operating for more than 3 months) were also studied. The microorganisms on the mature membrane were observed by field emission scanning electron microscopy (JSM-7001F) purchased from JEOL Ltd.

Figure 1 | Flow diagram of biological activated carbon (BAC) filter.
(Tokyo, Japan), to determine the mechanism of PAE removal.

**Analysis method**

The PAE concentrations were analyzed by an Agilent 1100 high-performance liquid chromatography system with a photodiode array detector set at 228 nm. A mixture of methanol and Milli-Q water (90:10) was used as the mobile phase, while the stationary phase was a C18 column (4.6 × 150 mm, 5 μm). A flow rate of 1.0 mL/min, an injection sample volume of 10 μL, and a column temperature of 30°C were used in the analysis.

**RESULTS AND DISCUSSION**

**Effect of carbon dosage**

Carbon dosage experiments were carried out in the range of 10–50 mg/L to assess the PAE adsorption capacity (PAE concentration, 10 μg/L). The removal efficiency was measured and the results are depicted in Figure 2.

It is suggested that the PAE removal efficiency is highly dependent on the activated carbon dosage. The removal rate increased with an increase in the activated carbon dosage, but its influence gradually weakened when the amount of activated carbon increased from 40 to 50 mg/L. When PAE concentration in the influent was 10 μg/L, DMP, DEP, DBP, and DEHP could be removed at rates of 77.4%, 57.6%, 72.9%, and 47.8%, respectively, with an activated carbon dosage of 40 mg/L. Theoretically, if a higher activated carbon dosage had been added, PAEs with high concentrations (>10 μg/L) could also have been removed effectively, but this is not financially viable. Therefore, further research on the degradation of PAEs with high concentrations by the BAC process is needed.

**Removal of COD\textsubscript{Mn}, NH\textsubscript{3}-N and PAEs during the cultivation period**

To form a biofilm on the GAC surface during the cultivation period, water with PAE micro-pollution was poured directly into the BAC filter to allow microorganisms to adhere and grow. Studies show that when the removal rate of comprehensive organic indices, such as COD\textsubscript{Mn} and NH\textsubscript{3}-N, reached 30% and 60% stably, respectively, the biofilm could be deemed mature (Nishijima et al. 1998). The cultivation was continued for 1 month in summer, with an average temperature of 29.5°C, until biofilms on activated carbon were formed integrally. The changes in COD\textsubscript{Mn}, NH\textsubscript{3}-N and PAE concentration with time in the BAC filter outlet are shown in Figures 3 and 4.

It can be seen from Figure 3 that the removal rates of COD\textsubscript{Mn} and NH\textsubscript{3}-N fluctuating for a period of 6 days after the start of BAC. After about 12 days, the removal rates began to increase gradually, and after 50 days of operation, the removal rate of COD\textsubscript{Mn} was stable at about 61%, and
that of NH$_3$-N was also stable above 50%, which indicated that the film had formed successfully.

The results shown in Figure 4 indicate that PAEs can be significantly reduced by the BAC process. Specifically, before the biofilm was formed (1 day), the removal efficiencies of DMP, DEP, DBP, and DEHP were 77.41%, 72.40%, 78.87%, and 56.17%, respectively, which were attributable to activated carbon adsorption. With the gradual formation of biofilm, the removal rate of PAEs increased steadily, except in the backwash cycle (7 days). After a 30-day cultivation period, the removal rates of DMP, DEP, DBP, and DEHP were sustained at above 99%, 96%, 80%, and 70%, respectively. Their residual concentrations were all below the limits set by ‘environmental quality standards for surface water’ (PRCNS 2002) and ‘standards for drinking water quality’ (PRCNS 2006). Therefore, after 1 month, the biofilm in the BAC filter achieved maturity, and performed the simultaneous functions of microbial degradation and activated carbon adsorption for PAE removal.

**Effect of EBCT**

In the BAC filter, EBCT was the key operational parameter and is defined as the time a fluid spends in the BAC column when the column is empty. Four EBCTs (5, 10, 15, and 20 min) in the BAC filter were investigated with a PAE concentration of 10 μg/L. Figure 5 shows the effects of EBCT on the PAE removal efficiency. When EBCT was changed from 5 to 10 min, the PAE removal efficiency increased slowly, except for DEHP, which showed a rapid increase. However, from 10 to 20 min, the removal rate of DMP, DEP, and DBP fluctuated within a small range, whereas that of DEHP declined markedly. Removal efficiencies of DMP, DEP, DBP, and DEHP reached 94%, 98%, 84%, and 78%, respectively, with 10 min EBCT. In other words, effluent concentrations of PAEs were 0.59, 0.14, 1.51, and 2.20 μg/L, respectively. According to ‘standards for drinking water quality’ (PRCNS 2006), the allowable DBP and DEHP concentrations in drinking water are below 3 and 8 μg/L, respectively, and 10 min EBCT was sufficient to achieve these standards.

**Effect of initial PAE concentration**

PAE concentration may vary between water bodies or seasons, and it is therefore important to analyze the effects of different initial PAE concentrations. Initial PAE concentrations in the experiments in this study were 10, 20, 50 μg/L, with the same EBCT (10 min) and carbon layer thickness (80 cm). When the PAE concentrations increased, the removal rates of DMP, DEP, DBP, and DEHP decreased (Figure 6). The removal efficiency of the BAC filter was sufficient with a PAE concentration of 10 μg/L for two possible reasons: firstly, some PAEs may have been toxic to microorganisms when PAE concentrations exceeded a certain threshold, and this might have inhibited the growth and...
reproduction of the bacteria. Secondly, it may have been due to the biodegradation constants of mixed PAEs often being higher than that of a single PAE species, which can increase the recognition of microbial degradation for the PAEs (Nishijima et al. 1998). It is suggested that the optimal PAE concentration in the experiments was 10 μg/L, as the removal rates of DMP, DEP, DBP, and DEHP reached 79.8%, 90.2%, 91.3%, and 100%, respectively.

**BAC operational stability**

After the microbial cultivation period and operation parameter optimization experiments, BAC operational stability experiments were conducted for more than 3 months. After the BAC process matured, the average concentrations of the PAEs in treated water were approximately 10 μg/L. PAE removal rates reached a steady state (Figure 7), and average DMP, DEP, DBP, and DEHP removal rates ranged from 70% to 95%, which suggested that the BAC process was efficient.

On the other hand, PAE removal rates decreased in the order of DMP > DEP > DBP > DEHP, which was related to the length of the alkyl side and branch chains. The short-chain PAEs (DMP and DEP) were removed at higher rates than the long-chain PAEs (DBP and DEHP). This fits well with a general finding in previous studies (Bajt et al. 2001; Li et al. 2006), which was that the nature of the identified by-products provides evidence for a major attack on the aliphatic chain; increased alkyl side and branch chain lengths may inhibit interaction with oxidative species produced in the aqueous phase.

**Biofilm analysis**

Activated carbon samples, including new and mature hanging membrane, were baked into dry solids and sprayed with gold film in advance for protection, and then studied for changes using field emission scanning electron microscopy.

The new carbon, which contains a large number of micropores and an irregular surface (Figure 8(a)), can not only adsorb impurities, but also offer appropriate attachment points for the growth of microorganisms. After hanging the film successfully (Figure 8(b)–8(d)), thick biofilms were formed on the surface of the activated carbon, with stable growth of microbial flora, such as bacillus and coccus.

During the early stage of the hanging membrane, the physical adsorption of organic matter by the activated carbon was the dominant mechanism. This is because its large initial specific surface area made its adsorption performance very strong. However, as time passed, the amount of adsorbed organic matter increased, and the adsorption capacity of the activated carbon decreased. However, when the biofilm had formed continuously and stably, biodegradation was enhanced, and then adsorption and biodegradation occurred simultaneously. Some researchers have postulated that the vitro enzymes secreted by microbes
were the main reason for the stable processing capacity of the BAC, because these enzymes can decompose the organic matter adsorbed by the activated carbon (De Laat et al. 1985). Therefore, when the biofilm had achieved maturity, biological function played a major role in the mechanism of the BAC process.

**CONCLUSIONS**

DMP, DEP, DBP, and DEHP removal by a BAC filter was investigated in this study. Overall, the results can be summarized as follows:

1. With an influent PAE concentration of 10 μg/L, DMP, DEP, DBP, and DEHP could be removed effectively by activated carbon adsorption. When activated carbon was used as an emergency treatment for excessive amounts of PAEs, the optimum activated carbon dosage was 40 mg/L.
2. In summer, the microorganism cultivation period was approximately 1 month, for its stable COD$_{Mn}$ and NH$_3$-N removal rates of about 61% and 50%. Further, the removal rates of DMP, DEP, DBP, and DEHP were stable at above 99%, 96%, 80%, and 70%, respectively, with the maturation of biofilm.
3. The optimum parameters of the BAC process were determined as 10 μg/L initial PAE concentration and 10 min EBCT.
4. The operational stability experiment showed that the BAC process was efficient, because average DMP, DEP, DBP, and DEHP removal rates ranged from 70% to 95%. The order of PAE removal efficiency was DMP > DEP > DBP > DEHP.
5. During the hanging membrane test in the BAC process, the PAE removal mechanism was different at different stages. During the early stage, adsorption of organic matter by activated carbon was the main mechanism. Both adsorption and biodegradation were active in the medium term, and as the film matured, biodegradation was the primary mechanism.

COMPETING INTERESTS

The authors declare no actual or competing financial interests.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (contract no. 21477027, 51278133, and 51609042), Science and Technology Projects of Guangdong province, China (contract no. 2014A020216049), and Key Laboratory for Water Quality Security and Protection in Pearl River Delta (Ministry of Education and Guangdong Province), Guangzhou University (contract no. ZSJ201602).

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First received 10 April 2017; accepted in revised form 23 June 2017. Available online 5 July 2017