



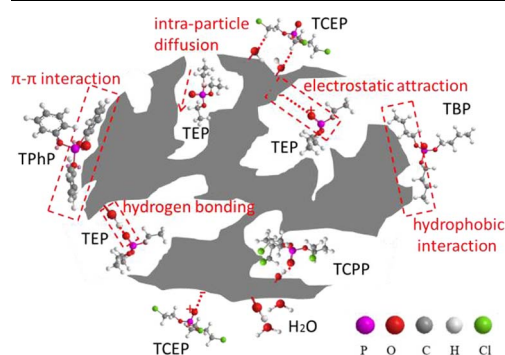
Sorption behavior and mechanism of organophosphate flame retardants on activated carbons



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GRAPHICAL ABSTRACT



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ABSTRACT

Organophosphate flame retardants (OPFRs) are widely distributed in aquatic environment, but their adsorptive removal is not clear. For the first time, the removal of OPFRs from water using activated carbons (ACs) was investigated in this study. Adsorption kinetics, effects of activated carbon characteristics, OPFR property, and solution pH, as well as adsorption mechanism and reuse were studied. Adsorbent size significantly affected the adsorption kinetics and capacity, and powdered activated carbon (PAC) exhibited much faster sorption and higher sorption capacity than granular activated carbon (GAC) due to the easier intraparticle diffusion of OPFRs. The sorption kinetics of OPFRs at the initial stage followed the intraparticle diffusion-controlled adsorption, and the molecular size and hydrophobicity influenced greatly the sorption rate. The reactivated GAC exhibited higher OPFR removal than GAC because more enlarged pores were produced and available for OPFR sorption. Based on the sorption behavior of OPFRs, hydrophobic, electrostatic, hydrogen bonding, and π - π interactions were proposed to be involved in the sorption process. Additionally, the spent ACs could be successfully regenerated and reused at least four times with stable sorption capacity. This work indicated that the appropriate ACs have a promising application in the water or wastewater treatment for OPFRs removal.

1. Introduction

Flame retardants (FRs) comprise a large group of chemicals widely

used in varnishes, polyurethane foams, plastics, electronics equipment, wood, textiles and so on [1,2]. Since the restriction of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) as FRs in

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Table 1
Physicochemical properties of selected OPFRs used in this study.

OPFRs	Chemical structure	Mol. weight (g/mol)	Density (g/cm ³)	Water solubility ^a (mg/L)	Mol. volume ^b (nm ³)	log <i>K</i> _{ow} ^c
TEP	(CH ₃ CH ₂ O) ₃ P=O	182	1.07	5.0 × 10 ⁵	0.170	0.8
TCEP	(ClCH ₂ CH ₂ O) ₃ P=O	285	1.39	7.0 × 10 ³	0.205	1.4
TCPP	(ClCH ₂ CH(CH ₃)O) ₃ P=O	328	1.29	1.6 × 10 ³	0.254	2.6
TBP	(CH ₃ (CH ₂) ₂ CH ₂ O) ₃ P=O	266	0.98	280	0.272	4.0
TPhP	(C ₆ H ₅ O) ₃ P=O	326	1.21	1.9	0.271	4.6

^a Ref. [2].

^b Calculated according to Ref. [15].

^c Ref. [4].

Europe and the United States [2,3], their alternative substances, like organophosphorus flame-retardants (OPFRs), have been widely used in a variety of industries [3–5]. The worldwide annual consumption of FRs amounts is more than 2 million tons, of which 16% is OPFRs, and will continue to grow at a global annualized rate of approximately 3.4%. However, OPFRs are not safe as expected. For example, tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloro-1-methylethyl) phosphate (TCPP) are proven carcinogens; triphenyl phosphate (TPhP) is bioaccumulative and very toxic to aquatic ecosystems [6].

Since OPFRs are primarily added to the product in a simple physical form, they are easily released into the surrounding environment. So far, OPFRs have been found in wastewater, oceans, river water, groundwater and drinking water all over the world [2,4]. Industrial and domestic wastewaters are important pollution sources of OPFRs. In a Spanish wastewater treatment plant, 10 OPFRs were detected with a total concentration up to 151 µg/L [7]. In South Korea, the total concentrations of ten OPFRs in drinking water were up to 1660 ng/L, and the main pollutants were TCEP, TCPP and tris(butoxyethyl) phosphate [8]. Some OPFRs are stable in water like TPhP, triethyl phosphate (TEP) and trimethyl phosphate with the half-life of 1.2–5.5 year under neutral conditions [9]. Therefore, some OPFRs have high environmental risks, and effective techniques are required to remove them from wastewater.

To date, only few papers about OPFR removal from wastewater have been published. It is reported that biological treatment and advanced oxidation can't significantly remove TCEP and TCPP [8,10]. Nearly 50% of OPFRs entering the wastewater treatment plant in Sweden can't be removed and go directly into natural water [11]. It has been demonstrated that adsorption is an efficient and economical method for the removal of many pollutants from wastewater, but very limited studies are available to remove OPFRs by adsorption. It was previously reported that TCPP in river sediment was up to 1300 (µg/kg dw), while the corresponding concentration in water was only 170 ng/L, suggesting that OPFRs tend to concentrate in sediment [12]. Grieco et al. found that zeolite exhibited good adsorption capacity for TCEP and the maximum adsorption capacity was up to 103 mg/g [13]. The oxygen-containing functional groups on CNTs are not conducive to the adsorption of OPFRs [14], indicating that the hydrophobicity of CNTs had a significant influence on the sorption of OPFRs on CNTs. Activated carbons (ACs) are widely used in wastewater treatment plants, but the adsorption of OPFRs on ACs has not been reported, and it is necessary to know whether ACs are effective for OPFR removal from water.

The objectives of this study are to evaluate the adsorption behavior of different OPFRs on ACs and elucidate the corresponding adsorption mechanism. Five OPFRs including TEP, TCEP, TCPP, tributyl phosphate (TBP) and TPhP were selected as model pollutants because they are commonly detected in wastewater and widely distributed in aquatic environment. They belong to the three typical groups including aliphatic OPFRs, chlorinated OPFRs and aromatic OPFRs, and these five OPFRs were commonly used in various commercial products. The adsorption kinetics and isotherms, the effects of properties of ACs and OPFRs as well as solution pH on OPFR adsorption were investigated, and the underlying adsorption mechanism for OPFR removal was also

proposed. Finally, the regeneration and reuse of the spent ACs was also evaluated.

2. Materials and methods

2.1. Chemicals and materials

Five OPFRs (purity > 98%) including triethyl phosphate (TEP), tri(2-chloroethyl) phosphate (TCEP), tri(chloropropyl) phosphate (TCPP), tributyl phosphate (TBP) and triphenyl phosphate (TPhP) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China), and their main physicochemical properties are shown in Table 1. The molecular structures of the five OPFRs are displayed in Fig. S1. The coal-based activated carbon (AC) was obtained from Jingke Activated Carbon Co. (Tangshan, China). Other chemicals are analytical reagent grade.

2.2. Preparation of activated carbons

Prior to adsorption experiments, all ACs were first rinsed with deionized water for several times and then dried in an oven at 105 °C for 24 h. Four types of ACs, including granular activated carbon (GAC), powdered activated carbon (PAC), reactivated GAC (R-GAC) and oxidized GAC (O-GAC) were selected to investigate the effect of AC properties on the sorption of OPFRs. PAC, R-GAC and O-GAC were all prepared from the same coal-based GAC. To prepare R-GAC with enlarged pores, GAC particles were impregnated by KOH solution at the KOH/C mass ratios of 1 for 48 h and then dried at 105 °C for 12 h, followed by heating at 800 °C in a tubular furnace for 1.5 h under N₂ flow protection. Thereafter, the obtained material was washed by 1 mol/L HCl solution and Milli-Q water until the pH of the supernatant was neutral. Finally, the R-GAC was dried in an oven at 105 °C for 24 h. In order to obtain a highly oxidized GAC, the O-GAC was made from the GAC by a HNO₃ oxidation treatment. An amount of 10 g GAC was added into 50 mL of 70% w/w HNO₃ solution in a 100 mL reaction vessel, and the oxidative treatment was conducted at 25 °C for 4 h. After the reaction, the residual oxidants and byproducts were removed from O-GAC by repeatedly rinsing the mixture with Milli-Q water until the pH of the wash water was approximately 7.

2.3. Characterization of activated carbons

The specific surface area and pore size distribution of the ACs were determined by nitrogen adsorption at 77 K using a gas adsorption instrument (Autosorb iQ, Quantachrome Corp., US). All samples were outgassed at 300 °C for 6 h in vacuum before determination. The elemental compositions were obtained by an elemental analyzer (EA3000, Italy). Their surface oxygen-containing functional groups were measured by Boehm titration. The zeta potentials of AC were determined by a zeta potential instrument (Delsa Nano C, Beckman Coulter, USA). The powder samples (below 300 mesh) were added into ultrapure water at 0.05 g/L. Solution pH values were adjusted with HCl or NaOH solution in the range of 3.0–9.0 before measurement. The properties of four ACs

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