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Removal and reduction of selected organic micro-pollutants in effluent sewage by the ozone-based oxidation processes

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HIGHLIGHTS

- Four organic micro-pollutants were selected using a developed screening system.
- HA, pH, and reaction time affected the performances of the ozone-based oxidation.
- Removal of target compounds increased during US/O_3 and O_3/PC combined processes.
- US/O_3 combined process could achieve the best removal of the target micro-pollutants.

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ABSTRACT

Four typical organic micro-pollutants in effluent sewage were subjected to the various treatments using three ozone-based oxidation processes, i.e. individual ozonation (O_3), ultrasonic ozonation (US/O_3) and photocatalytic ozonation (PC/O_3) under different experimental conditions involving supplied ozone dose, pH value and humic acid (HA) concentration of the effluent, ultrasonic radiation power, and photocatalyst dose. The target compounds, i.e. clofibric acid (CFA), nonylphenol (NP), 17α-ethinylestradiol (EE2) and carbamazepine (CBZ), were selected from 11 organic pollutants frequently detected in the aquatic environment through a developed screening system. The increase on the supplied ozone doses would improve the performances of ozonation of the target compounds. Besides, the removal rates of the compounds during the three ozone-based oxidation processes increased with the rise on pH value in the set range (3.7–9.5) of this study. However, the removal rates on the whole reduced with the increasing HA addition, especially during the US/O_3 combined process. Compared with the individual O_3, the two combined processes enhanced considerably the removal rates, by 13.9% or above for CFA, 12.6% or above for NP, over 13.3% for EE2, and no less than 14.8% for CBZ. The optimal removal of the target compounds was obtained at the ultrasonic power 240 W for the ultrasonic ozonation treatment. For the PC/O_3 combined process, the enhanced removal of the targets was mainly due to the larger amount of oxidizing species generated through the enhancement effects of photocatalysis as the adsorption of the targets to the photocatalyst was far less. The US/O_3 combined process could achieve the best removal of the target micro-pollutants.

1. Introduction

There are increasing concerns about many kinds of organic micro-pollutants including endocrine-disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs) at ng/L–μg/L levels present in natural aquatic environments [1–4]. For example, Liu et al. [4] investigated the occurrence of eight lipophilic pharmaceutically active compounds in the downstream rivers of sewage treatment plants in Nanjing, China. The results indicated that these compounds were widely detected in the surface water, with the mean concentrations of the total compounds being in the range of 15.4 and 384.5 ng/L. Besides, the detection frequency of EE2 was very high in the surface water and wastewater world widely [5,6]. Al-Ansari et al. [7] pointed out that an equivalent of trace EE2 even at ng/L level could cause the disorders of the reproductive systems of fish, and would also bring to humans diseases, such as infertility, spontaneous abortion and other reproductive harms, and increasing breast cancer, ovarian cancer, prostate cancer and other tumours.

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Adverse effects on human health potentially from EDCs and PPCPs present in the aquatic environments have been demonstrated in the following two aspects. One is the direct effects in that these organic micro-pollutants can cause the pollution of drinking water, and consequently affect human health directly [8]. The other is the indirect effects in that these organic micro-pollutants may contaminate soil and food [9], and thereby affect human health indirectly. It has been confirmed that eco-toxicities of some pharmaceuticals are relatively high, and their chronic toxicity thresholds are even less than 1 μg/L [10].

Once used, organic micro-pollutants are released into natural aquatic environments via different routes, such as wastewater effluent discharge, industrial waste discharge, agricultural runoff, or the improper disposal of unused chemical products [4]. Effluent sewage has been regarded as a main source of organic micro-pollutants in the aquatic environments [11]. So far, the most economic method for the reduction of organic pollutants of wastewater into the aquatic environments has been regarded as the biological treatment [12]. However, advanced oxidation processes (AOPs) are considered as more suitable to be adopted for the treatment of the toxic and refractory organic compounds, especially in the trace level [12,13]. The AOPs could improve their biodegradability, and enhance their mineralization. Among the AOPs, ozonation is one of the most widely used processes due to the high oxidation ability of ozone as well as no residual and no secondary pollution produced [12]. The technology has been designed and utilized for the treatment of wastewater containing some refractory organic micro-pollutants, such as residual pesticides [14], phenolic compounds and EDCs [15]. It could effectively degrade and remove these compounds. However, its performances can be still improved and enhanced when ozonation is combined with other oxidation technologies since these technologies will improve the availability and/or decrease the reaction selectivity of ozone. Zhou et al. [16] investigated the enhanced decolorization efficiency of triphenylmethane dye, malachite green using the ultrasound-assisted ozonation, compared to individual ozonation. The results indicated that when ultrasonic irradiation was applied with ozone simultaneously, the apparent pseudo-first-order rate constant (K_{app}) increased, leading to the reduction of reaction time; and the stoichiometric ratio (Z_{app}) between O_3 and malachite green was enhanced to 2.0 mol, saving 11% oxidant addition, comparing to individual ozonation. Therefore, the application of ultrasonic irradiation was believed to reduce the reaction time and the dose of ozone addition.

In this study, 4 typical organic micro-pollutants, i.e. blood lipid regulator clofibric acid (CFA, $C_{10}H_{11}ClO_3$), phenolic compound nonylphenol (NP, $C_{15}H_{24}O$), synthetic estrogen 17α-ethinylestradiol (EE2, $C_{20}H_{24}O_2$) and antiepileptic drug carbamazepine (CBZ, $C_{15}H_{12}N_2O$), were selected as target compounds through a developed screening system. Then the reduction and removal of the target compounds in effluent sewage was investigated using individual ozonation (O_3) and ozone-combined processes, i.e. ultrasonic ozonation (US/O_3) and photocatalytic ozonation (PC/O_3). The attempt was to determine whether the combined processes could promote the removal and reduction of the compounds in the effluent sewage. In addition, the effects of operating conditions on the removal rates were taken into account.

2. Materials and methods

2.1. Reagents and materials

The reference standards, CFA (CAS No. 882-09-7), NP (CAS No. 104-40-5), EE2 (CAS No. 57-63-6) and CBZ (CAS No. 298-46-4), as well as the internal standard, bisphenol A-d16 (BPA-d16), were purchased from ANPEL Co., Shanghai, China, and the purity of all the compounds were above 98.5%. The derivatization reaction reagent, N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), and Methyl tert-butyl ether (MTBE) were supplied by Sigma–Aldrich, USA. Acetone, methanol, and dichloromethane were purchased from Fisher, USA. All the solvents used were HPLC grade. Other used reagents, such as perchloric acid ($HClO_4$) and sodium hydroxide (NaOH), were of analytical grade or better. Ultrapure water was prepared with Aquapro Ultrapure Water System (China).

GF/B Glass fiber filters (1 μm) were obtained from Whatman, USA. Cartridges (C8 opposition, 6 cc/200 mg) for solid-phase extraction (SPE) were supplied by Supelco, USA. The photocatalyst, prepared by a research team in our laboratory, was a powder of TiO_2 hybrid composited with 5% (m/m) exfoliated g-C_3N_4 nanosheets (CNs) through a facile sol–gel method. The particle size of the TiO_2 hybrid was about 20 nm with the BET surface up to 140.13 m^2/g and the average pore size of 3.48 nm.

2.2. Experimental setup

Ozone-based oxidations of the target compounds in effluent sewage were carried out in the duplicate experimental systems. The individual system is shown in Fig. 1. Each designed column ozone reactor was made of plexiglass with the effective volume of 10 L, the diameter of 120 mm, and the height of 1160 mm. A spiral microporous aeration hose was set horizontally at the bottom of the reactor to distribute ozone evenly. The diameter of the hose was 15 mm, and its total length was 800 mm. The opening

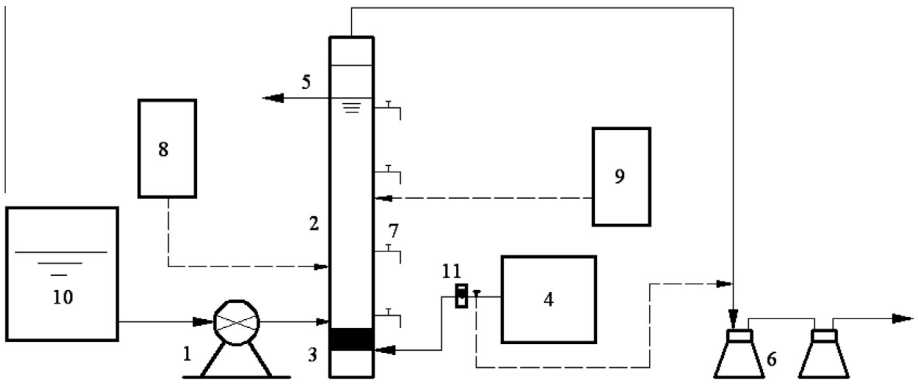

Fig. 1. Schematic diagram of ozone-based oxidation process (1 – peristaltic pump; 2 – ozone reactor; 3 – microporous aeration hose; 4 – ozone generator; 5 – treated effluent; 6 – conical flask with two-hole stoppers containing ferrous sulfate solution; 7 – sampling opening; 8 – ultrasonic generator; 9 – photocatalytic tank; 10 – water-supplying tank; 11 – gas flow meter).