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Degradation of endocrine-disrupting chemicals during activated sludge reduction by ozone

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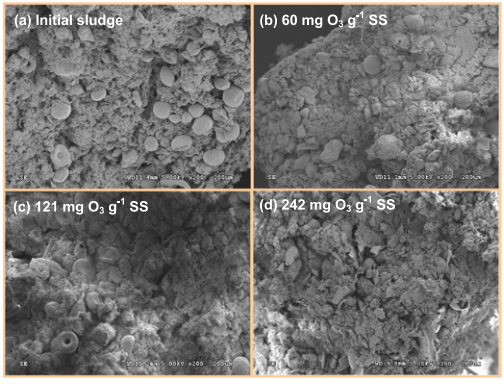
HIGHLIGHTS

- Ozonation was an effective means for excess sludge reduction.
- Sludge-bound EDCs were effectively removed during sludge ozonation.
- The adsorption of EDCs on sludge greatly retarded their degradation by O_3.
- EDCs degradation kinetics could be expressed by the pseudo-first-order model.
- Either H_2O_2 addition or pH adjustment enhanced the removal of most EDCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozonation has been considered to be an effective means for the reduction of excess sludge in recent years. However, it remains largely unknown whether hydrophobic organic micro-pollutants, which are originally adsorbed on activated sludge, will be released into wastewater upon ozonation because of sludge solubilization. This study investigated the degradation efficiencies of several typical endocrine-disrupting chemicals (EDCs) during sludge ozonation, including estrone (E1), estriol (E3), 17α-ethynylestradiol (EE2), bisphenol A (BPA), and 4-nonylphenol (NP). Results indicate that the EDCs present in activated sludge could be effectively removed by O_3 even though the apparent rate constants in sludge were 3–4 orders of magnitude lower than those in water. However, the applied O_3 dose should be prudently controlled because a low dose (e.g., 29 mg O_3 g^{-1} SS) may lead to an increase of BPA and NP concentrations in the liquid phase of activated sludge. Furthermore, H_2O_2 addition or pH adjustment could improve the removal of most studied EDCs, but exert a negative effect on the more hydrophobic and refractory compound, NP.

1. Introduction

The activated sludge process has been extensively used for treatment of municipal sewage, and over 90% of sewage treatment plants (STPs) adopt it as a core part of the treatment processes at present (Liu, 2003). However, the large amount of excess sludge produced daily has become the most troublesome problem. The conventional methods for sludge treatment and disposal (e.g., landfill and compost) are facing an increasing challenge because of the more stringent regulations as well as the social concerns for environment. Hence, various reduction technologies of excess sludge have recently been developed including

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Nomenclature

BPA	bisphenol A
BSTFA	*N*,*O*–bis(trimethylsilyl)trifluoroacetamide
COD	chemical oxygen demand
DOC	dissolved organic carbon
E1	estrone
E3	estriol
EDCs	endocrine-disrupting chemicals
EE2	17α-ethynylestradiol
EPS	extracellular polymeric substances
NP	4-nonylphenol
SEM	scanning electron microscope
STPs	sewage treatment plants
TMCS	trimethylchlorosilane
TN	total nitrogen
TP	total phosphorus
TSS	total suspended solids
VSS	volatile suspended solids

mechanical, thermal, chemical and biological methods, among which ozonation is considered to be an effective and practical way. Previous studies (Yasui et al., 1996; Lee et al., 2005) have reported that the sludge reduction efficiency by ozonation could reach 100% (i.e., zero yield of excess sludge). Furthermore, ozonation has been successfully applied in practice to reduce sludge in a few European countries and Japan (Yasui et al., 1996; Sievers et al., 2004). However, some problems associated with this technique are also obvious (Liu, 2003). For example, some refractory organic micro-pollutants originally adsorbed on sludge may get released into wastewater during sludge ozonation and thus probably deteriorate the effluent quality. Along with the effluent discharge, these refractory micro-pollutants tend to contaminate the receiving water bodies. Especially, the occurrence of endocrine-disrupting chemicals (EDCs) in aquatic environment has attracted great attention. It was reported that even a trace level (ng L^{-1}) of 17β-estradiol (E2) or 17α-ethynylestradiol (EE2) could induce vitellogenesis in trout, and the presence of vitellogenin in the plasma of fish was indicative of estrogenic stimulation (Purdom et al., 1994).

The effluent of STPs is one of the major sources of EDCs released to the aquatic environment (Ternes et al., 1999; Baronti et al., 2000). In general, two typical classes of EDCs are seriously concerned. One class is the steroid estrogens, including both natural and synthetic ones. Among them, estrone (E1), E2 and estriol (E3) are the most common natural estrogens mainly coming from urinary excretion, and EE2 is a typical synthetic estrogen used as contraceptive. The other class consists of 4-nonylphenol (NP) and bisphenol A (BPA), which are extensively used in household and industrial processes (e.g., textile, paper, detergents and polymeric material production). All these EDCs are hydrophobic, so a notable part of EDCs present in sewage could transfer to activated sludge in biological treatment processes (Johnson and Sumpter, 2001; Zhao et al., 2008; Nie et al., 2012). Therefore, two questions are to be answered regarding the practical application of sludge ozonation: (1) Will sludge solubilization lead to an increase of the concentrations of EDCs in wastewater? (2) Can ozonation effectively degrade the EDCs originally adsorbed by sludge? But to date, no answer is available.

According to these questions, a sensitive and selective method for detecting EDCs in both liquid and solid phases of activated sludge has been developed in our previous study (Nie et al., 2009). To move forward, this work was to investigate the degradation efficiency of studied EDCs during sludge ozonation. Besides, the effects of H_2O_2 addition and sludge pH adjustment, which were intended to enhance the generation of hydroxyl radicals (·OH), on the removal of EDCs were also examined. This study helps to optimize the sludge ozonation process to achieve a high efficiency in both sludge reduction and EDCs removal.

2. Materials and methods

2.1. Target compounds and sludge source

E1, EE2, E3, BPA and NP were selected as the representative EDCs whose structures, log K_{ow} and pK_a values are shown in Table S1 (Supplementa Data). E2 was not selected because its biodegradation by activated sludge was so fast that its removal efficiency could reach 90% within several minutes (Urase and Kikuta, 2005; Hashimoto and Murakami, 2009). The activated sludge was collected from a secondary sedimentation tank of Qing-he STP located in Beijing (200 000 $m^3\ d^{-1}$ treatment capacity), China. This STP employed basically an anaerobic/anoxic/oxic (A/A/O) biological treatment process. The concentrations of total suspended solids (TSS) and volatile suspended solids (VSS) were about 4.50 and 3.30 g L^{-1}, respectively, and the pH was around 7.1. The mean concentrations of total nitrogen (TN) and total phosphorous (TP) were 58.0 and 2.5 mg L^{-1} in the influent, respectively. About 70% of TN and 80% of TP could be removed by the A/A/O process.

2.2. Reaction system

A semi-batch reaction system (sludge: batch addition; O_3 gas: continuous supply) was used for sludge ozonation experiments (Fig. S1, Supplementary Data). The sludge sample was ozonated in a cylindrical glass reactor (∅ = 120 mm, H = 220 mm) with an effective volume of 2.0 L. The O_3 gas, produced from pure oxygen by using an ozone generator (CF-G-3-010G, Goulin, China; maximum yield = 10 g h^{-1}), was continuously bubbled into the reactor. At pre-selected times, the O_3 gas stream was stopped and the residual O_3 in the headspace of reactor was immediately stripped out by N_2 gas. The off-gas during and after ozonation was collected into 500 mL of 1% KI solution, which was then titrated by 0.1 M NaS_2O_3 to determine the amount of unreacted O_3. The inlet gaseous concentration of O_3 was determined by the same iodimetric method. The amount of consumed O_3 during the reaction was calculated as follows:

$$\text{Consumed } O_3 = C_{O_3,gas-in} \times Q_{O_3,gas-in} \times T - M_{O_3,out} \quad (1)$$

where $C_{O_3,gas-in}$ (mg L^{-1}) represents the gaseous concentration of O_3 at the inlet; $Q_{O_3,gas-in}$ (L min^{-1}) represents the flow rate of O_3 gas; T (min) is the time of sludge ozonation; and $M_{O_3,out}$ (mg) is the total mass of O_3 in the off-gas. The amount of consumed O_3 could be readily controlled through adjusting either the ozonation time or the electrical current of the O_3 generator.

Four series of experiments were performed under different ozonation conditions (Table S2, Supplementary Data). Series A was to determine the optimal range of O_3 dose by examining the solubilization characteristics of activated sludge. Series B was to investigate the degradation efficiency of studied EDCs in activated