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Removal of steroid estrogens from waste activated sludge using Fenton oxidation: Influencing factors and degradation intermediates

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HIGHLIGHTS

- Fenton oxidation is effective in removing estrogens from waste activated sludge.
- The proper reaction conditions are recommended for both estrogen removal and sludge solubilization.
- Hydroxyl radical takes the most important role in Fenton oxidation of estrogens in sludge.
- Pregn-4-ene-3,20-dione and pregn-4-en-20-yn-3-one are first observed as intermediates of estrogens.

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ABSTRACT

The presence of endocrine disrupting compounds (EDCs) in waste activated sludge (WAS) is raising concerns about their influence on animals and the overall food cycle. Traditional sludge stabilization processes cannot remove EDCs effectively. The main objective of this work was to study the removal of four estrogens (estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2)) in waste activated sludge treated with Fenton oxidation. The effects of H_2O_2 dosage, initial pH, reaction time, and Fe(II) to H_2O_2 molar ratio were investigated. Base on both the removal of estrogens and the solubilization of WAS, the proper reaction conditions were recommended as follows: H_2O_2 dosage = 15.62 mmol g^{-1}, initial pH = 3, reaction time = 60 min, Fe(II) to H_2O_2 molar ratio = 0.167. Under these conditions, the removal efficiencies of E1, E2, EE2, and E3 were 70%, 90%, 84% and 98%, respectively; compared with non-Fenton treatment, a 24-fold increase in STOC was achieved, and the extent of solubilization of TSS and VSS was close to 13 and 20%, respectively. The degradation intermediates were detected using GC/MS. Results showed that the phenol structures of targets were mostly oxidized to cyclohexenone moieties and quinone-like structures, which indicated that estrogenic activity was weakened. Pregn-4-ene-3,20-dione and pregn-4-en-20-yn-3-one were observed for the first time. Fenton oxidation was shown to offer a promising alternative method of removing EDCs from sludge in pretreatment applications.

1. Introduction

Endocrine disrupting compounds (EDCs) are chemicals that have negative effects on the endocrine systems of humans and wildlife. These include natural estrogens, natural androgens, artificial synthetic estrogens, phytoestrogens, and other industrial compounds (Liu et al., 2009). Among steroid estrogens, estrone (E1), 17β-estradiol (E2), estriol (E3), and 17α-ethinylestradiol (EE2) are reported to be highly disruptive to the endocrine system (Ternes et al., 1999).

During wastewater treatment, some estrogens present in sewage may be transferred to activated sludge in biological treatment systems due to their hydrophobic properties (Li et al., 2011). Ternes et al. (2002) reported that in activated and digested sludge, concentrations of E1, E2, and EE2 were in the ranges of <2–37, 5–49 and <2–17 ng g^{-1}, respectively. Nieto et al. (2008) indicated that estrogen concentrations in sludge exceeded 50–100 ng g^{-1} for E1 and 272–406 ng g^{-1} for E3. These concentrations are high enough to pose risks to the environment and human health (Muller et al., 2010). The presence of EDCs in sludge raises concerns regarding the use of sludge as fertilizer in agriculture (Kinney et al., 2006). Reducing the impact of EDCs in sludge systems is of considerable environmental relevance.

So far, the fate of estrogens during sludge stabilization process is poorly documented (Hamid and Eskicioglu, 2012). Little work has been done on degradation of E1, E2, EE2, and E3 in sludge treatment units despite the fact that these estrogens have been found to exert the majority of estrogenic activity (Nelson et al., 2007). Previously published articles show that effective removal of estrogens

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is not achieved during traditional sludge stabilization processes. Andersen et al. (2003) measured E1, E2 and EE2 in a wastewater treatment plant (WWTP) and found a notable increase in the concentration of E1 and E2 during sludge stabilization. Czajka and Londry (2006) monitored the concentration of EE2 over a 271-d period in a municipal WWTP anaerobic digester and suggested that EE2 degradation was minimal even though electron acceptors had been reduced and methanogenesis occurred. Muller et al. (2010) confirmed that full-scale anaerobic digestion did not remove estrogens from sludge efficiently. They further indicated that final sludge stabilization and dewatering using a thermal-pressurized treatment tended to increase the estrogen content from anaerobically digested sludge to dewatered sludge. This shows that alternative methods are needed to remove the estrogens from sludge prior to their release into receiving media.

Advanced oxidation processes (AOPs) have drawn particular attention for degradation of emerging micropollutants like EDCs, pharmaceuticals, and personal care products in various aqueous matrices (Klavarioti et al., 2009). However, only a few investigations into the ability of AOPs to remove EDCs from sludge have been conducted (Hamid and Eskicioglu, 2012). Bernal-Martinez et al. (2007) used O_3 to pretreat sludge for the removal of polycyclic aromatic hydrocarbon (PAH) and noted an increase in biodegradability of PAH. Carballa et al. (2007) studied the effect of O_3 on the removal of E1, E2, and EE2 from sludge and noted high removal efficiencies for natural estrogens. Qiang et al. (2013) studied the degradation of EDCs for O_3-treated activated sludge and indicated that the EDCs present in activated sludge were effectively removed.

The Fenton process has been used for organic compound oxidation due to its highly efficient generation of ·OH, as shown in Eq. (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\cdot}OH + OH^- \quad (1)$$

This is an attractive oxidation system because iron is an abundant, non-toxic element and H_2O_2 is environmentally safe (Frontistis et al., 2011). The Fenton process can also be used in sludge pretreatment because it can disintegrate extracellular polymer substances and rupture cell walls, releasing intracellular material. Fenton oxidation can transform refractory organic compounds into readily available and soluble compounds, which ultimately increases the generation of biogas (Tyagi and Lo, 2011). Dewil et al. (2007) investigated biogas production of sludge with Fenton peroxidation during anaerobic digestion and showed a 75% increase over non-Fenton treatments. To date, no studies on the removal of steroid estrogens from sludge with Fenton oxidation have been conducted.

This research investigated Fenton oxidation of E1, E2, EE2 and E3 in waste activated sludge (WAS). Its purpose was to produce and confirm a useful technology suitable for pretreatment of sludge containing estrogens. The bulk of the present work is concerned with (i) the effects of Fenton oxidation conditions on removal of estrogens in WAS and solubilization of WAS; (ii) degradation intermediates of tested estrogens identified by GC/MS to predict their degradation mechanisms and the changes in estrogenicity.

2. Materials and methods

2.1. Chemicals

Estrogens and all organic solvents of HPLC grade were purchased from Sigma–Aldrich (USA). Stock estrogen solutions (200 mg L^{-1}) were prepared by dissolving relevant amount of estrogen in methanol and stored at 4 °C. They were spiked into the sludge to produce the desired estrogen concentrations.

2.2. Was

The sludge was collected from a sludge thickener in a WWTP in Shanghai, China. The main characteristics (average data plus standard deviations of triplicates) were as follows: pH 6.2–6.8, total solids (TS) 28.5 ± 1.0 g L^{-1}, volatile solids (VS) 22.3 ± 0.2 g L^{-1}, total suspended solids (TSS) 26.8 ± 1.5 g L^{-1}, volatile suspended solids (VSS) 21.2 ± 0.3 g L^{-1}, soluble chemical oxygen demand (SCOD) 471 ± 86 mg L^{-1}, and total chemical oxygen demand (TCOD) 29.4 ± 5.9 g L^{-1}.

2.3. Fenton oxidation experiments

Fenton oxidation experiments were carried out in 500 mL of flasks stirred with magnetic stirrers at room temperature. 300 mL of sludge containing 1 mg L^{-1} of estrogens was transferred to the flask. The initial pH was adjusted by NaOH and HCl as appropriate. Specific amounts of ferrous sulfate (0.5 M) and H_2O_2 (30% v/v) were immediately added. The reaction was allowed to proceed for a specific length of time. Then 2 M NaOH was injected into the flask to increase the pH to 10 to terminate the reaction. Then the sludge was taken for analysis. Fresh H_2O_2 and $FeSO_4$ solutions were prepared daily.

Experiments evaluating the effects of H_2O_2 dosage, initial pH, reaction time, and Fe(II) to H_2O_2 molar ratio were conducted by changing one factor while keeping the others constant. Except where otherwise stated, the pH was around 3; the H_2O_2 dosage was 15.62 mmol g^{-1}; the Fe(II) to H_2O_2 molar ratio was 0.1, and the reaction time was 60 min. 6 pHs (1.6–6.8) were tested; the H_2O_2 dosage ranged from 1.56 to 46.86 mmol g^{-1}; Fe(II) to H_2O_2 molar ratios of 0.0667–0.25 were tested. Reaction times were set from 15 to 120 min. In order to verify the role of ·OH radicals, tert-butyl alcohol (t-BuOH, a ·OH scavenger) was added at a H_2O_2 dosage of 6.25 mmol g^{-1}, pH 3, reaction time of 60 min, and Fe(II) to H_2O_2 molar ratio of 0.146.

2.4. Analytical methods

2.4.1. Estrogen analysis

The sample preparation procedure followed the method of sludge samples described by Zeng et al. (2009). An HPLC equipped with a reversed-phase C-18 column (4.6 mm × 250 mm, 5 μm, Agilent, USA) was used to analyze samples. The injection volume was 50 μL and the flow rate was 1 mL min^{-1}. The separation was performed under gradient elution conditions using (A) acetonitrile and (B) water. The solvent program used for E2, EE2, and E3 was as follows: initial conditions 70% B linearly reduced to 30% B over 12 min, then linearly decreased to 0% B over 0.3 min, and then kept isocratic for 10 min. An excitation wavelength of 228 nm and emission wavelength of 316 nm were used for fluorescence detection of E2, EE2, and E3. For E1, a wavelength of 200 nm was used for UV detection at a temperature of 40 °C. The solvent program used for E1 was kept initial conditions of 50% B for 15 min. Under these experimental conditions, the quantification limits of target compounds were 62.5 ng g^{-1}. The recoveries were in ranges of 85–92%, 90–101%, 83–94% and 83–93% for E1, E2, EE2 and E3, respectively.

2.4.2. Other analysis

TSS and VSS were analyzed before the termination of reactions according to Standard Methods (APHA, 1999). STOC (soluble total organic carbon) was measured using a TOC-V_{CPN} analyzer (Shimadzu, Japan). TSS_0, VSS_0, and $STOC_0$ referred to as the parameters of