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Comparison of different advanced treatment processes in removing endocrine disruption effects from municipal wastewater secondary effluent

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HIGHLIGHTS

- The MWP secondary effluent had obvious estrogenic risk.
- Five ATPs were compared for EDEs and EDCs removal.
- Steroid estrogens like E1, E2 and EE2 were the main EDEs contributors.
- The ATPs are more efficient in steroid estrogens removal, and less so in artificial EDCs removal.
- ATPs treated effluents still showed significant *in vivo* EDEs risks.

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ABSTRACT

In this study, secondary effluent from the Wulongkou (WLK) municipal wastewater plant (Zhengzhou, China) was tested for its toxicity effects before and after five advanced treatment processes (ATPs, i.e. coagulation sedimentation, nan da magnetic polyacrylic anion exchange resin (NDMP) resin adsorption, activated carbon adsorption, ozonation and electro-adsorption). Results showed that estrogen disruption effects (EDEs) were particularly significant for the raw secondary effluent among the studied dioxin-like toxicity effect, androgenic/anti-androgenic response effect, EDEs, and genotoxicity effect. And E1, E2, and EE2 were the main endocrine disruption chemicals (EDCs) contributing to EDEs. Except coagulation sedimentation, all the other four ATPs were efficient in removing the steroid estrogens (i.e. E1, E2, and EE2), but were inefficient in the artificial EDC (i.e. DBP, OP and BPA) removal. In the ATPs treated samples, vitellogenin (VTG) in zebrafish were largely removed. However, they were still significant in comparison with the control, probably due to artificial EDCs. Therefore, finding ways to thoroughly remove EDEs and EDCs from the secondary effluent will be a new research direction in the future.

1. Introduction

Municipal wastewater, a mixture of liquids and chemicals, often flows or seeps into surface water. Exposure to these waters tends to result in acute or chronic toxicity effects including genotoxicity, carcinogenic toxicity, dioxin-like risks, and endocrine disrupting effects (Mathur et al., 2007; Zhang et al., 2013). Among them, the endocrine disrupting effects, especially the estrogen disruption effect (EDEs) attracts researchers increasingly. The EDEs in natural water bodies are largely due to endocrine disruption chemicals (EDCs) from municipal wastewater plant (MWP) effluents (Zhang and Zhou, 2005). There are many comprehensive studies on the occurrences of EDCs in the rivers, for example, Chang et al. had detect 18 EDCs in Koyama river, Japan (Chang et al., 2008); Shao

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et al. had detected phenolic EDCs in Yangtze River of Chongqing area (Shao et al., 2002); Chang et al. had detected more than 20 EDCs in the urban river around Beijing (Chang et al., 2009), Fan et al. even detected the EDCs in source of drinking water and chlorinated byproducts of BPA, NP, and estrogens in the drinking water (Fan et al., 2013). EDCs can induce the malformation in sexual organs, and also induce morphological deformations in both invertebrates and vertebrates, such as triphenyltin and tributyltin (Hu et al., 2009), while estrogenic chemicals are usually related to the intersexuality in fish species. Observed malformations vary from subtle changes to permanent alterations, including feminized and masculinized sex organs (Vos et al., 2000). There was a high incidence of intersexuality in roaches in British rivers (Jobling et al., 1998), and studies have found that bass and bullhead collected across the Hudson River have been disrupted by EDCs (Baldigo et al., 2006).

Several EDCs, including some phenols and phthalate, are synthetic chemicals introduced to the environment as a result of human activities, including the production and disposal of industrial chemicals, pharmaceuticals, and personal care products. EDCs can also occur naturally in the environment. For example, natural hormone testosterone (T), estrone (E1), and 17β-estradiol (E2) are EDCs excreted by animals, and are therefore ubiquitous in the same aquatic environment receiving sewage inputs (Duong et al., 2010; Chang et al., 2011); Chang et al. had evaluated the occurrence of five classes of hormones in MWPs and the receiving waters, and found that the hormones may be still detected in MWPs effluents (Chang et al., 2009). Many EDCs are sufficiently stable to survive sewage treatment processes and can be reactivated during those processes (Zhang and Zhou, 2005). Some studies have reported EDC removals by the conventional MWPs. For example, the removals of E1, E2, EE2, bisphenol A (BPA) and 4-*tert*-octylphenol (OP) were 58%, 91%, 18%, 50–69% and 14%, respectively; and their corresponding effluent concentrations were about 71 ng/L, 1.3 ng/L, 1.9 ng/L, 10–338 ng/L and 0.6 ng/L. Although the EDCs in the MWPs effluents remained stable in the ng/L range, they still posed EDEs risk (Mailler et al., 2015; Margot et al., 2013; Nakada et al., 2007).

Many studies have examined the removal of EDCs and EDEs by some advanced treatment processes (ATPs), however, these studies mainly used simulated wastewater, with EDCs at concentrations of μg/L or mg/L. Only a few studies have studied pilot ATPs in real wastewater treatment and these ATPs were mainly ozonation and activated carbon treatment (Nakada et al., 2007; Cao et al., 2009; Margot et al., 2013). The treatment conditions of the effluents and ATPs in these literature varied, making them hard to compare. Therefore, in this study, five typical ATPs, including coagulation sedimentation, ozonation, resin adsorption, electro-adsorption and activated carbon adsorption, were comparatively studied to evaluate their efficiencies in EDCs removal, toxicity reduction and EDEs reduction from the real MWP secondary effluent.

2. Material and methods

2.1. ATP operational conditions

The Wulongkou (WLK) MWP is located in the northwest of Zhengzhou city (treatment capacity: 150–200 kilotons daily), Henan province, China. Wastewater is processed with conventional biological activated sludge treatment (Fig. 1a). Water samples were collected daily on May 1–20, 2015. The following five ATPs are used to treat the effluent for further evaluation of EDCs removal and toxicity reduction.

Coagulation sedimentation: 100 kilotons of the secondary effluent in WLK MWP were treated per day using a coagulation sedimentation process (18 mg/L polyaluminium + 9 mg/L polyacrylamide) (Fig. 1b). Water samples were collected daily on May 1–20, 2015.

Nan da magnetic polyacrylic anion exchange resin (NDMP) resin adsorption: A pilot plant for NDMP-2 resin treatment was designed to treat 1000 t/d secondary effluent (Fig. 1c). The NDMP resin, a kind of magnetic anion exchange resin, has a retention time of 1 h; a suspension of 1–6% was tested. For regeneration, the resin used in the above adsorption was desorbed using a regeneration solution composed of 12% (m/m) NaCl and 0.5% (m/m) NaOH. The operation details are available in the reference of (Shuang et al., 2012).

Ozonation: A 100 t/d pilot plant for oxidation treatment was designed to treat secondary effluent (Fig. 1d). The ozone dose was 5–40 mg/L (amount of gaseous ozone injected) and the contact time was 20 min in the oxidation process (Fig. 1d). Ozone containing gas (4–12% w/w) was continuously produced by an ozone generator (JET, China). Ozone concentrations in the feed and off gas were continuously measured (BMT 964 S/RD probes, Germany). The remaining gaseous ozone was catalytically converted to oxygen before being released into the atmosphere.

Electro-adsorption: Experimental conditions of the bench-scale electro-adsorption process (or capacitive deionization technology) (Fig. 1d) were: 1.8 V of applied potential, 2 mm of plate distance, and 15 mL/min of flow rate for 10–100 min. The activated carbon electrode added to the electro-adsorption devices was 80 mm × 80 mm, and the powder activated carbon dose was 1.2 g. The activated carbon was changed after treating 50 L water. A previously published paper described the test procedure in detail (Wang et al., 2015).

Activated carbon adsorption: The powder activated carbon was purchased from Sigma (USA); it was 20–40 mesh with a specific surface area of 600 m^2/g. The bench-scale installation was done in a well-mixed contact reactor of 100 L. Powder activated carbon slurry was added continuously, in proportion to the wastewater flow, to reach a final dosage of 20–160 mg/L. The response time was 30 h (Zhang and Zhou, 2005).

2.2. EDCs analysis and E2 equivalent (ΣEEQ_{EDC}) calculation

EDCs in the water samples were extracted using Oasis HLB SPE cartridges (60 mg/3 mL, Waters Corp., USA) according to previous published study (Mathur et al., 2007). Then the EDCs (E1, E2, 17α-ethynylestradiol (EE2), OP, BPA and dibutylphalate (DBP)) were analyzed using a gas chromatography/mass spectrometry (GC/MS, Trace ISQ, Thermo Fisher, US) coupled with an HP-5 MS capillary column (30 mm × 0.25 mm, 0.25 μm film thickness). Target compound recoveries ranged from 74.2% to 103.5%. An EDC concentration at a signal-to-noise ratio of 3:1 was considered as the detection limit (Williams et al., 2003). In this study, EDCs detection limits were 0.14 ng/L for E1, 0.13 ng/L for E2, 0.12 ng/L for EE2, 0.10 ng/L for OP, 0.12 ng/L for BPA, and 0.22 ng/L for DBP. Experiments were independently performed in triplicate. Based on the measured EDCs concentration and the E2 equivalency factor (Murk et al., 2002a), the E2 activity equivalency of EDCs (ΣEEQ_{EDC}) was calculated using the following formula:

$$\sum EEQ_{EDC} = 1 \times 10^{-2} \times [E1] + [E2] + 1.2 \times [EE2] + 1 \times 10^{-5} \times [BPA] + 1 \times 10^{-5} \times [OP] + 1 \times 10^{-7} \times [DBP]$$