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Comprehensive evaluation of three sets of advanced wastewater treatment trains for treating secondary effluent: Organic micro-pollutants and bio-toxicity

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HIGHLIGHTS

- BOIs, OMPs and bio-toxicity were comprehensively investigated.
- Ozonation was effective in removing OMPs and bio-toxicity of SE.
- UV_{254} and TF showed high potential in indicating OMPs and genotoxicity removal.
- Estrogenic activity reduction was related well to OMPs removal during treatments.
- The removals of spectroscopic indicators indicated the risk mitigation of SE.

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ABSTRACT

The environmental presence of organic micro-pollutants (OMPs) has posed increasing risks on aquatic organism and human health. The performance of three commonly used advanced wastewater treatment trains, coagulation-sand filter, coagulation-biological aerated filter (BAF) and ozonation-biological activated carbon (BAC), in removing fifteen residual contaminants and bio-toxicity of the effluent from a local municipal wastewater treatment plant (WWTP) were investigated. Relatively high level of OMPs (0.69–14.71 μg/L), genotoxicity (22.64 μg 4-NQO/L) and estrogenic activity (1.4 μg E2/L) were observed from the secondary effluent (SE). Limited OMPs and bio-toxicity reduction was achieved during coagulation with 20 mg/L of polymeric aluminium and sand filter. Ozonation exhibited high advantage in OMPs, genotoxicity and estrogenic activity reduction. More than 80% of removal was achieved for most OMPs after ozonation with normalized dose of 1.25 mg O_3/mg DOC, and the removal of OMPs was consistent well with the second reaction kinetics constants of OMPs with ozone. Based on Pearson correlation analysis, spectroscopy indicators such as UV_{254} and total fluorescence (TF) exhibited a high positive correlation with genotoxicity reduction, while estrogenic activity was related well with OMPs variation. To sum up, spectroscopic indicators showed a high potential to indicate the OMPs and bio-toxicity of SE.

1. Introduction

An increasing number of organic micro-pollutants (OMPs) were detected in wastewater and surface water during the last decade (Michael-Kordatou et al., 2015). OMPs are incompletely or none removed in conventional wastewater treatment plants (WWTPs) making WWTPs major point sources of OMPs to the aquatic environment (Bui et al., 2016). Although they are present in water environment at extremely low concentration (ng/L or μg/L level), they could lead to potential acute and chronic toxicity to aquatic organisms and human health (Tang et al., 2014a; Zietzschmann et al., 2015). However, OMPs is such a large family that cannot be completely detected and the bioactivity of substantial OMPs is also unknown until now. Bio-toxicity test, such as acute toxicity, genotoxicity test, estrogenic activity and anti-estrogenic activity, may provide alternative and comprehensive information on the risk of SE. It has been reported that secondary effluent (SE) exhibited relatively high genotoxicity (Tang et al., 2014a). Therefore, exploring effective advanced treatment processes to reduce the risk

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of SE is an urgent issue.

Various advanced wastewater treatment processes were extensively initiated in recent years, such as coagulation (Tang et al., 2013), biofilter (Lee et al., 2012; Knopp et al., 2016), membrane filtration (Lee et al., 2012), activated carbon adsorption (Anumol et al., 2015; Zietzschmann et al., 2015), ozonation and advanced oxidation process (AOP) (Pocostales et al., 2010). Among the processes, membrane filtration, activated carbon adsorption and advanced oxidation process showed excellent performance in bulk organic matters, OMPs and bio-toxicity reduction (Macova et al., 2010; Anumol et al., 2015). However, the power consumption of reverse osmosis (RO) membrane filtration and AOP are at least 4–10 times greater than that consumed by ozonation (Lee et al., 2012), and the regeneration of saturated activated carbon is also a troublesome work (Zietzschmann et al., 2015). Therefore, high operating cost, strict requirement for influent quality (i.e. suspended solids and organic matter content) and by-products production restricted their applications in developing country and area. Coagulation, biofilter, ozonation and biological activated carbon (BAC), which are widely used in drinking water treatment, may serve as alternatives in advanced wastewater treatment to reduce the ecological risk of SE (Kalkan et al., 2011; Qian et al., 2013). Substantial researches related to coagulation, ozonation and BAC have been widely reported, but there is no parallel comparison research on how these advanced wastewater treatment processes work in OMPs removal and bio-toxicity reduction.

The ubiquitous nature of OMPs has been extensively reported, still there are lots of unknown chemicals in the aquatic environment. So it is of great significance to find inherent relationship between bulk organic indicators (BOIs) and OMPs in order to indicate the removal efficiency of OMPs during advanced wastewater treatments. Previous studies showed that BOIs such as UV absorbance and fluorescence exhibited good positive correlation with OMPs removal in ozonation and activated carbon adsorption (Gerrity et al., 2012; Altmann et al., 2015; Anumol et al., 2015). However whether this relationship is unified in different treatment process has not been investigated. In addition, bio-toxicity parameters (acute toxicity, genotoxicity, estrogenic activity and anti-estrogenic activity) of SE are important to indicate the comprehensive bioactivity of effluent organic matter (EfOM), which could be analyzed through laborious and time consuming *in vitro* bioassay (Nishikawa et al., 1999). Estrogenic compounds are also constituents of EfOM and OMPs (Macova et al., 2010), hence there may be an inherent relationship between BOIs and estrogenic activity. It is also expected to find out well related indicators to indicate the genotoxicity based the work herein.

In the present research, three advanced wastewater treatment trains were conducted to evaluate OMPs removal and bio-toxicity reduction of real SE. The goals of this research are to (1) evaluate OMPs removal behavior during the treatment processes and (2) investigate the bio-toxicity reduction efficiency, and (3) find out the relationships among simple BOIs, OMPs and bio-toxicity reduction.

2. Material and methods

2.1. Source of SE

SE from a local WWTP in Harbin, China, was used as the source water. The treatment process of the WWTP is in sequence of screen filtration, grit chamber, modified anaerobic/anoxic/oxic (25 days of average sludge retention time), secondary clarification and UV disinfection. The SE used for experiment was taken before UV disinfection and the water qualities are listed in Table 1.

2.2. Experimental set-up

The diagram of the three sets of advanced treatment trains (set 1: coagulation-sand filter (C-S); set 2: coagulation-biological aerated filtration (C-BAF) and set 3: ozonation-BAC (O3-BAC)) is depicted in Fig. S1. In coagulation process, 20 mg/L PACl was applied with the maximum COD and phosphorus removal (data not shown). Sand filter was packed with silica sand (grain size of 5–8 mesh), while BAF with globular ceramsites (grain size of 3–5 mm). Two hermetic glass columns with the same volume were used in ozonation process, one of the columns was bubbled with air containing ozone from an ozone generator (HY-003-20A, China), the other was at steady state to remove residual ozone in the effluent. The ozone concentration of the inlet was maintained at 5 mg/L with a flow rate of 500 mL/min, while ozone concentration in the outlet was monitored with an ozone detector (ES20B-O3, China). Ozone concentration in water was measured using standard indigo colorimetric method. Therefore, the normalized ozone dose was about 1.25 mg O_3/mg DOC in this study. The BAC column was 2 m in height and was filled with coconut shell activated carbon (grain size of 4–6 mesh) with packing density of 435.5 g/m^3. All the processes were continuously operated in steady state for over 2 months. The operational parameters are listed in Table 2.

2.3. Sample concentration

Solid phase extraction (SPE) was carried out using Oasis HLB cartridge (6 cc, 200 mg, Waters). Cartridges were first preconditioned with 5 mL of methanol, followed by 2 × 5 mL of ultrapure water. 250 mL sample passed through a 0.45 μm microfiber filter was then acidified to pH 2.5. Then the sample was introduced to the cartridges via a multi-channel peristaltic pump (LongerBT100-1L, China) at a flow rate of 10 mL/min. After dried under vacuum for 2 h, the cartridges were eluted with 2 × 5 mL methanol at a flow rate of 5 mL/min. The 10 mL extract was evaporated to near dryness under a gentle stream of nitrogen. Before analysis, 1 mL methanol was added, and mixed by a rotating mixer. 0.5 mL of the extract was used for OMPs analysis, and the rest 0.5 mL was dried under a gentle stream of nitrogen and re-dissolved by 0.5 mL 100% dimethylsulfoxide (DMSO) to obtain 250-fold concentration. The samples were subsequently diluted to different concentration with 30% DMSO for bio-toxicity analysis.

2.4. Analytical methods

Samples were filtered through a 0.45 μm filter for DOC analysis by a TOC-V_{CPH} analyzer (SHIMADZU, Japan). UV absorbance was measured using a UV–VISIBLE Spectrophotometer (SHIMADZUUV-2550, Japan). Chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonia, total nitrogen (TN) and total phosphorus (TP) were detected according to the standard methods (SEPAC, 2002). Fluorescence excitation-emission matrix (EEM) was measured using a Fluorescence Spectrophotometer (JASCO FP-6500, Japan). Fluorescence of Milli-Q water was subtracted from all sample spectra to remove Raman scatter (Antony et al., 2011), and Raleigh scatter was cutoff in data processing.

Molecular weight (MW) of EfOM was determined using a high pressure liquid chromatography (HPLC) system with a gel permeation chromatography (GPC) column (ultrahydroget™ linear 7.8 × 300 mm, waters), ultraviolet detector and phosphate buffer (1.39 g/L of $Na_2HPO_4 \cdot 12H_2O$, 0.73 g/L of KH_2PO_4 and 7.1 g/L of Na_2SO_4) was used as the mobile phase. Polystyrene sulfonate standards (PSS, American polymer standards) with MW of 1.7 K, 3.6 K, 7.5 K, 15.5 K and 41 K Da and acetone were used for GPC calibration.

Fifteen selected OMPs based on the detection frequency in SE, including norfloxacin (NOR), enrofloxacin (ENR), sulfamethoxazole (SMX), sulfamerazine (SMZ), chlorotetracycline (CRT), oxytetracycline (OTC), naproxen (NPX), ibuprofen (IBP), gemfibrozil (GFZ),