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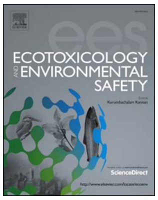

Removal characteristic of surfactants in typical industrial and domestic wastewater treatment plants in Northeast China

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ABSTRACT

Surfactants are widely used in household and industrial products for cleaning and/or solubilization in our daily life. Therefore, they are finally discharged into wastewater treatment plants (WWTPs), which may be the major point pollution source for environment if they were not completely removed during wastewater treatment. In this study, two typical industrial and domestic WWTPs with different wastewater treatment technologies were considered for the topic. Totally, two types of surfactants were analyzed in 24 h influent and each processing unit effluent. Four linear alkylbenzene sulfonates (LASs) with the alkyl chain from C10 to C13, and two benzalkonium chlorides (BACs) with the alkyl chain of C12 and C14 were selected as target compounds. The total concentrations of LASs in influent varied from 19.2 to 1889 μg/L and LAS-C11 and LAS-C12 were the predominant compounds with the concentration from 6.01 to 641 μg/L and 8.02–674 μg/L, respectively. The total concentrations of BACs were much lower than those of LASs, with the concentration ranging from 0.00935 to 1.85 μg/L. Significant positive correlations were observed between concentrations of LASs and BACs in influent, indicating their same and/or similar sources. Compared with the concentration of influent, the concentration of effluent was much lower, indicating the high removal efficiency by the two wastewater treatment processes. Biological treatment unit and cyclic activated sludge system were the main treatment units for the removing of surfactants, which suggested that these two types of surfactants can be easily degraded under aerobic condition. Seasonal variation indicated that the removal efficiencies of surfactants in autumn were a little higher than those in winter. The results of this study provided new insights into the environmental fate of surfactants in wastewater treatment system.

1. Introduction

Surfactants are a diverse group of chemicals with cleaning and/or solubilization properties. Generally, they consist of a polar head group (either charged or uncharged), which is well solvated in water, and a non-polar hydrocarbon tail, which is not easily dissolved in water (Mungray and Kumar, 2009). Therefore, surfactants combine hydrophobic and hydrophilic properties in one molecule. They are widely used in household cleaning detergents, personal care products and industries, like textiles, paint, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and paper industries (Ying, 2006). Generally, surfactants can be divided into four types: anionic, nonionic, cationic and amphoteric. They have been extensively used for over 40 years with an estimated global consumption of 18.2 million tones in 2003 (Hauthal et al., 2004). According to the reported statistics, the total production of surfactants in China was 1.4 million tones in 2006, ranking the second place in the world (Luo, 2007). Linear alkylbenzene sulfonate (LAS) is one of the important anionic surfactants. It has been extensively used for over 40 years with an estimated global consumption of 2.8 million tons in 1998 (VanGinkel, 1996). Commercial LAS consists of the alkyl chain (from C10 to C14) and isomers, in function of the position of the sulfophenyl group link with the alkyl chain (Leon et al., 2006). Benzalkonium chloride (BAC) is a mixture of alkyl benzyl dimethyl ammonium chlorides with C8 to C18 alkyl groups. BAC is a group of quaternary ammonium compounds, which were a sort of cationic surfactants (Zhang et al., 2011).

The wide applications and occurrences of BAC and LAS in environment raise concerns about their potential harm to ecosystem and

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human health. The risk assessment and toxicity of BAC and LAS to terrestrial plants and animals had been studied and reported previously (Mieure et al., 1990; Mungray and Kumar, 2008). For example, the short term median effective concentration values (EC_{50}) of BAC on algae, daphnids, rotifers and protozoans varied from 41 to 2941 μg/L (Kreuzinger et al., 2007). The growth inhibition test with the Gram-negative bacteria were applied to assess the toxicity of BAC. It was found that EC_{50} values of BAC for *Vibrio fischeri* and *P. putida* were reported at the concentration of 0.5 mg/L and 6.0 mg/L, respectively (Sütterlin et al., 2008). Furthermore, the toxicity of BAC and LAS in effluent from wastewater treatment system has received considerable attentions (Ying, 2006). Mieure et al., concluded that there were adequate margins of safety in the use of wastewater for the irrigation of plant species. Adverse effects on plant and animal species were observed at LAS concentration of 10 mg/L, however, LAS concentration in effluents are in a range 0.09 mg/L to 0.9 mg/L, which were much lower than 10 mg/L (Mieure et al., 1990). Mungray and Kumar (2008) found that for effluent from aerobic WWTPs, the risk quotient values were below 1, which means that the environment impact due to the LAS is less than that the target value having an adverse effect on organisms (Mungray and Kumar, 2008).

Sorption and biodegradation (biotransformation) are the two main processes influencing the fate of surfactants in different environmental compartments. It was found that biodegradation is an important process to eliminate LAS in WWTPs. The most important influencing factors are chemical structure, aerobic and anaerobic environments (Mungray and Kumar, 2009). Under aerobic condition, LAS co-metabolism generates shorter-chain homologues. LAS can also be mineralized to CO_2 and H_2O, but this normally requires the contribution of several species of bacteria (Scott and Jones, 2000). Degradation processes in anaerobic systems depends on alternative acceptors such as sulphate, nitrate or carbonate yielding, hydrogen sulfide, molecular nitrogen, methane and/or ammonia. LAS mineralization under anoxic conditions has not been documented and the known enzymatic steps involved in aerobic mineralization require molecular oxygen (Garcia et al., 2005). In wastewater treatment systems, an increased alkyl chain length of BAC homologues (Clara et al., 2007) and the decrease of temperature and sludge particle size (Ren et al., 2011) will result in an increased tendency to absorb to the activated sludge and the increased removal proportion via excess sludge. BAC is also generally considered biodegradable under aerobic conditions (Patrauchan and Oriel, 2003; Takenaka et al., 2007). With increasing alkyl chain length or the substitution of a methyl group with a benzyl group, the biodegradation rate of BAC would decrease (Grabińska-Sota, 2011).

Surfactants can reach the environment through discharge from WWTPs and/or through direct discharge of raw wastewater. Many previous studies have reported the occurrence of these compounds in WWTPs. For example, four LASs were found in all analyzed influent wastewater samples with the mean concentration from 240 ± 121 μg/L (LAS-C13) to 1224 ± 546 μg/L (LAS-C11), and in the 83% of the studied effluent wastewater from 7.49 ± 14.4 μg/L (LAS-C13) to 37.0 ± 51.0 μg/L (LAS-C11) (Camacho-Munoz et al., 2014). Total LASs (C10–C13) concentration were measured in another study, it was found that the mean concentration in the influent was 4200 μg/L (2400–6700 μg/L) and in the effluent was 28 μg/L (7.9–50 μg/L) (Clara et al., 2007). BACs were found in two WWTPs' influent wastewater with the concentration from 2.74 μg/L (C12) to 36.6 μg/L (C14) (Ferrer and Furlong, 2001). In another study, it was found that the mean concentrations in the influent were 39.3 μg/L for BAC-C14 and 55.1 μg/L for BAC-C12, and in the effluent of 0.18 μg/L for BAC-14 and 0.18 μg/L for BAC-C12 (Clara et al., 2007). However, most of them focused on the removal efficiency based on the influent and effluent. Their fates in different treatment units of WWTPs were not comprehensively studied. Furthermore, the hydraulic retention time was not considered for the wastewater sampling, which makes some uncertainty with the calculation of removal efficiency. In this study, the removal characteristic of BAC and LAS in typical industrial and domestic WWTPs was deeply studied. The objectives were: (1) to study the daily variations of concentrations of two BACs and four LASs in influent; (2) to study the fate of BACs and LASs in WWTPs; (3) to study their removal efficiency and characteristic in WWTPs.

2. Materials and methods

2.1. Materials and standards

Methanol (MeOH) and dichloromethane (DCM) were purchased from J. T. Baker (Philisburg, NJ, USA). Ultrapure water was prepared with a Milli-Q ultrapure system. The solid phase extraction (SPE) cartridge packed with 500 mg of Oasis HLB was purchased from Waters (Milford, MA, USA).

Standards of LASs mixture containing LAS-C10 (9.1%), LAS-C11 (37.8%), LAS-C12 (34.1%) and LAS-C13 (18.3%), and BACs with alkyl chain of C12 (76.8%) and C14 (23.2%) were purchased from Sigma-Aldrich, Inc. The detailed information for the six compounds was presented in Table S1 in Supporting information (SI). Stock solution of standards was prepared by dissolving each compound in MeOH at a constant concentration of 100 mg/L. All stock solutions were stored at − 20 °C. Working solution of standards were prepared by diluting the individual stock solution with the same solvent and were stored at − 20 °C before analysis.

2.2. Samples collection

Two WWTPs (WWTP 1 and WWTP 2) were selected for the study. The anaerobic-oxic treatment process (A/O) and cyclic activated sludge technology process (CAST) were applied in the WWTP 1 and WWTP 2, respectively. The detailed information for the two WWTPs is described in Table S2. In order to study the daily variation with influent concentration of BACs and LASs, 24 h influent wastewater samples were collected in December (winter) in 2016 from the two WWTPs. For each hour, one influent wastewater sample was collected by the automatic sampling device SIGMA 900 (Hach, USA). In order to study the fate of BACs and LASs along the wastewater treatment processing, wastewater samples from each treatment unit of the two WWTPs were collected consequently according to the hydraulic retention time (HRT). For each unit, four subsamples were collected at the HRT and then combined together as the typical sample for this unit. Two sampling programs were conducted in September (autumn) and in December (winter) in 2016 for both the two WWTPs in order to study the seasonal variation with their fate and removal characteristic. All the collected wastewater samples were stored in 1 L glass bottles. After collection, samples were transported to the laboratory in low temperature of 4 °C within 24 h to avoid microbial degradation. The wastewater treatment units and HRTs for the two WWTPs were depicted in Fig. 1.

2.3. Sample treatment

Wastewater samples were extracted by SPE. In brief, 20 mL of wastewater samples were diluted to 800 mL with ultrapure water. Oasis HLB SPE cartridge were conditioned with 6 mL of DCM, 6 mL of MeOH and 6 mL of ultrapure water passing through the HLB cartridge under gravity (~ 1 mL/min). Samples were percolated through cartridge at a flow rate about 3 mL/min (~ 1 drop/second) using a vacuum manifold system (12 hole, Agela, China) connected to a vacuum pump. Cartridge was dried for 1–2 h. Then, 7 mL DCM and 7 mL MeOH were used to elute the SPE cartridge under gravity. The combined elution was concentrated by soft nitrogen flow to 1 mL and transferred into 1.5 mL amber GC vial for analysis.