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Modeling and monitoring cyclic and linear volatile methylsiloxanes in a wastewater treatment plant using constant water level sequencing batch reactors

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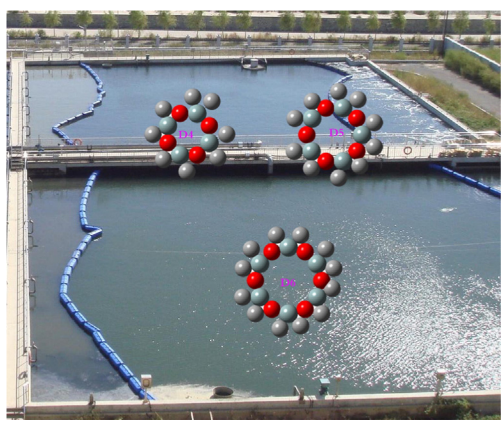
HIGHLIGHTS

- A mass balance model for siloxanes was developed in sequencing batch reactor.
- Total suspended solid in effluent has the most influence on removal efficiency.
- Enhancement of suspended solid removal reduces the release to aquatic environment.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate of cyclic and linear volatile methylsiloxanes (VMSs) was evaluated in a wastewater treatment plant (WWTP) using constant water level sequencing batch reactors from Dalian, China. Influent, effluent, and sewage sludge samples were collected for seven consecutive days. The mean concentrations of cyclic VMSs (cVMSs) in influent and effluent samples are 1.05 μg L^{-1} and 0.343 μg L^{-1}; the total removal efficiency of VMSs is >60%. Linear VMS (lVMS) concentration is under the quantification limitation in aquatic samples but is found in sludge samples with a value of 90 μg kg^{-1}. High solid-water partition coefficients result in high VMS concentrations in sludge with the mean value of 5030 μg kg^{-1}. No significant differences of the daily mass flows are found when comparing the concentration during the weekend and during working days. The estimated mass load of total cVMSs is 194 mg d^{-1} 1000 $inhabitants^{-1}$ derived for the population. A mass balance model of the WWTP was developed and derived to simulate the fate of cVMSs. The removal by sorption on sludge increases, and the volatilization decreases with increasing hydrophobicity and decreasing volatility for cVMSs. Sensitivity analysis shows that the total suspended solid concentration in the effluent, mixed liquor suspended solid concentration, the sewage sludge flow rate, and the influent flow rate are the most influential parameters on the mass distribution of cVMSs in this WWTP.

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1. Introduction

Pharmaceuticals, personal care products, endocrine disruptors and illicit drugs (PPCPs) are regarded as emerging environmental contaminants as many PPCPs are ubiquitous, persistent, and biologically active compounds. As one type of typical PPCPs, volatile methylsiloxanes (VMSs) are high-volume chemicals that are based on Si–O–Si bonds with both aliphatic and cyclic structures and methyl moieties, which are used in a number of commercial applications such as intermediates for the polymerization of polyorganosiloxanes, cosmetic and personal care products, defoamers, sealants, adhesives and coatings (Alaee et al., 2013). Like many PPCPs, the effluent of municipal wastewater treatment plants (WWTP) is an important way to discharge VMSs into the environment (Badjagbo et al., 2009; Dewil et al., 2007; Kaj et al., 2005b; McBean, 2008; Schweigkofler and Niessner, 1999; Surita and Tansel, 2014a; Xu et al., 2013). VMSs are suspected to have a potential ecotoxic impact on aquatic ecosystems (Borgå et al., 2012; Kierkegaard et al., 2013; Norwood et al., 2013; Parrott et al., 2013; Surita and Tansel, 2014b). Therefore, the removal efficiencies of VMSs in WWTPs play a vital role in the discharge of VMSs into the aquatic environment.

Typically, previous studies on WWTPs have been completed to demonstrate the presence or absence of VMSs in influent, effluent, and sludge (Liu et al., 2014; Wang et al., 2013c; Xu et al., 2013) or to develop detection methods of VMSs in these matrices (Cortada et al., 2014; van Egmond et al., 2013; Wang et al., 2013a). All of the studies have demonstrated that VMSs can be well removed by these WWTPs using secondary activated sludge processes. However, the details of the removal mechanisms on the influence of these parameters are not always clearly understood. In fact, removal efficiencies depend strongly on the physico-chemical properties of a substance. Moreover, WWTP operating conditions including sludge retention time, hydraulic retention time, and temperature have influence on the removal efficiencies of PPCPs (Pomiès et al., 2013).

Information about the influence of operating conditions on VMS removal is a key point to better understand removal mechanisms and improve removal efficiency. However, as shown above, the experimental results presented in the previous studies do not provide unambiguous conclusions. Modeling can help to resolve these questions because it enables the simulation of many operating conditions. Understanding the fate of VMSs through WWTP includes the knowledge of the influence not only of the WWTP operating conditions but also of the physico-chemical properties of the VMSs on the main removal mechanisms. The objective of this study is to investigate the four cyclic VMSs (cVMSs) and the four linear VMSs (lVMSs) in a municipal WWTP using the innovative process of constant water level sequencing batch reactors (CWSBR) in Dalian, China. To elucidate detailed removal mechanisms for the VMSs, the fugacity-based treatment plant model is used to simulate their fate in the WWTP.

2. Materials and methods

2.1. Chemicals

Octamethyltrisiloxane (L3; CAS No. 107-51-7; purity >97%), decamethyltetrasiloxane (L4; CAS No. 141-62-8; purity >95%), dodecamethylpentasiloxane (L5; CAS No. 141-63-9; purity >95%), tetrakis(trimethylsiloxy)-silane (M4Q; CAS No. 3555-47-3; purity >95%), hexamethylcyclotrisiloxane (D3; CAS No. 541-05-9; purity >98%), octamethylcyclotetrasiloxane (D4; CAS No. 556-67-2; purity >98%), decamethylcyclopentasiloxane (D5; CAS No. 541-02-6; purity >98%), and dodecamethylcyclohexasiloxane (D6; CAS No. 540-97-6; purity >98%) were purchased from Gelest (Morrisville, PA., U.S.A.), and $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6 were purchased from Moravek (purity >98%; Brea, CA., U.S.A.). Pesticide grade hexane, acetonitrile, and methanol were purchased from TEDIA (U.S.A.).

2.2. Study site and sampling

The municipal WWTP selected for this study discharges into the Bohai Sea, Dalian, China. The WWTP currently serves a population of approximately 130,000 and has a capacity of 30,000 $m^3\ d^{-1}$, which belongs to a small-scale municipal WWTP in China. The plant treats wastewater from homes and food processing facilities. The WWTP uses the process of CWSBR containing intake screens, grit tanks, SBR tanks, and an outfall pipe to the sea (Fig. 1). The innovative CWSBR process can maintain a constant water level, which is achieved with specially developed hydrosails dividing the pond into holding, SBR and balancing zones. Fig. 1 describes the basic stages of a cycle, indicating the constant water level at each stage with a constant inflow and discharge volume. Raw influent, effluent, and sewage sludge samples were collected during seven consecutive days at 10 AM from May 20th, 2014 to May 26th, 2014. Water samples were collected without headspace in 100-mL serum bottles and quickly crimp sealed with Teflon coated butyl septa and aluminum seals. Grab samples of waste sludge were taken from sludge tank outlet. Sludge samples were collected in prewashed amber glass containers. All samples were placed on ice and shipped to the laboratory for extraction and analysis within 2 h.

2.3. Extraction and analysis

Membrane-assisted solvent extraction technology was used to extract VMSs from the water samples. This method can extract the total concentration in the water sample. Each 100 mL water sample was spiked with 2-ng internal standards of $^{13}C_4$-D4, $^{13}C_5$-D5, and $^{13}C_6$-D6. A stainless steel membrane holder and membrane were inserted and held in the neck of the bottle. Hexane (0.5 mL) was added to the membrane as the extracting solvent. The bottle was immediately crimp capped with an aluminum seal fitted with a Teflon faced butyl rubber

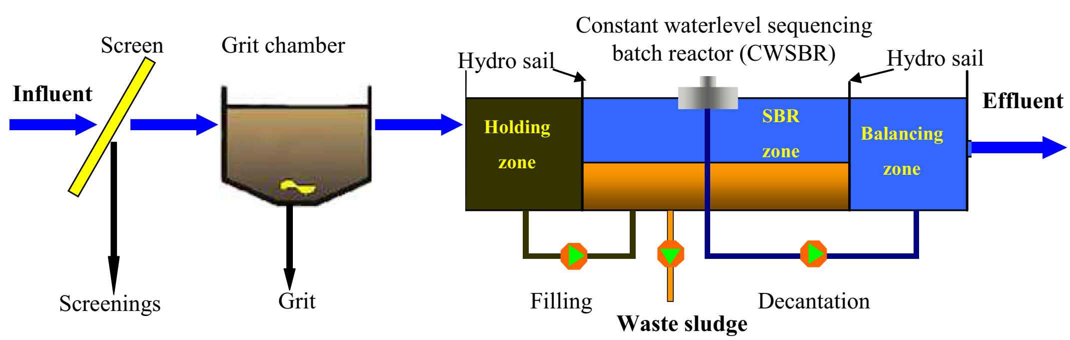

Fig. 1. Schematic of the treatment process of constant water level sequencing batch reactor (CWSBR) at the WWTP selected for this study. The boldfaced sampling sites are influent, effluent, and waste sludge.