DOCTORAL THESIS

Environmental occurrence of triclosan in wastewater and transformation fate and development of a method of derivatization of PFOS

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Abstract

Triclosan (TCS) as an antimicrobial agent in a variety of consumer products has drawn environmental and health care scientist's attention for over 40 years as it has been widely detected in environment. Once released to the environment, TCS can easily transfer to water bodies and soil due to its fair solubility and hydrophobicity. TCS is not considered as a toxic compound. However, two main reasons have bolded TCS occurrence important in the environment. Firstly, TCS can easily adsorb to and accumulate in the media possessing organic matter such as sludge, soli or tissue. Secondly, TCS can degrade/transform to other compounds with higher potential toxicity and persistency. While many degradation products have been observed in certain circumstances, the main easily-formed products can be pointed as 2,4-dichlorophenol (2,4-DCP), 2,8-dichlorodibenzoparadioxin (2,8-DCDD) and methyl triclosan (MTCS). 2,4-DCP is listed as the priority toxic pollutant by US Environmental Protection Agency. 2,8-DCDD is a member of dioxin family with a recently reported relative potency factor of 1×10^{-4}. This compound is suspected to transform to higher chlorinated dioxins when exposed to light or chlorine. MTCS, resulted from microbial methylation of TCS, has received much attention recently due to its persistency.

Although TCS has been studied vastly, it`s fate and behavior in wastewater and sludge as the first receiver in the environment has not been investigated deeply so far. In this research, attempt was done to answer some so far unanswered questions such as whether i) TCS occurrence is consistent within a single STP and between different

STPs, ii) TCS transformation is a factor of wastewater and sludge treatment, iii) TCS degradation occurs in aerobic/anaerobic sludge digestion, iv) TCS adsorption is predictable and obeys any equilibrium and kinetics model.

Two gas chromatography-mass spectrometry (GC-MS) based-methods were successfully developed for determination of TCS, 2,4-DCP, 2,8-DCDD and MTCS in wastewater and sludge. In the first method, liquid-liquid extraction (LLE) and silica column chromatography were applied for the extraction and cleanup of wastewater. In the second method, accelerated solvent extraction (ASE) and multilayer silica column chromatography were employed for the extraction and cleanup of sludge. For validation purpose, the methods were successfully applied to wastewater and sludge samples from three different municipal sewage treatment plants (STPs) in Hong Kong. Satisfactory mean recoveries for all target compounds were obtained as over 82% and 84% for wastewater and sludge samples, respectively. TCS degradation products were detected based on the treatment practice. 2,8-DCDD was detected in the plant utilizing UV disinfection at the mean level of 20.3(±4.8) $ng.L^{-1}$. 2,4-DCP was identified in chemically enhanced primary treatment (CEPT) applying chlorine disinfection at the mean level of 64.5(±4.5) $ng.L^{-1}$. Besides, MTCS was detected in the wastewater collected after biological treatment 33.3(±3.4) $ng.L^{-1}$ as well as in sludge samples that have undergone aerobic digestion at the mean level of 266.1 (±14.2) $ng.g^{-1}$ dry weight (d.w.).

Mass balance of TCS in three STPs and the extent of TCS transformation to the degradation compounds were investigated and adsorption behavior of some of the occurred compounds was studied. Moreover, TCS fate was probed in full scale plant

during wastewater and sludge aerobic/anaerobic treatment condition. Finally few correlations were investigated. For STP (I), 77.6% of the entering TCS mass flux to the plant was directly discharged to the receiving environment. The mass that was settled along the sludge underwent aerobic digestion treatment of which 52.2% was aerobically degraded in the digester. However 5.4% of the TCS in the sludge was observed to be transformed to MTCS and 47.8% was remained in the dewatered sludge to be disposed to landfill. TCS elimination in STP (II) wastewater treatment was 25.5%. Chlorination could cause 5.3% of TCS loss during disinfection process. Nevertheless, still 68.7% of the loading TCS was discharged to the environment through wastewater. TCS mass flux in pretreatment and post treatment sludge was almost constant. For STP (III), 14.2% and 8% of initial TCS mass flux was adsorbed to primary and secondary sludge, respectively. Mass balance between TCS lost in the biological treatment, the mass adsorbed to the sludge and the effluent revealed that 44.0% of the initial TCS mass flux was biodegraded in biological treatment of which 19.8% was transformed to MTCS. In addition, 10.3% of TCS mass was lost in UV irradiation disinfection unit of which 90.8% was transformed to 2,8-DCDD. Significant TCS mass loss (20.6%) was observed in anaerobic digestion of sludge and the remaining mass in dewatered sludge was disposed to landfill. No other degradation product was observed in the dewatered sludge except MTCS that showed insignificant change in mass flux after anaerobic digestion. K_d values were calculated for TCS, MTCS and 2,4-DCP for the first time based on the concentration of target compound in liquid and solid phase. Moreover, temporal-based variation of TCS and its degradation products were statistically proved. A relationship was attributed

between TCS fraction adsorbed to the particulates in raw wastewater and elimination efficiency in primary treatment (r = 0.83, 0.66 and 0.87 for STP (I), (II) and (III), respectively).

Adsorption behavior of TCS, 2,4-DCP and MTCS to primary and secondary sludge was investigated. For this purpose, a simple and efficient GC-MS-based method was developed for simultaneous determination of TCS, MTCS and 2,4-DCP in wastewater. Batch experiments were carried out and effect of various parameters such as pH, temperature and sludge concentration were studied. Three isotherm models, Linear, Freundlich and Langmuir were examined to fit the adsorption data. Amongst, Linear and Freundlich isotherm models were able to describe the system behavior well while Langmuir isotherm model did not exhibit satisfactory result. Relevant K_d values were derived for three compounds and were compared to the full scale. Pseudo-first and second order kinetics models were applied to describe the kinetic data. Pseudo-second order kinetic was found to fit well over the range of applied initial concentrations based on the regression coefficients and the relative error for the calculated equilibrium sorption capacity which implied the sorption of TCS, MTCS and 2,4-DCP onto the inactivated dried sludge proceeds predominantly through a pseudo-second order kinetics.

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