Int. J. Electrochem. Sci., 11 **(2016)** 6914 – 6921, doi: 10.20964/2016.08.04

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Removal of Cyclic and Linear Siloxanes in Effluents from a Cosmetic Wastewater Treatment Plant by Electrochemical Oxidation

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Received: 28 April 2016 / *Accepted:* 23 May 2016 / *Published:* 7 July 2016

The presence of cyclic and linear siloxanes in wastewater samples after different processing units of a cosmetic wastewater treatment plant (WWTP) in Beijing was investigated in the current study. Dodecamethylcyclohexasiloxane (D6) and linear siloxanes (L5 to L16) were detected in wastewater. D6, L14, L15 and L16 were the dominant siloxanes in wastewater. An electrochemical oxidation reactor was applied for advanced treatment of siloxanes in cosmetic WWTP effluents. The stainless steel plates were used as anode and cathode electrode. It concluded that the removal efficiency of siloxanes was significantly enlarged with the increasing applied current density when the reaction time was increased from 0 to 20 min. Under the optimal reaction conditions, with reaction time of 20 min, current density of 20 mA/cm^2, electrode plate distance of 1.0 cm and electrode plate amounts of 5 pairs, the removal efficiencies of of D6, L14, L15 and L16 were from 30.2% to 93.3%.

Keywords: Cyclic siloxanes, linear siloxanes, wastewater treatment plants (WWTPs), electrochemical oxidation, persistent organic pollutants (POPs)

1. INTRODUCTION

Siloxanes belong to a kind of silicones, consisting of a structure unit of alternating Si-O bonds with aliphatic chains attached to Si atoms [1, 2]. In past several decades, siloxanes, including both cyclic and linear siloxanes, have been used widely in the field of industrial applications, for example, fuel, automobile, decorative, as well as in cosmetic industries [3]. Because siloxanes are produced with high in the production process of consumer products, it has a probability that they will enter into outside environment. Inevitably, siloxanes may be discharged into wastewater systems. Some studies have been carried out to assess their occurrence in wastewater treatment plants (WWTPs) effluents and surface water environment [4]. Because of their stable characters, siloxanes could be persisted in the environment. Siloxanes also have the risk to bioaccumulate in organisms [5]. Up to now, cyclic siloxanes have been detected much more often than linear siloxanes in environment [6]. Especially, octamethylcyclotetrasiloxane (D_4, D refers to the dimethysiloxane unit, and the subscript refers to the number of silicon bonds), decamethylcyclopentasiloxane (D_5) and dodecamethylcyclohexasiloxane (D_6) have been seen as high production volume (HPV) chemicals by the Organization for Economic Cooperation and Development and the US Environmental Protection Agency [7, 8].

WWTPs have been believed as a source for siloxanes discharging into the environment [9]. Typically, all of previous studies on occurrence of siloxanes focused on municipal WWTPs [1]. Thus far, no study has been investigated the concentrations of siloxanes in the units of a cosmetic WWTP.

What's more, the current conventional and further treatment units in WWTPs of China mainly aiming to removal of COD, NH_3-N, TN, TP and other common organics in water. However, micro pollutants, including siloxanes and other persistent organic pollutants (POPs), are not designed for removal in the treating processes of WWTPs [10]. Thus, it is urgent to find a feasible method to remediate siloxanes in wastewaters. So far, lots of documents have described the determination or monitoring of siloxanes in wastewaters. However, only a small number of studies have been focused on the remediation of siloxanes in environment, mainly focusing in biogas and wastewater sludge. For example, Activated carbon and bio trickling filter have been tried for siloxanes removal in landfill gas [11]. Since the conventional wastewater treatment processes can only remove siloxanes partially, WWTP effluent can be one of the major sources of siloxanes discharged into natural water environment. Therefore, some advanced treatment methods are necessary for remediation of siloxanes in WWTPs effluents.

For the advanced treatment of siloxanes in WWTPs effluents, to date, nearly no research has been found. Conventional advanced treatment methods, including adsorption, photoelectrocatalysis, ultrasonic irradiation, and zerovalent iron, have been investigated to remove persistent organic pollutants (POPs) from WWTPs effluents. However, the above methods are expensive and inefficient [12].

Recently, electrochemical oxidation has attracted wide interesting because electrochemical oxidation is one of the economical and environmental–friendly methods in wastewater treatment processing [13]. The electrochemical oxidation has been successfully used in the treatment of some high organic concentration wastewaters, such as coke chemical, textile, tannery wastewater, solid waste leachate and some POPs in wastewater [14].

In this study, three cyclic siloxanes, D_4, D_5 and D_6, in addition 12 kinds of linear siloxanes (L_5 to L_{16}) in wastewaters of different processing units of a cosmetic WWTP in Beijing were determined. An effective electrochemical oxidation system was built for highly removal of siloxanes from wastewater effluents.

2. METHODS

2.1 Regents and Standards

All chemicals were of analytical grade and used without any further purification. Octamethylcyclotetrasiloxane (D_4, $C_8H_{24}O_4Si_4$), decamethylcyclopentasiloxane (D_5, $C_{10}H_{30}O_5Si_5$) and dodecamethylcyclohexasiloxane (D_6, $C_{12}H_{36}O_6Si_6$) were obtained from Tokyo Chemical Industry (Wellesley Hill, MA). PDMS 200 fluid (viscosity of 5 cSt), which contains linear siloxanes [L_5 ($C_{12}H_{36}O_4Si_5$), L_6 ($C_{14}H_{42}O_5Si_6$), L_7 ($C_{16}H_{48}O_6Si_7$), L_8 ($C_{18}H_{54}O_7Si_8$), L_9 ($C_{20}H_{60}O_8Si_9$), L_{10} ($C_{22}H_{66}O_9Si_{10}$), L_{11} ($C_{24}H_{72}O_{10}Si_{11}$), L_{12} ($C_{26}H_{78}O_{11}Si_{12}$), L_{13} ($C_{28}H_{84}O_{12}Si_{13}$), L_{14} ($C_{30}H_{90}O_{13}Si_{14}$), L_{15} ($C_{32}H_{96}O_{14}Si_{15}$), L_{16} ($C_{34}H_{102}O_{15}Si_{16}$)], was obtained from Sigma-Aldrich (St. Louis, MO). Tetrakis (trimethylsiloxy)-silane (M4Q; purity 97%) was purchased from Aldrich, used as surrogate standard. PCB-30 was obtained from AccuStandard (New Haven, CT) and was used as internal standard. All solutions were prepared using Milli-Q ultrapure water.

2.2 Collection of wastewater sample

The wastewater samples were collected in high-density polyethylene bottles from a cosmetic WWTP (founded in 2007, Beijing, China; Treatment process: primary setting, followed by ABR (Anaerobic Baffled Reactor), aeration biological treatment and final clarifier; Treatment capacity: 200 m^3/d) in spring and summer, 2015. In the wastewater treatment processing, the hydraulic retention times in the primary setting, ABR, aeration and final clarifier were 4.0, 48.0, 8.0 and 1.0 h, respectively. After settling in the final clarifier, part of the activated sludge was returned to ABR tank, and the excess was conveyed to be dehydrated. Samplings were carried out at influent, the primary setting effluent, ABR effluent, aeration effluent and effluent (Fig. 1).

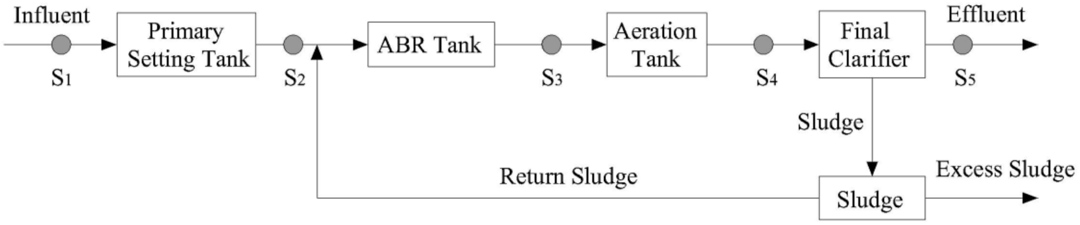

Figure 1. Flow scheme of the cosmetic WWTP with sampling locations S_1 - S_5: Sampling point

The COD concentrations of wastewater effluents were 33.7-114.5 mg/L. After sampling, sampling bottles were transported to the laboratory immediately within 4 h by an ice chamber. The bottles were preserved in refrigerator at 4 ºC.

2.3 Preparation of wastewater sample

The extraction of wastewater samples was applied by following the procedure described by Reiner and Kannan [15]. Briefly, 0.1 g of the sieved sample was spiked with 100 µL of 1 mg/L MQ solution as the internal standard. The spiked sample was extracted with 10 mL of ethyl acetate/HEX mixture (1:1) for 15 min in an ultrasonic bath, and the mixture was then centrifuged at 3500 rpm for 10 min. The supernatant was transferred to a new glass tube. The extraction procedure was repeated 3 times. The total extract was concentrated to 2 mL under a gentle stream of N_2 and then purified by a cartridge packed with 1.0 g anhydrous Na_2SO_4. Finally, the eluent was concentrated to 1 mL with a gentle stream of N_2 before GC/MS analysis.

2.4 Instrument analysis

Concentrations of siloxanes in the wastewater samples were identified and quantified by GC/MS (Agilent Technologies 7890A GC/5975C MSD) with an electron-impact (EI) ionization source. The target analytes were separated by a 5% phenyl methyl siloxane capillary column (HP-5 ms; 30 m×0.25 mm i.d. ×0.25 μm). The temperature of the GC injector port (splitless mode) was set as described by Liu et al. [16].

2.5 Quality assurance and quality control (QA/QC)

Laboratory personnel were forbidden to use any cosmetic products in experiments. No sampling or storage device was made of silica gel in the process of sampling collection. All devices were cleaned with methanol.

Good recoveries were found for siloxanes (75-107%) in matrix spiked samples. Limit of quantitation (LOQ) was determined as 10 times the standard deviation of the laboratory blank signals (n=7). For compounds not detected in procedural blanks, the limit of detection (LOD) and LOQ were determined based on a signal-to-noise ratio of 3 and 10. LOQs of siloxanes ranged from 0.5 to 3.6 ng/g.

2.6 Electrochemical oxidation procedure

The electrolytic device was made of parallelepipedic plexiglas. The valid working volume, length, width and height of device were 6000mL, 30cm, 20cm and 15cm, respectively. In all cases, stainless steel electrode plates (dimensions: 20 cm × 10 cm; thickness: 1mm) were used as anode/cathode. The cathode and anode electrodes were alternately arranged and placed inside of the device. The supplied power in this experiment was a MPS 702 DC power generator. The cell potential was controlled by a voltmeter.

3. RESULTS AND DISCUSSION

3.1 Siloxanes in wastewaters

The concentrations of the target siloxanes detected in different samples in wastewaters from the cosmetic WWTP are summarized in Table 1.

Table 1. Siloxanes concentrations in wastewater samples from a cosmetic WWTP* (μg/L)

Sampling unit	*S_1 Influent*		*S_2 After Primary Setting*		*S_3 After ABR*		*S_4 After Aeration*		*S_5 Effluent*	
Sampling time	*March 2015*	*June 2015*	*March 2015*	*June 2015*	*March 2015*	*June 2015*	*March 2015*	*June 2015*	*March 2015*	*June 2015*
D4	0.26	0.35	0.25	0.28	0.10	0.12	0.05	0.07	ND	ND
D5	0.33	0.46	0.30	0.42	0.13	0.15	0.08	0.10	ND	ND
D6	3.72	4.85	3.55	4.74	1.64	2.10	1.41	1.82	0.89	1.53
L5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L12	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L14	5.12	5.50	5.05	5.47	3.28	3.59	2.95	3.08	2.74	3.14
L15	5.74	6.15	5.90	6.13	4.19	4.42	3.71	4.29	3.55	4.25
L16	6.02	6.65	5.81	6.62	3.73	4.56	3.22	4.08	3.06	3.87

* ND: Not detected. The number of samples analyzed: 4. Because of the relatively constant emission, the wastewater samples were collected 4 times within 24 h and were well mixed with equal volume.

From the quantitatively determined siloxanes, D4, D5, D6, L14, L15 and L16 were detected in S_1, S_2, S_3 and S_4 samples. D6, L14, L15 and L16 were detected in effluent samples. In general, after the wastewater was treated by different units from primary setting tank to final clarifier step by step, the siloxanes were decreased accordingly. The main siloxanes in effluents of cosmetic wastewater were D6, L14, L15 and L16 siloxanes, both containing cyclic and linear siloxanes. Thus far, some former studies showed that cyclic siloxanes were the dominant siloxanes in wastewater [4, 17-18]. However, all of their researches were focused on civil wastewater. Lu et al [19] investigated the concentrations of 15 siloxanes in personal care products. The results indicated that the linear siloxanes were the dominant compounds. The wastewater sample was taken from cosmetic WWTPs, which belong to the personal care product industry. Our research results are not in conflict with previous studies. What’s more, some further treatment processes must be used to remediate siloxanes in effluents from the cosmetic wastewater.

3.2 Removal of siloxanes by electrochemical oxidation

3.2.1 Effect of current density and reaction time

It has been confirmed that the capability of electron transfer and hydroxyl radical generation control the removal efficiencies of target pollutants in the process of electrochemical oxidation [20]. The hydroxyl radical generation capability depends on the applied current density and reaction time. As a result, in our experiments, the applied current densities were set at 10, 15, 20 and 25 mA/cm^2 to evaluate the removal efficiency of COD in wastewater effluent samples. According to our former research results, the optimal electrode plate amount is 5 pairs, and the optical electrode distance is 1.0cm uniformly [21]. The initial concentration of COD was 56.6 mg/L. The COD removal efficiencies with reaction time were shown in Fig. 2.

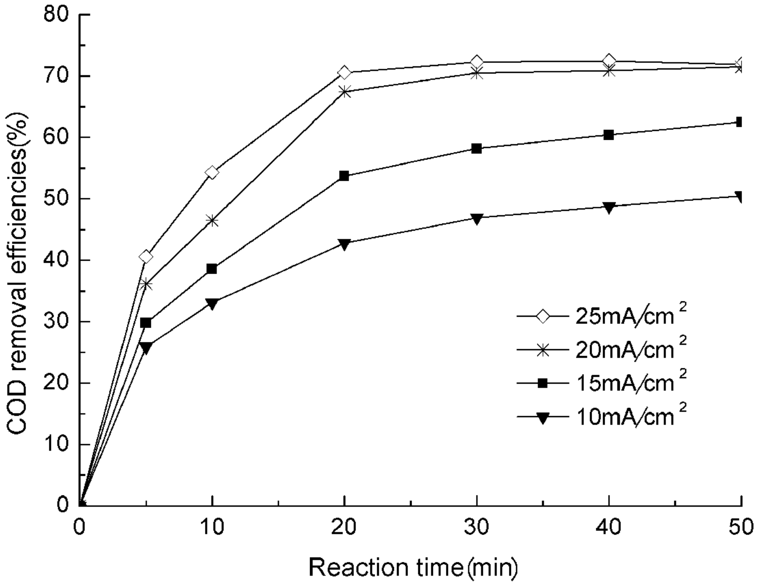

Figure 2. Removal efficiencies for COD in wastewater effluent samples

In Fig. 2, the removal efficiency of COD significantly increased with the increasing applied current density when the reaction time was less than 20 min. While the removal efficiency of COD changed little after the reaction time was above 20 - 50 min. The removal efficiencies of COD were almost same when applied current density was set at 20 or 25 mA/cm^2. For energy consideration, applied current of 20 mA/cm^2 and reaction time of 20 min were chosen as the optimal parameters of electrochemical oxidation during the following experiments.

3.2.2 Optimal removal efficiency of siloxanes

The electrochemical device was operated under above optimal reaction parameters, which indicates reaction time (20 min), current density (20 mA/cm^2), plate distance (1.0 cm) and electrode plate amounts (5 pairs). The removal efficiencies for siloxanes in wastewater effluents are summarized in Figure 3.

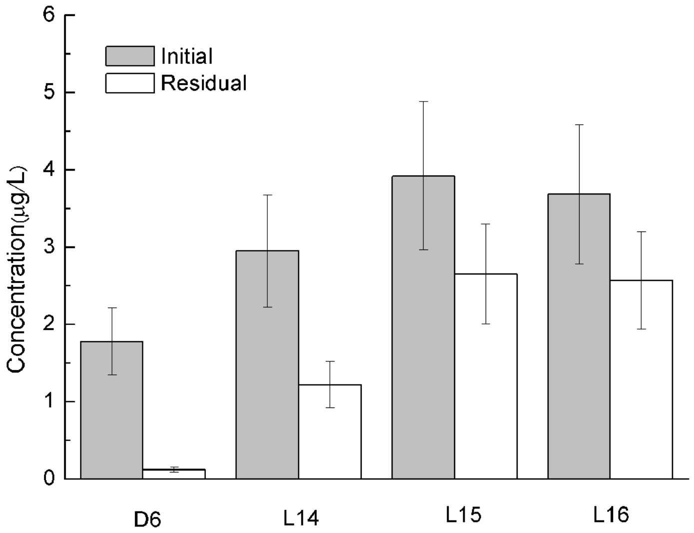

Figure 3. The removal effect of siloxanes after electrochemical oxidation (The number of samples analyzed: 4)

It can be seen from Fig. 3 that the removal efficiencies of target siloxanes were from 30.2% to 93.3% with the current density of 20 mA/cm^2, electrode plate distance of 1.0 cm, electrode plate amounts of 5 pairs and reaction time of 20 min. The removal efficiency of D6 was the highest, while the removal efficiencies of L15 and L16 were plain. The mechanism for siloxanes removal in water is based on direct oxidation and indirect oxidation. Firstly, the siloxanes are broken down to lower molecular weight siloxanes and partially oxidized to silicones and silica (SiO_2). Then, with the increase of electrolysis time, most of the siloxanes were degraded to CO_2 and H_2O [22]. The electrochemical oxidation could be a promising way for further treatment of siloxanes and other POPs in WWTP effluents.

4. CONCLUSIONS

In this study, the concentrations of target cyclic and linear siloxanes were determined in wastewaters from different processing units in a cosmetic WWTP from Beijing. The results showed that D6, L14, L15 and L16 were the predominant siloxanes in wastewater. The detected siloxanes were decreased after the wastewater treated by different processing units in WWTP.

An electrochemical oxidation device, stainless steel plates were used as anode and cathode electrode, was applied to remove siloxanes in WWTP effluents. The major conclusions are summarized as follows:

(1) The removal efficiency of COD was significantly increased with the increasing applied current density when the reaction time was increased from 0 to 20 min.

(2) With reaction time of 20 min, current density of 20 mA/cm^2, electrode plate distance of 1.0 cm and electrode plate amounts of 5 pairs, the removal efficiencies of D6, L14, L15 and L16 were from 30.2% to 93.3%.

The results obtained from this study showed that electrochemical oxidation is an effective method for remediation of siloxanes in effluents of WWTPs.

ACKNOWLEDGEMENTS
We gratefully acknowledge the financial support provided by Beijing Natural Science Foundation Fund (No. 8152025).

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