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Biological treatment of TMAH (tetra-methyl ammonium hydroxide) in a full-scale TFT-LCD wastewater treatment plant

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ABSTRACT

This study evaluated biological treatment of TMAH in a full-scale methanogenic up-flow anaerobic sludge blanket (UASB) followed by an aerobic bioreactor. In general, the UASB was able to perform a satisfactory TMAH degradation efficiency, but the effluent COD of the aerobic bioreactor seemed to increase with an increased TMAH in the influent wastewater. The batch test results confirmed that the UASB sludge under methanogenic conditions would be favored over the aerobic ones for TMAH treatment due to its superb ability of handling high strength of TMAH-containing wastewaters. Based on batch experiments, inhibitory chemicals present in TFT-LCD wastewater like surfactants and sulfate should be avoided to secure a stable methanogenic TMAH degradation. Finally, molecular monitoring of *Methanomethylovorans hollandica* and *Methanosarcina mazei* in the full-scale plant, the dominant methanogens in the UASB responsible for TMAH degradation, may be beneficial for a stable TMAH treatment performance.

1. Introduction

The amount of pollutants produced during manufacturing processes of TFT-LCD (thin-film transistor liquid crystal display) substantially increases due to an increasing production of the opto-electronic industry in Taiwan. Organic solvents used in TFT-LCD manufacturing processes account for more than 33% of the total organic wastes present in wastewater. The main components of these organic solvents are composed of the stripper (dimethyl sulfoxide (DMSO) and monoethanolamine (MEA)), developer (tetra-methyl ammonium hydroxide (TMAH)) and chelating agents. These compounds are recognized as slow-biodegradable organic compounds and very few information is available regarding their biological treatability (Chang et al., 2008; Park et al., 2001). In a previous study (Lei et al., 2010), it was found that MEA can be treated without difficulties under aerobic, anoxic, and anaerobic conditions, while a higher DMSO degradation rate can be achieved under anaerobic condition with the presence of external electron donors.

TMAH, a toxic and corrosive alkaline chemical, is widely used in the semiconductor and opto-electronic industries as developer (Hirano et al., 2001). It is a highly toxic compound and caused a few deaths in Taiwan (Wu et al., 2008). One way to treat this kind of wastewater is oxidation treatment. Hirano et al. (2001) developed a process which combined pyrolysis and catalytic oxidation to treat TMAH wastewater. Although this method avoids the production of noxious compounds like NO_x or NH_3, the cost of this method is still much higher than the biological ones and makes it difficult to be employed in full scale.

The treatment of TMAH-containing wastewaters using activated sludge treatment is usually difficult (Urakami et al., 1990). However, this can be achieved by some methylotroph and some *Paracoccus* spp., *Kluyveromyces delphensis, Bacillus circus, Acinetobacter* sp. (Anthony, 1982; Urakami et al., 1990). According to the proposed pathway for aerobic TMAH degradation, tetra-methyl ammonium ion is first degraded to trimethylamime, and then to dimethylamine, methylamine and finally to ammonia. Formaldehyde is produced in each of the reactions and can be quickly oxidized to carbon dioxide and water under aerobic conditions. In addition to aerobic conditions, methanogenic degradation of TMAH has been reported (Tanaka, 1994). Methanogens are strictly anaerobic archaea capable of producing methane as the end-product during anaerobic conversion of organic compounds (Ferry, 1993). An isolated methanogen has been grown on TMAH and degrade TMAH to methane gas and ammonium (Tanaka, 1994). In a recent study, Chang et al. (2008) successfully enriched

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anaerobic TMAH-degrading sludge under methanogenic conditions using a lab-scale up-flow anaerobic sludge blanket (UASB) fed with TMAH-containing wastewater. Their results indicated that the toxicity effects of TMAH up to 10,000 mg/L on enriched UASB sludge was negligible (Chang et al., 2008). Although anaerobic processes involving diverse microbes for industrial wastewater treatment have been successfully applied in full-scale for decades, their application to TMAH treatment at full-scale has not been evaluated. Furthermore, information for microbial community of methanogenic TMAH treatment processes is also quite limited at this time.

In this study, biological treatment of TMAH in a full-scale methanogenic UASB bioreactor followed by an aerobic bioreactor was evaluated. Batch experiments were conducted to evaluate aerobic and methanogenic TMAH biodegradation kinetics, and possible adverse effects on methnogenic TMAH degradation caused by potential inhibitors present in TFT-LCD wastewater. Finally, microbial community of methanogenic TMAH treatment processes was also evaluated using molecular methods.

2. Methods

2.1. Description of full-scale wastewater treatment bioreactors

The full-scale bioprocess for TMAH-containing wastewater treatment investigated in this study included an UASB bioreactor followed by a conventional activated sludge (CAS) system, as shown in Fig. 1. The influent wastewater of the UASB contained mainly TMAH, some domestic wastewater, and some other chemicals such as surfactants used during TFT-LCD manufacturing. The capacity of the UASB was about 1000 m^3/d and the hydraulic retention time (HRT) was 15 h. The influent and effluent TMAH concentrations of UASB were averaged around 1200 and 100 mg/L, respectively. During this study, the full-scale UASB was able to perform up to 92% of TMAH degradation efficiency and achieve a more than 90% in gas composition for methane. The CAS bioreactor with a total volume of 1000 m^3 treated 1000 m^3/d of wastewater effluent from the UASB. The CAS bioreactor, with an average biomass concentration of 2000 mg VSS/L, was operated at hydraulic retention time (HRT) and solids retention time (SRT) of 1 and 20 days, respectively. The influent COD of the CAS bioreactor varied between 400 and 1000 mg/L, depending on the TMAH removal efficiency of the UASB. Based on determined average TMAH loading of the UASB, two phases were defined in this study. In Phase I, the average influent TMAH was 1528 mg/L, while the average influent TMAH in Phase II was 1144 mg/L.

2.2. Batch experiments for TMAH biodegradation

A series of batch tests were performed in order to study biodegradation of TMAH under aerobic and methanogenic conditions. For aerobic batch tests, sludge was taken from the CAS bioreactor, while for methanogenic batch tests sludge was taken from the UASB. For the aerobic batch experiment, 800 mL of examined mixed-liquor-suspended solids (MLSS) were centrifuged at 10,000*g* for 10 min. The supernatant was discarded, and the solids were resuspended in a 1 L flask containing 800 mL of the nutrient medium with composition same as that previously described (Lei et al., 2010). The initial biomass concentrations in batch experiments were controlled at around 2000 mg/L. During the experiment, the MLSS in the flask was mixed using a magnetic stirrer and aerated for aerobic condition experiment to maintain the DO concentration above 3 mg/L. The pH of the batch reactor was controlled with a pH controller at 7 ± 0.1 by addition of 0.1 MHCl or 0.1 MNaOH. The batch tests were carried out in an incubator maintained at 27 ± 2 °C. Samples were frequently taken throughout the batch experiments for the determination of TMAH.

Methanogenic batch experiments were conducted to evaluate the effects of TMAH concentration and potential inhibitory chemicals present in TFT-LCD wastewater on TMAH degradation activity of the UASB sludge. Batch tests were conducted in 1L serum bottles sealed with a rubber stopper. The total liquid volume was 400 mL. UASB sludge and predetermined concentrations of TMAH (1000 mg/L for inhibitor batch tests) and potential inhibitors such as sulfate, surfactants, and DMSO were mixed using a shaker at 150 rpm and incubated at 35 ± 1 °C. The pH was frequently monitored and maintained at 7.0 ± 0.2 during experiments. Batches without inhibitors were conducted as control experiments, demonstrating TMAH degradation performance of UASB sludge. For each experiment, duplicated batches were conducted and samples were taken frequently for analyses.

2.3. Analytical methods

The composition of biogas in the headspace was analyzed using a gas chromatograph (China GC 8900, Taipei, Taiwan) equipped with a thermal conductivity detector (TCD). A 2 m stainless column packed with Hayesep Q (60/80 mesh) was installed in a 60 °C oven. The operational temperatures of the injection port, the oven, and the detector were all set at 60 °C. Nitrogen was used as the carrier gas at a flow rate of 15 mL/min. The concentration of TMAH was analyzed by an ion chromatography (IC) (Mrklas et al., 2003). The IC used was ICS-1000 (Dionex, California, USA) equipped with a IonPacCG-18 column as the guard and cation analytical column, a CSRS 3002-mm self-regenerated suppressor, and a conductivity detector. A 3 mM of methanesulfonic acid was used as the eluent at a flow rate of 0.25 mL/min. The pH, ORP, COD and volatile suspended solids (VSS) were measured according to standard methods (APHA, 1995).

2.4. Genomic DNA extraction and polymerase chain reaction (PCR) amplification

The UltraClean Soil DNA Isolation kit (Mo Bio Laboratories, Solana Beach, CA) was used to obtain genomic DNA from the batch

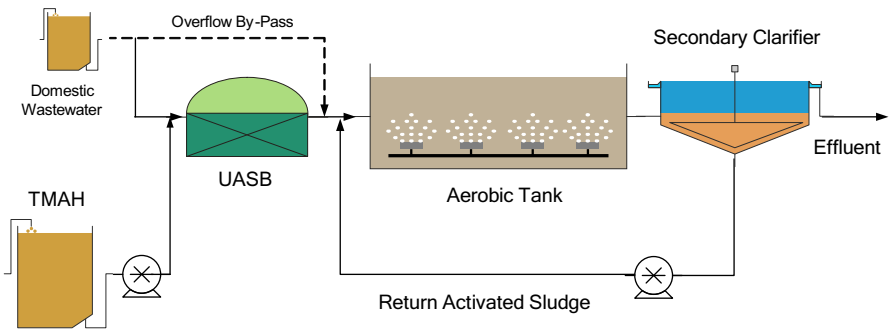

Fig. 1. Schematic of the full-scale bioprocess for TMAH-containing wastewater treatment.