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Biodegradation of tetramethylammonium hydroxide (TMAH) in completely autotrophic nitrogen removal over nitrite (CANON) process

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HIGHLIGHTS

- Biodegradation of TMAH was studied by CANON process in an anoxic upflow bioreactor.
- Effects of TMAH concentration on performance of CANON process were tested.
- A high removal efficiency of nitrogen from wastewater is achieved by CANON process.
- TMAH is almost completely biodegraded in CANON process.
- CANON process is efficient to convert TMAH into nitrogen gas.

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ABSTRACT

This study conducted a completely autotrophic nitrogen removal over nitrite (CANON) process in a continuous anoxic upflow bioreactor to treat synthetic wastewater with TMAH (tetramethylammonium hydroxide) ranging from 200 to 1000 mg/L. The intermediates were analyzed for understanding the metabolic pathway of TMAH biodegradation in CANON process. In addition, ^{15}N-labeled TMAH was used as the substrate in a batch anoxic bioreactor to confirm that TMAH was converted to nitrogen gas in CANON process. The results indicated that TMAH was almost completely biodegraded in CANON system at different influent TMAH concentrations of 200, 500, and 1000 mg/L. The average removal efficiencies of total nitrogen were higher than 90% during the experiments. Trimethylamine (TMA) and methylamine (MA) were found to be the main biodegradation intermediates of TMAH in CANON process. The production of nitrogen gas with ^{15}N-labeled during the batch anaerobic bioreactor indicated that CANON process successfully converted TMAH into nitrogen gas.

1. Introduction

Semiconductor and thin-film transistor liquid crystal display (TFT-LCD) industries are two of the most important parts of the manufacturing sector in Taiwan, which provide over 10% GDP (gross domestic product) for Taiwan's economy in 2014. In general, tetramethylammonium hydroxide (TMAH) is widely used as photographic or photoresist developers in integrated circuit and TFT-LCD manufacturing processes. Then, a large quantity of wastewater containing high concentrations of TMAH as well as ammonium are produced from semiconductor and TFT-LCD industries in Taiwan. TMAH is a bio-toxic and bio-resistant compound, and therefore the TMAH-containing wastewater has to be properly treated before being discharged to the environment (Chen et al., 2003; Chang et al., 2008; Lee et al., 2011; Mori et al., 2015). Because of the stringent environmental regulations for effluent disposal in future, the management of TMAH-containing wastewater has become an important issue in semiconductor and TFT-LCD industries.

Although the industrial wastewater containing high levels of TMAH (above 1000 mg/L) can be efficiently treated by the chemical (advanced oxidation) processes, such as Fenton oxidation and catalytic oxidation, the cost of these chemical process was at least two times that of biological treatment (Hirano et al., 2001; Kim et al., 2002). Ohara et al. (1990) successfully isolated a new species of tetramethylammonium-degrading bacteria from an activated sludge that was used for the treatment of TMAH contained in the wastewater from semiconductor manufacturing processes. Kim et al. (2001) also found that TMAH could be degraded under both aerobic and anaerobic conditions by a newly isolated denitrifying bacterium from the activated sludge. Recently, a lot of biological treatment approaches presenting both an economical and

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environmentally friendly solution for TMAH containing wastewater treatment have been investigated (Chang et al., 2008; Wu et al., 2008; Lei et al., 2010; Hu et al., 2012). The upflow anaerobic sludge blanket (UASB) system was able to remove more than 95% of THAM from the synthetic optoelectronic wastewater but its effluent still contained high concentration of ammonium (Chang et al., 2008). Also stable and high biodegradation efficiencies of TMAH were achieved in the aerobic sequencing batch reactor (SBR) and aerobic membrane bioreactor (MBR) and only nitrification was carried out in these bioreactor (Wu et al., 2008; Lei et al., 2010). A real optoelectronic industrial wastewater with high strength ammonium nitrogen (>3000 mg N/L) was successfully treated by the completely autotrophic nitrogen removal over nitrite (CANON) process in a single anoxic SBR (Daverey et al., 2013). In CANON process, NH_4^+ is first partially oxidized to nitrite by ammonia oxidizing bacteria under controlled oxygen concentration (Eq. (1)). Then the generated nitrite functioned as an electron acceptor oxidizing NH_4^+ to N_2 and NO_3^- by anaerobic ammonium oxidation (anammox) bacteria (Eq. (2)). The stoichiometric equation for CANON process is represented by Eq. (3) (Suzuki et al., 2000).

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+ \quad (1)$$

$$NH_3 + 1.32O_2 + H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2H_2O \quad (2)$$

$$NH_3 + 0.85O_2 \rightarrow 0.11NO_3^- + 0.44N_2 + 1.43H_2O + 0.14H^+ \quad (3)$$

The purposes of this study were to investigate the performance of CANON process operated in a continuous anoxic upflow bioreactor for treating synthetic optoelectronic industrial wastewater containing high concentrations of TMAH (200–1000 mg/L) over a long period of operation. In order to identify biodegradation pathway of TMAH in CANON process, metabolic intermediates were measured during the experiments. In addition, a batch anoxic bioreactor fed with ^{15}N-labeled TMAH was performed to confirm the conversion of TMAH into nitrogen gas in CANON process.

2. Methods

2.1. Reactor set-up and operational conditions

A stirring anoxic upflow reactor, with a working volume of 5 L and a settling zone of 2 L, was operated at ambient temperature and equipped with the probes for online monitoring of pH, oxidation–reduction potential (ORP) and dissolved oxygen (DO), respectively. The schematic diagram of continuous anoxic upflow reactor is shown in Fig. 1. Complete mixing inside the bioreactor was achieved by means of a magnetic mixer. An influent was supplied via the bottom of the reactor using a peristaltic pump with upflow rate of 0.8 mL/min. The whole biodegradation experiment was divided into three phases by influent TMAH concentrations of 200 mg/L (phase I, days 1–403), 500 mg/L (phase II, days 404–445) and 1000 mg/L (phase III, days 446–508), respectively. The reactor was operated with hydraulic retention time of 4.34 days. A separate peristaltic pump was used for effluent withdrawing from the reactor. DO level was maintained below 0.5 mg/L with a DO controller system (Insite IG model 1000CE, LA), which was equipped with DO meter and needle air flow valve. The alkalinity as $CaCO_3$ of effluent was controlled among 1000 and 3000 mg/L by dosing bicarbonate ($NaHCO_3$) in influent. In order to confirm the presence of anammox bacteria as well as ammonia-oxidizing bacteria (AOB), nitrite-oxidizing bacteria (NOB) and denitrifying bacteria, the completely mixed suspended biomass samples on day 442 (in the steady state of phase II) were collected from the reactor for microbial community analysis by the real-time quantitative polymerase chain reaction (real-time PCR). For real-time PCR analysis, specific primer set for total anammox bacteria (*Candidatus Brocadia anammoxidans*, *Candidatus Kuenenia stuttgartiensis* and most of anammox bacteria) was Amx809F/Amx1066R (Tsushima et al., 2007), for AOB was amoA-1F/amoA-2R (Rotthauwe et al., 1997), for NOB were Nitro1198f/Nitro1423r (Knapp and Graham, 2007) and NSR1113f/NSR1264r (Dionisi et al., 2002), for denitrifying bacteria was nirS-1F/nirS-6R (Braker et al., 1998), and for eubacteria was BACT1369F/ProK1492R (Suzuki et al., 2000). The details of the DNA extraction and real-time PCR procedure were described by Daverey et al. (2013) and Huang et al. (2013).

2.2. Seed sludge and feeding media

A 7 L of mixed liquor and total 80 carriers (polyurethane spheres of 3 cm diameter) attached with biomass, collected from the previous lab-scale bioreactor treating a synthetic wastewater, were used as seed for developing CANON process in the anoxic upflow reactor. During the experiment of TMAH biodegradation, the anoxic upflow reactor was re-inoculated with the same seed

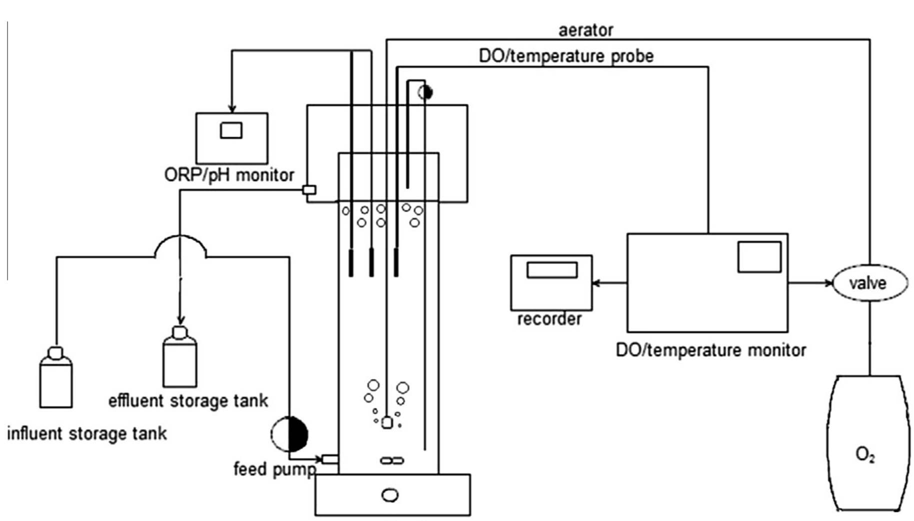

Fig. 1. The schematic diagram of continuous anoxic upflow reactor.