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Kinetic analysis of biological degradation for tetramethylammonium hydroxide (TMAH) in the anaerobic activated sludge system at ambient temperature



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ABSTRACT

With rapid development of thin-film transistor liquid crystal display industries, improvements of the wastewater treatments for spent developing fluid (Tetramethylammonium hydroxide (TMAH)) is essential. As an alternative to the conventional aerobic processes, an anaerobic process in ambient temperature composed of a suspended sludge reactor and subsequent two gravity thickeners with addition of flocculants was elaborated. Methylophilic TMAH-degraders were enriched from an anaerobic digester at a municipal wastewater treatment plant, feeding TMAH as a sole substrate. In the system TMAH was converted to methane via methanol whilst trimethylamine, dimethylamine, monomethylamine and ammonium were sequentially produced with the biomass yield of 0.14 gCOD/gTMAH, maximum specific growth rate at 0.372 d⁻¹ and specific decay rate at 0.017 d⁻¹ under 23 °C. The system could remove TMAH at 0.37–1.2 kgTMAH/m³/d with 2000–6000 mg/L of sludge concentration in the reactor, and achieved low effluent dissolved organics at about 2–5 mgC/L. A kinetic model of TMAH degradation, including cryptic growth of ordinary acidogens, acetotrophic and hydrogenotrophic methanogens from the decayed TMAH-degraders was built, and validated using a quantitative PCR method. Since the calculated fractions of bacterial and archaeal biomass were consistent with those detected, the kinetic model based on the metabolic pathways could be used as a design platform to maximise the target species and reaction rates in the new system.

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1. Introduction

Tetramethylammonium hydroxide (TMAH, [(CH₃)₄N][OH]) is a caustic developing fluid to produce thin-film transistor liquid crystal display (TFT-LCD), and has been widely used in the TFT-LCD manufacturing industries over Asia. As TMAH is a potent toxicant and may cause disorders of nerves and muscles in case of high exposure concentrations, leading to fatal difficulties in breathing, muscular paralysis [13]. Given its potential impacts to the environment, this emerging pollutant in the discharge from the TFT-LCD manufacturing plants has already been legislatively reg-

ulated in Taiwan and Japan. Therefore the wastewater containing several hundred mg/L of TMAH is basically transferred to their own wastewater treatment facilities equipped with biological processes (e.g. activated sludge process) whilst the concentrated fraction at the factories is physicochemically recovered and recycled [10]. Apart from the treatment of the toxicant, due to excessive demands to reduce TFT-LCD production cost, improvements of the wastewater treatment system is also highly desired. From this awareness the anaerobic process was pointed out to outcompete with conventional activated sludge processes, with which could reduce expenses for aeration and waste sludge treatment [10,11]. For treating the medium-strength TMAH wastewater using the anaerobic process, an up-flow anaerobic sludge blanket process (UASB process) was recently demonstrated in a full-scale plant in Taiwan [2,7,8]. The UASB process receiving about 1000 mg/L of TMAH successfully removed the compound by 70–90% at a mesophilic

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condition of 35 °C with corresponding biogas production. However, the UASB process still experienced operation instabilities, in particular the sludge wash-out due to poor granulation of sludge in the reactor.

Another potential drawback of UASB processes is that the substrate removal efficiency is usually inferior to that of the suspended growth system such as activated sludge process, because of the high substrate diffusion resistance in the UASB granules (e.g., the attached growth system) [18,12]. Therefore UASB processes are often required to equip a biological post treatment process, resulting in system complexity and high capital cost. To overcome this problem, applying anaerobic suspended growth process (anaerobic activated sludge process), would be of interest. The process has suspended anaerobic sludge in the reactor where the sludge is thickened at the subsequent gravity settler with a sludge recycle stream to the reactor. As the biomass grows in a suspended form, the high affinity with the substrates may enable to remove the organics in the influent down to the dischargeable level with minimum post treatments. Furthermore the alternative process has opportunities to retrofit the existing activated sludge processes since modification of the plant configuration would not be cumbersome (e.g. only covering the aeration basin to isolate from ambient air, and installing mixers after removing aerators).

When the anaerobic activated sludge process was listed as a possible option for the medium-strength TMAH wastewater treatment, it was noted that the process should be developed to operate under room temperature since heating wastewater was not attractive because of huge wastewater stream produced in the industries. In the context of this background, the study focused on the investigation of biological kinetics for the anaerobic TMAH-degraders at room temperature. Also, as these microorganisms were grown in a mixed culture, a study to catch the microbial community would help to maximise the target biomass and process rates in the system. In fact such integrated approach has not been tackled yet in conventional biological wastewater engineering. The process performance for the anaerobic activated sludge process was evaluated using a continuous lab-scale reactor whilst a mathematical model developed in this study was used to simulate the operational responses and the microbial population in the system.

2. Materials and methods

2.1. Enrichment of TMAH-degraders, and measurements of specific growth and decay rates

Fresh anaerobically digested sludge (8.8 gVSS/L) taken from Hiagari municipal wastewater treatment plant, Kitakyushu, Japan was mixed with TMAH reagent to be 1.0 gTMAH/L (Tama chemicals, Japan), and TMAH-degraders were enriched in a 4-L gas-tight reactor with stirring speed at 200 rpm for 2 months at 23 °C. The methane gas production from the reactor was monitored for the initial 45 days using a volumetric gas meter (Milligascounter, Ritter Apparatebau GmbH, Germany) after removing CO₂ and H₂O in the biogas with caustic pellets inserted between the reactor and the gas meter. Focusing on the exponential growth of volumetric methane production rate, TMAH-degrader's specific growth rate (μ) was estimated according to Eq. (1) (batch test #1) (see also Table 1 in the next section).

$$r_{MPR(t)} \cong \left(\frac{1-Y}{Y} \right) \mu \cdot X_{\text{Biomass}(0)} \cdot e^{(\mu-b)t} \quad (1)$$

where,

$r_{MPR(t)}$: volumetric methane production rate at t (mgCOD/L/d), t : time (d), Y : Biomass yield coefficient (gCOD/gCOD), $X_{\text{Biomass}}^{[0]}$: initial concentration of the biomass (TMAH-degraders) growing in the

batch incubation (mgCOD/L), μ : specific growth rate of the biomass (d^{-1}), b : specific decay rate of the biomass (d^{-1})

After the monitoring, the batch incubation was switched to a fill-and-draw mode and operated for a year where 100 mL of sludge was withdrawn from the reactor at every once or twice per week whilst equal volume of synthetic media was fed to the reactor (TMAH 60 g/L, KH₂PO₄: 80 mg/L, K₂HPO₄: 80 mg/L, NaHCO₃: 872 mg/L, CoCl₂: 1 mg/L, NiCl₂: 1 mg/L, in tap water). Reactor pH was controlled between 7.0 and 8.0 with addition of HCl. When the methane gas production rate exceeded 700 mgCOD/L/d, 400 mL of the enriched sludge was transferred to another gas-tight vessel to measure TMAH-degrader's specific decay rate. Without feeding the substrate to the vessel, the sludge was regularly sampled for 20 days. The sampled sludge was mixed with TMAH reagent to be 710 mgTMAH/L, and maximum methane production rates were then measured with a set of external batch reactors (0.5 L). The maximum methane production rates gradually decreased along with the starvation period, indicating that decay of the TMAH-degraders took place in the vessel. Based on the logarithmic maximum methane production rates against the starvation period, the specific decay rate (b) was calculated according to Eq. (2) (batch test #2) (see also Table 1 in the next section).

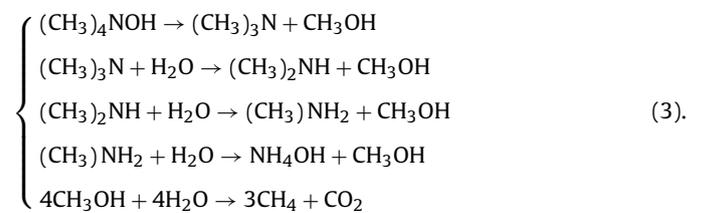
$$r_{MPR(t)} \cong b \cdot (1 - f_U) \cdot X_{\text{Biomass}(0)} \cdot e^{-bt} \quad (2)$$

where,

f_U : production of biologically inert particulates from decay (gCOD/gCOD)

2.2. Development of kinetic model

Using the enriched sludge, the TMAH anaerobic degradation kinetics and stoichiometrics were obtained under a batch condition with addition of TMAH reagent to be 710 mgTMAH/L (batch test #3). According to [19] and following Eq. (3), the TMAH-degraders were assumed to be methylotrophic methanogens, and hence concentrations of trimethylamine (TMA), dimethylamine (DMA), monomethylamine (MMA) and methanol (MeOH) were analysed as the intermediates of the biological TMAH demethylation whilst methane gas production rates were logged simultaneously. Volatile fatty acids (e.g. acetate) were not detected in a preliminary analysis (data not shown).



During the batch test a small portion of the sludge sample was taken at 1.5–3.0 h interval and immediately filtered. The MeOH concentration in the filtrates were analysed with a gas chromatography equipped with flamed ionisation detector (7890A, Agilent Technologies, 3m × 3 mm of glass column, injection port temperature = 240 °C, column temperature = 110 °C and detector temperature = 240 °C, carrier gas = Helium at 12 psi, quantitative detection limit of methanol = 0.1 mg/L). For the analysis the methylamines, anion chromatography was used (ICS-1000, Dionex, CS-10 cation analytical column, eluent = 25 mM-H₂SO₄, quantitative detection limits for each compounds = 0.01 mg/L).

Based on the above datasets (batch tests #1–3), the kinetics and stoichiometrics of each biochemical reactions were calibrated to match the data plots using a process simulator (GPS-X ver. 6.4, Hydromantis, Canada). To simulate the TMAH removal of a continuous lab-scale reactor as described in the next subsection, the

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