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Hybrid Treatment of Tetramethyl Ammonium Hydroxide Occurring from Electronic Materials Industry

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Abstract–TMAH (tetramethyl ammonium hydroxide) originating from etching and photo-developing processes was treated with Fenton oxidation followed by an activated sludge. Additionally, a Microtox test was performed to address any potential toxicity of TMAH against mixed cultures of microorganisms in the activated sludge. The Microtox test revealed that toxicity of TMAH against *Photobacterium phosphoreum* was highly effective showing 5% of EC_{50}, but its toxicity was completely dissipated showing 100% of EC_{50} being recovered after being treated with Fenton reagents. BOD_5 test showed that acclimated cultures to TMAH could readily decompose TMAH in an order of magnitude higher than that of not-acclimated culture. Feasibility tests showed that TMAH was readily biodegraded after being oxidized by the Fenton process, while TMAH fed directly into the activated sludge was laggardly decomposed during longer adaptation period. In the presence of acetic acid, activity of acclimated mixed cultures to TMAH was considerably reduced by dominant presence of predators competitively utilizing acetic acid.

Key words: Fenton Oxidation, Activated Sludge, Tetramethyl Ammonium Hydroxide

INTRODUCTION

TMAH [$(CH_3)_4NOH$] is a chemical which has been used for etching and photo-developing in the electronic materials industry and its application has been recently increased [Merlos et al., 1995; Thong et al., 1997; Sato et al., 1999]. Other than application in electronic materials processing, TMAH has been used for critical analysis of humic substances forming in-situ methylation [Hatcher and Clifford, 1994]. It has also been used for sustaining a certain level of moisture in hydrophobic silicone wafers and for solvent extraction in the Purex process [Uetake et al., 1989; Jeon and Raghavan, 1993]. Its carcinogenic property has not yet been clearly classified by the National Toxicology Program in the USA. However, it has been regulated under the Toxic Substance Control Act since 1976 due to the relatively high toxicity of quaternary ammonium salts. Nonetheless, there have not been any attempts given to properly treat TMAH present in wastewater. In reality, the biological treatment of organic wastewater receiving TMAH would provoke an operational problem due to its potential toxicity against mixed cultures of microorganisms [Qureshi et al., 1980]. Their activities would also be degenerated by mixtures of other rinsed chemical reagents, peroxide and organic/metallic contaminants in the semi-conductor processing industry. It is thus postulated that an advanced oxidation treatment can agreeably treat TMAH so that a biological treatment may successfully be implemented. Fenton oxidation has been generally used to degrade non-biodegradable high molecular organic compounds. Sato et al. reported that polyvinylalcohol was oxidized as high as 60% by the Fenton, which further degraded up to 90% in the activated sludge [Sato et al., 1999]. Bowers revealed that substrate uptake rate in treating 2,4-dichlorophenol was escalated up to 3.47 mg TOC/gVSS·hr, once 2,4-dichlorophenol (DCP) had been degraded by the Fenton [Bowers, 1987]. In addition, its toxicity against microcosm was reduced to one forties. However, low molecular organic acids and alcohols cannot be efficiently decomposed by the Fenton oxidation solely applied [Condren and Etzel, 1966]. Sedlak and Andren found that 1 mole of chlorobenzene was completely oxidized by 5 moles of H_2O_2 at pH 3 [Sedlak and Andren, 1991]. In the absence of oxygen molecules, benzene started to produce a number of daughter compounds, which in turn were progressively oxidized in the presence of oxygen molecules. Most of the organic compounds in the reductive form, generally classified into non-biodegrables, were transformed into biodegradables by the Fenton oxidation. It suggests that the Fenton oxidation can be used as a pretreatment process of TMAH for a biological process following.

Photobacterium phosphoreum has been used for Microtox test as demonstrated by Curtis et al. and Qureshi et al. [Qureshi et al., 1980; Curtis et al., 1980]. It can examine biodegradability of unknown organic compounds flowing into a biological process [Yim, 1990]. *Vibrio fischeri* was also used to observe a degree of fluorescent diminishing in response to a span of exposure against a potential toxic chemical [Algae, growth inhibition test, 1984].

This study was conducted to investigate if TMAH can be biologically degraded in combination with Fenton oxidation, and then to verify toxicity of TMAH against *photobacterium phosphoreum* as a representative microorganism in activated sludge. It was further attempted to treat wastewater containing TMAH in the activated sludge followed by the Fenton oxidation. It was compared to biological degradation of TMAH in an activated sludge process as a control. Finally, we studied the effect of acetic acid, generally present in electronic materials industry wastewater, on degrading TMAH if they were present together in wastewater. It was also tested with

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or without Fenton oxidation.

MATERIALS AND METHODS

1. Chemicals

2.38 w/v% of TMAH (Tokyo Ohka Kogyo) was diluted to a desired concentration for each experiment. Fenton's reagent was prepared in various ratios by using H_2O_2 (Extra pure, Daejung) and $FeSO_4 \cdot 7H_2O$ (Extra pure, Yakuri). H_2SO_4 (Extra pure, Daejung) and NaOH (Extra pure, Duksan) were used to adjust pH in the Fenton oxidation. Anionic polyelectrolyte (i.e. SA-307, Songwon) was used as a flocculent to separate suspended solids originating from the Fenton oxidation.

Biodegradability of TMAH in the presence of organic compound was examined by using CH_3COOH (99% purity, Duksan). In the activated sludge, KH_2PO_4 (>99% purity, Duksan) was solely amended to provide phosphorus at 5 mg/*l*.

2. Fenton Oxidation

1 L of diluted TMAH solution was placed into a 2 L jar. pH was adjusted ranging from 2 to 6 using 1 N H_2SO_4. Fenton reagent was added at a ratio of 0.6 : 1, 0.8 : 1, 1 : 1, 1.2 : 1, 1.4 : 1 for H_2O_2 (30 v/v%) to Fe^{2+} ($FeSO_4 \cdot 7H_2O$, >98%), respectively. The sample was then mixed at 200 rpm and 20 °C for 90 minutes. A sample was taken every 10 minutes. After the Fenton oxidation was completed, pH in the sample was raised to 8 by 1 N NaOH so that iron salts were removed as iron hydroxides. At the same time, 3 mgL^{-1} of anionic polyelectrolytes (SA-307) was mixed at 50 rpm for 20 minutes; thereafter sludge subsequently settled for 30 minutes. TMAH in the supernatant were consequently analyzed by an electro-spray mass spectrometer as a mass detector for high-performance liquid chromatography (Model 440, Waters).

3. Degradation of TMAH Employing Activated Sludge in Combination with Fenton Oxidation

Degradation of TMAH was simultaneously compared between the activated sludge and pre-Fenton oxidation with the activated sludge process. A bench scale of activated sludge was made with Pyrex glass such that the aerator was 5 L and settling tank was 2.5 L. Four pieces of diffuser were built on the bottom of the aerator, thereby filtered air was supplied to sustain 2 mgL^{-1} of dissolved oxygen in the reactor [Lee and Hano, 2001]. The reactor was operated for 1 day of HRT (Hydraulic Retention Time) at 20±0.5 °C. A high alkaline TMAH sample was adjusted to pH 5.5 by adding 1 N H_2SO_4 and then slowly increased to pH 7(±0.5) by adding 0.005 N $NaHCO_3$. Phosphorus concentration in the activated sludge was sustained at 5 mgL^{-1} by supplying 0.2 N KH_2PO_4. A biological inoculum taken from an activated sludge at a municipal wastewater treatment plant was inoculated into the reactor.

4. Toxicity Test

Employing Microtox TestTM [Micro Mutatox Manual, 1993] we performed a toxicity test on bioluminescent bacteria, i.e., *photobacterium phosphoreum*. The test was conducted in the same manner as suggested by OECD [Algae, growth inhibition test, 1984]. The test was conducted on *photo- bacterium phosphoreum*. The bacteria frozen at –20 °C was incubated at 1,000 µl and then 10 µl was diluted into a test tube. Bioluminescent intensity was initially observed for the dilute sample, and after 15 minutes a degree of its diminished intensity was measured. A control was also simultaneously observed. Bioluminescent loss was calculated in Eq. (1).

$$\text{Bioluminescent loss } (\%\,\Delta) = \{(I_o - I_t)/I_o\} \times 100 \quad (1)$$

where I_o is initial bioluminescent intensity, I_t is a bioluminescent intensity observed after 15 minutes.

The ratio of bioluminescent loss was estimated as given in Eq. (2).

$$\text{Ratio of bioluminescent loss } (\gamma) = \%\,\Delta/(100 - \%\,\Delta) \quad (2)$$

Effective concentration (EC_{50}, %) was obtained as γ being 1, which consequently corresponds to 50% of bioluminescent loss (% Δ) for 15 minutes since bacteria was exposed to toxic compounds. Water quality parameters such as pH, dissolved oxygen, BOD_5, alkalinity and NH_4^+-N were observed as given in Standard Methods [APHA, 1994].

RESULTS AND DISCUSSION

1. Optimal Fenton Oxidation of TMAH

Optimal condition for effectively decomposing TMAH was obtained with regard to each varying pH, dosage of Fenton reagent, ratio of Fenton reagent (Fe^{2+} to H_2O_2) and reaction time, respectively. For this purpose, the concentrations of BOD_5 and residual H_2O_2 have been observed since each parameter was varied. Determining optimal pH, 1,000 mgL^{-1} of TMAH was mixed with 1,000 mgL^{-1} of Fe^{2+} to 1,000 mgL^{-1} of H_2O_2 at 200 rpm for 1 hr while pH was varied from 2 to 6. Fig. 1A shows that the lowest level of residual H_2O_2 was observed at pH 3 with the highest BOD_5 value. pH 3 was then preferably selected to maximally decompose the given concentration of TMAH.

To determine optimal dosage of Fenton reagent, 1 : 1 for Fe^{2+} : H_2O_2 was each prepared between 200 and 1,000 mg/*l*, which was each mixed at 200 rpm for 1 hr with 1,000 mg/*l* of TMAH at pH 3. Fig. 1B shows that the optimal dosage of the reagent was found at 400 mgL^{-1} such that BOD_5 was at the highest value observed for the lowest extent of residual H_2O_2.

In the following, optimal reaction time for Fenton oxidation was assessed as 1,000 mgL^{-1} of TMAH at pH 3 was mixed at 200 rpm with 400 mgL^{-1} of Fe^{2+} and 400 mgL^{-1} of H_2O_2. The sample was obtained at every 10 min. As shown in Fig. 1C, H_2O_2 was completely consumed for the first 30 min. BOD_5 showed that TMAH completely transformed into biodegradables after 70 min. Consequently, it suggested that the Fenton reaction should be satisfactorily accomplished after 70 min.

The ratio of Fenton reagent is also one of important parameters efficiently performing the Fenton oxidation. The ratio of Fe^{2+} : H_2O_2 was varyingly investigated at 200 rpm for 70 min with 1,000 mgL^{-1} of TMAH at pH 3.0. The concentration of Fe^{2+} was varied ranging from 300 to 700 mgL^{-1} over 500 mgL^{-1} of H_2O_2. As shown in Fig, 1D, residual concentration of H_2O_2 decreased as the ratio of the reagent increased. Concentration of BOD_5 culminated at the ratio of 3 : 1. Consequently, the ratio of 3 : 1 was obtained as an optimal ratio of Fenton reaction efficiently implemented.

2. Toxicity Test

EC_{50} was comparatively obtained for 300 and 700 mgL^{-1} of TMAH, respectively, after they were oxidized by the Fenton reagent at the ratio of 3 : 1 for Fe^{2+} : H_2O_2; thus Fe^{2+} concentration ranged

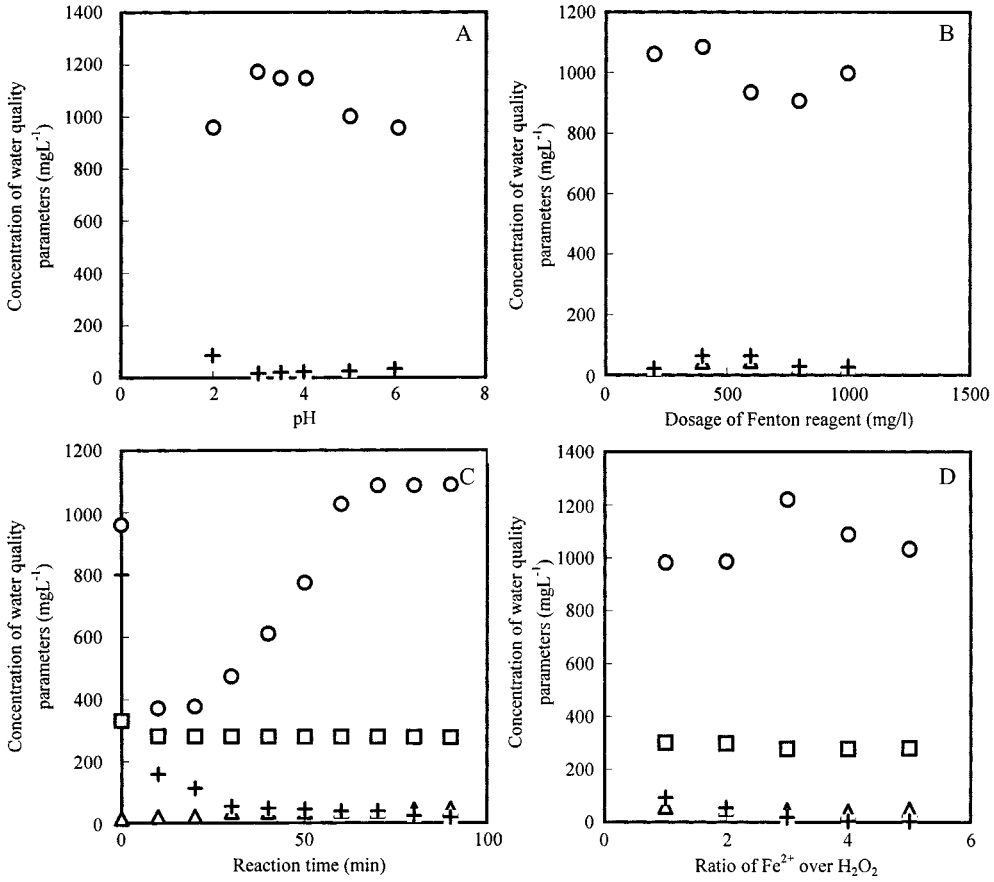

Fig. 1. Effects of parameters on Fenton oxidation of 1,000 mg/*l* of TMAH: A. pH 2 to 6 at 1,000 mg/*l* H_2O_2; B. Dosage of the Fenton reagent (1 : 1 Fe^{2+} : H_2O_2=200 to 1,000 mg/*l*); C. Reaction time (1 : 1 Fe^{2+} : H_2O_2 at 400 mg/*l* for 90 min); D. Ratio of Fenton reagent as varying concentration Fe^{2+} (300 to 700 mg/*l*) over 500 mg/*l* of H_2O_2; O BOD_5; + Residual H_2O_2.

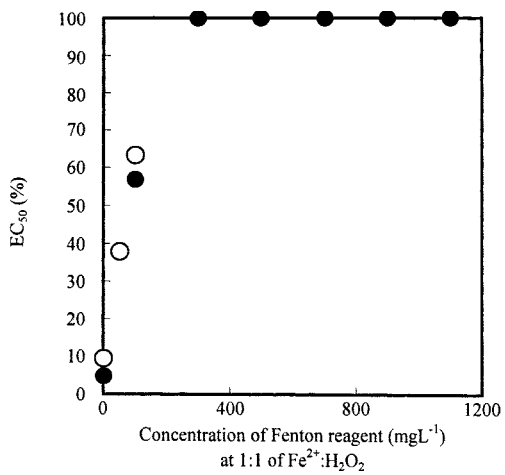

Fig. 2. EC 50 (%) according to varying concentrations of Fenton reagent addition at 1 : 1 of Fe^{2+} : H_2O_2; ○ 300 mg/*l* TMAH; ● 700 mg/*l* TMAH.

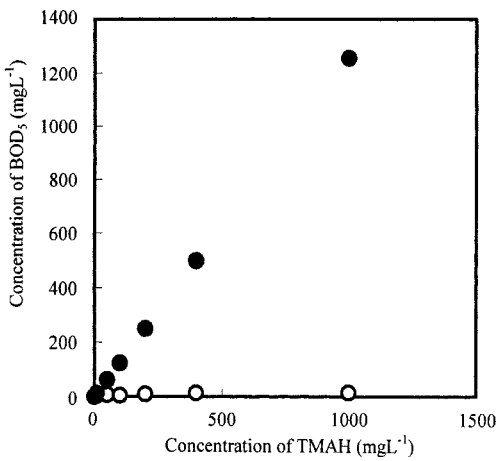

Fig. 3. Comparison of BOD_5 observed between unacclimated and acclimated inocula: ○ unacclimated BOD_5; ● acclimated BOD_5.

from 50 to 1,100 mgL^{-1}. As shown in Fig, 2, EC_{50} was extremely low at 10% and 5% for 300 and 700 mgL^{-1} of TMAH, respectively, for the Fenton oxidation not employed. However, it started to recover up to 100% after the Fenton reagent was introduced at 300 mgL^{-1} of Fe^{2+}. Fenton oxidation may help in reducing the degree of toxic influence on microorganisms in the activated sludge.

BOD_5 for TMAH ranging from 10 to 1,000 mgL^{-1} was comparatively observed to address its toxicity against two kinds of inocula, i.e., acclimated and not-acclimated. As shown in Fig. 3, concentrations of TMAH in acclimated culture were readily convertible to BOD_5. It showed a much higher correlation factor of 0.99 compared to 0.79 obtained from BOD_5 for not-acclimated inocula.

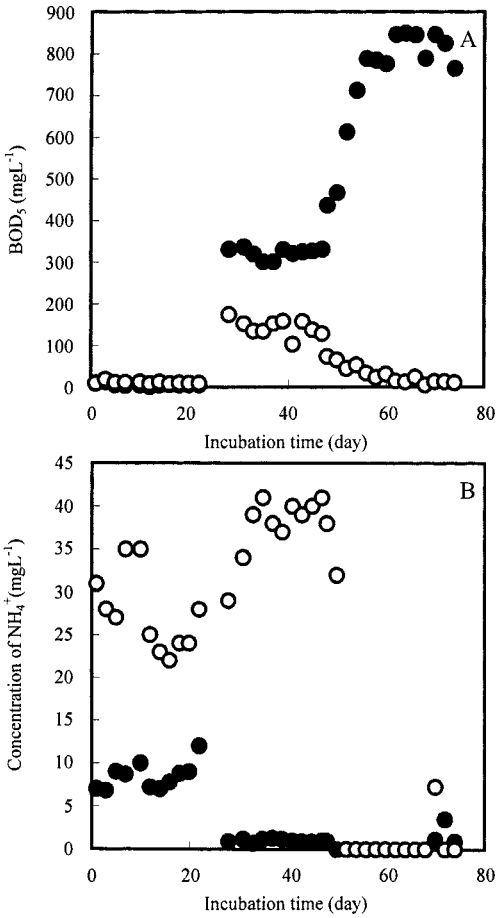

Fig. 4. Biological degradation of TMAH in activated sludge for consecutively increasing the concentration of TMAH from 300 (at start) to 500 (at 28 day) and finally to 700 mg/*l* (at 48 day): A. BOD_5; B. NH_4^+; ● Influent concentration; ○ Effluent concentration.

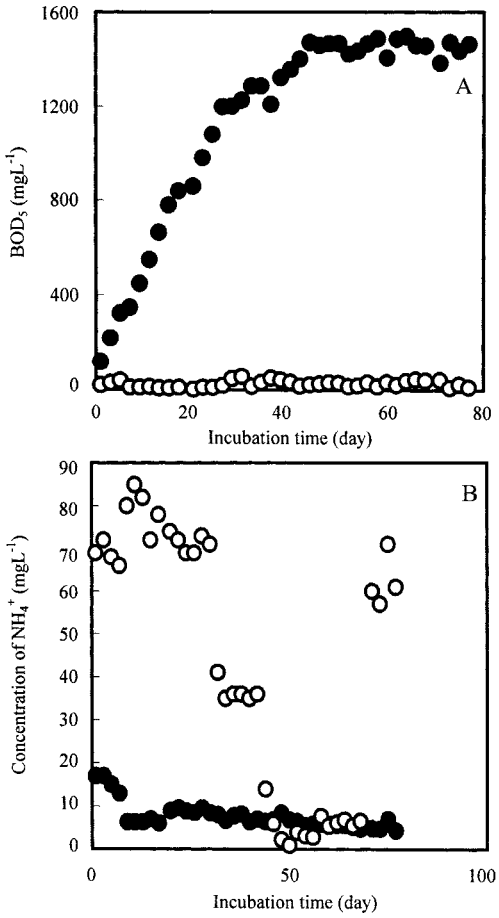

Fig. 5. Biological degradation of TMAH in activated sludge after the Fenton oxidation implemented by 3 : 1 of Fe^{2+} : H_2O_2 at 1,000 mg/*l* of Fe^{2+}: A. BOD_5; B. NH_4^+; ● Influent concentration; ○ Effluent concentration.

This indicates that TMAH can be readily degraded in the activated sludge process once microcosm has acclimated to TMAH.

3. Activated Sludge

At first, 300 mgL^{-1} of TMAH was acclimated for 7 days and then continued to incubate for 22 days (Fig. 4A-B). Fig. 4A illustrates that there was found no significant reduction on BOD_5 for the first 22 days while ammonification increased (Fig. 4B). After 22 days of incubation, TMAH concentration increased up to 500 mg/*l*. BOD_5 was unvaryingly removed up to 68%, while nitrification was initiated at 47 days (Fig. 4B). Finally, TMAH concentration increased to 700 mg/*l* at 48 days of incubation.

As shown in Fig. 4A, the level of BOD_5 had increased to approximately 800 mgL^{-1} at 58 days since it was initially observed at 400 mgL^{-1} for 48 days. It was continued to be escalated up to 870 mg/*l*, which indicates that microorganisms were still being processed into acclimation. Acclimation was eventually completed at 61 days of incubation. At that time, BOD_5 was removed as high as 98%. Nitrification had been initially occurring at 47 days of incubation; thereafter the concentration of NH_4^+-N was negligibly observed at 53 days of incubation.

4. Activated Sludge Accommodating Fenton Oxidation

Activated sludge experiment was conducted in the same manner as previously performed. As shown in Fig. 5A, there was no retardation found for activated sludge. Nevertheless, BOD_5 in the influent had increased until the 42th day of incubation. It simply means that it still takes a specific duration for microorganisms to completely acclimate oxidized products of TMAH even though no adaptation period is necessarily required. Fig. 5B shows that nitrification was hitherto started from 30 days of incubation as 70 to 90 mgL^{-1} of NH_4^+-N decreased to less than 40 mg/*l* of NH_4^+-N. Subsequently, at 45 days of incubation, the concentration of NH_4^+-N was reduced down to as low as 10 mgL^{-1}.

In general, the wastewater originating from the semi-conductor industry includes acetic acid solution other than TMAH. In this regard, the influence of acetic acid on decomposition of TMAH was tested. 500 mgL^{-1} of acetic acid was added in the activated sludge in the presence of 500 mg/*l* of TMAH. It was also tested after Fenton oxidation had been implemented. The Fenton oxidation was performed at pH 3.0 for 70 min with 3 : 1 ratio of Fe^{2+} : H_2O_2 for 500 mgL^{-1} of Fe^{2+}. Fig. 6A shows that BOD_5 was efficiently removed as high as 97%, but, from 40 days of incubation, BOD_5 in effluent steeply increased due to the occurrence of filamentous bacteria such as *Microthrix*, *Nocardia*, *Glaucoma* and *Uronema*. In the meantime, the concentration of NH_4^+ in effluent gradually increased for the duration of the test (Fig. 6B). It simply means that acetic

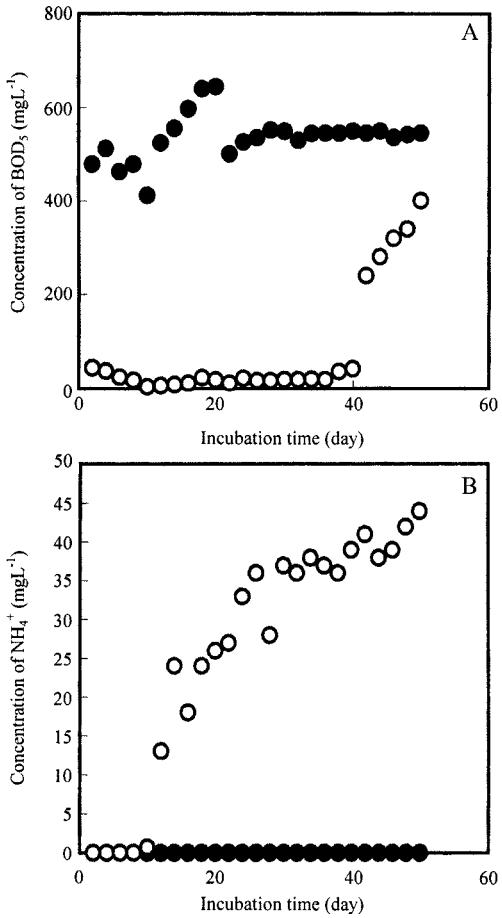

Fig. 6. Effects of coincident presence of 500 mg/*l* of acetic acid on biological degradation of 500 mg/*l* of TMAH in activated sludge: A. BOD_5; B. NH_4^+; ● Influent concentration; ○ Effluent concentration.

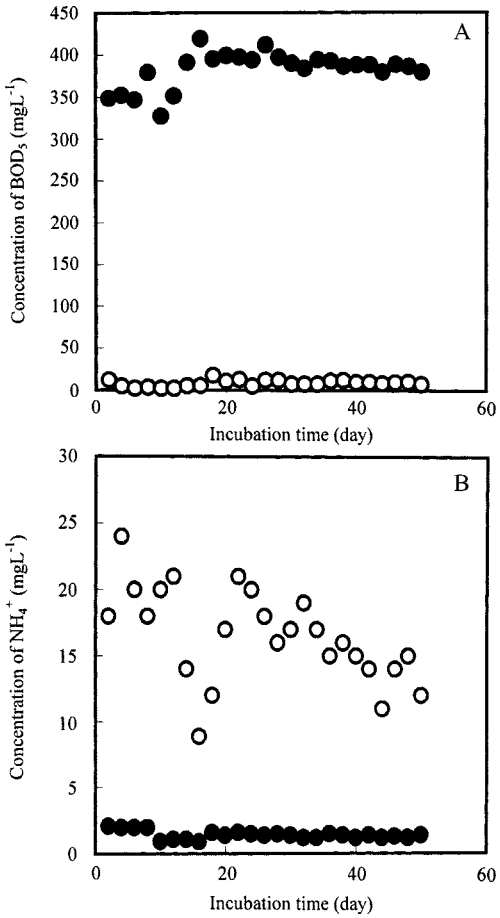

Fig. 7. Effects of coincident presence of 500 mg/*l* of acetic acid on biological degradation of 500 mg/*l* of TMAH after the Fenton oxidation implemented at 1 : 1 of Fe^{2+} : H_2O_2 at 500 mg/*l*: A. BOD_5; B. NH_4^+; ● Influent concentration; ○ Effluent concentration.

acid in the presence of TMAH could competitively be degraded by microcosms. It also suppressed the degree of nitrification. However, after Fenton oxidation was implemented, less than 2 mg/*l* BOD_5 in effluent was observed for the whole test duration as shown in Fig. 7.

Generally, the types of microorganisms observed in the activated sludge followed by Fenton oxidation were different from activated sludge solely applied without the Fenton oxidation. *Aoelosoma hemprechi*, *Aspidisca*, *Lepadella* and *Vorticella* were predominantly observed in the activated sludge combined with the Fenton oxidation. In the meantime, NH_4^+ had declined to 12 mg/*l* since it was initially observed at 24 mg/*l*. It simply indicates that nitrification had been accomplished up to 50%.

CONCLUSIONS

EC_{50} showed that microorganisms could cope with the oxidized products originating from the Fenton oxidation of TMAH. It is unlikely that they were vulnerably inactivated by contacting with concentrations of TMAH untreated by the Fenton oxidation.

The sole application of activated sludge could degrade TMAH efficiently, but it needed to have more time to acclimate, whereas the activated sludge receiving the Fenton oxidized compounds can shorten the adaptation period. In other words, the products originating from the Fenton reaction immediately started to decompose without observable adaptation span. Nitrification was retardedly occurring from degradation of TMAH at 47 days of incubation in activated sludge solely implemented, but it was more shortened to 30 days of incubation after Fenton oxidation was initiated.

It was also suggested that Fenton oxidation be previously implemented to decompose TMAH in the presence of acetic acid. Otherwise, degradation of TMAH and nitrification were deteriorated even though acetic acid can be readily biodegraded.

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