Kinetic Study of Aerobic Degradation of Tetramethylammonium Hydroxide (Tmah) Waste Produced in Electronic Industries

Ida DE MICHELIS*, Alessia DI RENZO, Matteo SARULLO and Francesco VEGLIO’

DIIIE- University of L’Aquila, Via Giovanni Gronchi 18 - Zona industriale di Pile, 67100 L’Aquila, Italy

*Corresponding author

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Abstract. Tetramethylammonium hydroxide is used in the electronic industry during the photolithography process to produce memories. The effluent produced in this process must be treated before discharging due to its toxicity. The aim of this research is to evaluate the feasibility of biological treatment to remove this molecule from the effluent by aerobic process at room. Experiments were carried out on real effluent, in which TMAH concentration was about 1800 mg/L. Like C-source for microorganisms another effluent coming from the same industries was used. Batch reactor tests have showed an efficiency of TMAH removal of about 99%. Kinetic studies have provided the following kinetic parameters able to describe the trends vs time of TMAH, ammonium ions and biomass concentration in the reactor: $K_S = 0.8 \text{ g/L}; \mu_{\text{max}} = 0.42 \text{ h}^{-1}; Y_{X/S} = 0.34 \text{ g}_{S}/\text{g}_{X}$.

Introduction

Tetramethylammonium hydroxide (TMAH) is a quaternary ammonium salt widely used in semiconductor industry. TMAH toxicity for human beings and environment was demonstrated [1, 2] and for this reason it is necessary to treat it before discharging. Many processes have been studied. The degradation of TMAH through biological way was proven by different authors. Another research has demonstrated the possibility to treat wastewater containing also TMAH in anaerobic and aerobic conditions [3]. Asakawa [4] obtained methane and other products feeding bacteria with TMAH as unique substrate. The anaerobic study was also performed in a UASB reactor (TMAH degradation yield 95%) [5]. Researchers have applied ANAMOX process to treat effluent that contains TMAH, they found a nitrogen removal yield of about 90% [6]. Also adsorption process was studied. Research work reports results about the use of different kinds of activated carbons, the authors have obtained a maximum sorption capacity of 27.7mg/g [7]. Kelleher [8] have found an equilibrium concentration on solid phase of 270mg/g on mesoporous silicate material, whereas other researchers have studied strongly and weakly acidic cation exchange resin to remove this molecule [9, 10]. Also TMAH chemical oxidation was studied [11].

In the present study, biological treatment of wastewater containing TMAH and photoresist, provided by an electronic plant located in Italy, was investigated. Main goal of the research is to check the efficiency of aerobic degradation to treat this kind of wastewater by the measurement of the reduction of concentration of this molecule. Moreover the collected data was used to evaluate kinetics parameters useful to build a model able to describe the biological system.

Materials and Methods

Wastewater Characterization

Wastewater, contains TMAH, comes from Photo Area of an electronic industry, located in Italy. The average characteristics of wastewater are set out in Table 1. A second effluent, called photoresist (PR), coming from the same electronic plant contains mainly 1-Methoxy-2-Propanol. Besides was used as C-source.
Table 1. Average characteristics of wastewater used as feed for pilot plant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.30</td>
</tr>
<tr>
<td>TMAH concentration</td>
<td>1800 mg/l</td>
</tr>
<tr>
<td>TOC</td>
<td>1800 mg/l</td>
</tr>
<tr>
<td>Turbidity</td>
<td>0.09 FAU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>4800 µS</td>
</tr>
</tbody>
</table>

**Biological Tests**

Biological tests was carried out in a bioreactor BIOSTAT® B (Fig. 1) in batch condition. This equipment present a control unit for setting parameters; steel impeller; double glass cylindrical and a capacity of 6.6 L. Table 2 reports the operating condition adopted during the tests.

Table 2. Operation parameters for the biological tests.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity</td>
<td>70 rpm</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5/L/min for the first test and 2 L/min for the next test</td>
</tr>
</tbody>
</table>

Figure 1. Bioreactor BIOSTAT® B.

From literature analysis results that the optimal C/N ratio for the survival of the microorganisms is equal to 20/1, in TMAH molecule this ratio is only 3.43. To increase this value it will be necessary to add a carbon source, so, for this purpose, biological tests was carried out by the addition of photoresist (PR), another wastewater produced by the same company with high content of carbon. The amount of each effluent was calculated by solving the following system.

\[
\begin{align*}
V_1 + V_2 &= V_{TOT} \\
\frac{c_1 \cdot V_1 + c_2 \cdot V_2}{c_{N-TMAH} \cdot V_1} &= \frac{20}{1}
\end{align*}
\]

Where: \( c_1 \) = carbon mass concentration in TMAH: 1056 [g/L]; \( c_2 \) = carbon mass concentration in the photoresist: 615 [g/L]; \( c_{N-TMAH} \) = nitrogen mass concentration in TMAH: 0308 [g/L]; \( V_1 \) = volume of TMAH wastewater; \( V_2 \) = volume of pr wastewater; \( V_{TOT} \) = total volume of wastewater treated in the reactor.

Total volume of wastewaters treated was 1.5L (1488mL of TMAH wastewater + 12mL of PR wastewater), to which was added the same volume of micronutrient solution called growth medium (table 3 reports its composition).
### Table 3. Additional growth medium composition [g/L].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl₂</td>
<td>0.13</td>
</tr>
<tr>
<td>Na₂MoO₄</td>
<td>0.23</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.82</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.21</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0.51</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Six sequential batch cycles were performed and for each batch a make-up of TMAH and PR wastewaters was carried out (1488mL of TMAH wastewater + 12mL of PR wastewater).

PH was adjusted to the optimal value (about 7) by the addition of H₂SO₄ (96%) or NaOH (35%) solutions.

Every day a sample was collected and analyzed to determine: COD (HACH-Lange kit: LCK 514), pH (HI254 pH-meter), TMAH (Ion Chromatograph Donex DX5000) and ammonium ions (HACH-Lange kit: LCK 302) concentrations. Samples volume was refilled by growth medium addition.

**Results and Discussion**

The following figures show results obtained for each parameter measured in the six batch cycles.

It is possible to observe that:

- pH values change during each cycle, but are still close to the optimum value 7, it means that the system is able to buffer the production of acids and bases connected to the biological process that occurs in the reactor;
- COD decrease in the time, this means that degradation process occurs in the reactor;
- NH₄⁺ concentration during the time increase, this is an indication of ammonium compounds degradation;
- TMAH concentration trend show an initial decrement followed by an increment and subsequent decrement. By comparison with the evolution of ammonium ion, one would expect a downward trend, it is possible to hypothesize that at the beginning TMAH is adsorbed on the biomass and after gradually released in the bulk where it is degraded until to reach concentration values close to zero.

Figure 3 shows the yields of TMA⁺ degradation and NH₄⁺ formation for each batch to confirm that ammonium is a product of the degradation of TMAH molecules.

Figure 4 shows the stoichiometry of biomass growth when TMAH is the substrate.

\[
C_4H_{12}N + 4 \ C_4H_{10}O_2 + 26,413 \ O_2 \rightarrow 1,75 \ C_4H_{17}O_{0.45}N_{0.20} + 18,25 \ CO_2 + 0.65 \ NH_3 + 26,413 \ H_2O
\]  

(3)
The equations (4), (5) and (6) describes batch system.

\[ \frac{dX}{dt} = (\mu - D) \cdot X \]  \hspace{1cm} (4)

\[ \frac{dS}{dt} = (S_0 - S) \cdot D - \sigma \cdot X \]  \hspace{1cm} (5)

\[ \frac{dP}{dt} = (P_0 - P) \cdot D + \pi \cdot X \]  \hspace{1cm} (6)

Where:

\[ \mu = \frac{\mu_{\text{max}} \cdot S}{K_s + S} \]  \hspace{1cm} (7)
\[ \sigma = \frac{1}{Y_{X/S}} \cdot \mu + m \]  
\[ \pi = \alpha \cdot \mu + \beta \]  

Figure 5. Model and experimental trends: TMAH (a); Ammonium ions (b) and biomass (c).

Variable \( D \), in previous equations, is the dilution rate and it is the inverse of the residence time, whereas \( S_0 \) (0.992 g/L), \( X_0 \) (0 g/L) and \( P_0 \) (0.006 g/L) are the inlet concentrations of TMAH, biomass and ammonium ions, respectively.

Equations (4-9) represent a differential system of 6 equations in 6 unknowns which can be solved by the Runge-Kutta methods. System resolution provides the following kinetic parameters:

\( K_S = 0.8 \) g/L;
μ_{max} = 0.42 \text{ h}^{-1} \\
Y_{XS} = 0.34 \text{ gS/gX}

The following figures (Figure 5-a and b) show that the model (solid line) describes enough the experimental data trend of batches 1-4.

Summary

Lab-scale biological tests, on effluent contains TMAH molecules and coming from an electronic industry, were carried out to evaluate the potential use of an aerobic process to treat this kind of waste. The experiments on wastewater, with a TMAH content of about 1800 mg/L, have showed that biological treatment is able to remove TMAH with and efficiency greater than 99%, as TMAH removal yield, after about 6 days of process, this means the microorganism population present in the sludge is able to adapt its metabolism and use TMAH like substrate. Moreover, PR effluent can be used like a C source for the microorganism, in other words also this effluent can be treated by biological process. Kinetic model could simulate the process response, by this model it is possible to find also the trend of biomass in the reactor.

Acknowledgement

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References