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Aerobic Treatment of Waste Process Solutions from the Semiconductor Industry: From Lab to Pilot Scale

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Abstract: Tetramethylammonium hydroxide (*TMAH*) is widely used as a solvent in the semiconductor industry. After the photo-impression process, it is necessary to remove the photoresist (PR) layer from the surface of the circuits; for this purpose, a *TMAH* solution is usually used. This chemical compound is highly toxic and corrosive and cannot be discharged into the environment. This study was carried out in collaboration with LFoundry (SMIC group), in order to prove the feasibility of biodegradation under aerobic conditions, using microorganisms coming from the LFoundry's wastewater treatment plant (WWTP) at different operating conditions. The feed composition was modified in order to add a small but increasing amount of *TMAH* and PR. The aim was to verify if the increase of *TMAH* concentration was harmful to bacteria. The feed stream, containing *TMAH* and PR, was the only carbon source for the metabolism of the aerobic microorganisms. The results of this study demonstrated an effective biological degradation of *TMAH* and showed a total removal efficiency of more than 99.3%, with a final concentration of 7 mg/L. Moreover, the kinetic parameters of the Monod model were also calculated. The results obtained from the experimental campaign were used to design a pilot plant that will treat around 25 L/h of waste *TMAH*/PR solution.

Keywords: tetramethylammonium hydroxide; *TMAH*; anaerobic digestion; photoresist; wastewater

1. Introduction

In several production processes, special chemical compounds are often used; such chemicals cannot be easily replaced with other ones, as no substances with similar physicochemical properties are available so far. This is the case of *TMAH*, which is a quaternary ammonium salt extensively used in the semiconductor industry.

The problem lies in the high toxicity for the biota, as demonstrated by various studies [1,2]. The exposure to *TMAH* causes harmful effects on human health, whether ingested or inhaled: being very corrosive is harmful to both the mucous membranes and the skin in general. If *TMAH* is ingested, it causes burns and ulcers [3]. The acute *Daphnia similis* toxicity test demonstrated that the 48-h lethal concentration 50 (LC50) of *TMAH* is only 0.75 mg/L. The acute toxicity of N-NH_4^+ to *Daphnia similis* varied with the pH of the collected wastewater: the 48h LC50 values were found to vary in the range of 18.5–155 mg/L from pH 7.0 to pH 6.5 [2].

Mori et al. [4] also studied the *TMAH* effects on the aquatic environmental: the tests were carried out on seaweed and freshwater fish, in particular, the microalga *Pseudokirchneriella subcapitata*, the bacterium *Vibrio fischeri*, the fresh fish *Oryziaslatipes* (or rice fish) and the microcrustacean *Daphnia magna*. The results highlighted a strong impact on the development of these organisms because of *TMAH* in high concentration. The damage varies depending on the exposure level and can also lead to the death of the organisms; for this reason, it is necessary to treat it before discharging.

Adsorption is an effective technique that can be used to remove the *TMAH* molecule. In particular, graphene oxide (GO) was tested in the adsorption of *TMAH* in different operating conditions; it was demonstrated that the adsorption capacity is around double to that of granular (GAC) and powdered (PAC) activated carbon [5] as well as zeolite Na-Y [6].

The adsorption of *TMAH* was also tested with ion-exchange resins like Amberlite IR-120 and Dowex HCR-W2 [7]. The adsorption with different kinds of activated carbon was also studied by Prahas et al. [8]; other studies were performed to evaluate mesoporous silicate materials or strongly and weakly acidic cation exchange resins, as well as electrodialysis in the removal of such a molecule [9–11].

Catalytic oxidation is another interesting technique investigated in the past for the removal of *TMAH*. Suitable catalysts, usually based on active metals like Pd-V_2O_5-WO_3or Pt supported on titania-silica or alumina, were used [12]. Catalytic oxidation involves the catalyzed reaction of *TMAH* to TMA^+ and the further decomposition of TMA^+ to nitrogen, water, and carbon dioxide [13].

Membrane distillation is another effective treatment for the removal of *TMAH* and the recovery of process water in the nano-electronics industry [14].

Different authors have studied the biological degradation of *TMAH*, both in anaerobic and aerobic conditions, but the biological treatment of such waste solutions is still difficult in standard activated sludge plant [15].

Few studies investigated the treatment of waste solutions containing *TMAH* by biological processes in up-flow anaerobic sludge blanket (UASB) reactors with *Methanosarcina* and *Methanomethylovorans* bacteria: removal yields of around 90% were achieved, together with 90% of methane production [15,16]. Lei et al. [15] showed that effective removal is carried out under aerobic conditions in sequencing batch reactors (SBR). Hence, the anaerobic methanogenic degradation of *TMAH* was fully demonstrated in a batch operating mode with a 1000 mg/L synthetic solution, where the appropriate substrate composition was added. The specific *TMAH* degradation rate and the half-saturation constant of the enriched methanogens were 39.5 mg *TMAH*/gVSS·h and 820 mg/L, according to the Monod kinetics for *TMAH* degradation. The concentration of sulphides higher than 20 mg/L showed a heavy inhibition and slowed down the specific *TMAH* degradation rate of *Methanomethylovorans* and *Methanosarcina* [17].

An interesting study was carried out by means of real wastewater from a full-scale methanogenic UASB reactor that treats the sewage from the manufacturing of thin-film transistor liquid crystal displays (TFT-LCD). The batch trials demonstrated that *Methanomethylovorans hollandica* and *Methanosarcina mazei* are the dominant methanogens in the UASB responsible for *TMAH* degradation. In anaerobic conditions, the UASB sludge achieved a specific degradation rate of 9.5 mg *TMAH*/gVSS·h, even when the original concentration of *TMAH* was 1500 mg/L [18]. Aerobic batch trials were also investigated, and the results showed a maximum specific degradation of 8.8 mg *TMAH*/gVSS·h with an initial *TMAH* of 145 mg/L, but inhibition occurred when the *TMAH* concentrations reached 150 mg/L [18].

Anaerobic conditions were also tested by Liu et al. [19]. The anaerobic treatment of waste solution containing 340 mg/L of *TMAH* at room temperature was conducted in lab-scale experiments, where the methane conversion yield of *TMAH* reached nearly 90%.

Autotrophic nitrogen removal over nitrite in a continuous anoxic up-flow bioreactor was investigated by Chen et al. [20]. Such a process was used to treat synthetic wastewater containing *TMAH* in a concentration range of 200–1000 mg/L. The nitrogen average removal yield was always greater than 90% in all the trials, with a peak of 98% after a retention time of around 4.3 days. Trimethylamine and methylamine were the main biodegradation intermediates detected in the solution.

Great attention is paid to waste solutions from the semiconductor industry in those countries where many factories are located, in particular, China, Taiwan, South Korea, and Japan. This is demonstrated by the high percentage of scientific papers dealing with such a topic that comes from the aforementioned countries. Instead, Europe and the USA seem not to be aware of this problem, and this has resulted in a lack of research. The present study assesses the biological treatment in a laboratory-scale aerobic reactor of a liquid waste stream containing tetramethylammonium hydroxide (*TMAH*)/photoresist blend. The results were then used to design a pilot-scale plant with a capacity

of 25 L/h in continuous operation mode. The goal of the paper was to minimize the concentration of *TMAH* in the treated sewage released into the environment, considering the toxicological aspects and looking for the best biological technique; in particular, the objective was focused on the efficiency of the aerobic degradation as a function of the feed composition, optimized for such purpose. The novelty of the present research lies in the aerobic degradation of *TMAH* in high concentration (around 1800 mg/L) with specialized microorganism strains, using a second waste stream as a carbon source.

2. Materials and Methods

2.1. Feed Composition

The wastewater (R1), provided by the company that manufactures semiconductors (LFoundry, Avezzano, Italy), contains 1600–2000 mg/L of *TMAH*, and the relevant pH is usually in the range of 12–13. The European Waste Code (EWC) of such a solution is 11 01 12. The *TMAH* solution was neutralized by 5 mol/L H_2SO_4 solution to pH 7, that is a value suitable for the microbial growth.

For a correct and optimal bacterial growth, the following two streams were added to the *TMAH* waste solution:

- a photoresist solution (R2), EWC 14 06 03. This solution is an additional waste stream produced by the manufacturing processes of LFoundry: it is a mixture of organic substances, mainly 1-methoxy-2-propanol, with a total organic carbon (TOC) concentration of around 615 g/L. It was added as a source of carbon, in order to supply the optimal C/N ratio for the bacterial metabolism, that should be 20 by weight [21]. Such a ratio is indeed too low, around 3.5 in the *TMAH* molecule, thus the second waste stream R2 was added to the previously mentioned stream R1;
- a growth medium, whose composition is shown in Table 1.

Table 1. Composition of the growth medium.

Compound	Concentration (mg/L)
$CuCl_2$	140
Na_2MoO_4	250
$NaHCO_3$	820
K_2HPO_4	210
$MgSO_4$	510
$FeCl_3$	110
Yeast Extract	12

The amount of the mixture of *TMAH* and PR effluents was calculated by solving the following mass balance given by the equation system:

$$V_1 + V_2 = V_{TOT} \quad (1)$$

$$\frac{C_1 \times V_1 + C_2 \times V_2}{C_{N-TMAH} \times V_1} = \frac{20}{1} \quad (2)$$

where C_1 is the carbon mass concentration in *TMAH* solution, 1.1 g/L; C_2 is the carbon mass concentration in the photoresist solution, 615 g/L; $C_{N\text{-}TMAH}$ is the nitrogen mass concentration in the *TMAH* molecule, 0.31 g/L; V_1 is the volume of the *TMAH* solution R1; V_2 is the volume of the photoresist solution R2; and V_{TOT} is the total volume of the wastewater treated in the reactor. The total volume of the wastewater blend solution treated in the lab-scale bioreactor was set to 3 L.

2.2. Biological Tests

The seeding activated sludge was taken from the wastewater treatment plant located in the LFoundry's site, that usually treats all the sewage coming from toilets, cleaning of some process

equipment from the process and the canteen. The activated sludge, containing neither *TMAH* nor photoresist, was stored in wide neck plastic bottles. They were kept under a fume hood and left open—in contact with atmospheric air—for 14 days, to allow the complete oxidation of residual organic matter. Thus, the substrate, whose composition is listed in Table 1, was added. The feeding for the reactor was obtained by mixing 1.93 L of *TMAH* residue, 20 mL of photoresist, and 50 mL of culture mineral medium. The experimental reactor was kept at room temperature (20 ± 2 °C), stirred at 70 rpm with air-oxygen saturation. Colony counts, Lowry's protein assay, and the biodiversity indexes were calculated according to the methods detailed in Moretti et al. [22]. Colony count was performed on Luria–Bertani enriched medium and AGAR-*TMAH* selective medium. Lowry's protein assay was carried out on lysate cells to assess the biomass production, hence the bacterial DNA was extracted from the samples. The biodiversity indexes, in particular, the range-weighted richness, functional organization, Simpson diversity index, and Simpson evenness index, were evaluated. Main genus representation in sequence reads were *Comamonas* (18.3 ± 5.7%), *Pseudomonas* (18.1 ± 5.3%), *Stenotrophomonas* (12.3 ± 3.1%), and *Brevundimonas* (11.4 ± 3.8%), while others sequence reads were spread in various groups belonging to families *Sphingomonadaceae* (8.1 ± 1.0%), *Sphingobacteriaceae* (4.05 ± 2.2%), *Methylophilaceae* (4.05 ± 3.18%), *Xanthobacteraceae* (3.30 ± 0.14%), *Xanthobacter* (2.55 ± 0.07), and *Rhodococcus* (1.90 ± 0.57%). The microorganism community was inoculated and adapted quickly to the change of nutrients, and stabilized over a new equilibrium state within a week when in the constant presence of *TMAH* and any further perturbation did not change the community structure. The biomass enrichment was obtained by means of some sequential batches, according to the sequence: (1) Batch T, from day 1 to day 6 (2 L of inoculum and 2 L of feeding solution); (2) Batch R, from day 7 to day 12, Batch A from day 13 to day 18, and Batch M from day 19 to day 24: at the beginning of each batch from the 7–24th day, 1 L of activated sludge coming from the previous batch was left in the reactor and fed with 2 L of feeding solution; (3) Batch M, from day 25 to day 30, where 1 L of activated sludge resulting from Batch M was added to 2 L of distilled water and 50 mL of mineral culture medium [22].

The biological results showed an organized and stable community over time, even in the long run, composed of specialized species that were also the best selected for the desired function. After that, the biomass was concentrated by gravity and stored at 4 °C in order to be used as inoculum for the two batch cycles.

The biological tests were carried out in a bioreactor BIOSTAT® B (Sartorius, Goettingen, Germany) (Figure 1) in batch operating mode. The process conditions for the tests were: temperature 25 °C, pH 7, stirring speed 70 rpm, oxygen flow-rate of 2.0 L/min, controlled and regulated by the control unit of the bioreactor, whose nominal capacity was 3.5 L.

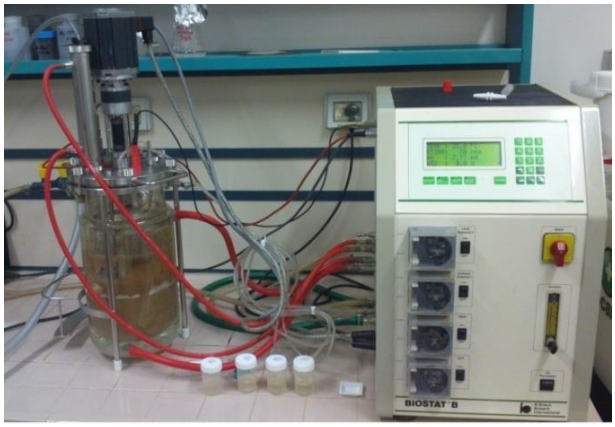


Figure 1. BIOSTAT®B and its control unit.

Two sequential batch cycles were carried out; such cycles were consecutive in order to confirm the results with different waste solution samples. At the end of the first cycle, mixing and aeration

were switched off, so that the biomass could settle; thus, the supernatant was removed by a peristaltic pump and disposed of, whereas the settled biomass was centrifuged in order to remove the remaining solution. Afterward, the fresh mixture (2678 mL of *TMAH* +22 mL of PR solutions) was added together with 300 mL of growth medium and the recycled biomass. At the end of each cycle, the total volume of the *TMAH*/PR wastewater mixture and growth medium was removed and disposed of. The concentration of *TMAH*, after dilution with the photoresist and sludge, was 1780 mg/L and 1625 mg/L for batch cycle 1 and 2, respectively. The batch time for each cycle was 21days, whereas the solid retention time (SRT) was 42 days. The composition of the two solutions, after blending, is listed in Table 2.

Table 2. Composition of the solutions for the two batch tests.

Parameter	Batch 1 (mg/L)	Batch 2 (mg/L)
pH	7.20	6.95
COD	5085	4863
TMAH	1780	1625
NH_4^+	75	62
F^-	0.04	0.02
NO_3^-	<0.01	<0.01
Cl^-	0.09	0.06
Sb, As, Cd, Cr, Hg, Ni, Pb, K, Se, Cu	<0.01	<0.01
Na	0.55	0.71

The mixture's pH was adjusted to the optimal value (i.e., 7) by the addition of H_2SO_4 (96%wt) or NaOH (35%wt) from the initial value of 12.4.

Every day, one sample of 100 mL was collected and centrifuged at 5000 rpm. The supernatant was used to determine the pH (Seven Compact pH-meter, Mettler Toledo), *TMAH* (Ion Chromatograph Dionex DX5000), and ammonium ion (Nessler's reagent method) concentrations, whereas the total suspended solids (TSS) were determined after drying of the settled material at 105 °C for 24 h.

The sample's volume was refilled by the addition of the growth medium. The kinetic parameters of the Monod model were also calculated for the design of the pilot bioreactor [21].

3. Results and Discussion

3.1. Kinetic Model

It was assumed that the kinetics of the microorganism population could be represented by the Monod model (Equation (3)):

$$\mu = \frac{\mu_{max} \times S}{K_S + S} \tag{3}$$

where μ is the specific growth rate of the microorganisms (h^{-1}), μ_{max} is the maximum specific growth rate (h^{-1}), S is the concentration of the limiting substrate for growth (mg/L), and K_S is the half-velocity constant, that is, the value of S corresponding to μ/μ_{max} = 0.5 (mg/L). The specific growth rate (μ) was calculated from an overall mass balance for the biomass at stationary conditions.

One single batch test was sufficient to derive the specific growth rate, by solving the system of linear first order differential equations:

$$\frac{dX}{dt} = \mu \times X \tag{4}$$

$$\frac{dS}{dt} = -\sigma \times X \tag{5}$$

$$\frac{dP}{dt} = \pi \times X \tag{6}$$

where X, S, and P are the concentrations of microorganisms (mg/L), *TMAH* (mg/L), and ammonium ion (mg/L), respectively, and μ, σ, and π are the specific growth rate, substrate consumption rate, and product generation rate (h^{-1}). These three equations have to be coupled with the well-known Monod (Equation (3)), Pirt (Equation (7)), and Luedeking–Piret (Equation (8)) equations:

$$\sigma = \frac{1}{Y^{G}_{X/S}} \times \mu + m \tag{7}$$

$$\pi = \alpha \times \mu + \beta \tag{8}$$

where the coefficients m and β are null (product associated to the growth), the biomass yield $Y^{G}{}_{X/S}$ is 0.34 g of biomass per g of substrate, and α = 0.2 g of ammonium per g of biomass (experimental values). The detailed calculation can be found in Innocenzi et al. [21]. Such an approach allows the fitting of substrate depletion data versus time to the integrated Monod equation by using nonlinear regression, which is advantageous since μ_{max} and K_S may be calculated from a single progress curve [23].

From the analysis of the data collected from the tests carried out with the bench bioreactor, the following kinetic parameters were calculated:

- μ_{max} = 0.0425 ± 0.0034 h^{-1};
- K_S = 800 ± 51 mg/L.

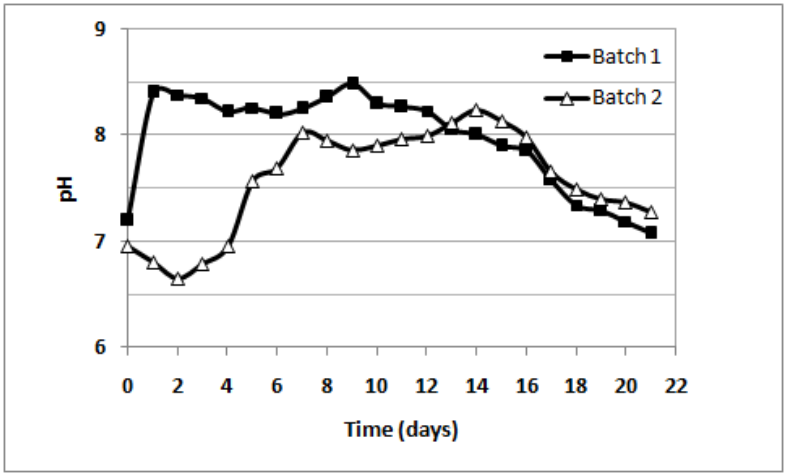
These data were used to design the optimal configuration of the biological equipment for the pilot plant.

3.2. Biological Tests

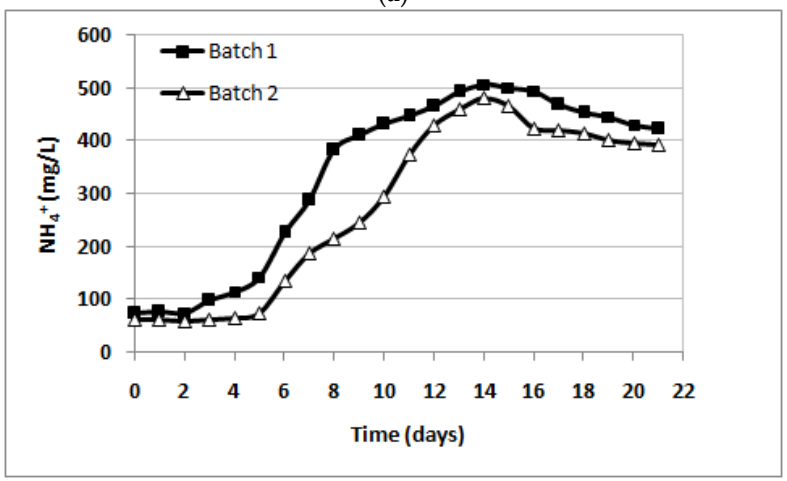
Figure 2 shows the pH, $NH_4{}^+$, *TMAH* and TSS trends for each batch cycle. From Figure 2, the following conclusions can be inferred:

- the pH value changed during each cycle: it increased to alkaline values and then came back towards neutral values after several days. This was apparently due to a buffering effect of the growth medium;
- $NH_4{}^+$ concentration increased with time: this was a clear indication of the *TMAH* degradation and indeed started after the adaptation period of 36–48 h;
- the *TMAH* concentration trend showed a rapid degradation and a further decrease toward zero, after the adaptation period. It is possible to hypothesize that, after nearly two days, the *TMAH* was adsorbed on the biomass and, afterward, was gradually decomposed, reaching concentrations very low if compared to the initial one. The final *TMAH* concentration obtained in the two batch cycles was 7 and 4 mg/L;
- the biomass concentration increased up to the tenth/eleventh day, but after that, it was rather constant, at around 1300–1500 mg/L.

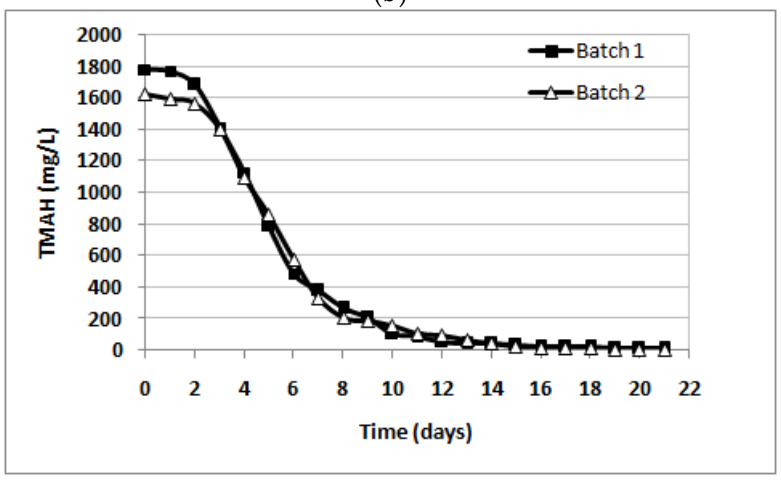
Figure 3 shows the *TMAH* degradation and the resulting $NH_4{}^+$ production for each cycle; the *TMAH* removal was higher than 99%, and this confirms the effectiveness of the biological process carried out in the experimental campaign. Hu et al. [18] stated that the aerobic sludge with a concentration of 2000 mg/L can gradually decompose *TMAH*, after several hours of inhibition, but the reduction in such ability usually occurs when the *TMAH* concentration reaches 150 mg/L. Instead, Lei et al. [15] found that an acclimated aerobic sludge reduces the inhibitory effect of *TMAH* up to 300 mg/L, but the aerobic process is not recommended for wastewater containing more than 1000 mg/L of such a molecule. Nevertheless, the 14-day acclimated strains were able to degrade higher concentrations of *TMAH*.



(**a**)

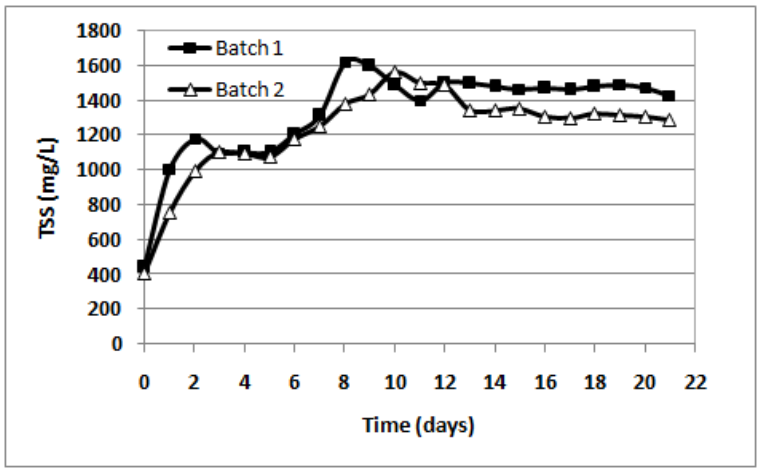


(**b**)



(**c**)

Figure 2. *Cont.*



(**d**)

Figure 2. pH (**a**), NH_4^+ (**b**), *TMAH* (**c**),and TSS (**d**) trends for the effluent in batches 1 and 2.

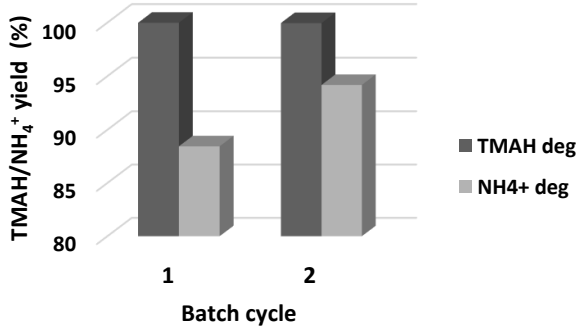


Figure 3. Degradation and NH_4^+ ion production for each cycle.

Comparing these results with those obtained in other prior experiments, where the feeding conditions were different (i.e.,1.5 L of *TMAH*/PR mixture feed (1.488 mL of *TMAH* mixed with 12 mL of PR) plus 1.5 L of growth medium, with a *TMAH* concentration of 992 mg/L), it is possible to observe that the increase in the initial *TMAH* concentration from 992 mg/L to 1780 g/L does not cause harmful effects on bacteria: as a matter of fact, the population of the microorganisms did not show any slowdown in their metabolic activity. The results of such tests are reported in Figure 4: six batch cycles were carried out with the same procedure described in Section 2.2 (25 °C, stirring at 70 rpm, 2 L/min of O_2, batch time 21 days). The final *TMAH* concentration was in the range of 2–5 mg/L.

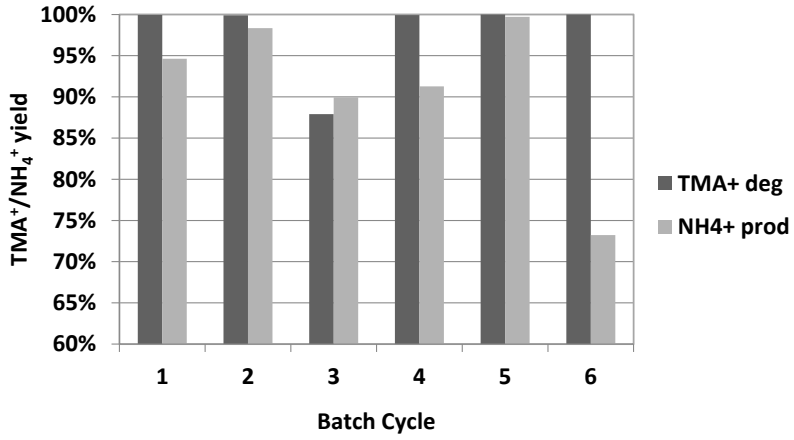


Figure 4. Degradation and NH_4^+ ion formation for previous experiments with different feed condition (50% waste solution (*TMAH*-PR)/50% growth medium), *TMAH* C_0= 992 mg/L.

4. Pilot Plant

At the moment, LFoundry neutralizes the *TMAH* by H_2SO_4 and NaOH, and the solution passes through an ion exchange resin filter from which the *TMAH* is stripped by another solution: in this manner, the *TMAH* can be concentrated and the resulting volume is lower. This solution is thus stored in a big tank and sent to an external plant authorized for the treatment of such waste. In addition, LFoundry also owns a conventional activated sludge system that already treats the wastewater from toilets, the canteen, the solution from which the *TMAH* is removed (from the ion-exchange) and other process wastewaters. Hence, the aim of LFoundry is to construct an upstream plant that can treat such particular liquid stream, instead of being disposed of externally, saving a significant amount of the annual operating costs relevant to the waste treatment.

The Monod model was used to design the pilot-scale bioreactor. The design was optimized by applying the minimization of the total volume, using three reactors in series [24].

Such a configuration, in continuous operating mode, is composed of three bioreactors in series that allow a remarkable saving in the total volume required for the treatment of the *TMAH*/PR solution. The volume of each bioreactor is indeed around 1.1 m^3 (total volume 3.3 m^3), whereas the volume of one single bioreactor would have been 10 m^3. The pilot plant is housed in two 40 ft standard containers and can treat three types of industrial effluents produced by LFoundry: line 1 treats the *TMAH*/PR mixed stream by the biological process, whereas line 2 (BOE) and line 3 (SEZ) treat other two waste streams containing high concentrations of nitrates, fluorides, and acetic acid. The first container includes one neutralization reactor, a storage tank and three biological reactors in series; the second container houses the equipment to treat the other two waste solutions by using physicochemical operations, in particular, one reactor, a plate and frame filter, and some tanks to store the effluents before and after the treatments. Some pictures of the pilot plant are shown in Figure 5.

(**a**) (**b**) (**c**)

Figure 5. 40 ft container housing the pilot plant (**a**), storage tank (**b**), and the three bioreactors (**c**).

The pilot-scale tests began in the winter 2018 and are currently being carried out for optimization purposes; the overall results will be published as soon as the experimental campaign ends. Nonetheless, a preliminary design of the full-scale plant was also carried out, considering that the amount of the *TMAH*/photoresist mixture currently produced at LFoundry is 6300 t/year. The optimized configuration with three reactors in series, 30 m^3 each, with pumps, two tanks for neutralization and final storage, PLC, and control devices, electricals, and more, will require an investment of around € 1.64 million. The total operating costs were estimated to be nearly 90 €/t, lower than the current cost paid for the external disposal of such solutions, that amounts to 140 €/t. The payback time is 4.75 years. LFoundry will evaluate the possibility of constructing the fully automated plant once a more accurate economic analysis, based on the pilot-scale data, is available.

5. Conclusions

The experiments carried out with *TMAH*/PR wastewater showed that the aerobic biological treatment is able to remove the *TMAH* molecule. In the present case, the mixture was composed

of 10% of growth medium and 90% of *TMAH*/PR wastewater, while in other previous experiments, such a composition was 50% growth medium and 50% *TMAH*/PR. For each cycle that lasted 21 days, the *TMAH* concentration was reduced to 4–7 mg/L, with removal yields greater than 99.3%: this means that the microorganism populations already present in the sludge from the LFoundry's WWTP can adapt their metabolism and use the *TMAH* as substrate, when photoresist, another waste solution, is dosed as carbon source. Moreover, the optimal composition of the growth medium and all the process parameters like pH, temperature, O_2flow-rate, and stirring were optimized. The kinetic parameters of the Monod model were also obtained in order to design the pilot plant, whose capacity was set at 25 L/h. The adapted microorganisms were thus used for the inoculum in the pilot plant, where three bioreactors in series were chosen in order to reduce the total volume required by the process. The volume of each reactor is around 1.1 m^3. The pilot-scale experimental campaign is currently being carried out.

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