Aerobic degradation of tetramethyl ammonium hydroxide (TMAH) from effluents of semiconductor industries: kinetic studies of laboratory and pilot experiments

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Abstract
Aerobic degradation of effluents contains tetramethylammonium hydroxide molecules (TMAH), coming from an electronic industry, was studied at laboratory and pilot scale. At the first, the preliminary experiments were conducted using a lab scale reactor inoculated with activated sludge coming from urban wastewater treatment. Several batches have been performed on real effluent, in which TMAH concentration was about 1800 mg/L. The results showed that after acclimation, the microorganisms removed 99% of TMAH in seven days. Kinetic studies have provided the following kinetic parameters able to describe the trends of TMAH, ammonium ions and biomass concentration as a function of time in the reactor: K_S = 0.8 g/L; μmax = 0.042 h-1. Then, in a second phase the experiments were conducted at pilot scale using a pilot plant realized within Life Bitmpas project (LIFE15 ENV/IT/000332). The plant has three biological reactors of 1 m^3 and it is possible to feed up to 25 L/h of TMAH effluent. The experiments were conducted in a continuous mode and the results showed that in 8 days the total degradation of TMAH was 99%; moreover, from kinetic study have been determined the following kinetic parameters: Ks = 0. 83 g/L and μmax = 0.0074 h^{-1}.
Keywords: TMAH, Aerobic process, Biological degradation, Kinetic modelling, pilot experiments

1. Introduction

In the electronics industry, the production of semiconductors is a process that involves several operations with the usage of large quantities of ultra-pure water. Consequently, a significant amount of wastewater is produced. These residual solutions should be treated to remove pollutants: inorganic substances, metals and organic contaminants as acetic acid, CH_3COOH, and tetramethylammonium hydroxide, $C_4H_{13}NO$ (TMAH) before discharging or re-using it for the production cycles [Degremont, 2015]. The first two groups of pollutants can be removed by traditional processes usually adopted for the treatment of semiconductor industry sewage [Huang et al., 1999] as lime precpitation, whereas the organic pollutants are only partially degraded by the conventional depuration treatments. Residual solutions with TMAH poses several problems if are not properly treated due to its toxicity.

In this paper a combined process to treat three types of wastewater (WW1, WW2, WW3) produced by a microelectronic industry was described. WW1 contained TMAH, the second one contained fluorides and phosphates, while the lasted (WW3) was rich in nitrates, fluorides and acetic acid. The treatments have been studied in the laboratory scale to define the optimal operative conditions for wastewater treatments. In the second phase, it has been design a pilot plant that can be treated these wastewaters. A process anlysis of the pilot plant has been performed, assuming the capacity of the plant 33 times smaller of the future industrial plant for wastewater treatments produced by the microelectronic industry. The treated water output from the three treatment lines can be stored and after sent to biological plant of the industry to complete remove of the residual impurities, after that the water can be reused and/or discharged to surface waters. These activities have been performed within European Life Bitmaps Project (Grant Agreement N. LIFE 15 ENV/IT 000332).

2. Process Design. From Laboratory Experiments to Process Analysis: Overview of the Experimental Results.

A series of laboratory experiments have been performed to define the optimal operative conditions for wastewater treatments from electronic manufactory. Three types of wastewaters were produced by LFoundry Srl, located in Avezzano (L'Aquila, Italy): WW1, WW2 and WW3. The first residual liquid flow contained in TMAH, the second one contained fluorides and phosphates, while the lasted was rich in nitrates, fluorides and acetic acid. The first liquid was biologically treated by activated sludge: the initial wastewater contained around 2 g/L of TMAH was used to perform experimental tests in a biological reactor with useful volume of 1.5 L. The fermenter consisted in a control unit for setting parameters, it had of double glass cylindrical with stirring system. The wastewater had an initial pH of 12 and it has been neutralized with sulfuric acid (98%) to reduce the pH value until 7. This current was added to a mixture of micronutrients (growing medium). Several experiments were performed in the presence of oxygen (2 L/min) at 70 rpm for a maximum residence time of 13 days. The results of these studies demonstrated an effective biological degradation of TMAH and showed a TMAH removal efficiency of about 99%: the microorganism population present in the sludge could adapt its metabolism and use TMAH like substrate. The specific growth rate (μ) was calculated from an overall mass balance for the biomass. It was assumed that the kinetics of the microorganism population could be defined by the Monod equation (3):

$$\mu = \frac{\mu_{max} \cdot S}{K_S + S} \quad (1)$$

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 substrate (mg/L) and K_S is the half-velocity constant, e.g. the value of *S* corresponding to μ/μ_{max} = 0.5 (mg/L). From the analysis of the data collected, the following kinetic parameters were calculated: μ_{max} = 0.042 h^{-1} and K_S = 0.8 g/L. These data were used to design the optimal configuration of the biological equipment for the pilot plant. Such configuration, in continuous operating mode, foresees three bioreactors in series that allow a remarkable saving in the total volume required for treatment of the TMAH solution. The volume of each bioreactor is indeed 1 m^3, whereas the volume of one single bioreactor would have been 10 m^3.

The second and the third wastewaters were chemically treated with lime in presence of aluminum sulfates. The solutions were neutralized with lime to precipitate the impurities: the results showed that lime as a precipitating agent was effective to remove pollutants from residual solutions. For WW2, according to calculations lime (20 % solution) consumption in the process of wastewater treatment was 364 kg/m^3 and aluminum sulfate (powder) consumption was 12.9 kg/m^3.

Instead for WW3, according to calculations lime (20 % solution) consumption in the process of wastewater treatment was 579.5 $kg/m^{3.}$

More details about the biological and chemical processes adopted for the wastewater treatments were described in a recent work [Innocenzi et al., 2019].

3. Pilot Plant Construction

The pilot plant has been realized in two 40 ft standard containers and can treat the three types of industrial effluents produced by LFoundry. The first container includes one neutralization reactor, a storage tank and three biological reactors in series of 1 m^3 (Fig.1); the second container has the equipment to treat the other two waste solutions by using physical-chemical operations, in particular one reactor, a plate & frame filter and five tanks to store the effluents before and after the treatments.

4. Conclusions

The present work showed that the aerobic biological treatment is able to remove TMAH with and efficiency greater than 99%. The results of the biological experiments has been used to define the kinetic parameters of the Monod model and to optimize the volume of the pilot plant equipment. At present, the pilot plant has been realized and experimental tests are in progress in order to check the data obtained during the lab experiments. The results will be used to define the parameters for the industrial plant.

Figure 1. Storage tank and biological reactors

References

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