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Effect of the Hydrodynamic Cavitation for the Treatment of Industrial Wastewater

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In the present work, the degradation of tetramethyl ammonium hydroxide (TMAH) from synthetic liquid waste of electronic industry was investigated by using hydrodynamic cavitation process. The core of the experimenal apparatus was a Venturi tube having a diameter of 12 mm and a convergent of 2 mm. The experiments were performed using synthetic solutions with an initial TMAH concentration of 2 g/L. A factorial plant with 2 factors and 2 levels was planned to prove that the hydrodinamic cavitation was an effective methodf to degrade TMAH. The investigated factors were: solution pH (3 – 20) and time (5 -20 min). The experiments have been carried out at a fixed temperature of 20°C and a pressure of 4 bar. The inlet pressure of 4 bar was chosen as a result of preliminary experiments that showed as at this value the degradation yields were higher than those obtained at other pressure values. The experiments showed that pH solution was significant with a negative effect. The optimal performance (around 44%) of process for degradation of tetramethyl ammonium hydroxide was achieved at pH=3 after 20 minutes.

1. Introduction

Tetramethyl ammonium hydroxide (TMAH, $(CH_3)_4NOH$) is an organic compound used for the production of semiconductors by the microelectronic industry. This substance is poisonous (Lin et al., 2011) corrosive, slow to biodegrade and eutrophic to aquatic environments. The production of semiconductors requires a large amount of ultra-pure water and makes use of large amounts of chemical reagents, as TMAH, that at the end of the production cycle must be appropriately disposed to avoid the dispersion of toxic substances in the environment and aquatic system. The microelectronic industry produces a large amount of wastewater with relevant concentrations of inorganic compounds (as hydrofluoric, sulfuric, phosphoric, and nitric acid, ammonium hydroxide) and heavy metals (as copper, iron, aluminum, etc.) and organic compounds. Traditional industrial processes are successfully used for the removal of inorganic substances from wastewater (Huang and Liu, 1999). On the contrary the removal of the organic compounds as TMAH is already an open issue. A list of processes for the degradation of TMAH is reported in the following. The treatments are divided into chemical/physical processes (e.g. advanced oxidation processes (AOP) and adsorption) and biological processes (e.g. anaerobic digestion). Wang and Liang (2014) studied the AOP using UV activated persulfate ($S_2O_8^{2-}$). The results of the experiments showed that the removal of TMAH increased with increasing persulfate dosage, temperature and UV irradiation. The acidic conditions support the removal of the organic substance. The authors suggested that TMAH was degraded into nitrate and ammonium according to the demethylation mechanism as the main degradation pathway. The advanced oxidation processes with UV, H_2O_2 and O_3 and their combination with SiO_2/Fe_3O_4 catalyst were also studied by Chiou et al. (2013). Results suggested that UV/O_3 process provided the best condition for the mineralization of TMAH (40 mg/L). Adsorption process was studied by several authors (Kelleher et al., 2001; Chang et al., 2013; Nishihama et al., 2013). Shibata et al. (2006) performed the removal of TMAH using cation exchange resins. The tetra-methyl ammonium ion was captured and released as tetra-methyl ammonium chloride into aqueous solution by the action of dilute hydrochloric acid, with an 89.4 % of total recovery of TMAH in the cation exchange and elution steps. Tetramethylammonium hydroxide can be also removed by biological treatments as described by several scientific works (Hu et al., 2012; Kim et al., 2002; Lei et al., 2000; Asakawa et al., 1998; Chang et al. 2008). Upflow anaerobic sludge blanket (*UASB*) technology (Hu et al., 2012) and Fenton process (Kim et al.,

2002) were successfully applied for the removal of TMAH from wastewater. A different study (Asakawa et al., 1998) verified the possibility of degrading TMAH using methanogen bacterium (family of Methanosarcinaceae) where TMAH was used as substrate for methane production. Chang et al. (2008) reported their biological studies in which the efficiency of Archaea microorganisms was described obtained a total degradation of TMAH of 95%. The organic substance was converted into CO_2, CH_4 and NH_3. Overall TMAH conversion was 95%.

The treatments described are technically complex and costly. They require a series of chemical and biological processes and a lot of space for equipment installation; therefore, the problem of the treatment of micro-electronic wastewaters containing TMAH is still open. The authors already developed a method to remove TMAH from aqueous solutions (Tortora et al., 2018) using a micellar enhanced ultrafiltration (MEUF) process. Two tubular ceramic membranes (210 kDa and 1 kDa) were tested in presence of surfactant (SDS). The results showed a sensible improvement in the rejection coefficient when the molecular weight cut-off of the membrane is reduced (99.75% with 1 kDa cut-off membrane in the presence of SDS). The tests were performed within the European project LIFE BITMAPS to study the removal of TMAH using several processes. The second investigated method in the cited project is the hydrodynamic cavitation by using a Venturi tube. This phenomenon includes the formation of bubbles and their subsequent collapse in a solvent. During the collapse several phenomena occur: a) local pressure and temperature increase until to reach extreme values: b) radical species, $OH^{\cdot}$, are released by the dissociation of water molecules (Capocelli et al., 2013; 2014a; b, Chianese et al., 2016). In order to obtain the removal of pollutants, the substances should react with the radicals produced by the hydrodynamic cavitation. The potential of the process for the wastewater treatment was discussed by several authors.

For example, Dular et al. 2016 discussed the efficiency of this method for removal of pharmaceuticals (clofibric acid, ibuprofen, ketoprofen, naproxen, diclofenac, carbamazepine), toxic cyanobacteria (*Microcystis aeruginosa*), green microalgae (*Chlorella vulgaris*), bacteria (*Legionella pneumophila*) and viruses (Rotavirus) from water and wastewater. Other works can be found for the disinfection of natural water and sewage (Kovalet al., 2011), and for the Microbial Cell Disruption (Capocelli et al., 2014c).

In this paper the experimental tests regarding the removal of TMAH by hydrodynamic were presented. The hydrodynamic cavitation occurs thanks to a Venturi tube connected to reactor with a recycle line. The experiments were performed with a synthetic solution with an initial concentration of TMAH equal to 2 g/L and the effect of two operative conditions (solution pH and inlet pressure) on pollutant degradation was investigated.

2. Materials and Methods

2.1. Materials

Sulfuric acid (Carlo Erba, 96%) and sodium hydroxide (Fluka Chemika, >97%) was used to adjust the solution pH. Aqueous solutions were prepared using tetramethylammonium hydroxide (TMAH) solution at 2.38% (Elga Europe Srl, Figure 1) that was provided by LFoundry (Avezzano, Italy). The experimental tests were performed using solutions with a concentration of 2 g/L of TMAH, that are prepared by diluting the initial sample with bi-distilled water. All experiments were performed at a constant temperature of 20°C.

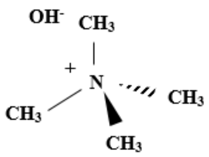

Figure 1: Chemical formula of Tetramethylammonium hydroxide (TMAH)

2.2. Experimental apparatus

Figure 2 shows the laboratory apparatus used for the hydrodynamic cavitation experiments.

The system includes a feed tank with a useful volume of 1000 mL (T1), a centrifugal pump (P1) and two valves (V1 and V2). The feed flowrate crosses the principal pipe and passes through the Venturi tube (VT1) therefore is reinjected in the tank T1. In order to control the liquid flowrate in this main line an additional pipe (by–pass line) with a valve (V2) is provided. The diameter of the main and by-pass line is equal to 12 mm. The centrifugal pump (Fluid -o – Tech, TMFR2) has a maximum electric power of 375 W and a rotation speed range of 1100-3500 rpm. The reactor T1 has a jacketed system to control temperature.

The flow was measured by an automatic flow meter (Comac Cal, Flow 38) while the pressure was checked by two electric manometers (M1 and M2, (Barksdale Control Products, UPA2 KF16809D). The pressure signals were sent to a computer and recorded by process software Labview.
The geometrical characteristics of the Venturi are shown in Figure 3; the divergence angle value is 5.74°. The Venturi is made of plexiglass. All other system components are in Rilsan and stainless steel.

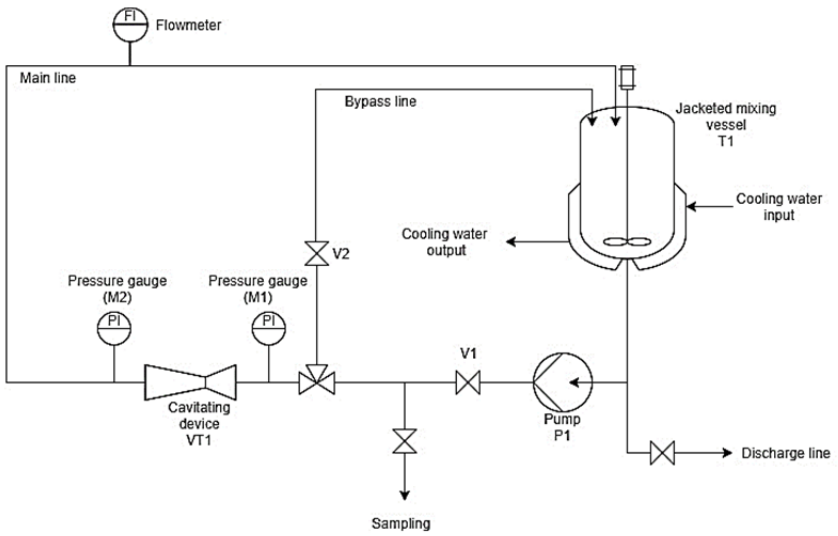

Figure 2: Layout of the experimental apparatus used for the hydrodynamic cavitation tests.

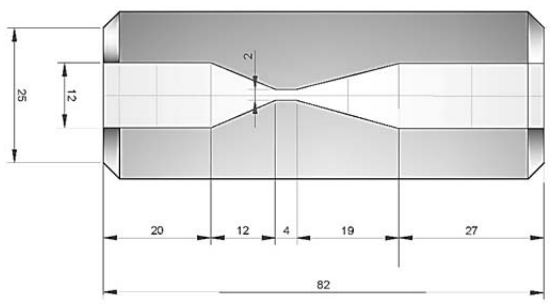

Figure 3: Sketch of the Venturi tube

2.3 Experimental procedures

The preliminary tests with distilled water were carried out for analysing the hydraulic characteristics of the system. The rotation speed was set to 1100 rpm and the inlet pressure to the Venturi has been varied up to 0.66 MPa, checking the water flowrate through the line.
After this first series of tests, the hydrodynamic cavitation experiments of TMAH were performed in according to a full factorial plan with two factors and two levels (2^2). In these tests, the factors were solution pH values (3.5 and 7) and reaction time (5 and 30 min). The aim of experiments was to mainly define the effect of pH on TMAH degradation. Process conditions are listed in Table 1 and 2.
The experiments were conducted at an inlet pressure of 4 bar. It was chosen this value because preliminary tests (here not reported) showed that the pressure had a positive effect on degradation yields of TMAH and an optimal pressure value was 4 bar.
The samples were collected in according to the experimental plan and after analysed to define the degradation of TMAH.
Before each test, the apparatus was washed fluxing for 15 minutes to remove traces of residual solutions of the previous test, moreover at the beginning of each experiments the solutions were recirculated at the minimum inlet pressure to monitor the initial TMAH concentration and let the system to degas and stabilize.

Table 1: Factors studied in the second series of experiments

Factors		**Levels**	
		−1	**+1**
A	pH value	3	5
B	Reaction time	5	20

Table 2: Full factorial design with two factors and two levels

Test	Treatment	pH value	Time reaction, min
1	1	3	5
2	a	7	5
3	b	3	20
4	ab	7	20

2.4 Quantitative analysis TMAH concentration

Liquid samples were analyzed by DX500 Thermofisher ionic chromatography equipped with CG17 guard column, to check the concentrations of TMAH residual and calculate the degradation yield values.
The removal yields of TMAH were calculated according to the equation (1):

$$\eta = \frac{TMAH_{o} - TMAH_{t}}{TMAH_{o}} \times 100 \qquad (1)$$

where $TMAH_o$ was the initial concentration of the solutions and $TMAH_t$ was the concentration of TMAH at the sampling time t.

3. Results and discussion

3.1. Hydraulic study of the experimental apparatus

The preliminary tests with distilled water were carried out for analysing the hydraulic characteristics of the system. The rotation speed was set to 1100 rpm and the inlet pressure to the Venturi has been varied from 0.026 until 0.6 MPa, checking the flow of the water that go through the line.

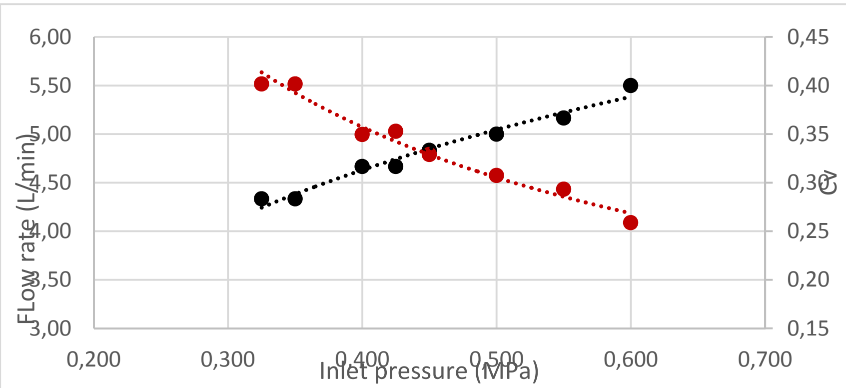

Figure 2: Hydraulic features of the system (See Fig 2): flow rate (black line) and cavitation number Cv (red line) as a function of the inlet pressure. Rotation speed 1100 rpm

In Figure 2, it is also reported the cavitation number (Cv), equation (2):

$$C_v = \frac{p_2 - p_v}{0{,}5 \rho v_0^2} \qquad (2)$$

C_v is dimensionless number, specific for this type of apparatus. p_2 is the downstream pressure, p_v is the vapor pressure of the liquid, v_0 is the fluid velocity at the convergent.
The analysis of the Figure showed that as the inlet pressure increases the flowrate increased, on contrary as expected the C_v decreased because of a higher kinetic energy of the liquid flow. Moreover, it was observed an increase of the turbulence as consequence of the more bubbles in the flow [Capocelli 2014a].

3.2 TMAH degradation

The experiments were conducted in according to the operative conditions described in Table 2.
During these tests, the initial conditions of TMAH was constant and equal to 2 g/L and inlet pressure of 4 bar, as stated above.
Table 3 shows the results of this series of experiments.

Table 3: Results of the factorial plan described in Table 2.

Test	Treatment	TMAH degradation (%)
1	1	40.26
2	a	27.47
3	b	44.45
4	ab	25.82

The maximum yields of TMAH removal (around 40%) were obtained in the test #1 and #3, when the pH was at low value (pH = 3). Analysis of variance was applied to investigate, more in details, the effect of the two factors on system response. For the variance of the experimental error was used the value previous found during hydrodynamic cavitation experiments. The significance of main factors and their interactions was assessed by *F*-test method with a confidence level of 95%. The results were showed in Table 4.

Table 4: Analysis of variance for the results showed in Table 3.

Source of variation	Value	Sum square	Significance (%)
A, pH value	-15.71	246.80	99.33
B, Reaction time	1.27	1.61	30.18
AB Interaction	-2.92	8.53	60.79

The factor A was significant with negative effect. It means that an increase of pH resulted in a reduction of the TMAH degradation. The effect of time was negligible, in the investigated conditions 5 minutes were sufficient to reach the maximum efficiency of removal.

4. Conclusions

The present work is a preliminary study of the research activity, whose main goal was to degrade the TMAH in an industrial wastewater coming from the electronic production of microprocessors. The initial result of this work has clearly established the efficiency of hydrodynamic cavitation process for the removal of this specific organic substance. The cavitation apparatus used for the experiments was a Venturi tube.
The efficiency of the process was significantly influenced by the pH value of the initial solutions: the yields increased by decreasing the pH; an efficiency of TMAH removal equal to 44.45% was obtained operating with a pH = 3 at an initial concentration of pollutant equal to 2 g/L and after 20 minutes of reaction.
Future research activities will be aimed to test the efficiency of a combined treatment with adding hydrogen peroxide during the hydrodynamic cavitation process in order increase the degradation efficiency and show how this process could be a viable alternative to the conventional treatment processes.

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