SARDINIA2021 HYBRID EVENT / 11-15 OCTOBER 2021 / CAGLIARI / ITALY
18TH INTERNATIONAL SYMPOSIUM ON WASTE MANAGEMENT AND SUSTAINABLE LANDFILLING

A CASE STUDY ON THE WASTEWATER TREATMENT IN THE SEMICONDUCTOR INDUSTRY

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ABSTRACT: Microelectronics manufacturing typically generates large amounts of toxic wastewater. Three wastewater of various composition, provided by a semiconductor company (L'Foundry, Avezzano, Italy), were tested in a laboratory and pilot plant scale to confirm the feasibility of an integrated treatment system. One stream contained TMAH (WW1), the second contained fluorides and phosphates (WW2), and the last was rich in nitrates, fluorides, and acetic acid (WW3). The process analysis showed that the treated liquids can be sent to the existing biological plant of the company for further treatment. After that, the treated water can be reused and/or discharged to surface waters.

Keywords: electronics industry, wastewater treatment plant, tetramethylammonium hydroxide, photoresist, fluorides, laboratory and pilot scale tests

1. INTRODUCTION

The production of microelectronics is characterized by the formation of a significant amount of wastewater containing toxic inorganic and organic pollutants (Lin et al. 2010; Lee at all. 2016). Several thousand tons per year of phosphate, fluoride and tetramethylammonium hydroxide (TMAH) discharge in the form of wastewater which cause many environmental issues. They can be removed from wastewater by means of several techniques.

Ion exchange technology and adsorption process, well established method to treat TMAH effluent and recovery TMAH reagent. The adsorption with different kinds of activated carbon (Chang et all. 2015; Prahas et all. 2012), cubic mesoporous silica (Kelleher at all. 2001) and weakly acidic cation exchange resins (Shu et all. 2016) were studied recently.

TMAH can be degraded under both aerobic and anaerobic conditions. Recently, a lot of biological treatment approaches presenting both an economical and environmentally friendly solution for TMAH containing wastewater treatment have been investigated (Hu et ll. 2012; Liu at all. 2016; Ferella et all. 2019).

Many alternatives methods have been developed for Fluoride and Phosphate removal (Zulfiqar et all. 2014). Among them adsorption (Hue and Tung. 2018; Xu et all. 2017), precipitate flotation (Warmadewanthi and Liu. 2009), coagulation (Chuang et all. 2006; Venditti et all. 2018) and membrane based process (Damtie et all. 2019).

In most chemical treatments, phosphorus can be removed by precipitation with a metal salt, e.g., iron, aluminum and mainly calcium containing ores (Wang et all. 2019). In wastewater with high fluoride content, the most commonly adopted method is precipitation under calcium fluoride form (CaF_2), using different calcium salts ($CaCl_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and hydrated lime $Ca(OH)_2$) as precipitants. However, as said before, precipitation by use of metal salts and lime results in the formation of large quantities of sludge which, though characterized by potential value, are difficult to treat for extraction of valuable components.

The goal of this work was to create an integrated wastewater treatment scheme for wastewater treatment of an semiconductor company (LFoundry, Central Italy), that would save a significant amount of water by organizing a ZLD and, therefore, annual operating costs.

LFoundry currently has two processing lines: concentrating of wastewater containing TMAH (WW1) (by ion exchange process), followed additional treatment at an external Wastewater Treatment Plant (WWTP) and biological treatment of domestic wastewater. The remaining two streams (WW2 and WW3) are directly sent for treatment to external WWTP. In addition, the company faced the problem of low efficiency of the ion-exchange resin due to its contamination with one of the components present in the effluent (photoresist). The objective of this work was to propose suitable treatment process for three types of wastewater.

2. MATERIALS AND METHODS

Three wastewater of various composition, provided by a semiconductor company (LFoundry, Avezzano, Italy), were tested in a laboratory and pilot plant scale to confirm the feasibility of an integrated treatment system. One stream contained TMAH (WW1), the second contained fluorides and phosphates (WW2), and the last was rich in nitrates, fluorides, and acetic acid (WW3) (Table 1).

Table 1. Composition of studied wastewater samples

Waste water	**pH**	**F^-, mg/L**	**PO_4^{3-}, mg/L**	**NH_4^+, mg/L**	**NO_3, mg/L**	**COD, mg/L**	**CH_3COOH, mg/L**	**Surfactants, mg/L**		**TMAH, mg/L**	**Photoresist, mg/L**
								Anion.	**Kation.**		
WW1	12	0	0	0	0	6000	0	0	0	2470	9900
WW2	8.7	20100	1450	25700	13800	500	0	0	0	0	0
WW3	1.6	16600	0	0	120970	109000	26112	14.3	0.075	0	0

Hydrated lime (calcium hydroxide) 20 % (w/v) and aluminum sulfate were used for the precipitation tests. For all fluoride-containing solutions, only polypropylene (PP) vessels were used for sample preparation and storage.

Fluoride, nitrate and COD were measured with Dr. Lange's kit, cuvette-test LCK 153 and LCK 114A. A XRF spectrophotometer (Spectro XEPOS 2000) and atomic spectroscopy Agilent Synchronous Vertical Dual View (5100 ICP-OES) were used to perform the chemical analyses of wastewater and precipitate of wastewater.

2.2 Experimental Procedures

2.2.1. Biological tests

The wastewater (WW1), provided by the company was neutralized by 5 mol/L H_2SO_4 solution to pH 7, that is a value suitable for the microbial growth.

The seeding activated sludge was taken from the wastewater treatment plant located in the L'Foundry's site, which usually treats all the sewage coming from toilets, cleaning of some process equipment from the process and the canteen.

The lab scale biological tests were carried out in a bioreactor BIOSTAT® B (Sartorius, Goettingen, Germany) in batch operating mode. The process conditions for the tests were: temperature 25 ºC, 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.

2.2.2. Chemical Treatment

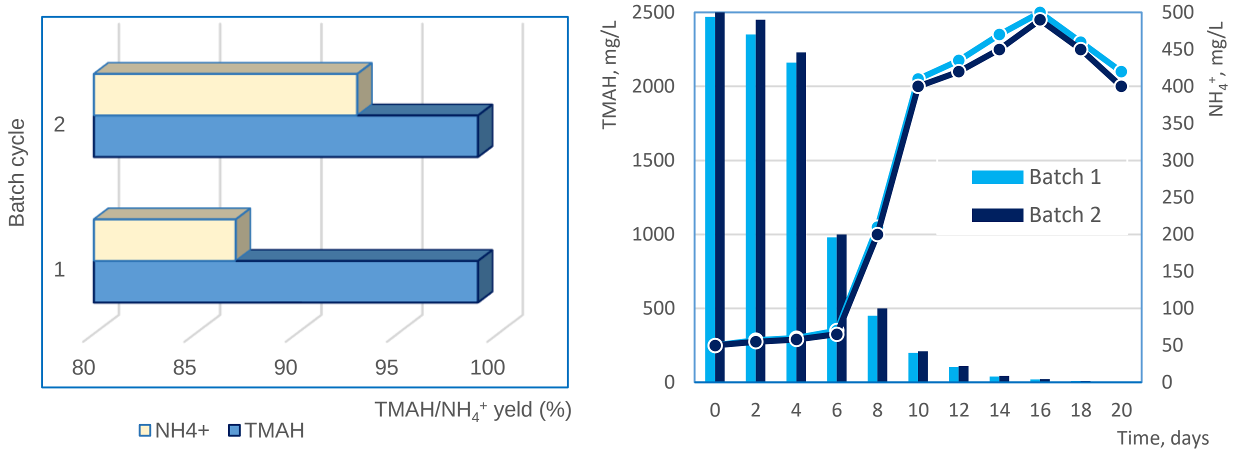
Lab scale batch adsorption experiments where carried out at constant temperature (232 ºC) by adding different amounts of reagents. During the precipitation step, suspension of lime (20%) and aluminum sulphate was gradually added under constant stirring until reaching the around desired pH. The mixture was stirred further for 2h in order to ensure precipitation equilibrium. Precipitation tests were performed in a pH range of 1.4–12, at room temperature (25±2 ˚C). The final pH was then was measured and the precipitate was separated from the slurry by centrifugation, and then dried at 105 ◦C overnight. For each considered pH, the obtained filtrate was analyzed for determining the residual composition.

3. RESULTS AND DISCUSSIONS

Different strategies were chosen for each of the streams. Aerobic treatment of WW1 was investigated by using a lab scale reactor inoculated with an activated sludge coming from the company municipal wastewater treatment plant. For WW2 and WW3, a pollutant removal of 99% was obtained by chemical precipitation with lime.

3.1 Biological Tests. WW1 treatment process.

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 each cycle, the total volume of the TMAH/PR wastewater mixture and growth medium was removed and disposed off. The batch time for each cycle was 21 days, whereas the solid retention time (SRT) was 42 days. As can be seen from Figure 1(a), the decomposition of TMAH and the resulting formation of NH_4^+ exceeds 99% after the second cycle, which confirms the effectiveness of the biological process carried out in the lab scale experiments. The final TMAH concentration was in the range of 2–5 mg/L.



(a) (b)

Figure 1. Degradation of TMAH and NH_4^+ ion production for each cycle.

Beside this, every day, one sample of 100 mL was collected and centrifuged at 5000 rpm. The supernatant was used to determine the TMAH (Ion Chromatograph Dionex DX5000) and ammonium ion (Nessler's reagent method) concentrations (Figure 1(b)).

As it can be seen from the results of exeperiments the pH was increasing to alkaline values and then caming back towards neutral values after several days, due to a buffering effect of the growth medium.Possibly, after 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.

3.2 Chemical Treatment

3.2.1. WW2 treatment process.

The effect of the pH on fluoride and phosphate precipitation was examined in a series of experiments that used wastewater WW2 while maintaining the pH at different values between 8.7 and 12.0.

It was found that Lime as a precipitating agent was effective for fluorides and phosphate removal (Figure 2). Along with increase in the pH value from 8.7 to 11-11.5 removal efficiency of F ions increased up to 99.9 % phosphate – 100 %. Whereas the total degree precipitation of F^- reached maximum at pH 11.5 (99.9 %) with further increasing pH up to 12 effect of fluoride removal decreased.

In order to facilitate separation for cleaning with the use of calcium hydroxide slurry coagulant of aluminum sulfate ($Al_2(SO_4)_318H_2O$) was investigated. As original wastewater characterized by high pH value, coagulant was added at the beginning, before adding of calcium hydroxide. In this case, the aluminum salt hydrolysis products were the centers of the formation of calcium phosphate and calcium fluoride during the addition of lime. Wastewater + powder $Al_2(SO_4)_3$ form positively charged complex: $[Al_8(OH)_{20}]^{+4}$.

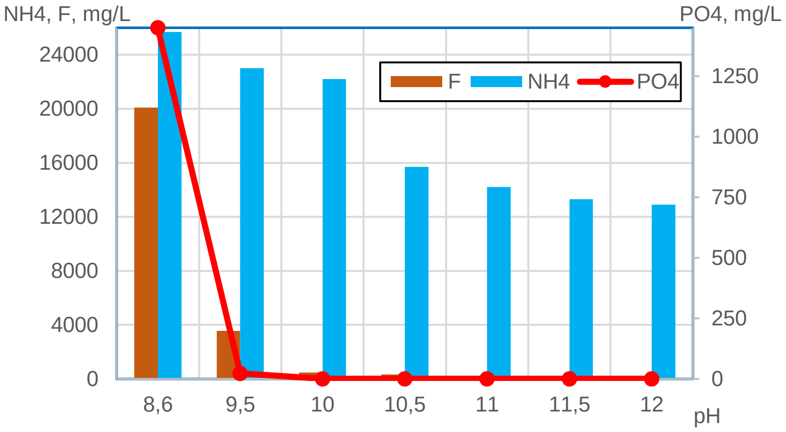


Figure 2. The effect of pH $Ca(OH)_2$ dosage on the WW2 treatment efficiency

The composition of sediment after precipitation with $Ca(OH)_2$ and $(Al_2(SO_4)_318H_2O$ are given in Table 2. No other elements were detected at concentrations greater than 0.01 wt %.

Table 2. Quantitative analysis (XRF) of the solid phase of wastewater after treatment with $Ca(OH)_2$ (I) and after treatment with $Ca(OH)_2$ and $Al_2(SO_4)_3$ (II)

	pH	% (w/w)						
		Na	**Si**	**Ca**	**Fe**	**S**	**P**	**Al**
I	11.4	1.20	1.6	94.6	0.10	1.6	0.60	0.01
II	11.2	1.55	0.01	75.8	0.06	12.5	0.42	9.44

This research has proven that joint use of aluminum sulfate and lime was effective in treatment of NH4F wastewater. Results of experiment identify optimum dosage of reagents to get maximum of Fluoride and Phosphate sedimentation and allow us to draw the following conclusions:

The process is more effective if staggered as follows:

1. Adding powder of Aluminum Sulfate and stirring for 15 min. This time is required for hydrolysis of reagent and formation positively charged complex $[Al_8(OH)_{20}]^{+4}$ that can play role of nucleating agent.
2. Adding of 20% solution of $Ca(OH)_2$ up to pH=11.2-11.4 at constant mixing for 1h 45 min.

Following centrifugation to separate precipitate. Centrifugation instead of filtration is recommended in order to avoid air pollution working zone by vapor of ammonium.

It is recommended to provide additional filtering to avoid getting residual sludge particles on the stage of biological treatment. Concentration of SST after centrifugation step <0.001 g/L.

Under these conditions effect of removal of Fluoride was 99.9 %, Phosphate – 100%. Concentration of Fluorides and Phosphate in NH_4F wastewater after treatment was below Limits for sewerage.

3.2.1. WW3 treatment process.

The effect of the pH on fluoride precipitation was examined in a series of experiments that used the wastewater WW3 while maintaining the pH at different values between 1.4 and 11.8.

It was found that Lime as a precipitating agent was effective for fluorides. Along with increase in the pH value from 1.4 to 4.7 removal efficiency of F ions increased up to 99.9 %. Whereas the total degree precipitation of F- reached maximum at pH 4.4 (99.9 %) with further increasing pH up to 9.9 effect of fluoride removal decreased. Optimum for Fluoride removal was pH=4.4-4.7 ($Ca(OH)_2$ dosage 80 g/L). In this case F^- concentration in the solution after treatment will be 11,5 mg/L (initial concentration in wastewater was 16861 mg/L). Farther increasing of pH value from 4.4 up to 6.4 do not increase effect of F removal, but result in increasing of calcium consumption up to 100 g/L.

Results of experiment identify optimum dosage of lime to get maximum of Fluoride sedimentation after neutralization with 20% solution of $Ca(OH)_2$ up to pH=4.4-5.4 at moderate mixing in order to avoid foaming effect. Under these conditions effect of removal of Fluoride was 99.9 %. Concentration of Fluorides in WW3 after treatment was below Limits for sewerage. Appart of this high concentration of nitrate and acetate (Figure 3) make it nutrient medium during biological treatment.

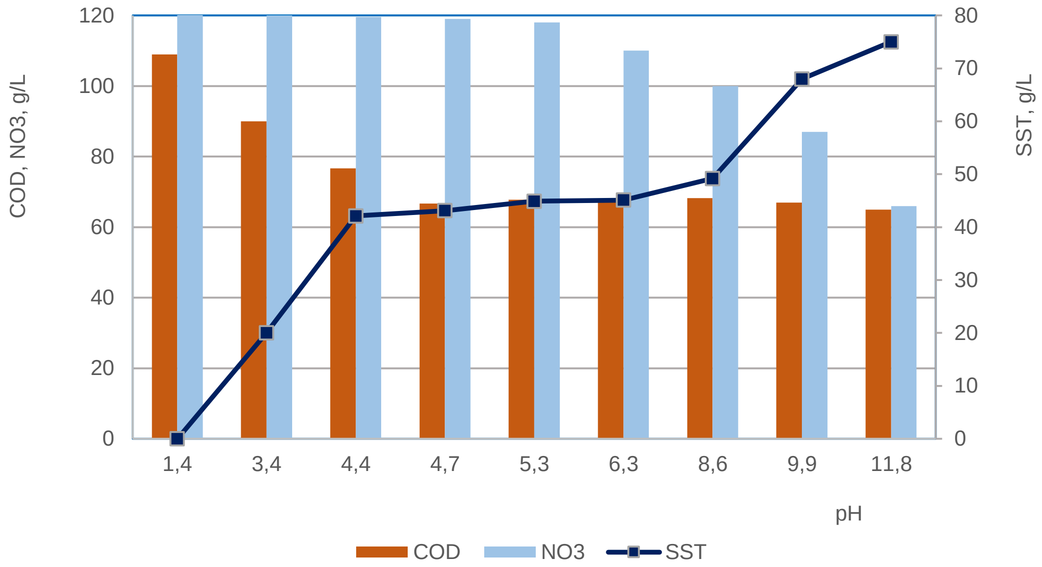


Figure 3. Concentration of COD, NO3 and TSS as function of pH

It has to be checked if WW3 after neutralization up to pH=5.4 (for example after mixing with TMAH waste water in ratio 1:10) can be send for farther biological treatment.

3.3 Integrated treatment processes

The results showed that with the correct sequence of continuous and batch processes, integrated treatment of the studied effluents can be carried out simultaneously and directly on site (Figure 4).

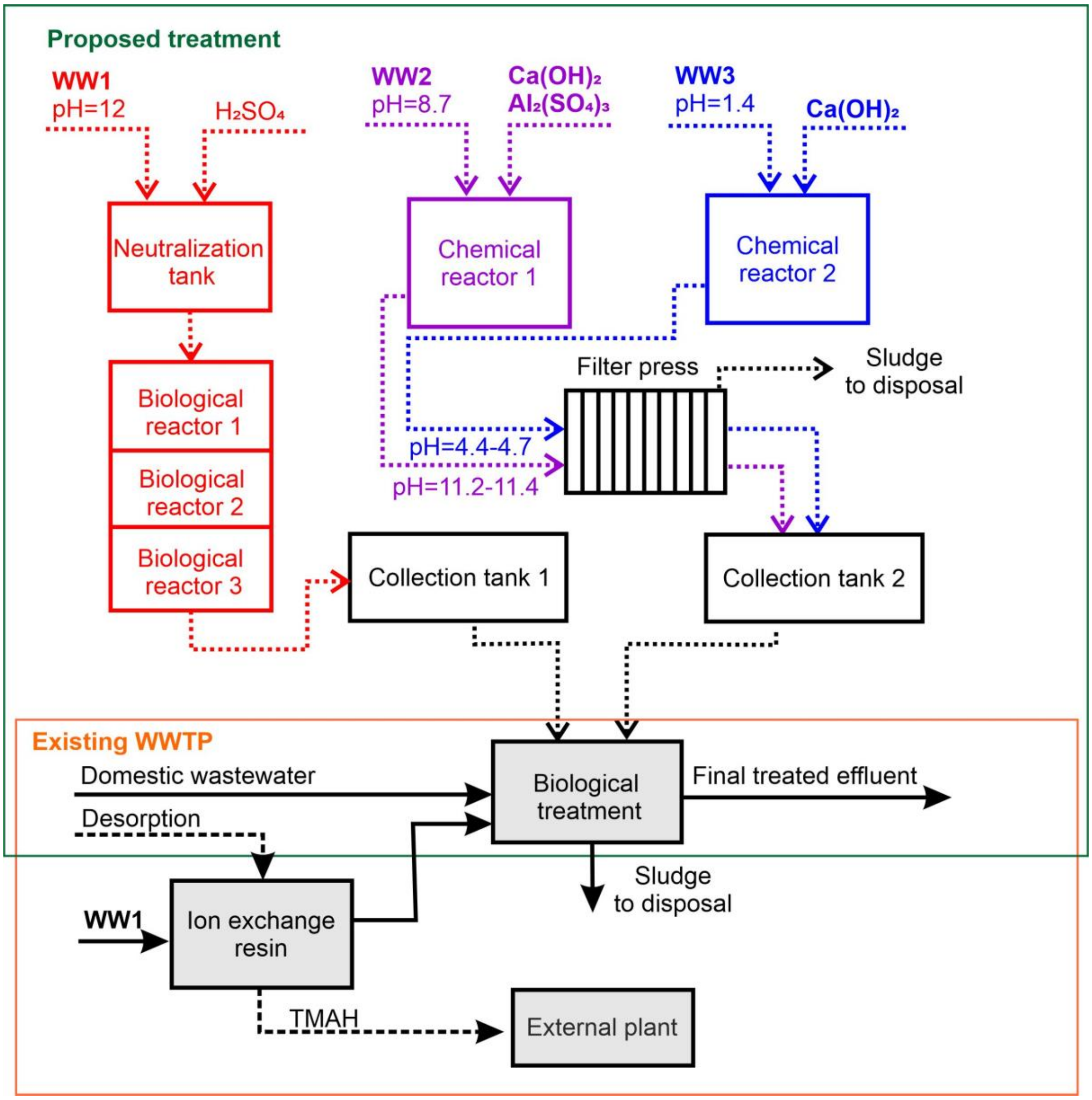


Figure 4. Existing Sewerage System and Future Plans

An attempt was made to implement the research results obtained in the laboratory on a pilot scale. The pilot plant was housed in two 40 ft standard containers and can treat three types of industrial effluents produced by LFoundry: WW1 (TMAH/photoresist mixed stream) by the biological process, whereas WW2 and WW3 by physicochemical operations. Two series of experiments were carried out on a pilot plant in batch and continuous mode, started in June 2018 and finished at December 2019.

A pilot-scale field experiment was performed in a pilot plant, which was composed of chemical reactors, filter press and scrubber, built at LFoundry. Studied wastewater (WW1, WW2 and WW3) were pumped into the pilot plant, passed through the all process steps. The pilot plant was housed in two standard containers and was designed for wastewater produced by LFoundry: line 1 treats the WW1 stream using a biological process, while WW2 and WW3 treat two other waste streams containing high concentrations of nitrates, fluorides and acetic acid, were treated by chemical methods.

The first container included one neutralization reactor, a storage tank and three successive biological reactors. Biological treatment took place in the first container and consisted of three bioreactors connected in series, each with a volume of 1.1 m^3 (total volume of 3.3 m^3).

The second container contained equipment for physicochemical wastewater treatment, in particular, one reactor, a plate and frame filter, and tanks for storing eluents before and after treatment.

This research was funded by the EUROPEAN COMMISSION, grant number LIFE15 ENV/IT/000332, Project LIFE BITMAPS and carried out in collaboration with LFoundry Srl (SMIC group), Italy, University of L'Aquila, Italy, BME Biomaterials & Engineering Srl, Italy and BFC Sistemi Srl, Italy.

4. CONCLUSIONS

Different strategies were chosen for each of the streams. Aerobic treatment of WW1 was investigated by using a lab scale reactor inoculated with an activated sludge coming from the company municipal wastewater treatment plant. Another residual industrial effluent (photoresist) was added, together with several micronutrients, to guarantee a good carbon/nitrogen ratio and a nutrient supply for bacterial growth. The results showed that 99% of TMAH degradation was reached in seven days. For WW2 and WW3, a pollutant removal of 99% was obtained by chemical precipitation with lime.

The process analysis showed that the treated liquids can be sent to the existing biological plant of the company for further treatment. After that, the treated water can be reused and/or discharged to surface waters.

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