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1. Introduction

In the electronic industry, the production of semiconductors is a process that involves several treatments with the usage of large quantities of ultra-pure water. Consequently, a relevant amount of polluted process water is produced, that must be treated to remove impurities before discharging or re-using it for the production cycles [1]. One of these residual solutions contains organic contaminants, as tetramethylammonium hydroxide, $C_4H_{13}NO$ (TMAH) that is only partially degraded by the conventional depuration treatments.

Moreover, semiconductor industries discharge also several thousand tons of phosphate and fluoride per year into the open atmosphere in the form of wastewater which cause many environmental issues as well as loss of drinking water. They can be removed from wastewater by means of several techniques, such as biological treatment, precipitation and crystallization.

About TMAH, this compound is corrosive, lethal if ingested, slow to biodegrade and eutrophic to aquatic environments [2]. Therefore, it must be necessarily removed from wastewaters to avoid environmental and human health problems. Recently, the scientific community is approaching the problem of its disposal to avoid the dispersion of substance if the TMAH containing wastewaters are not properly treated before disposal.

The proposed treatments include chemical/physical processes and biological processes. Lei et al. [3] studied biological treatments to treat residual solutions containing TMAH and other compounds (dimethyl sulfoxide and mono-ethanolamine). The experiments were performed in aerobic and anaerobic conditions. In both cases, TMAH degradation was possible but in anaerobic conditions some inhibitory effects were recorded with high concentration of this salt. On the contrary, during aerobic process NO_x were produced. Asawaka et al. [4] and Chang et al [5] conducted anaerobic treatments to remove TMAH from wastewaters. The degradation yields were about 95% and the processes produced a gas flow containing methane and carbon dioxide.

TMAH could be removed from solutions by using chemical oxidation [6]. In this case, a poisonous gas containing nitrogen oxides could be produced and should be added a conversion process to decompose these oxides into nitrogen, water and carbon dioxide [7]. Other studies showed that TMAH effluents could be treated by absorption with active carbon [8], zeolites [9] and silicate materials [10].

The efficiency for TMAH removal of micellar enhanced ultrafiltration (MEUF) was tested with very good results [11].

About effluents that contain phosphates and fluorides, many alternatives methods have been developed, including precipitate flotation [12], flotation–microfiltration [13], nano-magnetite aggregation [14], selective separation [15,16], fluoride removal in a fluidized bed reactor [17,18] or in packed fixed bed with granular calcite [19-21].

In most chemical treatments, phosphorus can be removed by precipitation with a metal salt, e.g., iron, aluminum and mainly calcium salts [22]. In wastewater with high fluoride content, the most commonly adopted method is precipitation under calcium fluoride form (CaF_2) [23], 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 [24-28].

In the present research activity, treatment of wastewaters containing TMAH, phosphates and fluorides (in the following called BOE and SEZ) were investigated using a pilot scale plant, in which two sections are present, first one is a biological section where TMAH was treated by activated sludge supplied by urban wastewater plant of LFoundry, second one is a chemical physical section where SEZ and BOE were treated by lime addition.

Objectives of this study were to check: the feasibility to treat biologically the aqueous residue contains TMAH by adapting a common wastewater microbial community and the removal efficiency of fluoride by treatment with lime.

2. Materials and methods

2.1 Operation of the pilot plant

Fig. 2.1 shows the block scheme of the pilot plant realized in the LFoundry site. The pilot plant has been built in two containers and treats three types of wastewaters (WW) by using biological and chemical processes. WW1 contains TMAH instead the other two residual solutions (WW2 and WW3) are rich in acetic acid, fluorides, nitrates and other compounds. It has been decided to propose a biological treatment for the first type of wastewater and chemical-physical operations for the second and the third solutions. The equipment for the treatment of WW1, to remove TMAH, have been constructed into the first container, shown in Fig.2.2, instead in the second one it was allocated the reactor and the filtration system for the treatment of the WW2 and WW3.

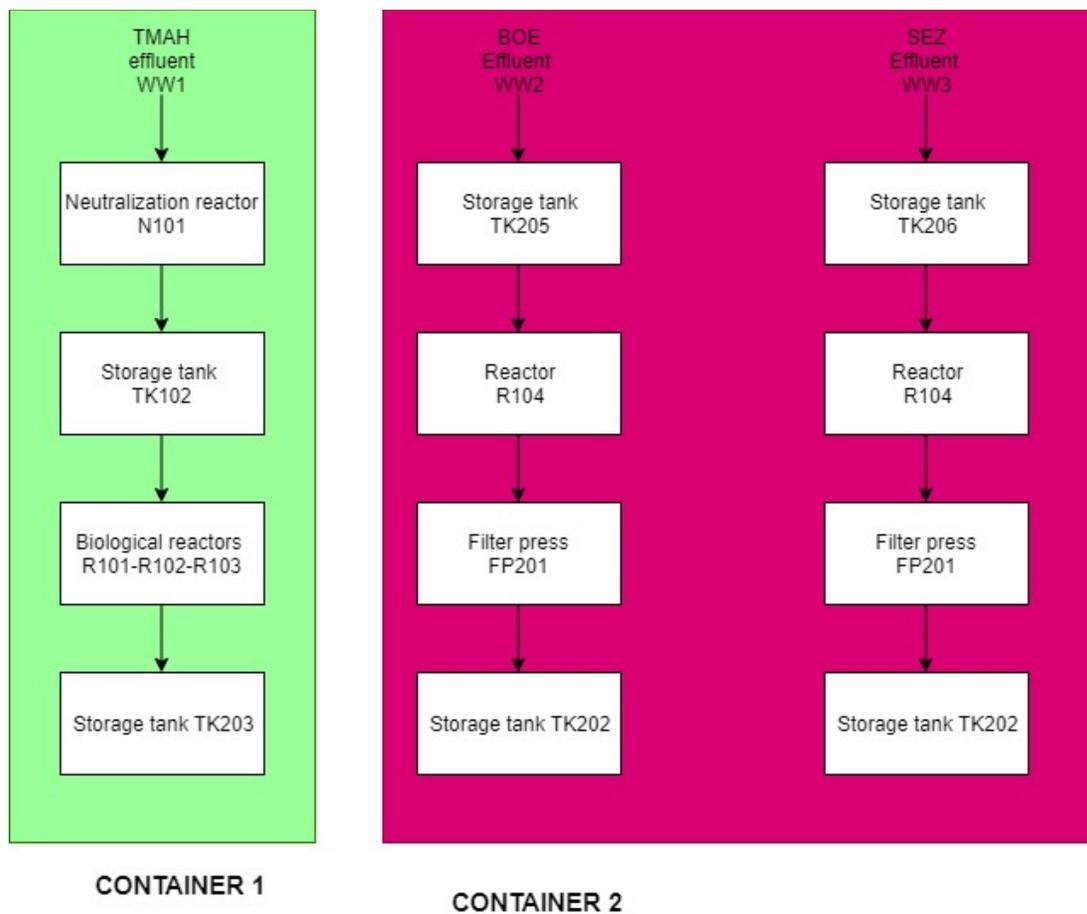


Fig.2.1: Simple block scheme of the pilot plant

Table 2.1 reports the list of the equipment of the pilot plant.



Fig.2.2: Image of the first container

Pilot plant: list of the equipment		
First container		
Item	Volume [m ³]	Material
R101	1.24	AISI 304
R102	1.24	AISI 304
R103	1.24	AISI 304
TK101	0.5	
TK102	0.2	Polypropylene
N101	0.12	Polypropylene
Second container		
Item	Volume [m ³]	Material
R104	0.3	Polypropylene
FP201	0.02	AISI 304
TK201	1	Polyethylene
TK202	0.6	Polyethylene
TK203	1.5	Polyethylene
TK204	1.5	Polyethylene
TK205	0.3	Polyethylene
TK206	0.3	Polyethylene

Table 2.1: Equipment of the pilot plant

2.1.1 Description of Treatment of WW1

In this section it will be discussed the pilot plant experiments conducted for the first type of WW1. TMAH residual solution (produced by LFoundry as industrial wastewater to disposal) is sent into reactor N101 (Fig 2.3a) in which sulfuric acid is added to reduce the pH values from 12 to 7, after that the solution is sent to a storage tank, TK102 (Fig. 2.3b), and fed to R101, R02 and R103 (Fig. 2.3c), that are biological reactors in series.

The suspension from the last reactor is sent to another storage tank, TK203 (Fig. 2.3d), and finally fed to the biological plant of the company. This plant presents an oxidation reactors, that transform ammonium ions into nitrates and denitrification reactors that transform the nitrates in nitrogen.

The average composition of WW1, that contains TMAH, comes from Photolithographic processes of the LFoundry facility, is reported in following table 2.2.

pH	12
TMAH	2161 mg/L
N-NH ₄	7.4 mg/L
N-NO ₃	< 0.15 mg/L
Dimethylamine (DMA)	< 0.05 mg/L

Table 2.2: Average composition of WW1

Three series of experiments have been performed in batch and continuous mode. The first cycle started 05/06/2018 until 12/07/2018; the second one started 15/10/2018 until 10/12/2018, the third one started 16/05/2019 until 27/06/2019. During first and second phases, batch and continuous activities have been alternate as a consequence of some technical problems identified on start-up. The last one has carried out only in continuous condition.

At the initiation of each cycle, the reactors R101, R102 and R103 were inoculated with around 800 L of activated sludge (approx. 2.5 g/L of TSS) from LFoundry site and as shown in the following pages, WW1 was fed in R101 with specific flows after neutralization of the wastewater.

The pHs in the reactors were checked by pH -meter and recorded. Oxygen was controlled at 2 mg/L by air blowing (Fig. 2.4) and mixing system. The temperature was kept constant (around 20°C) with the aid of heat exchanger serving to the jacket reactors.

Table 2.3 summarizes the batch and continuous experiments performed during the two cycles of the scientific activity.

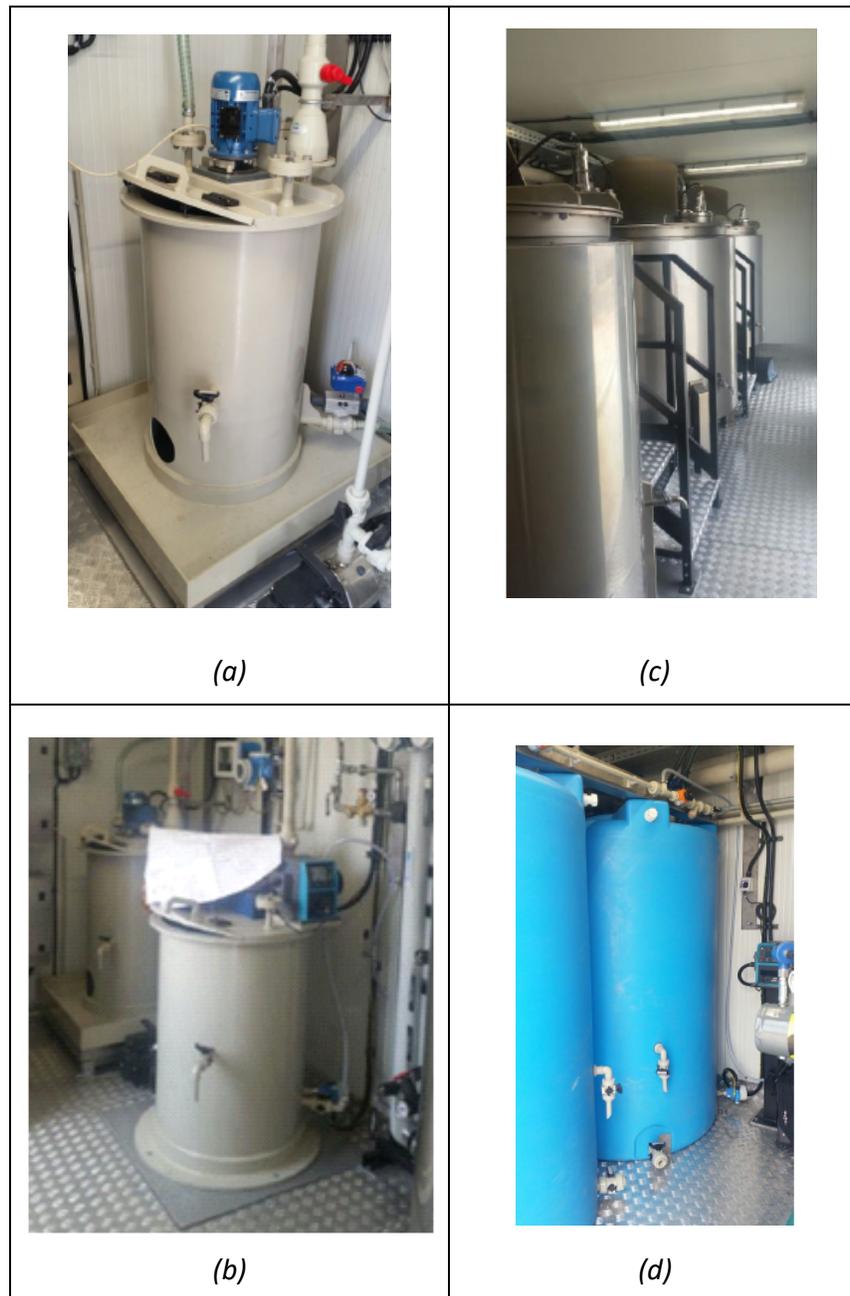


Fig.2.3: Biological section of the pilot plant. a) N101; b) TK102; c) R101, R102 and R103) and d) TK203 and TK204



Fig.2.4: Biological section of the pilot plant: air blowing

2.1.1 Description of Treatments of WW2 and WW3

In this section it will be discussed the pilot plant experiments conducted for the second and third types of WW (WW2 and WW3). WW2 and WW3 (produced by LFoundry as industrial wastewater to disposal) are charged in two storage tanks (TK201 and TK202) from which R104 is load by one of this WW per time. Treatments of these WW are carried out in batch condition and a series of three experiments are carried out per each effluents.

The suspension from the reactor is sent to the filter-press, FP201 and finally filtrate is stoked in the tank TK206 before to send it to the biological plant of the LFoundry site, whereas solid cake are stored and after send to disposal.

The average composition of the effluents is reported in following table.

The pH in the reactor (R104) was checked by pH -meter and recorded.

First cycle of experiments		
Date	Operation	Note
5/06/2018	Start-up of the plant and inoculation of the reactors	
8/06/2018	Loading of WW1 with a flow of 3 L/h	Continuous charging until 11/06/2018
11/06/2018	Loading of WW1 with a flow of 5 L/h	
12/06/2018	No WW1	Batch mode until 21/06/2018
21/06/2018	Loading of WW1 with a flow of 5 L/h	Continuous charging until 25/06/2018
25/06/2018	Loading of WW1 with a flow of 2 L/h	
26/06/2018	Loading of WW1 with a flow of 5 L/h	Continuous charging until 2/07/2018
2/07/2018	Loading of WW1 with a flow of 2 L/h	Continuous charging until 4/07/2018
4/07/2018	No WW1	Batch mode until 12/07/2018
12/07/2018	Stop pilot plant	
Second cycle of experiments		
16/10/2018	Start up and Loading of WW1 with a flow of 5 L/h	Continuous charging until 31/10/2018
31/10/2018	No WW1	Batch mode until 23/11/2018
23/11/2018	Loading of WW1 with a flow of 10 L/h	Continuous charging until 3/12/2018
3/12/2018	Loading of WW1 with a flow of 20 L/h	Continuous charging until 10/12/2018
10/12/2018	Stop pilot plant	

Table 2.3: Summary of the experiments performed by using pilot plant

Waste water	pH	F, mg/L	PO ₄ ³⁻ , mg/L	NH ₄ ⁻ , mg/L	NO ₃ ⁻ , mg/L	COD, mg/L	CH ₃ COOH, mg/L	TSD, mg/L	TSS, mg/L	Ca, mg/L	Si, mg/L	K, mg/L	Al, mg/L	Surfactants, mg/L	
														Anion.	Cation.
SEZ	1.6	16600	0	0	120970	109000	26112	4095	0	0.05	314	1.14	1.83	14.3	0.075
BOA	8.7	20100	1450	25700	13800	500	0	27400	0	3425	23.5	0.46	0.04	0	0

Table 2.4: Average composition of WW2 (BOE) and WW3 (SEZ)

2.2 Analytical procedures

About WW1, Regular sampling of N101 and R101, R102, and R103 have been made to analyze the concentration of ammoniacal nitrogen, nitrates, chemical oxygen demand (COD), that is an indirect measure of the bacterial activities, total suspended solid (TSS), that is an indirect measure of the quantity of cells, TMAH and DMA. The samples were centrifugated and after analyzed. Ammoniacal nitrogen, nitrates, chemical oxygen demand (COD) have been checked by Kit LCK 304 HACH LANGE Ammonium, Kit LCK 339 HACH LANGE Nitrate and Kit LCK 514 HACH LANGE COD. For TSS, the solid residue after centrifugation was dried at 105°C for 24 h and weighted to define the concentration of the suspended solids considering the volume of suspensions centrifugated. TMAH and DMA were analyzed by LFoundry and in a second phase by Technosib Company.

Finally, a fraction of the samples was stored for biological characterization.

About WW2 and WW3, at the end of each process a sample has collected from R104 and filtrated, solid cake has dried at 105°C. On the liquor, 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. Infrared spectroscopy (FTIR, Impact 410 Nicolet spectrophotometer) were made to characterize the obtained precipitate.

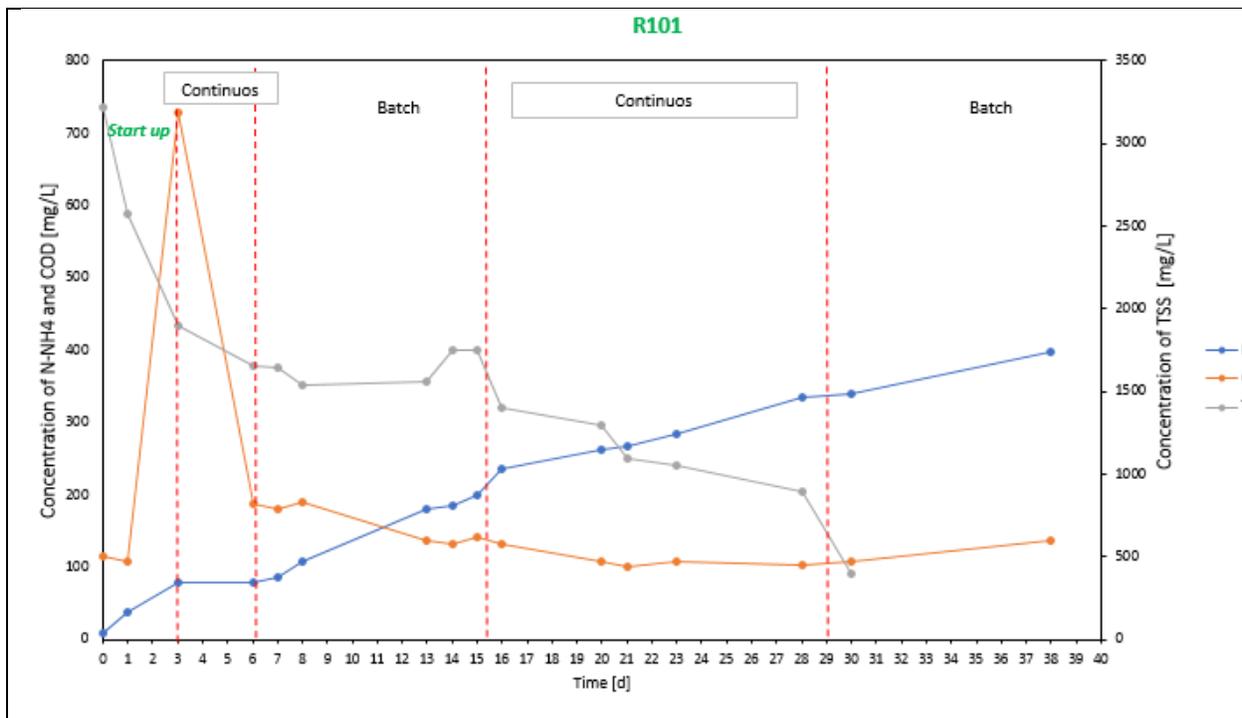
3. Results and discussions on TMAH treatment

3.1 First cycle of experiments (5/06/2018 -12/07/2018)

Table 3.1 and Fig. 3.1 show the results of the first series of experiments.

[L/h]	Sampling data	Day	R101					R102					R103				
			N-NH4 [mg/l]	COD [mg/l]	pH	SST [g/l]	SST [mg/L]	N-NH4 [mg/l]	COD [mg/l]	pH	SST [g/l]	SST [mg/L]	N-NH4 [mg/l]	COD [mg/l]	pH	SST [g/l]	SST [mg/L]
0	05/06/2018	0	9.56	115	6.82	3.22	3220	0.74	82.8	8.14	4.45	4450	0.36	79	8.22	4.54	4540
0	06/06/2018	1	36.8	107	5.54	2.58	2580	4.46	86.4	6.33	4.05	4050	0.5	64.7	7	4.05	4050
3	08/06/2018	3	80	726	4.62	1.9	1900	28.2	101	5.8	3.95	3950	6.4	89.1	6.16	3.65	3650
5	11/06/2018	6	80	187	7.24	1.66	1660	56	124	5.97	3.37	3370	37.8	227	6.58	3.7	3700
0	12/06/2018	7	86.5	180	7.08	1.65	1650	57.8	143	5.72	3.41	3410	37.6	219	5.99	3.5	3500
0	13/06/2018	8	107.5	190	6.95	1.54	1540	59.6	145	5.26	3.54	3540	47.6	251	5.53	3.28	3280
0	16/06/2018	13	180	137	7.12	1.56	1560	81	151	5.09	3.4	3400	75	205	4.97	3.22	3220
0	19/06/2018	14	185	131	7.16	1.75	1750	89.5	158	5.37	3.02	3020	78.5	213	5.12	3.1	3100
0	20/06/2018	15	200	142	7.55	1.75	1750	93	175	5.66	3.05	3050	81.6	228	5.56	3.05	3050
5	21/06/2018	16	236	131	7.05	1.4	1400	108	178	6.18	2.8	2800	94	347	6.06	2.8	2800
2	25/06/2018	20	262	108	7.28	1.3	1300	181	161	6.95	2.15	2150	125	277	5.82	2.55	2550
5	26/06/2018	21	268	99.6	7.03	1.1	1100	193	166	7.07	1.95	1950	143	269	6.25	2.3	2300
5	28/06/2018	23	284	108	5.71	1.05	1050	220	202	6.88	1.8	1800	157	273	6.88	2.05	2050
2	02/07/2018	28	336	102	6.46	0.9	900	252	178	6.31	1.8	1800	188	253	6.42	2.1	2100
0	04/07/2018	30	340	108	5.97	0.4	400	248	198	6.01	3.6	3600	175	244	5.91	4.85	4850
0	12/07/2018	38	397	138	6.4			284	208	6.84			203	301	6.75		

Table 3.1: Results of the first cycle of experiments



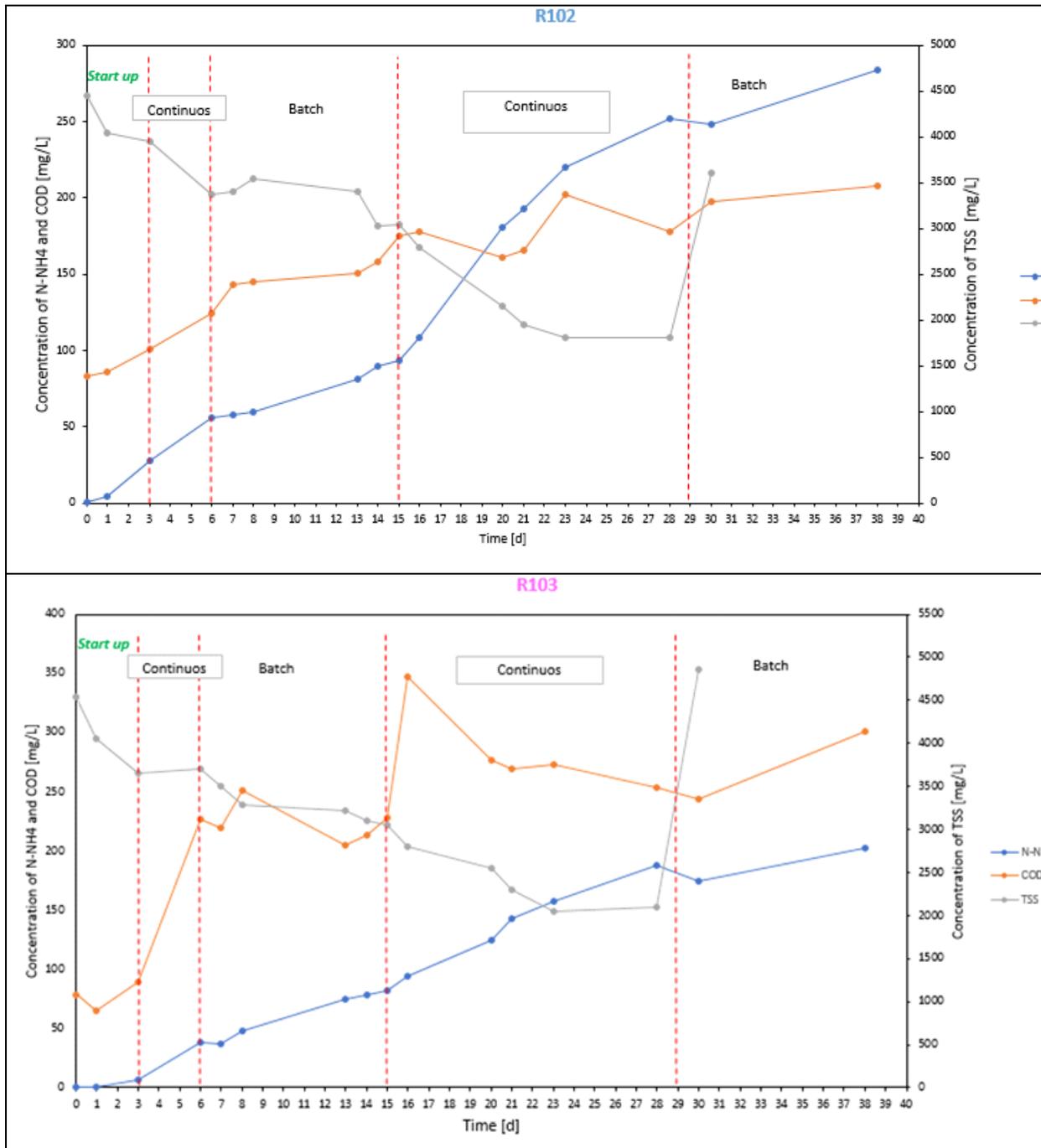


Figure 3.1: Concentration of N-NH₄, COD and TSS [mg/L] for each bio-reactors

For R101: in the first two days (start-up of the plant) COD concentration was constant at 100 mg/L, after that the value increased until 700 mg/L. This trend was probably due at the loading of TMAH wastewater (5 and 3 L/h). Then as the days passed COD concentration decreased and remains constant at 100 mg/L for the whole cycle of experiments. Initial concentration of N-NH₄ was about 10 mg/L, it regularly increased showing that in this phase there was the biological degradation of TMAH in ammoniacal

products. The maximum concentration of N-NH₄ at the end of the cycle was about 400 mg/L. TSS decreased, in the first period, until 1600 mg/L. During batch procedure TSS remained constant and then decreased during continuous loading of WW1. Minimum concentration of TSS was 400 mg/L.

For R102: COD remained fairly constant for the whole cycle of experiments and in the last period the concentration was about 200 mg/L. N-NH₄ increased exponentially, in particular during the continuous operation, the maximum concentration at the end of the experiments was 284 mg/L. TSS constantly decreased until to 1800 mg/L.

For R103: COD had a less regularly trend respect to the COD trend measured for R101 and R102. At the end of the cycle COD concentration was 300 mg/L. N-NH₄ increased on a regular way until to 200 mg/L. TSS decreased during the various phases of the cycle less respect to the trend of TSS in R101 and R102. The minimum concentration was 2100 mg/L (28 day), after that the concentration increased until to 4850 mg/L during the last batch phase. The same trend was also observed for TSS in R102. It is clear that the bacteria in the first reactor (R101) most suffers of TMAH in the WW1 and are the main player of TMAH degradation during the first phase of the biological treatment.

Fig. 3.2 reports the data for TMAH, DMA, N-NH₄⁺ and NO₃⁻ during the batch period between 12/06/18-19/06/18. DMA, N-NH₄⁺ and NO₃⁻ are the products of the biological degradation of TMAH. Their presence and the reduction of TMAH concentration demonstrated the effective removal of TMAH.

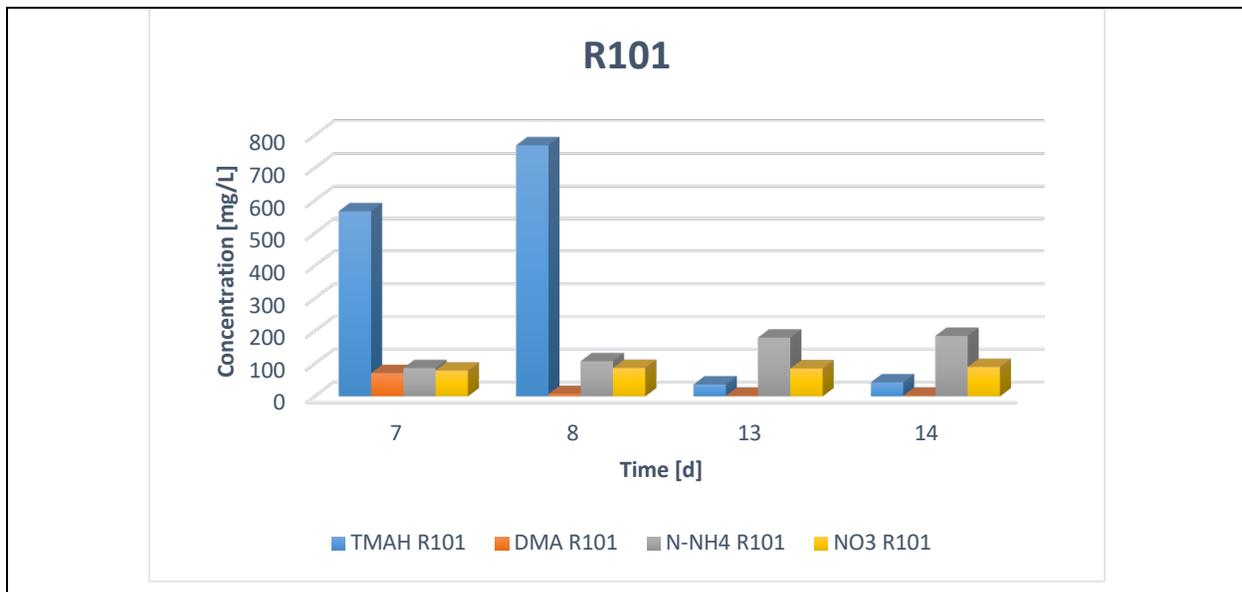




Figure 3.2: Concentration of TMAH, DMA, N-NH₄⁺ and NO₃⁻ for R101, R102 and R103 during the period 12/06/18 – 19/06/18 (batch operation)

TMAH concentration in R101 was about 600-800 mg/L, after that decreased until to 30 mg/L during 13th and 14th day of the cycle. TMAH in R102 and R103 was near to 3 and 1 mg/L, respectively. TMAH was completely degraded in the first biological reactor, moreover considering that the plant was in batch operation, no flow of WW1 with fresh TMAH moved from R101 to R102 and R103. DMA in the samples of R101 was around 70 mg/L the first day of the batch cycle, after that was near to 2 mg/L. Concentration of DMA in R102 and R103 was near to 0 mg/L for all days of the cycle. The most of DMA was degraded in R101 during the first 24 h of reaction. N-NH₄⁺ (second product of bio degradation of TMAH) was more concentrated in R101 respect to R102 and R103. Instead NO₃⁻ was more concentrated in R102 and R103. These data showed that in R101 took place the first biodegradation of TMAH in DMA and N-NH₄⁺, instead

in R102 and R103 took place the degradation of N-NH_4^+ in NO_3 , the bacteria in the last two reactors oxidised the N-NH_4^+ in NO_3 (nitrification reaction).

3.2 Second cycle of experiments (15/10/2018 – 10/12/2018)

Table 3.2 and Fig. 3.3 show the results of this series of experiments

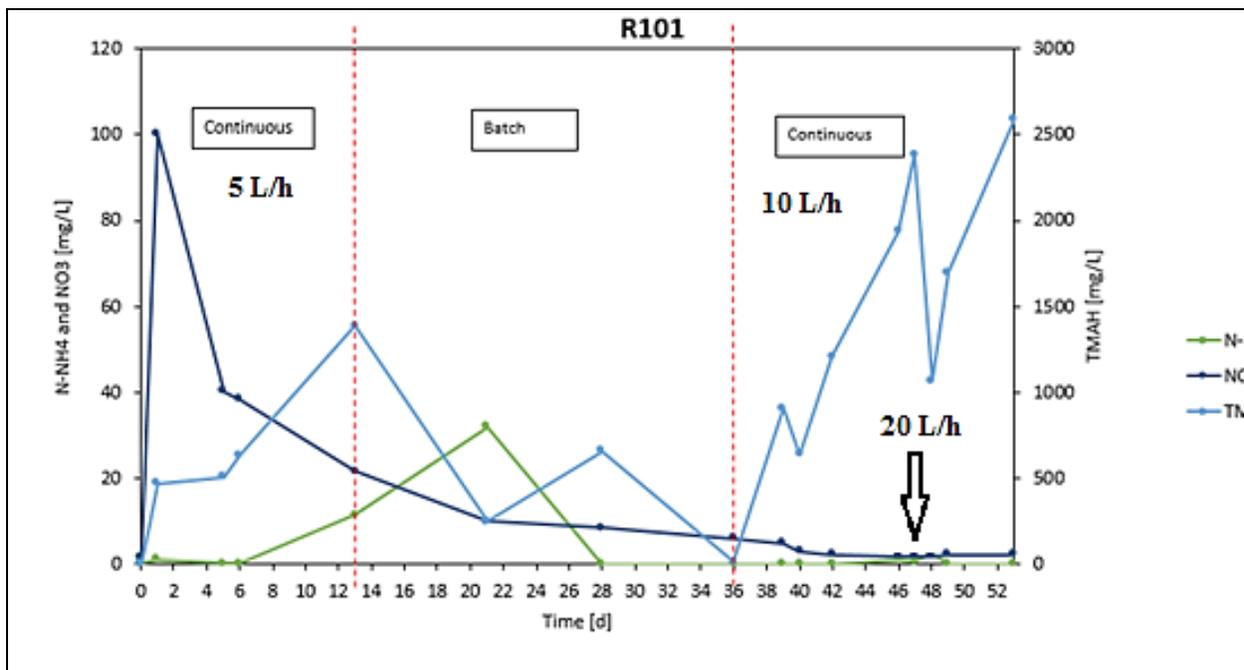
L/h	Date	Day	R101							DMA [mg/L]	NO3 [mg/L]
			N-NH4 [mg/L]	COD [mg/L]	pH	SST [g/L]	SST [mg/L]	TMAH [mg/L]			
5	16/10/2018	0	0.358	143	7.13	2.52	2520	0	0	1.65	
5	18/10/2018	1	1.2	90.2	7.21	1.88	1880	470	62	100	
5	23/10/2018	5	0.147	187	6.59	1.04	1040	507	44	40.2	
5	24/10/2018	6	0.136	182	7.03	0.94	940	633	27	38.4	
BATCH 0	31/10/2018	13	11.5	183	7.01	0.34	340	1388	0	21.6	
0	08/11/2018	21	32	109	5.89	0.68	680	247	14.6	9.92	
0	15/11/2018	28	0.045		6.45	1.46	1460	660	0	8.4	
From 23 10 L/h	23/11/2018	36	0.03	128	4.14	0.1	100	14.8	0	5.9	
10	26/11/2018	39	0.045	129	4.2	0.4	400	906	0	4.94	
10	27/11/2018	40	0.067	120	4.19	0.24	240	641	0	2.93	
10	29/11/2018	42	0.001	220	4.73	0.2	200	1209	0	2.19	
10	03/12/2018	46	1.08	114	6.54	0.02	20	1936	0	1.78	
20	04/12/2018	47	0.471	149	6.75	<0.02	20	2383	0	1.8	
20	05/12/2018	48	2.39	139	6.87	<0.02	20	1066	0	1.8	
20	06/12/2018	49	0.05	80		0.16	160	1695	0	2.27	
20	10/12/2018	53	0.024	87.6				2591	0	2.188	

L/h	Date		R102						DMA [mg/L]	NO3 [mg/L]
	Day		N-NH4 [mg/L]	COD [mg/L]	pH	SST [g/L]	SST [mg/L]	TMAH [mg/L]		
5	16/10/2018	0	0.204	161	6.84	3.24	3240	0	0	1.54
5	18/10/2018	1	1.14	83.2	6.85	2.83	2830	37.1	89	126
5	23/10/2018	5	0.276	146	6.38	2.16	2160	18.6	68	225
5	24/10/2018	6	0.938	150	6.62	2.28	2280	58.1	61	180.8
BATCH 0	31/10/2018	13	0.34	154	6.81	1.18	1180	422	0	120
0	08/11/2018	21	1.064	80.3	5.92	1.46	1460	0	0	92.9
0	15/11/2018	28	0.015		6.5	1.9	1900	0	0	159
From 23 10 L/h	23/11/2018	36	0	105	5.53	0.18	180	0	0	118
10	26/11/2018	39	0.003	137	4.61	0.9	900	165	0	70.3
10	27/11/2018	40	0.028	137	3.94	0.94	940	269	0	51.2
10	29/11/2018	42	0.033	201	3.71	0.58	580	514	0	31.2
10	03/12/2018	46	0.122	127	4.03	0.2	200	1051	0	12.8
20	04/12/2018	47	0.033	131	4.31	0.04	40	1561	0	7.84
20	05/12/2018	48	0.226	144	4.87	0.1	100	1548	0	5.16
20	06/12/2018	49	0.008	94.4		0.26	260	1516	0	3.1
20	10/12/2018	53	1.5	91.4				2465	0	2.31

L/h	Date	GIORNO	R103							
			N-NH4 [mg/L]	COD [mg/L]	pH	SST [g/L]	SST [mg/L]	TMAH [mg/L]	DMA [mg/L]	NO3 [mg/L]
5	16/10/2018	0	0.186	112	6.89	1.88	1880	0	0	1.29
5	18/10/2018	1	0.28	74.4	7.08	1.78	1780	2.84	96	126
5	23/10/2018	5	3.9	109	6.03	2.26	2260	<0,05	122	275
5	24/10/2018	6	3.2	118	6.23	2.1	2100	2.04	89	252
BATCH 0	31/10/2018	13	2.77	138	6.36	1.78	1780	12.6	0.05	254
0	08/11/2018	21	3.98	82.8	6.28	1.96	1960	0	0	251
0	15/11/2018	28	0.014		5.9	1.76	1760	0	0	227.5
From 23 10 L/h	23/11/2018	36	0.006	108	6.07	1.3	1300	0	0	234
10	26/11/2018	39	0.005	118	4.37	1.28	1280	16.2	0	203
10	27/11/2018	40	0	118	3.91	1.3	1300	0	0	162
10	29/11/2018	42	0.036	200	3.65	1	1000	81.7	0	113
10	03/12/2018	46	0	134	3.72	0.72	720	406	0	54.4
20	04/12/2018	47	0.004	141	3.7	0.56	560	514	0	38.2
20	05/12/2018	48	0.07	141	3.8	0.54	540	886	0	38.4
20	06/12/2018	49	0.032	88				1377	0	14.7
20	10/12/2018	53	0.221	97.8		0.2		2154	0	2.85

Table 3.2: Results of the second cycle of experiments

These data are reported in the following figures.



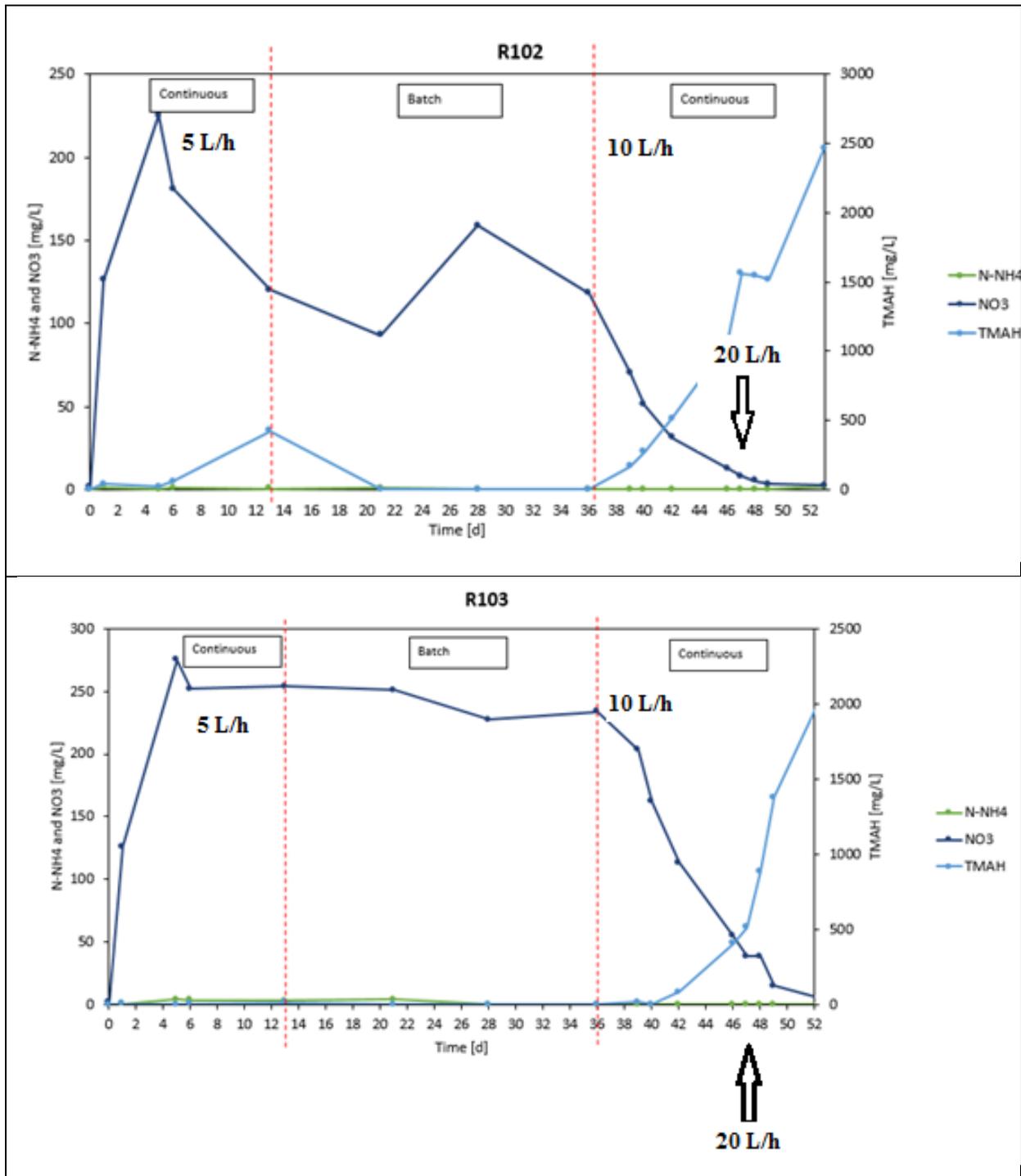


Figure 3.3: TMAH and its degradation products

Fig. 3.4 reports the pH value during the whole cycle.

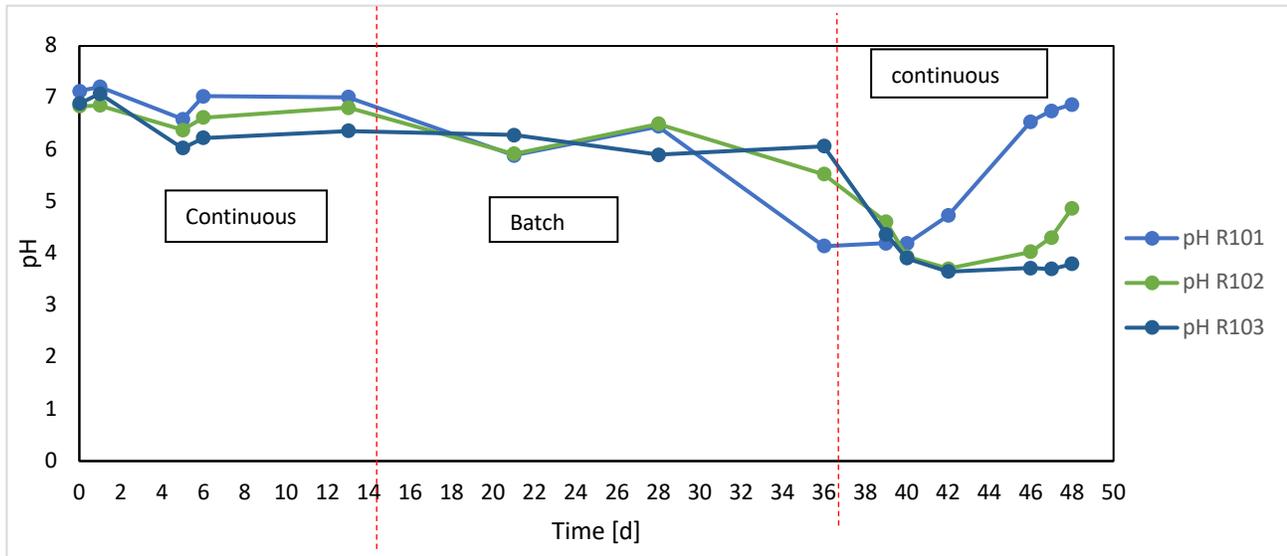


Figure 3.4: pH value for R101, R102 and R103

pH values were constant for the continuous and batch period and near to 7. pH in R101 started to decrease until 4 during the last days of the batch operation: it can be explained considering the low activity of the bacteria and as consequence low production of basic compounds as nitrate and ammonium. It means that TMAH degradation yields substantially decreased. pH increased in the last continuous period: it can be explained considering that from 36th WW1 that had a pH 7 was charged with a flow of 10 and 20 L/h.

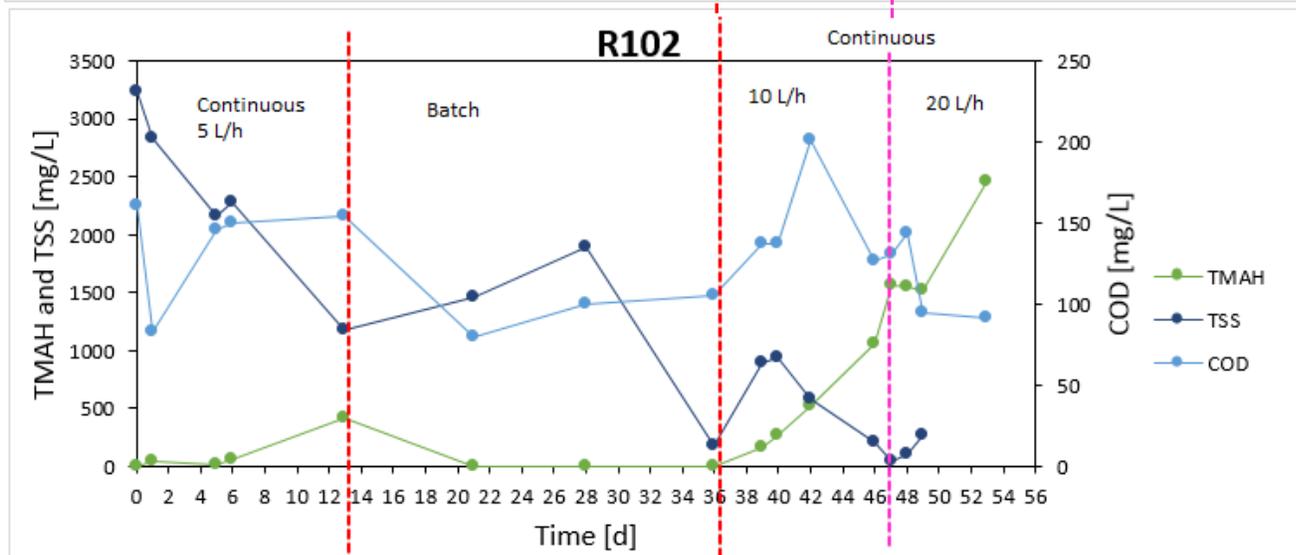
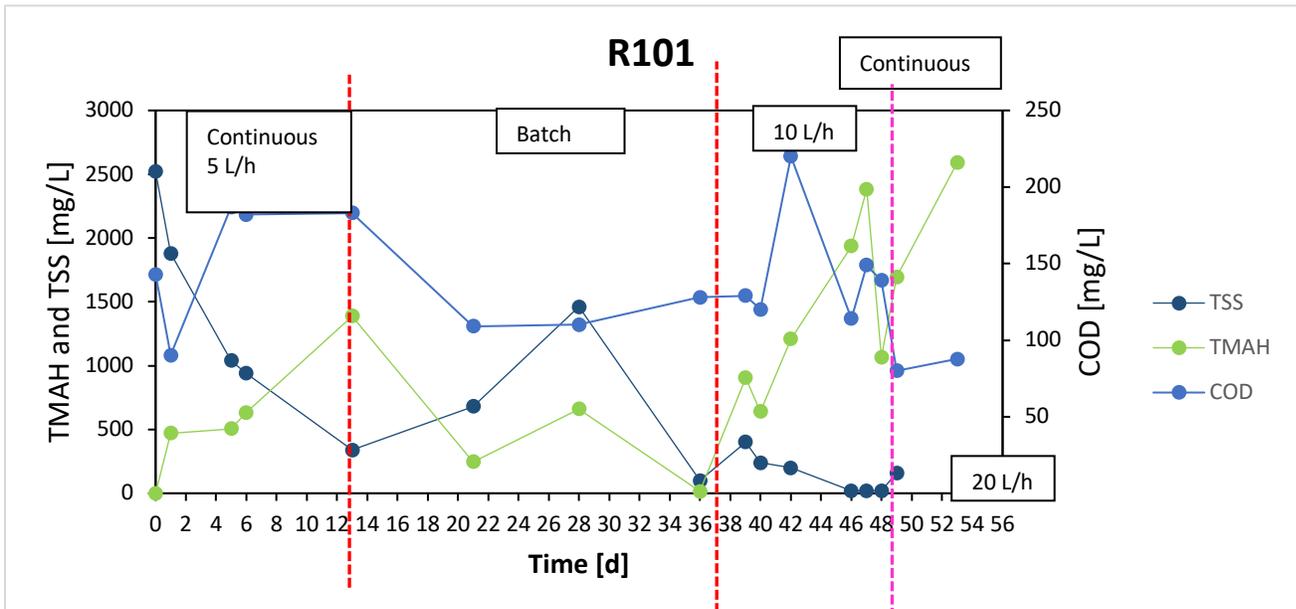
Also, for R102 and R103 the pH value decreased during the last days, in these reactors the activity of bacteria had just finished, probably for aging population and for wash out.

As it is possible to observe by the data reported in Table 3.2, as a consequence of the low activity of the biomass (TSS concentration), TMAH was not degraded and there were not present the degradation products as N-NH₄ and nitrates, hence pH decreased until acidic values.

In R101 TMAH concentration was fluctuating and it was near to zero at the end of the batch cycle, after that it increased when the flow was constant to 10 and 20 L/h and at the end of the entire cycle the concentration was near to 2.5 g/L (equal to initial concentration of TMAH in WW1). It was clear that there was low degradation of TMAH during the last days of the cycle (low activity of the bacteria). As a consequence, also the concentration of N-NH₄ and nitrates decreased.

In R102 and R103, TMAH concentration was near to zero, especially during the first days and batch operation; N-NH₄⁺ was near to 1 mg/L instead the nitrates concentrations were higher respect to the concentrations in R101: it means that the bacteria made nitrification process of the N-NH₄⁺. In the last days, the nitrates concentrations rapidly decreased as a consequence of the low activity of the bacteria.

Following Fig. shows the concentrations of COD, TSS and TMAH as a function of time.



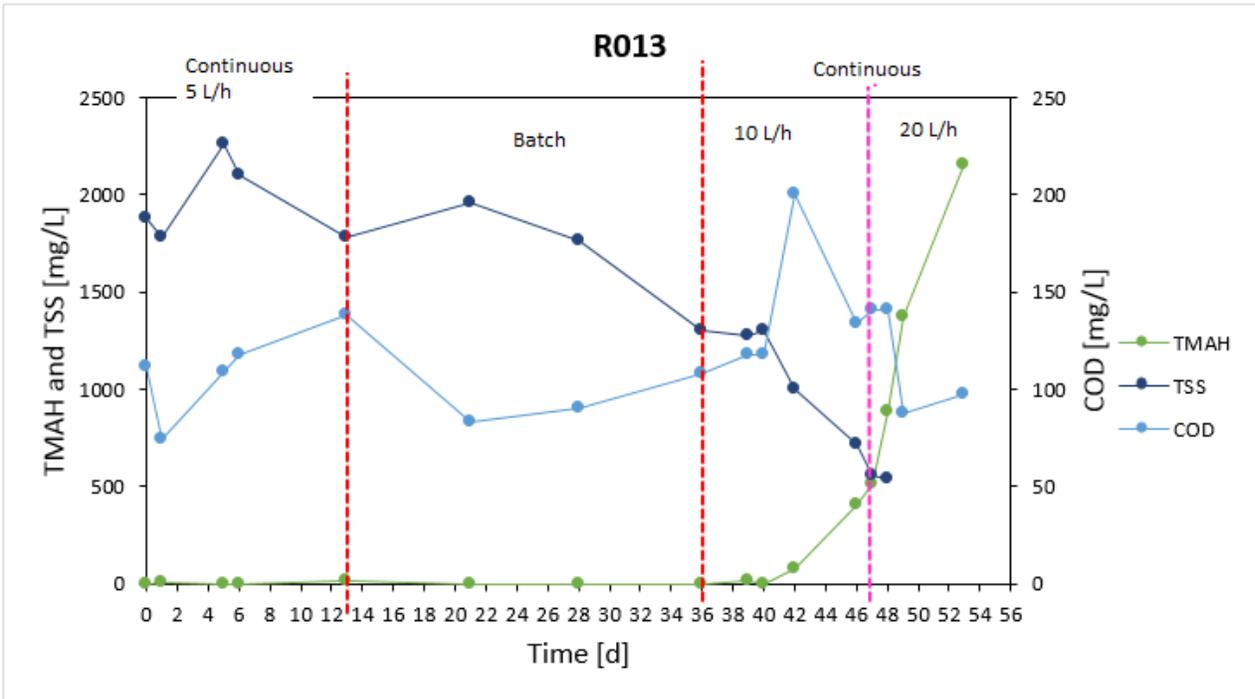


Figure 3.5: COD, TMAH and TSS as a function of time

In the first 48 hours, COD concentration decreased as a consequence of TMAH degradation; after that it increased until batch cycle in which decreased until its minimum value since there was not load pollutant (flow of WW1 equal to zero). In the last continuous operations COD concentration increased with non-regular evolution. This trend could be caused by complex activity of the bacteria that in the last period were slowing down their growth, as demonstrated also TMAH evolution. COD trends are similar for each reactor.

TSS had a downward trend: this phenomenon can be due by the severe shock suffered by the bacteria during the start – up of the plant and/or possible inhibition by substrate (TMAH) and/or products (ammonium, nitrates, ...).

3.2.1 Microbial community behavior into 3 pilot-scale reactors (October 2018 – December 2018)

To have more information about the various phenomena occurred in R101, R102 and R103, bacterial populations are analyzed to define if there are some structure and DNA modifications.

Microbial community analyzed in this work, encountered three phases between October 2018 to December 2018.

We were not able to identify all the OTUs (species) with genus taxonomy, due to unspecific reports into online databases used as template for alignment and taxonomy assignment, and the shortness of the DNA segment sequenced (300 pb). However, NGS Illumina reads data were processed to respect the proportions of OTUs and to wipe out chimeras and PCR noise, so we are confident with the correctness of community analysis.

In the first section of time, community adapted to a not very high-strength tetramethylammonium sulphate (tma-sulphate) inlet at 5 L/h.

As shown in picture (Fig 3.6), reactors 101 102 and 103 show the same proportions between the major populations of bacteria for each time interval, respectively. Usually this indicates adapted communities that survive in environments with stable conditions, such as continuously fed sludge reactors.

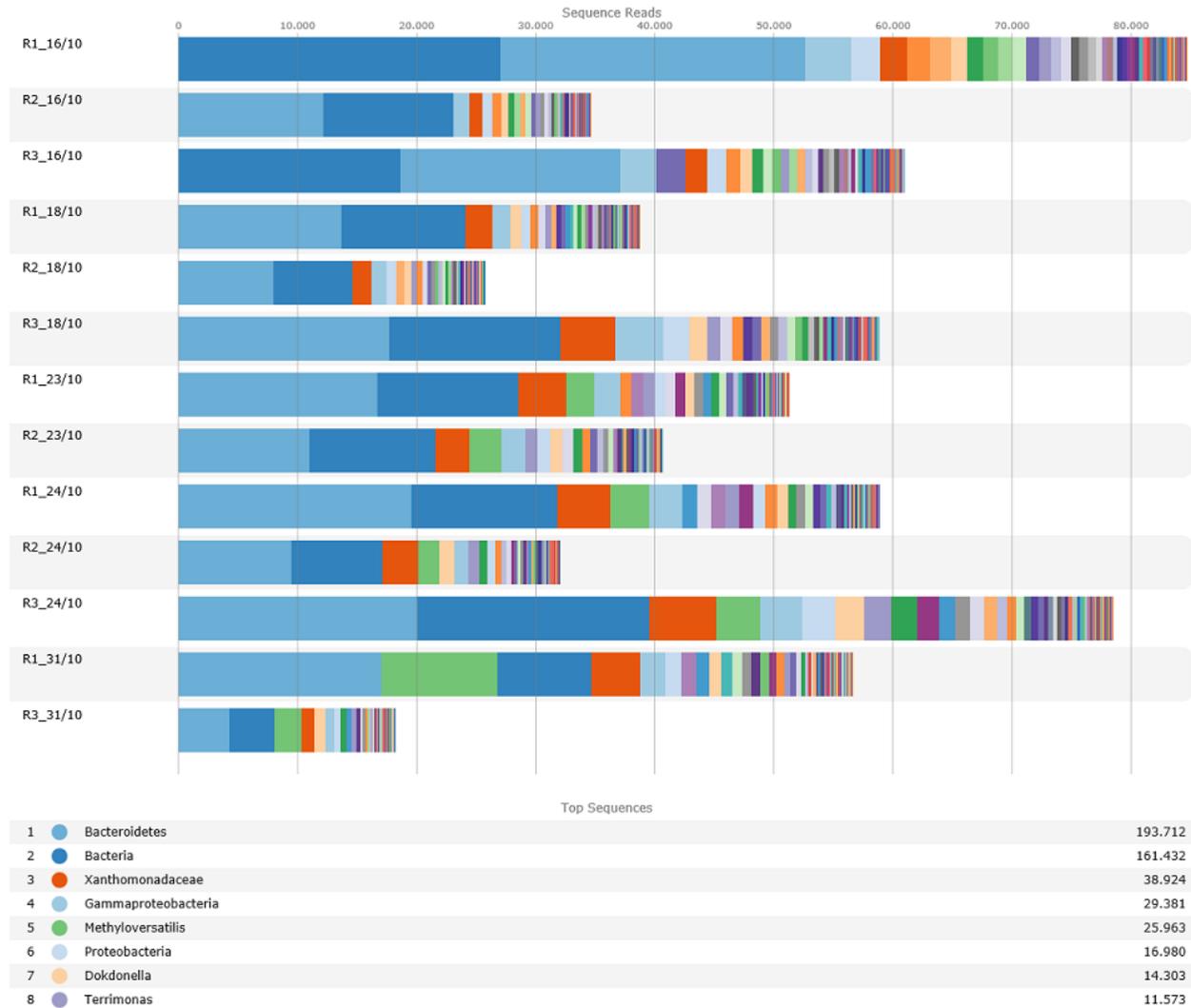


Fig 3.6: In this phase OTU 179 (Uncultured Bacteroidetes), OTU 108 (uncultured bacteria) where dominant in the community, representing at least 50% of the sequence reads in each point of time, if taken together.

Other members of the community that may have a role in TMAH abatement are Xanthomonas, gammaproteobacteria and methyloversatilis, that where present in all samples in this phase.

In the second phase, all reactors were left without inlet for 15 days. During the batch phase, from sludge biomass only the first and last day were sampled for DNA sequencing and analysis.

The community changed significantly while the TMAH was completely consumed and pH decreased from 7.1 to 4.5. This could have led to a change in adaptation to different conditions, like the toxicity of TMAH solution that was not the major selective force (Fig. 3.7).

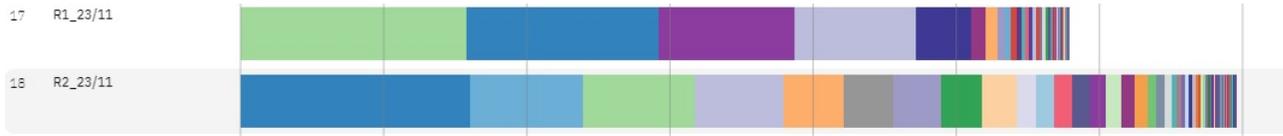


Fig 3.7: Thermomonas (light green), Mycobacterium (blue), and Rhodanobacter (grey) were dominant at the end of batch.

After the batch phase, reactors were alimented at very high rate, but microbial community totally lost the adaptation capacity and TMAH -sulphate concentrated through all reactors, because it was not consumed anymore.

The change of selective conditions could have caused the substitution of some species like Xanthomonas (known, from a previous article, to be able to consume TMAH in aerobiosis) with others like Thermomonas, that disappeared during the last phase. (Fig 3)

Dominant genera during the last phase were Dyella, Mycobacterium, and Rhodanobacter that were found in all samples. OTUs 108 and 179, like Xanthomonas, disappeared during the second phase, and there were not found in samples taken afterwards. Progressively during the last phase populations of Pseudomonas, Serratia, and Sphingobacterium, all of them known to be able to metabolize tetramethylammonium (TMAH) under particular conditions, or to be resistant to it, disappeared.

3.2.2 TMAH degradation yields

Using a file excel, TMAH degradation yields have been defined from mass balance for substrate (equation 1) in the absence of TMAH consumption:

$$F c_0 - F c = V \frac{dc}{dt} \quad (1)$$

Where

F = load of WW1 [L/h]

c₀ = Initial concentration of TMAH [mg/L]

c = Output concentration of TMAH [mg/L]

V = suspension liquid in the reactor [L]

t = time [h]

The following data are known: F = 5 L/h, Co = 2161 mg/L, 900 L. For the calculation of TMAH degradation it was chosen to work with the experimental values obtained during the first days of the continuous cycle, in that on days the bacteria had more activity than the last period.

Solving the mass balances of TMAH for each reactor (see schema reported in Fig. 3.8), it is possible to obtain the evolution C_0 , C_1 , C_2 and C_3 reported in Fig. 3.9.

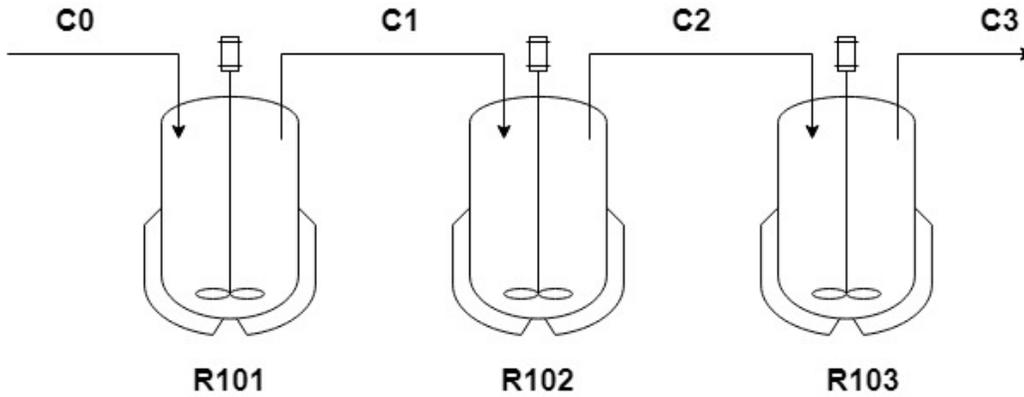


Figure 3.8: Block scheme of the bioreactors in series

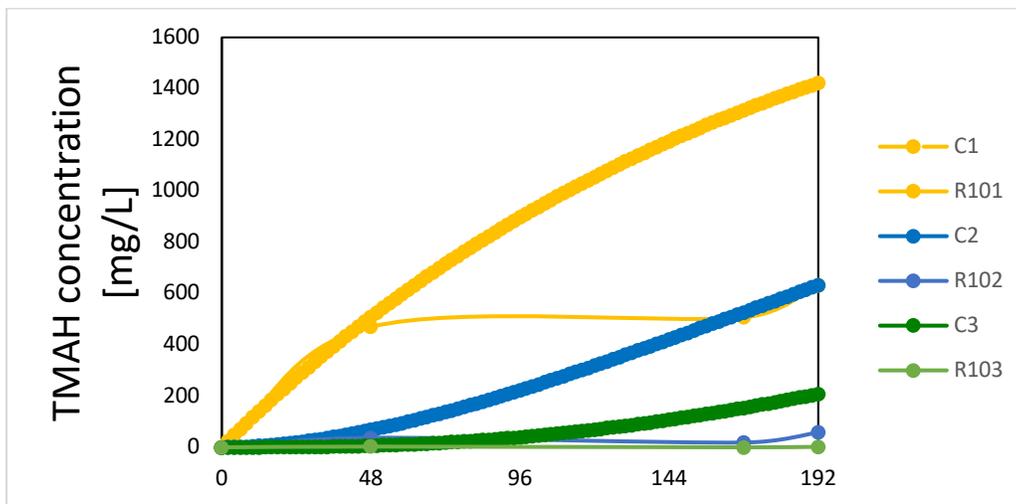


Figure 3.9: TMAH concentration obtained from simulation (C_1 , C_2 and C_3) and experimental concentrations obtained during the first cycle of experiments ($R101$, $R102$ and $R103$)

The same data were reported in Table 3.3 and 3.4.

Sampling	Time [d]	Time [h]	TMAH concentration in R101	TMAH concentration in R102	TMAH concentration in R103
16/10/2018	0	0	0	0	0
18/10/2018	2	48	470	37.1	2.84
23/10/2018	7	168	507	18.6	0.05
24/10/2018	8	192	633	58.1	2.04

Table 3.3: TMAH concentrations [mg/L] obtained during the first cycle of experiments (R101, R102 and R103)

Time [d]	C1	TMAH concentration in R101	C2	TMAH concentration in R102	C3	TMAH concentration in R103
0	0	0	0	0	0	0
2	508.30	470	67.58	37.1	6.37	2.84
7	1315.63	507	526.63	18.6	154.04	0.05
8	1421.71	633	633.14	58.1	208.18	2.04

Table 3.4: Comparison between TMAH concentrations [mg/L] obtained during the first cycle of experiments (R101, R102 and R103) and TMAH concentration obtained with simulation (C1, C2 and C3)

Using the data reported in Tables 3.3 and 3.4 it is possible to calculate the TMAH degradation yields (equation 2):

$$X_s = \frac{C_i - R_i}{C_i} * 100 \quad (2)$$

Where

C_i = TMAH concentration [mg/L] obtained by simulation in the bioreactor R10i

R_i = Experimental TMAH concentration [mg/L] in the bioreactor R10i

Table 3.5 shows the degradation yields calculated by using equation 2.

Time [h]	R101	R102	R013
48	7.53%	45.10%	55.38%
168	61.46%	96.47%	99.97%
192	55.48%	90.82%	99.02%

Table 3.5: TMAH Degradation yields (%) for each reactor

It is possible to observe that after 192 h of reaction in continuous mode (WW1 5 L/h) the degradation yields of TMAH were: 55.48%, 90.82% e 99.02% for R101, R012 and R103, respectively.

The same procedures were repeated for 10 L/h. The degradation yields after 144 h were: 22.50%, 35.78%, and 73.68%, respectively. The reduction of TMAH degradation yields could be attributed at the progressive ageing of the bacteria population.

Speciation of bacterial strains is underway, a different colour and density of the biological sludge is already visible, which seems to attest to a different type of sludge.

3.2.3 Kinetic parameters of TMAH degradation

Experimental data were used to define the kinetic parameters of the growth of bacteria. It was considered the following scheme (Fig. 3.10).

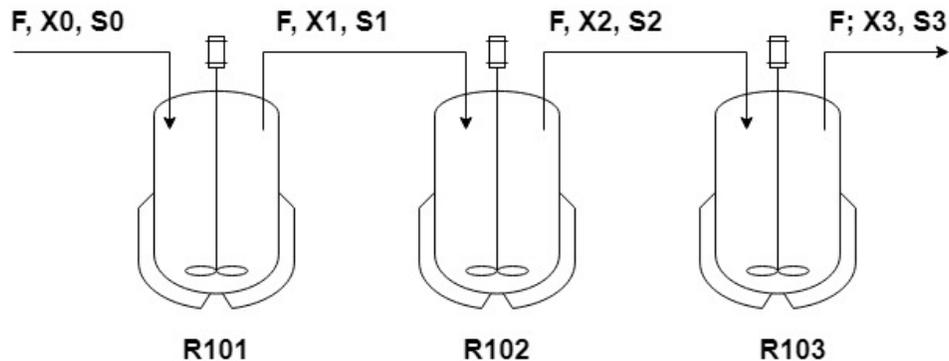


Figure 3.10: Block scheme of the bioreactors in series

It was calculated the specific growth rate (μ) performing a mass balance for the biomass at stationary conditions for each bio-reactor. After that it was assumed as growth rate the Monod equation (3):

$$\mu = \frac{\mu_{max} \times S}{K_s + S} \quad (3)$$

According to the data, Monod model (μ equation) is the kinetic model able to describe the growth of the bacteria, μ_{max} is the maximum specific growth rate of the microorganisms, K_s is the half-velocity constant. Experimental data was reported in the Fig. 3.11.

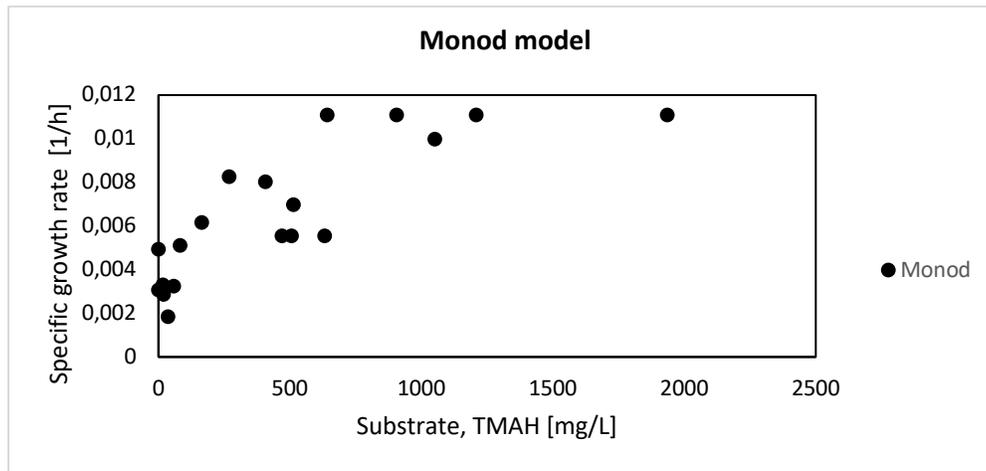


Figure 3.11: Specific growth rate (μ) as a function of TMAH concentration

From the analysis of the Fig. 3.11 it was obtained the following kinetic parameters:

$$\mu_{\max} = 0.011 \text{ h}^{-1}$$

$$K_s = 0.25 \text{ g/L}$$

These data were used to define the optimal configurations of the bioreactor at the full scale.

3.3 Third cycle of experiments (16/05/2019 – 27/06/2019)

Third cycle of plant tests was carried out at 5L/h with the aim to validate the results obtained during previous tests and selecting the best flowrate value. After was decide to improve the flowrate at 7L/h to check if it is possible to operate at higher flowrate, that allows to design smaller volume reactors.

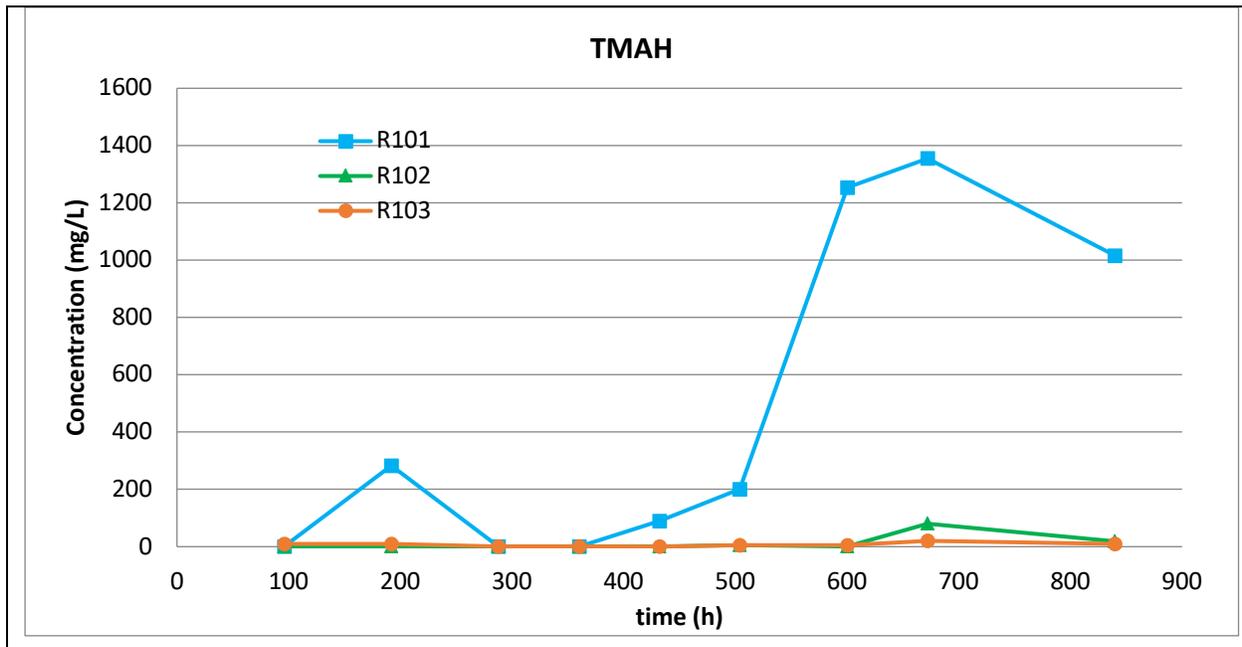
Table 3.6 and Fig. 3.12 show the results of this set of experiments.

R101								
Flowrate (L/h)	Date	Relative time (h)	TSS (mg/L)	NO3 (mg/L)	NH4 (mg/L)	N-Amm (mg/L)	COD (mg/L)	TMAH (mg/L)
5	20/05/2019	96	1854,17	2,49	7,8	6,4	163	0,483
	24/05/2019	192	1413,17	6,78	12,4	9,8	149	283,459
	28/05/2019	288	1164,68	2,3	343	267	158	0,412
	31/05/2019	360	1259,16	5,07	422	328	153	0,357
	03/06/2019	432	1314,14	2,49	432	336,4	186	88,612
	06/06/2019	504	359,74	2,76	392,4	305,2	217	199,7
	10/06/2019	600	292,51	2,67	260,8	203,2	159	1253,75
	13/06/2019	672	253,14	2,86	190	148	137	1354,82
	17/06/2019	840	275,96	3,12	139	108	126	1016,72
7	20/06/2019	24	241,95	2,75	154,5	122,5	127	1497,7
	25/06/2019	144	295,61	3,22	126	99	123	1345,94
	27/06/2019	192	343,78	2,9	71,5	55,5	105	
R102								
Flowrate (L/h)	Date	Relative time (h)	SST (mg/L)	NO3 (mg/L)	NH4 (mg/L)	N-Amm (mg/L)	COD (mg/L)	TMAH (mg/L)
5	20/05/2019	96	2646,35	56,1	33	25,7	111	0,119
	24/05/2019	192	2511,62	83,7	183,8	142,6	136	0,317
	28/05/2019	288	2733,66	126	164	128	164	0,33
	31/05/2019	360	2577,84	113	252	196,8	166	0,567
	03/06/2019	432	1616,62	68	326,8	254,4	190	0,619
	06/06/2019	504	850,84	46,2	404	315,2	194	6,11
	10/06/2019	600	916,27	12,44	460	358,4	177	0,38
	13/06/2019	672	842,39	6,1	492	384	163	80,18
	17/06/2019	840	833,99	8,75	510	395	152	17,94
7	20/06/2019	24	653,63	3,46	17,5	14	147	463,61
	25/06/2019	144	528,62	3,95	19,5	15,5	136	815,26
	27/06/2019	192	594,45	5,1	16,5	12	109	

R103								
Flowrate (L/h)	Date	Relative time (h)	SST (mg/L)	NO3 (mg/L)	NH4 (mg/L)	N-Amm (mg/L)	COD (mg/L)	TMAH (mg/L)
5	20/05/2019	96	2881,03	5,18	1,76	1,38	90,4	8,688
	24/05/2019	192	2632,85	15,3	25,7	20	96,5	10,411
	28/05/2019	288	2590,34	147	176	138	94,7	0,313
	31/05/2019	360	2976,92	167	97,4	75,8	121	0,353
	03/06/2019	432	2751,56	167	142,6	111	151	0,119
	06/06/2019	504	2855,23	147	292	228	169	5,999
	10/06/2019	600	1954,45	84,8	329,6	256,4	151	4,33
	13/06/2019	672	1453,72	74,1	382	297,2	141	20,34
	17/06/2019	840	1308,21	39,9	425	330,5	138	10,6
7	20/06/2019	24	1278,81	3,14	17,5	12,5	139	149,57
	25/06/2019	144	818,80	3,11	285	222,5	116	413,74
	27/06/2019	192	902,23	2,56	23	18	111	

Table 3.6: Results of the third cycle of experiments

These data are also reported in the following figures.



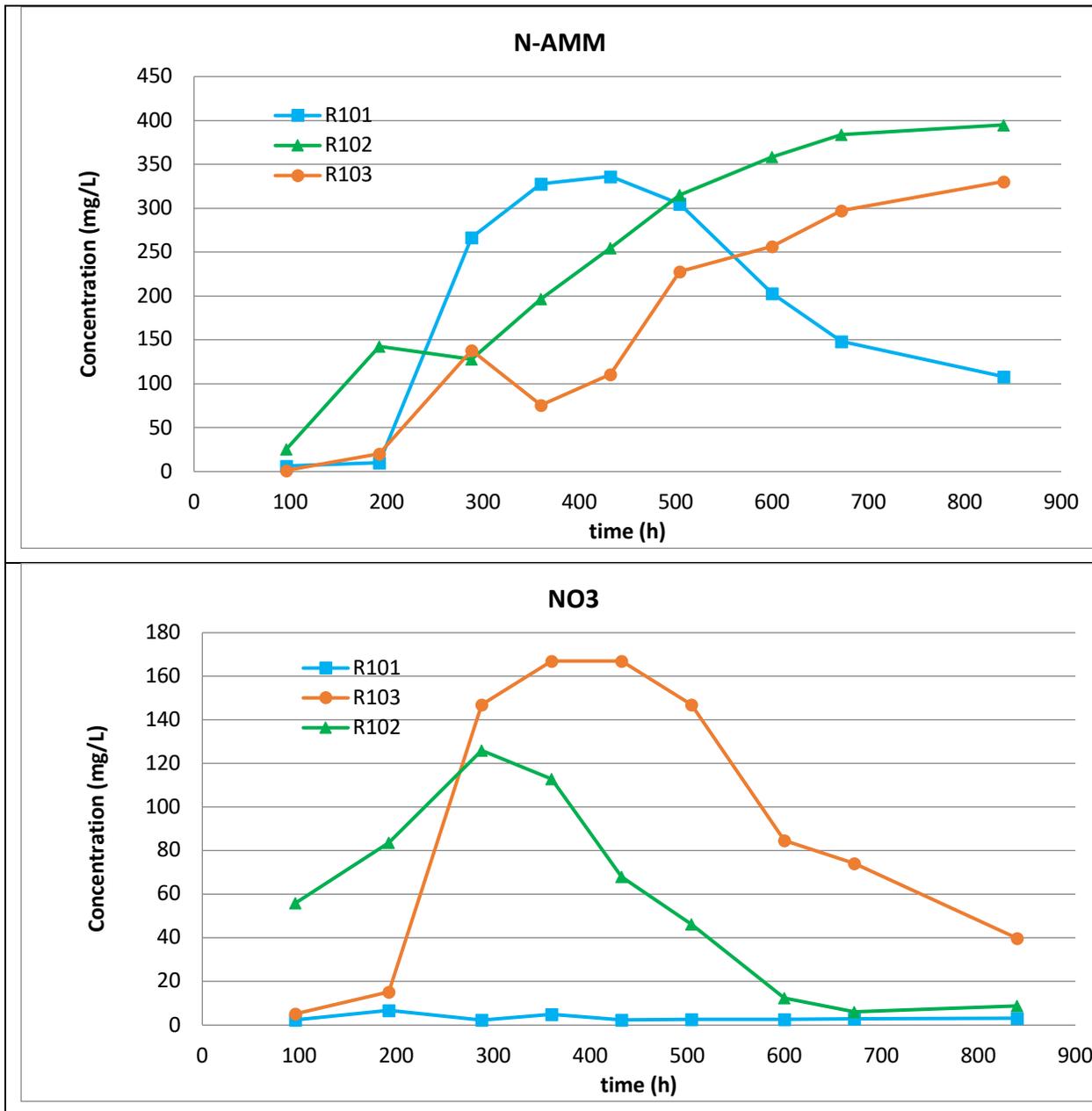
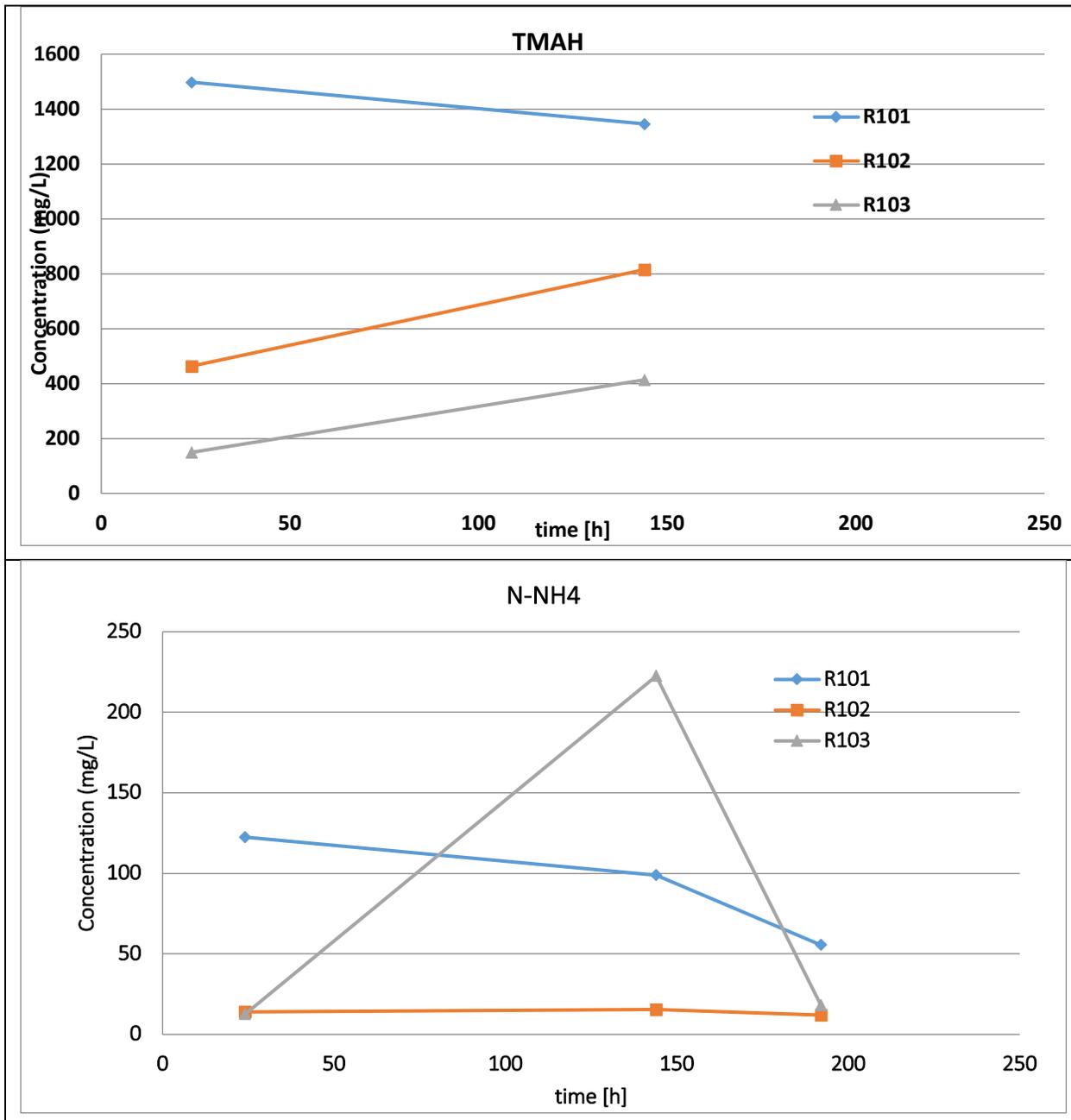


Figure 3.12: TMAH and its degradation products at flowrate of 5L/h

From the data it is possible to observe that after about 500h the biological system in the reactor R101 start to failure (see TMAH trend), but the others two reactors work like to keeping protector system able to reduce TMAH concentration under 12mg/L.



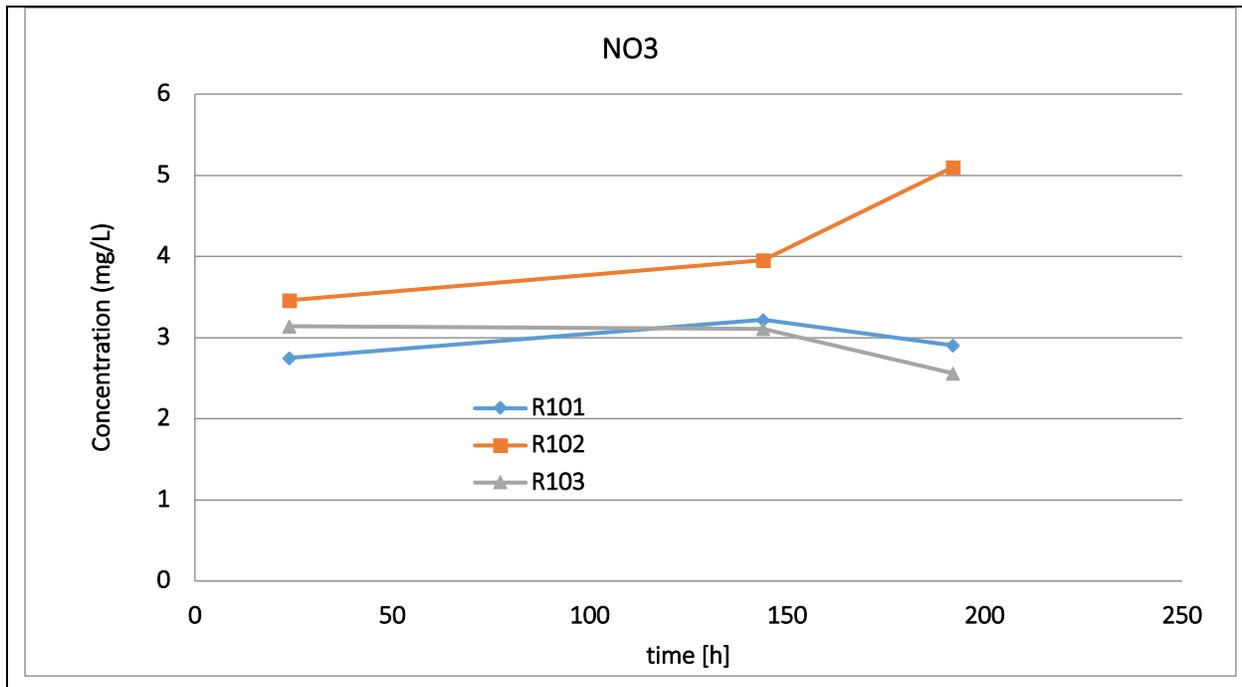


Figure 3.13: TMAH and its degradation products at flowrate of 7L/h

When the flowrate was increased to 7L/h TMAH concentration becomes to increase also in the last two reactors and the test was interrupted.

Probable, it is possible to justified biological system failure by microorganism suffering due to carbon deficiency; in fact during the tests no additional source of carbon was added. It is possible to hypothesize that in the initial phase the system is not affected by the lack of carbon since the adaptation of the sludge to the new diet leads to the death of many bacterial strains, establishing a necrophilic metabolism (dead cells represent the additional source of carbon).

The adaptation to TMAH feed results in a decrease in the concentration of sludge; this means that with time the system will reach a condition in which the carbon coming from necrophilic metabolism will not enough to compensate the lack of carbon in the feed, so biological system failures.

Fig. 3.14 reports the pH value during the whole cycle.

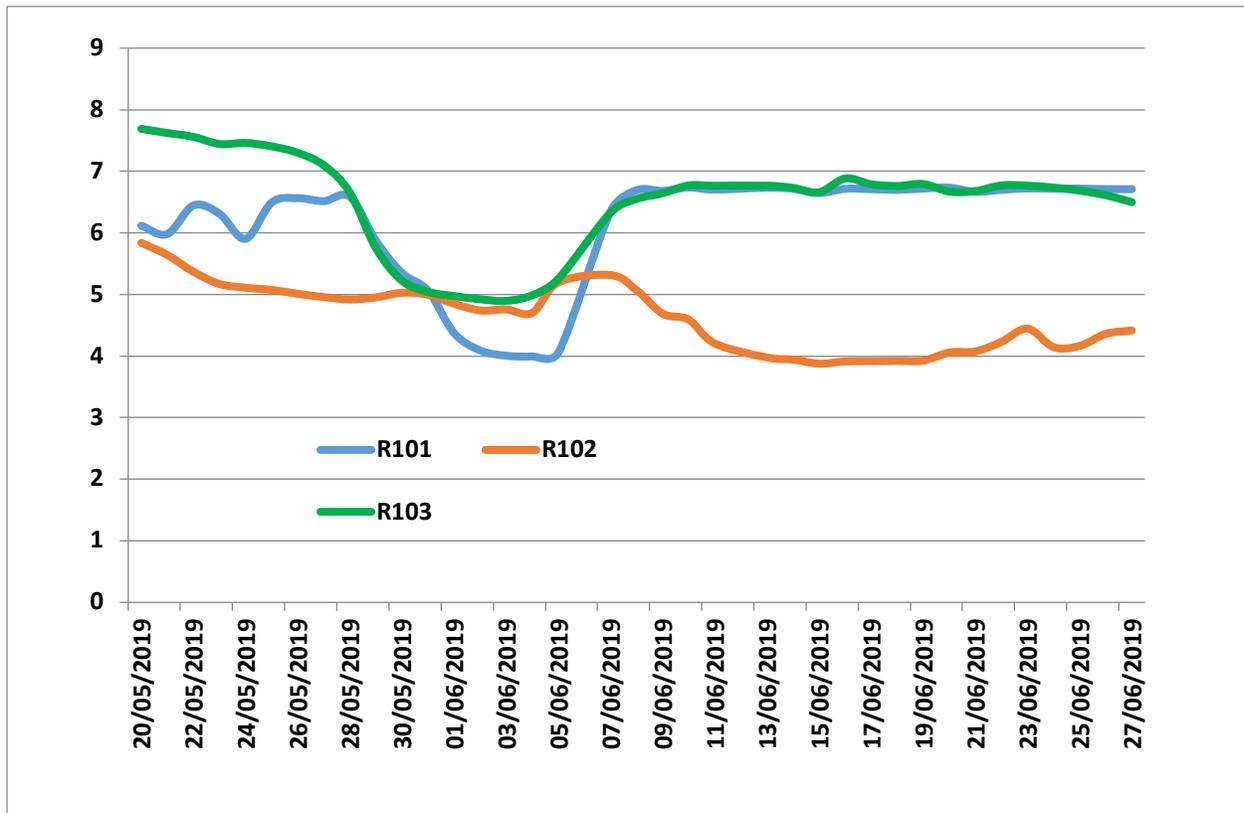
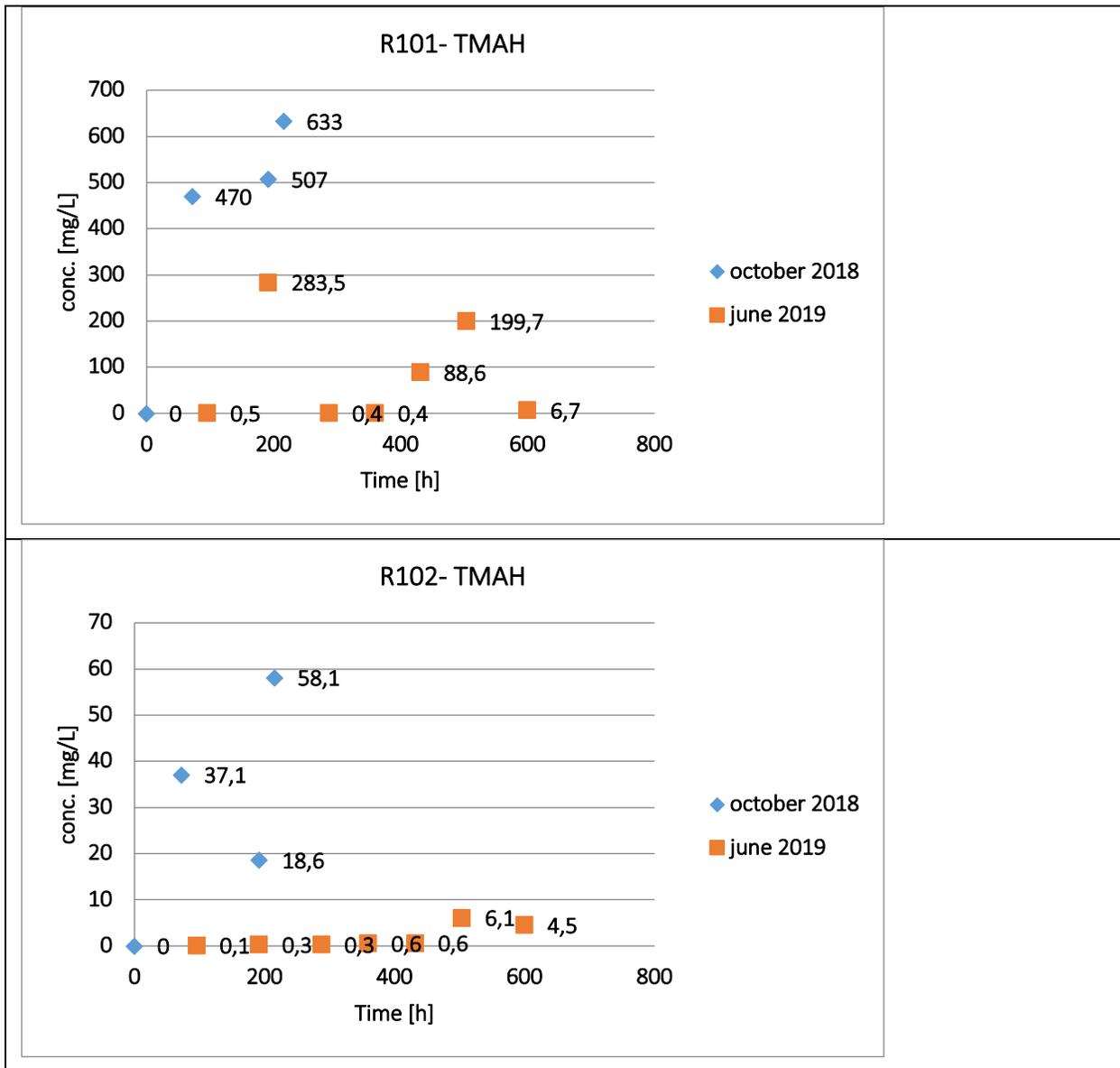


Figure 3.14: pH value for R101, R102 and R103 (from 19/06/2019 the system was fed at 7L/h)

pH trends in the reactors R101 and R103 are quite similar, they present a deviation for about one week (decrease and after increase), then the value becomes constant around to 6.8. Whereas, pH values in reactor R102 are lowest then the values measured in the others reactors.

To conclude, from the comparison of the tests at 5L / h conducted in October 2018 and June 2019, a first observation to make is that: despite the thermostat control system, the average temperature in biological reactors, during the 2018 tests, was below 20 ° C, while in tests conducted in June 2019 the temperature was on average around 25 ° C (optimal temperature according to laboratory data).

The following graphs show the concentration values of TMAH vs time in the three reactors for the two series of tests.



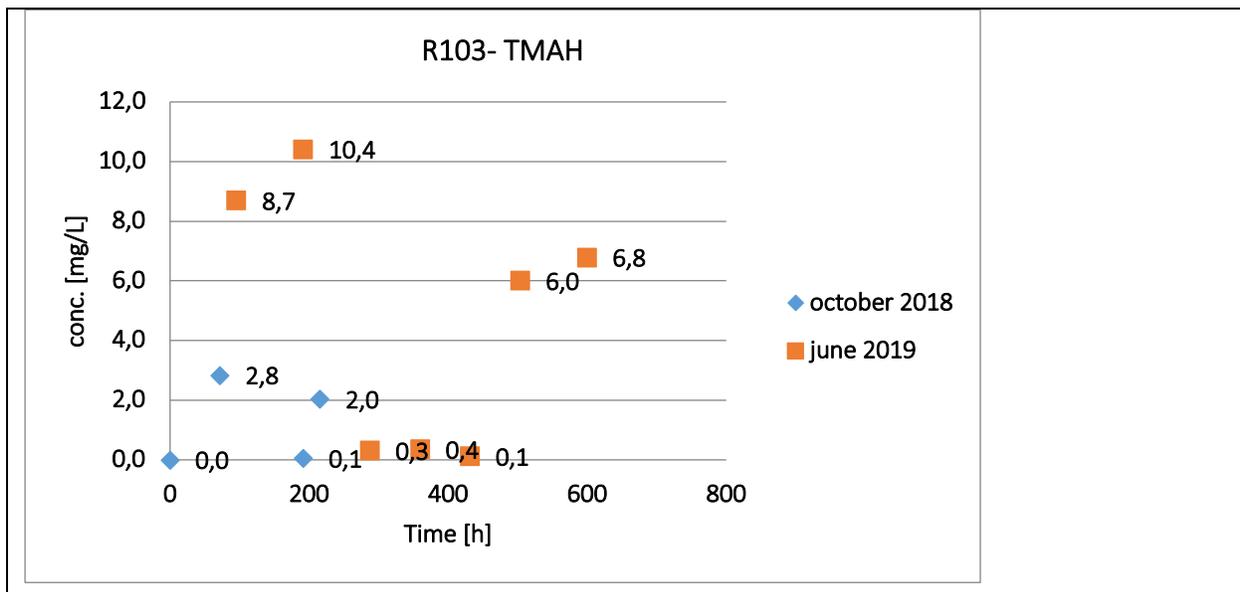


Figure 3.15: TMAH concentration trend for the treatment at 5L/h carried out in October 2018 and June 2019.

Observing the data, it is possible to see that generally TMAH concentrations in R101 during the June test are lower than the values obtained in October. This result confirms that the flow rate of 5L/h guarantees a residence time in the reactor such as to allow the biomasses both to adapt and, consequently, to degrade the amine molecule, but on the other side it shows that the higher temperature at which the system operates has a positive effect by improving the removal yield. The same observation can be applied to the reactor R102.

About the data collected on the reactor R103, some anomalies are highlighted, in fact in the time frame in which the two series of tests are directly comparable it would seem that the system presents higher concentrations of TMAH in the June tests, these data (i.e. 8.7 mg/L and 10.4 mg/L) are in conflict with the data of R102, in that at the same "time instant" of sampling and, above all, in the initial phase of the process (the average residence time in the reactors is equal to 6.6 days) it would seem that the concentration of TMAH in R103 is greater than that in R102. This result is inconsistent, in fact, independently to the TMAH degradation process, due to the dilution effect, the concentrations in R103 should be lower than those in R102, probably the TMAH measurement presents interferences that have determined values affected by a high error.

As done with previous data, (see paragraph 3.2.2), in the following graph the experimental data were compared with the data calculated from a descriptive model of the system in the absence of reaction (biological degradation).

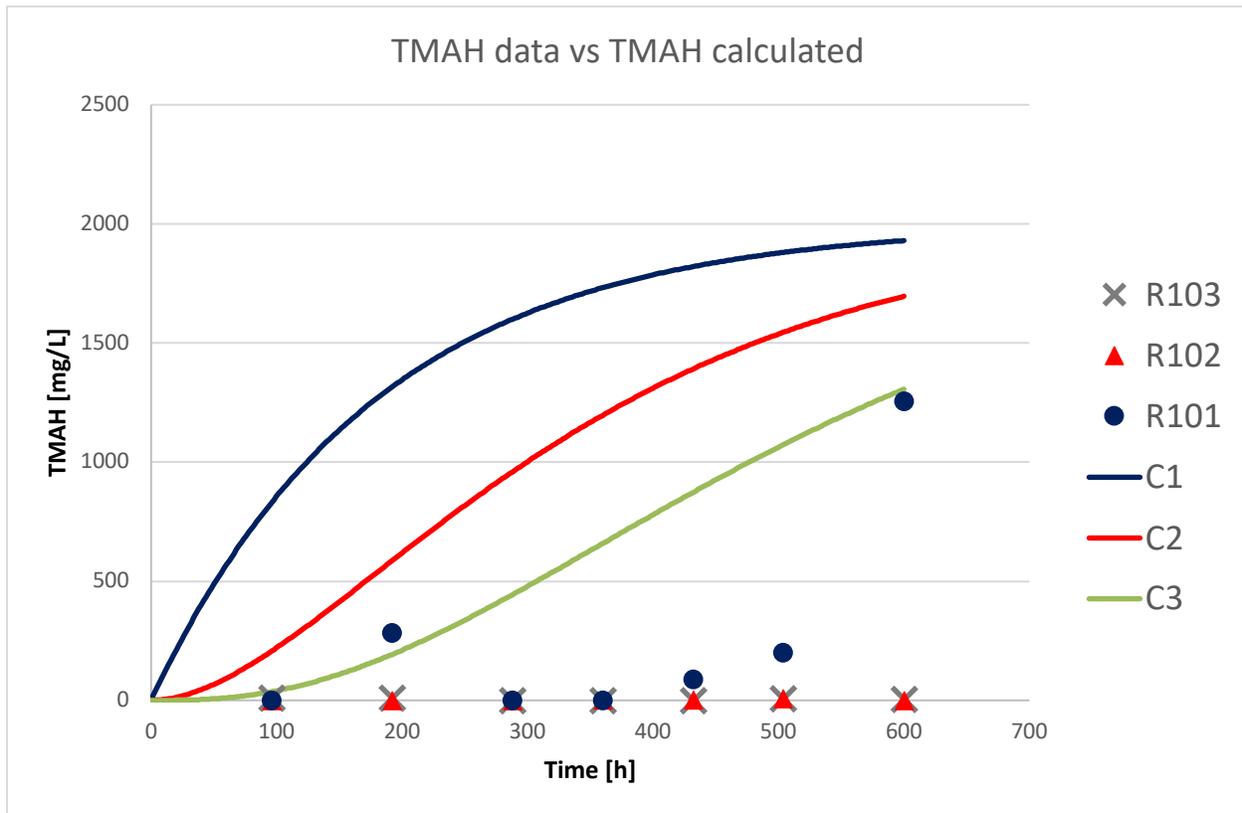


Figure 3.16: TMAH concentration obtained from simulation (C1, C2 and C3) and experimental concentrations obtained during the first cycle of experiments (R101, R102 and R103)

It is possible to observe that the experimental values are below the "model" curves; this comparison is useful to understand if a "reactive" process (degradation) happens in the reactors and to carry out an evaluation of the degradation yield by deducting the dilution effect.

By the comparison between data coming model and plant tests, it is possible to conclude that a degradation process takes place (as previously stated) and therefore concentrations lower than 2000mg/L (average TMAH concentration value of the plant feed) are due to the TMAH degradation.

The following table shows the yield values, calculated with respect to the simulation data.

During this experimental campaign TMAH removal yields of about 99% were obtained, confirming the previous results. Therefore, it is possible to conclude that the process carried out at flowrate of 5L/h is validated, furthermore, during these tests it was demonstrated that the temperature increment leads to an increase in the biological system kinetics. The bacterial flora also showed the same behavior as the previous test, or rather, the change in the concentration of sludge in the three reactors (increasing from R101 to R103), as well as their coloring, both phenomena indicate an adaptation and a different specialization in the three reactors.

About the other measured parameters (COD, N-amm, and Nitrates), all reactors are shown concordant values (for the overlapping period of time) with the previous ones. It should be emphasized that: in the tests conducted in June 2019, for times greater than 200h, an increment of the N-amm concentration was detected, this is one of the degradation products of TMAH, therefore its increment is an indication of the increase of the degradation kinetics of TMAH or, also, the degradation of the by-products of TMAH (like

dimethyl- or methyl-amine) in R101. The same trend was not highlighted in the previous tests, probably because it was interrupted after 216h.

Time (h)	Model Data [mg/L]			TMAH Removal Yield		
	R101	R102	R103	R101	R102	R103
96	830,20	206,31	36,48	99,9%	99,9%	76,2%
192	1315,79	585,96	192,67	78,5%	99,9%	94,6%
288	1599,81	959,50	443,69	100,0%	100,0%	99,9%
360	1732,34	1197,03	658,74	100,0%	100,0%	99,9%
432	1820,99	1391,35	873,40	95,1%	100,0%	100,0%
504	1880,27	1545,03	1073,83	89,4%	99,6%	99,4%
600	1929,97	1696,54	1306,19	99,7%	99,7%	99,5%

Table 3.7: TMAH removal yield with respect to theoretical value

3.4 Treated TMAH wastewater disposed to the WWTP

In this section, it has been reported the simulation of the WWTP of LFoundry with the aim to define the final concentration of TMAH output from biological plant. Fig. 3.17 shows the block scheme of the WWTP that which receives 25 L/h of treated WW of TMAH.

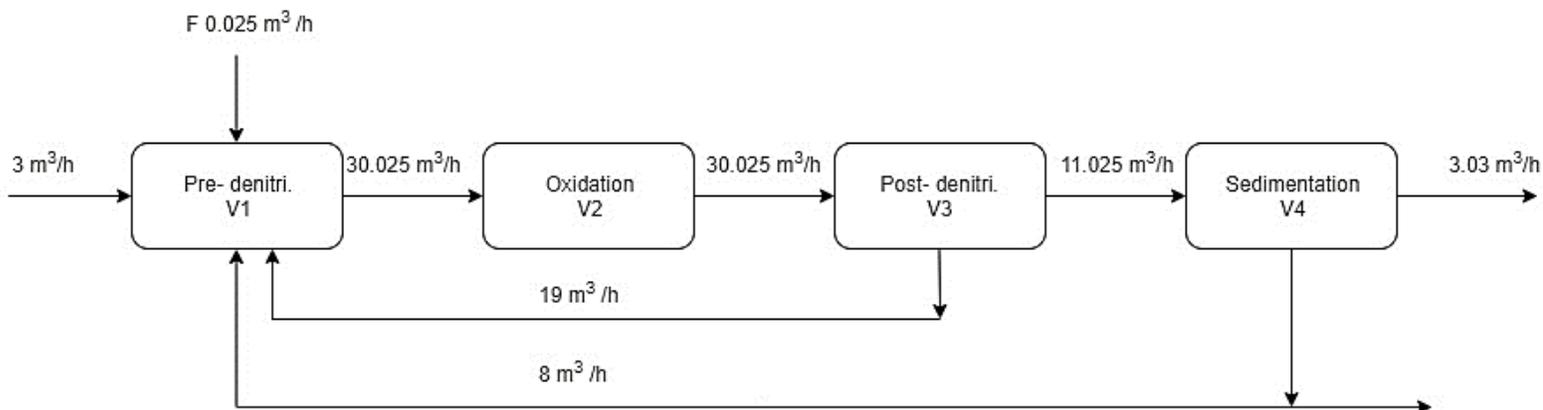


Figure 3.17: Block scheme of WWTP of LFoundry site

F is the output of the pilot plant with an average concentration of TMAH equal to 34 mg/L (from TK203, experimental data obtained during the tests with 5 L/h). Fig.3.18 shows the results of the simulation considering that batteries of WWTP do not degrade TMAH (conservative assumption). The final concentration of TMAH was less than 0.03 mg/L (law limit of 7 mg/L).

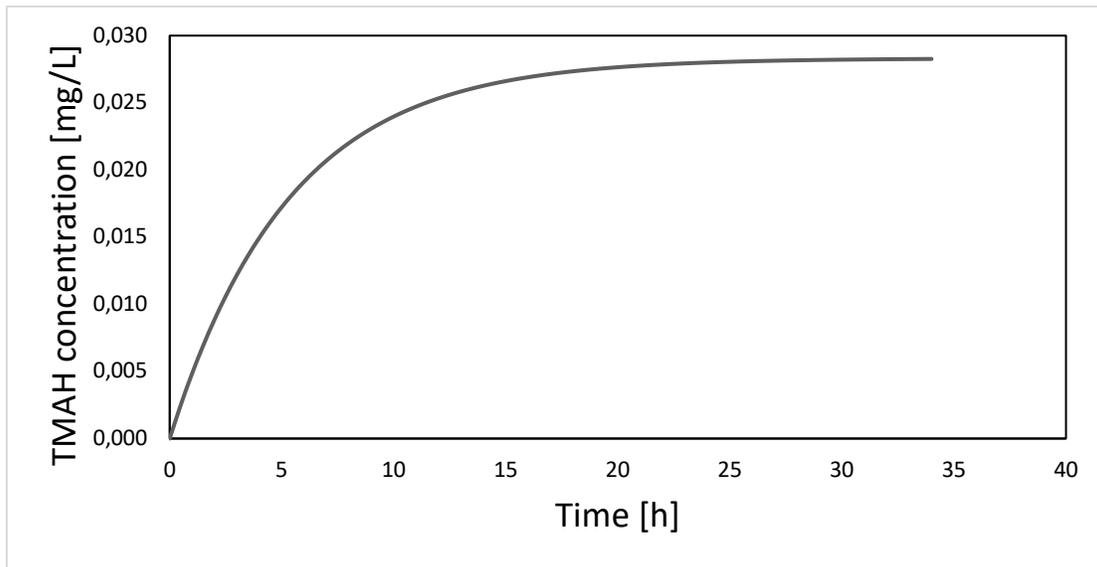


Figure 3.18: Simulation of TMAH concentration as a function of time for WWTP

3.4.1 Effect of treated wastewater on the LFoundry depuration plant

The potential effect of treated WW on the biological system of depuration plant, present in the industrial site, was preliminary evaluated by tests carried out on lab scale reactor. Experimental system and experimental design were projected to simulate the real plant, reactor was loaded with sludge (5L) coming from LFoundry oxidation basin and feed with effluent coming from industrial plant (civil WW) and effluent coming from pilot plant (after treatment). Table 3.8 report the three different feed tested.

Test N°	TMAH WW (mL)	SEZ WW (mL)	BOE WW (mL)	Civil WW (mL)
1	130	3	10	500
2	286	6.6	22	550
3	430	10	33	550

Table 3.8: Composition of feed to biological reactor to simulate WW plant

Test N° 1 was carried out preserving the actual volume ratio of the four effluents in the industrial site; the other two tests were carried out at higher volume ratio with the aim to evaluate the effect of highest flow-rate on the biological system. These tests have also the goal to appraise the strength of the system in the case of an increase in production.

Samples were periodically collected to measure COD, sulphate, nitrate, fluoride and ammonium. The following tables report these data.

time (h)	SST (mg/L)	SO4-- (mg/L)	NO3 (mg/L)	F- (mg/L)	NH4 (mg/L)	COD (mg/L)
0,00	4,00	35,6	41,4	3,54	0,152	278
2,00	4,27	42,6	60,7	1,16	0,05	207
3,50	-	-	36,3	-	-	-
5,50	4,20	45,9	66,2	0,348	0,837	72,1
6,50	-	-	77	-	-	-
22,00	4,03	45,7	120	0,297	0,042	55,6
23,00	-	-	125	-	-	-
25,00	-	42	120	0,257	0,011	50,7
26,00	-	-	127,5	-	-	-
28,67	-	-	115	-	-	29,8
29,67	-	-	24,75	-	-	-
47,50	4,23	40,5	1,05	0,562	0,045	38,7
60,47	4,67	0	0	0	0	35

Table 3.9: Results of test N°1: solid concentration and concentrations of the mains factors of interest

time (h)	SST (mg/L)	SO4-- (mg/L)	NO3 (mg/L)	F- (mg/L)	NH4 (mg/L)	COD (mg/L)
0,00	3,73	101,00	126,50	0,35	0,03	110,00
2,75	3,60	101,00	100,00	0,40	0,02	114,00
2,75	-	-	-	-	-	131,80
3,92	-	-	45,80	-	-	178,00
71,75	3,80	85,30	150,50	0,29	-	33,70
71,75	-	-	-	-	-	105,80
73,50	-	-	31,50	-	-	-
75,25	4,20	106,00	32,70	1,16	0,02	84,30
95,25	5,00	89,50	106,50	0,34	0,10	33,70

Table 3.10: Results of test N°2: solid concentration and concentrations of the mains factors of interest

From the data it is possible to observe that in the test N°1 the biological system is able to tolerate the presence of other wastes in the feed. When the ratio of other WW with respect to civil WW is duplicated biological system react correctly, in terms of COD degradation, whereas about sulphate concentration it is possible to observe that it increases. If the flowrate of others WW is triplicate with respect of civil WW the biological degradation efficiency decreases, this probable means that the sludge it not able to tolerate some compounds, present in these additional WWs, in the amount added. Also the COD trend (see fig. 3.19) in the test N°1 is more regular respect to others.

This is more evident if compare the slope ($\Delta\text{COD}/\Delta t$) vs time of the three experiment (see fig. 3.20)

time (h)	SST (mg/L)	SO ₄ ⁻⁻ (mg/L)	NO ₃ (mg/L)	F- (mg/L)	NH ₄ (mg/L)	COD (mg/L)
0,00	3,33	163	269	0,333	0,006	139
2,75	3,50	158	271,5	0,398	0,02	53,5
2,75	-	-	-	-	-	202,8
3,75	-	-	157	-	-	274
6,00	3,53	155	58,5	1,28	0,009	146
23,50	3,70	150	79	0,543	0,025	85
24,00	-	-	-	-	-	235,8
25,17	-	-	45,45	-	-	-
26,75	3,87	148,6	34	1,41	0,175	285
71,50	4,40	147,8	84	0,38	0,032	63,6
72,16	-	-	-	-	-	185,8
74,33	-	-	20,4	-	-	339

Table 3.11 Results of test N°3: solid concentration and concentrations of the mains factors of interest

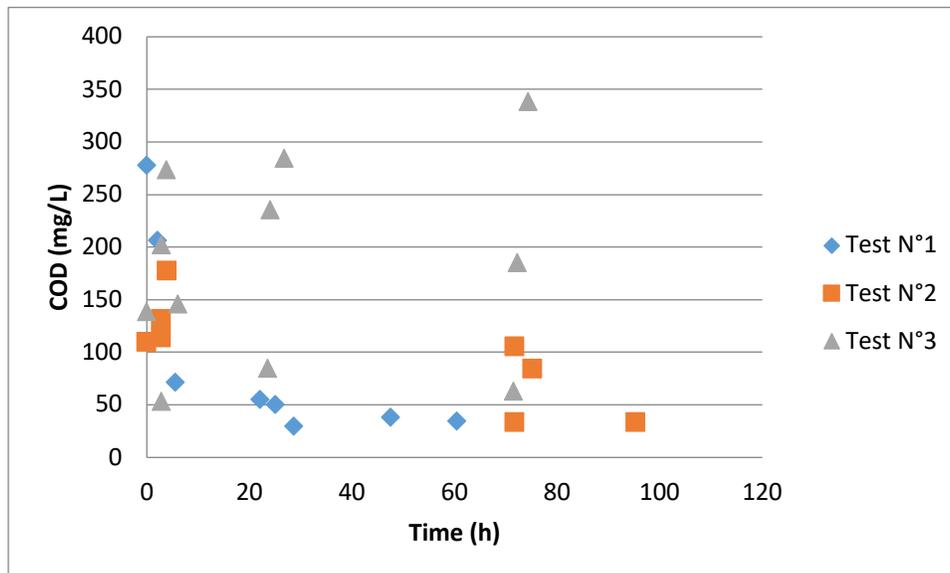


Figure 3.19: COD concentration evolution in an activated sludge reactor

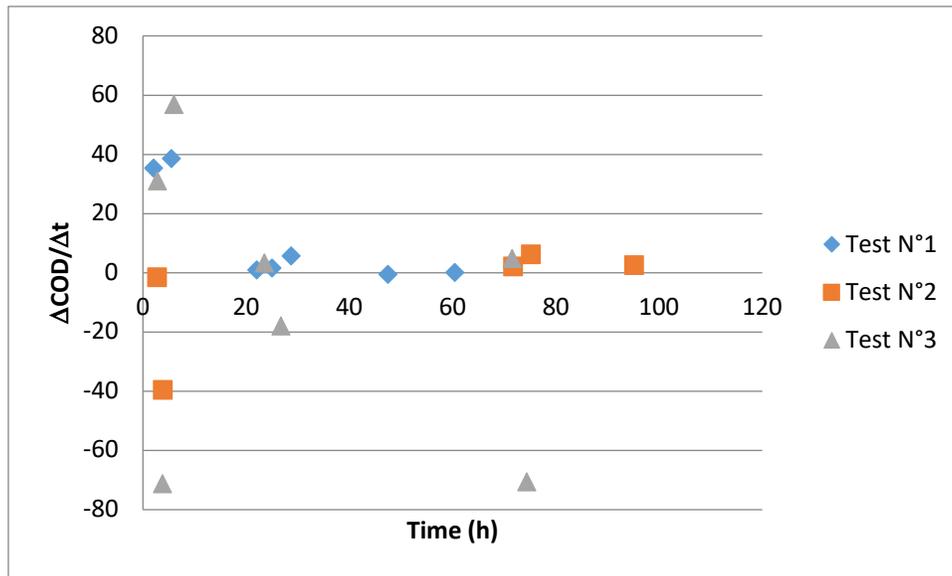


Figure 3.20: $\Delta\text{COD}/\Delta t$ concentration evolution in an activated sludge reactor

4. Scale up from pilot plant to industrial plant (TMAH)

Several configurations have been tested in order to define the optimal configuration of the full-scale plant to bio-degrade TMAH contained in WW1. It was assumed a flow of 800 L/h and for design the kinetic parameters found in the previous section were considered.

Table 4.1 shows the results of the simulations.

Configuration	Useful volume (80%) of the total volume
Single bio reactor	982 m ³
Single bio reactor with partial recirculation of bacteria	196 m ³
Bioreactors in series	R101 = 80 m ³ R102 = 59 m ³ R103 = 35 m ³ Vtot= 174 m ³
Bioreactors in series with partial recirculation of bacteria in R101	R101 = 29.50 m ³ R102 = 30.62 m ³ R103 = 29.41 m ³ Vtot= 89.52 m ³

Table 4.1: Results of the simulation for the design of the full biological plant to degrade TMAH in WW1

From results of the Table 8 it is possible to observe that to have a removal of around 99% of TMAH (0.02 g/L TMAH) contained in WW1 can be used:

- single bioreactor with a volume of 982 m³;
- bioreactor with partial recirculation of bacteria the volume is 196 m³ (volume reduction of 80%);
- three bioreactors in series with a total volume of 174 m³ (volume reduction of 82%);
- three bioreactors in series with partial recirculation of bacteria in R101, total volume of 89.52 m³ (volume reduction of 90%)

It has been chosen the fourth alternative to perform a simulation with SuperPro Designer.

5. Results and discussion on SEZ and BOE treatments

A pilot-scale experiment was performed in a pilot plant, which was composed of chemical reactors, filter press and scrubber, built at LFoundry. BOA and SEZ wastewater were pumped into the pilot plant, passed through the all process steps.

In detail, each wastewater was treated in the reactor, under mixing, with aluminium sulphate and lime (about 16%w/w). Lime was added gradually until to reach pH value around the optimal range value estimated during lab-scale experiments (pH=4.4-5.4 and pH=11.2-11.4 for SEZ and BOE respectively).

Reached the optimal pH value, the system is left to react, under constant stirring, for about 2h.

Suspensions, after completing the process, are sent to the filter press.

Results of pilot plant tests are presented in the Tables 5.1÷5.4, XRF of obtained precipitate after filter press are presented in the table 5.5 (main element detected).

Date	pH		Volume of wastewater, L	Reagent consumption, kg	
	initial	final		Al ₂ (SO ₄) ₃	Ca(OH) ₂ , 16%
24/09/18	1.5	4.5	102.14	3.00	200.0
8/11/18	1.5	4.9	99.10	3.04	95.4
15/11/18	1.5	5.2	101.3	3.00	144.3

Table 5.1: Reagent consumption for SEZ treatment

Date	Waste water		Precipitate, %					
	F, mg/L		Water content	Ca	Al	Na	P	S
	initial	final						
24/09/18	20600	7.8	65.5	62.1	3.5	6.8	19.2	7.7
8/11/18	16400	9.6	56.4	58.5	4.6	6.8	19.4	10.1
15/11/18	17500	5.1	55.7	62.4	2.1	7.7	23.4	3.8

Table 5.2: Wastewater SEZ parameters before and after treatment

About SEZ treatment, Fluoride removal Yield is greater than 99% in all treatments. About lime consumption (see table), it is possible to assert that this value is hard connected to the age of the lime (more is old, more is the consumption), due to loss of activity.

Date	pH		Volume of wastewater, L	Reagent consumption, kg	
	initial	final		Al ₂ (SO ₄) ₃	Ca(OH) ₂ , 16%
04/10.18	4.8	11.8	100	4.0	182.8
15/10/18	5.3	9.2	105	4.0	120
31/10/18	5.4	9.9	94.3	4.0	89

Table 5.3: Reagent consumption for BOA treatment

Date	Wastewater					Precipitate, %				
	F, mg/L		PO ₄ , mg/L		NO ₃ , mg/L	Water content	Ca	Al	P	Na
	initial	final	initial	final						
04/10.18	97	5.3	245	0	29000	48.1	91.7	1.9	4.8	1.1
15/10/18	418	4.6	333	0	762000	51.2	90.4	2.5	5.2	1.2
31/10/18	25700	9.9	380	0	16500	53.4	90.9	2.2	5.0	1.4

Table 5.4: Wastewater BOE parameters before and after treatment

About BOE, from the data of initial characterization is evident that this effluent show high variability with respect of fluoride and nitrate concentration, also in this case lime consumption is connected to the age of the reactant, moreover it depends also from the initial composition

Average mass of the precipitate after filter press according lab-scale tests were **221.4 kg/m³** (water content 55%) for SEZ wastewater and **162 kg/m³** (water content 50%) for BOE wastewater.

Elements	Na	Al	P	S	Ca
BOE	0.23%	0.40%	0.04%	1.00%	19.10%
SEZ	1.64%	0.85%	4.64	1.86%	14.97%

Table 5.5: Solid cake characterization by XRF analysis

Solid residuals have also been characterized for landfill disposal, this analysis have showed that these wastes are not dangerous.

6. Operational problems and recommendations for the industrial plant

The tests carried out on a pilot scale plant have also the purpose to evaluate any technical problems that may occur on this type of system.

About biological system, the main problems detected are been:

- 1) Clogging of piping and pumps due to microorganism proliferation. This phenomenon is happens particularly after a period of process stop, because of fluid in static condition inside the piping.
- 2) Fouling or growth of bacterial agglomerates occurs inside the reactors.

About physical-chemical section of the plant, the main problems detected are been:

- 1) Malfunction of the load / transfer pump of the SEZ due to the presence of hard rubbery material inside the pump. This material derives from the residual of WW remained inside the equipment after one test.
- 2) Lime precipitation inside the pipe that feed the reactor (pipe clogging).
- 3) High ammonia emissions during the filtration phase (treatment of WW2)
- 4) Corrosion of pH probe.
- 5) Foam formation (treatment of WW3).

From these observations mains recommendations for the industrial plant are:

- 1) The pipes of the biological section must be sized to allow that they can be easily inspected and cleaned.
- 2) Pump section must be sized so that they can be easily inspected and cleaned, or adopt pumps capable of processing suspensions.
- 3) Predict periodical cleaning cycles.
- 4) A solid/liquid separation system will be necessary to separate biological sludge from the treated water.
- 5) A system to charge an additional carbon source (photoresist or other) will be necessary.
- 6) Installation of level control.
- 7) Protection on the pump that transfer TMAH from the equalization reactor to feed the tank.
- 8) Pumps, in which the SEZ flows, must be work continuously or must be clean always after a stop.
- 9) Lime must be stored in a tank with mixer.
- 10) The emission aspiration system must be properly designed.
- 11) Charge of aluminium sulphate must be automated.
- 12) A foam breaking system must be present on the chemical-chemical reactor.
- 13) To limited pH-probe corrosion it is necessary provide an automatic mechanical system that dips and removes periodically pH-probe from the reactor, moreover, at each cycle pH-probe must be clean.

7. Chemical usage, capital and operation and maintenance costs in view of full scale size

During the experiments campaigns carried out on pilot plant the following compounds have been used:

- Sulfuric acid (50%w/w);
- Aluminum sulphate;
- Lime solution (16%w/v)

Aluminum sulphate and lime have been used in the treatment of SEZ and BOE, whereas sulfuric acid has been used in the treatment of TMAH (acidification of effluent) and in the scrubber basin (treatment of emissions).

The following table reports specific chemical consumption respect to: unit mass of wastewater treated (WW1, WW2 and WW3) for the treatments; the amount of water in the scrubber basin and number of solution make-up for the scrubber.

	Ca(OH)₂, 16% (kg/kg of WW)	Al₂(SO₄)₃ (kg/kg of WW)	H₂SO₄ 50% (kg/kg of WW)	H₂SO₄ 50% (kg/kg of H₂O/n° of make-up)
WW1			0.002	
WW2				
WW3	1.5	0.03		
Scrubber				0.07

Table 6.1 Chemical Reagents Consumption

During the experimentation, water make-up of the scrubber was not necessary, because the number of experiments carried out and, consequently, the amount of emissions was not sufficient to exhaust the acid. From theoretical calculation, it is possible to assert that scrubber water make-up will be necessary every 15 treatments of BOE (this is the effluent that present the highest problems of emissions, calculation with respect to this WW allows to have a conservative value).

8. Environmental performance and regulation prescriptions

Environmental performance is fundamental to meet the prescriptions given by the authorization of the plant and also a significant indirect component in order to demonstrate the cost effectiveness of the proposed solution when comparing it with other plants adopting different technologies.

The authorization to put into operation the Lif-BitMaps pilot plant was issued by the Authority with the communication “AIA n. 238/38 del 28/12/2015 – Ditta LFoundry S.r.l. – Riscontro a parere ARTA su comunicazione di modifica non sostanziale per installazione impianto TMAH del 20/10/2017 “ of the 2/22/2018.

Relevant regulation prescriptions expected by the authorization are focused on the monitor and control of the follow environmental matrices and topics:

- Air Emissions
- Water emissions
- Waste

Samplings and chemical analyses as required by the Authorization, were executed by a third party certified laboratory (Accredia LAB N° 1340)

The whole set of monitoring results were sent to the Authorities.

8.1 Air Emissions

The test was carried out by simulating the worse conditions in terms of emissions into the atmosphere, through the simultaneous operation of both the chemical-physical treatment and the biological one;

Two different operating conditions were verified:

- 1) Physical chemical treatment of wastewater contains BOE + biological treatment of wastewater containing TMAH
- 2) Chemical physical treatment of wastewater containing SEZ + biological treatment of wastewater containing TMAH

The Air sampling has been executed on an air flow deriving from the process reactors and storage tanks present in the two treatment sections. .

Considering the wastewater types, the following pollutants were expected to be released into the atmosphere: ammonia, mineral acids (HF, HNO₃, and H₃PO₄) and organic acids (CH₃COOH).

For the abatement of such pollutants a wet Scrubber has been installed, charged with a sulfuric acid solution 2%wt concentrated, able to treat a maximum effluent flow rate of 1,720 Nm³/h.

The gaseous stream treated through the Scrubber is expelled into the atmosphere through a dedicated chimney named as emission point E1.

Emission limits according to the authorization are reported in the below table:

Emission Point	Plant	Flow (Nm ³ /h)	Time of run (h/d)	Frequency	Temp. (°C)	Pollutants	Limit Value		Chimney size		Abatement system (*)	O ₂ Amount (%)
							Concentration (mg/Nm ³)	Mass Flow (Kg/h)	Height (m)	Diameter (m)		
E1	Pilot plant	1.720	24	Continuous	20	NH ₃ (Class IV Table C)	175	0,3	4,19	0,20	AU	n.a.
						COT	75	0,13				
						HF (Class II Table C)	2	0.003				
						HNO ₃	3.5	0.006				
						H ₃ PO ₄	3.5	0.006				

Table 8.1: Air emission control system data of the pilot plant and authorized limits.

8.1.1 Air Emissions Results

In terms of air emissions, negligible concentrations have been measured for the foreseen pollutants (NH₃, dust acids) deriving from the two treatments processes even in the case they were simultaneously operated.

All the values registered are significantly below the limits indicated by the authorization.

Test Reports 1

- RDP n° 18LA02588 - 1 Run – BOE + TMAH
- RDP n° 18LA02662 - 2 Run - BOE + TMAH

Test reports 2

- RDP n° 18LA02779 - 1 Run – SEZ + TMAH
- RDP n° 18LA02864 - 2 Run – SEZ + TMAH

8..2 Water emissions

The pilot plant processes generate two types of downstream wastewaters:

- 1) One from the biological treatment of the stream containing TMAH combined with the wastewater coming from the abatement system
- 2) The second one containing the wastewaters derived from chemical-physical treatment (Wastewater flow named BOE and SEZ)

The test was carried out only with the type 1) wastewater, sent downstream to the site civil treatment plant by connecting the collection tanks (TK203) to the oxidation tank of civil site treatments, in order to provide a further biological treatment process of the organic substances.

Differently, the wastewater from the chemical-physical treatment process 2) was collected in special tanks and disposed as wastes.

To management the wastewater coming from the pilot plant it wasn't necessary to activate other water discharges but it was used the already authorized discharge point S2.

The authorized limit values to be respected at the S2 discharge are the same currently foreseen by the Coordinating beneficiary (LFOUNDRY) environmental permit (table 3 annex 5 third part of the legislative dlgs. 152/2006). In relation to TMAH the current limit reported in the LFOUNDRY environmental authorization is 7 mg / L.

The authorized monitoring plan is reported in the table below:

Area		Pollutants	Sampling Method	Analytic Method	Frequencies
Emission point	Name				
S2	Final discharge Biological Civil plant	Odour	APAT-IRSA/CNR2003	APAT-IRSA/CNR2050	Monthly
		Colour	APAT-IRSA/CNR2003	APAT-IRSA/CNR2020.A	
		pH	APAT-IRSA/CNR2003	APAT-IRSA/CNR2060	
		Material coarse	APAT-IRSA/CNR2003	APAT-IRSA/CNR2090.B	
		Material settleable	APAT-IRSA/CNR2003	APAT-IRSA/CNR2090.C	
		SST	APAT-IRSA/CNR2003	APAT-IRSA/CNR2090.B	
		BOD 5	APAT-IRSA/CNR2003	APAT-IRSA/CNR5120	
		COD	APAT-IRSA/CNR2003	APAT-IRSA/CNR5130	
		Chloride	APAT-IRSA/CNR2003	APAT-IRSA/CNR4020	
		Fluoride	APAT-IRSA/CNR2003	APAT-IRSA/CNR4020	
		Sulphate	APAT-IRSA/CNR2003	APAT-IRSA/CNR4020	
		Ammonium nitrogen	APAT-IRSA/CNR2003	APAT-IRSA/CNR4030 A2	
		Nitric nitrogen	APAT-IRSA/CNR2003	APAT-IRSA/CNR4020	
		Nitrous nitrogen	APAT-IRSA/CNR2003	APAT-IRSA/CNR4050	
		Total phosphate	APAT-IRSA/CNR2003	APAT-IRSA/CNR4110	
		Aluminium	APAT-IRSA/CNR2003	APAT-IRSA/CNR3050.B	
Chromo VI	APAT-IRSA/CNR2003	APAT-IRSA/CNR3150C			
iron	APAT-IRSA/CNR2003	APAT-IRSA/CNR3160.A			

Area		Pollutants	Sampling Method	Analytic Method	Frequencies
Emission point	Name				
		acute toxicity test (Daphnia Magna)	APAT-IRSA/CNR 1030	UNI EN ISO 6341/99	
		TMAH	APAT-IRSA/CNR2003	I.C. colonna CS17	

Table 8.2: Water monitoring plan.

The test was run continuously for a month, using a supply flow rate from the pilot plant to the civil plant of about 5 L/h.

The process control was realized monitoring the process parameters and the chemical analysis at TK203 (final tank for the TMAH section) twice a week, while the civil biological plant was monitored every day by internal chemical laboratory.

3 consecutive weekly official samples at the S2 final discharge were taken by the third party certified laboratory;

8.2.1 Water Emissions Results

The analytic results at the discharge showed for all pollutant substances values below the legal limits, the concentration of TMAH has been found below the detection value (< 0.05 mg/l) with analytic method.

The process did not alter the functioning of the existing civil biological plant, so it was not necessary to change the setup of the operating parameters of that plant.

Test reports

RDP: n° 19LA01502, sampling date 07/06/2019

RDP: n° 19LA01652, sampling date 14/06/2019

RDP: n° 19LA01765, sampling date 21/06/2019

8.3 Solid Waste

With regard to solid wastes (sludges) resulting from the chemical-physical line of the pilot, for both the treated streams (ammonium fluoride and acid mix solutions) they have been classified as “non-hazardous” (CER code 060503)

Test reports

- RDP n° 18LA02586 - sludges from BOE treatment
- RDP n° 18LA02780 - sludges from SEZ treatment

9. Conclusions

The aim of the present document has been that to describe and analyse the experimental results for TMAH degradation obtained during the pilot scale activity. The experiments have been performed between June and December 2018. The pilot plant is realized in two containers and can treat three types of industrial effluent: line 1 that contains TMAH by biological process, line 2 (BOE) and line 3 (SEZ) rich in nitrates and fluorides an acetic acid.

The first container has a neutralization reactor N101, a storage tank TK102 and three biological reactors in series R101-R102 and R103; in the second container there are the equipment to treat BOE and SEZ by using chemical -physical operations, in particular there are a reactor R104, a filter press FP201 and a several tanks to storage the effluents before and after the treatments.

For TMAH degradation, two series of experiments have been performed in batch and continuous mode. The first cycle started 05/06/2018 until 12/07/2018; the second one started 15/10/2018 until 10/12/2018. In this phase the batch and continuous activities have been alternate as a consequence of some technical problems identified on start-up. A third cycle in continuous condition started in May 2019 to validate previous results.

At the initiation of the two cycles, the reactors R101, R102 and R103 was inoculated with around 800 L of activated sludge (approx. 2.5 g/L of TSS) from LFoundry site and WW1 was fed in R101 with specific flows after neutralization of the wastewater. The pH values in the reactors were checked by pH -meter and recorded. Oxygen was controlled at 2 mg/L by air blowing and mixing system. The temperature was kept constant (around 20°C) with the aid of heat exchanger serving to the jacket reactors.

The experiments have been performed varying the flow of TMAH effluent fed into R101, in particular it has been studied the following flows: 2-3- 5- 10 - 20 L/h.

The parameters checked were: TMAH, DMA, $N-NH_4^+$, NO_3 , COD, pH and TSS concentration. The experimental results showed that the TMAH can be degraded in DMA by using biological process. After that DMA degrades in ammonium and nitrates. The results of the second series of experiments have been analysed to calculate the degradation yields of TMAH: the data showed that using a loading of TMAH solution of 5 L/h and after 192 h of reaction it has been possible to reach 55.48%, 90.82% and 99.02% of removal in R101, R102 and R103, respectively.

Moreover, DMA appears after 48 h and it is degraded by bacteria in 192 h that product ammonium. The concentration of ammoniacal nitrogen is higher in R101 respect to the other two reactors. Nitrate concentration is similar in the three reactors and decreased at the end of the cycles, probably as results of ageing process of the biomass. The nitrification process was more relevant in the last bioreactor.

The experimental results of the second cycle of experiments have been used to define the kinetic parameters of TMAH biodegradation, assuming Monod model of bacteria growth. The following kinetic parameters have been estimated:

$$\mu_{max} = 0.011 \text{ h}^{-1}$$

$$K_s = 0.25 \text{ g/L}$$

These data were used to define the optimal configurations of the bioreactor at the full scale (flow of TMAH effluent equal to 800 L/h). Several configurations have been proposed and it has been chosen the optimal configuration to reduce the volume of the equipment: three bioreactors in series with partial recirculation of bacteria in R101, total volume of 89.52 m³ (volume reduction of 90% respect to a single bio reactor).

Third cycle has validated previous results, moreover has highlighted that the temperature improve the kinetic of the process. Moreover, to maintain the efficiency it will be necessary to provide an additional carbon source.

About the chemical-physical treatments of SEZ and BOE it is possible to assert that: both effluents can be treated by the addition of lime and aluminium sulphate as precipitation coadjuvant; fluoride removal yield is around 99% for both effluents; lime consumption depends from initial composition of the effluent and from the age of the lime. Due the last consideration a recommendation is design a tank for lime storage able to satisfy only a week's plant demand, thereby lime activity loss will be limited.

About environmental performance, it is possible to asset that the process respects all the prescription for the emission and the water. Also solid wastes produced are classified as no-dangerous.

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