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Effects of Coagulation and Ozonation Pretreatments on Biochemical Treatment of Fluid Catalytic Cracking Wastewater

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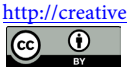


Abstract

Fluid catalytic cracking (FCC) salty wastewaters, containing quaternary ammonium compounds (QACs), are very difficult to treat by biochemical process. Anoxic/oxic (A/O) biochemical system, based on nitrification and denitrification reactions, was used to assess their possible biodegradation. Because of the negative effects of high salt concentration (3%), heavy metals and toxic organic matter on microorganisms' activities, some techniques consisting of dilution, coagulation and flocculation, and ozonation pretreatments, were gradually tested to evaluate chemical oxygen demand (COD), ammonia-nitrogen (ammonia-N) and total nitrogen (TN) removal rates. In this process of FCC wastewater, starting with university-domesticated sludge, the ammonia-N and TN removal rates were worst. However, when using domesticated SBR's sludge and operating with five-fold daily diluted influent (thus reducing salt concentration), the ammonia-N removal reached about 57% while the TN removal rate was less than 37% meaning an amelioration of the nitrification process. However, by reducing the dilution factors, these results were inflected after some days of operation, with ammonia-N removal decreasing and TN barely removed meaning a poor nitrification. Even by reducing heavy metals concentration with coagulation/flocculation process, the results never changed. Thereafter, by using ozonation pre-treatment to degrade the detected organic matter of di-tert-butylphenol and certain isoparaffins, COD, ammonia-N and TN removal rates reached 92%, 62% and 61%, respectively. These results showed that the activities of the microorganisms were increased, thus indicating a net denitrification and nitrification reactions improvement.

Keywords

Ammonia-N, Anoxic and Oxic (A/O) Reactor, Coagulation and Sedimentation, FCC Wastewater, Ozone, Total Nitrogen (TN)

1. Introduction

The fluid catalytic cracking (FCC) process is a major unit used worldwide in refinery operations [1] [2]. It is used to convert low-value high-boiling, high molecular weight feedstock of petroleum by "cracking" C-C bonds into lighter, high-value products such as liquefied petroleum gas (LPG), olefinic gases, gasoline, diesel, and other products. The FCC process is based on the application of various heterogeneous catalysts such as quaternary ammonium compounds (QACs) [3] [4] whose generated wastewater is not environmentally friendly as reported by various research and studies. In fact, this wastewater is high salt, low COD, and high ammonia-nitrogen wastewater, so that using the general activated sludge to treat this effluent is difficult to meet the standard. In addition, these petrochemical wastewaters, when rejected in the environment without any treatment, have adverse impacts (soil degradation, surface water eutrophication and underground water contamination) on the entire environment [1] [2] [3] [4] [5]. In addition, this industrial wastewater has an impact on the health of living organisms, both animals and plants, as well as on aquatic life and in addition to water pollution [1] [6] [7] [8].

Therefore, a huge production of FCC wastewater becomes a big challenge for environmental protection and has also serious consequences for the development of oil refineries and other petrochemical industries. To face these problems, governmental stringent regulations have been implemented progressively in order to prevent further exacerbation. Several methods were used to manage these kinds of wastewater. A pre-treatment process was required to reduce metallic and organic pollutants prior to biological treatment.

Various conventional methods, which include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, and the application of membrane technology, were used to achieve the wastewater's pre-treatment [7] [9] [10]. Coagulation and flocculation are crucial processes used for pre- (or post-) treatment of most wastewater treatment plants prior to subsequent biochemical processes [11]. Their objective consists to bring together and agglomerate colloidal particles and other finely divided matter to form larger-sized particles that can subsequently be removed by sedimentation and filtration techniques [11] [12] [13]. These techniques were used very early in the treatment of domestic and industrial wastewater. Benschoten *et al.* [14] have reported that the dissolved organic can be removed by adsorption on aluminum precipitation by using coagulation process. Dennett *et al.* [15] have observed that the mechanism of coagulation for aluminum salts is controlled by the hydrolysis speciation. In ad-

dition, the use of coagulation process shows an efficient removal of many other pollutants, such as metals, toxic organic matter, viruses, and radionuclides [16] [17]. Many studies have been reported on the efficiency of coagulation/flocculation for the treatment of industrial wastewater treatment based on the selection of the most appropriate coagulant and assessment of experimental parameters, such as pH and technique of flocculant addition. Panhwar *et al.* [18] have reported that coagulation with different chemicals alum, ferric chloride, lime, PACl, PVA and ferrous sulfate is very effective for removing pollution. Pernitsky *et al.* [19] have concluded that the chemical and electrical means of water and wastewater treatment were achieved by using coagulation as the most important physicochemical operation. Lee *et al.* [20], working on swine wastewater treatment, by the application of a flocculent, non-ionic polyacrylamide (NPAM), have reported high removal rates of more than 90% of copper and zinc metal ions as well as ammonia-nitrogen (NH_4^+-N), total phosphate (TP), and total nitrogen (TN). In addition, Bharti [21] has summarized the efficiency of the application of a number of biopolymers for their flocculation behavior for treating various industrial as well as agricultural wastewaters via chemical alteration onto its backbone. It was found that minute quantities of dosage were sufficient to reduce the organic, biological and suspended loads from wastewater sample.

In the same context of pre-treatment, ozonation process has also been applied as pre- (or post-) treatment to degrade wastewater's organic matter and color [22]. Ozonation is defined as a process where ozone (a molecule containing three oxygen atoms) is produced in situ by an ozone generator, and the yielded ozone gas is dissolved in wastewater in order to degrade organic and inorganic pollutants and kill microorganisms. Given its high capacity to degrade pollutants, ozone has the potential to be considered a multi-purpose disinfectant and a powerful oxidizer for wastewater treatment. A wide variety of organic matter could be effectively removed by ozone from water and wastewater as well as microorganisms during pre-treatment or post-treatment [23]. According to numerous reports, ozone-based technologies, such as non-catalytic ozonation, ultraviolet irradiation-catalyzed ozonation, hydrogen peroxide and various heterogeneous catalysts, can be used as alternatives or pre-treatment methods prior to the biological treatment of actual agro-industrial wastewater. They showed an improvement in their biodegradability by greatly reducing toxicity [23] [24] [25].

The A/O method is one of various activated sludge methods used in wastewater treatment process [26]. Its main purpose is to remove nutrients such as nitrogen and phosphorus from wastewater. Compared with the biological treatment system used in the traditional coal chemical wastewater treatment, the A/O process does not need to add additional carbon source, the main reason is that the process directly uses the organic matter in the original water as the carbon source needed for microorganisms. The A/O process also reduces COD during denitrification process. The aerobic segment is located after the anoxic section so

that the aerobic section can fully use the alkalinity produced by microbial denitrification inside the anoxic section, and can reduce effectively the external alkalinity demand of the system. The A/O process is equipped with anoxic section and aerobic section, and its internal mixed flora can alternate between the states of anoxia and aerobic so that the whole reactor is in dynamic flow which allows effective control of sludge expansion problem [26] [27].

In this study, the used FCC wastewater is very complex and difficult to treat biologically, therefore two pre-treatment techniques are required. The objective is to evaluate the biological removal of ammonia-N, TN and COD using the A/O bioreactor by carrying out preliminary treatments of this wastewater for coagulation/sedimentation of residual metals and ozonation of persistent organic matter. These two pre-treatment effects on the biodegradation of nitrogen species are assessed by A/O system.

2. Materials and Methods

2.1. Principle of A/O System

The used process is an A/O-activated sludge treatment system, also known as the anterior denitrification biological treatment system, which consists of the denitrification reactor in front of the system followed by the nitrification reactor at the rear. The combined A/O-activated sludge treatment system is shown in **Figure 1**.

The fully reactive sewage within the oxic reactor (pool O) is partly returned to the anoxic reactor (pool A). Meanwhile, microorganisms of the pool A take wastewater's organic matter as the carbon source, and the oxygen in the reflux liquid as the electron receptor for respiration and life activities; so that the system does not require any addition of carbon source [6]. On the other hand, the nitrification microorganisms inside pool O reactor, located after the anoxic pool A section, can fully use the alkalinity produced by the microbial denitrification of the anoxic pool A reactor so to reduce the external alkalinity demand of the system. The A/O process also degrades COD during denitrification inside anoxic pool A reactor process. In addition, the A/O process's internal mixed flora can

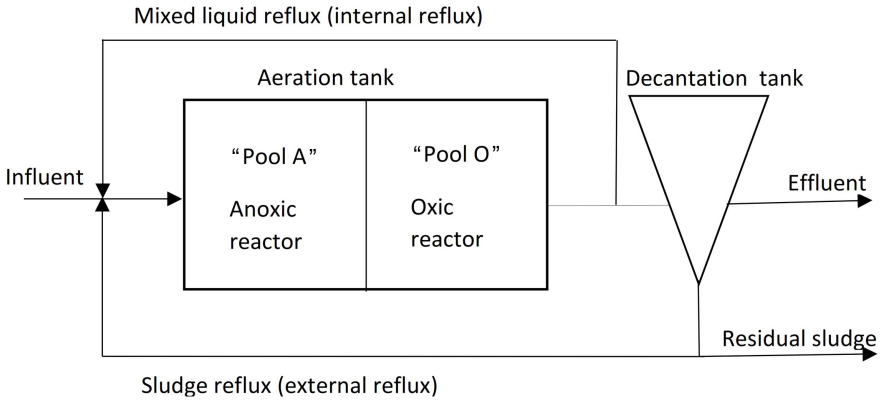


Figure 1. Flow diagram of A/O process.

alternate between the anoxic and the oxic states so that the whole system is in the dynamic flow, which allows effective control of sludge expansion problem [7].

2.2. Water Quality Analysis of FCC Raw Wastewater

In order to understand the water quality of raw FCC wastewater's COD, total salt percentage, and ammonia-N and total nitrogen concentrations were measured as shown in Table 1.

Meanwhile, in Table 1, the concentrations of Cl^- and SO_4^{2-} ions are in accordance with the design's parameters.

2.3. Experimental Procedure

The sludge domestication was performed with the sewage of treatment plant, and at the end of this process the discharge of wastewater was completely low of ammonia-N concentration. Then, the removal efficiency of wastewater's COD, ammonia-N and TN, through the above domesticated sludge, were measured.

The system consisted of a 10 L daily intake wastewater. First, anoxic pool A operations were performed with a 48 h HRT and 0.5 mg/L DO, meanwhile the concentration of DO in the oxic pool O was maintained between 2 to 4 mg/L; and both pools pH values were adjusted between 7.0 to 8.0. During the whole experiment, glucose was added to control the wastewater's C/N ratio to 4:1. Wastewater reflux ratio and sludge reflux ratio were controlled to r = 142% and r = 70%, respectively. The temperature was maintained around 24˚C. The second operation consisted of increasing HRT to 55 h and reducing daily water intake to 8.7 L. For each cycle, the effluent wastewater's ammonia-N, TN and COD concentrations along with sludge efficiency in terms of SV_{30}, MLSS and SVI were measured.

2.4. Coagulation-Settlement Pretreatment and Biochemical Treatment of FCC Wastewater

Considering whether the presence of heavy metals into catalysts wastewater has toxic effects on microorganisms, therefore the pretreatment of heavy metals

Table 1. Quality analysis of FCC wastewater data.

Item	Physicochemical Test
COD (mg/L)	50
Ammonia-N (mg/L)	330
TN (mg/L)	280
Cl^- (mg/L)	6200
SO_4^{2-} (mg/L)	12,051
pH	8.59
Total salt (%)	3

settleability was realized by means of coagulation operation so as to improve the wastewater's microbial treatment efficiency. For this reason, a certain concentration of flocculant was priory used in order to form flocculates which should be deposited and filtered, and thereafter a fresh sludge was replaced and the same process was continued.

2.5. Ozonation

The GC-MS, Agilent 8890-5977B with Mass range number 2-800 m/z, analysis has determined that the persistent toxic organic compounds which inhibited nitrification reaction was mainly di-tert-butylphenol. Therefore, ozone pre-oxidation was used to degrade the di-tert-butylphenol so as to facilitate an effective microbial treatment of ammonia-N. The experimental device for ozonation process was as shown in Figure 2. The selected ozone generator model Cf-G-3-10 is made by Qingdao Yilin Industrial Co. Ltd., PR China. According to the product manual, the ozone output of the ozone generator was directly related to the O_2 intake and electric current output. The ozone output volume was inversely proportional to the intake air volume, and proportional to the electric current output value. During the experiment, the air's O_2 intake was controlled to 1 L/min, the output electric current value was adjusted, and the ozone yield obtained under various values of electric current was investigated so that it will be convenient to determine the current value required for subsequent experiments.

As it can be seen in Figure 2, the experimental device is mainly composed of three 3 parts: Ozone generator (2), ozone reactor (5) and exhaust absorption bottle (7). The ozone generator was taking oxygen as the gas source (1), the rotor flowmeter (4) was set to 1 L/min, and ozone concentration could be increased by adjusting the current value. At the beginning of the experiment, the wastewater

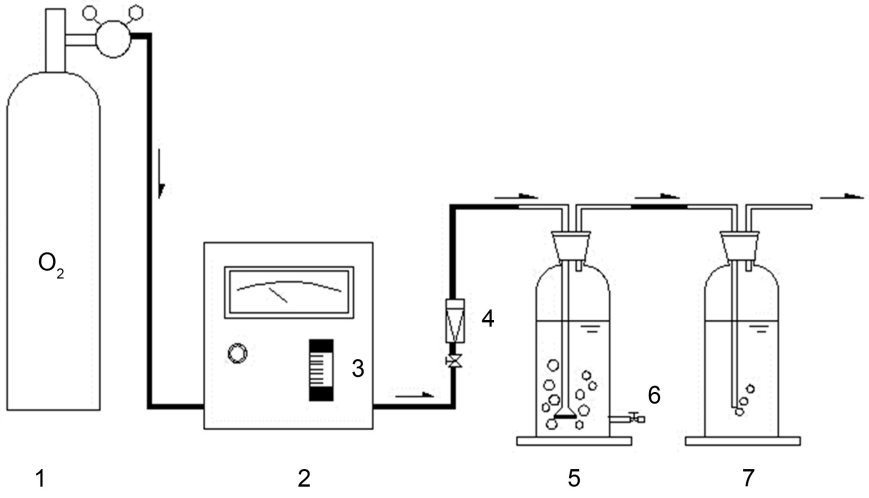


Figure 2. Experimental device for ozone oxidation reaction. 1: Oxygen tank; 2: Ozone generator; 3: Rotor flowmeter (O_2); 4: Rotor flowmeter (O_3); 5: Reactor; 6: Sampling port; 7: Exhaust absorption bottle.

was added to the reactor, and ozone generator was activated in order to stabilize the ozone airflow into the reactor; thereafter ozone through the aeration head was mixed with simulated water into the reactor resulting in two-phase gas and liquid reactions, and the ozone exhaust gas was absorbed by the exhaust absorption bottle containing KI solution.

3. Results and Discussion

3.1. Effect of Individual Biochemical Method on FCC Wastewater

For the set of 20 days' operations, the first activity was the sludge domestication process which ended when the effluent was completely of low ammonia-N concentration. Thereafter, followed by different tests of the treatment of salty QAC wastewater. During the experiment, both influent and effluent COD, ammonia N, and TN concentrations were measured, as well as SV_{30}, MLSS, and SVI. Compared with the A/O process, the result showed that the SBR process was more suitable for acclimating the microorganisms of activated sludge. The specific influent parameters, sludge treatment efficiency and sludge performance are shown by the SBR process in Table 2.

When starting the experiment (shown No. 1 in Table 2), the influent was diluted 4-fold in order to obtain low ammonia-N wastewater. After 3 days experiment, the concentrations of ammonia-N and TN were 82 mg/L and 81 mg/L, respectively. The measured effluent's ammonia-N and TN were higher than that of the influent water. This is due to some microorganisms' death during the adaptation of sludge to high-salt wastewater and the sludge's self-decomposition. However, the maximum COD removal rate can reach around 87% from 3 days of experiment. The concentration of ammonia-N in the effluent was 17.1%

Table 2. Status of FCC influent water and experimental results (SBR reactor).

Serial No.	1	2	3	4	5
Influent water ammonia-N (mg/L)	70	93	140	280	280
Effluent ammonia-N (mg/L)	82	80	121	284	267
Removal rate of effluent ammonia-N (%)	-	14	14	-	5
Influent water's TN (mg/L)	70	93	140	280	280
Effluent's TN (mg/L)	81	81	121	360	322
Removal rate of effluent's TN (%)	-	13	14	-	-
Influent COD (mg/L)	280	373	560	1120	1120
Effluent COD (mg/L)	37	40	79	186	267
COD removal rate (%)	87	89	86	83	76
SV_{30} (%)	73	85	79	78	73
MLSS (g/L)	5413	4752	4536	4453	4413
SVI (mL/g)	135	179	174	175	165

higher than that in the influent. Thereafter, the low ammonia-N influent was 3-fold diluted. After 4 days of domestication experiments (shown No. 2 in **Table 2**), it was observed that ammonia-N and TN were slightly degraded, and the COD removal rate reached 89%. Then, the wastewater was twice (or 2-fold) diluted. No. 3 in **Table 2** illustrates after 7 days of experiment, the removal rate of ammonia-N and TN concentrations reached 14%, while the COD removal rates was 86%. After passing the above experiment, the influent was no longer diluted. After 6 days and 10 days of experimentation from No. 4 and No. 5 in **Table 2**, the measured effluent's ammonia-N concentration was higher than that of the influent. This is probably due to the presence of high chlorides Cl^- ions in wastewater which killed the microorganisms and in turn increased the effluent ammonia-N. At the same time, the TN in the effluent was higher than that of the influent, which reason was related to poor denitrification phase. However, the resulted COD removal rates were 83% and 76%, respectively, indicating that the microorganisms were still active, so operation can be continued to acclimate and to evaluate the denitrification effect on the system. The result shows that the sludge acclimated by SBR process [28] was more efficient than that one prepared by the A/O process so that it was chosen for this A/O process. However, the removal rate of ammonia-N has not yet been improved. The reason may be due to the complexity of QACs in wastewater, which has a great resistance to various microrganisms' activities [3] [4] [5] such as nitrifying bacteria as confirmed by certain studies. In fact, Pati *et al.* [3] have reported that the degradation of QACs in the natural environment by both microorganisms and photolysis is slow. Hence, the activated sludge was acclimated again. Subsequently, the wastewater was first diluted 5 times before being treated by the A/O process and the results obtained are presented in **Table 3**.

After that, domesticated SBR's activated sludge was added to the A/O reactor and the pH value and DO content of pool O were adjusted. The 33-days domestication process in A/O treatment system is shown in No. 1 in **Table 3**. It can be seen that the effluent's ammonia-N and TN concentrations are higher than that of influent, while the removal rate of COD is 66%. Therefore, it is necessary to domesticate the microorganisms in sludge to achieve nitrification and denitrification of ammonia-N. As it can be seen from No. 3 in **Table 3**, another 20 days were required for domestication. At this time, the removal rate of ammonia-N was only 3%, but the TN was not removed. Meanwhile, the COD removal rate reached 92%. In this A/O system, after 25 days of acclimation, the COD removal rate was 90%, while the recorded ammonia-N and TN removal rates were 57% and 37%, respectively as listed in serial No. 5 in **Table 3**. These results can indicate that microbial acclimation of sludge is still needed.

To this end, the wastewater was diluted 4-fold for treatment as shown in **Table 4**. After 3 days of operation, as it can be seen in serial No. 1 in **Table 4**, the effluent's ammonia-N and TN removal rates were about 27% and 24%, respectively. In No. 3 in **Table 4**, the effluent's ammonia-N and TN removal rates were

Table 3. Status of FCC inlet wastewater and experimental results (5-fold diluted, A/O process).

Serial No.	1	2	3	4	5
Influent ammonia-N (mg/L)	60	60	60	60	60
Effluent ammonia-N (mg/L)	63	59	58	35	26
Ammonia-N removal rate (%)	-	1	3	42	57
Influent TN (mg/L)	60	60	60	60	60
Effluent TN (mg/L)	65	62	65	50	38
TN removal rate (%)	-	-	-	17	37
Influent COD (mg/L)	240	240	240	240	240
Effluent COD (mg/L)	81	21	20	21	23
COD removal rate (%)	66	92	92	92	90
SV_{30} (%)	64	64	64	64	63
MLSS (g/L)	4162	4358	4353	4258	4324
SVI (mL/g)	154	147	147	150	146

Table 4. Status of FCC inlet wastewater and experimental results (4-fold diluted, A/O process).

Serial No.	1	2	3	4	5
Influent ammonia-N (mg/L)	70	70	70	70	70
Effluent ammonia-N (mg/L)	51	45	61	70	73
Ammonia-N removal rate (%)	27	36	13	-	-
Influent TN (mg/L)	70	70	70	70	70
Effluent TN (mg/L)	53	54	63	72	73
TN removal rate (%)	24	23	10	-	-
Influent COD (mg/L)	280	280	280	280	280
Effluent COD (mg/L)	40	30	33	35	32
COD removal rate (%)	86	89	88	88	89
SV_{30} (%)	64	63	63	62	63
MLSS (g/L)	4243	4268	4231	4332	4323
SVI (mL/g)	151	148	149	143	146

decreased to 13% and 10%, respectively.

It can be found from serials No. 4 and No. 5 in Table 4 that the influent's ammonia-N and TN concentrations were not much different when compared with those of the effluent. Nitrogen species were barely removed meaning the nitrification reaction did not occur at all. On this basis, it was considered that there must be the presence of other substances in the wastewater that have toxic side effects on microorganisms. Given that, the wastewater produced by refining catalytic operations contained heavy metals poisons [1] [4] [5] [6] [8], and con-

sidering their possible toxic side effects on microorganisms, the coagulation and sedimentation method was considered. To this end, the pretreatment of heavy metals must be conducted by means of the following coagulation-settlement process before assessing ammonia-N removal efficiency by microbial method.

3.2. Coagulation Settlement Pretreatment and Biochemical Treatment of FCC Wastewater

A certain concentration of flocculants was added to the wastewater to form coagulant flocs which were sedimented and filtered out. Thereafter, a fresh sludge was used for biological treatment expecting, of course, to achieve nitrogen species removal. Thereafter, the experimental tests were conducted with 4-fold diluted inlet wastewater. And both influent and effluent's COD, ammonia-N and TN concentrations along with sludge's SV_{30}, MLSS and SVI were determined as shown in Table 5.

As it can be seen in serial No. 1 in Table 5, the ammonia-N removal rate was about 24%. But from serial No. 2, there was no more ammonia-N removal. In fact, the effluent's ammonia-N concentration was higher than that one of the influent wastewaters. After 15 days of experiment, it was found that the effluent's ammonia-N and TN concentrations were still higher than those in the influent. In one month of experiment, the removal rate of COD by A/O system was basically fluctuated between 86% - 89%, indicating that the activity of sludge still exists. Despite coagulation and sedimentation operations, neither wastewater's ammonia-N concentration nor TN removal rate have been improved over the next days. As mentioned above, the complexity of QACs compounds [3], with amphiphilic structure containing very long carbon chains (more than 10 C atoms) made them difficult to degrade. And their presence in the influent

Table 5. Status of inlet FCC wastewater and experimental results.

Serial No.	1	2	3	4	5
Influent ammonia-N (mg/L)	70	70	70	70	70
Effluent ammonia-N (mg/L)	53	80	82	76	77
Ammonia-N removal rate (%)	24	-	-	-	-
Influent total nitrogen (mg/L)	70	70	70	70	70
Effluent total nitrogen (mg/L)	55	82	84	80	83
Total nitrogen removal rate (%)	21	-	-	-	-
Influent COD (mg/L)	280	280	280	280	280
Effluent COD (mg/L)	40	38	30	32	33
COD removal rate (%)	86	86	89	89	88
SV_{30} (%)	63	64	63	64	63
MLSS (g/L)	4324	4298	4268	4283	4231
SVI (mL/g)	146	149	148	149	149

wastewater can cause the death of sludge's microorganisms responsible for the increase of the effluent's ammonia-N concentration. In fact, as reported by García *et al.* [8] and Tezel *et al.* [6], QACs always showed poor or no biodegradation under anaerobic/anoxic conditions.

4. Ozone Pretreatment and FCC Wastewater Treatment

4.1. Identification of Wastewater's Organic Matter by GC-MS

As the above results of the microbial treatment with and without coagulation/sedimentation method were both ineffective for ammonia-N removal; hence, whether there are organic substances in the wastewater that have toxic and harmful effects on microorganisms should be considered. Thus, the organic matter in the catalyst's wastewater was analyzed. To this end, gas chromatography-mass spectrometry (GC-MS), a new established analytical window which allowed the measurement of more polar compounds and led to the discovery of a wide range of (biologically active) organic micropollutants in municipal wastewater [29]) was chosen for this analysis and the results are shown in the following **Figures 3(a)-(d)**.

From the GC-MS analysis' results (**Figures 3(a)-(d)**), it was found that concluded that the persistent components of the wastewater's organic matter were di-tert-butylphenol and some isoparaffins. In fact, phenol-based compounds with long alkyl chains are particularly toxic to microorganisms [6]. According to the literature reported by Zhao *et al.* [25], the di-tert-butylphenol has toxic side effects on some plants and soil microorganisms with particular toxicity to anoxic and oxic-activated sludge. Thus, the discovery of di-tert-butylphenol and long carbon branched chains isoparaffins in this wastewater may hinder its biodegradability. Hence, the need to use ozonation for their removal as a pretreatment prior to nitrogen species biodegradation.

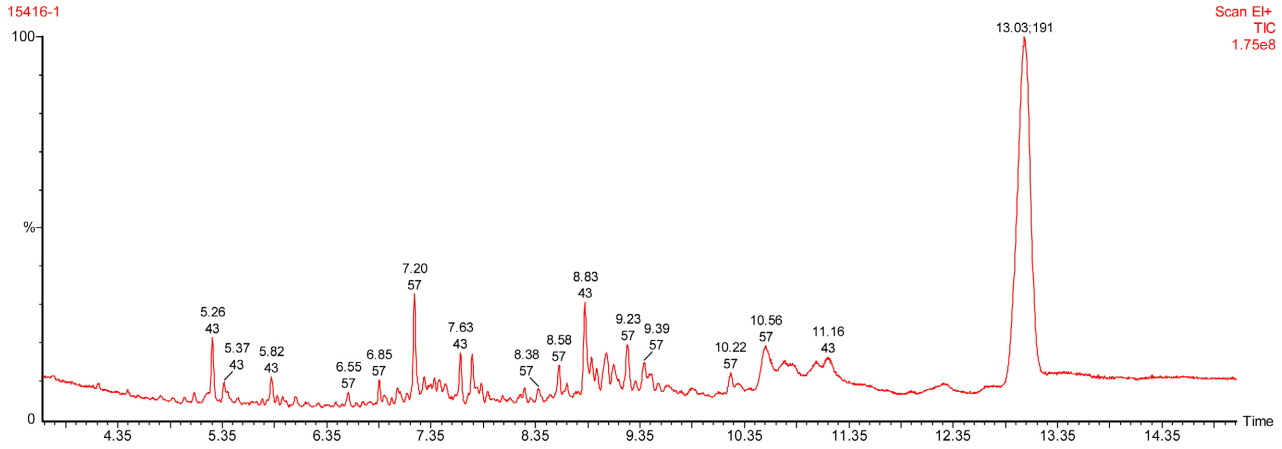
4.2. Effects of Ozonation on Biochemical Treatment of Wastewater

According to the experimental results, the variation curves of ozone concentration under different electric flows are shown in **Figure 4**.

Figure 4 shows that when the oxygen intake was 1 L/min, under different current values comprised between 0.03 A - 0.2 A, the yielded ozone concentration at the outlet increased significantly from 9 mg/L, 33 mg/L, 64 mg/L, 104 mg/L to 115 mg/L, respectively. Subsequent experiments were performed by varying current values to obtain the best ozone concentrations which were used to carry out experimental operations.

As it can be seen in **Table 6**, by comparing the results of wastewater quality parameters before and after ozonation, a decrease of COD concentration from 113 mg/L to 66 mg/L was observed. However, no change in ammonia-N and TN concentrations was registered. Based on these results, half part of organic matter was degraded by ozonation as shown by COD reduction. Which indicates that

there are still existed some recalcitrant organic compounds. This is a little bit in contrast with the findings of Wei *et al.* [23], Amor *et al.* [24] and Zhao *et al.* [25] who reported an improvement in the biodegradability of QACs organic compound's structure which greatly reduce their toxicity. Thereafter, the treated wastewater was diluted and poured into the bioreactor with fresh activated sludge to realize domestication. As shown in **Table 7**, both influent and effluent's COD, ammonia-N, TN concentrations were measured.



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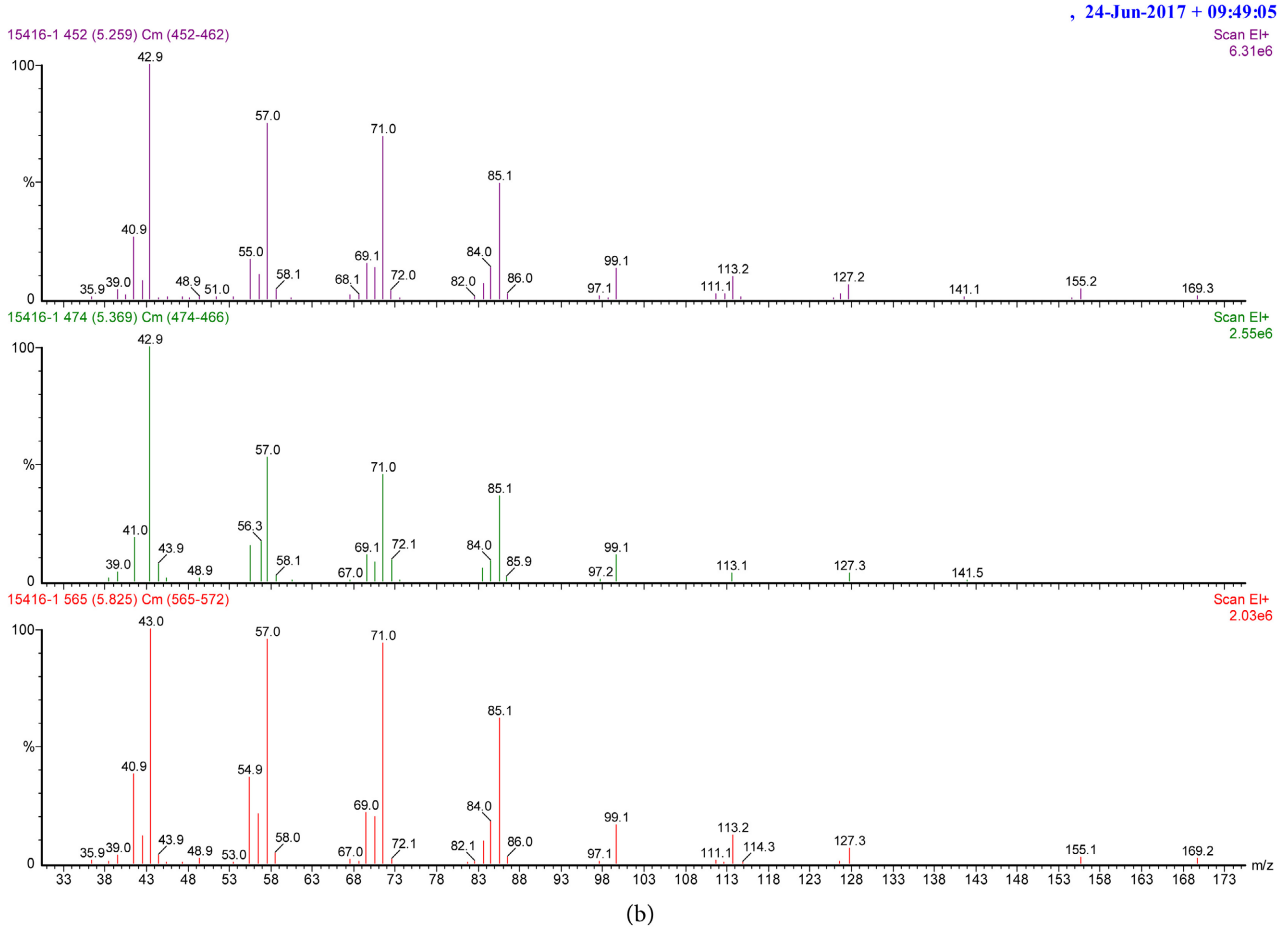

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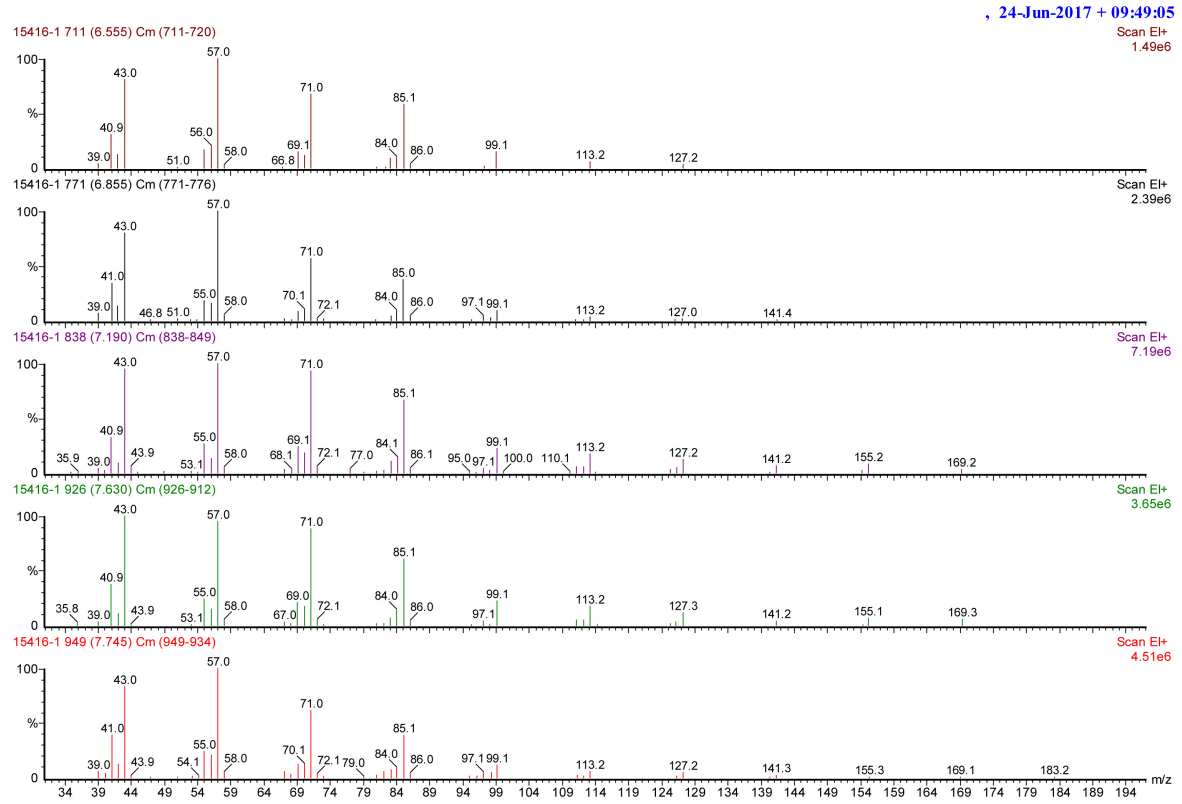

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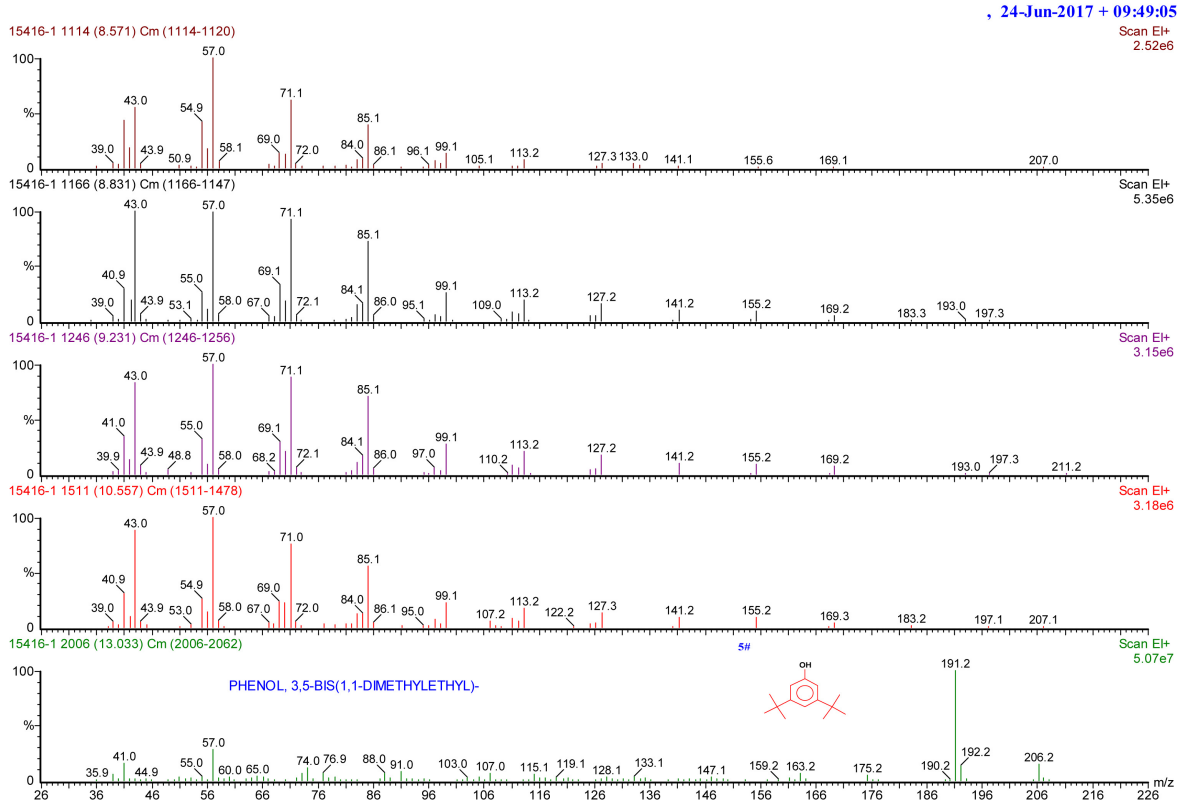

(d)

Figure 3. GC-MS analysis for organic matter determination.

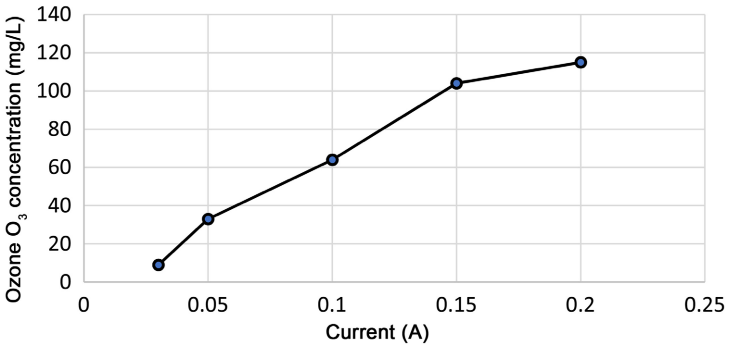

Figure 4. Ozone variation as a function of electric current.

Table 6. Wastewater quality parameters before and after ozonation.

Parameters	COD	Ammonia-N	TN
Before ozone pre-oxidation (mg/L)	113	323	325
After ozone pre-oxidation (mg/L)	66	319	320

Table 7. Water inlet and experimental results.

Serial No.	1	2	3
Influent's ammonia-N sludge loading rate ($kg/m^3 \cdot d$)	0.05	0.08	0.10
Effluents ammonia-N concentration (mg/L)	16	28	38
Ammonia-N removal rate (%)	70	67	62
Influent TN's sludge loading rate ($kg/m^3 \cdot d$)	0.05	0.08	0.10
Effluents TN concentration (mg/L)	17	30	40
TN removal rate (%)	69	66	61
Influent COD sludge loading rate ($kg/m^3 \cdot d$)	0.5	0.5	0.5
Effluent COD concentration (mg/L)	40	37	38
COD removal rate (%)	92	93	92

As it can be seen from No. 1 in Table 7, the removal rate of ammonia-N reached about 70% corresponding to effluents' ammonia-N concentration of 16 mg/L. And when the influent's ammonia-N concentration was gradually increased while the dilution ratio of wastewater was reduced, then the ammonia-N removal rate decreased somewhat as shown by serials No. 2 and No. 3 with 67% and 62%. The same improvement was observed with TN removal, which varies between 61% to 69%. Thus, the resulted ammonia-N and TN removal rates were much higher than that those when operating without pretreated wastewater by ozonation. The use of ozonation for pre-treatment has been beneficial to the removals of ammonia-N, TN and COD in this wastewater.

5. Conclusions and Perspectives

Microorganisms require a long time to acclimate in order to degrade ammo-

nia-N contained in highly salty FCC catalyst wastewater. However, with SBR's acclimated sludge, the ammonia-N removal rate was significantly improved. In Table 2, during the treatment of 5-fold dilution of FCC wastewater, the ammonia-N removal rate reached about 57%. It is suggested that the dilution factor of wastewater could be gradually reduced in order to further increase the acclimation of microorganisms.

The use of coagulation and sedimentation techniques to remove suspended pollutants or heavy metals, so that the microbial acclimation to wastewater could achieve nitrification and denitrification standards, needs to be deeply investigated in the future.

Through GC-MS analysis, the detected di-tert-butylphenol and isoparaffin compounds in the FCC wastewater showed toxic side effects on microorganisms, which inhibited nitrification and denitrification reactions. The use of ozonation pre-treatment to degrade the above compounds showed an improvement in the ammonia-N, TN and COD removal rates.

Since, the experimental sludge has just begun to be domesticated, as the sludge activity has not been fully restored, so the subsequent experiments will further increase the influent water's ammonia-N sludge loading rate to perform further acclimation.

Also, what was the real effect of the ozone pre-oxidation on the ammonia-N biochemical removal in such wastewater can be investigated by using various ozone amounts, adding other auxiliary agents, and adjusting the HRT and the duration of each operating cycle of the A/O system.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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