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Electrochemical Treatment of Oil Refinery Wastewater for NH_3-N And COD Removal

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The electrochemical treatment of industrial effluents is an alternative to conventional treatments because of its advantages, such as environmental compatibility, process versatility and efficiency. The use of indirect oxidants with this technology is important to accelerate the process; however, it can also compromise the performance of the electrodes through corrosion processes, mainly due to variations in the pH. In this work, the electrochemical treatment of sour water from an oil refinery was performed using a parallel-plate electrochemical reactor with Ti/RuO_2 anodes and carbon steel cathodes. NaOCl was used for indirect oxidation. The results demonstrated that the electrochemical treatment proved to be effective for removing NH_3-N and decreasing the chemical oxygen demand (COD) in the oil refinery sour water. In addition, the indirect oxidant concentration directly affected the media pH and the generation of chloramine.

Keywords: electrochemical treatment, ammonia, COD, indirect oxidation

1. INTRODUCTION

The electrochemical treatment of wastewater is an attractive and environmentally friendly process that can be performed in industrial areas under ambient temperature and pressure. Electrochemical treatment processes efficiently eliminate pollutants such as nitrogen compounds [1,2], cyanides [3], organics [4,5], and chemical oxygen demand (COD) [6]. In addition, the selection of appropriate electrodes and an appropriate electrochemical system minimizes losses and optimizes energy consumption [7-9].

The electro-oxidation of ammonia and ammonium ions during the electrochemical process includes several steps and results in the formation of different compounds, such as N_2 and nitrate ions in their highest oxidation state, as shown in Equation (1) [10,11]:

$$\begin{array}{lll} NH_3 \leftrightarrow NH_2OH_{ad} \leftrightarrow NOH_{ad} \leftrightarrow & NO \leftrightarrow NO_2^- \leftrightarrow NO_3^- & \qquad (1) \\ \updownarrow & \downarrow\ \downarrow & \\ NH_4^+ & N_2\ \ N_2O \rightarrow N_2 & \end{array}$$

The selectiveness of these reactions depends on the potential and the pH value selected for the electrochemical process. The possibility of unstable intermediate species generated at the anode undergoing cathodic reactions must also be considered, as certain products can be reconverted to ammonia at the cathode, thereby reducing the efficiency of this process [10-17]. The electrochemical treatment of ammonia effluents could also result in the generation of hydrogen gas in addition to nitrogen gas, and both compounds are stable species under a wide range of pH conditions [12]. The produced H_2 can also be an important clean energy source for the process itself.

The pH dependence is important because it determines the decomposition pathway of the species. In an aqueous solution, ammonia and ammonium ions are in a pH-controlled equilibrium, as shown in Equation (2):

$$\begin{array}{ll} NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O & \qquad (2) \\ pKb = 4.74 & \end{array}$$

In alkaline media with pH values greater than 10, the predominant species is NH_3, whereas NH_4^+ predominates at $pH \leq 7$. Between pH 7 and 10, both species coexist in equilibrium. The electro-oxidation of ammonia and ammonium ions in alkaline media proceeds through a mechanism that is based on the adsorption of the NH_3 species [10,11]. First, ammonia adsorbs onto the surface of the electrode, and at higher potentials, these species are oxidized to yield N_2 through several steps [18]. At $pH \leq 7$ where the predominant species is NH_4^+, the direct electrochemical decomposition that forms nitrogen occurs rather than the adsorption/oxidation mechanism [10,11,19].

In addition to nitrogen compounds, wastewater also contains compounds that consume the available oxygen present in the ecosystem. The chemical oxygen demand, or COD, is a measure of the amount of the oxygen that is consumed during the chemical oxidation of inorganic and organic matter present in wastewater. COD is an estimate of the biodegradability of the system, and it is an indicator of the potential environmental impacts of the discharge of wastewater into bodies of water. This parameter is also regulated by environmental laws [6].

Indirect oxidants play an important role during electrochemical treatment processes. Substances such as O_3, H_2O_2 and hypochlorite ion have high oxidation potentials, and their use in electrochemical treatment systems improves the performance of the electrochemical process by accelerating the oxidation reactions in the effluent [2,10,12,17,19-24]. Additionally, the incompletely oxidized adsorbed NH_x species and the OH^- generated during the electrochemical process can block the electrode surface, which diminishes the efficiency of the oxidation process [12,22]. This unfavorable situation can be avoided by indirect oxidation [1]. Importantly, the effect of the indirect oxidant is also dependent on the material selected for the anode [24].

Chloride is widely used for indirect oxidation during electrochemical processes, and it is often present in liquid effluents or is added to the system [4,24,25]. The presence of sufficiently high chloride ion concentrations (concentrations greater than 300 mg L^{-1}) is sufficient for the formation of HOCl at certain pH values and potentials [10,11,14,21,23,25]. The overall indirect oxidation reactions involving $N\text{-}NH_3$ and COD are described in Equations (3) - (5) [26]. Typically, chloride is regenerated; however, depending on the parameters of the electrochemical process, some chloride can also escape from the solution in the form of gaseous chlorine [14,21]. The Cl^- regeneration is described by Equations (6)-(8).

$$2\ NH_3 + 3\ HOCl \rightarrow N_2 + 3\ H^+ + 3\ Cl^- + 3\ H_2O \qquad (3)$$

$$3\ HOCl + 2\ NH_4^+ \rightarrow N_2 + 3\ H_2O + 5\ H^+ + 3\ Cl^- \qquad (4)$$

$$COD + yOCl^- \rightarrow \text{final product} \qquad (5)$$

$$2\ Cl^- \rightarrow Cl_2 + 2e^- \qquad E_{0(SCE)} = -1.6\ V \qquad (6)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad K_a = 3.94 \times 10^{-4} \qquad (7)$$

$$3\ Cl_2 + 6\ OH^- \rightarrow 3\ Cl^- + 3\ H_2O \qquad (8)$$

Depending on the pH, OCl^- species are also formed from Cl^-, as described by Equation (9):

$$HOCl \rightarrow H^+ + OCl^- \qquad (9)$$

The OCl^- species are strong oxidants, and they are capable of oxidizing COD to its final product. Ammonia and ammonium ions are indirectly oxidized to N_2 according to Equations (3)-(4) and (10)-(11), respectively:

$$2\ NH_3 + 2\ OCl^- \rightarrow N_2 + 2H^+ + 2Cl^- + 2\ H_2O \qquad (10)$$

$$3\ NH_4^+ + 4\ OCl^- \rightarrow 3/2\ N_2 + 4H^+ + Cl^- + 4\ H_2O \qquad (11)$$

However, indirect oxidation also contributes to a decrease in the pH of the media due to the hydrolysis reaction of chlorine according to Equation (7) [4]. Chloride ions are also responsible for significant corrosion issues that can compromise the performances of the electrodes in the electrochemical system [2,7,21,23].

The formation of chloramines during electrochemical treatments is also possible and mainly depends on the pH value, the temperature and the concentration ratios between active chlorine and ammonia [25,27]. Li *et al.* [16], Li and Liu [21], Gendel and Lahav [25] and Kapalka *et al.* [27] have reported that chloramines are highly unstable and that the final concentration of chloramine could be zero. In addition, conditions can be created during the treatment in which, relative to the concentrations of ammonia and ammonium ion, an excess of electro-generated active chlorine is ensured [27]. The cathode is also capable of decomposing chloramines that are formed at the anode primarily to N_2 [25].

The critical parameters for the electrochemical treatment of ammonia and ammonium ions are the current density/potential value, the pH, the species concentration and the electrode material [8,14,22,24,25,27-29]. The design of the electrochemical reactor, which includes the type and the presence or absence of a separator, the mass transport conditions, the arrangement and format of the electrodes and the materials selection, is also a fundamental choice [30].

The selection of materials for the electrode is an important consideration for the development of an effective and economical method for the electrochemical treatment of ammonia and ammonium ion-containing effluents [1,12,11,13,14,17,21,31-37]. Many inexpensive materials have attracted considerable attention [1,16,18,38]. The use of carbon steel as the cathode is an attractive option because suitable electrochemical conditions can be created in which a proper current density is applied to favor the reduction of nitrate and nitrite ions to N_2 [16]. In addition, the proper amount of indirect oxidant and its effect on the pH conditions contribute to the improvement of the electrochemical performance [17,25,27,29,38,39].

Therefore, the purpose of this work was to evaluate the performance of a parallel-plate electrochemical reactor for the removal of ammonia and ammonium ions, which are also referred to as NH_3-N, and COD from an oil refinery effluent, or so-called sour water. Sodium hypochlorite was used as the indirect oxidant, and the treatment was performed using Ti/RuO_2 DSA-type electrodes as the anodes and carbon steel as the cathodes.

2. EXPERIMENTAL SETUP

2.1. Electrochemical reactor

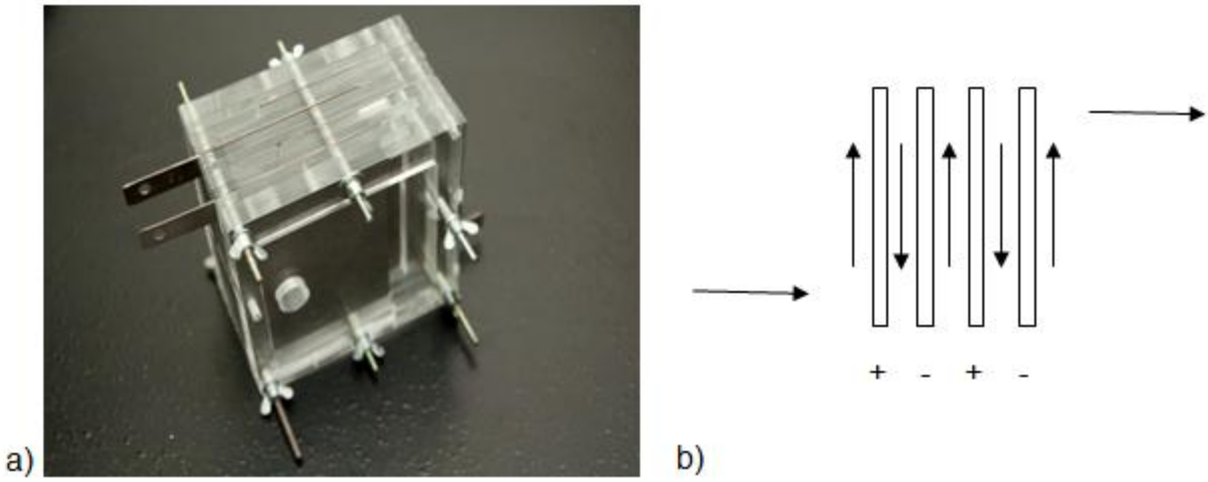

Figure 1. a) Parallel-plate electrochemical reactor; b) Electrode positions scheme according to the effluent flux that is indicated by the arrows.

A parallel plate configuration was used for the electrochemical reactor. The outer body was constructed of an inert material, and two pairs of electrodes were used: two Ti/RuO_2 DSA® (dimensionally stable anode) electrodes produced by De Nora®, with a total surface area of 192 cm^2, and two carbon steel cathodes with the same dimensions. The electrodes were positioned with a gap of 10 mm between them. Figure 1 indicates the positioning of the electrodes and the reactor.

A constant current density of 26 $mA.cm^{-2}$ was applied to the electrodes, which was provided by a Minipa MPL-3305M DC power supply. The electrochemical system was composed of an effluent/mixture tank, an electrochemical reactor with a power supply, a filter and a pump for recirculation, as indicated in Figure 2. The experiments were performed in batch mode. Each test was conducted at room temperature and ambient pressure.

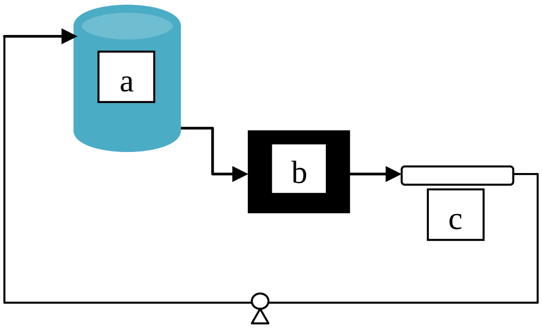

Figure 2. Simplified scheme of the electrochemical treatment system: a) effluent/mixture tank; b) electrochemical reactor; c) filter.

2.2. Effluent and indirect oxidation

Oil refinery sour water samples were provided by Petrobras S.A. The main components of this type of effluent are NH_3-N and H_2S, and their concentrations prior to treatment can reach up to 6 $g.L^{-1}$ and 4 $g.L^{-1}$, respectively, according to the operational conditions. The average pH was 9.38. The sour water volume used for each test was 1.3 L.

A commercial 4-6% NaOCl solution was used for the indirect oxidation at a proportion of 17.8 mL_{NaOCl} per 1 L of sour water sample. This sodium hypochlorite concentration was based on previous studies and literature reports [10,11,14,21,23,25].

2.3. Sample analysis

The concentrations of NH_3-N, NO_2^-, COD, chloramines and soluble Fe were determined using standard methods from the American Society for Testing and Materials (ASTM) and the United States Environmental Protection Agency (USEPA): the Nessler Method for NH_3-N determination, the phenanthroline method for soluble Fe determination, the ferrous sulfate method for NO_2^- determination and the dichromate method for COD determination. Chloramines were determined after the determination of total chloride and free chloride by the DPD Method. Hanna Instruments photometers were used for these tests.

2.4. Current efficiencies and energy consumption

The average current efficiency (ACE) and energy consumption (EC) were determined using Equations (12) and (13) after considering the removal of NH_3-N [1,20]:

$$\mathbf{EC} = (\Delta Ec \times I \times t)/(3600 \times V) \quad \text{kWh. L}^{-1} \qquad (12)$$

where **t** (s) is the time of the electrochemical treatment, **ΔEc** (V) is the average cell voltage, **I** (A) is the electrochemical treatment current and **V** (L) is the sample volume;

$$\mathbf{\%ACE} = \{3 \times [(NH_3\text{-}N)_i - (NH_3\text{-}N)_f] \times F \times V\}/(14 \times I \times t) \qquad (13)$$

where **t** (s) is the time of the electrochemical treatment, $\mathbf{(NH_3\text{-}N)_i}$ and $\mathbf{(NH_3\text{-}N)_f}$ are the initial and final concentrations of NH_3-N (g.L^{-1}), respectively, **I** (A) is the electrochemical treatment current, **F** is the Faraday constant (96,485 C mol^{-1}), **V** (L) is the sample volume, **3** is the number of exchanged electrons for the electrochemical oxidation of ammonia and **14** (g.mol^{-1}) is the molecular mass of nitrogen.

3. RESULTS AND DISCUSSION

3.1. Electrochemical reactor

The parallel-plate reactor is well known for its efficiency [30]. In this work, a hydrodynamic study was developed to demonstrate the suitability of this reactor design for the proposed electrochemical treatment and to obtain the mass transfer coefficient (K_l) for the process. A typical expected K_l value in industrial applications can range from 10^{-6} to 10^{-4} m.s^{-1}, depending on manufacturing costs, maintenance and process efficiency [30].

In the case of the parallel-plate reactor design, a turbulent flow regime takes place, and the mass transfer coefficient can be defined by Equation (14):

$$\mathbf{K_l} = 0.023\, Re^{0,8} Sc^{1/3} D_i/de \qquad (14)$$

where:

Di is the diffusion coefficient of NH_4^+, and $D_i = 1.957 \times 10^{-9}$ $m^2.s^{-1}$, assuming the slowest ion-controlling process, ***de*** is the hydraulic diameter, $de = 9.41 \times 10^{-3}$ m, ***Sc*** is the Schmidt number, $Sc = \mu / (\rho \times D_i)$, **μ** is the water viscosity, $\mu = 1 \times 10^{-3}$ N.s.m^{-2}, **ρ** is the water density, $\rho = 1000$ kg.m^{-3}, ***Re*** is the Reynolds number, $Re = (de \times \rho \times \nu) / \mu$, **ν** is the fluid velocity and $\nu = Q / A$ m.s^{-1}, **Q** is the fluid output and $Q = 8.5 \times 10^{-5}$ $m^3.s^{-1}$, **A** is the fluid passage hydraulic area and $A = 4 \times 10^{-4}$ m^2.

According to Equation (14) and process data, $\mathbf{K_l} = 1.64 \times 10^{-5}$ m.s^{-1}.

In terms of industrial applications, this K_l is an acceptable value. Therefore, the reactor design was suitable for the electrochemical treatment developed in this work.

3.2. Electrodes

When a current density of $j = 26$ mA.cm^{-2} was applied during preliminary tests, the potential values at the anode and cathode remained constant during the entire electrochemical process. This behavior indicated that the system was electrochemically stable.

The Ti/RuO_2 DSA anodes did not exhibit any visible signs of surface damage, in agreement with the results discussed in the literature. This type of electrode is known for its significant surface and structural stability. According to Pourbaix [40], the potential achieved by the cathode during the electrochemical process (-3 V to -4 V) and at a solution pH of 9.4 are conditions in which Fe is thermodynamically immune to corrosion.

However, before the electrochemical treatment was initiated and while the current density was zero, the potential value of the carbon steel electrode was approximately 0.4 V. Under these conditions, corrosion processes are thermodynamically favorable for this material [40]. Several minutes were required to allow adjustments of the system parameters, and this time was sufficient for the corrosion processes to occur at the carbon steel electrode. The corrosion processes during system shut-down were expected and were not expected to interfere with the electrochemical treatment process. Additionally, a decrease in pH was observed during some tests, which was attributed to the hydrolysis of chlorine, according to Equation (7) [4]. This phenomenon created thermodynamic conditions in which carbon steel corrosion was possible. Through the optimization of the systems parameters it is possible to soften the corrosion processes during the electrochemical treatment.

3.3. NH_3-N removal

After the preliminary hydrodynamic study and electrodes tests, the electrochemical treatment of the industrial sour water was performed. Three groups of tests were accomplished to verify the response of the system according to the optimization of the use of indirect oxidant. The treatments lasted for 7 hours.

Table 1. Average characteristics of oil refinery sour water

pH	NH_3-N mg.L^{-1}	NO_2^- mg.L^{-1}	COD mg.L^{-1}	Soluble Fe mg.L^{-1}	Chloramines mg.L^{-1}
9.38	2350	3400	5690	6200	8

As previously mentioned, a sample volume of 1.3 L of sour water was used for each electrochemical treatment.

In Test 1, NaOCl was added once only at the beginning of the process. In Test 2, NaOCl was added at the beginning and at two additional instances during the process at the same proportion of

17.8 mL_{NaOCl} per 1 L of sour water sample. In Test 3, NaOCl was added at the beginning and at one additional instance during the process at the same proportion. The concentrations of NH_3-N, NO_2^-, COD, chloramines and soluble Fe and pH value were measured at specific time intervals. The H_2S content was not considered in this work because the treatment was performed with samples obtained after this compound has been already removed.

The basic characteristics of the sour water effluent, not considering H_2S, are indicated in Table 1, which report the average values. The variations in NH_3-N content and in pH are shown in Figures 3 and 4, respectively.

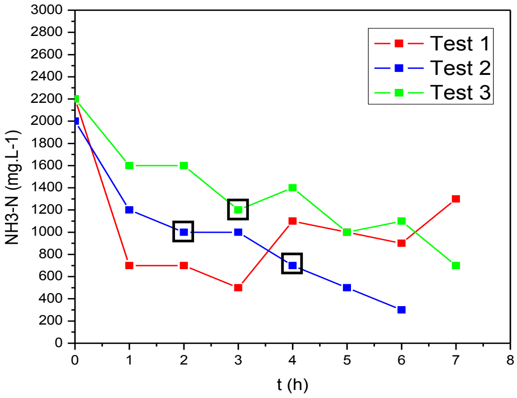

Figure 3. Variations in NH_3-N content according to the NaOCl injection system. Test 1: NaOCl added at the beginning of the process; Test 2: NaOCl added at the beginning and at two additional occasions during the process; Test 3: NaOCl added at the beginning and once more during the process. Intermediary NaOCl injections are indicated by the squares.

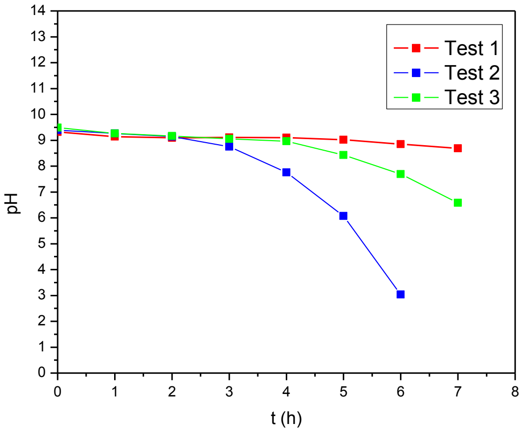

Figure 4. Variations in pH according to the NaOCl injection system.

In Test 1, hypochlorite was added to the system at the beginning of the electrochemical treatment (t=0), and the pH remained stable under these conditions. As shown in Figure 3, however, the NH_3-N content profile exhibited a significant initial decay that was followed by a positive variation. According to Vitse *et al.* [12], Lima *et al.* [14], Li *et al.* [16], Bonnin [41], and Seed *et al.* [42], the use of DSA anodes during the electrochemical removal of ammonia compounds leads to a final product that is free of nitrogen oxides. According to the same references, the final product is primarily N_2. However, depending on the conditions of the system, nitrate and nitrite are possible co-products. Additionally, as shown in Equation (1), only the N_2 formation pathway is irreversible, which means that the NH_3-N content variation in Figure 3 likely indicated the reversible nitrite and nitrate formation reactions. Thus, the ammonia and ammonium ions were not completely transformed to N_2. This observation was reinforced by the variation in NO_2^- content, which is shown in Figure 5.

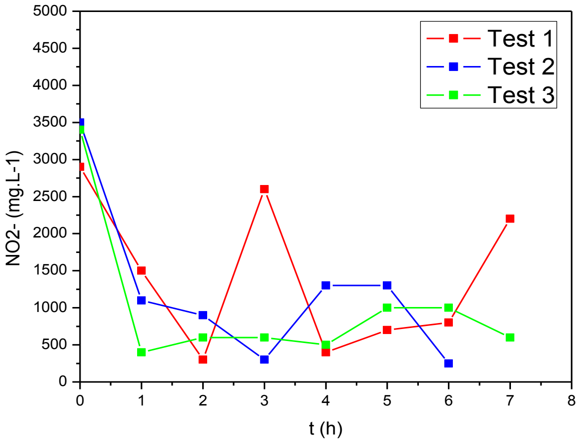

Figure 5. Variation in NO_2^- content according to the NaOCl injection system.

The NO_2^- and NH_3-N profiles were complementary. The nitrite content increased as the ammonia and ammonium ions were reduced, as discussed previously. Nevertheless, NO_2^- and NO_3^- can be reduced at the cathode if the electrochemical conditions are satisfactory for these reactions. These results thus indicated a difference between the oxidative and reductive kinetics: the indirect oxidation contributed to the generation of anodic reaction products faster than the cathode reductive capacity was able to handle in this system configuration.

In Test 1, the removal percentage of NH_3-N with the addition of indirect oxidant at the beginning of the electrochemical treatment was only 40.9%. The optimization of the NaOCl addition was then investigated to improve the removal of NH_3-N and decrease the reversible nitrite reactions to lead to the final product N_2.

Based on the positive NH_3-N content variation in Figure 3, 3 points of NaOCl addition were established at $t = 0$ (beginning of the test), $t = 2$ and $t = 4$ hours. The results from the 3 additions of NaOCl are indicated by the curve labeled Test 2 in Figure 3. The variations in pH and NO_2^- content are indicated by the curves labeled Test 2 in Figures 4 and 5, respectively. Under these new conditions, the removal percentage of NH_3-N was 85%, and the final nitrite content was lower than in Test 1, which indicated that the reaction followed the N_2 generation pathway. However, the pH value decreased over time, and its final value was 3.04, which is considered to be too low for effluent disposal according to environmental laws [43]. As mentioned previously, the indirect oxidation can contribute to a decrease in the pH of the media due to chlorine hydrolysis reactions, according to Equation (7) [4].

Test 3 was then performed with one extra point of NaOCl injection in addition to the NaOCl added initially. Thus, 2 points of NaOCl addition were established at in t = 0 (beginning of the test) and t = 3 hours. The results from the 2 additions of NaOCl are indicated by the curve labeled Test 3 in Figure 3. The variations in pH and NO_2^- content are indicated by the curves labeled Test 3 in Figures 4 and 5, respectively. Test 3 included the best operating conditions with regard to the pH value. According to Figure 4, the pH profile for Test 3 was nearly constant, and the final value was 6.58, which is considered to be adequate for effluent disposal according to environmental laws [43]. This result also indicated that there existed an optimum value for the indirect oxidant in which the reaction of hydrolysis of chlorine would not be predominant and pH would remain stable. The removal percentage of NH_3-N in Test 3 was 68.2%. This result was not as satisfactory as the removal from Test 2, however, the pH value was higher in Test 3 than in Test 2. The nitrite profile appeared to follow the NH_3-N profile, and the reactions also appeared to follow the N_2 generation pathway.

In general, the removal of NH_3-N increased by increasing the indirect oxidant content, as discussed in the literature and demonstrated in this work. However, the pH was strongly affected by the indirect oxidant content. Therefore, despite the promising results in Test 3, the electrochemical system could be further optimized to achieve the best configuration for higher NH_3-N removal. Additionally, the generated nitrite could be separated and used, for example, as a corrosion inhibitor.

3.4. COD removal

The COD concentrations and the removal percentage of COD are shown in Table 2.

Table 2. COD removal from the electrochemical treatment.

Tests	Initial COD concentration mg.L^{-1}	Final COD concentration mg.L^{-1}	Removal %
1	6040	380	93.7
2	2170	550	74.6
3	7790	1150	85.2

The results in Table 2 suggest that the indirect oxidant also influenced the removal rate of COD in addition to the removal rate of NH_3-N. Nevertheless, the highest COD removal was achieved with Test 1, and the lowest removal was achieved with Test 2, indicating that the hypochlorite content directly affected the electro-oxidation process. These results were correlated with the pH values, as COD electrochemical removal is favored by more alkaline pH values [26]. In Test 2, the indirect oxidant content was the highest, which lowered the observed pH. The low pH affected the COD removal in Test 2, which produced the lowest COD removal compared to the other tests. In Test 1, the pH remained stable, providing a more alkaline and suitable environment for the oxidation of the compounds that were expressed by the COD index.

According to the presented results, the optimal conditions for COD and NH_3-N removal were achieved with Test 3.

3.5. Soluble Fe and chloramines

The soluble Fe content provided information about the stability of the cathode material in the sour water media. Although the initial thermodynamic conditions were favorable to Fe immunity toward corrosion, corrosion was still possible due to variations in the pH [40]. The corrosion of Fe at varying pH was indeed observed: in Test 1, the final soluble Fe content remained stable at approximately 7000 mg.L^{-1}, while in Tests 2 and 3, it increased by approximately 20%.

Chloramines were also evaluated, as their formation depends mainly on pH, temperature and the concentration ratios between active chlorine and ammonia [25,27]. Some authors have previously reported that chloramines were highly unstable and that the final concentrations of chloramines were zero [16,21,25,27]. The results obtained in this work are presented in Figure 6.

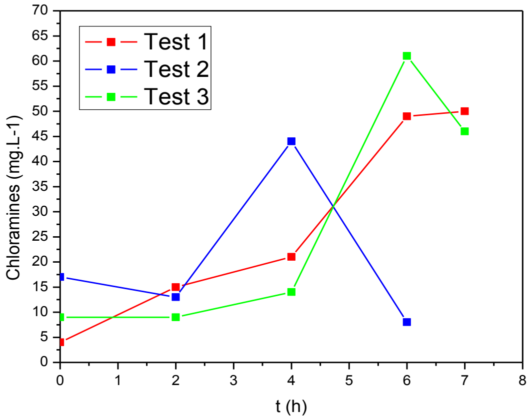

Figure 6. Chloramine content variation according to the NaOCl injection system.

According to Figure 6, the pH affected the chloramine generation during the tests. In Test 2 in which the lowest pH value was achieved, the final chloramine concentration was lower than the initial concentration, indicating a removal of 52.9%. In this case, the chloride in the solution was subjected to hydrolysis according to Equation (7), and chloramines were more easily decomposed. In contrast, the higher pH values in Tests 1 and 3 contributed to the generation of chloramines.

3.6. Average current efficiencies and energy consumption

The average current efficiencies (ACE) and the energy consumption (EC) were calculated for each test according to Equations (12) and (13) considering the NH_3-N removal data. The results are shown in Table 3. In Test 2, the test time was different because the experiment was finished early due to the low pH value, as indicated in Figure 4. According to Chen *et al.* [1], an increase in the indirect oxidant content promoted an increase in the ACE. This was demonstrated by the Test 2 results, which showed the highest average current efficiency. In addition, according to Table 3, the energy consumption decreased with increased indirect oxidant concentrations, which would indicate lower operating costs as well.

Table 3. ACE and CE during the electrochemical treatment of oil refinery sour water.

Tests	$[(NH_3\text{-}N)_i - (NH_3\text{-}N)_f]$ g.L^{-1}	V (L)	ΔEc (V)	I (A)	t (s)	%ACE	EC kWh.L^{-1}
1	0.9	1.3	8.40	5	25200	19	226.15
2	1.7	1.3	8.48	5	21600	42	195.69
3	1.5	1.3	7.77	5	25200	32	209.19

Considering the composition of the sour water used in this study, which contained elevated NH_3-N and COD concentrations in addition to other compounds, the obtained current efficiencies were not considered too low when compared to the literature data. Additionally, the energy demand was not too high, although it could be considered elevated when compared to biological processes. However, the electrochemical treatment process presents more reliable results compared to biological processes [1,20,44].

The electrochemical treatment proposed in this study presented promising NH_3-N and COD removal efficiencies. The configuration of the electrochemical system could be further optimized to achieve a lower EC, a higher ACE and a greater removal percentage of NH_3-N to guarantee that the final solution parameters are in accordance with the limits established by environmental laws for effluent disposal [43] and to guarantee that the energy consumption is satisfactory for industrial applications. Although the energy demand was high, the electrochemical treatment is still an attractive and environmentally friendly process that occupies less area and is typically performed under ambient temperature and pressure, which makes the process easier to operate, control and maintain. The electrochemical system can be further optimized both in terms of current density and energy consumption [7-9].

4. CONCLUSIONS

- The parallel-plate configuration is a suitable design for the electrochemical reactor. The hydrodynamic parameters indicate the applicability of this design to further industrial scale.
- There is a NaOCl concentration limit in which the indirect oxidation remains active without lowering the pH of the media. In addition, the electrochemical treatment with the indirect oxidation is an interesting alternative process for NH_3-N and COD removal.
- The best system configuration for the electrochemical treatment for NH_3-N and COD removal in this work was achieved in Test 3 with the use of two points of addition of the indirect oxidant NaOCl. The pH remained stable and favored the removal of COD. Additional studies are required to improve the removal percentage of NH_3-N and COD to guarantee that the final solution parameters are in accordance with the limits established by environmental laws for effluent disposal.
- Additional studies could be performed to decrease the energy demand and to improve the current efficiency.

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