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STUDY OF THE EFFECTIVENESS OF MEMBRANE AERATION SYSTEMS ON THE REMOVAL OF AMMONIUM IONS FROM NATURAL WATERS

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The experimental results obtained through the operation of a pilot laboratory facility designed to increase the efficiency of the water oxygenation process and increase the efficiency of ammonium ion removal from natural and wastewater were presented. To study the efficiency of the aeration process, was identified the influence of the composition of the aqueous environment, of the type of membrane, of the air stripping flow rate and of the height of the fluid layer. It was found that the membrane with the larger hole diameter reaches dissolved oxygen concentration values, DO, higher than the saturation values, in the specific working conditions. Increasing the bubbled air flow rate increases the degree of oxygen saturation in all the environments studied. The concentration of dissolved salts in the aqueous environment has a negative effect on the DO concentration, the higher the concentration, the lower the DO concentration. This is determined by its consumption in oxidation processes. The decrease in the height of the water column has negative effects on the DO concentration due to the decrease in the contact time between water and air. The efficiency of the ammonium ion removal process is influenced by the air flow rate, the initial concentration of the ammonium ion, and the pH of the system. The efficiency increases as the air flow rate increases, decreases with increasing of ammonium concentration and increases with increasing pH.

Following the obtained results, can be stated that the constructive solution proposed for the aeration system is efficient and can be improved based on the obtained results.

Keywords: natural water treatment, aeration, oxygen dissolved, ammonium, removal efficiency

1. Introduction

The new European legislation for drinking water, Directive 2020/2184/EC harmonized in Romanian legislation by Ordinance 7/2023 imposes new restrictions on water treatment processes, [1]. Considering the new legislative requirements, innovative technical solutions for water treatment must be identified to ensure the achievement of the required parameters.

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The main components that create problems in drinking water process when used as raw materials underground waters or deep surface waters are compounds in reduced form of ammonium type, hydrogen sulphide and sulphides, organic compounds, iron, manganese ions, arsenic and others. To be able to remove these compounds, they must undergo the oxidation process. Normally, the oxidation of compounds in reduced form in natural waters is carried out by pre-chlorination using chlorine gas, hypochlorite, chlorine oxides, ozone, $KMnO_4$, etc. [2, 3]

Chlorination has been used successfully, being a very efficient method of oxidation which, however, has the disadvantage that in the presence of organic compounds, chlorine can form in water trihalomethanes and organochlorine substances, toxic and carcinogenic compounds. [4, 5]. Another problem generated using chlorine compounds is the desorption of gaseous chlorine from water that reaches the atmosphere where it participates in the destruction of the ozone layer and the formation of acid rain. [6] Under these conditions, less toxic solutions must be identified for the peroxidation process to avoid unwanted effects.

NH_4^+ cation is present in natural surface and underground waters, and also in wastewater. NH_4^+ concentrations in the natural water can reaches under 10 mg/L and in the industrial and agricultural wastewater concentrations can reach 40-50 mg/L [2, 4, 7]. The removal of ammonium ion from water is a highly developed subject in research studies, however it continues to pose problems especially in natural water sources used as a source of drinking water that have concentrations higher than 5 mg/L. The removal of ammonium ion from water can be done by numerous methods: oxidation with or without catalysts, by desorption (stripping) in the presence by bubbling some gases (air, oxygen, ozone, etc.), by adsorption, ion exchange, membrane processes, biological processes A convenient process for removing the ammonium ion from natural waters is aeration [8-13].

Through aeration, it is possible to ensure a concentration of oxygen in the water at a higher concentration or at least equal to the saturation concentration for the working temperature [15]. To achieve this performance, it is necessary to identify an optimal solution from a constructive point of view that allows a uniform distribution of air bubbles in the fluid mass. In the purification stations, membrane diffusers with orifices are used, which are evenly distributed over the surface of the nitrification zone. Perforated pipes are used in treatment stations for aeration, which have a reduced efficiency.

In the current study, it has been presented an efficient solution for water aeration, by stripping of the air under pressure through two perforated membranes, a bubble diffusion aerator. The performance of the aeration system was monitored from the point of view of aeration, but also the efficiency of the aeration process on the removal of the ammonium ion from the water. The influence of the membrane type (pore size), the air flow, the gas volume and the initial concentration of the ammonium cation on the concentration of dissolved oxygen, DO, and the removal efficiency of the ammonium ion was studied.

2. Materials and methods

2.1. Pilot laboratory installation, Laboratory aeration system, LAS

In this study, the following elements have been used: a pilot laboratory installation, a bubble diffusion aerator, called Laboratory aeration system, LAS, with the aim of ensuring a high concentration of dissolved oxygen (at values above the concentration at saturation), to ensure the oxidation of oxidizable compounds in the water, and, at the same time, to allow the desorption of gases dissolved in water as well.

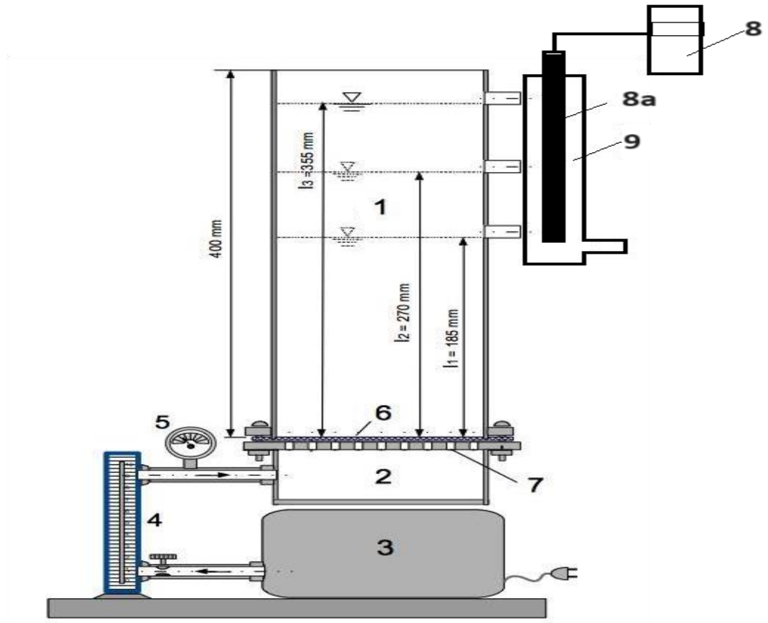

Fig. 1. The Laboratory aeration system, LAS, of the water treatment plant
1 – Reaction chamber;
2 – Air chamber;
3 – Air pump;
4 – Air flow meter;
5 Manometer;
6 – Membrane;
7 – Membrane support plate,
8- Oxygen-meter;
8a -Dissolved oxygen sensor;
9 -Sampling vessel.

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The installation is represented in Fig. 1 and consists of a reaction chamber (1), where the physic-chemical processes of reaction and gas desorption take place, air is introduced under pressure by a pump (3) into the air chamber (2), from where it is evenly distributed through the membrane (6) in the reaction chamber. The gas pressure was measured with a manometer (5), and the air flow rate with a flowmeter (4). The membrane rests on a support (7). The concentration of dissolved oxygen, DO, was measured online with an Oxygen-meter type HQ30d, HACH, Loveland, CO, USA. The concentration was measured with a dissolved oxygen sensor (8a) inserted in the sampling chamber (9), connected to a data storage device (8).

In Table 1, the characteristics of the perforated membranes of the water aeration installation are presented:

Table 1.

The characteristics of the perforated membranes of the water aeration installation, diffusion bubble aerator

Characteristics	Membrane 1, M1	Membrane 2, M2
Material	Soft rubber	Soft rubber
Thickness	2 mm	2 mm
Diameter of membrane	14.4 cm	14.4 cm
Area	162.77 cm^2	162.77 cm^2
Number of perforations	320	320
Perforations density	2 / cm^2	2 / cm^2
Diameter of perforations (diameter of needle used for perforating the membrane)	1.5 mm	0.5mm
The approximate size of the bubbles in the water in the aerator vessel, starting from its base, depending on the pumped air flow rate	1.0.....2.5 mm	0.3.....2.0 mm

2.2. Efficiency of aeration - oxygen dissolved concentration

In the research carried out, the two membranes with characteristics mentioned in Table 1 were used. The work was done under static conditions regarding the liquid phase. Distilled water and synthetic solutions containing ammonium chloride (Sigma Aldrich) with concentrations between 9 mg/L and 39 mg/L were used as the liquid system. The pH in the systems was of 6.5, and the temperature was around 20 °C;

Different liquid volumes were introduced into the Reaction chamber: 5, 3.74, 2.76 L, the geometric characteristics of the vessel: diameter D= 144 mm, height, H =300 mm, 230 mm and 168 mm respectively. The air flows were of 5 L/min, 10 L/min, 15 L/min, and 20 L/min. The ammonium ion concentration was determined according to SR ISO 7150-1 /2001. Jenway Aquanova spectrophotometer was used to determine the ammonium ion.

The concentration of dissolved oxygen in distilled water and in ammonium synthetic solutions was monitored until the DO concentration remained constant. DO was measured every 10 seconds. The results are shown in Figs. 2- 7.

2.3. Efficiency of aeration on ammonium removal

To determine the efficiency of removing the ammonium ion from water by stripping, we worked on three initial concentrations of the synthetic ammonium chloride solution: 9, 23 and 39 mg/L, and on two stripping air flows: 5 and 10 L/min, using membrane M1. The pH in the systems was varied between 5 and 9;

the temperature was around 20 °C, the working time 30 minutes, and samples were taken every 2 minutes.

The efficiency of the aeration (stripping) process was calculated with the relation [15]:

$$\text{Efficiency, \%} = \frac{DO_i - DO_t}{DO_i} \text{x}100 \qquad (1)$$

where DO_i *-and* DO_t represent dissolved oxygen concentrations, in mg/L, at initial and at moment t.

The experimental results are shown in Fig. 8. The influence of pH on the removal efficiency of the ammonium ion was also studied (see Fig. 9). To maintain the pH at a constant value, a mixture of phosphoric acid, nitric acid and boric acid was used in equal ratios and different volumes of sodium hydroxide. The working pHs were of: 5.02, 6.09, 6.59, 7.00, 7.96, 8.69, 9.15. For each system, 5 ml of buffer solution was introduced into the 5 L system.

3. Results and discussion

3.1. Efficiency of aeration - oxygen dissolved concentration

In order to study the efficiency of the aeration process, two membranes, M1 and M2, distilled water and synthetic ammonia solutions of ammonium chloride with concentrations of 9 and 24 mg/L, respectively, were used. The temperature in the system was around 20 °C. The liquid volumes in the reaction chamber were of 5L, 3.74 L and 2.76 L, height, H =307 mm, 230 mm and 168 mm respectively; four air flow rates were used: 5, 10, 15, 20 L/min. The dissolved oxygen present in the aqueous media before the beginning of the experiments was removed by bubbling nitrogen gas with a purity of 99.8%, under pressure (Linde). Figs. 2 - 7 show the variation of the dissolved oxygen concentration in distilled water and ammonium synthetic solutions, until reaching the maximum DO concentrations by stripping the air on M1 and M2 membranes.

To characterize the aeration efficiency of the membranes, the degree of saturation, S, was calculated as the ratio between the DO reached in the system and the concentration at saturation for the working conditions, in this case being of 9.07 mg/L. From the comparative analysis of Figs. 2 and 3, an important parameter that influences DO is the diameter of the perforations in the membranes. The M1 membrane with an opening diameter of 1.5 mm is much more efficient than the M2 membrane with an opening size of 0.5 mm. For all air flows bubbled in distilled water, the maximum DO concentration provided by M1 reaches supersaturation at values between 102.7% and 103.2%. The time required to reach these values was between 350 and 200 seconds.

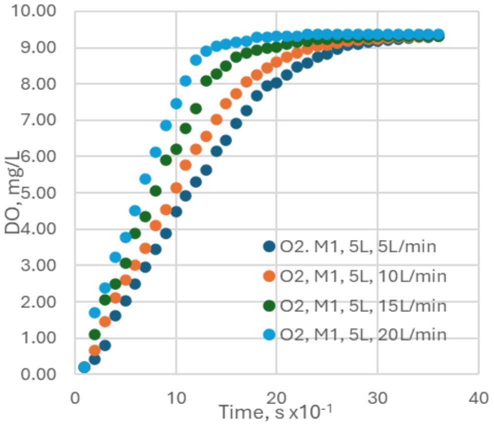

Fig. 2. Variation of the DO in distillated water, striping air flow rate 5, 10, 15 and 20 L/min, by M1, volume liquid 5 L

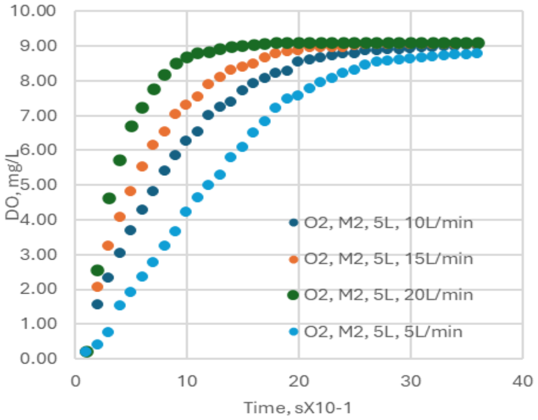

Fig. 3. Variation of the DO in distillated water, striping air flow rate 5, 10, 15 and 20 L/min, by M2, liquid volume 5 L.

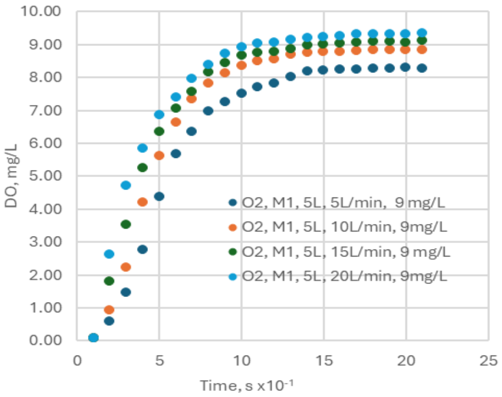

Fig. 4. Variation of the DO in synthetic solution of NH_4Cl, concentration 9 mg/L, the striping flow rate was 5, 10, 15 and 20 L/min introduce by M1, liquid volume 5 L.

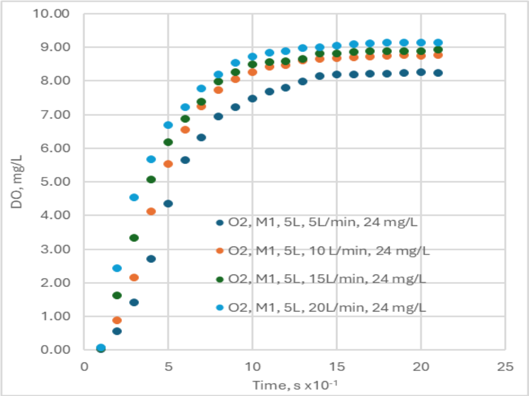

Fig. 5. Variation of the DO in synthetic solution of NH_4Cl, concentration 24 mg/L, the striping flow rate was 5, 10, 15 and 20 L/min, by M1, liquid volume 5 L.

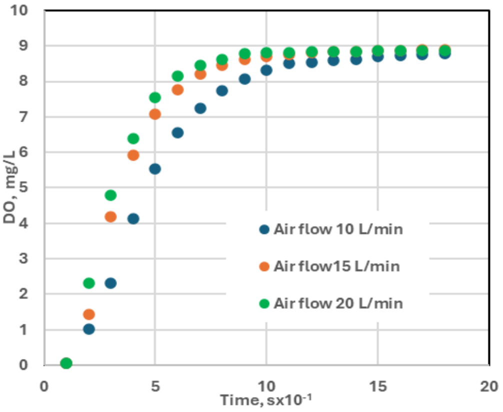

Fig. 6. Variation of the DO in synthetic solutions NH_4Cl, concentration 24 mg/L, the striping flow rate was 5, 10, 15 and 20 L/min, M1, liquid volume 3.74 L.

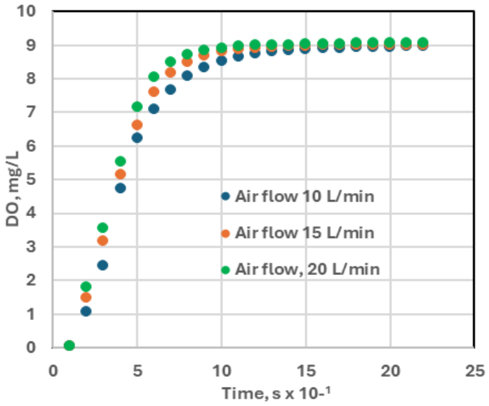

Fig. 7. Variation of the DO in synthetic solutions NH_4Cl, concentration 24 mg/L, the striping flow rate was 5, 10, 15 and 20 L/min, M1, liquid volume 2.76L.

For the M2 membrane, the DO values reach S saturation values between 96.7% and 100.3% after 350 and 200 seconds, respectively. Since M1 proved to be more efficient than M2, the following experiments were carried out using only this one.

When synthetic ammonia solutions are used under the same conditions as for distilled water but with concentrations of 9 mg/L and 24 mg/L ammonium chloride (see Figs. 4 and 5), it can be observed that the degree of saturation decreases with increasing concentration of ammonium, so that it reaches values between 91.4% and 102.7%.

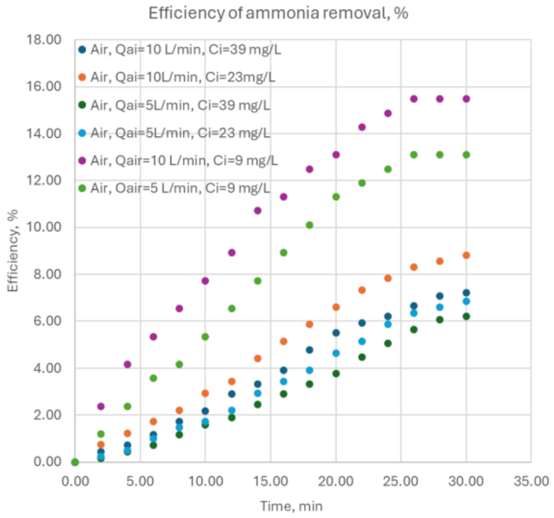

Fig. 8. Efficiency of ammonium removal, concentration initial 9 mg/L, 23 mg/L and 39 mg/L, flow rate of air: 5 L/min and 10 L/min. pH =6.5.

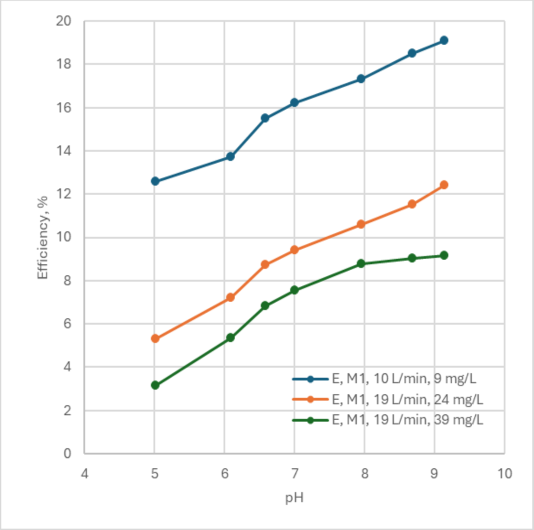

Fig. 9. Efficiency of ammonium removal, concentration initial 9 mg/L, 23 mg/L and 39 mg/L, air flow rate o 10 L/min, pH in range 5-9

These values are reached after 200 seconds of air bubbling, at the four working flow rates for an ammonium concentration of 9 mg/L. For concentrations higher than 24 mg/L, it can be observed that the degree of saturation decreases and reaches values between 90.8% and 100.77%. after 200 seconds of air bubbling at the four air flow rates. This proves that in the presence of ammonium part of the dissolved oxygen is consumed in oxidation processes. At lower dissolved oxygen flow rates, oxygen consumption is higher.

Another important parameter that influences the degree of oxygen saturation is the height of the water column (see Figs. 2, 6 and 7). It can be observed that the decrease in the height of the water column is from 307 mm to 168 mm, while the degree of saturation decreased from values between 102.7% and 103.2%, to values between 98.7% and 99.8%. Although the difference does not seem significant, if these techniques are applied to industrial installations, then the influence will be significant.

To demonstrate the effectiveness of these in the case of synthetic solutions with high ammonium content, three synthetic solutions of ammonium chloride were used, with concentrations of 9 mg/L, 23 and 39 mg/L, air flow rates of 5 and 10 L/m, working pH of 6.5 (see Fig. 8). Naturally, as the concentration of ammonium increases, the efficiency of its removal decreases. The highest efficiency was recorded in the case of the concentration of 9 mg/L at an air flow rate of 10 L/min is 15.47%. For a concentration of 39 mg/L, the efficiency is only 6.8%, at a flow rate of 10 L/min air. Although these effective values seem small, since the concentrations of the ammonium ion are very high, they assume losses of concentrations between 1.45 and 2.8 mg/L ammonium. This loss is assured by the installation and demonstrates that the constructive solution with performing membranes can be a solution for the partial removal of the ammonium ion that can be improved.

Aeration is a complex process that involves the simultaneous development of several processes such as: decomposition of ammonium in ammonia species (gaseous or dissolved form); desorption of ammonia in gaseous form, and oxidation of ammonia. In water, the ammonium cations (NH_4^+) are in equilibrium with molecular ammonia (NH_3) and introduce the acidity in aqueous solution. The characteristic reactions are [17]:

$$NH_4^+\,[aq] + H_2O\,[l] \leftrightarrow NH_3\,[aq] + H_3O^+[aq] \tag{1}$$

$$NH_4Cl[s] + H_2O[l] \leftrightarrow NH_3\,[aq] + HCl\,[aq] \tag{2}$$

The acidity introduced by ammonium in water gives a pH of 4.6 to 7, depending on the initial concentration of the ammonium ion, a high concentration of the ammonium ion determines a higher acidity**.**

In basic medium, the ammonium reacts with hydroxyl ions and form the ammonia and water after reaction [17, 18]:

$$NH_4^+\,[aq] + HO^-[aq] \leftrightarrow NH_3\,(aq] + H_2O[l] \tag{3}$$

In the stripping process, we intend to remove as much ammonia as possible (which is a slightly volatile compound). So, it is desired to transform ammonium into ammonia and eliminate it, by entrainment with gases (air). From the relationship of the equilibrium constant of reaction (3), it is possible to determine the value of the ammonia concentration in water depending on the pH [17].

$$[NH_3] = \frac{[NH_3 + NH_4^+]}{1 + [\,H^+]/Ka} \tag{2}$$

where $[NH_3]$ represents the ammonia concentration, $[NH_3 + NH_4^+]$ represents the total ammonia concentration, $[H^+]$ is the hydrogen ion concentration, and Ka is the acid ionization constant. From relation (2) results that high values of the ammonia concentration are obtained if the acidity is reduced, so the basicity increases. However, the increase in alkalinity is limited by the legislation in force, which imposes the maximum pH value for drinking water at 9.5 pH units [1], but also the costs of reagents and dosage. In this sense, a balance must be made between them [18].

By air stripping, the ammonia formed in the system is removed, so that the balance of equation (4) is driven to the right, according to Le Chatelier's principle.

In Fig. 9, one can see that the removal efficiency of the ammonium ion decreases with the increasing of the concentration of ammonium. This does not exceed 9.14%, 12.4% and 19.1% for 39 mg/L, 24mg/L and 9 mg/L, respectively. It also increases with increasing of pH; for the concentration of 9 mg/L, the effective increase is 1.5 times and, at the concentration of 39 mg/L, it increases 2.9 times, in the pH range studied, although the dose of sodium hydroxide was kept constant for each pH. Therefore, besides the chemical reaction between ammonium and the hydroxyl group, there are other processes that stimulate the removal of the ammonium.

4. Conclusions

The pilot laboratory installation, LAS, developed and used in this study has given gratifying results.

The membrane M1**,** with an opening diameter of 1.5 mm was more efficient; the maximum DO concentration reaches supersaturation at values between 102.7% and 103.2% in distillated water, and the values of saturation between 90.8% and 102.7 % in solution with high concentration of ammonium, after 4-5 minutes of air bubbling. The decrease of height of water column from 307 mm to 168 mm, decreasing the saturation in DO from 103.2 % to 99.8 %, in the same work conditions. The efficiency of ammonium removal decreases with ammonium concentration increasing. The highest efficiency is recorded in the case of the concentration of 9 mg/L for an air flow rate of 10 L/min is 15.47%. by comparation of concentration of 39 mg/L, where the efficiency is only 6.8% at the same flow rate. The efficiency of ammonium removal increases with pH increasing; for the concentration of 9 mg/L, the effective increase is 1.5 times and, at the concentration of 39 mg/L, it increases 2.9 times, in the pH range studied, although the dose of sodium hydroxide was kept constant for each pH.

Based on the results obtained, the operation of the pilot plant can be optimized to raise the performance level.

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