



Ammonia removal from leachate by photochemical process using H₂O₂ (doi:10.4136/ambi-agua.136)

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ABSTRACT

In this work, it was studied the optimization of the photochemical process using H₂O₂/UV in order to reduce the concentration of ammonia in leachate. It was used landfills leachate previously treated in the development of studies. A photochemical reactor with the capacity of 1.7 liters equipped with refrigeration system and recirculation of leachate was employed in the research. The influence of temperature, the light bulb power, the concentration of H₂O₂ and treatment time were tested during the study. A removal of 97% of ammonia was observed at 90 min.

Keywords: landfill leachate; photochemical oxidation; solid waste.

Remoção de nitrogênio amoniacal de percolado de aterro por processo fotoquímico utilizando H₂O₂

RESUMO

Neste trabalho foi estudada a otimização do processo fotoquímico utilizando H₂O₂ /UV com o propósito de reduzir a concentração de nitrogênio amoniacal. A matriz poluente em estudo foi o percolado de aterro previamente tratado. No tratamento fotoquímico utilizou-se um reator com capacidade para 1,7 litros equipado com sistema de refrigeração e recirculação do percolado. Durante o estudo foram otimizados a influência da temperatura, da potência da lâmpada, a concentração de H₂O₂ e o tempo de tratamento. Foi possível observar uma alta remoção de nitrogênio amoniacal na ordem de 97%.

Palavras-chave: percolado de aterro; oxidação fotoquímica; resíduo sólido.

1. INTRODUCTION

The leachate is generated in landfills, resulting from the water passage through the solid waste originating from household and industrial waste in the process of decomposition (Lin and Chang, 2000). Leachate may contain high levels of organic compounds, heavy metals, ammonia, chlorine and many other soluble compounds (Cabeza et al., 2007). The physico-chemical composition varies greatly depending on factors ranging from rainfall conditions, time of disposition, age of the landfill, environmental conditions and characteristics of the dump (Bertazzoli and Pelegrini, 2002; Jeong-Honn et al., 2001; Marnie et al., 2005).

Among the classes of pollutants found in leachate, ammonia has caused particular concern due to its high toxicity. Considerable concentrations of nitrogen, in ammoniacal form, can become toxic to organisms especially when present in aquatic environments. The

most toxic form of ammonia is the one non-ionized (NH₃), because it interacts with the nervous system of vertebrate organisms such as fish.

Excessive nitrogen in water, in the form of nutrient, can result in eutrophication. This effect is usually characterized by the increase of aquatic plants to determined levels which may be considered the cause of interference so that, compromising the use of the water body (Kim et al., 2005).

Several biological processes of nitrification can decompose ammonia by techniques of aerobic and anaerobic treatment, however these methods have not been satisfactory (Kim et al., 2006). The photochemical technique using ultraviolet radiation and hydrogen peroxide has been portrayed in the oxidation of organic matter, and in the efficiency to reduce color in effluent, however, it has been reported that this method is inefficient to remove ammonia (Cabeza et al., 2007).

In this study, we have researched several methods of photochemical oxidation using hydrogen peroxide and UV radiation for the degradation of ammonia found in the leachate.

1.1. Photochemical Mechanisms

One way to employ the Homogeneous Photochemica is based on the generation of the hydroxyl radical (OH[·]) from hydrogen peroxide. The use of hydrogen peroxide combined with UV radiation generates the hydroxyl radical, which is a chemical agent with great power of oxidation. Radiation below 400 nm is capable of photolize H₂O₂ causing the split of the molecule into two hydroxyl radicals (Equation 1).



The reaction of the hydroxyl radical is very efficient because its oxidation potential (E^o= +2.8 V) is much higher than that of the molecular hydrogen peroxide (E^o= +1.78 V), and it can cause a stronger oxidation. Furthermore, the hydroxyl radicals react with almost any type of substance, subtracting from it hydrogen atoms or electrons or even being added to the substrate (Dominguez et al., 2005; Xu et al., 2005).

When ferrous ions are present, the photolysis with hydrogen peroxide can be catalyzed to the hydroxyl radical formation (Photo-Fenton process). In this case, the Fe²⁺ ions decompose the H₂O₂ into a redox reaction that leads to the generation of hydroxyl radicals (Equation 2) (Walling, 1975).



The Fe³⁺ ion, formed during the process, can be regenerated to Fe²⁺ with the generation of more hydroxyl radical (Equation 3). This shows the catalytic character of ferrous ions, which can be regenerated in the Photo-Fenton process (Gozzo, 2001).



1.2. The Chemical Oxidation of Ammonia by the Hydroxyl Radical

Kim and collaborators (2005), studied the chemical oxidation of ammonia by the hydroxyl radical in its several complicated steps. The decomposition of ammonia can occur through direct oxidation with the hydroxyl radical so that, forming various compounds of nitrogen, among them, the nitrogen gas, nitrogen oxides (NO_x) and ionic compounds such as nitrite and nitrate (Equations 4 and 5).



The oxidation of ammonia can also be enhanced by increasing the concentration of hypochlorous acid or hypochlorite ions in solution (Equations 6 and 7) (Kim et al., 2006; Cabeza et al., 2007).



Hypochlorous acid can be generated through the reaction of chloride with the hydroxyl radical (Equations 8 and 9), and the oxidation of ammonia may happen via indirect reaction with the hydroxyl radical (Brito, 2008).



2. MATERIALS AND METHODS

The photochemical experiments were performed in a Pyrex glass reactor with the volume capacity of 1.7 L (100 mm internal diameter, 145 mm external diameter and total height of 300 mm) equipped with cooling water system in order to control temperature. The source of ultraviolet radiation was provided by a high pressure mercury light bulb (Philips HPL-N, 250 W and 400 W) by the removal of the outer medulla and it was placed in the center of reactor. The shake of the process was continuously maintained by the recirculation of the leachate through a hydraulic pump (Invensys BAV 1115-02U, 220 V 60 Hz 34 W). The oxygen supply to the photochemical process was held by bubbling air through a sintered glass at the bottom of the reactor using a compressor with a flow control valve (Sniff Compact) (Figure 1).

The leachate used in this study was collected in the city landfill located in the city of Limeira (São Paulo, Brazil). The experiments were performed with pre-treated leachate by slow land filtration. Some physicochemical characteristics of the leachate are shown in Table 1.

Table 1. Landfill leachates characterization.

Parameters	In nature leachate	Pretreated leachate
Nitrogen NH ₄ ⁺ (mg L ⁻¹)	446,67	432,01
Nitrite NO ₂ ⁻ (mg L ⁻¹)	0,22	0,15
Nitrate NO ₃ ⁻ (mg L ⁻¹)	2,66	2,30
Chloride (mg L ⁻¹)	1825	1770
Fe (mg L ⁻¹)	54,16	17,87
pH	8,01	8,14

Source: Brito (2008).

In this study, for verify the efficiency of the photochemical treatment of leachate the following parameters were used: ammonia nitrogen, nitrite, nitrate, pH, residual hydrogen peroxide.

The analysis of ammoniacal nitrogen, nitrite and nitrate were performed according to the colorimetric method, according to Standard Methods for the Examination of Water and Wastewater, 20th Edition (APHA, 1998).

The determination of leachate pH values was carried out according to potentiometric method, according to Standard Methods for the Examination of Water and Wastewater, 20th Edition (APHA, 1998).

The study of residual hydrogen peroxide was a colorimetric process measured in wavelengths of 446 nm, based on the reaction between hydrogen peroxide and vanadate ion (VO₃⁻) in acidic medium (Oliveira et al., 2001).

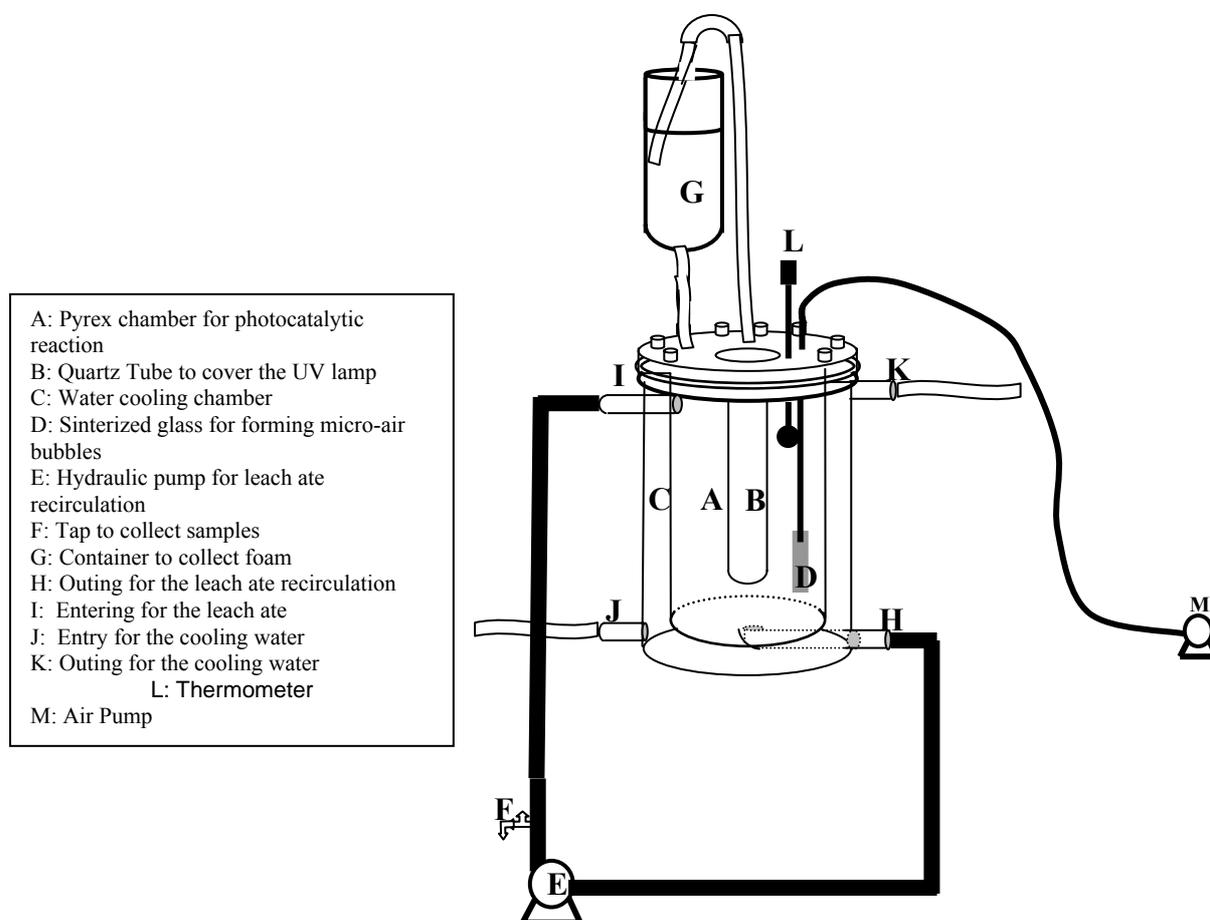


Figure 1. Schematic experimental apparatus.

3. RESULTS AND DISCUSSION

3.1. The optimization of the photochemical process

To initiate the studies of degradation of ammonia in the leachate, a 2³ factorial design (Barros Neto et al., 1995) was developed to optimize some parameters of the treatment (Table 2). In all tests performed, it was added a volume of 50 mL H₂O₂ 10% (2.93 g L⁻¹) and it was maintained with an air flow of 15 L min⁻¹. The influence of two levels in the factorial design was evaluated, one lower and one higher, for each parameter in order to reduce the ammonia concentration in leachate. It was studied: light bulb power (250 and 400W), temperature (35 and 45°C) and time of treatment (90 and 180 min). After each test the concentration of the hydrogen peroxide residual was evaluated.

For a better interpretation about the effects of the combination in the parameters of reducing the concentration of ammonia, a geometric diagram was built (Figure 2), where it could be observed that the increase in temperature had a significant influence on photochemical yield showing an improvement of around 8% when the temperature increases from 35°C to 45°C in both the lower level (with 250W lamp) and the upper level (with 400W lamp).

Table 2. 2³ Factorial Design. Optimization of the photochemical treatment for reduction of ammonia concentration in the leachate. Conditions: Volume of H₂O₂ 10% 50 mL; air flow 15 L min⁻¹.

Tests	Lamp	Temperature	Time	Ammonia Reduction (%)	H ₂ O ₂ residual (mg.L ⁻¹)
1	-	-	-	54,55	0,143
2	-	-	+	65,82	0,057
3	-	+	-	62,33	0,094
4	-	+	+	78,63	0,026
5	+	-	-	75,10	0,045
6	+	-	+	78,41	0,003
7	+	+	-	84,12	0,028
8	+	+	+	86,45	0,000

Parameters: Level (-) 250 W, 35°C, 90 min./ Level (+) 400 W, 45°C, 180 min.

With the increase of the light bulb power to 400W the efficiency of the process made an improvement from 21 to 22% at temperatures of 35°C and 45°C respectively, at the 90 min mark of the treatment. The same efficiency was not observed at the 180 min mark of the treatment, which remained between 8 and 12%. Observing the terms of the lower level (temperature 35°C, time 90 min and 250W light bulb) and the highest level of efficiency (time 180 min temperature 45°C and 400W lamp) the yield was above 32%.

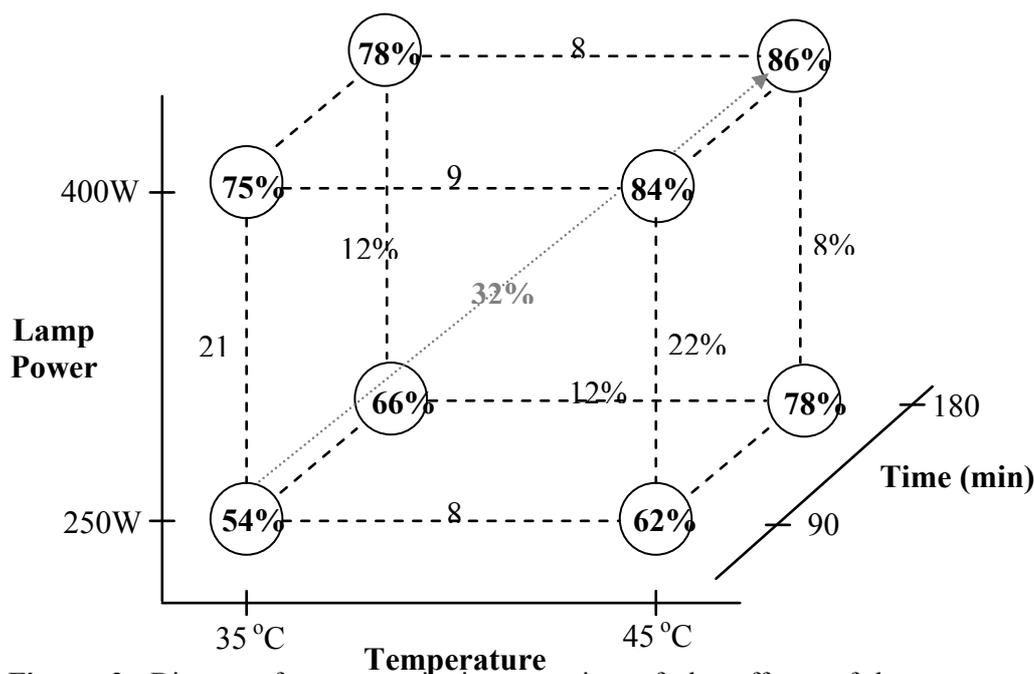


Figure 2. Diagram for geometric interpretation of the effects of lamp power, temperature and time of photochemical treatment to reduce ammonia concentration in the leachate.

By taking into account these optimized conditions, a new 3² factorial design was developed aiming to study three concentration levels of H₂O₂ and air flow (Table 3), considering that the efficiency of the process has always been assessed by reducing the concentration of ammonia in the leachate.

Table 3. 3² Factorial Design. Optimization of photochemical treatment for reduction of ammonia concentration in the leachate. Conditions: Lamp 400 W, temperature 45°C, treatment time 180 min.

Tests	Volume H ₂ O ₂	Air Flow	Ammonia Reduction (%)
1	-	-	76,53
2	-	+	73,47
3	-	Θ	75,48
4	+	-	89,01
5	+	+	86,42
6	+	Θ	88,14
7	Θ	-	91,08
8	Θ	+	87,36
9	Θ	Θ	88,64

Parameters: Level (-) 20 mL, 1.17 g.L⁻¹ H₂O₂ e 0,0 L.min⁻¹ vazão de ar;
 Level (Θ) 35 mL, 2.05 g.L⁻¹ H₂O₂ e 5.0 L.min⁻¹ vazão de ar;
 Level (+) 50 mL, 2.93 g.L⁻¹ H₂O₂ e 15.0 L.min⁻¹ vazão de ar.

For best visual results of the study, a geometric diagram was built, as shown in Figure 3. Comparing the results of photochemical treatment in each level, it was observed that when a volume of 35 mL with a 10% solution of H₂O₂ (concentration 2.05 g L⁻¹) without the addition of air was used, the process showed a 91% reduction of ammonia concentration.

Following the work, the volumes of about 35 mL and addition of several aliquots at different times were studied. The four best methods are shown in Table 4.

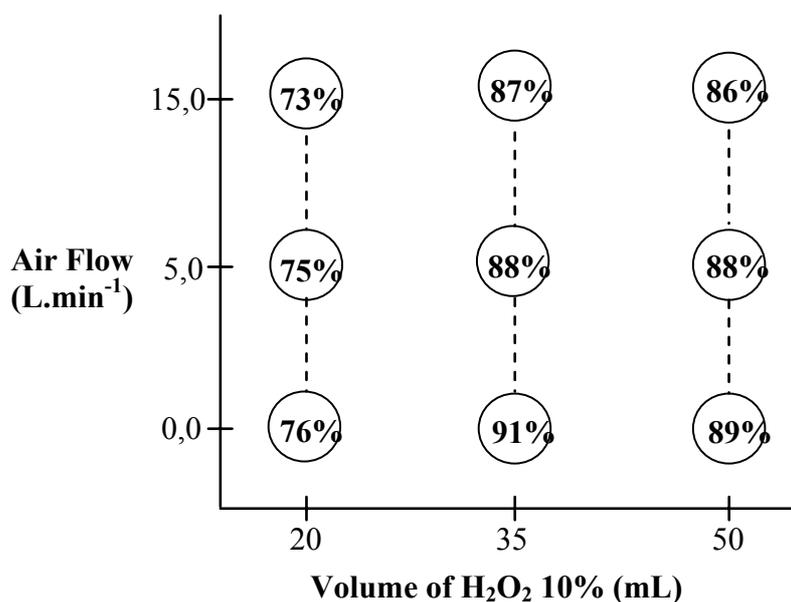


Figure 3. Diagram for the geometric interpretation on the effects of air flow and volume of H₂O₂ 10% in the photochemical treatment to reduce ammonia concentration in the leachate.

Table 4. Results of the % reduction of ammonia concentration in leachate and sequential evaluation of residual H₂O₂. Photochemical conditions: 400 W light bulb, temperature 45°C, air flow 0.00.

Time (min)	Test A (% Ammonia Reduction)	Test B (% Ammonia Reduction)	Test C (% Ammonia Reduction)	Test D (% Ammonia Reduction)
0	0	0	0	0
30	75,53	73,30	74,25	75,59
60	93,26	92,59	87,35	86,80
90	97,89	(96,91)	(95,56)	89,28
120	97,92	97,36	96,00	90,71
180	97,90	98,10	96,42	91,82
Methodology □	40 mL: 20; 10; 10 [2,35 g.L⁻¹ H₂O₂]	35 mL: 15; 10; 10 [2,05 g.L⁻¹ H₂O₂]	35 mL: 20; 10; 5 [2,05 g.L⁻¹ H₂O₂]	30 mL: 20; 10 [1,75 g.L⁻¹ H₂O₂]
Treatment Time	H₂O₂ residual (mg.L⁻¹)	H₂O₂ residual (mg.L⁻¹)	H₂O₂ residual (mg.L⁻¹)	H₂O₂ residual (mg.L⁻¹)
90 min	0,053	0,008	0,012	0,000
180 min	0,000	0,000	0,000	0,000

Note: Methodology and volumes:
Test A (40 mL: 20 mL at 0 min, 10 mL at 30 min and 10 mL at 60 min);
Test B (35 mL: 15 mL at 0 min, 10 mL at 30 min and 10 mL at 60 min);
Test C (35 mL: 20 mL at 0 min, 10 mL at 30 min and 5 mL at 60 min);
Test D (30 mL: 20 mL at 0 min, 10 mL at 30 min).

For better interpretation of this study a new geometric diagram was built, prioritizing the results of reduction on ammonia concentration at times of 90 and 180 min (Figure 4). This figure shows that the tests A, B and C presented very similar results. However, no significant differences were found in reducing the ammonia concentration when the time of treatment increased from 90 min to 180 min. By observing the concentration of residual H₂O₂ at the 90 min mark, it was observed that "Test B" shows the lowest concentration (0.008 mg L⁻¹). In this study, the methodology developed in "Test B" in time of 90 min was chosen, as optimized conditions for the photochemical treatment of ammonia in the leachate. Figure 5 shows a curve of the trend of ammonia degradation. Other results of environmental importance were also obtained using this method of treatment (Table 5).

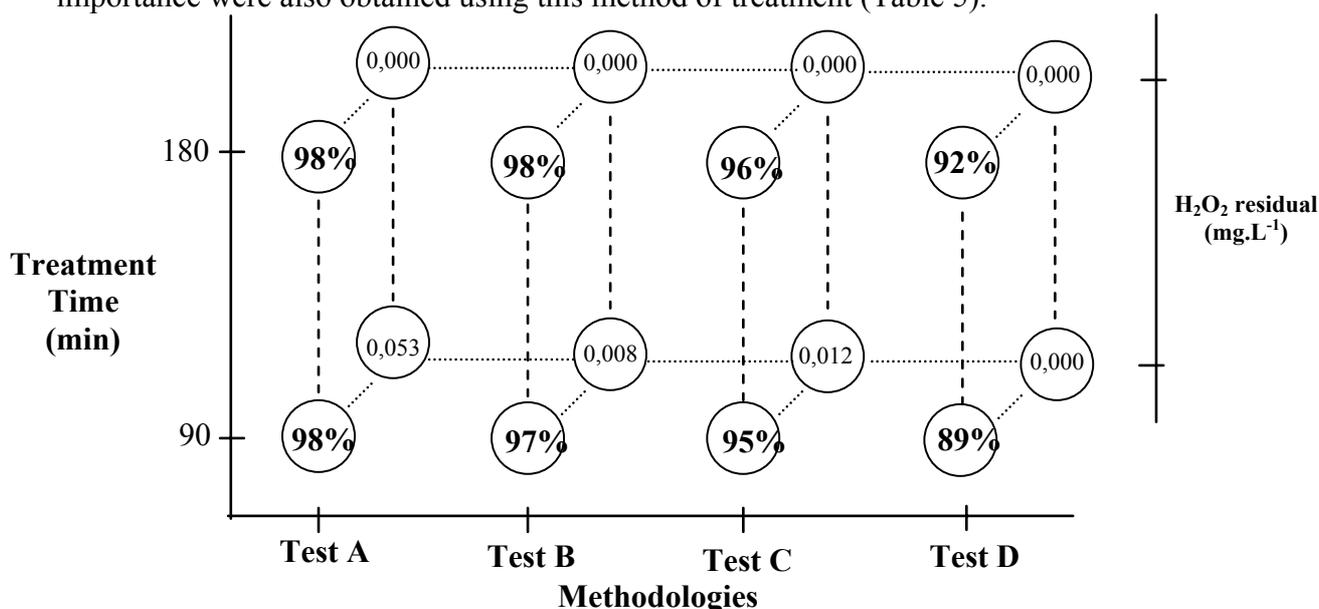


Figure 4. Diagram for the geometric interpretation of the effects of photochemical treatment time versus Methodologies of Addition to the H₂O₂ and evaluation of residual H₂O₂ to reduce the ammonia concentration in the leachate.

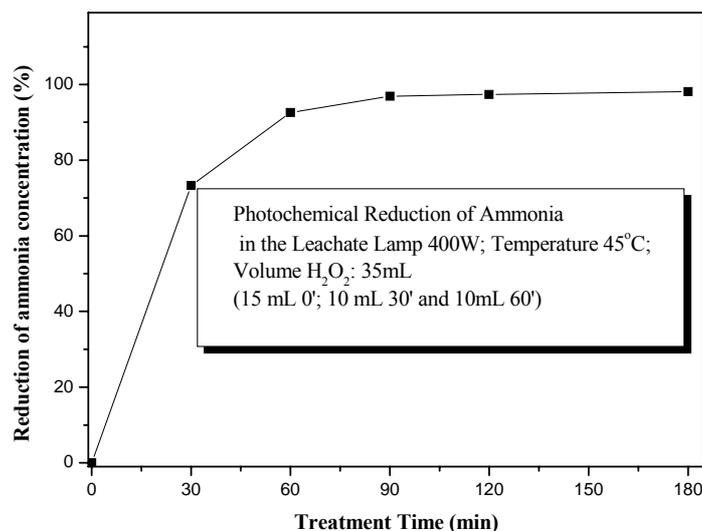


Figure 5. Evolution of the percentage of degradation of the ammonia concentration in the leachate treated by photochemical processes using H₂O₂.

Table 5. Landfill leachates characterization after the photochemical process.

Parameter	Pretreated leachate	Photochemical post-treatment	% Reduction
Nitrogen NH ₄ ⁺ (mg L ⁻¹)	432,01	13,3	97,0
Nitrite NO ₂ ⁻ (mg L ⁻¹)	0,15	0,05	66,7
Nitrate NO ₃ ⁻ (mg L ⁻¹)	2,30	0,73	68,3
pH	8,14	8,54	-

3.2. Ammonia Oxidation in Leachate

Considering the equation 1, it is observed the generation of hydroxyl radical from homolytic cleavage of H₂O₂ caused by UV radiation. The degradation of ammonia may have followed this photochemical path. However, in the leachate studied there is a concentration of Fe²⁺ around 18 mg L⁻¹ (Table 1), leading to the production of hydroxyl radicals via mechanisms provided by equations 2 and 3, and the process would be via photo-Fenton. The leachate also presented high concentrations of chloride (1770 mg L⁻¹) which can react with hydroxyl radical generating HClO and ClO⁻ (Equations 7 and 8). These species can cause the degradation of ammonia (Equations 5 and 6).

Considering the high efficiency of the degradation of ammonia in the leachate, certainly part of the remediation was via direct mechanism of H₂O₂ cleavage through the redox reaction of Fe²⁺ and Fe³⁺ ions and also through the formation of species-HClO and ClO, which would be a significant contribution in the treatment of leachate.

4. CONCLUSIONS

The technique of photochemical proved to be an excellent alternative in the treatment of complex wastewaters such as leachate. The optimization of the process made it possible to treat high concentrations of ammonia. It was observed that the parameters of light bulb power (400 W) and temperature (45°C) are decisive factors in the efficiency in the photochemical process. Allied to this, the method of adding the H₂O₂ solution, at rates, favored the results of this study significantly.

It was also observed through by photochemical process H₂O₂/UV and Photo Fenton process a decrease in the ammonia concentration in the order of 97%, but was also observed reductions in the concentration of nitrite (66%) and nitrate (68%). Thus concludes that oxidation of ammonia occurs via direct oxidation (Equation 4) or can also be enhanced by increasing the concentration of hypochlorous acid or hypochlorite ions in solution with gaseous nitrogen production (Equations 5 e 6).

5. ACKNOWLEDGEMENT

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