Ambiente & Água - An Interdisciplinary Journal of Applied Science
ISSN 1980-993X – doi:10.4136/1980-993X
www.ambi-agua.net
E-mail: ambi.agua@gmail.com

Evaluation of the aerobic process performance for treating tannery effluent in the fungicide presence and ammoniacal nitrogen high concentration

ARTICLES doi:10.4136/ambi-agua.3007

Received: 08 May 2024; Accepted: 13 Oct. 2024

Andressa Corso[1]; Fábio Orssatto[2*]; Leandro Fleck[3]; Flavia Manente da Silva[4]

[1]Programa de Pós-Graduação em Tecnologias Ambientais. Universidade Tecnológica Federal do Paraná (UTFPR), Câmpus Medianeira, Avenida Brasil, n° 4232, CEP: 85722-332, Medianeira, PR, Brazil. E-mail: andressa.c.corso@gmail.com
[2]Departamento Acadêmico de Ciências Ambientais e Biológicas. Programa de Pós Graduação em Tecnologias Ambientais. Universidade Tecnológica Federal do Paraná (UTFPR), Câmpus Medianeira, Avenida Brasil, n° 4232, CEP: 85722-332, Medianeira, PR, Brazil.
[3]Núcleo de Ciências Biológicas e da Saúde. Universidade Estadual de Mato Grosso do Sul (UEMS), Cidade Universitária de Dourados, Caixa Postal 351, CEP: 79804-970, Dourados, MS, Brazil. E-mail: leandro.fleck@uems.br
[4]Departamento Acadêmico de Ciências Ambientais e Biológicas. Universidade Tecnológica Federal do Paraná (UTFPR), Câmpus Medianeira, Avenida Brasil, n° 4232, CEP: 85722-332, Medianeira, PR, Brazil. E-mail: flavia@alunos.utfpr.edu.br
[*]Corresponding author. E-mail: orssatto@utfpr.edu.br

ABSTRACT

Leather processing is characterized by the generation of effluents with a high concentration of ammonia nitrogen ($N^-NH_4^+$) and the presence of fungicides. This study evaluated the interference of these two constituents on the removal of chemical oxygen demand (COD) and $N^-NH_4^+$. To this end, an aerated reactor operating in a batch system was used. The effects of cycle time, fungicide volume, and initial $N^-NH_4^+$ concentration on COD and $N\text{-}NH_4^+$ removal was evaluated using a Centralized Rotational Composite Design. The highest COD removal (45.45%) occurred under the conditions of 72 h, 0.55 mL of fungicide, and 62.5 mg L^{-1} of $N^-NH_4^+$, and the lowest removal (8.24%) occurred under the conditions of 24 h, 0.28 mL of fungicide and 84.8 mg L^{-1} of $N\text{-}NH_4^+$. The highest removal of $N\text{-}NH_4^+$ (38.49%) occurred under the conditions of 42 h, 0.55 mL of fungicide, and 62.5 mg L-1 of $N\text{-}NH_4^+$, and the lowest removal (4.26%) occurred under the conditions of 24.1 h, 0.82 mL of fungicide and 84.8 mg $^{L-1}$ of $N^-NH_4^+$. Through statistical analysis, it was possible to obtain mathematical models for the two response variables, which satisfactorily described the removal efficiency of COD and $N^-NH_4^+$, and through the desirability analysis, it was possible to optimize the treatment process operation with a cycle time of 58.15h, with the addition of 0.62 mL of fungicide and 57.91 mg L^{-1} of ammoniacal nitrogen. Although the removal of $N^-NH_4^+$ via nitrification is an efficient technique in industrial effluent treatment, the results obtained in this work indicate that the removal of $N^-NH_4^+$ was significantly affected by the presence of the fungicide.

Keywords: biological treatment, chemical oxygen demand, DCCR, TCMTB.

Avaliação do desempenho do processo aeróbico de tratamento de efluente de curtume na presença de fungicida e alta concentração de nitrogênio amoniacal

RESUMO

O processamento do couro, tem como característica a geração de efluentes com elevada concentração de nitrogênio amoniacal ($N\text{-}NH_4^+$) e a presença de fungicidas. O objetivo desse estudo, foi avaliar a interferência desses dois constituintes sobre a remoção de demanda química de oxigênio (DQO) e $N\text{-}NH_4^+$. Para isso, utilizou-se um reator aerado, operando em sistema de batelada. Foram avaliados os efeitos do tempo de ciclo, do volume de fungicida e da concentração inicial de $N\text{-}NH_4^+$, sobre a remoção de DQO e $N\text{-}NH_4^+$, utilizando um Delineamento Composto Central Rotacional. A remoção mais elevada de DQO (45,45%), ocorreu nas condições de 72 h, 0,55 mL de fungicida e 62,5 mg L^{-1} de $N\text{-}NH_4^+$, e a menor remoção (8,24%) ocorreu nas condições de 24 h, 0,28 mL de fungicida e 84,8 mg L^{-1} de $N\text{-}NH_4^+$. A maior remoção de $N\text{-}NH_4^+$ (38,49%), ocorreu nas condições de 42 h, 0,55 mL de fungicida e 62,5 mg L^{-1} de $N\text{-}NH_4^+$, e a menor remoção (4,26%), ocorreu nas condições 24,1 h, 0,82 mL de fungicida e 84,8 mg L^{-1} de $N\text{-}NH_4^+$. Através das análises estatísticas foi possível obter modelos matemáticos para as duas variáveis respostas, os quais descreveram satisfatoriamente a eficiência de remoção de DQO e $N\text{-}NH_4^+$, sendo que por meio da análise de desejabilidade foi possível otimizar o processo de tratamento operando com tempo de ciclo de 58,15h, com adição de 0,62 mL de fungicida e 57,91 mg L^{-1} de nitrogênio amoniacal. Embora a remoção de $N\text{-}NH_4^+$ via nitrificação tem-se mostrado uma técnica eficiente em tratamentos de efluentes industriais, os resultados obtidos neste trabalho indicam que a remoção de $N\text{-}NH_4^+$ foi significativamente afetada devido a presença do fungicida.

Palavras-chave: DCCR, demanda química de oxigênio, TCMTB, tratamento biológico.

1. INTRODUCTION

The tanning industry is of significant importance in the economy of several developing countries, including Brazil, which ranks second in world leather production. The importance of the sector has intensified due to high demand for the product and the commercial value acquired (Moysés *et al.*, 2017).

However, this sector stands out among the most polluting, due to the presence of toxic substances in wastewater. Among these substances are solid materials such as chromium salts, tannins, oils, fats, detergents, and biocides (El Mouhri *et al.*, 2024). Fungicides are one example of biocides that can be applied to the skin to preserve it, and which, consequently, are incorporated into the effluent (Saira and Shanthakumar, 2023).

One compound that can be used as a fungicide is 2-(thiocyanomethylthio)benzothiazole (TCMTB). Derived from the benzothiazole group, it is widely used in the leather industry, and due to its characteristics, it is classified as an emerging contaminant (Bertoldi *et al.*, 2020). TCMTB can have toxic effects on non-target organisms, such as bacteria, so the presence of this compound in the effluent can compromise the efficiency of biological treatment processes (Fernández-Alba *et al.*, 2002), as well as having high toxicity if inhaled and irritating effects on the skin (Širvaitytė *et al.*, 2012).

In addition to the compounds mentioned, ammonium salts are used to remove the alkaline material used in liming, which provide a high concentration of ammonia nitrogen ($N\text{-}NH_4^+$), with values that can vary between 2,000 and 4,000 mg L^{-1} (Hashem *et al.*, 2024). Biological treatment has been widely used as an economical and effective method for removing ammonia nitrogen from wastewater. This process consists of a combination of two steps, nitrification and denitrification.

In the nitrification stage, ammoniacal nitrogen is converted into nitrite and later into nitrate; however, this stage is extremely sensitive, and to ensure the efficiency of the process it is necessary to monitor some parameters, such as pH, alkalinity, temperature, oxygen concentration dissolved (Bassin *et al.*, 2012) and organic carbon/nitrogen ratio (Hu *et al.*, 2009).

Furthermore, the rate of development of bacteria responsible for nitrification can also be inhibited due to toxic substances present in tannery effluent, such as excess ammonia nitrogen, as this causes an imbalance between the concentrations of nutrients essential for the development of these organisms. (Hashem *et al.*, 2024) and fungicides applied to leather conservation (Jochimsen and Jekel, 1997; Ganesh and Ramanujam, 2009). Ganesh and Ramanujam (2009) add that, although fungicides are extremely important in preserving leather, they have low biodegradability and a high degree of toxicity.

Given the challenge encountered in carrying out the nitrification stage in the treatment of wastewater from the tanning industry, and based on information about the possibility of effluent constituents being responsible for inhibiting this stage, the objective of the present work was to verify the effect of the fungicide and the excess ammoniacal nitrogen over the nitrification stage to make the process more efficient.

2. MATERIALS AND METHODS

2.1. Experimental system

The experimental system used to carry out this study consists of an aerated reactor, operating in a batch system. The reactor was built in Polyvinyl Chloride, with a working volume of 5 L, 240 mm in diameter, and 250 mm in height. Aeration was provided through a compressed air system and the flow rate introduced into the system was 6 L min $^{-1}$, adjusted manually with the aid of a rotameter. Air diffusion in the liquid medium occurred through a porous rubber, with micro holes at its ends.

2.2. Preparation and characterization of synthetic effluent

A synthetic effluent was used as a substrate, prepared following the composition proposed by Canto *et al.* (2008), composed of proteins, carbohydrates, and lipids. Proteins represented 50% of the COD, being obtained by adding meat extract (179 mg L^{-1}). Carbohydrates accounted for 40% of COD, obtained by adding sucrose (36 mg L^{-1}), commercial starch (112 mg L^{-1}), and cellulose (41 mg L^{-1}). To the 10% lipid fraction, soybean oil (0.056 mL L^{-1}) was added and emulsified with 3 drops of commercial detergent. The effluent was also enriched with mineral salts: sodium chloride (5 mL L^{-1}), magnesium chloride (5 mL L^{-1}), and calcium chloride (5 mL L^{-1}).

The substrate had a COD concentration equal to 1000 mg L^{-1} and was diluted in a proportion of 1:20, thus, the effluent had a COD of 50 mg L^{-1}. Analysis of this effluent was carried out and a concentration of 50.4 ± 1.27 mg L^{-1} was found. Ammonium chloride was used as a source of ammonia nitrogen. In addition, Buckman's Busan® 30L fungicide, whose active ingredient is TCMTB 30%, was added to the substrate.

The effluent was produced with each batch and no inoculum was introduced into the reactor. The development of the bacteria responsible for the process began with favorable environmental conditions for development. As the preparation followed previously defined concentrations, its characteristics were similar in all tests.

2.3. System evaluation

Analytical monitoring involved analyses of Chemical Oxygen Demand (5220 D), and Ammonia Nitrogen (4500 - NH_3 F). The parameters pH (4500 - H^+ B) total alkalinity (2320

B) and temperature were monitored to guarantee the stability of the nitrification process, following the methodologies proposed by APHA *et al.* (2012). Samples were collected at the bottom of the reactor, at the beginning and end of each test, to evaluate the efficiency of COD and $N\text{-}NH_4^+$ removal and thus observe whether the presence of the fungicide and/or excess of ammonia nitrogen interfered in the process.

2.4. Experimental planning

The methodology applied was the Rotational Central Composite Design (DCCR). Three independent variables were evaluated: cycle time, fungicide volume, and initial ammonia nitrogen concentration. The selection of cycle time levels and initial ammonia nitrogen concentration was based on preliminary studies. The selection of levels for the volume of fungicide applied was defined based on some operational parameters similar to those of the industry. The response variables studied were the removal of COD and ammonia nitrogen. A 2^3 factorial was performed, including 6 axial tests and 3 repetitions at the central point, totaling 17 tests. Table 1 shows the treatment design matrix, with coded and real values.

Table 1 . Design of treatments with coded and real values.

Tests	Cycle time		Fungicide volume		Initial concentration $N\text{-}NH_4^+$	
	Coded values	Real values (h)	Coded values	Real values (mL)	Coded values	Real values ($mg\ L^{-1}$)
1	-1	24.1	-1	0.28	-1	40.2
2	1	59.9	-1	0.28	-1	40.2
3	-1	24.1	1	0.82	-1	40.2
4	1	59.9	1	0.82	-1	40.2
5	-1	24.1	-1	0.28	1	84.8
6	1	59.9	-1	0.28	1	84.8
7	-1	24.1	1	0.82	1	84.8
8	1	59.9	1	0.82	1	84.8
9	0	42	0	0.55	0	62.5
10	0	42	0	0.55	0	62.5
11	0	42	0	0.55	0	62.5
12	-1.68	12	0	0.55	0	62.5
13	1.68	72	0	0.55	0	62.5
14	0	42	-1.68	0.1	0	62.5
15	0	42	1.68	1	0	62.5
16	0	42	0	0.55	-1.68	25
17	0	42	0	0.55	1.68	100

For the response variables COD removal and ammonia nitrogen, quadratic mathematical models representing the process were generated. These were obtained from the statistical adjustment of the results, corresponding to all tests carried out, using the *software* Statistica (Version 11.0). Equation 1 represents the coded mathematical model for the removal of COD and $N\text{-}NH_4^+$.

$$\gamma = \alpha_1 + \alpha_2 x_1 + \alpha_3 x_1^2 + \alpha_4 x_2 + \alpha_5 x_2^2 + \alpha_6 x_3 + \alpha_7 x_3^2 + \alpha_8 x_1 x_2 + \alpha_9 x_1 x_3 + \alpha_{10} x_2 x_3 \quad (1)$$

Where y: response variable; α: regression coefficients; X_1: encoded cycle time value; X_2: volume of fungicide; X_3: initial concentration of ammonia nitrogen.

The statistical significance of the mathematical models was tested using Analysis of Variance (ANOVA), with a 90% confidence interval. We chose to adopt a 90% confidence interval, due to the variability inherent to biological treatment, parameters with p-values lower than 10% ($p< 0.1$) are considered significant.

Subsequently, the mathematical models were validated based on COD and ammonia nitrogen removal data, obtained from a validation test. The conditions used in the validation test were found through the desirability function, a methodology proposed by Derringer and Suich (1980), using the *software* Statistica (Version 11.0). The desirability function aims to find the optimal operational values of the independent variables, which result in better removals of the response variables simultaneously.

3. RESULTS AND DISCUSSION

3.1. Process monitoring

The pH, alkalinity, and temperature parameters were monitored to ensure the stability of the nitrification process. A reduction in pH values was observed in all tests, with the average pH of the tests before and after the aeration period equal to 7.31 ± 0.046 and 7.11 ± 0.092, respectively. There are optimal values for the nitrification process, which, according to Wef *et al.* (2005) is in the range 6.5 to 8.0. In all tests, there was a consumption of alkalinity, with average values before and after the aeration period of 135.29 ± 5.42 ppm and 119.05 ± 9.35 ppm respectively. The tests took place in a closed environment with low thermal variation. The average operating temperature of the system was 26.35 ± 1.5°C. Although Wef *et al.* (2005) cite optimal values between 35 to 42ºC, they mention that the process can occur in a wide temperature range between 4 and 45ºC.

3.2. Removal efficiency

Figure 1 shows the COD and ammonia nitrogen removal efficiency in the 17 tests of the experimental design.

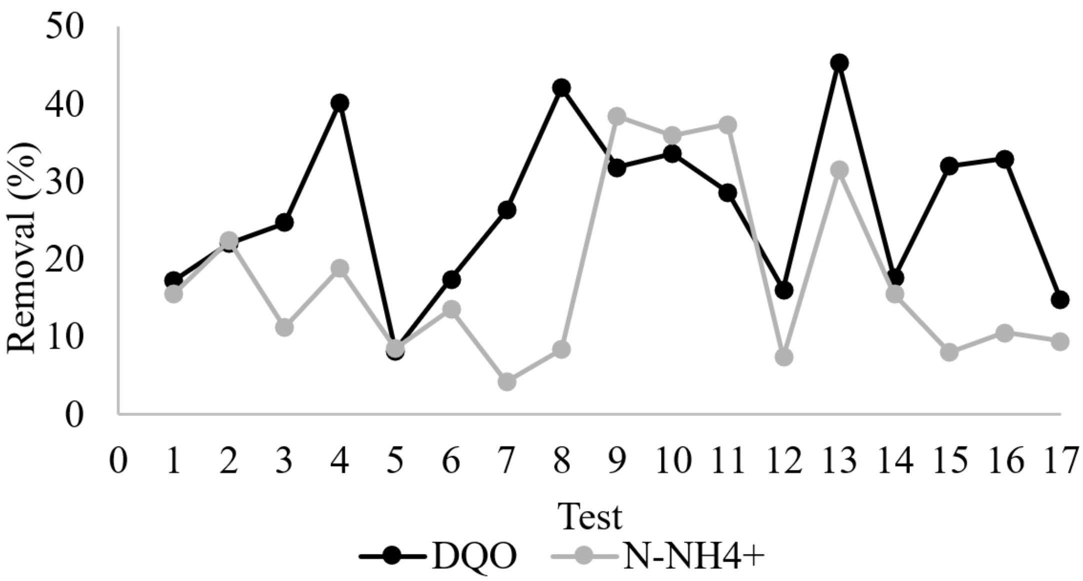

Figure 1. COD and $N\text{-}NH_4^+$ removal efficiency.

It can be seen that the highest COD removal of 45.45% occurred in Test 13, under conditions of 72 h, 0.55 mL of fungicide, and 62.5 mg L^{-1} of $N\text{-}NH4^+$, this being the test carried out with the longest cycle time. Considering the high concentration of organic matter in real wastewater, it is necessary to combine different treatment processes to meet the standards required for disposal.

In comparing the previous results in the literature (Table 2), this work obtained poor removal efficiency, probably due to the fungicide interference.

Table 2. Conditions and findings of the previous literature.

	Wastewater	Cycle time	Airflow	$N\text{-}NH_4^+$ concentration	DQO removal (%)	$N\text{-}NH_4^+$ removal
Mees *et al.* (2011)	Poultry slaughterhouse	10.15 h	3 L min^{-1}	-	50%	-
Dallago *et al.* (2012)	Poultry slaughterhouse	16 h	-	80 mg L^{-1}	-	87%
		20 h	-	100 mg L^{-1}	-	92%
Lima *et al.* (2014)	Cattle slaughterhouse	16 h	0.725 L min^{-1}	150 mg L^{-1}	-	100%

The result was obtained by Mees *et al.* (2011), who, when evaluating the efficiency of a sequential batch reactor, applied to the treatment of wastewater from a poultry slaughterhouse, obtained an average COD removal efficiency of approximately 50%; however, this efficiency was obtained under conditions of lower cycle time and airflow, being 10.15 h and 3 L min^{-1} respectively. The lowest COD removal occurred under conditions of 24 h, 0.28 mL of fungicide, and 84.8 mg L^{-1} of $N\text{-}NH_4^+$, which was 8.24%.

The highest removals of ammoniacal nitrogen from 38.49%, 35.99%, and 37.43% were obtained in the central point tests, under conditions of 42 h, 0.55 mL of fungicide, and 62.5 mg L^{-1} of $N\text{-}NH_4^+$. Dallago *et al.* (2012), evaluated the influence of cycle time and $N\text{-}NH_4^+$ concentration on the removal efficiency of $N\text{-}NH_4^+$ from poultry slaughterhouse wastewater, obtaining removal efficiency between 87% and 92% under conditions of 16 and 20 h, and 80 to 100 mg L^{-1}, combined with an air flow equal to 3 L min^{-1}.

The lowest removals of $N\text{-}NH_4^+$, of 4.26%, 7.42%, and 7.97% occurred under conditions 24.1 h, 0.82 mL of fungicide and 84.8 mg L^{-1} of $N\text{-}NH_4^+$, 12 h, 0.55 mL of fungicide and 62.5 mg L^{-1} of $N\text{-}NH_4^+$ and 42 h, 1 mL of fungicide and 62.5 mg L^{-1} of $N\text{-}NH_4^+$, respectively. In comparison, when evaluating the influence of airflow and $N\text{-}NH_4^+$ concentration on $N\text{-}NH_4^+$ removal efficiency, Lima *et al.* (2014) obtained 100% removal under conditions of 0.725 L min^{-1} L$_{reactor}$$^{-1}$, 150 mg L^{-1} of $N\text{-}NH_4^+$, combined with 16 h cycle time in the treatment of wastewater from a cattle slaughterhouse.

The high ammonia nitrogen removal efficiencies of the works mentioned above can be attributed to the addition of an acclimated inoculum to carry out the experiments. This acclimatization phase of nitrifying organisms allows the conversion of ammonia nitrogen to nitrate to stabilize. Since in the present study, there was no addition of inoculum, this factor may have been one of those responsible for the low efficiency of ammonia nitrogen removal.

Another factor responsible for the low efficiency of ammonia nitrogen removal can be attributed to competition for dissolved oxygen between bacteria. According to Hu *et al.* (2009), the high C:N ratio reduces the efficiency of the process, as it induces competition for dissolved oxygen between autotrophic and heterotrophic bacteria.

During the tests, it was possible to notice that the fungicide applied increased the concentration of organic carbon in the effluent, since, although the substrate used to carry out the tests had a COD concentration of 50 mg L^{-1}, it was observed in all the tests that, after adding the fungicide, there was an increase in the initial COD concentration. It was also found that this increase was proportional to the volume of fungicide applied, so the C:N ratio differs between the tests. By comparing the factorial tests (1 to 8), it is possible to observe the effect of the C:N ratio on the removal of COD and ammonia nitrogen (Figure 2).

Tests 1 and 3 have the same cycle time (24.1 h) and the same initial concentration of ammonia nitrogen (40.2 mg L^{-1}); what distinguishes both is the volume of fungicide applied, being 0. 28 and 0.82 for Tests 1 and 3, respectively, so the C:N ratio differs between the two tests. It is noted that Test 1 obtained removals of 17.29% of COD and 15.46% of $N\text{-}NH_4^+$, while in Test 3 with the increase in the C:N ratio, an increase in COD removal was observed, 24.66%, while the removal of $N\text{-}NH_4^+$ reduced to 11.20%. A similar result occurred between Tests 2 and 4, 5 and 7, 6 and 8, where the increase in the C:N ratio favored the removal of COD; however, the reduction in the efficiency of $N\text{-}NH_4^+$ removal is noticeable.

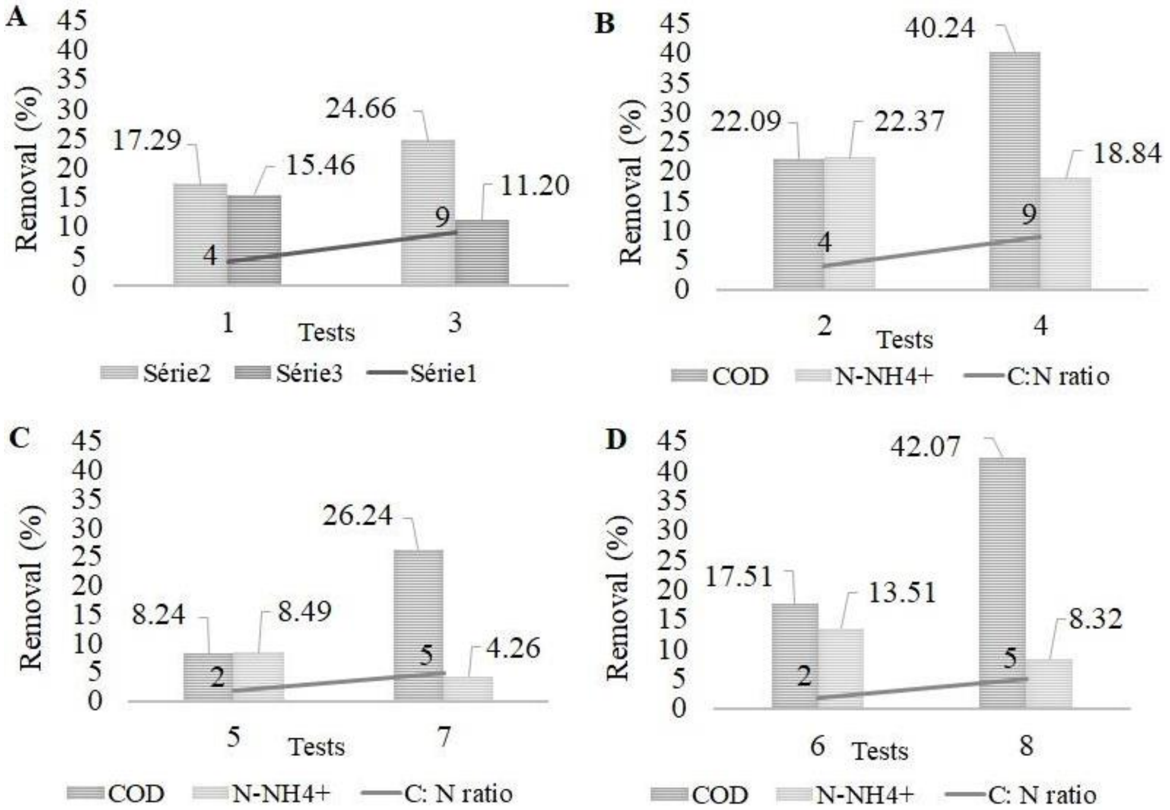

Figure 2. Effect of the C:N ratio on the COD and $N\text{-}NH_4^+$ removal efficiency.

3.3. Process optimization

The effects of independent variables on the removal of COD and ammonia nitrogen were studied. For COD removal, cycle time (linear term), fungicide volume (linear term), and ammonia nitrogen concentration (linear and quadratic terms) had a significant influence on COD removal, since the p-value obtained is lower than the adopted significance level of 10%. Cycle time and fungicide volume (linear terms) showed a positive effect, which means that increasing these variables results in increased COD removal.

For the removal of ammonia nitrogen, the linear and quadratic terms of the three independent variables studied exerted a significant influence on the removal. However, only cycle time (linear term) showed a positive effect, indicating that increasing cycle time results in increased ammonia nitrogen removal. However, non-significant terms were kept in the mathematical model, as a way of increasing the proportion of total response variability explained by the regression model.

The representative mathematical models of the process for optimizing the removal of COD and ammonia nitrogen, for the ranges and variables studied, are presented in Equations 2 and 3, respectively.

$$DQO\ Removal(\%) = 31{,}46 + 6{,}95x_1 - 0{,}520{x_1}^2 + 6{,}76x_2 - 2{,}63{x_2}^2 - 3{,}00x_3 - 2{,}98{x_3}^2 + 2{,}17x_1x_2 + 0{,}59\,x_1x_3 + 2{,}13x_2x_3 \quad (2)$$

$$N - {NH_4}^+\ Removal(\%) = 37{,}27 + 4{,}69x_1 - 6{,}21{x_1}^2 - 2{,}18x_2 - 8{,}64{x_2}^2 - 2{,}57x_3 - 9{,}55{x_3}^2 - 0{,}03x_1x_2 - 0{,}68x_1x_3 - 0{,}20x_2x_3 \quad (3)$$

Where X $_1$: coded cycle time value; X $_2$: volume of fungicide; X $_3$: initial concentration of ammonia nitrogen.

The Analysis of Variance (ANOVA) for the statistical validation of the mathematical models representing the process, indicated that the mathematical models are statistically significant, presenting p-values of 0.0067 and 0.00036, lower than the adopted level of significance (10%), explaining the total variability of responses at 90.82% and 96.18%, for COD and ammonia nitrogen removal, respectively. Therefore, it can be inferred that mathematical models have a satisfactory adjustment to the experimental data. Figures 3 and 4 show the response surfaces for COD and ammonia nitrogen removal, respectively.

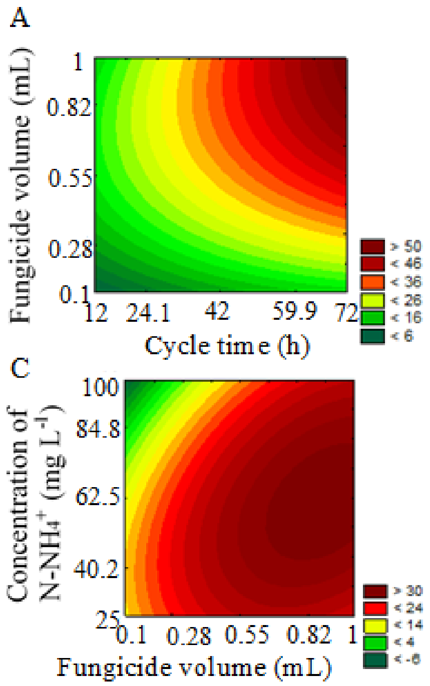

Figure 3 . Response surfaces for COD removal.

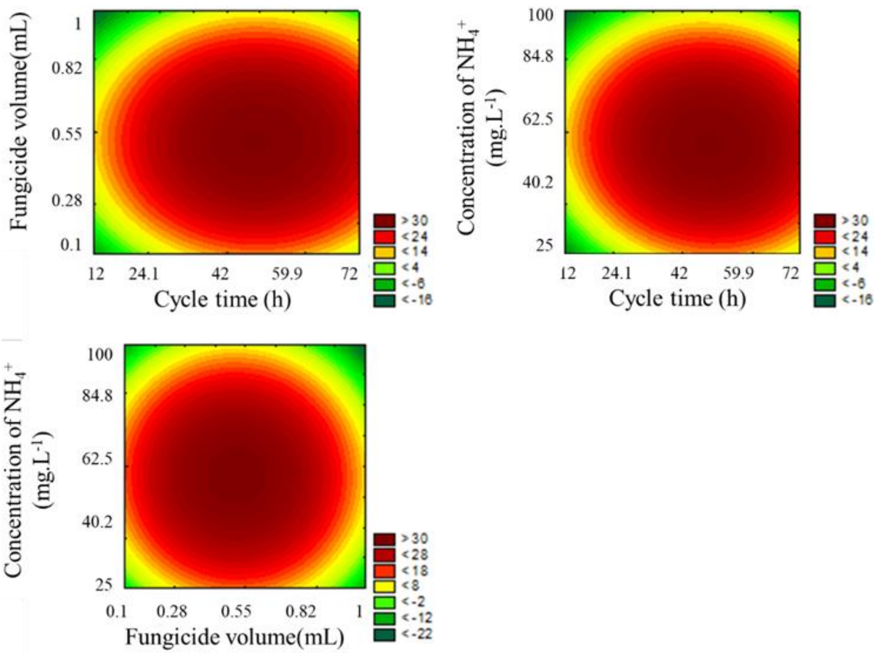

Figure 4 . Response surfaces for N-NH_4^+ removal.

As can be seen in Figure 3, for greater COD removal, the optimal regions of fungicide volume and initial ammonia nitrogen concentration are between 0.68 to 1 mL and 73.6 to 40.2 mg L^{-1}, respectively. It can also be seen that there is a tendency towards increased COD removal efficiency at cycle times longer than those studied in this work.

According to Figure 4, for greater ammonia nitrogen removal efficiency, the reactor must operate close to the central point conditions for the factors fungicide volume and initial ammonia nitrogen concentration 0.55 mL and 62.5 mg L^{-1} respectively, and the optimum operating range of the reactor in terms of cycle time is between 42 and 59.9 h.

To obtain the operational condition that allows optimizing the removal of COD and $N\text{-}NH_4^+$ simultaneously, a desirability analysis was carried out. The results of this analysis indicate that the ideal cycle time is 58.15h, with the addition of 0.62 mL of fungicide volume and 57.91 mg L^{-1} of ammonia nitrogen.

Using the optimal conditions found in the desirability function, a validation test of the mathematical models representing the process was carried out. The predicted and observed efficiencies for COD removal were 38.71% and 37.65 and for ammonia nitrogen 35.55% and 33.95%. The average error between the predicted and observed efficiencies for the COD and $N\text{-}NH_4^+$ removal model was only 2.81% and 4.71%, respectively, indicating that the mathematical models representing the process have a good fit and describe satisfactorily the removal efficiency of COD and $N\text{-}NH_4^+$.

4. CONCLUSION

The removal of ammonia nitrogen via nitrification has proven to be an efficient technique in treating industrial effluents. However, given the results obtained and considering the parameters evaluated, it can be concluded that the removal of ammonia nitrogen was significantly affected in the presence of the fungicide. Regarding COD removal, it can be seen that there is a tendency to increase removal efficiency in cycle times higher than those studied in the present work, indicating that in this situation the increase in cycle time tends to increase the COD removal efficiency. In future works, the increase in the cycle times can be tested.

Through statistical analysis, it was possible to obtain mathematical models for the two response variables. Furthermore, seeking to optimize the treatment process, it is necessary to operate with a cycle time of 58.15h, with the addition of 0.62 mL of fungicide and 57.91 mg L^{-1} of ammonia nitrogen, with it is possible to obtain an average removal of 38.18% COD and 34.75% for $N\text{-}NH_4^+$.

From an environmental point of view, the low efficiency in removing ammoniacal nitrogen is unsatisfactory, given the impact of this nutrient on the watercourses that receive the effluent. It is, therefore, necessary to try to replace the fungicide with products that are less harmful to biological treatment or to segregate the effluent containing the fungicide and look for a treatment capable of guaranteeing adequate efficiency. It is possible to evaluate the interference of other fungicides, looking for a more sustainable option that is easily degraded.

5. REFERENCES

APHA; AWWA; WEF. **Standard Methods for the examination of water and wastewater**. 22nd ed. Washington, 2012. 1496 p.

BASSIN, J. P.; KLEEREBEZEM, R.; ROSADO, A. S.; VAN LOOSDRECHT, M. C. M.; DEZOTTI, M. Effect of different operational conditions on biofilm development nitrification, and nitrifying microbial population in moving-bed biofilm reactors. **Environmental Science & Technology**, v. 46, n. 3, p. 1546−1555, 2012. https://doi.org/10.1021/es203356z

BERTOLDI, C.; PENA, A. C. C.; DALLEGRAVE, A.; FERNANDES, A. N.; GUTTERRES, M. Photodegradation of Emerging Contaminant 2-(tiocyanomethylthio) Benzothiazole (TCMTB) in Aqueous Solution: Kinetics and Transformation Products. **Bulletin of Environmental Contamination and Toxicology**, v. 105, p. 433–439, 2020. https://doi.org/10.1007/s00128-020-02954-2

CANTO, C. S. A. do; RODRIGUES, J. A. D.; RATUSZNEI, S. M.; ZAIAT, M.; FORESTI, E. Feasibility of nitrification/denitrification in a sequencing batch biofilm reactor with liquid circulation applied to post-treatment. **Bioresource Technology**, v. 99, p. 644-654, 2008. https://doi.org/10.1016/j.biortech.2006.12.040

DALLAGO, R. C.; GOMES, S. D.; BORTOLI, J.; MEES, R. Nitrification and denitrification of a poultry slaughterhouse wastewater according to cycle time and ammonia nitrogen using concentration surface response methodology. **Journal of Food Agriculture and Environmental**, vol. 10, p. 856-860, 2012.

DERRINGER, G. C.; SUICH, R. Simultaneous optimization of several response variables. **Journal of Quality Technology**, v. 12, p. 214-219, 1980. https://doi.org/10.1080/00224065.1980.11980968

EL MOUHRI, G.; ELMANSOURI, I.; AMAKDOUF, H.; BELHASSAN, H.; KACHKOUL, R.; EL OUMARI, F. *et al.* Treatment of wastewater from the leather tanning industry by the coagulation-flocculation method: An ecological approach. **Heliyon**, p. e27056, 2024. Available at: https://doi.org/10.1016/J.HELIYON.2024.E27056

FERNÁNDEZ-ALBA, A. R.; HERNANDO, M.D.; PIEDRA, L.; CHISTI, Y. Toxicity evaluation of single and mixed antifouling biocides measured with acute toxicity bioassays. **Analytica Chimica Acta**, v. 456, n. 2, p. 303-312, 2002. https://doi.org/10.1016/S0003-2670(02)00037-5

GANESH, R.; RAMANUJAM, R. A. Biological waste management of leather tannery effluents in India: current options and future research needs. International Journal of Environmental **Engineering**, v. 1, n. 2, p. 165-186, 2009. https://doi.org/10.1504/IJEE.2009.027313

HASHEM, M. A.; ISLAM, S.; MIMI, A. A.; ENAN, E. T.; MIEM, M. M.; RAHMAN, M. T.; ZAHIN, M. E. H. Solid dicarboxylic acid assisted deliming in beamhouse to reduce nitrogen compounds in tannery wastewater. **Journal of Cleaner Production**, p. 141440, 2024. https://doi.org/10.1016/J.JCLEPRO.2024.141440

HU, Z.; LI, D.; LIU, Q.; TAO, Y.; HE, X.; WANG, X. *et al.* Effect of organic carbon on nitrification efficiency and community composition of nitrifying biofilms. **Journal of Environmental Sciences**, v. 21, p. 287-394, 2009. https://doi.org/10.1016/S1001-0742(08)62281-0

JOCHIMSEN, J. C.; JEKEL, M. R. Partial oxidation effects during the combined oxidative and biological treatment of separated streams of tannery wastewater. **Water Science and Technology**, v. 35, p. 337-345, 1997. https://doi.org/10.1016/S0273-1223(97)00389-2

LIMA, A. N. de; GOMES, B. M.; GOMES, S. D.; CARVALHO, K. Q. de; DIVAIR, C. Application of response surface methodology to study the biological removal of nitrogen from effluent of cattle slaughterhouse in a sequencing batch reactor. **Engineering Agrícola**, v. 34, p. 363-371, 2014. https://doi.org/10.1590/S0100-69162014000200017

MEES, J. B. R.; GOMES, S. D.; GOOD, M. A. V.; GOMES, B. M.; PASSIG, F. H. Kinetic behavior of nitrification in the post-treatment of poultry wastewater in a sequential batch reactor. **Engineering Agricultural**, v. 31, p. 954-964, 2011. https://doi.org/10.1590/S0100-69162011000500013

MOYSÉS, F. dos S.; BERTOLDI, K.; ELSNER, V. R.; CECHINEL, L. R.; BASSO, C.; STÜLP, S. *et al.* Effect of tannery effluent on oxidative status of brain structures and liver of rodents. **Environmental Science and Pollution Research**, v. 24, n. 18, p.15689-15699, 2017. https://doi.org/10.1007/s11356-017-9149-4

SAIRA, G. C.; SHANTHAKUMAR, S. Zero waste discharge in tannery industries – An achievable reality? A recent review. **Journal of Environmental Management**, v. 335, p. 117508, 2023. https://doi.org/10.1016/J.JENVMAN.2023.117508.

ŠIRVAITYTĖA, J.; ŠIUGŽDAITĖB, J.; VALEIKAC, V.; DAMBRAUSKIENE, E. Application of essential oils of thyme as a natural preservative in leather tanning. **Proceedings of the Estonian Academy of Sciences,** v. 61, n. 3, p. 220–227, 2012. https://dx.doi.org/10.3176/proc.2012.3.12

WEF; ASCE; WERI. **Biological nutrient removal (BNR) operation in wastewater treatment plants**. 29. ed. New York: McGraw-Hill, 2005.