Revista Brasileira de Ciências Ambientais
Brazilian Journal of Environmental Sciences

Comparison of electrocoagulation and physicochemical coagulation/flocculation in the treatment of synthetic textile wastewater

Comparativo dos processos de eletrocoagulação e tratamento físico-químico de coagulação/floculação aplicado no tratamento de efluente têxtil sintético

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ABSTRACT

This study aimed to compare the efficiency of coagulation/flocculation and electrocoagulation treatments applied to synthetic textile wastewater containing navy blue dye (AM-16). For the coagulation/flocculation process, polyaluminum chloride (PAC 18%) and aluminum sulfate ($Al_2(SO_4)_3$) were used as coagulants, and cationic polymer (CP) as a coagulation aid. Coagulation/flocculation treatments were assessed at the concentrations of 150–350 mg L^{-1} for dye, 10–50 mg L^{-1} for PAC 18%, and 0.1–0.5 mg L^{-1} for CP, with initial pH ranging from 5 to 9. The same ranges were applied for the $Al_2(SO_4)_3$ tests, except for initial pH, which ranged between 4 and 8. Aluminum electrodes were used for electrocoagulation, as well as the same dye concentration range (150–350 mg L^{-1}) and applied current of 0.3–0.9 A. The response variables were contaminant (AM-16) removal, color removal, chemical oxygen demand, total organic carbon, and reduced toxicity using the microcrustacean *Artemia salina* as bioindicator. The aim was to compare the performance of different treatment methods (coagulation/flocculation and electrocoagulation) and assess how all independent variables and their interactions affected process efficiency. The results obtained through statistical analysis demonstrated that the most influential factor in coagulation/flocculation in removing AM-16 dye concentration was the initial pH, for both PAC 18% and $Al_2(SO_4)_3$. However, for aluminum sulfate, dye concentration also had an influence, indicating that an increase in pH and dye concentration favored the removal of contaminant. With respect to wastewater toxicity after treatments, there was a maximum average reduction of approximately 11% for treatment with $Al_2(SO_4)_3$. Electrocoagulation showed no significant variables at the

RESUMO

O presente estudo foi realizado buscando comparar a eficiência dos tratamentos de coagulação/floculação e eletrocoagulação aplicados a um efluente têxtil sintético contendo o corante azul marinho (AM-16). Para o processo de coagulação/floculação, utilizou-se policloreto de alumínio (PAC-18%) e sulfato de alumínio ($Al_2(SO_4)_3$) como coagulantes e o polímero catiônico (PC) como auxiliar de coagulação. Os tratamentos de coagulação/floculação foram avaliados nas concentrações do corante na faixa de 150–350 mg L^{-1}, concentração do PAC-18% (faixa de 10–50 mg L^{-1}), concentração do PC (faixa de 0,1–0,5 mg L^{-1}), pH inicial (faixa de 5–9). Para os ensaios com o $Al_2(SO_4)_3$ as mesmas faixas de estudo foram aplicadas, com exceção apenas do pH inicial, para o qual a faixa utilizada foi de 4 a 8. Para o processo de eletrocoagulação, utilizaram-se eletrodos de alumínio, que foi conduzido utilizando-se a faixa de concentração para o corante de 150 a 350 mg L^{-1} e a corrente aplicada de 0,3 a 0,9 A. As variáveis de resposta foram remoção do contaminante (AM-16), remoção de cor, demanda química de oxigênio, carbono orgânico total e redução de toxicidade empregando-se o microcrustáceo *Artemia salina* como bioindicador. O objetivo foi comparar o desempenho dos diferentes métodos de tratamento (coagulação/floculação e eletrocoagulação), bem como avaliar como todas as variáveis independentes e suas interações afetaram a eficiência dos processos. Os resultados encontrados por meio da análise estatística demonstraram que fator de maior influência no processo de coagulação/floculação para a remoção da concentração do corante AM-16 foi o pH inicial, tanto para o PAC-18% quanto para o sulfato de alumínio ($Al_2(SO_4)_3$). No entanto, para este último a concentração do corante também teve influência, mostrando que o aumento no pH e na concentração do

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Conflicts of interest: the authors declare no conflicts of interest.

Funding: Coordination for the Improvement of Higher Education Personnel (CAPES), National Council for Scientific and Technological Development (CNPq), Research Support Foundation of the State of Rio Grande do Sul (FAPERGS), and the Federal University of Fronteira Sul (UFFS) (Process nº 73/GR/UFFS/2023).

Received on: 10/30/2023. Accepted on: 04/07/2024.

https://doi.org/10.5327/Z2176-94781803

levels studied but good average performance in removing dye (83.68%) and color (95.1%) from the wastewater. Both treatments (coagulation/flocculation and electrocoagulation) demonstrated efficiency for the variables studied and their levels. However, coagulation/flocculation performed better considering the removals obtained in the set of response variables assessed.

Keywords: navy blue dye; coagulation/flocculation; electrochemical treatment; textile wastewater.

corante favorecem a remoção. Quanto à toxicidade do efluente após os tratamentos, houve redução média máxima de aproximadamente 11% para o tratamento com o $Al_2(SO_4)_3$. A eletrocoagulação não apresentou nenhuma variável significante nos níveis estudados, entretanto apresentou bom desempenho médio na remoção da concentração do corante (83,68%) e da cor (95,1%) do efluente. Os dois processos de tratamento avaliados (coagulação/floculação e eletrocoagulação) demonstraram eficiência para as variáveis estudadas e seus níveis. Entretanto, os processos de coagulação/floculação tiveram melhor desempenho se levarmos em consideração as remoções obtidas no conjunto das variáveis de resposta avaliadas.

Palavras-chave: corante azul marinho; coagulação/floculação; tratamento eletroquímico; efluente têxtil.

Introduction

Water resources undergo different treatments before being used, and similarly, industrial wastewater must be treated before being released into water bodies. In both cases, physical, chemical, and biological methods are used for decontamination (Mazzutti et al., 2023), depending exclusively on the characteristics of the wastewater to be treated.

The textile industry is important for the economy, but fabric production and dyeing result in the discharge of wastewater rich in dyes and other substances that can cause serious environmental impacts if released without proper treatment (Stone et al., 2020). The Brazilian Textile and Apparel Industry Association (ABIT, 2022) reported an estimated revenue of R$ 190 billion in 2021, with the clothing sector representing the second-largest employer in the manufacturing industry, creating jobs and income (Cavalcanti and Santos, 2021).

Among the various contaminants that may be present in textile wastewater, synthetic dyes stand out due to their lower cost when compared to their natural counterparts, making them a valid option. They are considered emerging contaminants because they belong to the category of pollutants not included in environmental monitoring programs, are largely recalcitrant, and are used globally in different industrial processes. When released into the environment, they can alter the color of receiving bodies of water, even at low concentrations (Silva and Fracacio, 2021).

The textile and clothing industry accounts for approximately 20% of the wastewater generated worldwide (Ma et al., 2024). In addition to the large volume produced, the composition of these wastewaters is heterogeneous and toxic (Barcellos et al., 2016). The main problems related to this sector are high water consumption and low input use, since it is estimated that 50% of the chemical species used in dyeing are discarded with the wastewater (Soler and Xavier, 2015). These wastewaters have high chemical oxygen demand (COD), color intensity, toxicity, and turbidity (Mcyotto et al., 2021). Their chemical composition makes them difficult to remove, with high stability due to extensive conjugation of synthetic chromophores and high aromaticity (Mcyotto et al., 2021; Schallemberger et al., 2023). The synthetic dyes present are stable to light, heat, and display low biodegradability due to their complex structure and high molecular weight (Mcyotto et al., 2021). Color in water inhibits light penetration, preventing the development of photosynthetic beings and thus interfering with the base of the food chain (Tranker, 2021). Furthermore, studies have shown a correlation between cancer and synthetic dyes (Rodrigues et al., 2017; Arl et al., 2019; Bharti et al., 2019).

Technological advancements have made treatment methods increasingly cheaper and more efficient. Among the various technologies applied today are coagulation/flocculation, electrocoagulation, chemical degradation with ozone, Fenton processes, adsorption, membrane separation, among others (Macedo et al., 2019; Al-Ansari et al., 2022; Albahnasawi, 2023; Asfaha et al., 2022).

A number of studies have been conducted to minimize environmental contamination, a topic addressed by several authors (Gao et al., 2007; Shi et al., 2007; Dalvand et al., 2017; Kamiwada et al., 2020; Mcyotto et al., 2021; Al-Ansari et al., 2022; Asfaha et al., 2022; Albahnasawi, 2023), but comparative studies between coagulation/flocculation and electrocoagulation technologies are scarce.

It is known that a single treatment method is inadequate for removing these contaminants, especially color, due to the complex structure of dyes. Hybrid processes are often applied (Mcyotto et al., 2021). However, this study aimed to compare two competing techniques applied to remove color, COD, turbidity, and toxicity produced by the AM-16 dye, in addition to investigating the influence of different parameters that may affect the processes and their correlations. The idea for this study arose from questions about the differences between coagulation/flocculation and electrocoagulation technologies in some companies in southern Brazil.

Additionally, Brazilian law has become strict in relation to textile wastewater, where no discharge is allowed without proper treatment for dye removal, thus reducing ecological and toxicological impacts on receiving bodies of water (Brasil, 2011; Soler and Xavier, 2015). This makes wastewater treatment mandatory before discharge, validating research that seeks treatment alternatives for companies. Another issue to consider is the global scenario, since the present study addresses several of the 17 Sustainable Development Goals (SDGs) proposed by the United Nations (UN) in 2015. Among the aims of this study are SDG 6 — clean water and sanitation for all; SDG 9 — industry, innovation, and infrastructure; and SDG 14 — life below water. Thus, the concern for preserving water resources goes beyond the needs of industries alone but is a social and political concern that permeates all these areas.

As such, this study aimed to compare the efficiency of electrocoagulation and coagulation/flocculation techniques applied in removing navy blue synthetic dye (AM-16) in wastewater samples prepared from this dye, analyzing different parameters and how they interfere with the efficiency of these treatments.

Materials and Methods

Synthetic wastewater

Was prepared in Jar-test tanks (PoliControl — Floc Control II) containing 2 L of water alkalized with calcium carbonate ($CaCO_3$ buffering agent), preventing the acidifying action of the coagulants (Oliveira and Baltar, 2020). Next, navy blue commercial dye 16 (AM-16 — Tingecor Guarani) was used at concentrations of 150, 200, 250, 300, and 350 mg L^{-1}, which were homogenized at 30 rpm for 2 min. The specific calibration curve was used to analyze a range of light spectra linked to the parameter intended to be monitored (Rosa, 2020). All tests were performed in triplicate, and the determination coefficient R^2=0.997 was obtained from the curve.

Coagulants

Comprised polyaluminum chloride (PAC 18%), and aluminum sulfate ($Al_2(SO_4)_3$), and cationic polymer (CP) acted as a coagulant aid. Solutions of HCl (0.05 M) and NaOH (0.05 M) were used to adjust the pH.

Experimental procedure

Coagulation/flocculation process

In this process, PAC 18% or aluminum sulfate at the established concentrations was added to the wastewater samples, which were then agitated at 150 rpm for 30 s. Next, the CP solution was added at the established concentrations, and the mixture was agitated for 30 min at 20 rpm. The treated wastewater was filtered using qualitative filter paper (125 mm). The independent variables analyzed were CP concentration, coagulant concentration, initial pH, and dye concentration. A Central Composite Rotatable Design (CCRD 2^4) containing 28 tests was used (Table 1).

Table 1 – Independent variables of coagulation/flocculation and electrocoagulation treatments.

Independent variables	Levels				
Coagulation/flocculation	**-2**	**-1**	**0**	**1**	**2**
CP (mg L^{-1})	0.1	0.2	0. 3	0.4	0.5
PAC 18% (mg L^{-1})	10	20	30	40	50
Initial pH (PAC 18%)	5	6	7	8	9
AM-16 dye (mg L^{-1})	150	200	250	300	350
Coagulation/flocculation	**-2**	**-1**	**0**	**1**	**2**
CP (mg L^{-1})	0.1	0.2	0. 3	0.4	0.5
$Al_2(SO_1)_3$ (mg L^{-1})	10	20	30	40	50
Initial pH ($Al_2(SO_4)_3$)	4	5	6	7	8
AM-16 dye (mg L^{-1})	150	200	250	300	350
Electrocoagulation	**-2**	**-1**	**0**	**1**	**2**
Electric current (A)	0.3	0.45	0.6	0.75	0.9
AM-16 dye (mg L^{-1})	150	200	250	300	350

All the tests presented in the table were performed in triplicate.

Electrocoagulation process

The electrocoagulation process lasted for 10 min, and aluminum electrodes (3 cm × 5 cm × 2 mm) placed 8-cm apart were used. The independent variables were the electric current and dye concentration, and sodium chloride (NaCl) was used as the electrolyte at a concentration of 1 g L^{-1} (De Maman et al., 2022a). A CCRD containing 11 tests was used (Table 1).

Analytical methodology

Color analysis (method 2120) and COD (method 5520 D) were determined using the methodology presented in the Standard Methods for Examination of Water and Wastewater (APHA et al., 2005). The hydrogen ion potential of the wastewaters was determined using potentiometric methods. The dye concentration was calculated using a standard curve produced by the direct UV-VIS spectrophotometric method (Nova Instruments, 1800 Series) at a wavelength of 562 nm (obtained by scanning). Total organic carbon (TOC) was determined using a TOC analyzer (Shimadzu TOC-L CPN), reading samples in triplicate before and after treatment. Toxicity analyses were carried out via acute toxicity tests with 50 *Artemia salina* individuals for each sample, counting how many specimens survived after 24 h of exposure (Meyer et al., 1982). Tests were conducted before and after treatment, including a control sample without wastewater (only saline solution).

The treatment results were submitted to ANOVA, allowing validation of the three-dimensional models. The results of the dependent variables obtained in the designs were analyzed using the Minitab 19.0 software, with data treated with a 95% confidence level.

Results and Discussion

Removal of AM-16 Dye

Tables 2 and 3 present the dye removal and color results of the 28 coagulation/flocculation and 11 electrocoagulation tests, respectively. The results obtained for coagulation/flocculation with a combination of PAC 18% and the CP indicated 77–99% removal of the AM-16 dye present in the synthetic wastewater, except for test 22, where no removal occurred. The average removal was 93.43%.

In the process using $Al_2(SO_4)_3$ combined with CP, an average of 71% AM-16 dye removal was obtained, with values ranging between 37 and 99.9%. The best results were obtained in tests 12 and 28. The former had a pH in the range of 5, with CP, dye, and coagulant concentrations of 0.4, 300, and 40 mg L^{-1}, respectively. In contrast, in test 28, the initial pH was in the range of 6, with respective CP, dye, and coagulant concentrations of 0.3, 250, and 30 mg L^{-1}. In terms of color removal, the tests showed that both PAC and $Al_2(SO_4)_3$ were efficient. However, it is important to note that this parameter does not indicate effective contaminant removal but may only be related to the cleavage of bonds responsible for the dye color (De Maman et al., 2022a).

Mcyotto et al. (2021) reported that a PAC dose between 200 and 400 mg L^{-1} promoted peak color removal efficiency, with a subsequent increase in coagulant not improving efficiency, showing the importance of studying coagulant concentration in the coagulation/flocculation process.

Table 2 – Removal of AM-16 dye and color in synthetic wastewater by coagulation/flocculation using PAC 18% and $Al_2(SO_4)_3$ coagulants.

Test	Initial AM-16 dye concentration (mg L^{-1})	Final concentration (mg L^{-1})	Dye removal (%)	Color removal %	Final concentration (mg L^{-1})	Dye removal %	Color removal (%)
		PAC 18%[a]			$Al_2(SO_4)_3$[b]		
1	200	8.89	95.56	57.89	5.56	97.22	99.90
2	200	5.56	97.2	99.00	3.33	98.33	99.90
3	200	14.44	92.78	98.20	5.56	97.22	99.90
4	200	4.44	97.7	99.80	5.56	97.2	99.90
5	200	10.0	95.00	97.45	55.56	72.22	99.90
6	200	7.78	96.1	98.80	126.67	36.6	36.16
7	200	4.44	97.78	99.90	111.11	44.44	39.66
8	200	3.33	98.33	99.90	116.67	41.67	38.49
9	300	66.67	77.78	73.71	167.78	44.07	34.50
10	300	2.22	99.26	92.55	162.22	45.93	39.00
11	300	3.33	98.89	98.96	158.89	47.04	42.98
12	300	2.22	99.26	96.07	0.00	99.90	92.82
13	300	5.56	98.15	97.20	140.00	53.33	43.80
14	300	5.56	98.15	97.80	161.11	46.30	35.80
15	300	6.67	97.78	97.00	183.33	38.89	29.20
16	300	6.67	97.78	96.40	172.22	42.5	28.80
17	250	5.56	97.78	96.20	42.22	83.11	74.66
18	250	5.56	97.78	94.60	103.33	58.67	49.51
19	250	4.44	98.22	97.00	110.00	56.00	38.24
20	250	3.33	98.67	96.80	7.78	96.89	87.15
21	250	10.0	96.00	95.60	10.00	96.00	84.66
22	250	-	-	65.00	123.33	50.67	48.65
23	150	4.44	97.04	96.20	5.56	96.3	80.10
24	350	5.56	98.41	96.40	10.00	97.14	95.40
25*	250	3.33	98.67	99.80	38.89	84.44	79.27
26*	250	3.33	98.67	99.00	44.44	82.22	75.08
27*	250	3.33	98.67	99.90	31.11	87.56	83.33
28*	250	3.33	98.67	99.60	3.33	98.67	98.68

[a]Center point standard deviation (PAC 18% [AM16 dye], no deviation; color=0.04%); [b]Center point standard deviation ($Al_2(SO_4)_3$ [AM16 dye]=18.25 mgL^{-1}; color=10.29%).

Table 3 – AM-16 dye and color removal from synthetic wastewater using electrocoagulation with aluminum electrodes.

Tests	Initial AM-16 dye concentration (mg L^{-1})	Final AM-16 dye concentration (mg L^{-1})	AM-16 dye removal (%)	Color removal (%)
1	300	22.22	92.59	96.09
2	200	22.22	88.89	97.45
3	300	26.67	91.11	96.92
4	200	34.44	82.78	91.46
5a	250	35.56	85.78	96.01
6 a	250	37.78	84.89	95.29
7 a	250	43.33	82.67	95.33
8	250	48.89	80.44	96.43
9	250	57.78	76.89	95.77
10	150	45.56	69.63	93.72
11	350	53.33	84.76	93.95

[a]Center point standard deviation [AM-16]=4.0 mg L^{-1}; color=0.4%.

Gao et al. (2007) used three different coagulants and found that increasing the dose enhanced color removal efficiency. Controlling coagulant concentration between 350 and 450 mg L^{-1} used in the treatment of three real wastewaters demonstrated better color removal efficiency (Islam and Mostafa, 2020). In addition to coagulant concentration, other variables can also affect color removal, including wastewater pH, contaminant concentration, sedimentation time, temperature, agitation, and coagulant potential, all of which are influencing factors in dye removal (Obiora-Okafoet al., 2020; Iloamaeke et al., 2021). Table 3 presents the results of AM-16 navy blue dye removal from synthetic wastewater through electrocoagulation using aluminum electrodes.

In electrocoagulation, 69.93–92.59% removal was observed, with an average of 83.68%. The best results were obtained in tests 1 and 3. In test 1, a continuous current of 0.45 A was used and a dye concentration was 300 mg L^{-1}; while in test 3, the applied current was 0.75 A and dye concentration was 300 mg L^{-1}. The overall color removal results were better than for dye removal, suggesting that, in addition to physical removal, there was also a change in the chromophore groups of the dye, explaining this potential difference. Electrocoagulation removal efficiency was also demonstrated by Tones et al. (2020), who used a mixture of Turquoise Blue (TB) and Scarlet Red (SR) dyes, achieving up to 99.26% removal.

Figure 1 presents Pareto charts for the AM-16 dye removal results using coagulation/flocculation with PAC 18% and aluminum sulfate. For electrocoagulation, none of the parameters assessed was significant within the range and conditions studied. The results obtained by ANOVA indicated that pH was the only significant influencing factor in AM-16 dye removal using coagulation/flocculation and PAC, while with aluminum sulfate, both initial pH and dye concentration affected the coagulation/flocculation process.

Since a variation in pH affects hydroxide precipitation and alters hydrolysis production, pH changes can directly affect clot formation (Islam and Mostafa, 2020). Thus, as a determining factor in color removal (Kamiwada et al., 2019), it is important to control pH during coagulation/flocculation in order to optimize and increase coagulant efficiency (Seneda et al., 2020). Shi et al. (2007) assessed Direct Black 19, Direct Red 28, and Direct Blue 86 dye removal using aluminum sulfate, PAC, and purified aluminum sulfate as coagulants, achieving higher efficiency at pH levels of around 5 and 6, which are similar to those assessed in the present study. Figure 2 represents the contour plot for AM-16 dye removal using aluminum sulfate as coagulant.

As observed on the Pareto chart, both dye concentration and initial wastewater pH showed a linear effect, where an increase in pH and AM-16 concentration favored contaminant removal. However, the electrocoagulation results showed no parameter that significantly influenced AM-16 dye removal at the levels of the variables assessed. In contrast to these results, Pathak et al. (2021) used electrocoagulation for Acid Violet 17 (AV 17), Malachite Green (MG), Methylene Blue (MB), and Congo Red (CR) dye removal, observing a negative linear effect of pH on dye removal, with a removal rate of 59.17 and 58.28% for wastewater with acidic and alkaline dyes, respectively. According to Mcyotto et al. (2021), the PAC dose is a determining factor in dye removal. Shi et al. (2007) agree with a previous study, indicating that different coagulants (aluminum sulfate, PAC 18%, and purified aluminum sulfate) interfere with the removal of Direct Black 19, Direct Red 28, and Direct Blue 86 dyes. In relation to CP, the concentration used was the same for the different coagulants, with a view to assisting in floc formation. The results showed that it was successful in its function, since AM-16 dye concentrations of 150 and 350 mg L^{-1} resulted in 97.04 and 98.41% efficiency, respectively.

Total organic carbon removal

TOC results showed no mineralization but rather partial removal. The highest removal (80.3%) was achieved with electrocoagulation (test 11); while in coagulation/flocculation with PAC 18% and $Al_2(SO_4)_3$, the best results were in tests 1 (77.1%) and 28 (63.7%), respectively. The values obtained are presented in Figure 3.

Albahnasawi (2023) used iron chloride in coagulation and demonstrated that the pH range directly influences TOC removal, with a suitable pH range of 5.9, where the average removal was 40.8%. Figure 4 presents the statistical analysis results using Pareto charts for TOC removal in wastewater samples containing the AM-16 dye. ANOVA results indicated significant interaction between $Al_2(SO_4)_3$ and AM-16 dye concentration in coagulation/flocculation. Electrocoagulation and coagulation/flocculation with PAC 18% were not significantly influenced by any of the independent variables.

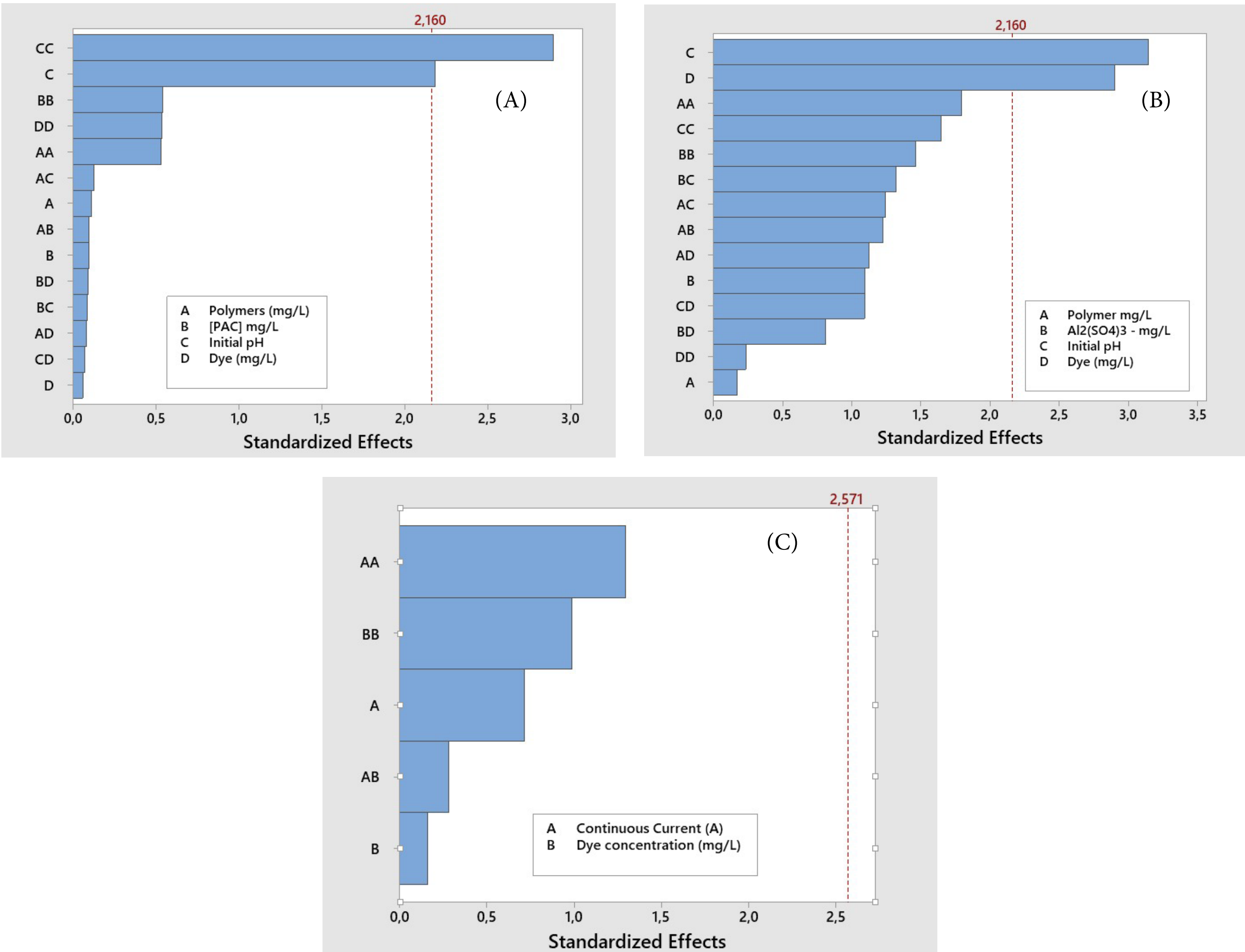

Figure 1 – Pareto chart for AM-16 dye removal in coagulation/flocculation treatments using (A) PAC 18%, (B) $Al_2(SO_4)_3$, and (C) electrocoagulation.

Doses over 50 mg L^{-1} of ferric chloride as a coagulant showed no significant variations in TOC removal when used to treat wastewater containing Direct Red 23 dye (Dalvand et al., 2017). This was also reported by Yuksel et al. (2012), who found no increase in TOC removal above this dosage. In the present study, the best result was obtained at a coagulant concentration of 30 mg L^{-1} of $Al_2(SO_4)_3$ and 250 mg L^{-1} of the AM-16 dye. The chemical characteristics of contaminants in wastewater or drinking water to be treated are a determining factor in coagulant efficiency, as well as in the concentration required to make coagulation/flocculation effective. According to Lara et al. (2016), a concentration of 40 mg L^{-1} of $Al_2(SO_4)_3$ was required to remove TOC from drinking water. The results obtained showed that initial dye concentration alone was not an influencing factor in TOC removal using aluminum sulfate as coagulant, and the highest removal was observed at a concentration of 250 mg L^{-1}, supported by Kadam et al. (2015), who obtained similar results.

Asfaha et al. (2022) used electrocoagulation with aluminum electrodes in the treatment of Vivizol Red 3BS dye (150% VR 3BS), obtaining TOC removal of around 47%, similar to the values recorded in the present study. De Maman (2022a, 2022b) used iron scrap and iron slag as electrodes in the electrocoagulation treatment of synthetic wastewater prepared with indigo blue and real wastewater collected at a textile company, both treated under electric voltages of 300–900 mA, indicating that TOC removal was also not significantly influenced by any independent variables.

However, according to the literature, determining factors in wastewater contaminant removal by electrocoagulation include electrolysis time and electric current applied in the process (Kabdasli et al., 2000; Nariyan et al., 2017; Azarian et al., 2018; Bener et al., 2019; De Maman et al., 2022b). However, Asfaha et al. (2022) indicated that initial pH also affected electrocoagulation results.

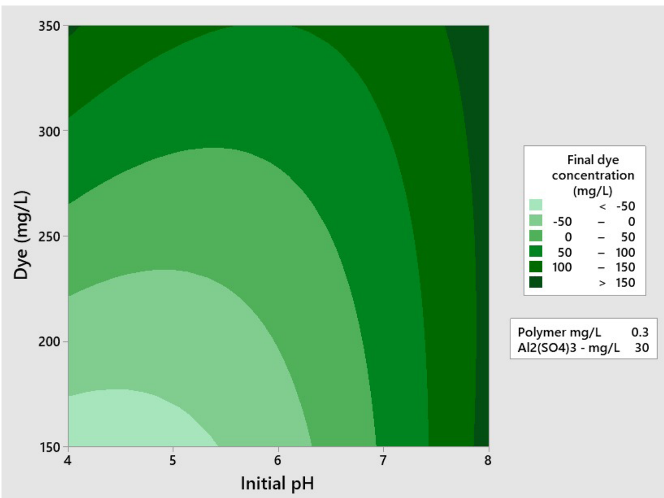

Figure 2 – Contour plot for AM-16 dye removal by coagulation/flocculation using $Al_2(SO_4)_3$ and cationic polymer.

Removal of chemical oxygen demand

The results of COD removal indicated that the best rates were obtained by coagulation/flocculation using aluminum sulfate as coagulant, as shown in Figure 5.

Figure 6 represents ANOVA analysis of the COD removal results, indicating that the removal efficiency of coagulation/flocculation using PAC (18%) was influenced by interaction between the dye and CP concentration (Figure 6A). However, coagulation/flocculation using aluminum sulfate showed a linear effect of AM-16 dye concentration and quadratic terms for the dye and polymer concentration (Figure 6B), making it possible to obtain the contour curve for this behavior in COD removal (Figure 7). For electrocoagulation, none of the independent variables influenced the removal of this parameter (Figure 6C).

Interaction between the independent variables dye and CP concentration in the treatment with PAC 18% (Figure 6A) favored COD removal. COD is an extremely relevant parameter in aquatic environments because it can directly affect microbial reproduction and may damage the ecosystem (Meng et al., 2018). Figure 7 represents the effect of the independent variables CP (quadratic) and AM-16 dye concentration on COD removal with aluminum sulfate. Higher contaminant concentrations associated with greater CP concentrations favor COD removal from the wastewater. It is also important to note the linear effect of the dye, as shown by the Pareto chart (Figure 6B), where an increase in dye concentration improved COD removal.

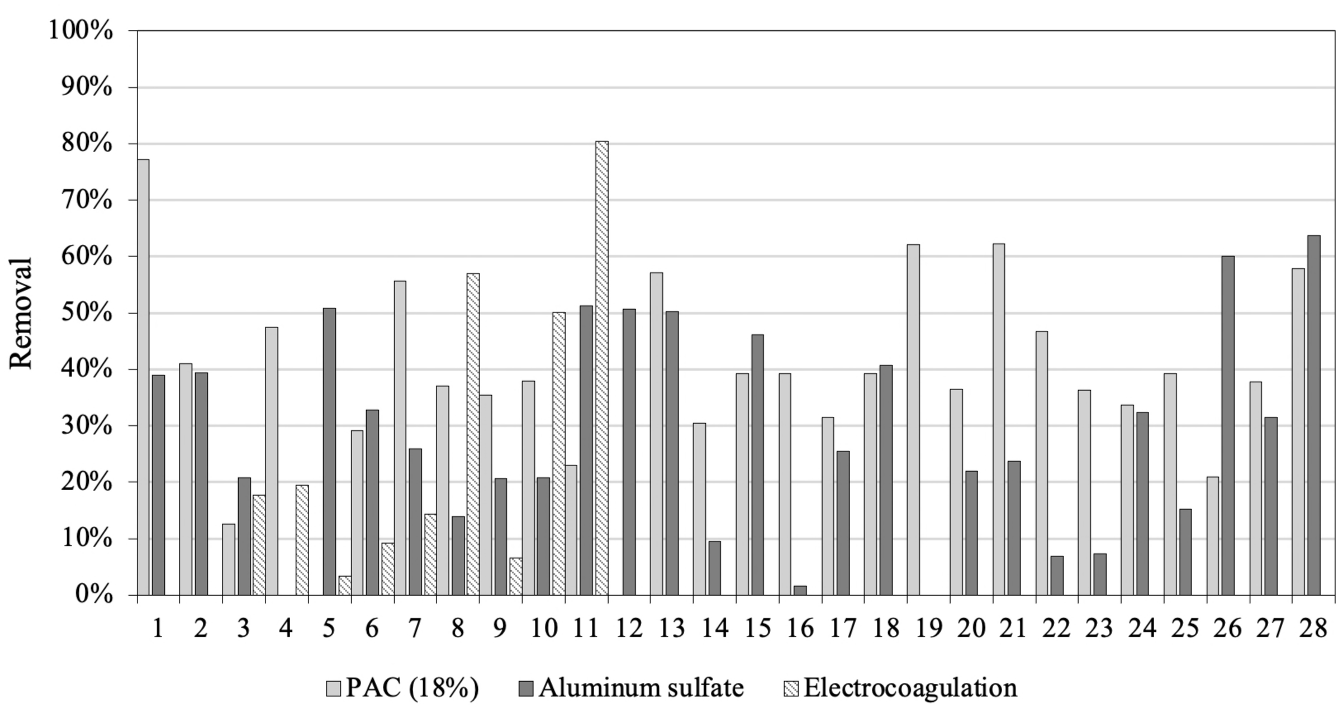

Figure 3 – Total organic carbon removal for coagulation/flocculation and electrocoagulation treatments.

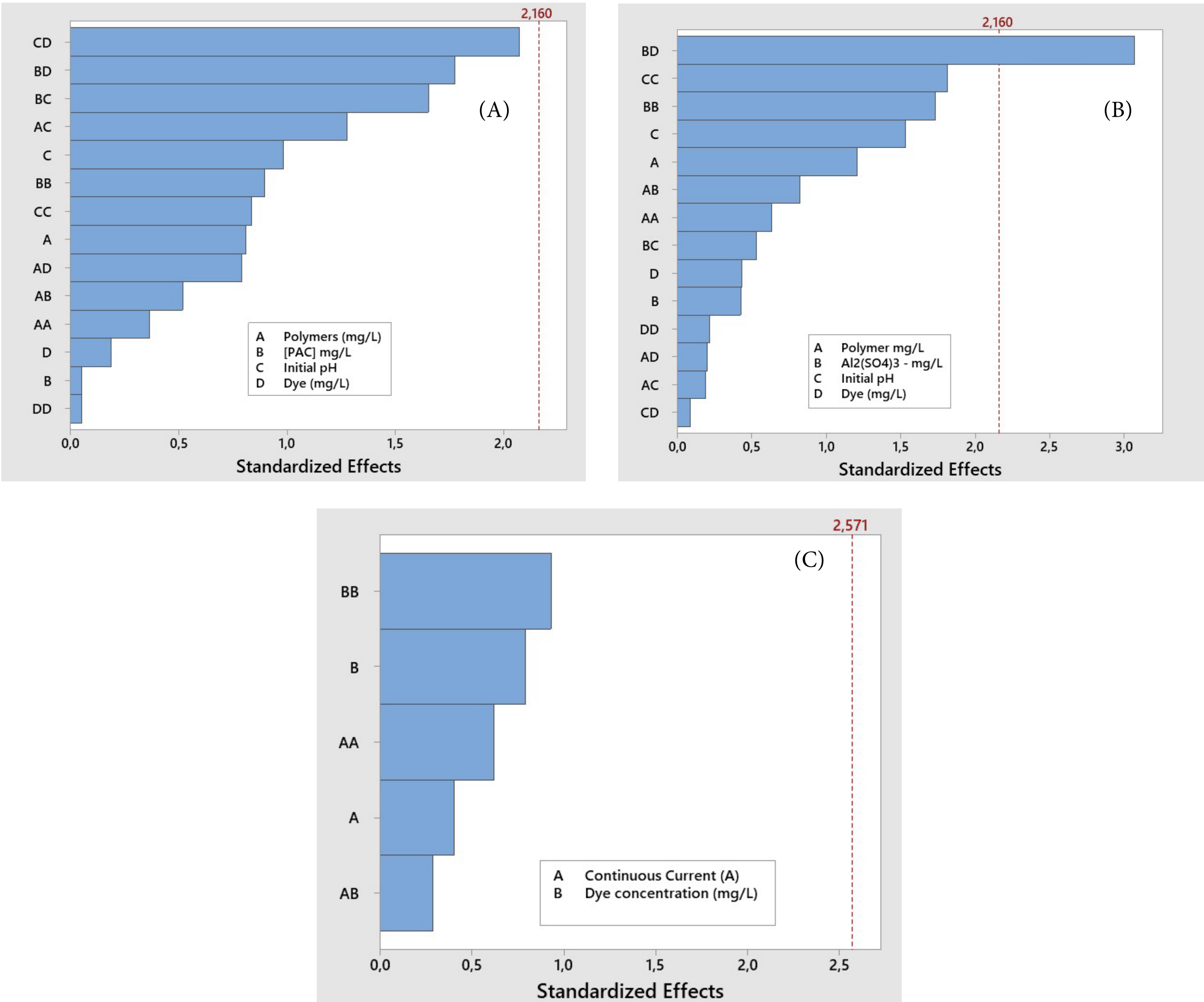

Figure 4 – Pareto chart for total organic carbon removal of synthetic wastewater containing the AM-16 dye in coagulation/flocculation treatments using (A) PAC 18%, (B) $Al_2(SO_4)_3$, and (C) electrocoagulation.

In the case of electrocoagulation, research conducted by Ardhan et al. (2022) using iron electrodes and focusing on COD removal indicated that the type of dye directly influences process efficiency. According to the study, there is a direct relationship between dye solubility and COD removal. However, the results obtained by Marquez et al. (2022) showed no significant influence of any independent variable on removal efficiency, corroborating the present study. The average values obtained for COD removal from synthetic wastewater treated with different coagulants (PAC 18%, $Al_2(SO_4)_3$) and electrocoagulation showed that aluminum sulfate was the most efficient coagulant in COD removal (38.04%), followed by electrocoagulation (29.32%) and PAC 18% (21.95%) under the conditions used in this study.

Toxicity tests

Figures 8–10 present the results of toxicity tests with the raw wastewater containing the AM-16 dye and after treatments (coagulation/flocculation (PAC 18%, $Al_2(SO_4)_3$, and electrocoagulation), showing the mortality percentages. For this analysis, the brine shrimp *Artemia salina* was used.

ANOVA data demonstrated that none of the variables in the different treatments at the levels assessed significantly influenced the mortality rate in the wastewater samples containing *Artemia salina*.

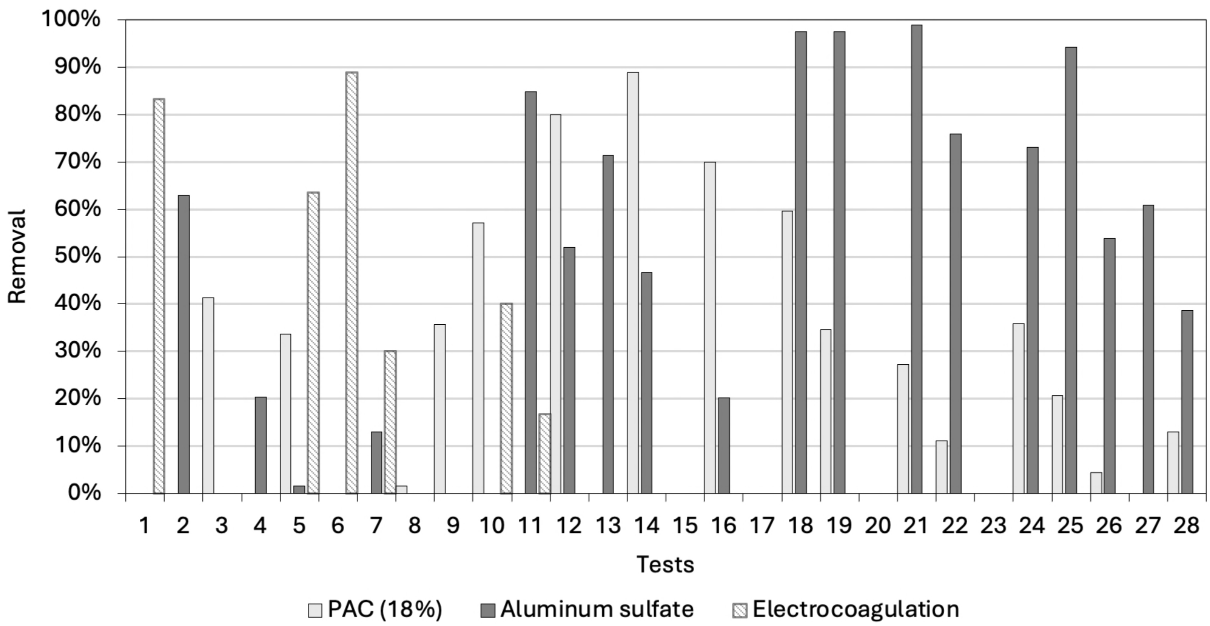

Figure 5 – Comparative results of % chemical oxygen demand removal for the different coagulation/flocculation and electrocoagulation treatments.

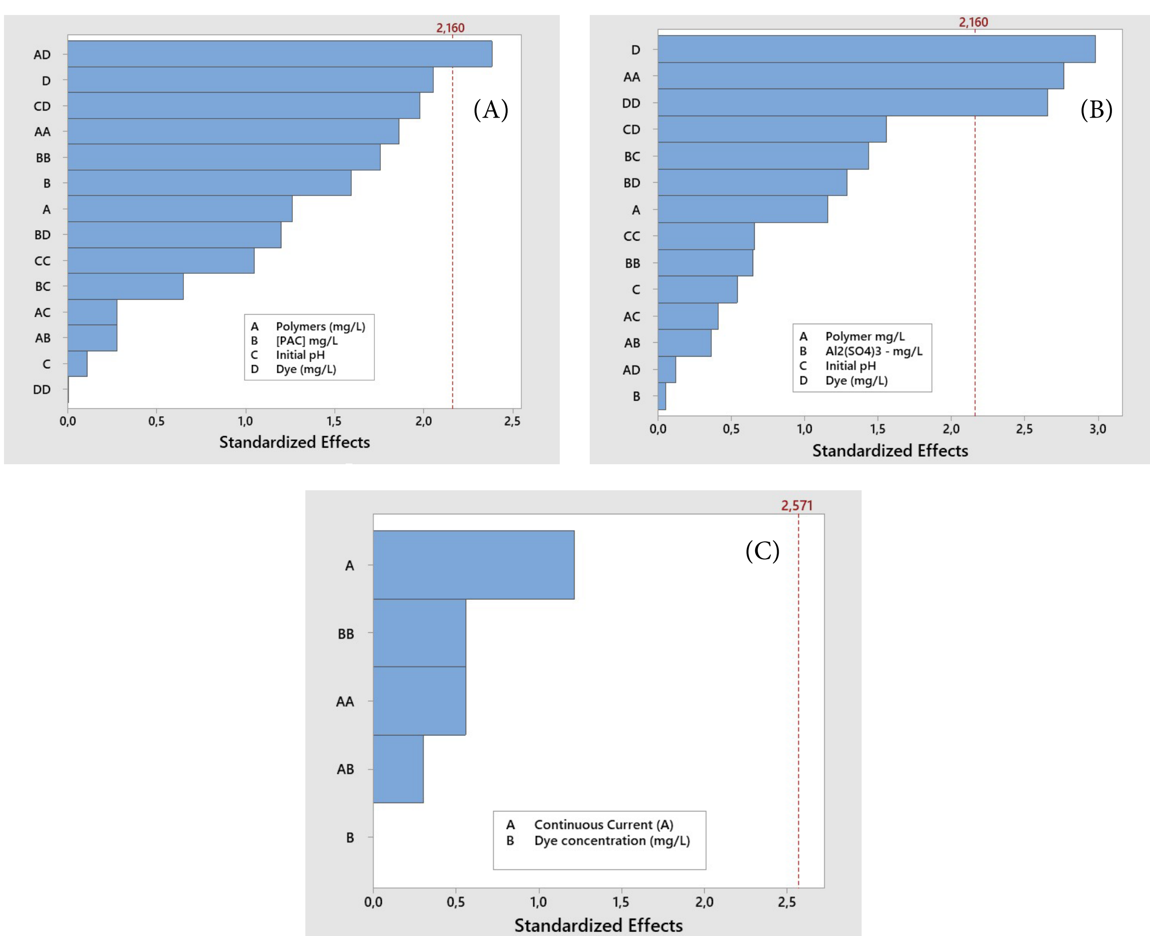

Figure 6 – Pareto chart for chemical oxygen demand removal from synthetic effluent containing AM-16 dye in coagulation/flocculation treatments using PAC 18% (A); $Al_2(SO_4)_3$ (B); electrocoagulation (C).

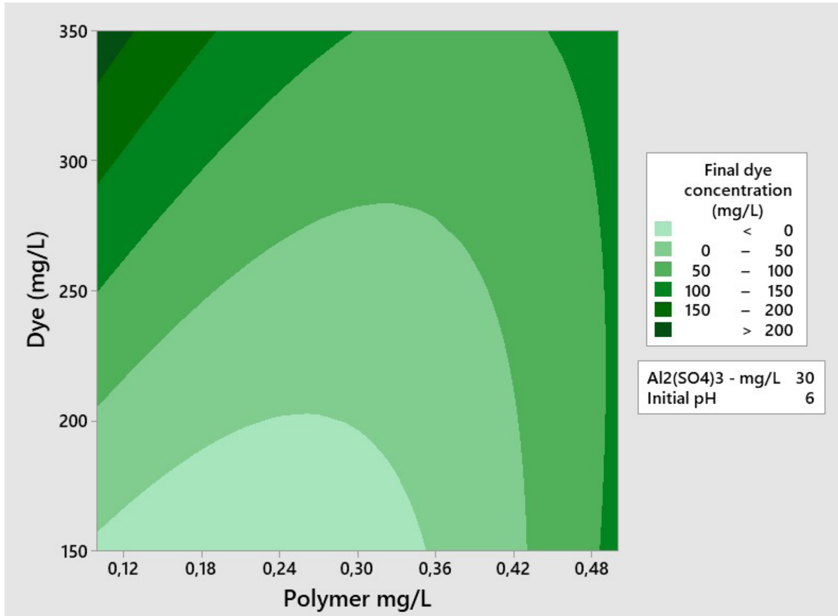

Figure 7 – Response surface for chemical oxygen demand removal from synthetic wastewater containing AM-16 dye in the coagulation/flocculation treatment using $Al_2(SO_4)_3$.

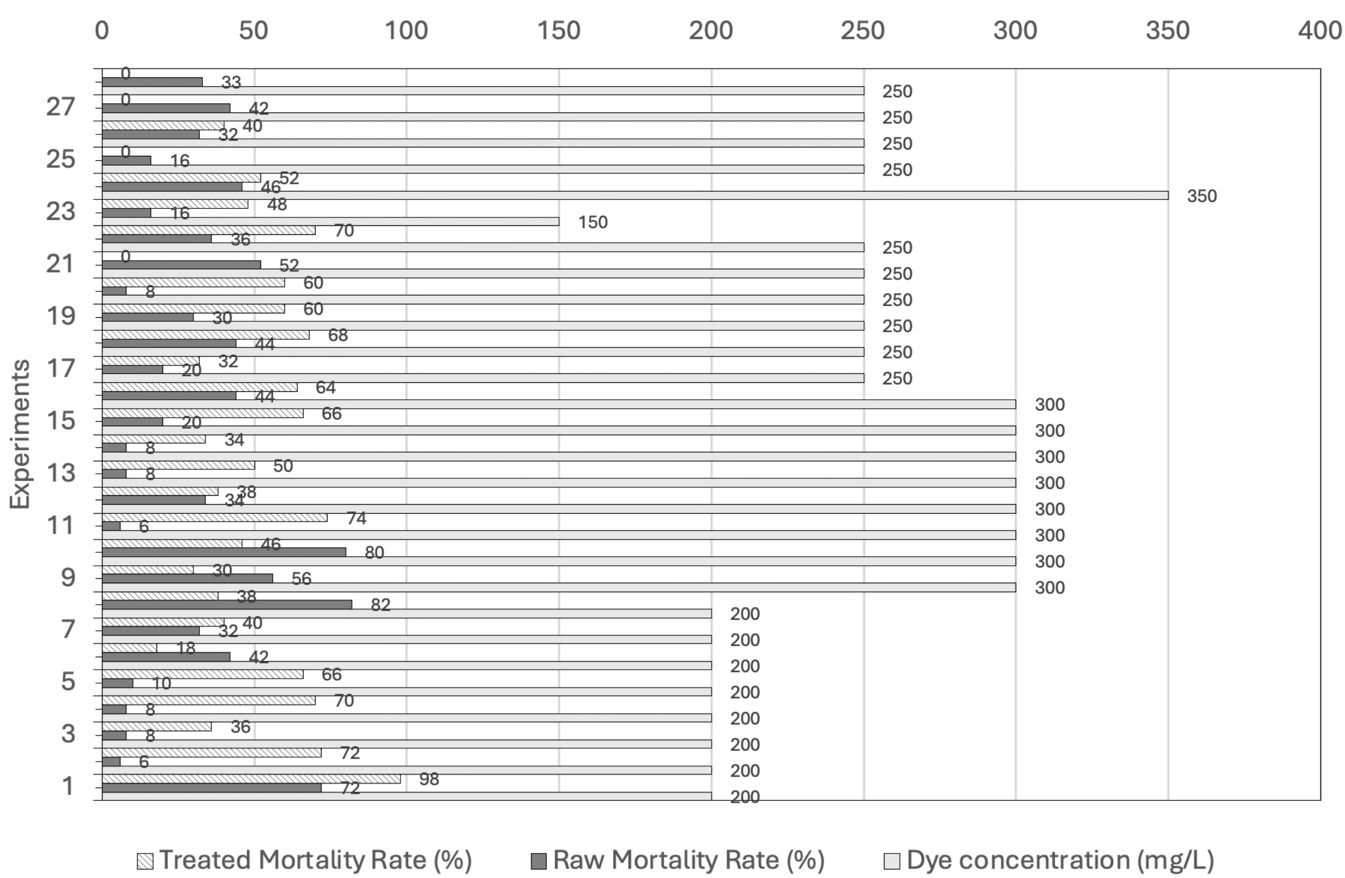

Figure 8 – Mortality rate of Artemia salina exposed to raw wastewater containing the AM-16 dye and that treated by coagulation/flocculation with PAC 18%.

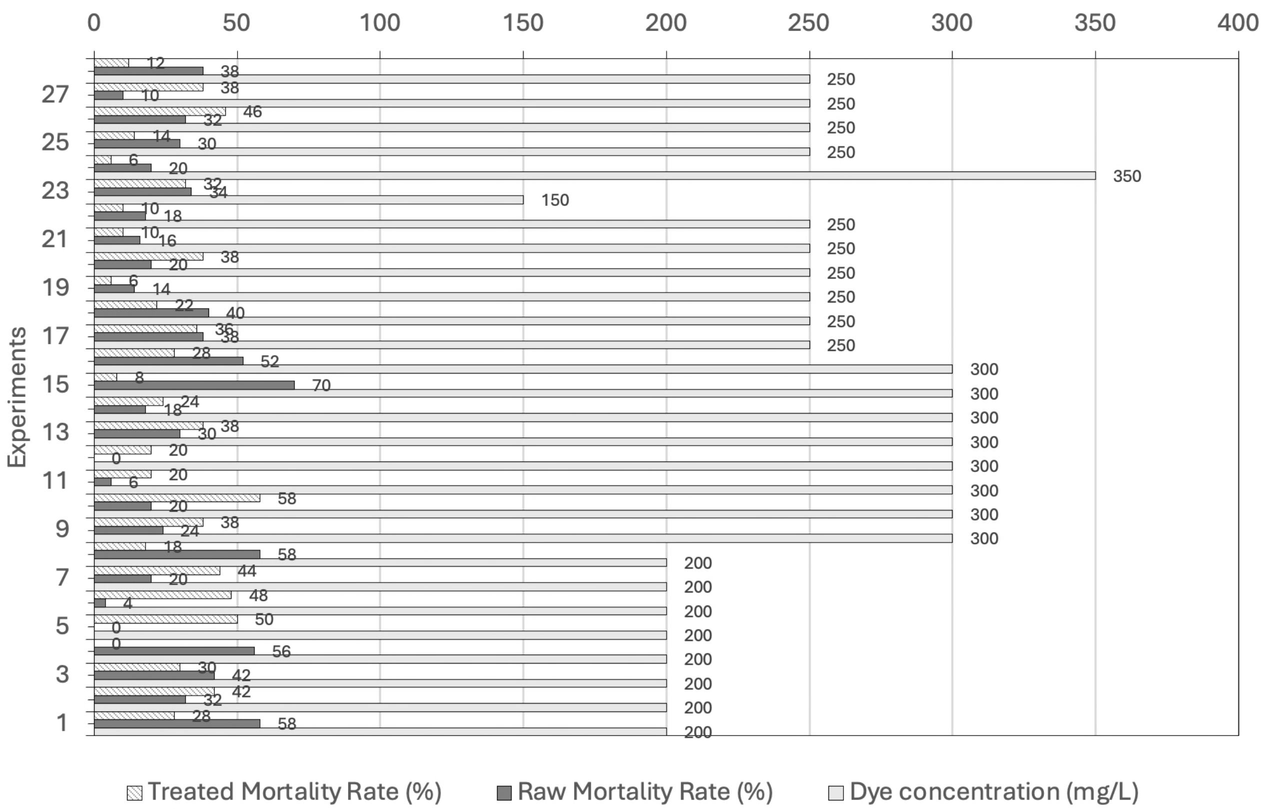

Figure 9 – Mortality rate of Artemia salina exposed to raw wastewater containing the AM-16 dye and that treated by coagulation/flocculation with $Al_2(SO_4)_3$.

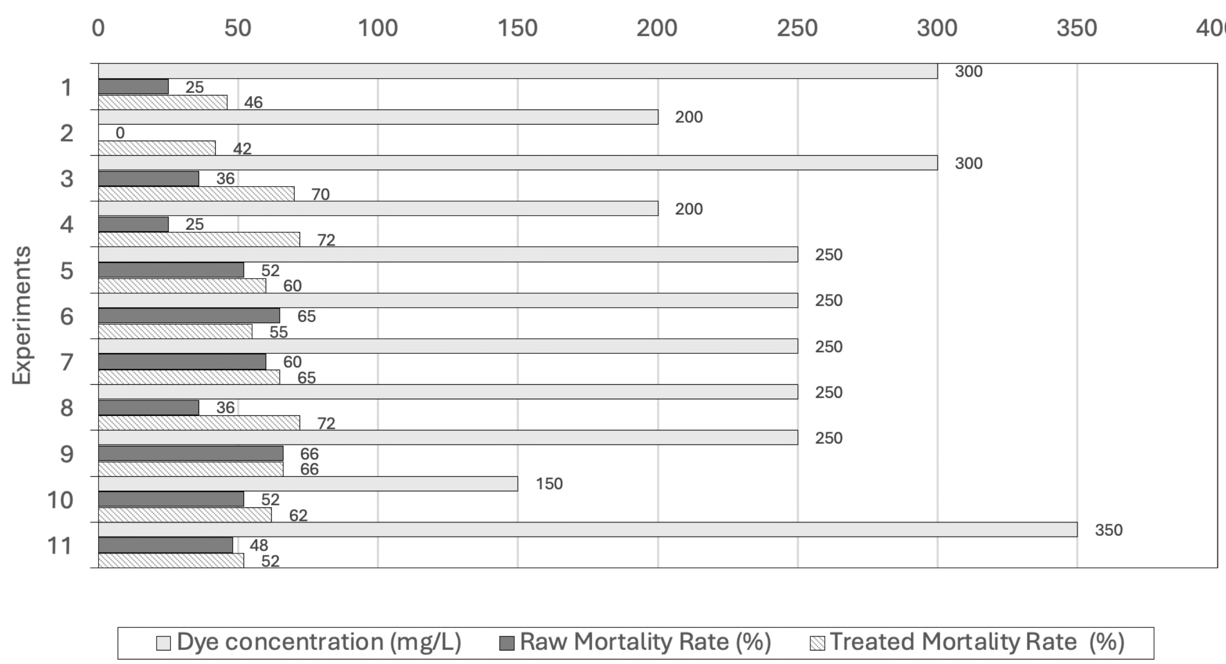

Figure 10 – Mortality rate of Artemia salina exposed to raw wastewater containing the AM-16 dye and that treated by electrocoagulation.

However, according to Al-Ansari et al. (2022), the decolorization of textile wastewater containing azo dyes (methyl orange, Congo red) improved the survival rate (91.7±2.9%) of *Artemia* larvae after 24 h. As mentioned earlier, the removal of wastewater color via treatment does not mean the removal of intermediate compounds that are often more toxic than the raw wastewater itself, given that only bond cleavage related to the chromophore group of the dye may occur rather than contaminant mineralization.

Overall, with respect to the mortality percentage after treatment, this effect possibly occurred during electrocoagulation treatment of wastewater containing AM-16 and coagulation using PAC 18%. Along with the intermediate compounds, the final pH of the process may also have influenced the result. In addition to the acute effect assessed in this study, attention should be paid to the long-term effects that may be triggered by the exposure of aquatic organisms to wastewater containing dyes. Alderete et al. (2020) assessed synthetic wastewater containing the azo dye Amido Black 10B (AB10B), using toxicity tests with *Daphnia magna* and the *Allium* strain to evaluate acute toxicity and chromosomal mutagenesis, respectively. It was observed that the raw wastewater did not exhibit acute toxicity but induced chromosomal mutations in the *Allium* species.

It is important to note that the species used in toxicity tests may also influence the results obtained. A study using lettuce seeds (*L. sativa*) demonstrated that even after electrocoagulation, the germination rate remained low, indicating high toxicity, in agreement with the present study (Martins et al., 2023). However, research conducted by Lach et al. (2022) with the microcrustacean *Daphnia magna* indicated a reduction in toxicity after treatment.

Comparative analysis of the average removal results

Figure 11 shows the average removal results of the different parameters studied with the treatments presented in this research.

Coagulation/flocculation using PAC-18%, aluminum sulfate, and electrocoagulation indicated average dye concentration removal of 93.43, 71.1, and 83.68%, respectively. In terms of toxicity, the best reduction was observed in the tests using $Al_2(SO_4)_3$ to treat synthetic wastewater, where an average of 11.57% was obtained. Electrocoagulation proved to be efficient for average AM-16 dye (83.68%) and color removal (95.31%), while for the other parameters assessed, the average results were lower than those obtained with coagulation/flocculation.

Conclusion

Despite being a traditional coagulant, aluminum sulfate exhibited a high degree of removal efficiency for the parameters assessed, with the treatment exhibiting the lowest residual toxicity. However, the data showed the possibility of using PAC-18% as a coagulant, given

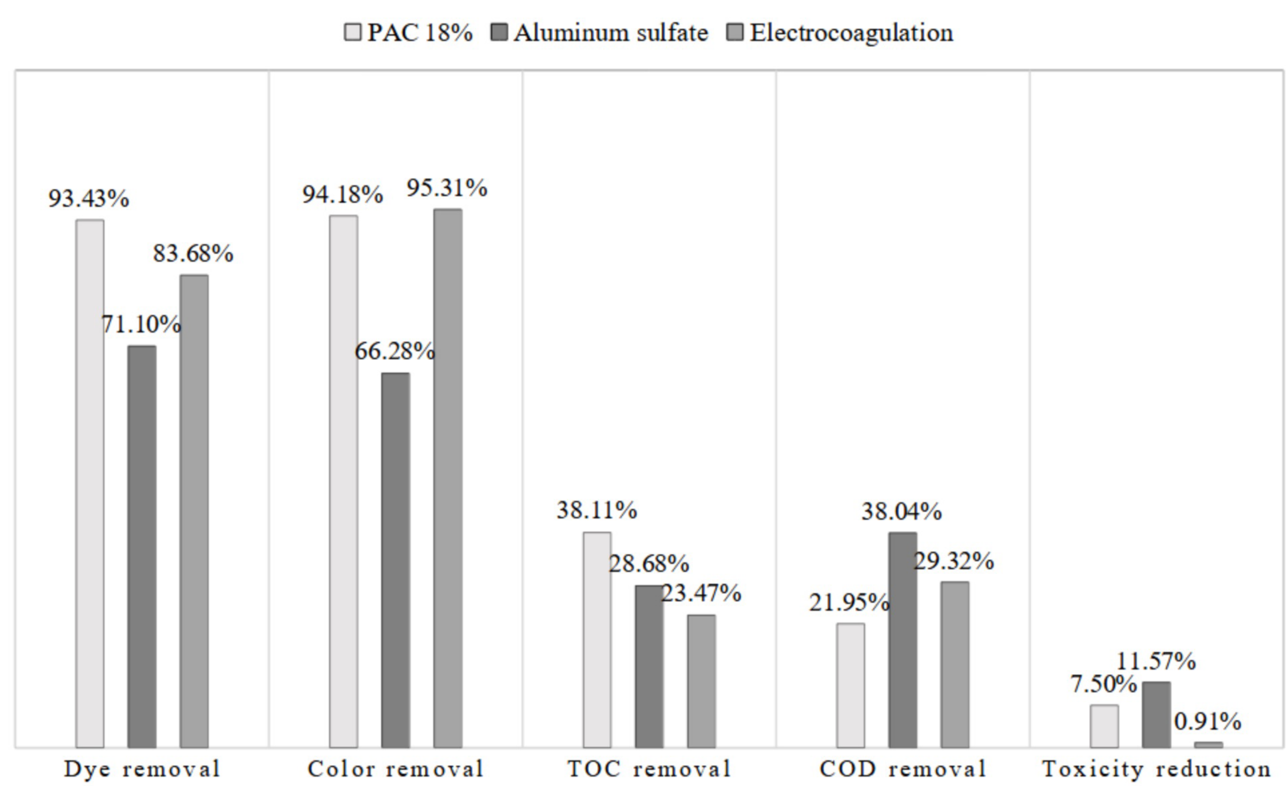

Figure 11 – Average removal in response variables for the tests conducted in each treatment applied to the synthetic wastewater containing the AM-16 dye.

its high removal rates for contaminants, color, and TOC. Electrocoagulation showed reasonable performance compared to the other methods, since it had good removal rates for AM-16, color, and COD but obtained the highest residual toxicity. Thus, it is concluded that the different treatment processes used were efficient, but treatments using coagulants are still competitive when compared to electrochemical methods under the conditions used in this study.

Acknowledgments

This study was supported by the Coordination for the Improvement of Higher Education Personnel (CAPES). We also thank the National Council for Scientific and Technological Development (CNPq) and the Research Support Foundation of the State of Rio Grande do Sul (FAPERGS) for providing research grants, and the Federal University of Fronteira Sul (UFFS) for the funding provided.

Authors' contributions

BRESSAN, L.G.: conceptualization; data curation; formal analysis; research; methodology; writing – original draft. FLORES, G.C.P.: data curation; formal analysis; research. BIOLCHI, N.J.: data curation; formal analysis; research. MENDES, M.E.M.: data curation; formal analysis; research. DERVANOSKI, A.: conceptualization, supervision; formal analysis; research; methodology; validation; visualization. KORF, E.P.: conceptualization, data curation; formal analysis; research; validation. PASQUALI , G.D.L.: conceptualization, supervision; data curation; formal analysis; research; methodology; validation; visualization; writing – review & editing.

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