

Radical decomposition of hydrogen peroxide catalyzed by iodide for degradation of organic dyes

Decomposição radicalar do peróxido de hidrogênio catalisada por iodeto para a degradação de corantes orgânicos

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Abstract

The decomposition of hydrogen peroxide into hydroxyl radical, a powerful oxidizing agent, has aroused the interest of the scientific community due to the numerous possible applications, mainly in the treatment of effluents. In this work, the potential of using iodide ions as precursors of the hydroxyl radical was evaluated. Iodide, in addition to being theoretically viable, simultaneously leads to the production of molecular iodine, which also has an oxidizing characteristic, and can contribute to the efficiency of the process. The results demonstrated that iodide ions act by promoting the radical decomposition of H_2O_2 and that the process is dependent on the pH of the reaction medium, with the generation of radical hydroxyl only manifesting itself at pH 2.5 and 3.0. The removal results proved that the anionic or cationic nature of the dye interferes with the reaction mechanism. For methylene blue, a cationic dye, a small portion of TOC was removed by oxidation (7.9 to 20.6%) and the remainder occurred by adsorption (79.4 and 92.1%). The interaction of methylene blue with the surface of molecular iodine prevents its contact with the iodide ions present in the reaction medium, allowing it to remain in a solid state in solution and act as an adsorbent,

contributing to better efficiency. For the tartrazine yellow dye, an anionic dye, there was no formation of solid iodine, indicating the absence of an adsorptive process, with the oxidation mechanism, showing removal of 11.3 to 18.9%, similar to the results found for the removal of blue methylene by oxidation.

Keywords: Advanced oxidative processes. Hydroxyl radical. Hydrogen peroxide. Iodide ions.

Resumo

A decomposição do peróxido de hidrogênio em radical hidroxila, um agente oxidante poderoso, despertou o interesse da comunidade científica devido às inúmeras possíveis aplicações, principalmente no tratamento de efluentes. Neste trabalho, avaliou-se o potencial do uso de íons iodeto como precursores do radical hidroxila. O iodeto, além de ser teoricamente viável, leva simultaneamente à produção de iodo molecular, que também possui característica oxidante, podendo contribuir para a eficiência do processo. Os resultados demonstraram que os íons iodeto atuam promovendo a decomposição radicalar do H_2O_2 e que o processo é dependente do pH do meio reacional, com a geração de radical hidroxila manifestando-se apenas em pH 2,5 e 3,0. Os resultados de remoção comprovaram que a natureza aniônica ou catiônica do corante interfere no mecanismo de reação. Para o azul de metileno, um corante catiônico, uma pequena porção de TOC foi removida por oxidação (7,9 a 20,6%) e o restante ocorreu por adsorção (79,4 a 92,1%). A interação do azul de metileno com a superfície do iodo molecular impede seu contato com os íons iodeto presentes no meio reacional, permitindo que permaneça em estado sólido na solução e atue como adsorvente, contribuindo para uma melhor eficiência. Para o corante amarelo tartrazina, um corante aniônico, não houve formação de iodo sólido, indicando a ausência de um processo adsorptivo, com o mecanismo de oxidação, mostrando remoção de 11,3 a 18,9%, semelhante aos resultados encontrados para a remoção do azul de metileno por oxidação.

Palavras-chave: Processos oxidativos avançados. Radical hidroxila. Peróxido de hidrogênio. Íons iodeto.

1. Introduction

Advanced oxidation processes (AOPs) have been extensively studied as they are effective treatment technologies to degrade recalcitrant and toxic organic contaminants in wastewater. These technologies generally use the hydroxyl radical, a powerful oxidizing agent capable of promoting the mineralization of organic pollutants (Mukherjee *et al.*, 2023). Among the AOPs, the Fenton process stands out. This process has already been used on an industrial scale to degrade organic contaminants in industrial wastewater and effluent treatment units (Kadioğlu *et al.*, 2024; Miklos *et al.*, 2018). The process involves the catalytic reactions of ferrous ions (Fe^{2+}) in the decomposition of hydrogen peroxide (H_2O_2) into hydroxyl radical ($^*\text{OH}$).

The success of this process can be attributed to the ease of operation and flexibility for implementation, in addition to the high efficiency in the mineralization of pollutants (Bokare & Choi, 2014; Nidheesh *et al.*, 2023). On the other hand, the use of large amounts of ferrous ions makes a post-treatment step of the effluent necessary for its removal, increasing the cost of the process by adding chemical products (Mirzaei *et al.*, 2017). Considering the proven feasibility of implementation and efficiency of the Fenton process, as well as the disadvantage in the use of iron, research has focused on exploring new catalysts for the radical decomposition of hydrogen peroxide to replace ferrous ions (Menino *et al.*, 2021; Wang *et al.*, 2016).

As the Fenton reaction basically consists of a redox reaction, it is essential to evaluate the standard reduction potential (E°) of the chemical species involved in the process. For the reaction to occur spontaneously and for the H_2O_2 to undergo reduction and decompose generating the hydroxyl radical ($^*\text{OH}$), it is necessary that the catalytic precursor has an E° value lower than that of H_2O_2 ($E^\circ = 1.77\text{V}$) (Menino *et al.*, 2021; Miotto, 2021).

In our previous study, the E° values for the halogen's iodine, chlorine, and bromine, in the form of iodide (I^-), chloride (Cl^-), and bromide (Br^-) ions were analyzed, and it was found that I^- is a potential catalytic precursor in the decomposition of hydrogen peroxide, as it meets the

electrochemical criterion ($E^\circ_{\text{catalyst}} < E^\circ_{\text{H}_2\text{O}_2}$), with a value of $E^\circ_{\text{(I}_2/\text{I}^-)} = 0.53\text{V}$. Furthermore, the product formed in the iodide oxidation reaction is iodine (I_2). Iodine is a water-insoluble oxidizing agent and can contribute to the oxidative degradation of organic compounds and enhance the oxidative process (Hou *et al.*, 2023; Khaled *et al.*, 2011). Due to its low solubility in aqueous medium (0.0013 mol.L^{-1}) the I_2 formed crystallizes in the form of crystals that have a metallic shine (Lee, 1999). For this reason, iodine can be easily removed at the end of the reaction by a sedimentation or filtration process, enabling its reuse after a reduction step.

In a previous study (Miotto, 2013), the reduction potential values (E°) for the iodide (I^-), chloride (Cl^-), and bromide (Br^-) ions were analyzed, and it was found that iodide (I^-) is a possible catalytic precursor for the radical decomposition of hydrogen peroxide, as it meets the electrochemical criterion ($\text{catalyst } E^\circ < E^\circ_{\text{H}_2\text{O}_2}$), with an $E^\circ_{\text{(I}_2/\text{I}^-)}$ value equal to 0.53V . Furthermore, the product formed in the iodide oxidation reaction is molecular iodine (I_2). Iodine is an oxidizing agent that is insoluble in water and can contribute to the oxidative degradation of organic compounds and enhance the oxidative process (Hou *et al.*, 2023; Khaled *et al.*, 2011). Due to its low solubility in aqueous media (0.0013 mol.L^{-1}), the I_2 formed appears in solid form, as a metallic precipitate (Lee, 1999), and can be easily removed at the end of the reaction through a sedimentation process or filtration, enabling its reuse after a reduction stage.

In this context, the objective of this study was to optimize the use of iodide as a catalytic precursor for the radical decomposition of hydrogen peroxide in degradation tests of model organic dyes. The effect of pH and type of acid on the radical decomposition of hydrogen peroxide, as well as the degradation potential of methylene blue and tartrazine yellow dyes, was evaluated.

2. Materials and Methods

2.1 Materials

The reagents used in the experiments were: acetic acid (CH_3COOH) (Synth); hydrochloric acid (HCl) (Vetec), nitric acid (HNO_3) (Vetec), sulfuric acid (H_2SO_4) (Vetec), methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) (Vetec), tartrazine yellow ($\text{C}_{16}\text{H}_9\text{N}_4\text{Na}_3\text{O}_9\text{S}_2$) (Brastok), potassium iodide (KI) (Synth), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) (Vetec), hydrogen peroxide (H_2O_2) (Sigma-Aldrich), and deionized water.

2.2 Evaluation of the influence of pH and different acids on the radical decomposition mechanism of H_2O_2

The catalytic activity of iodide in the radical decomposition of H_2O_2 was evaluated using the gasometry technique, monitoring the volume of oxygen gas (O_2) generated using deionized water or methylene blue solution as a reaction medium (Menino *et al.*, 2021; Moretto, 2011). The experiments were carried out using 9.5 mL of deionized water or methylene blue solution (20 mg.L^{-1}). After adjusting the desired pH (2.5, 3.0, 4.0, 5.0, 6.4, and 7.0) with a solution of H_2SO_4 (5%), 1 mL of a solution of potassium iodide (0.5 mol.L^{-1}), and 0.2 mL of H_2O_2 . The solution was homogenized, and the volume of oxygen gas generated was monitored.

After evaluating the influence of pH on the radical decomposition of hydrogen peroxide, new tests were conducted by correcting the pH of the reaction medium with different acids (HNO_3 , HCl , and CH_3COOH) that differ in their properties (oxidizing, reducing, and complexing, respectively).

2.3 Effect of reaction time on oxidative degradation

A preliminary study was carried out to evaluate the effect of reaction time on oxidative degradation. Two organic molecules with different characteristics were used as models: methylene blue (MB) with a cationic characteristic and tartrazine yellow (TY) with an anionic characteristic (Figure 1).

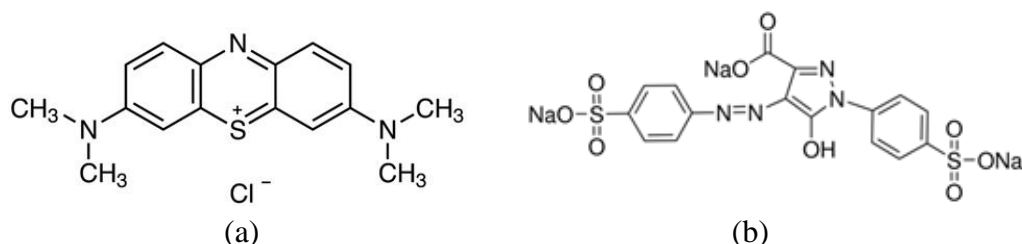


Figure 1 - Structural formula of the dyes used in this study, (a) methylene blue and (b) tartrazine yellow.

The oxidative degradation tests were carried out in batch in glass reactors at room temperature (23 – 25 °C). First, 100 mL of the solution of the dyes blue methylene or tartrazine yellow at the concentration of 100 mg.L⁻¹ was added to the reactor. After adjusting the pH to 2.5 using a solution of H₂SO₄ (5%), 5 mL of potassium iodide (0.5 mol.L⁻¹) and 2 mL of H₂O₂ were added. The system was kept under magnetic stirring for 60 minutes.

Oxidative degradation tests were carried out in batches in glass reactors at room temperature (23 – 25 °C). First, 100 mL of methylene blue or tartrazine yellow dye solution at a concentration of 100 mg.L⁻¹ was added to the reactor. After adjusting the pH to 2.5 using an H₂SO₄ solution (5%), 5 mL of a potassium iodide solution (0.5 mol.L⁻¹) and 2 mL of H₂O₂ (30%) were added. The system was kept under magnetic stirring for 60 minutes.

For kinetic studies on color removal from solutions, 1 mL aliquots were removed at intervals of 1, 3, 5, 7, 10, 15, 30, and 60 minutes. After dilution steps to 10 mL with distilled water and centrifugation (3500 rpm for 10 minutes), the samples were analyzed spectrophotometrically at 665 nm for MB and 426 nm for TY to determine the concentration of the dyes. The efficiency of the oxidative degradation process in the mineralization of the samples was evaluated by the Total Organic Carbon (TOC) content (Shimadzu, model TOC-V CSH). The insoluble iodine formed was removed by centrifugation prior to analyzing the TOC, which was analyzed after 15, 30, and 60 minutes of reaction.

2.4 Factorial experimental design

The effects of the iodide concentration and H₂O₂ concentration variables on the efficiency of the oxidative process were evaluated using a 2² factorial experimental design, with four (4) factorial points and three (3) central points, totaling 7 experiments, which were carried out randomly to minimize systematic errors.

The tests were conducted in batches, under mechanical agitation at 25 °C, using 100 mL of dye solution (100 mg.L⁻¹) with the pH adjusted to 2.5 using a 5% H₂SO₄ solution. The definition of the levels of independent variables (Table 1) was based on reaction stoichiometry. The central point represents, stoichiometrically, the concentrations necessary for the total mineralization of the dye.

Table 1 - Levels of independent variables of factorial design 2².

Variable	Methylene Blue Levels (C ₁₆ H ₁₈ ClN ₃ S)			Tartrazine Yellow Levels (C ₁₆ H ₉ N ₄ Na ₃ O ₉ S ₂)		
	-1	0	1	-1	0	1
(I) / mg. L ⁻¹	275	550	825	166	332	498
(H ₂ O ₂) / mg. L ⁻¹	20	60	100	10	35	60

The recovered iodine mass and the TOC value were the dependent variables used to assess the efficiency of the process after a 15-minute reaction period. The experimental data were statistically evaluated using the Statistica 5.0 software, with a 95% confidence level.

2.5 Iodine reduction for reuse

The molecular iodine formed and separated by centrifugation in the experimental design tests was subjected to drying at 80 °C for 12 hours. It was later reduced to iodide with a solution of sodium metabisulfite (0.5 mol.L^{-1}) for reuse in new oxidative degradation tests. The necessary amount of sodium metabisulfite added for complete solubilization of iodine was 15 mL, a standardized value in all experiments. After solubilization, water was added until the final volume of the solution reached 100 mL.

3. Results and Discussion

Initially, the influence of pH and the use of different acids on the activity of iodide in the radical decomposition of H_2O_2 was studied. Subsequently, an experiment was conducted to evaluate the effect of reaction time on the oxidative degradation of dyes. Finally, an experimental design was applied to evaluate the degradation of two dyes, methylene blue and tartrazine yellow.

3.1 Influence of pH and different acids on the radical decomposition mechanism of H_2O_2

The volume of O_2 generated in the catalytic decomposition reaction of hydrogen peroxide by iodide, in the presence and absence of methylene blue, at different pH's is shown in Figure 2.

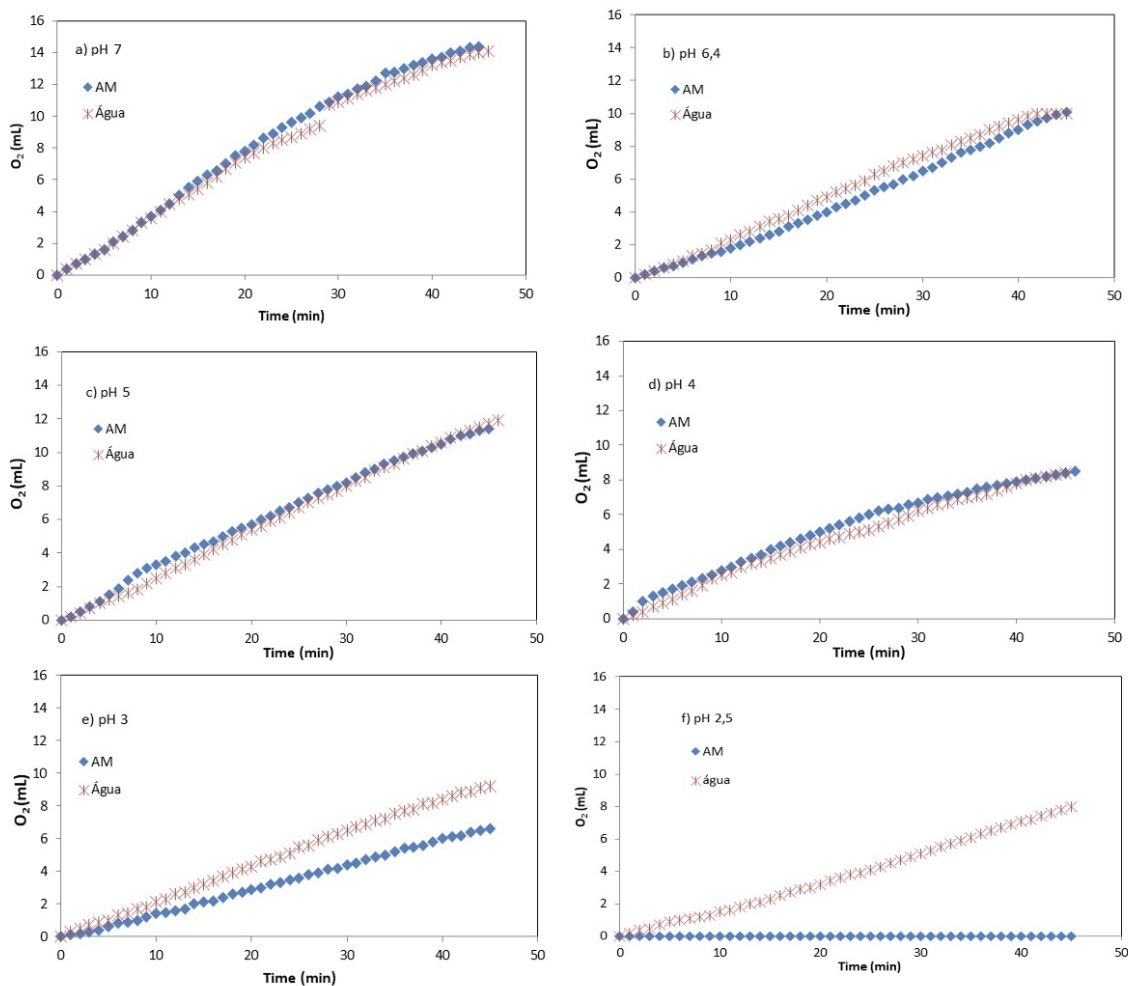


Figure 2 - Volume of O_2 generated in the catalytic decomposition of H_2O_2 , at different pHs, corrected with sulfuric acid: (a) pH = 7.0, (b) pH = 6.4, (c) pH=5.0, (d) pH = 4.0, (e) pH = 3.0, and (f) pH = 2.5.

The amount of O₂ produced as a function of the pH of the reaction medium shows trends between the experiments conducted in the presence and absence of methylene blue dye (Figure 2). The tests conducted with pH between 4 and 7 show similar trends, but differ from the tests conducted with pH 3 and 2.5.

Tests carried out at pH 7; 6.4; 5 and 4 in the presence of methylene blue dye (MB) showed O₂ production similar to that observed for their pairs conducted in the absence of MB. This similarity in the production of O₂ in the presence and absence of MB indicates that there was no generation of hydroxyl radicals in this pH range and the decomposition mechanism of H₂O₂ is not radical. The absence of removal of the blue color from the reaction medium in the test conducted in the presence of MB corroborates this hypothesis, indicating that there was no structural change in the MB, that is, that it was subjected to an oxidative process.

In organic molecules, structural changes, such as those caused by oxidative processes, lead to the loss or alteration of their ability to absorb radiation, that is, color, due to the decrease in their resonance structure (Skoog *et al.*, 2017). Therefore, the maintenance of the color after the test is an indication that the methylene blue molecule remains with its chemical structure intact and that there was no oxidative process.

The opposite is observed for tests carried out at pHs ≤ 3. The reactions carried out in the presence of MB provided a marked decrease in the amount of O₂ produced in relation to the reaction with only water and H₂O₂. The reaction conducted at pH 2.5 stands out, which did not show oxygen generation in the test conducted in the presence of MB.

This trend observed for the volume of O₂ suggests that the process of decomposition of hydrogen peroxide by iodide ions in these pH conditions is radical and is leading to the formation of the hydroxyl radical, responsible for the oxidation of MB. The manifestation of the oxidative process, by incorporating oxygen into the dye structure, prevents it from converting into molecular oxygen, thus restricting its formation. The removal of the blue color from the reaction media at the end of the tests conducted at pHs 2.5 and 3.0 corroborates these results.

According to Bray and Liebafsky (1931), complete oxidation of iodide to iodine is only possible at a high concentration of H⁺ ions. The traditional Fenton process presents conditions similar to those of the present study, with the optimum pH being between 2.5 and 3.0. pH's below 2.5 were not tested, as pH levels <2.5 result in the consumption of hydroxyl radicals (Wang *et al.*, 2016).

After the end of the catalytic activity tests, the pH of the reaction medium was analyzed, and all tests, in the absence and presence of MB, showed an increase in pH close to neutrality (between 6.5 and 7), which represents a advantage as it eliminates the need to adjust the pH at the end of a hypothetical treatment.

This increase in pH is consistent with the mechanism of the proposed reaction system (Equation 1), which generates the hydroxyl ion, an alkaline agent responsible for the increase in pH, as one of the reaction products.



Regarding the effect of the character (oxidizing, reducing or complexing) of the acid used to adjust the pH, no variation was found in the volume of O₂ generated for the different acids evaluated, indicating that the reaction system is dependent on the pH, but not on the type of acid.

Tests carried out with acetic acid did not show O₂ generation in the absence of the organic contaminant MB. This tendency was linked to the organic nature of acetic acid, characterizing it as a potential pollutant, which is subject to oxidation by the hydroxyl radicals generated, minimizing or ceasing the generation of molecular oxygen. Based on these results, the use of organic acids for pH adjustment is not recommended, as they can act negatively on the process, competing with pollutants for the hydroxyl radicals generated in the reaction medium. Considering that sulfuric acid

is commonly used in traditional Fenton processes, it was decided to continue studies with this acid (Ertugay & Acar, 2017; Zheng *et al.*, 2016).

3.2 Oxidative degradation: effect of reaction time

The evolution of the loss of color in the methylene blue solution as a function of reaction time is shown in Figure 3.

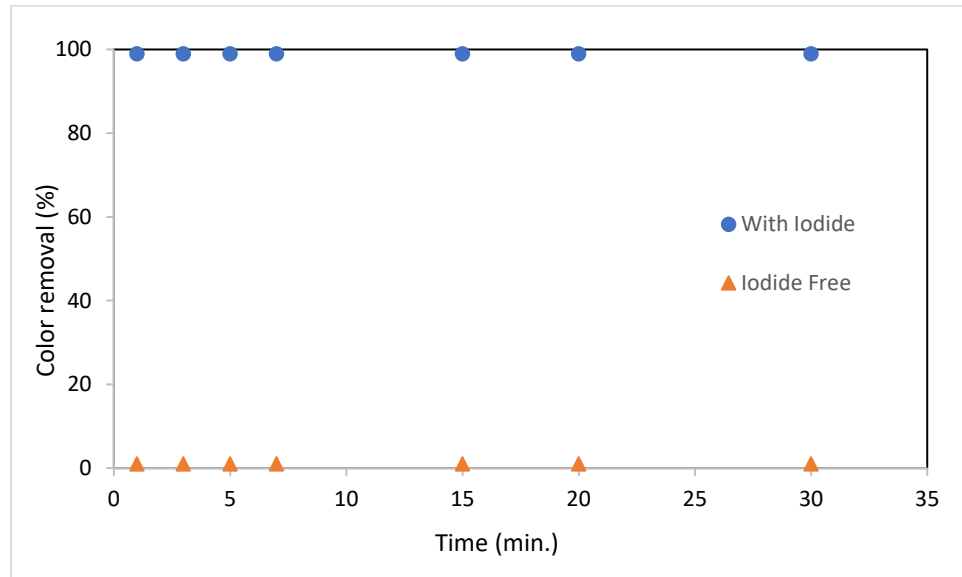


Figure 3 - Color removal (%) in the AM oxidative degradation test.

Conditions: [AM] = 100 mg.L⁻¹; [H₂O₂] = 600 mg.L⁻¹; [I⁻] = 132 mg.L⁻¹; pH_{initial} = 2,5.

A rapid discoloration of the MB solution is observed, with 99% of the blue color removed in the initial three minutes (Figure 4), as well as the formation of insoluble molecular iodine and iodine in solution, indicated by the brown color of the reaction medium. Iodine in the presence of iodide ions leads to the formation of the tri-iodide complex (I₃⁻) (equation 2), with high solubility in water (Santos & Afonso, 2013).



Unlike what was observed for MB, the test carried out with the AT dye did not lead to the formation of a precipitate, showing only a visual change in color, from light yellow to brown/amber when hydrogen peroxide was added to the reaction medium. The brown color observed in the AT test was more intense than in the AM test, being characteristic of the presence of iodine in solution, in the form of the tri-iodide ion, demonstrating that the redox reaction occurred.

However, the discoloration of the AT dye cannot be monitored by spectrophotometry due to the overlap of the absorbance spectrum of the tri-iodide ion with that of the tartrazine yellow dye. Therefore, AT degradation was monitored only by COT results.

The results of the TOC analyze obtained for the two dyes after 15, 30 and 60 reaction minutes are presented in Table 2.

Table 2 - Results of the TOC analysis. Conditions: [AM] = 100 mg.L⁻¹; [AT] = 100 mg.L⁻¹ [H₂O₂] = 600 mg.L⁻¹; [I⁻] = 132 mg.L⁻¹; pH_{initial} = 2,5; Time: 1 hora.

Dye	Sample (mg.L ⁻¹)	Amount Removed (mg.L ⁻¹)			Removal %		
		15'	30'	60'	15'	30'	60'
AM	37.4	34.04 ^a ± 0.53	34.63 ^a ± 0.49	34.71 ^a ± 0.76	91.0	92.2	93.0
AT	28.8	4.61 ^b ± 0.38	4.68 ^b ± 0.82	4.74 ^b ± 0.44	16.1	16.3	16.5

Mean ± standard deviation followed by equal letters does not differ statistically at the 5% level (Tukey test).

According to Table 2, organic matter was removed for the two dyes evaluated and that there was no statistical difference between the reaction times evaluated, indicating how quickly the reaction manifests itself.

Between the two dyes evaluated, methylene blue showed the best results, with a TOC removal of 93%, that is, 5.6 times higher than that observed for tartrazine yellow, with a removal of 16.5%.

This trend was linked to the different surface properties of the dyes, more specifically to the cationic (positive) characters of AM and anionic (negative) of AT, the discussion of which will be further discussed in the results obtained for experimental planning.

Considering that there was no variation in TOC removals between the times evaluated, for the continuity of the studies it was decided to use 15 minutes of reaction.

3.3 Experimental planning for methylene blue dye

Table 3 presents the factorial planning matrix with the tests carried out with the methylene blue dye and the results referring to the amount of TOC (mg. L⁻¹) removed and the mass of iodine (I₂) (mg) recovered after 15 minutes rational.

Table 3 - Factorial design matrix 2² with encoded values and (real) and response in terms of removed COD (mg.L⁻¹) and recovered iodine mass (mg).

Essay	Mass of I ⁻ (mg)	Equivalent of I ₂ (mg)	Mass of H ₂ O ₂ (mg)	COT (mg. L ⁻¹)	Mass of I ₂ (mg)
1	-1 (275)	137.5	-1 (20)	38.8	19.0
2	1 (825)	412.5	-1 (20)	38.3	14.1
3	-1 (275)	137.5	1 (100)	37.3	14.3
4	1 (825)	412.5	1 (100)	37.6	8.3
5	0 (550)	275.0	0 (60)	38.4	16.7
6	0 (550)	275.0	0 (60)	38.4	16.8
7	0 (550)	275.0	0 (60)	38.5	18.3

The results for the amount of carbon removed were similar between the evaluated conditions. The mass of iodine recovered was lower than the equivalent amount added at the beginning of the reaction in the form of iodide, showing that an amount of iodide remains in solution providing solubilization of iodine as tri-iodide ion.

For the removal of TOC (mg.L⁻¹), H₂O₂ showed a significant negative effect (p < 0.05), the interaction between H₂O₂ versus I⁻ showed a significant positive effect, while the mass concentration of iodide did not show a significant effect.

For the mass of iodine recovered, the variables H₂O₂ and I⁻ showed a significant negative effect, indicating that the greater the mass of these variables, the lower the mass of iodine recovered. This result is consistent with the mechanism of the iodine solubilization reaction in an aqueous

medium, which uses iodide as a solubilizing agent through the formation of the triiodide ion (Eq. 2). Therefore, increasing the mass of iodide will favor the solubilization of iodine, reducing the amount of precipitate formed. Based on these results, first-order empirical models were proposed for TOC removal (mg) and for iodine mass recovered (mg), which are represented by Equations 3 and 4.

$$\text{COT}_{(\text{removed})} = 38.182 - 0.054(\text{H}_2\text{O}_2) + 0.22(\text{I} \cdot \text{H}_2\text{O}_2) \quad (3)$$

$$\text{Iodo}_{(\text{recovered})} = 15.34 - 2.7(\text{I}) - 2.63(\text{H}_2\text{O}_2) \quad (4)$$

The analysis of variance (ANOVA) presented a $F_{\text{calculated}}$ greater than the $F_{\text{tabulated}}$ for the two responses evaluated, with a confidence level of 95% and a percentage of explained variation of 84% for TOC removal and 92% for the iodine mass recovered. First-order empirical models have been validated and can be used for predictive purposes.

The response surfaces referring to the effects of the independent variables H_2O_2 and I^- in relation to TOC removal and recovered iodine are shown in Figure 4.

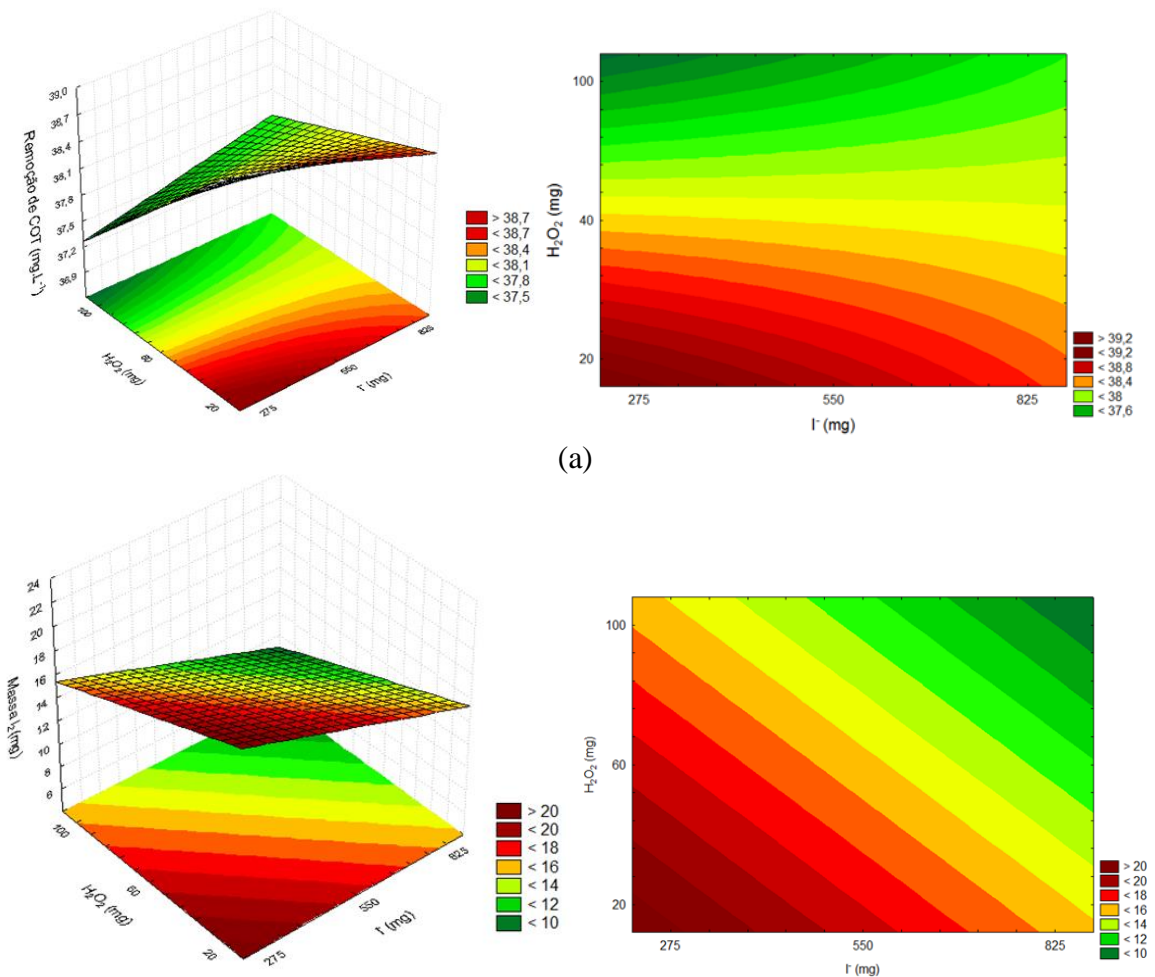


Figure 4 - Response surface and contour curve for (a) TOC removal and (b) recovered iodine mass.

According to the response surface (Figure 4), the best results for TOC removal and recovered molecular iodine (I_2) are observed in the region corresponding to the lowest amounts of hydrogen peroxide (20 mg) and iodide (275 mg).

This trend, mainly for the recovery of iodine (I_2), is consistent with the mechanism of the iodine solubilization reaction in an aqueous medium, which uses iodide (I^-) as a solubilizing agent

to form the triiodide ion (Eq. 2). Therefore, increasing the iodide concentration will favor the solubilization of molecular iodine, reducing the amount of precipitate formed.

Furthermore, the results suggest a correlation between iodine mass and TOC removal, indicating that insoluble molecular iodine may be contributing to methylene blue removal.

3.4 Iodine reduction for reuse

The insoluble molecular iodine formed in the AM degradation tests, after the centrifugation and drying steps, was subjected to a reduction step, using iodide ions, with sodium metabisulfite (Equation 5) with a view to possible reuse.



The reduction reaction of iodine (I_2) to iodide ions with sodium metabisulfite leads to its solubilization. During this test it was observed that the solution resulting from this redox process, which should remain colorless, since both reaction products (iodide and persulfate) are colorless, presented an intense blue color, indicating the presence of methylene blue dye, the which was confirmed through spectrophotometric tests, as the solution presented a characteristic absorption spectrum of methylene blue.

The blue coloration after the reduction step suggests that, concomitantly with the oxidative process, a non-destructive adsorptive process is occurring with solid molecular iodine behaving as an adsorbent for methylene blue, a cationic dye.

This adsorptive process is linked to the intrinsic properties of both compounds involved, more specifically to the positive character of methylene blue and the high electronic density of molecular iodine (I_2), which present contrasting characteristics in terms of charges, favoring the adsorptive process through electrostatic attraction.

The absence of precipitate formation and the intensification of the characteristic amber color of iodine in solution observed in the test carried out with tartrazine yellow, a dye with anionic characteristics, suggest that the adsorptive process of methylene blue is responsible for the stability of solid molecular iodine (I_2) in solution. This stability was linked to the coating of the iodine crystals, generated in the oxidative stage, by methylene blue molecules, as shown in the mechanism shown in Figure 5, preventing the iodine crystals, now coated with MB, from being solubilized by excess iodide, in the form of triiodide ion, thus allowing its recovery from the reaction medium.

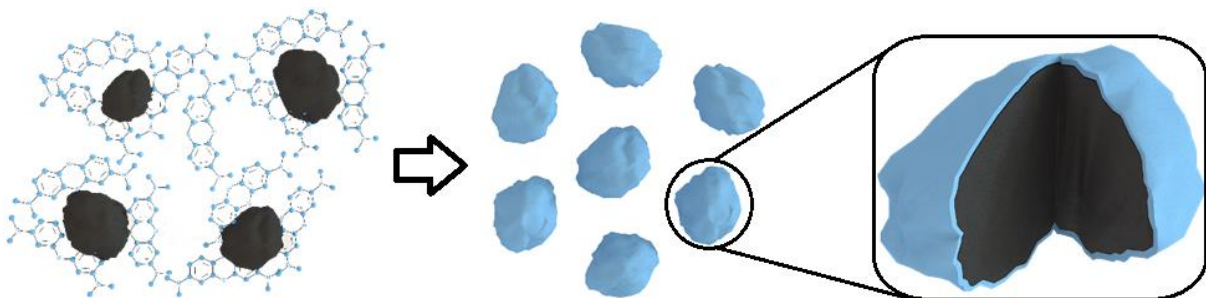


Figure 5 - Schematic representation of the adsorption process of methylene blue molecules, coating the formed I_2 crystals.

To confirm this hypothesis, new adsorption tests were carried out with methylene blue using molecular iodine (550 mg) with different particle sizes (one spherical and the other in the form of crystals) with adsorbent.

Both tests led to the removal of the color from the methylene blue solution, with the removal speed being inversely proportional to the particle size. Crystals, with smaller particle size and,

consequently, greater total surface area showed faster removal compared to spheres with lower total surface area.

After adsorption of methylene blue, the solid iodine containing the adsorbed dye obtained by the three tests (oxidative reaction and adsorption) was subjected to a resolubilization step with iodide. In parallel, an assay was carried out using pure molecular iodine, without dye. The visual result of this test is shown in Figure 6.



Figure 6 - Result of resolubilization with potassium iodide solution of molecular iodine containing adsorbed AM obtained by adsorptive tests with (a) fragmented commercial iodine, (b) commercial iodine spheres, (c) iodine recovered from the degradation oxidative process with hydrogen peroxide and (d) only commercial iodine without AM adsorbed.

The test carried out with pure iodine, the addition of the iodide solution provided total solubilization of the iodine (Figure 6d). An opposite trend was observed for tests carried out with iodine formed in oxidative tests with hydrogen peroxide, which contains methylene blue adsorbed on its surface. For this iodine, all tests (Figures 6a, 6c and 6c) maintained high amounts of molecular iodine in insoluble form even after the addition of iodide ions (solubilizing agent for iodine), proving the hypothesis that the methylene blue dye, when adsorbed, it acts as a protective barrier that hinders the solubilization of molecular iodine.

Furthermore, the color of the solutions varied between tests, showing greater intensity for the molecular iodine in spheres when compared to the sample with fragmented iodine in the form of crystals, suggesting that this effect is directly related to the size of the iodine particles.

With the increase in the size of iodine particles, more MB molecules are needed for their coating, favoring the formation of surface gaps that serve as access points for iodide ions to molecular iodine, leading to their solubilization.

In this context, the absence of the amber color observed in the test carried out with the iodine generated in the oxidative process suggests that the surface coating of the particles occurs more effectively, probably concomitantly with its generation, that is, in very small particles, allowing a more effective coating. efficient and uniform, completely preventing the access of iodide ions to iodine, which would lead to its solubilization.

The presence of excess iodide in the medium was proven by qualitative tests with copper ions, which in the presence of iodide lead to the generation of iodine in solution and copper (I) iodide, gray in color, according to the Equation 6.



The results obtained suggest the presence of two sequential mechanisms during the degradation process of MB with peroxide and iodide as catalyst: an oxidative one, observed by the reduction of organic load, where iodide is oxidized to iodine, followed by an adsorptive process, promoted by iodine formed.

With the samples measured to 100 mL with distilled water in a volumetric flask, new analyzes were carried out in relation to the organic carbon content, thus allowing us to stipulate the contribution of each process (oxidative and adsorptive) in removing the methylene blue dye from the solution.

The TOC values in the solutions generated after the solubilization of the iodine generated in the oxidative stage through the addition of metabisulfite, correspond to the methylene blue removed by adsorption, thus allowing the contribution of each process to be quantified through Equation 7. The results referring to each stage of the process (oxidative and adoptive) are presented in Table 4.

$$\text{COD removed by oxidation} = \text{Initial COD sample} - \text{COD adsorbed on I}_2 \quad (7)$$

Table 4 - 2² factorial planning matrix with coded and (real) values and response in terms of % oxidative process and % removal by adsorptive process.

Tests	I ⁻ (mg. L ⁻¹)	H ₂ O ₂ (mg. L ⁻¹)	Removal by oxidation		Removal by adsorption	
			mg.L ⁻¹	%	mg.L ⁻¹	%
1	-1 (275)	-1 (20)	3.1	7.9	35.7	92.1
2	1 (825)	-1 (20)	5.7	15.0	32.5	85.0
3	-1 (275)	1 (100)	5.1	13.7	32.2	86.3
4	1 (825)	1 (100)	7.7	20.6	29.9	79.4
5	0 (550)	0 (60)	6.0	15.7	32.4	84.3
6	0 (550)	0 (60)	6.5	16.9	31.9	83.1
7	0 (550)	0 (60)	6.6	17.2	31.9	82.8

The results presented in Table 4 indicate that the adsorptive process is predominant in relation to the oxidative process for all conditions evaluated. The contribution of the oxidative process varied between 7.9 and 20.6%, while the adsorptive process varied between 79.4 and 92.1%.

Among the conditions evaluated, experiments 1 and 4 stand out, carried out with the smallest and largest amounts of peroxide and iodide, respectively. Experiment 1 presented the lowest removal by oxidation and the highest by adsorption and experiment 4 presented the highest removal by oxidation and the lowest by adsorption. Corresponding with this trend, with regard to adsorption, the iodine masses recovered (Table 3), with experiment 1, with the lowest removal by adsorption, presenting the highest mass, and experiment 4, with the highest removal by adsorption, presenting the lowest mass.

Statistical analysis demonstrated that the independent variables, quantity of H₂O₂ and I⁻ ions, presented a significant positive effect ($p < 0.05$) for removal by oxidation and a significant negative effect ($p < 0.05$) for the removal process. adsorption. From these results it was possible to construct first-order empirical models for both responses (oxidation and adsorption), which are represented by Equations 8 and 9.

$$\% \text{ removal by oxidative process} = 15.28 + 3.48(I^-) + 2.83(H_2O_2) \quad (8)$$

$$\% \text{ removal by adsorptive process} = 84.76 - 3.48(I^-) - 2.83(H_2O_2) \quad (9)$$

The results of the variance analysis show that $F_{\text{calculated}}$ was greater than $F_{\text{tabulated}}$ for the two responses evaluated, with a confidence level of 95% and percentage of explained variation of 92%, validating the proposed empirical models.

Validation of the empirical models allowed the construction of the response surfaces and contour curves presented in Figure 7. Figure 7(a) shows the interaction between the amounts of hydrogen peroxide and iodide in relation to the percentage of removal by the oxidative process, while Figure 7(b) shows the interaction of these variables for the percentage removed by adsorption.

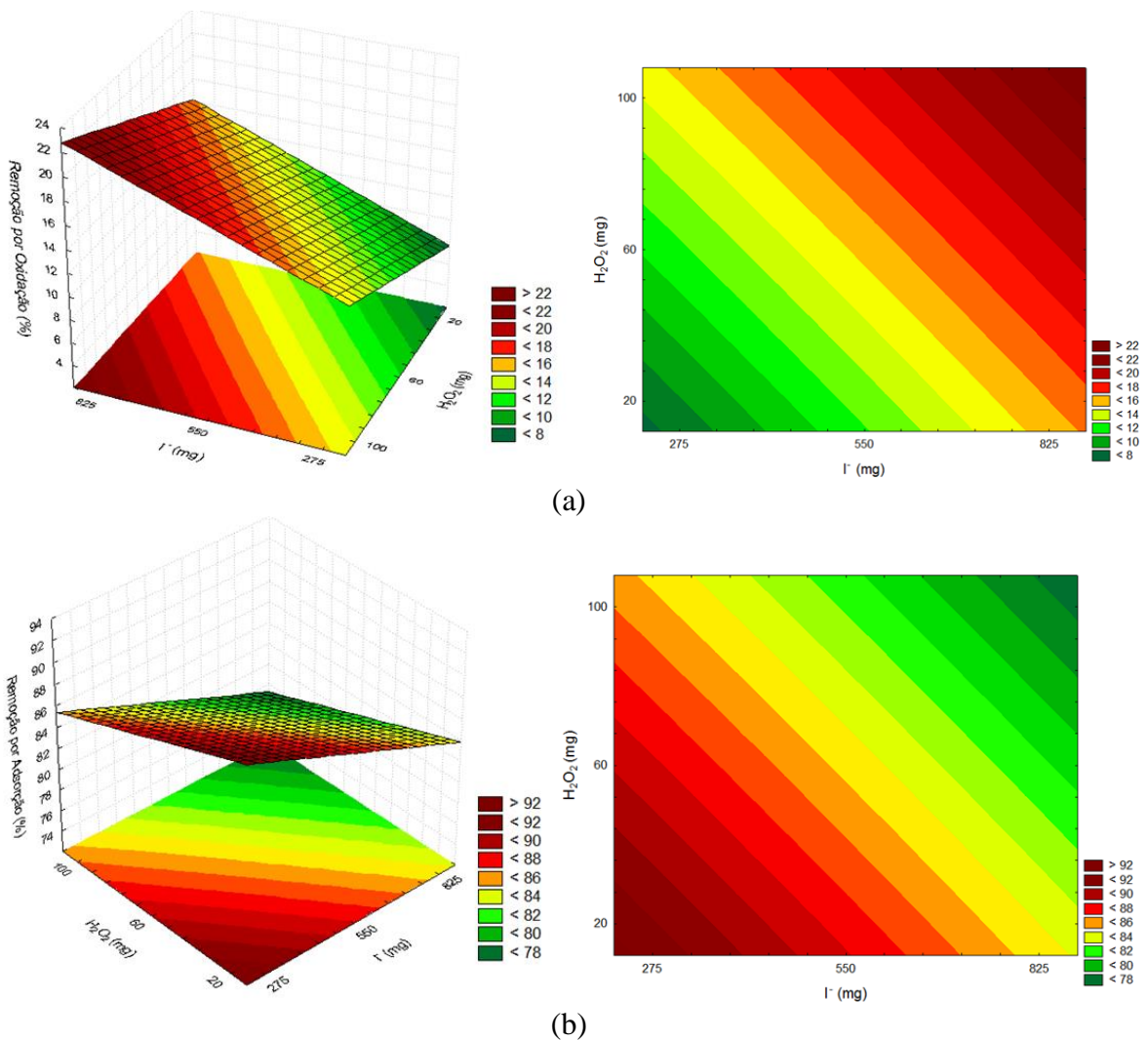


Figure 7 - Response surface and contour curve for percentage of methylene blue removal (a) by oxidative process and (b) by adsorptive process.

Through the analysis of the response surfaces, it is observed that the variables present opposite trends in relation to the monitored responses, with increasing amounts of hydrogen peroxide and iodide favoring oxidation (positive effect) and disfavoring adsorption (negative effect).

This trend observed for both processes was linked to iodide ions, which directly interfere with the solubilization of molecular iodine generated during the oxidative process through the production of tri-iodide ion, a complex with high solubility in water. The increase in iodide mass, by favoring the solubilization of molecular iodine, minimizes its precipitation, negatively interfering with the adsorptive process, which requires the presence of a solid adsorbent to occur.

3.5 Experimental planning for the yellow dye tartrazine

The 2² factorial planning matrix for the tests carried out with the yellow dye tartrazine (AT), together with the results regarding TOC removal (mg.L⁻¹ and %) are presented in Table 5.

Table 5 - 2² factorial planning matrix with coded and real values, as well as the response in terms of TOC removal.

Test	I ⁻ (mg)	H ₂ O ₂ (mg)	Removed of COT	
			mg.L ⁻¹	%
1	-1 (166)	-1 (10)	3.28	11.39
2	1 (825)	-1 (10)	5.31	18.44
3	-1 (275)	1 (60)	4.71	16.35
4	1 (825)	1 (60)	5.47	18.99
5	0 (332)	0 (35)	4.13	14.34
6	0 (332)	0 (35)	5.39	18.72
7	0 (332)	0 (35)	5.17	17.95

According to the statistical analysis, none of the variables were significant ($p < 0.05$) for TOC removal, not allowing the construction of the empirical model and response surfaces.

It is worth mentioning that in the oxidative degradation of the AT dye, with anionic characteristics, there was no formation of solid I₂, indicating no contribution from the adsorptive process. Therefore, the amount of TOC removed is linked only to the action of the oxidative process.

In terms of TOC removal percentage, with values between 11.3 and 18.9%, a similarity is observed between the percentages of removal by oxidation observed for methylene blue, suggesting that the effect of the oxidative mechanism is similar for both the dyes.

Oancea and Meltzer (2013) present similar results in tests with tartrazine yellow, in which they found a 17% reduction in tartrazine concentration in the traditional Fenton process (Fe²⁺/H₂O₂). These authors stated that only the Fenton process was not able to completely degrade the dye, suggesting that the dye is degraded into small molecules, such as aldehydes and organic acids, which contribute to the TOC content, since they were not mineralized. The highlight of this study was the application of photo – Fenton, which showed a removal of up to 80% of the TOC, therefore being a suggestion for improving results.

Conclusions

The results demonstrated that iodide ions act by promoting the radical decomposition of H₂O₂ and that the process is dependent on the pH of the reaction medium.

The adsorption of methylene blue onto molecular iodine, covering its surface, avoids contact with the iodide ions present in the reaction medium, allowing the molecular iodine to remain in a solid state in solution.

The trends observed for both dyes in relation to the formation or not of precipitate suggest that the chemical characteristics of the organic molecules influence the reaction mechanism, and may favor the removal, through adsorption processes, of molecules with cationic characteristics.

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