

Evaluation of catalytic precursors of radical hydrogen peroxide decomposition

Avaliação de precursores catalíticos da decomposição radicalar do peróxido de hidrogênio

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Abstract

The decomposition of radical hydrogen peroxide has aroused great interest from the scientific community due to the numerous possible applications, mainly concerning to the treatment of effluents. However, it is important to find new precursors for radical H_2O_2 decomposition. The potential of halogens (non-metals) iodine, chlorine, and bromine, in the form of iodide (I^-), chloride (Cl^-), and bromide (Br^-) ions, as catalytic precursors of the radical decomposition of the hydrogen peroxide, was evaluated. A solution of methylene blue was used as a model molecule of a contaminant to prove the radical mechanism from the effect of the organic compound on the volume of O_2 generated. The results of the experiments showed that iodide at acidic pH can act as a catalyst for the radical H_2O_2 decomposition mechanism in a spontaneous redox process (positive ΔE°). In contrast, the chloride ion showed slow decomposition kinetics of hydrogen peroxide (more than 72h), and the bromide ion was not characterized as a catalyst for H_2O_2 decomposition. Finally, a reduction in the production of O_2 is observed for the reaction with iodide ion in the presence of the organic contaminant in relation to the experiment with only water and H_2O_2 .

Keywords: H_2O_2 , iodide, chloride, bromide, methylene blue, gasometry

Resumo

A decomposição do peróxido de hidrogênio radicalar tem despertado grande interesse da comunidade científica devido às inúmeras aplicações possíveis, principalmente no que se refere ao tratamento de efluentes. No entanto, é importante encontrar novos precursores para a decomposição radicalar do H_2O_2 . O potencial dos halogênios (não metais) iodo, cloro e bromo, na forma de iodeto (I^-), cloreto (Cl^-) e íons brometo (Br^-), como precursores catalíticos da decomposição do peróxido de hidrogênio, foi avaliado. Uma solução de azul de metileno foi utilizada como molécula modelo de um contaminante para comprovar o mecanismo radicalar a partir do efeito do composto orgânico sobre o volume de O_2 gerado. Os resultados dos experimentos mostraram que o iodeto em pH ácido pode atuar como catalisador para o mecanismo de decomposição radicalar do H_2O_2 em um processo redox espontâneo (ΔE° positivo). Em contraste, o íon cloreto apresentou cinética de decomposição lenta do peróxido de hidrogênio (mais de 72h), e o íon brometo não foi caracterizado como catalisador para decomposição de H_2O_2 . Por fim, observa-se redução na produção de O_2 para a reação com o íon iodeto na presença do contaminante orgânico em relação ao experimento apenas com água e H_2O_2 .

Palavras-chave: H_2O_2 , iodeto, cloreto, brometo, azul de metileno, gasometria

Introduction

Hydrogen peroxide (H_2O_2) is a strong oxidizer that has been highlighted in emerging water treatment technologies [1], such as advanced oxidation processes for the degradation of organic pollutants [2, 3]. Since the by-product of H_2O_2 -mediated oxidation is water and oxygen, it has been recognized as a “green oxidizer” and environmentally friendly [4, 5]. Unlike chlorine-based oxidizing agents that generate harmful by-products to the environment, H_2O_2 does not leave harmful residues in the environment [6–9].

Since H_2O_2 is stable at room temperature, it is necessary to have a chemical species that acts as an activator, catalyst or promoter of H_2O_2 decomposition [10]. For this purpose, metallic catalysts such as iron, manganese, copper, among others, are used in homogeneous or heterogeneous form. Physical routes can also be used, such as ultraviolet radiation, ultrasound, microwave and heat treatment to activate H_2O_2 [1, 8, 11–15].

The catalytic decomposition of hydrogen peroxide in solution is a reaction that can occur via a radical intermediate and a non-radical route. The non-radical reaction is a direct and simple reaction (Equation 1), producing water and oxygen gas [16, 17].



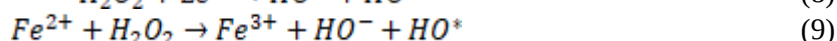
The reaction via a radical intermediate occurs through a redox mechanism. The chemical species (catalyst) oxidizes and transfers electrons to H_2O_2 , which uses these electrons to decompose radically through a reduction reaction, resulting in the formation of the HO^* radical (Equation 2). This radical is one of the main known oxidizing agents [18] ($E^\circ=2.8$ V [19]), with a non-selective characteristic that can react with a wide variety of classes of organic compounds that do not have an easy degradation, promoting its total mineralization [20].



However, during the radical reaction, it is possible that other reaction intermediates (hydroperoxyl radical, superoxide anion or hydroperoxide anion) are also generated, especially when the decomposition reaction occurs in the absence of organic contaminants or in excess of peroxide. In both conditions, the hydroxyl radicals formed react with each other in radical-radical and radical-hydrogen peroxide reactions (Equations 3 to 6), resulting in water and gaseous molecular oxygen, which are the same products of the non-radical reaction [21, 22].



A classic example of the reaction via a radical intermediate is the Fenton reaction, in which ferrous ions (Fe^{2+}) when oxidized to ferric ions (Fe^{3+}) generate electrons (Equation 7) [19], promoting the radical decomposition of hydrogen peroxide (Equations 8 and 9).



Considering that metallic catalysts such as iron, in metallic forms ($Fe^0_{(s)}$) or ferrous ions ($Fe^{2+}_{(aq)}$), generally used for H_2O_2 decomposition, require a post-treatment process for its removal, it is important to find new precursors for radical H_2O_2 decomposition. Therefore, through the potential patterns of reduction of the elements (E°) it is possible to select new precursors for the catalytic

decomposition of hydrogen peroxide. Conceptually, a galvanic cell represents an electrochemical system where oxidation and reduction reactions, which when spontaneously occur, lead to the generation of energy (positive ΔE). To occur spontaneously, the element or compound that acts as an anode, responsible for the generation of electrons through an oxidation reaction, must necessarily present a standard reduction potential (E°) lower than that of the element or compound that acts as a cathode, in the case of H_2O_2 ($E^\circ=1.77V$), responsible for the consumption of electrons through a reduction reaction [23]. It should be noted that the species that acts as an anode must be used in a reduced and not oxidized form.

A technique widely used in the literature to evaluate the ability of a chemical species to act as an activator of the radical decomposition of H_2O_2 is the gasometry technique, which is based on monitoring the volume of gas generated during a chemical reaction in a given time, in this case, the amount of oxygen gas generated [24, 25]. Through this technique, it is possible to verify whether the reaction occurs via a radical mechanism or not, through tests with hydrogen peroxide and the selected chemical species, being conducted in the absence and in the presence of an easily oxidizable organic contaminant, such as methylene blue or phenol in the reaction medium [26–29].

The aim of the present study was to evaluate the potential of halogens (non-metals) iodine, chlorine and bromine, in the form of iodide (I^-), chloride (Cl^-), and bromide (Br^-) ions, as catalytic precursors of the radical decomposition of the hydrogen peroxide, since they have lower reduction potentials (E°) than H_2O_2 . In addition, to prove the radical mechanism from the effect of the organic compound on the volume of O_2 generated, a solution of methylene blue was used as a model molecule of a contaminant.

Material and Methods

Materials

All reagents used in the present study were analytical grade. Sulfuric acid (Vetec), methylene blue (Vetec), potassium iodide (Synth), potassium bromide (Vetec), sodium chloride (Vetec) and hydrogen peroxide (Sigma-Aldrich). The water used in all experiments was deionized in the URI - Erechim laboratory.

Evaluation of catalytic activity in H_2O_2 decomposition

The potential of the catalytic activity of iodide, chloride and bromide in the decomposition of H_2O_2 was evaluated by the gasometry technique monitoring the volume of oxygen gas (O_2) generated in the reaction, using the experimental system shown in Figure 1. The volume of O_2 formed in the reaction between H_2O_2 and the catalyst was measured by the displacement of the water column in an inverted burette.

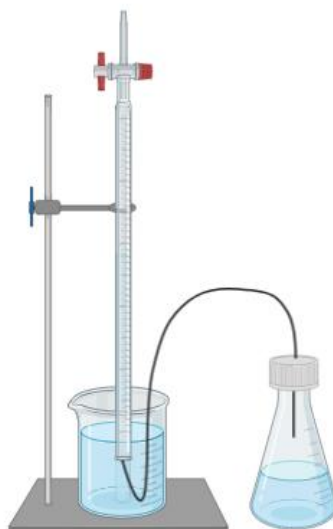


Figure 1: Scheme of the System used to evaluate H_2O_2 decomposition

The experimental conditions established were based on the study carried out by Moretto [30]. Initially, catalytic activity tests were carried out with deionized water with a pH adjusted to 3.0 with a 5% solution of sulfuric acid (H_2SO_4). As in the Fenton process, this is considered the ideal pH for the catalytic decomposition of H_2O_2 [31]. Afterwards, 9.5 ml of deionized water, 0.2 ml of H_2O_2 (30% v/v) and 1 ml of the catalyst solution (KI, NaCl or KBr in a concentration of 0.5 mol.L^{-1}) were added in a 25 ml glass flask. After adding the reagents, the flask was closed and the reaction was monitored by measuring the volume of oxygen (O_2) generated as a function of the reaction time. In parallel, a blank test was performed, using only deionized water and hydrogen peroxide.

Evaluation of the H_2O_2 radical decomposition mechanism

In the second stage, the tests were carried out using a methylene blue solution to replace water. Methylene blue was used as a model molecule of a contaminant to prove the radical mechanism from the effect of the organic compound on the volume of O_2 generated. In these tests, 9.5 ml of the methylene blue solution (20 mg.L^{-1}) were added to the glass flask. Afterwards, the pH of the solution was adjusted to 3.0 and 0.2 mL of H_2O_2 (30% v/v) and 1 mL of the catalyst solution (KI, NaCl or KBr with a concentration of 0.5 mol.L^{-1}) were added. The analysis procedure was performed as previously described.

Results and Discussion

Catalytic decomposition of H_2O_2 in the presence of different ions

The methodology used to evaluate the potential use of different chemical elements as promoters of the catalytic decomposition of hydrogen peroxide considers the amount of O_2 generated, as a function of time, in the decomposition of H_2O_2 . The amount of O_2 generated as a function of the reaction time for the catalytic decomposition reaction of hydrogen peroxide in the presence of different amounts of halogen ions (I^- , Cl^- and Br^-) is shown in Figure 2.

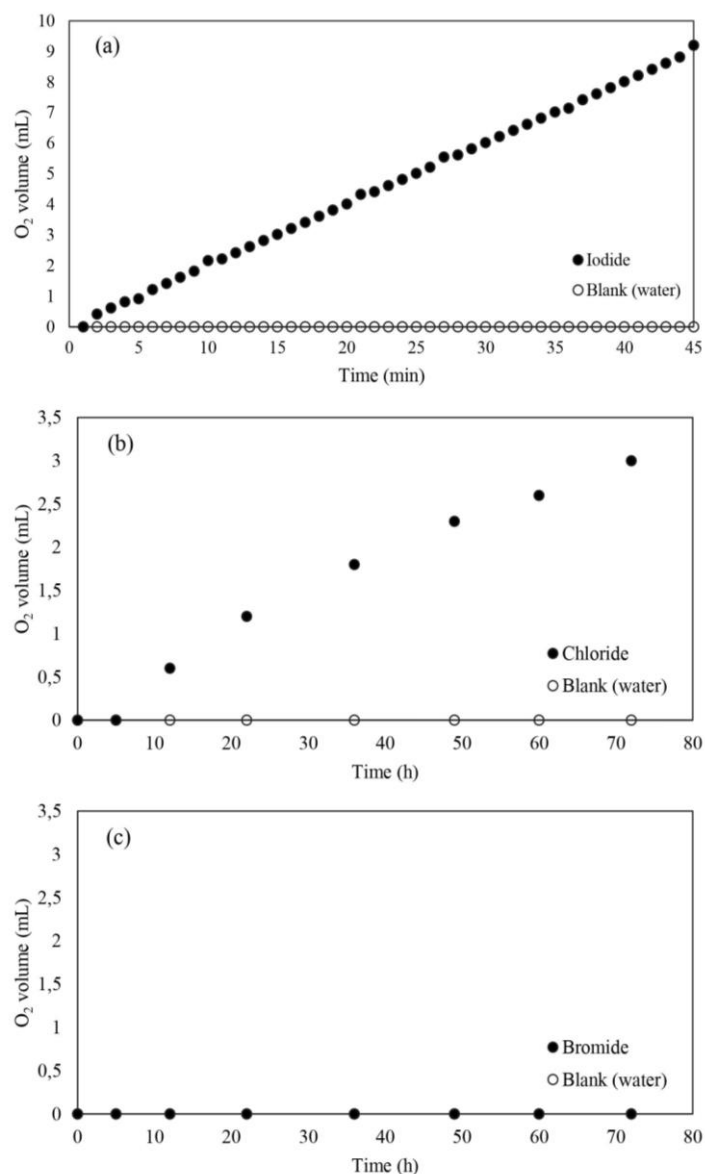


Figure 2: Volume of O_2 generated in the catalytic decomposition of H_2O_2 using as catalyst: (a) iodide (I^-), (b) chloride (Cl^-), and (c) bromide (Br^-)

It is observed that in the experiment carried out with iodide (Figure 2a) the generation of molecular oxygen (O_2) occurred in the first minutes. There was a gradual increase in the generation of O_2 during 45 reaction minutes, totaling 9.2 mL of gas generated at the end of the experiment. The blank test (water and H_2O_2) did not generate O_2 in the observed reaction time, showing that the iodide acted as a catalyst for the decomposition of hydrogen peroxide.

The decomposition of H_2O_2 in the presence of the chloride anion (Figure 2b) was slow, as it started after 12 hours and the evolution of the generation of O_2 bubbles took long periods of time to manifest. Because of this, the reaction was monitored during the 72-hour period, totaling 3.0 mL of O_2 generated at the end of the 3 days. With the generation of O_2 , it was proven that chloride contributes to the catalytic decomposition of H_2O_2 . However, the reaction is slow and this prevents the use of the chloride anion in the H_2O_2 decomposition reaction.

For bromide (Figure 2c), O_2 generation was not evidenced. Thus, the bromide ion does not act as a catalyst for H_2O_2 decomposition. This result indicates that the mechanism shown theoretically does not reproduce in practice. No foundations were found in the literature that can justify or contribute to clarify the difference in activity in relation to chloride and bromide ions.

Experiments using methylene blue as an organic contaminant

To prove whether the hydrogen peroxide decomposition process is occurring in a radical form, with radical HO^* generation or not, the experiments were conducted in the presence of an organic contaminant, methylene blue. The experiments were carried out using the iodide ion, which showed the best results in relation to the tested ions.

The evolution of the O_2 volume generated in the catalytic decomposition reaction of hydrogen peroxide by iodide ions, in the presence of methylene blue, are shown in Figure 3. Analyzing Figure 3, a reduction in the production of O_2 for the reaction conducted in the presence of the organic contaminant is observed in relation to the experiment conducted only with water and H_2O_2 . This result is characteristic of a radical mechanism for the catalytic decomposition of hydrogen peroxide [26].

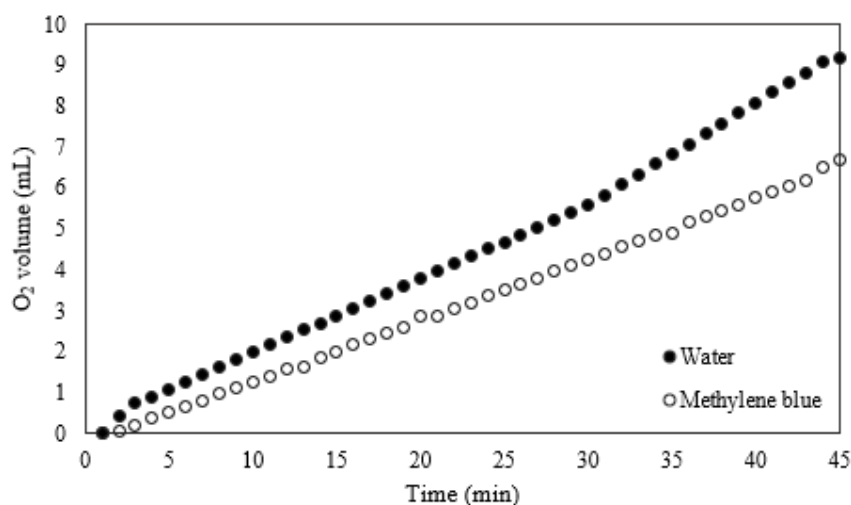


Figure 3: Volume of O_2 generated in the catalytic decomposition of H_2O_2 using iodide as a catalyst in the presence of methylene blue

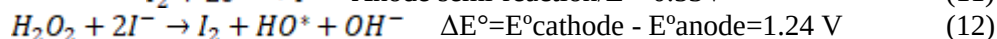
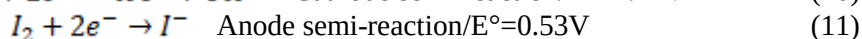
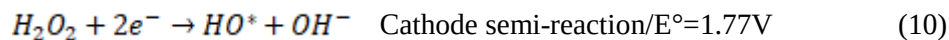
For the reaction to be radical, hydroxyl radicals are highly oxidizing species when in the presence of organic compounds, and these formed radicals will react instantly with the organic molecules oxidizing them, that is, incorporating oxygen into their structure instead of leading to the generation of molecular oxygen, thereby decreasing or ceasing the release of oxygen gas in the reaction, reducing the volume of oxygen produced in relation to the blank experiment, which is conducted in the absence of the organic contaminant. If the mechanism is not radical, the volumes of oxygen produced by both tests (with and without organic contaminants) will be very similar.

Oliveira et al. (2008) reported that when the H_2O_2 decomposition mechanism is via free radicals, in experiments conducted in the presence of an organic compound, a competitive effect by the HO^* radicals can be observed between the H_2O_2 decomposition reactions and the oxidation of the organic pollutant, leading to a decrease in O_2 generation. This hypothesis corroborates two different situations observed for the reaction system under analysis, one of an experimental and the other of a theoretical character:

(i) Experimentally the test provided, in addition to the lower O_2 production, the removal of the blue color from the reaction medium. This removal is indicative of the oxidative character of the medium, which through oxidation reactions provided by the hydroxyl radicals, leads to a structural rearrangement in the methylene blue molecule. When oxidized and with a lower number of resonant bonds (conjugated doubles), the molecule loses its radiation absorption capacity in the visible region of the spectrum.

The removal of color in aqueous systems, whether in synthetic or effluent solutions, using oxidative agents is reported by several authors in the literature and is used by some as an indicator of the efficiency of oxidative processes [32–34].

(ii) Theoretically or conceptually, the proposed reaction system has a positive electromotive force for the oxidation-reduction reaction between hydrogen peroxide and iodide, indicating that the redox reaction occurs spontaneously, that is, it behaves like a galvanic cell, according to the following reactions (Equations 10 to 12).



The results prove, both theoretically and experimentally, that the iodide ions act as catalysts for the radical decomposition of H_2O_2 . Another advantage observed for this system is related to one of the reaction products, more specifically to the iodine (I_2) formed (Figure 4), which for being an apolar molecule with low solubility in water ($0.0013 \text{ mol.L}^{-1}$), presents itself in the form of a precipitate [35].



Figure 4: Reaction system after catalytic decomposition experiment of H_2O_2 by iodide ions in the presence of methylene blue

In this context, after the reaction, the iodine can be easily removed or recovered from the reaction system, by a physical process of sedimentation or filtration, which makes the process cyclic and increases the possibilities of application. I_2 is practically insoluble in water and can be easily removed by means of a physical separation step, without requiring the addition of other chemicals. Finally, the research proposal for these new precursors is characterized by the search for a new route for the generation of an advanced oxidative process, meeting the national and world demands for alternative, fast, efficient, and clean processes, which allow to completely degrade persistent organic compounds.

Conclusions

The results of the experiments showed that iodide at acidic pH can act as a catalyst for the radical H_2O_2 decomposition mechanism. The radical mechanism observed experimentally is in agreement with the theoretical data of the redox reaction between hydrogen peroxide and iodide, in which the iodide acts as a reducing agent for H_2O_2 , leading to a spontaneous redox process (positive ΔE°). In addition, the chloride ion showed slow decomposition kinetics of hydrogen peroxide (more than 72h), and the bromide ion was not characterized as a catalyst for H_2O_2 decomposition.

Acknowledgements

The authors thank to IFRS, URI-Erechim, National Council for Scientific and Technological Development (CNPq), Coordination for the Improvement of Higher Education Personnel (CAPES) and Research Support Foundation of the State of Rio Grande do Sul (FAPERGS).

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