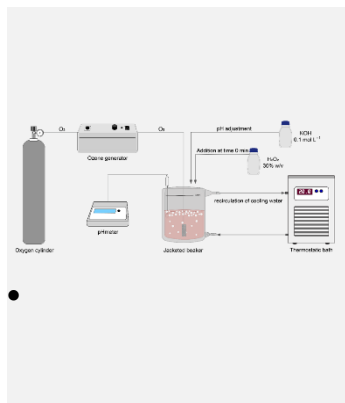


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Reactive oxygen species such as peroxide, superoxide and hydroxyl radicals are very important in the degradation of organic matter in the industrial waste water. The degradation of carotenoids in wastewater has been investigated using H₂O₂ and O₃ as oxidants. In this study pH, O₃ dosage and initial H₂O₂ concentration were optimized through design of experiments. The degradation of the carotenoids was carried out by injecting H₂O₂ and O₃ bubbling into the real raw wastewater from annatto industry. Efficiency and Kinetics of this H₂O₂/O₃ degradation process has been investigated and considerations about the possible mechanism has been made. Results showed that: (1) O₃ flow rate affect significantly carotenoid degradation; and (2) O₃ flowrate, initial H₂O₂ concentration and pH affected the rate of degradation. Radicals and radical cations from carotenoids can initially be formed by H₂O₂/O₃ due to their strong oxidation power and acceptance electrons from carotenoids molecules.

Introduction

Carotenoids are a category of terpenes known for their vibrant colors. Their molecules are formed by a long polyene chain composed of isoprene units which may terminate in a cyclohexene or isoprene residues at one or both ends. In plants, there are generally two types of C40 carotenoids: (1) carotenes, which are pure hydrocarbons such as β -carotene, its isomers, and lycopene; and (2) xanthophylls, which contain oxygen including lutein, zeaxanthin, canthaxanthin, and violaxanthin [1]. Carotenoids react with free radicals such as peroxides, superoxides and hydroxyl leading to their degradation. The primary mechanism involves an addition of a peroxide radical to a π bond of the carotenoid (Car) molecule followed by an abstraction of a hydrogen and a radical Car \cdot formation then, an electron transfer from Car \cdot generates a radical cation Car \cdot^+ [2]. Bixin is the primary carotenoid in annatto, making up about 80% of the carotenoids in the seed. Therefore, bixin, norbixin, their salts and by-products correspond to the predominant coloring mass of the present annatto industry wastewater. Its oxidation involves a two-electron process, with potentials of ~ 0.94 V and ~ 1.14 V in THF [3]. Therefore, aqueous systems are different from organic solvents; consequently studies have been conducted under equilibrium conditions in micellar aqueous media for five different Car/Car \cdot^+ pairs and the results showed that their redox potentials are around 1,02V [4]. These findings are significant, as H₂O₂ in acidic conditions and O₃ have higher potentials; therefore, carotenoids can be oxidized by them. Considering all the above mentioned, this work aimed to study the degradation of carotenes of a real wastewater from annatto industry using H₂O₂/O₃ process in aqueous acidic conditions.

Material and Methods

Carotenoid degradation has been performed using a batch process (liquid phase). 50 mL of raw wastewater were transferred to a 100-mL jacketed beaker with a predefined initial concentration of H₂O₂. Ozone bubbles were sparged at 1.0 L min⁻¹ through a sintered glass diffuser (15 x 20 mm) with t = 60 min. O₃ was generated *ex-situ* by the corona effect with Ozone & Life equipment, model O&L 3.0 RM. O₂ (purity >99%, White Martins Inc.) fed the ozone generator. pH and temperature were monitored with Tecnal equipment, model R-TEC-7/2-MP. Temperature control was performed using a Solab thermostatic bath, model SL-152/18. The pH of the experiments was adjusted using 1 mol L⁻¹ KOH solution and the temperature was kept at 20 °C. Samples were withdrawn periodically and carotenoids concentration were obtained using a double-beam UV-Visible spectrophotometer (Thermo Scientific) with $\lambda = 453$ nm and $\epsilon = 2850$, in order to investigate its kinetics degradation. A 2³ factorial design of experiments has been used to evaluate the effects of pH, ozone mass flowrate, and initial H₂O₂ concentration on carotenoid degradation and pseudo-first order kinetic constant (k_t).

Results and Discussion

Results from degradation studies showed that only Ozone flowrate was statistically significant at a 95% confidence level having a positive effect. Initial H₂O₂ concentration and pH did not affect degradation showing that no pH or initial H₂O₂ concentrations were necessary. The dynamics of carotenoid degradation was evaluated analyzing the pseudo-first order kinetic constant, whose values ranged from 0.0310 to 0.0805 min⁻¹. The Analysis of Variance

indicated that all linear independent variables (pH, O₃ and H₂O₂) were statistically significant at a 95% confidence level. In addition, only the interaction term between pH and ozone exhibited an impact on k . Analyzing the effects of independent variables, a positive effect was verified for O₃ and H₂O₂, which means that the higher the ozone supply and the hydrogen peroxide content, the faster the carotenoid degradation. On the other hand, pH affects negatively the k values, indicating that the faster carotenoid degradation was achieved in lower pH. This means that in industrial conditions, no pH adjustment would be necessary to provide rapid carotenoid degradation conditions. Cizmek et al [5] proposed mechanisms for the oxidation of astaxanthin, β -carotene and lutein. The first oxidation was irreversible and cation radical was formed in the center of the poly-isoprenoic chain. A second electron transfer, also irreversible, involved the reaction of the radical cation with water forming, probably, diols. Formation of epoxides was also considered but they are not stable in acidic media. Fontinele et al [6] studied the electrochemical behavior of Norbixin and its oxidation involved two irreversible electron transfers and protons from the

acidic. All these studies have been carried out in acidic aqueous media and the carotenoids were in the solid state on the electrodes. Considering that all these conditions are similar to that presented by the wastewater studied in this work, the similarities in the structure of the all the carotenoids above mentioned, probably, Norbixin and Bixin, which are the most prominent carotenoids in the effluent, may be forming cation radical in the first electron transfer followed by another electron transfer and chemical reaction with water generating diols.

Conclusions

The results showed that only O₃ flowrate affect significantly the degradation of the carotenoids and pH, initial H₂O₂ concentration and O₃ flowrate affect the rate of the reaction. Norbixin and Bixin from the effluent may form radical cations and reacting with water to form diols in irreversible oxidation process.

Acknowledgments

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