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Treatment of a biodiesel effluent by coupling coagulation-flocculation, membrane filtration and Fenton reactions

Bárbara R. Gonçalves, Antonio E.H. Machado, Alam G. Trovó*

Universidade Federal de Uberlândia, Instituto de Química, P.O. Box 593, CEP 38400-902, Uberlândia, MG, Brazil

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ABSTRACT

The conditions for treatment of a biodiesel effluent, combining coagulation-flocculation and membrane filtration with Fenton/photo-Fenton reactions, in order to ensure the reuse of water, are presented in this work. Coagulation-flocculation and membrane filtration were applied as a first stage to remove the turbidity, suspended solids, apparent color and oil & fats. In the second stage, Fenton/photo-Fenton reactions were used to reduce the organic load. Under the best condition achieved for this stage (3500 mg L⁻¹ H₂O₂, 25 mg L⁻¹ Fe²⁺ and pH between 2.5 and 2.9), 90% of the dissolved organic carbon and the same percentage of chemical oxygen demand were removed after 24 of irradiation. In addition, the same acute ecotoxicity to *Vibrio fischeri* was obtained, when compared to the effluent treated in the first stage and diluted to 20% v/v. These results demonstrate the effectiveness of coupling physical processes with photo-Fenton reactions to promote the treatment of biodiesel effluent.

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1. Introduction

Biodiesel effluent has as main characteristics the presence of high levels of chemical oxygen demand (COD), biochemical oxygen demand after five days (BOD₅), suspended solids (SS) and oil & fat (Daud et al., 2015).

Two review articles recently published point out the need for further studies on the integration of processes for the treatment of this kind of effluent, since low efficiencies has been obtained by application of isolated processes (Daud et al., 2015; Veljkovic et al., 2014). In order to contribute to the solution of this problem, in this study we evaluated the applicability of a two-stage treatment involving firstly the application of coagulation-flocculation and membrane filtration, followed by reactions of Fenton. The first stage was applied to break the emulsion, as well as reducing the turbidity, apparent color, SS and oils & fats, while the Fenton reactions were responsible for mineralization of the organic load. The evolution of the acute ecotoxicity for *Vibrio fischeri* during the Fenton reactions was also monitored to verify the feasibility of its application.

2. Material and methods

2.1. Procedures

The raw effluent was firstly treated during 70 min by coagulation-flocculation, using 243 mg L⁻¹ of Al³⁺, added as Al₂(SO₄)₃·18H₂O, at pH 9.7 (natural pH of the biodiesel effluent), under aeration and stirring (Gonçalves et al., 2016). This procedure was followed by filtration through membranes of 0.45 μm of mean pore size, and dilution of the filtered fraction to 20% v/v, using distilled water. This dilution was necessary, although not mandatory, since the volume of effluent available for these experiments was limited.

Then, 300 mL of this effluent were submitted, under magnetic stirring, to the photocatalytic process (100 mg L⁻¹ Fe²⁺ as FeSO₄·7H₂O, at pH 2.5–2.9 and different concentrations of H₂O₂, ranging from 500 up to 4000 mg L⁻¹). Two 10 W black light lamps (Irradiance of 35 W m⁻²), separated by a distance of 3.5 cm and positioned on the reaction container (5.9 cm deep, 9.2 cm diameter and surface area of 66.5 cm²), at 1 cm of the level of effluent, were used as radiation font. The reaction was monitored by the consumption of H₂O₂ (added in eight aliquots of 500 mg L⁻¹ - after the complete consumption of an aliquot, a new one was added, until a cumulative concentration of 4000 mg L⁻¹) and removal of dissolved organic carbon (DOC) and COD. In parallel the added amount of

* Corresponding author.

E-mail addresses: barbara.rezende08@gmail.com (B.R. Gonçalves), ahmachado@gmail.com (A.E.H. Machado), alamtrovo@ufu.br (A.G. Trovó).

H₂O₂ was optimized.

The concentration of Fe²⁺ was optimized in experiments similar to the above, using 3500 mg L⁻¹ H₂O₂ and four different concentrations of Fe²⁺ (15, 25, 50 and 100 mg L⁻¹) (Trovó et al., 2013).

Finally, using the best concentrations of Fe²⁺ (25 mg L⁻¹) and H₂O₂ (3500 mg L⁻¹), a comparison between the Fenton and photo-Fenton processes was performed, maintaining the temperature of the reaction medium in 25 °C during the exclusively thermal process, and 32 °C under irradiation.

In the experiments in which the concentration of Fe²⁺ was evaluated (except in the analyses of H₂O₂ and Fe²⁺), after sampling and before analyses, an equivalent amount of Na₂SO₃ was added to ensure the decomposition of the remaining H₂O₂. Further, the pH was adjusted (between 6 and 8), followed by filtration through membranes with a mean pore size of 0.45 μm. For samples for which the acute ecotoxicity for *V. fischeri* was evaluated, 0.4 g L⁻¹ of solution of bovine catalase were added after the pH adjustment, followed by filtration using membranes of 0.45 μm.

2.2. Analytical determinations and ecotoxicity assays

Turbidity, apparent color and pH were measured using respectively a turbidimeter 2100Q (Hach), a spectrophotometer (Shimadzu UV, 1800), and a pH-meter (Bel Engineering), after calibration with standard solutions.

The H₂O₂ concentration was quantified by methodology proposed by Nogueira et al. (2005). The concentration of total dissolved iron was determined according to a Standard Method (Clesceri et al., 2005).

DOC decay was followed using a TOC analyser (Shimadzu TOC-VCPH/CPN), while COD determinations were carried out according to the 5220D Standard Method (Clesceri et al., 2005).

The total solids, SS and oil & fats were determined according to a Standard Method (Clesceri et al., 2005).

Acute ecotoxicity for *V. fischeri* was estimated according to ABNT NBR 15411-3:2012 method (Brazilian Association of Technical Standards, 2012).

3. Results and discussion

The raw biodiesel effluent under study is opaque with milky appearance, apparent color of 12,775 mg L⁻¹ Pt/Co, turbidity of 1350 NTU, 3440 mg L⁻¹ of total solids, being 670 mg L⁻¹ of SS, 2095 mg L⁻¹ of oil & fats, and a pH equal to 9.7. The soluble fraction presents a high organic load (DOC = 3671 mg C L⁻¹ and COD = 17,016 mg O₂ L⁻¹), and 100% of acute ecotoxicity to *V. fischeri*. After the coagulation-flocculation process, more than 98% of turbidity, apparent color, SS, and oil & fats were removed. In addition, a reduction of 34% in the inhibition to *V. fischeri* was achieved, and only 32% of DOC and 35% of COD were removed.

After filtration and dilution of the pre-treated effluent, the catalytic step, involving Fenton and photo-Fenton reactions, was then applied (Fig. 1). A DOC and COD removal of respectively 25% and 75% was reached using 2000 mg L⁻¹ H₂O₂. The expressive COD removal should be related to the oxidation of organic and inorganic species, susceptible of being oxidized by HO• or H₂O₂, while DOC is only a measure of the remaining organic matter.

The DOC removal could be improved using 2500 mg L⁻¹ H₂O₂. For concentrations higher than this value and up to 4000 mg L⁻¹, the level of removal remained almost constant (Fig. 1). This stabilization seems to be due to the formation of carboxylic acids of low molar mass, which besides being recalcitrant to oxidation (Trovó et al., 2012), tend to form complexes with iron (Baba et al., 2015), reducing its concentration (Fig. 1).

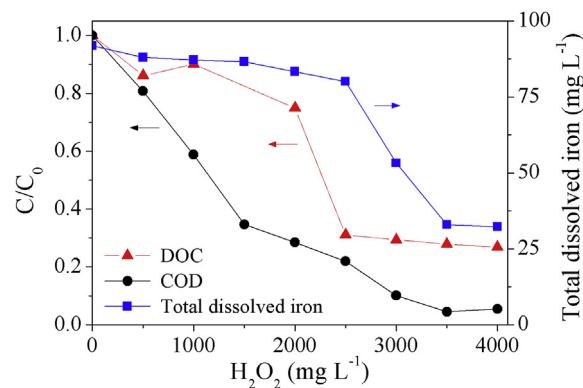


Fig. 1. Influence of the dosage of H₂O₂ on DOC and COD removal, and behavior of the concentration of total dissolved iron. Initial conditions: [DOC] = 514 mg C L⁻¹; [COD] = 1685 mg O₂ L⁻¹; [Fe²⁺] = 100 mg L⁻¹; pH = 2.5–2.9.

The DOC removal follows a sigmoidal behavior, being slow until 2000 mg L⁻¹ of H₂O₂ (Fig. 1), followed by an expressive increase in the rate between 2000 and 2500 mg L⁻¹, when it becomes slow again. The behavior above this concentration is possibly related to the growing availability of HO•. It is likely that the lower DOC removal with the addition of up to 2000 mg L⁻¹ of H₂O₂ can be due to the regeneration of Fe²⁺ (Silva et al., 2007) and consumption of HO• by inorganic species present in the effluent. This effect cannot be attributed to inner filter effects caused by components of the effluent, as suggested by Silva et al. (2015), since there is no significant overlap between the absorption spectrum of this effluent and the emission peak typical of this kind of lamp (Fig. 2). So, the degradation of the organic load in the effluent should be being caused primarily by HO• produced by thermal Fenton reactions, with a secondary role of the photo-Fenton reactions, but no less important, since the regeneration of the Fe²⁺ is essential to support the process.

Using 3500 mg L⁻¹ H₂O₂ a removal of respectively 72% and 95% of DOC and COD, was possible (Fig. 1). In view of this and considering that this concentration is very close the required to treat an initial COD of 1685 mg O₂ L⁻¹ (considering that 1 g COD ≡ 0.03125 mol O₂ ≡ 0.0625 mol H₂O₂ = 2.125 g H₂O₂ (Gernjak et al., 2003), the required concentration of H₂O₂ is 3580 mg L⁻¹), the role of Fe²⁺ concentration was evaluated using 3500 mg L⁻¹ H₂O₂. The removal of DOC was evaluated using four different concentrations

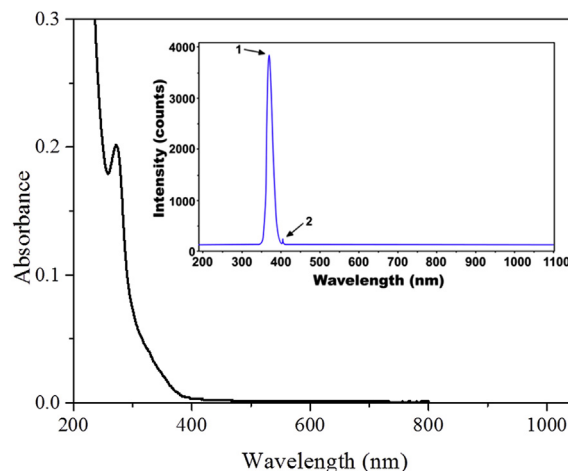


Fig. 2. Absorption spectrum of the effluent after pre-treatment using Al³⁺, diluted to 20% (v/v), at pH 2.7. Insert: Spectrum typical of a black light fluorescent lamp.

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