



## Residue-based iron catalyst for the degradation of textile dye via heterogeneous photo-Fenton



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### ABSTRACT

In this work, the use of a residue-based catalyst for heterogeneous photo-Fenton of Reactive black 5 (RB5) textile dye was evaluated. The catalyst was prepared by chemical vapor deposition of ethanol on a red mud residue, an important waste of the aluminum industry rich in iron oxide. The catalyst was characterized by different techniques, i.e., Mössbauer spectroscopy, Raman spectroscopy, CHN elemental analysis, BET surface area, and scanning and transmission electron microscopies. Results showed that the iron phases present in the red mud are reduced and a carbon coating is formed, protecting the catalyst from excessive iron leaching. The photo-Fenton experiments were carried out by varying pH, H<sub>2</sub>O<sub>2</sub> concentration and radiation power and assessing dye conversion as the response variable. Studies on textile dye degradation showed that low pH favors the reaction and 100% photo-degradation efficiency was obtained, reducing the toxicity of the dye. The best operational condition was achieved at pH 3 and H<sub>2</sub>O<sub>2</sub> initial concentration of 11 mM, after 60 min of reaction. Kinetic data related to RB5 dye degradation were well fitted to the Langmuir–Hinshelwood model in the range of 20–50 mg L<sup>-1</sup> of RB5 initial concentration with obtained initial rate constant of  $9.4 \times 10^{-8} \text{ mol L}^{-1} \text{ min}^{-1}$ . A reaction pathway was proposed in which the H<sub>2</sub>O<sub>2</sub> is activated by surface Fe<sup>2+</sup> sites on RM based catalyst, especially in the presence of light, producing •OH radicals in a heterogeneous photo-Fenton-like mechanism to oxidize the organic pollutant Reactive black 5 dye.

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### 1. Introduction

Red mud (RM) is a by-product of the Bayer process for alumina production. This process has been used for over 120 years and residues are primarily disposed of in long-term storage in a number of different forms [1]. Ideally, this residue could be used as an industrial by-product for other applications, leading to a zero waste situation. Despite over 50 years of research and hundreds of publications and patents on the subject, little evidence exists of any significant way that RM has been put to use [2].

Brazil has a large capacity for alumina production and 1.0–1.5 tons of RM are generated per ton of alumina produced. It is estimated that just in Brazil more than 20 Mt of red mud are generated every year without proper destination [3].

The main constituents of RM include Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, CaO and MgO, which are very interesting species for chemical applications. However, due to its high alkalinity RM is harmful to water, land and air, and demands much space for storage. It is expensive to contain and to build reservoirs to prevent RM spills into the environment. A worldwide effort has been made recently to find appropriate applications for RM residue [4], such as CO<sub>2</sub> capture [5,6], polymer and cements additives [7], heavy metals adsorption in contaminated soils [8,9] and contaminants adsorption from aqueous solution [10–12]. Moreover, the high iron content of RM motivates its use in catalytic applications [2,13–20], such as wastewater treatment. Brazil houses important industrial centers, including industries based on textile dye processing. The lack of treatment of wastewater from this industry, combined with high water scarcity, represents a serious environmental issue.

The textile industry produces large amounts of effluents contaminated with dyes, which are toxic to humans and environment. Textile dyes are generally recalcitrant compounds with high molecular weight. These dyes are highly resistant to microbiological

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degradation and may not be degraded readily by biological treatment methods [21]. Adsorption processes have been widely used to remove these pollutants from wastewater but these processes merely transfer them from an aqueous to a solid phase, which does not solve the problem. Given this, advanced oxidation processes (AOPs) have been studied in the recent years as a technique for the degradation of pollutants in wastewater treatment [22,23].

AOPs are based on the generation of  $\bullet\text{OH}$  radicals, powerful reactive species, capable of oxidizing a wide range of organic compounds [23–25]. Homogeneous photo-Fenton is a common AOP, in which soluble iron II is the catalyst; but the difficulty of catalyst recovery is a process drawback [26]. Thus, efforts have been made to find efficient heterogeneous iron catalysts such as Fe-clays [27], Fe/TiO<sub>2</sub> [28] and Fe<sub>3</sub>O<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [29]. A number of heterogeneous photo-Fenton studies have identified the optimized operational variables, e.g., the pH (from 2.8 to 7.0), H<sub>2</sub>O<sub>2</sub> concentration (from 0.1 to 5.0 mmol L<sup>-1</sup>) and concentration of solid catalyst (from 0.1 to 5.0 g L<sup>-1</sup>) [17–20]. Zero-valent iron (Fe<sup>0</sup>) has been also studied as a solid catalyst in the so called photo-Fenton-like reaction [30]. In this process, the Fe<sup>0</sup> is converted into ferrous ion (Fe<sup>2+</sup>) that acts as a catalyst for the Fenton reaction to produce  $\bullet\text{OH}$  [31].

Few studies have been reported on the application of RM as catalyst for AOPs. Saputra et al. [32] used red mud supported Co catalysts for phenol degradation in aqueous phase. Oliveira et al. [33,34] and Costa et al. [35] studied modified red mud for degradation of dyes, thiophene, quinoline and dibenzothiophene.

A concern about the heterogeneous photo-Fenton process is that attention has been focused on the photo-degradation of toxic compounds under UV irradiation. The use of artificial ultraviolet lamps for degrading industrial effluents consumes a large amount of expensive electrical energy. It is known that the sunlight that reaches the Earth surface contains only about 4% of UV radiation spectra [36]. Therefore, it is desirable to find heterogeneous photo-Fenton catalysts based on sunlight irradiation instead of an artificial UV light source, particularly in Brazil, where there is high availability of sun irradiation throughout the year.

In this contribution, we have studied the degradation of Reactive black 5 (RB5) textile dye using a magnetic carbon coated catalyst based on red mud residue and simulated sunlight irradiation by heterogeneous Fenton and photo-Fenton processes.

## 2. Experimental

### 2.1. Preparation and characterization of the catalyst

The catalyst RM/C was prepared by chemical vapor deposition (CVD) reaction. RM was previously washed with deionized water to reduce its alkalinity and was dried at 60 °C over 24 h. After drying, the RM (50 mg) was heated at a rate of 5 °C min<sup>-1</sup> up to 700 °C in an horizontal furnace (Lindberg Blue) with ethanol (Vetec 99.5%, Brazil) as the carbon source at ca. 6% in N<sub>2</sub> (30 mL min<sup>-1</sup>) and maintained at this temperature for 3 h. After this time, the system was cooled down to room temperature under ethanol/N<sub>2</sub> flow. The produced material, RM/C, was characterized by Mössbauer spectroscopy (room temperature in a spectrophotometer CMTE MA250, with constant acceleration, Co source, Rh matrix and  $\alpha$ -Fe as reference), Raman spectroscopy (Bruker SENTERRA, helium–neon laser at wavelength 633 nm), scanning electron microscopy – SEM (microscope SEG – Quanta 200–SEI) and transmission electron microscopy – TEM (microscope Tecnai G2 200 kV – SEI). In order to obtain the values of band gap, the catalyst was analyzed by diffuse reflectance. The diffuse reflectance spectra were obtained using a Varian Cary 5 instrument equipped with diffuse reflectance accessory.

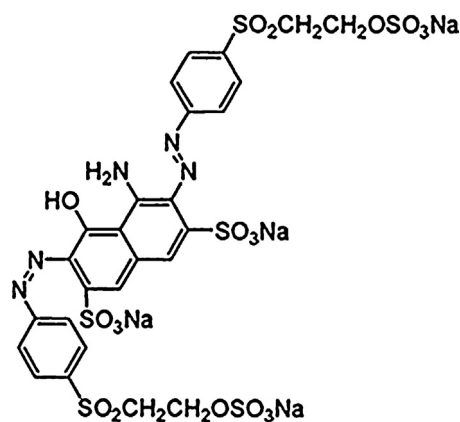


Fig. 1. Structure of the Reactive black 5 (RB5) textile dye.

### 2.2. Degradation of Reactive Black 5 textile dye

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 30%, Vetec) and a commercial textile dye RB5 (Hangzhou Color Rich Chem Co., China), Fig. 1, were used as reagents and H<sub>2</sub>SO<sub>4</sub> (98%, Vetec) and NaOH (99%, Vetec) were used for pH adjustment. The degradation of the dye was performed with a 2<sup>2</sup> factorial experimental plan using as independent variables the initial concentration of hydrogen peroxide (11 mM, 22 mM, 33 mM) and pH (3, 6 and 9). The influence of H<sub>2</sub>O<sub>2</sub> concentration was studied in the range of 11–97 mM H<sub>2</sub>O<sub>2</sub>, at pH 3. The degradation of the RB5 dye was used as the dependent variable. A catalyst concentration (RM/C) of 0.5 g L<sup>-1</sup> and a dye concentration of 50 mg L<sup>-1</sup> were held constant. The dye concentration was measured over time by UV–vis analysis in a Biochrom Libra S12 spectrophotometer using the peak of higher absorption at 595 nm. A batch reactor with 300 mL solution under stirring of 450 rpm was used. The lamp used in the tests was a SunLight Osran 300 W lamp, which has a light spectrum similar to sunlight. The radiation in the system was measured with a radiometer UVA/UVB MRU-201 in the range between 8.5 and 36 W m<sup>-2</sup>. The RB5 solution (50 mg L<sup>-1</sup>) was stirred in the dark for 30 min before reaction under light and H<sub>2</sub>O<sub>2</sub> addition.

### 2.3. Toxicity

The toxicity analysis of the degraded dye was performed according to the method reported by Mamindy-Pajany et al. [37]. This method uses photosynthetic enzyme complexes (PECs) and stabilized aqueous photosynthetic system (SAPS) in a LuminoTox-Lab Bell analyzer. Photosynthetic activity is based on the fluorescence production. The fluorescence photosynthetic efficiency (quantum yield  $\Phi$ ) is measured when the PECs/SAPS are unexposed ( $\Phi_{\text{zero}}$ ) or exposed ( $\Phi_{\text{SAMPLE}}$ ) to different concentrations of a toxic compound. 2.0 mL of pure deionized water or samples of RB5 solutions after reaction and neutralization were added to a cuvette at room temperature (25 °C), followed by the addition of 100  $\mu$ L of PECs/SAPS, gentle mixing and resting for 15 min in the dark before reading the photoluminescence in the LuminoTox analyzer. The inhibition is calculated as follows: Inhibition (%) =  $[(\Phi_{\text{zero}} - \Phi_{\text{SAMPLE}})/(\Phi_{\text{zero}})] \times 100$ .

## 3. Results and discussion

### 3.1. Characterization of the catalyst

The RM/C catalyst was produced by a chemical vapor deposition (CVD) process of RM residue and ethanol at 700 °C. Characterization results show that during the CVD process ethanol reacts with RM to

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