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Research article

# Ferrous ions reused as catalysts in Fenton-like reactions for remediation of agro-food industrial wastewater



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## ABSTRACT

Cassava is the most important tuberous root in tropical and subtropical regions of the world, being the third largest source of carbohydrates. The root processing is related to the production of starch, an important industrial input, which releases a highly toxic liquid wastewater due to its complex composition, which inhibits high performances of conventional effluent treatments. This study aims to evaluate Fenton-like and photo-Fenton-like reactions for treatment of cassava wastewater, reusing ferrous ions from the preliminary coagulation stage. Pre-treated cassava wastewater was submitted to oxidation in three variations of hydrogen peroxide concentrations, with more relevant analytical responses verified in color, turbidity, COD (Chemical Oxygen Demand), and acute toxicity in *Artemia salina*, besides the action of radicals during Fenton-like reactions. At higher peroxide concentrations, a decrease of 68% in turbidity and 70% in COD on the photo-Fenton-like system was observed, even at slow reaction rates (fastest rate constant  $k = 2 \times 10^{-4} \text{ min}^{-1}$ ). Inclusion of UV increases the viability of the Fenton-like reactions by supplementing the reaction medium with hydroxyl radicals, verified by the tert-butanol tests. The oxidation process leads to high EC<sub>50</sub> values in 24 h of incubation in Fenton-like reactions and 48 h in photo-Fenton-like reactions. Final COD and turbidity suggests that the reuse of iron, which remains in the preliminary treatment step shows a great potential as a catalyst for Fenton-like advanced oxidation processes. Tertiary treatment can be less expensive and harmful to the environment, reducing production of residual sludge and metal content in the final effluent, which reduces polluting potential of the effluent regarding solid waste.

## 1. Introduction

The increase in world population has induced the expansion of food production and consequently, the generation of waste. Among the food industries, cassava (*Manihot esculenta* Crantz) production (a root widely consumed in Asia and America) (ElMekawy et al., 2015) is increasing. According to the Food and Agriculture Organization of United Nations (FAO), world production of cassava remains in an accelerated rate of growth, with an average rate of 281 million tons/year and is a carbohydrate source for more than 400 million people worldwide, especially in developing countries. For industrial and value-added purposes, starch derivatives (starch, sour starch, tapioca, modified starch) and farinaceous products (white flour, toast, Biju) are produced from the cassava root (Avancini et al., 2007). Its beneficiation generates two types of residues: solids, composed of the woody parts of roots, fibrous portions retained in sieves, bagasse (Bhatnagar et al., 2015);

and liquids, consisting of root washing water and pressing water of cassava (Nasu et al., 2010).

The pressing water is better known as cassava wastewater (“manipueira”), resulting from the production of flour and the process of extraction and purification of starch. Cassava wastewater is a liquid residue rich in sugars, starch, proteins, salts and other substances (Rebouças et al., 2015). It is extremely toxic effluent because it contains high organic load, with biochemical oxygen demand (BOD) ranging from 14000–34000 mg L<sup>-1</sup>, besides having great volume produced, from 300 to 3000 L per ton of processed roots. It contains high concentration of linamarin (a cyanogenic glycoside), which is released after cell disruption of the root structure and, being soluble in water, this compound is almost completely eliminated with the wash water from the processing of cassava (Souza et al., 2014). Consequently, the release of this waste can lead to the reduction of dissolved oxygen, eutrophication and reduction of the capacity of autodepuration of water

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bodies, and death of aquatic fauna and animals that consume water with an excess of cyanide gas (Campos et al., 2006; Rajbhandari and Annachhatre, 2004). In humans, cyanide causes rapid breathing, tremors, and other neurological effects in short-term exposure, and long-term exposure causes weight loss, thyroid effects, neural damage, and even death (Vedula et al., 2013).

Conventional techniques for treating water and effluents, such as physico-chemical processes, are the most widespread in the industrial environment. Coagulation and flocculation, for example, are used to increase the size of colloidal and finely divided particles, as well as to destabilize and aggregate them, forming larger and denser flakes liable of separation (Liang et al., 2016). The phenomenon is observed with the use of coagulating agents, such as salts of iron and aluminum, and with synthetic polyelectrolytes as flocculants (Kim, 2016). However, they are preliminary steps and generate solid waste, only occurring with phase transfer of pollutants.

Cassava wastewater cannot be fully remedied by these routes due to molecular complexity, organic matter content and high concentration of toxic substances (Matilainen and Silanpää, 2010). Moreover, global guidelines on water use management suggest that the “end of pipe” approach to water and effluent treatment should be replaced by cleaner production, integrating environmental objectives into production processes to reduce waste and emissions in terms of quantity and hazard. Practices that involve the rational use of water, reuse, reduction of liquid and polluting effluents, may allow the consideration of water consumption in the productive process, generation of effluents at each stage of process and proposals to reduce the water load and organic effluents to be achieved (Amorim et al., 2007).

Advanced Oxidation Processes (AOPs) provide cleaner production technologies. Their main proposal is to complete mineralization of organic contaminants with the use of highly oxidant species by the generation of free radicals, mainly the hydroxyl radical ( $\cdot\text{OH}$ ), with the standard oxidation potential of 2.8 V. This radical rapidly and indiscriminately reacts with many organic compounds and inorganic solutes with high rate constants. The result of these reactions is the formation of organic radicals that react with molecular oxygen and start chain reactions, taking the organic substrate to innocuous species, such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and inorganic ions (Doumic et al., 2015; Ibáñez et al., 2014; Melo et al., 2009).

Classical Fenton reaction is an AOP discovered by Fenton (1894), where the production of reactive oxygen species is given by decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) catalyzed by the ferrous ion ( $\text{Fe}^{2+}$ ), following a series of reactions (summarized by Eqs. (1) and (2)) in solution (Bokare and Choi, 2014).

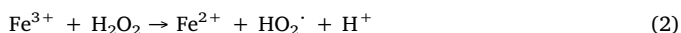
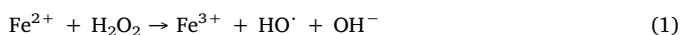
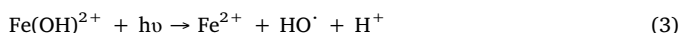


Photo-Fenton process combines Fenton's reaction with ultraviolet radiation and therefore increases the oxidation efficiency as it regenerates  $\text{Fe}^{2+}$  for the reaction with  $\text{H}_2\text{O}_2$  (Eq. (3)), in addition to producing additional hydroxyl radicals (Eq. (4)) (Melo et al., 2009).



Both techniques use readily available and safe reagents and can be applied at ambient temperature and atmospheric pressure (Babuponnusami and Muthukumar, 2014). Researchers have been investigating the applicability of these AOPs in several environmental matrices. Riaño et al. (2014) investigated color and organic matter removals in swine effluent by applying the Fenton process to reuse/recycling wastewater, achieving reductions of 96 and 78%, respectively. The system was also successfully employed in the removal of COD, suspended solids and turbidity in sugarcane vinasse (Guerreiro et al., 2016) and effluent from the manufacture of crystallized fruits

(Rodríguez-Chueca et al., 2016). In addition to the high removal efficiency in organic load, there are reports of degradation of organic refractory molecules such as polycyclic aromatic hydrocarbons (PAH) in domestic waste leachate (Li et al., 2016) and pesticides in the industrial effluent (Costa Filho et al., 2016).

Despite being extensively studied, Fenton reactions still have some disadvantages, such as high operating cost, strict pH range, generation of large volumes of iron sludge, difficulties in reusing catalyst, as well as restrictions on release patterns for iron established by environmental agencies (Wang et al., 2016). Thus, studies have been investigating other types of catalysts replacing  $\text{Fe}^{2+}$  with the purpose of preventing inconveniences of technique, resulting in reactions known as Fenton-like (Bokare and Choi, 2014), including  $\text{Fe}^{3+}$  species in the class of substituent catalysts. In Fenton-like processes, the chain reactions are initiated according to Eq. (2). Pesticides, dyes, and drugs are some contaminants whose treatment via Fenton-like reactions has already been investigated (Wang et al., 2016).

In this way, the purpose of this research was to evaluate the efficiency of the Fenton-like process, reusing  $\text{Fe}^{3+}$  remaining from the physico-chemical stage of coagulation with ferric chloride ( $\text{FeCl}_3$ ) and use of ultraviolet radiation (UV) for treatment of cassava wastewater. Performance of treatments was evaluated mainly in terms of turbidity and decay of absorbance in the UV region. The motivation for the study is mainly related to sustainability of the proposed process. In addition to being less expensive - because it is not necessary to supplement the reaction medium with iron species - the amount of sludge generated will be substantially less than in conventional Fenton reactions.

## 2. Material and methods

### 2.1. Cassava wastewater

The research was carried out using effluent obtained after the pressing stage of cassava in a starch production factory in the north-central region of Paraná - Brazil. It was stored under refrigeration at 4 °C. As pretreatment, a coagulation/flocculation step was performed with a stock solution of 1200  $\text{mg L}^{-1}$  of  $\text{FeCl}_3$  (Sigma-Aldrich/Vetec, Rio de Janeiro, Brazil) and cationic polymer (Purewater, São Paulo, Brazil) 2%, pH 6.0 (optimal condition previously obtained by experimental design 3<sup>2</sup>, data omitted), for reducing the total solids content and turbidity of the sample.

For purposes of characterization, analyses were performed to determine COD [closed reflux as described in APHA (2012)], TOC (Shimadzu carbon analyzer model TOC 5000-A, Kyoto, Japan), pH (pHmeter Tecnopon model mPA210, Piracicaba, Brazil), turbidity (turbidimeter Del Lab model DLT-WV, Araraquara, Brazil), electrical conductivity (Digimed model DM-3 conductivity meter, São Paulo, Brazil), total solids, volatiles, fixed [gravimetry as described in A.O.A.C. (2000)] and sedimentable [Imhoff cone method according to NBR 10561 (1988)], volatile acidity, alkalinity, total phosphorus and iron (APHA, 2012). Results are expressed in triplicates and by standard deviation. The obtained data was subjected to statistical inference analysis by Tukey's test (95% confidence limit), using the software Statistica - StatSoft® version 10.

### 2.2. Fenton-like reactions

In each experiment, 200 mL volume of pre-treated cassava wastewater was subjected to Fenton and photo-Fenton-like processes in a jacketed reactor, with a constant temperature aided by a thermostatic bath (Visomes Plus model V550, São Paulo, Brazil, at 25 ± 1 °C). There was constant stirring (90 rpm) in batch mode. The pH in all experiments was 3.0 ± 0.2 adjusted with a solution of  $\text{H}_2\text{SO}_4$  1  $\text{mol L}^{-1}$ , and different concentrations of  $\text{H}_2\text{O}_2$  were studied (1000, 3000 and 5000  $\text{mg L}^{-1}$ , from solution 30% w/w Sigma-Aldrich/Vetec, Rio de Janeiro, Brazil). In photo-Fenton-like reactions, the filament of a

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