Investigation of the reaction pathway for degradation of emerging contaminant in water by photo-Fenton oxidation using fly ash as low-cost raw catalyst

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Abstract
In this work, fly ash from a Brazilian thermal power plant was employed as a low-cost raw catalyst for Procion red degradation by photo-Fenton process. The ash was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), nitrogen adsorption/desorption isotherms (BET), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrometry (EDX). The material had an iron content of 4.10 wt%, distributed homogeneously on the solid surface. The ash particles showed mainly spherical morphology between 0.5 and 20 µm. The catalyst presented promising activity, reaching 93% of dye decolorization at 60 min of reaction, and 85% of organic load removal at 240 min. The predominant oxidizing species involved on the degradation of dye molecules during the photo-Fenton reaction were the hydroxyl radicals (HO·). The material showed remarkable stability and reusability after five successive cycles of reuse. The reaction intermediates were identified by LC/MS analysis and a reaction pathway was proposed.

Highlights
• Reaction pathway for degradation of an emerging contaminant by photo-Fenton
• Fly ash was a promising catalyst for the degradation of Procion red
• The catalytic efficiency was 93.6% decolorization and 85% TOC removal
• Fly ash presented good stability and low level of deactivation after five uses

Keywords Fly ash · Photo-Fenton · Degradation · Dye · Mechanism · Scavenger

Introduction
The coal burning in thermoelectric plants has generated large amounts of ash (Dash et al. 2018), which can represent up to 50% of the original coal (Pires and Querol 2004). These ash are classified as heavy and fly, corresponding to about 5–15% and 85–95%, respectively (Yao et al. 2015). Currently, the amount of fly ash generated worldwide is approximately 750 million tons (Yao et al. 2015) and around 3 million tons are produced in Brazilian thermoelectric plants (Mushtaq et al. 2019). The appropriate disposal of these wastes is still a problem faced by many thermoelectric plants, where most of it is placed in abandoned mines or landfills (Depoi et al. 2008; Yao et al. 2015), which can cause soil and groundwater pollution (Patra et al. 2018).
The fly ash is collected from mechanical cyclones or electrostatic precipitators in thermoelectric units and are composed of fine particles (Singh et al. 2016). The largest application of this type of ash is in the cement production, widely used for civil construction (Cho et al. 2019; Yao et al. 2015). Other applications are in ceramic manufacturing (Luo et al. 2017), glass (Depoi et al. 2008), soil pH correction (Shaheen et al. 2014), and synthesis of zeolite (Sivalingam and Sen 2019; Koshy and Singh 2016), geopolymer (Somna et al. 2011), and adsorbent (Hsu 2008).

Due to the presence of iron oxide on its composition (Pires and Querol 2004; Sideris et al. 2018), ash from thermoelectric power plant has also been employed as Fenton catalyst for the treatment of wastewater containing recalcitrant organic compounds (Drumm et al. 2019; Ramirez-Franco et al. 2019; Zhang et al. 2012). Few studies concerning applicability of these residues, in raw state, as Fenton catalysts have been highlighted in the literature, and therefore, further efforts need to be made to investigate their intrinsic catalytic properties, to be applicable for other organic pollutants, such as, Procion Red dye. It is known that iron decomposes the hydrogen peroxide (H₂O₂) during the Fenton reaction, generating hydroxyl radicals (HO·), which are the main reactive species responsible for the degradation of recalcitrant molecules (Grassi et al. 2020; Oliveira et al. 2016; Schmachtenberg et al. 2019; Xu et al. 2017). This reaction can be accelerated by the presence of light irradiation (known as photo-Fenton reaction) due to the additional generation of hydroxyl radicals (OH) because of the light (Xu et al. 2017; Mossmann et al. 2019).

Taking the above background into consideration, this work aims to evaluate the performance of Brazilian coal fly ash as a photo-Fenton catalyst for the degradation of Procion Red dye in water. The material was characterized by different techniques, and the effects of catalyst load, initial pH and H₂O₂ concentration on the degradation efficiency were investigated. Catalyst reuse tests and quantification of the leached iron to the aqueous phase were performed to evaluate the stability of the catalyst. In addition, the reaction intermediates were identified and a reaction mechanism of textile dye oxidation by photo-Fenton process was proposed.

**Materials and methods**

**Chemicals**

Procion Red HE7B dye (CI: Reactive Red; CAS Number: 17804-49-8; chemical formula: C₁₉H₁₀Cl₂N₆O₇S₂) is widely used in the textile industry and used herein as a model molecule (Fig. 1). Chemicals such as hydrogen peroxide (30% w/w), sulphuric acid (H₂SO₄), isopropyl alcohol (IPA), and benzoquinone (BQ) were purchased from Sigma Sigma-Aldrich.

**Preparation and characterization of material**

The fly ash was supplied by the Presidente Médici Thermoelectric Power Plant located at Candiota city (State of Rio Grande do Sul, Brazil). The residue was dried at 110 °C for 4 h, and subsequently sieved on 150 mesh. The chemical composition of the fly ash was determined by X-ray fluorescence spectrometry (XRF) in a Bruker S8 Tiger spectrometer. The crystalline phases were identified by X-ray diffraction (XRD) using a Rigaku Miniflex model 300 diffractometer, and operated with Cu-Kα radiation (λ = 1.5418 Å), 30 kV, 10 mA, step size of 0.03° and a count time of 0.5 s per step. N₂ adsorption/desorption isotherms were obtained on a Micromeritics ASAP 2020 instrument. The specific surface was determined by the Brunauer–Emmett–Teller (BET) method, and pore size and volume distribution were defined by the Barret–Joyner–Halenda (BJH) method. FTIR spectrum of sample pressed into KBr pellet (10 mg ash/300 mg KBr) was recorded by a Shimadzu IR-Prestige-21 spectrometer. Particles morphology and iron mapping were obtained by scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM/EDX, Carl Zeiss equipment, Sigma 300VP). Catalyst stability was evaluated by the amount of iron leached to the aqueous solution after the photo-Fenton reaction. The iron content in the aqueous solution was determined by flame atomic absorption spectrometry (Agilent 240FS).

**Photo-Fenton tests and analytical procedures**

Photo-Fenton catalytic tests were carried out on a glass reactor of 250 mL. The irradiation required for the catalyst...
activation was provided by a fluorescent lamp (85 W, Philips, light efficiency = 65 lumens W⁻¹), positioned 10 cm above from the reaction medium surface. Initial dye concentration was 50 mg L⁻¹. The variables evaluated during the process and ranges tested were: catalyst load (0.2–0.8 g L⁻¹), pH (2–4) and concentration of H₂O₂ (2, 4 and 6 mmol L⁻¹). H₂O₂ concentration of 4 mmol L⁻¹ corresponds to the stoichiometric amount needed for the total mineralization of 50 mg L⁻¹ of Procion Red dye. The pH adjustments were made with H₂SO₄ (0.1 mol L⁻¹). The catalyst was added to the dye solution and the system was kept under magnetic stirring for 60 min to reach the adsorption equilibrium. Then, H₂O₂ was added and the lamp was turned on. Aliquots of 4 mL were collected at predetermined times and centrifuged for catalyst removal. The absorbance was measured on a UV–vis spectrophotometer (Bel Photonics, SP1105) at wavelength of 544 nm (Silvestri et al. 2018). The decolorization efficiency (DE, %) was determined by Eq. (1):

\[
DE(\%) = \left[1 - \left(\frac{C_t}{C_0}\right)\right] \cdot 100, \quad (1)
\]

where \(C_t\) is the dye concentration at time \(t\) and \(C_0\) is the initial dye concentration. Kinetic analysis was performed using the pseudo-first order kinetic model (Ifelebuegu et al. 2016; Salla et al. 2018; Wang et al. 2019a; Zhou et al. 2015), according to Eq. (2):

\[
\ln \left(\frac{C_t}{C_0}\right) = -k \cdot t, \quad (2)
\]

where \(k\) is the reaction rate constant (min⁻¹).

To evaluate the dye mineralization during the reaction, the organic load (TOC, total organic carbon) of liquid samples was measured on a TOC-L-CPH/CNP analyzer (Shimadzu). The dye mineralization was expressed as TOC/TOC₀, where TOC is the organic carbon concentration at the reaction time \(t\) and TOC₀ is the initial concentration of the total organic carbon. The iron leaching from ash during the reaction was measured by atomic absorption spectroscopy (Agilent Technologies, 200 series AA).

It is well known that the photo-Fenton process can degrade recalcitrant molecules due to the generation of several oxidizing radicals, such as HO₂⁻, O₂⁻, and HO⁻ (Wang et al. 2017, 2019b). Isopropyl alcohol (IPA) and benzoquinone (BQ) was used as scavengers of HO⁻ and HO₂⁻/O₂⁻ radicals, respectively (Pan and Zhu 2010; Zhuang et al. 2010).

Electrospray ionization mass spectrometry was employed to identify the intermediates (Agilent 6460 Triple Quadrupole). The gas temperature was 300 °C and the dry gas flow was 5 L min⁻¹. The capillary voltage and fragmentor voltage were 3500 V and 10 V, respectively. The aliquots were introduced in equipment at a flow rate of 5 μL min⁻¹. Nitrogen was used as nebulizing gas and collision gas. Molecular ions were detected using the negative mode in the SCAN method.

### Table 1 Chemical composition of fly ash

| Oxides     | wt%  |
|------------|------|
| SiO₂       | 65.50|
| Al₂O₃      | 23.94|
| Fe₂O₃      | 4.10 |
| CaO        | 2.16 |
| K₂O        | 1.85 |
| MgO        | 1.05 |
| TiO₂       | 0.65 |
| SO₃        | 0.32 |
| Na₂O       | 0.30 |
| P₂O₅       | 0.01 |
| ZrO₂       | 0.06 |
| MnO        | 0.03 |
| SrO        | 0.01 |
| ZnO        | 0.01 |

![Fig. 2 XRD pattern of fly ash](image)

### Results and discussion

#### Characterization of fly ash

Table 1 shows the chemical composition of fly ash. It can be noticed that silicon dioxide (SiO₂) is the largest constituent (65.50 wt%), followed by alumina (Al₂O₃) with 23.94 wt% Iron oxide (Fe₂O₃), the active phase in Fenton reaction, represents 4.10 wt% of the fly ash. Fe₂O₃ content of about 5 wt% has been reported by other researchers to be sufficient to catalyze Fenton reactions (Drumm et al. 2018; Oliveira et al. 2016; Zhang et al. 2018).

X-ray diffractogram of fly ash is shown in Fig. 2. The result presents the typical structure of quartz (SiO₂) (JCPDS 85-1780) and mullite (3Al₂O₃·2SiO₂) (JCPDS 88-2049) (Fukasawa et al. 2017; Nascimento et al. 2009).
In addition, a peak related to magnetite (Fe₃O₄) is observed at 2θ = 35.06° (JCPDS 19-0629), confirming the presence of iron oxide on the sample. Figure 3 displays the N₂ adsorption/desorption isotherms of ash sample. According to the IUPAC classification, isotherms can be classified as type IV, with H3 hysteresis loop, indicating that the particles are mesoporous (Thommes et al. 2015). This characteristic can be confirmed by the pore size distribution (inset to Fig. 3). The fly ash has an average pore size of 34 nm, which is located in the mesoporous region (between 2 and 50 nm). The values of specific surface area and total pore volume were 0.50 m² g⁻¹ and 8.55 × 10⁻⁴ cm³ g⁻¹, respectively. These low values found may be explained by the high temperature during the coal burning, causing sintering of the material and consequently decreasing porosity (Ramírez-Franco et al. 2019).

Figure 4 presents the FTIR spectrum of fly ash. The bands at 3423 cm⁻¹ and 1630 cm⁻¹ are associated with O–H groups due to the presence of water absorbed in the ash (Grassi et al. 2020). The band at 1060 cm⁻¹ can be attributed to Si–O–Si asymmetrical stretching vibrations (Soon and Hameed 2013). The band at 790 cm⁻¹ can be attributed to the symmetrical stretching vibrations Si–O–Si (Mazumder and Rano 2015). The band centered at 465 cm⁻¹ can be attributed to the Fe–O stretching vibration of iron oxides (Ramírez-Franco et al. 2019; Rendon 1981).

SEM image (Fig. 5) shows a predominance of spherical particles with size in the range of 0.5–20 µm. The spherical shape can be attributed to the fusion of oxides due to the high temperature that occurs in coal burning (Kutchko and Kim 2006; Liu et al. 2016). The iron mapping in Fig. 5 (inset) shows a homogeneous distribution on the solid matrix. This characteristic can be considered a positive factor, since it may favor the performance of the material as a promising catalyst in the photo-Fenton process.

**Preliminary catalytic tests**

Preliminary tests were developed under different conditions to determine the best process of dye decolorization catalyzed by fly ash, as follows: (a) H₂O₂/dark, (b) H₂O₂/Vis, (c) catalyst/dark, (d) catalyst/Vis, (e) catalyst/H₂O₂/dark (Fenton), and (f) catalyst/H₂O₂/Vis (photo-Fenton).

As shown in Fig. 6, inexpressive results were obtained for the following systems: (a), (b), (c), and (d). For Fenton reaction (system “e”), the solution decolorized about 15%, whereas remarkable decolorization efficiency (about 72%) was observed in the presence of light (photo-Fenton reaction; system “f”). The higher percentage of decolorization in the photo-Fenton system can be attributed to the increased generation of hydroxyl radicals (HO·) by the energy provided by light irradiation. This radical is capable of accelerating the decomposition of dye molecules (Xu et al. 2017). In addition, despite low surface area, the ash presented remarkable catalytic activity for the decolorization of Procion Red dye from aqueous medium under visible irradiation, which can be attributed to the uniform distribution of iron on the surface of the particles, as shown in Fig. 5.

**Effect of catalyst load**

Figure 7 shows the influence of catalyst load on the Procion Red decolorization efficiency by photo-Fenton reaction. The decolorization efficiency increased from 47.34% (k = 0.010 min⁻¹) to 93.6% (k = 0.043 min⁻¹) at 60 min of reaction using catalyst load of 0.2 and 0.6 g L⁻¹.
respectively. This result is associated with an increase in the number of active sites available for H₂O₂ decomposition and the consequent generation of more HO· radicals (Guo et al. 2014). However, no increase in decolorization efficiency and reaction constant was observed when a catalyst load of 0.8 g L⁻¹ was employed. This could be attributed to reduction of irradiation incidence on the solution due to the excess of particles present in the reaction medium (Drumm et al. 2018; Soon and Hameed 2013). Therefore, 0.6 g L⁻¹ was the catalyst load used for further studies in this work.

**Effect of initial pH**

The degradation of organic molecules during the photo-Fenton reaction is significantly affected by pH of the aqueous solution. (Guo et al. 2014). It is known that the photo-Fenton reaction possess superior efficiency in acidic media (Drumm et al. 2018; Severo et al. 2016), thus the color removal was analyzed at different initial pH (2, 3 and 4), according to Fig. 8. The decolorization efficiencies and correspondent rate constants at pH 2, 3, and 4 were 71.99% \((k=0.021 \text{ min}^{-1})\), 93.6% \((k=0.046 \text{ min}^{-1})\), and 52.2% \((k=0.012 \text{ min}^{-1})\), respectively. The decrease in the degradation efficiency at pH below 3 can be attributed to the excess of H⁺ ions present in the solution, which can act as hydroxyl radical scavengers (Soon and Hameed 2013). On the other hand, the H₂O₂ decomposes rapidly into molecular oxygen at pH above 3, resulting in reduced generation of hydroxyl radical (Akay and Demirtas 2015). Thus, pH 3 was considered as ideal condition due to best catalytic activity presented by the fly ash in the photo-Fenton reaction. A similar pH behavior can be found in other studies presented in the literature (Akay and Demirtas 2015; Drumm et al. 2018; Oliveira et al. 2016).

**Effect of H₂O₂ concentration**

The Procion red decolorization was investigated as a function of H₂O₂ concentration (2, 4, and 6 mmol L⁻¹), and the results are shown in Fig. 9. The concentration of 4 mmol L⁻¹...
corresponds to the stoichiometric amount of \( \text{H}_2\text{O}_2 \) required for total mineralization of 50 mg L\(^{-1} \) of Procion Red. As shown in Fig. 9, the increase of the \( \text{H}_2\text{O}_2 \) concentration from 2 to 4 mmol L\(^{-1} \) leads to an increase in the decolorization efficiency (and rate constant) from 71.5% \((k = 0.021 \text{ min}^{-1})\) to 93.2% \((k = 0.046 \text{ min}^{-1})\) at 60 min of reaction. However, no change in values of decolorization efficiency and constant rate occurs when the \( \text{H}_2\text{O}_2 \) concentration is increased to 6 mmol L\(^{-1} \). In general, the addition of \( \text{H}_2\text{O}_2 \) enhances the efficiency due to the greater generation of hydroxyl radicals. However, in larger quantities, \( \text{H}_2\text{O}_2 \) can generate hydroperoxyl radicals \((\text{HO}_2\cdot)\), that are less reactive and thus, leading to a decrease in reaction rate (Sohrabi et al. 2017). Therefore, 4 mmol L\(^{-1} \) was considered as the optimum \( \text{H}_2\text{O}_2 \) concentration in the present study.

Finally, some studies have investigated the catalytic efficiency of fly ash from several regions of the world for...
removal of organic molecules in water, as shown in Table 2. The results reveal that the fly ash has a remarkable catalytic performance for removal of different organic contaminants in aqueous solutions. For instance, fly ash from a Brazilian thermal power plant has shown promising activity for degradation of Procion Red HE7B dye in water.

Mineralization assays

To evaluate the mineralization of Procion Red by the ash-catalyzed photo-Fenton process, tests were performed to verify the concentration of total organic carbon (TOC) present in the reaction medium during the reaction. The results are shown in Fig. 10, where it can be seen that around 19% of Procion Red degradation was achieved at 60 min of reaction. In this condition, the solution was practically discolored, indicating that the Procion Red decolorization occurs faster than the molecule mineralization. This behavior can be attributed to the initial attack of •OH radicals to the double N=N bonds of the dye azo chromophore groups, resulting in the cleavage of these coloring groups (Chen and Zhu 2007). Therefore, a longer reaction time is required to evaluate the Procion Red mineralization. According to Fig. 10, about 85% of TOC removal was observed at 240 min of reaction, demonstrating that the fly ash is an efficient catalyst for degrading Procion red.

Oxidation radicals generated in the ash-catalyzed photo-Fenton process

Radical scavengers were used to evaluate which species were responsible in the decolorization of Procion Red dye using the as catalyzed photo-Fenton process. Figure 11 shows the efficiency in color removal using two different oxidation radical scavengers (IPA and BQ). The addition of isopropanol (IPA), an •OH scavenger, revealed a negative effect on Procion Red decolorization efficiency. After 60 min, only 20.51% of the color was removed with 10^{-4} mol of IPA. The addition of 10^{-4} mol p-benzoquinone (BQ), an O_2^- scavenger, did not affect the Procion Red color removal (remaining around 93.6%). These results indicate that OH radicals were the predominant species responsible for the decolorization of Procion Red during the ash-catalyzed photo-Fenton reaction.

Reusability and stability

Important properties of a catalyst, such as reusability and stability are strongly desired from environmental and economic points of view. In this sense, several photo-Fenton experiments were performed in the following optimum experimental conditions (at 60 min of reaction): catalyst load = 0.6 g L^{-1}, pH 3, and H_2O_2 concentration = 4.0 mmol L^{-1}. At the end of every run, the catalyst was separated and dried at 100 °C for later reuse. Thus, the operational stability and reusability characteristics of ash were evaluated by five consecutive cycles of reuse in the photo-Fenton process. According to Fig. 12, the results indicated that the catalyst exhibited remarkable reusability, since the efficiency decreased only 14.34% until the fifth cycle of reuse. Regarding material stability, the leached iron content in each assay is shown in Table 3. In the first test, 1.4 mg L^{-1} of leached iron was found, representing 8.1% of the total iron content initially added to the reaction system. In the fifth cycle, only 5.9% of the initially added concentration was identified. For all tests, the amount of leached iron into aqueous phase remained below the limit (15 mg L^{-1}) established by the Brazilian environmental legislation (CONAMA) for effluent disposal.

Intermediate products analysis

Through LC–MS/MS analysis for samples taken at 0 min (initial), 120 and 240 min, it was possible to identify some fragments from cleaving the Procion red molecule (Fig. 13a) as well as propose a possible pathway for degradation reactions of dye (Fig. 13b). Cleavage of the dye molecule occurs mainly by the action of hydroxyl radicals generated by fly ash and H_2O_2 added when both are exposed to radiation. Superoxide radicals were not effective in dye degradation, since the oxidizing potential is about 2.5 times lower than the oxidizing potential of the hydroxyl radical (0.94 V and 2.31 V, respectively). All intermediate species detected by LC–MS/MS had a mass lower than the molecular weight of Procion Red dye (m/z 613.92). Sodium ions (Na^+) easily ionize in aqueous medium, generating the species m/z 567.94. This species can replace two chlorines with two hydroxides (m/z 533.02) which by cleavage the azo bond (N=N) is capable of generating three fragments (m/z 407.00, 317.97, and 128.03). The loss of phenylamide produces the species m/z 479.92, which by cleavage of the azo bond converts to m/z 162.97 and the loss of sulfite group to m/z 399.97, followed by the loss of another sulfite group generates m/z 320.01. From the low intensity of the peaks corresponding to m/z 575.00 and 324.04, in the chromatogram of Fig. 13a, it is believed that cleaving the triazine ring may occur, but with low probability.

Conclusions

Fly ash from a Brazilian thermal power plant was used as a low-cost raw catalyst for the photo-Fenton process. The presence of iron homogeneously well distributed on the particles surface makes it a promising catalyst for the degradation of Procion red in water. The ash presented particles shape predominantly spherical, with
Table 2 Catalytic performance towards removal of organic pollutants by fly ash from different world regions

| Region           | Target pollutant | Technique/operating conditions                                                                 | Removal efficiency (%) | References                              |
|------------------|------------------|-----------------------------------------------------------------------------------------------|------------------------|-----------------------------------------|
| Kaohsiung, Taiwan | Rhodamine B (RhB) | Fenton process; $[\text{H}_2\text{O}_2] = 6.10^{-3}$ M, pH 3, $[\text{RhB}]_0 = 100$ mg L$^{-1}$ | 97% RhB decolorization within 2 min and 72% COD removal at 30 min | Chang et al. (2009)                      |
| Wuhan, China     | n-butyl xanthate (n-BX) | Fenton process; catalyst dosage = 1 g L$^{-1}$, pH 3, $[\text{H}_2\text{O}_2] = 1.76$ mmol L$^{-1}$, $[\text{n-BX}]_0 = 90$ mg L$^{-1}$ | 96.9% n-BX degradation and 96.66% COD removal within 120 min | Chen and Du (2014)                      |
| Quang Ninh, Vietnam | Reactive Blue 182 (RB182) | Fenton process; $[\text{H}_2\text{O}_2] = 3.92$ mM, catalyst dosage = 1 g L$^{-1}$, pH 3 | 93% RB182 decolorization within 50 min | Dao et al. (2017)                      |
| Hebei, China     | Acid Orange 3 (AO3) | Ultrasonic assisted Fenton process; $[\text{H}_2\text{O}_2] = 5.4$ mM, $[\text{AO3}]_0 = 100$ mg L$^{-1}$, pH 3, catalyst dosage = 2.5 g L$^{-1}$, ultrasonic frequency = 25 kHz | 96% AO3 degradation in 160 min | Li et al. (2010)                        |
| Punjab, India    | Reactive Black 5 (RB5) | Solar Fenton process; $[\text{H}_2\text{O}_2] = 2.2$ mM, pH 3, $[\text{RB5}]_0 = 100$ mg L$^{-1}$ | 90% RB5 degradation within 30 min and 93% decolorization in 15 min | Rajput et al. (2016)                    |
| Santander, Colombia | Amoxicillin (AMX) | Photo-Fenton process; catalyst dosage = 1 g L$^{-1}$, pH 7.1, $[\text{H}_2\text{O}_2] = 10$ mmol L$^{-1}$, $[\text{AMX}]_0 = 50$ mg L$^{-1}$, UV irradiation lamp (150 W) | 36.1% AMX degradation | Ramírez-Franco et al. (2019)            |
| China            | Rhodamine B (RhB) | Microwave assisted Fenton process; $[\text{H}_2\text{O}_2] = 2$ mmol L$^{-1}$, catalyst dosage = 15 g L$^{-1}$, pH 3, $[\text{RhB}]_0 = 10$ mg L$^{-1}$, $P_{\text{MW}} = 0.1$ Kw | 91.6% RhB decolorization in 20 min | Wang et al. (2019a, b)                   |
| Dalian, China    | $p$-Nitrophenol ($p$-NP) | Fenton process; pH 2, $[\text{H}_2\text{O}_2] = 166.5$ mg L$^{-1}$, catalyst dosage = 10 g L$^{-1}$, $[\text{p-NP}]_0 = 100$ mg L$^{-1}$ | 98% COD removal | Zhang et al. (2012)                     |
| Candiota, Brazil | Procion Red HE7B | Photo-Fenton process; Vis irradiation lamp (85 W), $[\text{HE7B}]_0 = 50$ mg L$^{-1}$, catalyst dosage = 0.6 g L$^{-1}$, pH 3, $[\text{H}_2\text{O}_2] = 4.0$ mmol L$^{-1}$ | 93% HE7B decolorization in 60 min and 85% TOC removal in 240 min | This work                              |
The catalytic efficiency of ash under optimum experimental conditions (catalyst load = 0.6 g L⁻¹; pH 3.0; H₂O₂ concentration = 4.0 mmol L⁻¹) was 93.6% decolorization at 60 min, and 85% TOC removal at 240 min, proving to be a promising cost low catalyst for photo-Fenton reaction. Also, the ash presented good stability and low levels of deactivation even after five consecutive uses. The reaction intermediates in photo-Fenton system were identified and an associated reaction pathway was proposed.

**Fig. 10** Dye mineralization in photo-Fenton process. Experimental conditions: C₀ = 50 mg L⁻¹; catalyst load = 0.6 g L⁻¹; pH 3.0; H₂O₂ concentration = 4 mmol L⁻¹

**Fig. 11** Effect of the oxidation radicals on the Procion Red decolorization efficiency. Experimental conditions: C₀ = 50 mg L⁻¹; catalyst load = 0.6 g L⁻¹; pH 3.0 and H₂O₂ concentration = 4 mmol L⁻¹

**Fig. 12** Catalyst reusability assays. Experimental conditions: C₀ = 50 mg L⁻¹; catalyst load = 0.5 g L⁻¹; pH 3.0; H₂O₂ concentration = 4 mmol L⁻¹

| Run  | Leached iron (mg L⁻¹) | %, leached Iron |
|------|-----------------------|-----------------|
| 1    | 1.4                   | 8.1             |
| 2    | 1.2                   | 7.5             |
| 3    | 0.9                   | 6.1             |
| 4    | 0.83                  | 6.03            |
| 5    | 0.77                  | 5.95            |

The size in the range of 0.5–20 µm. The catalytic efficiency of ash under optimum experimental conditions (catalyst load = 0.6 g L⁻¹; pH 3; H₂O₂ concentration = 4.0 mmol L⁻¹) was 93.6% decolorization at 60 min, and 85% TOC removal at 240 min, proving to be a promising cost low catalyst for photo-Fenton reaction. Also, the ash presented good stability and low levels of deactivation even after five consecutive uses. The reaction intermediates in photo-Fenton system were identified and an associated reaction pathway was proposed.
Fig. 13  a Mass spectra of Procion Red dye and b proposed mechanism of dye degradation reaction

- Mass spectra of Procion Red dye
- Proposed mechanism of dye degradation reaction
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