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Catalytic wet hydrogen peroxide oxidation of phenolic compounds in coffee wastewater using Al–Fe-pillared clay extrudates

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ABSTRACT

The effluents from the biological treatment of coffee wet processing wastewater (CWPW) contain non-biodegradable compounds, which are toxic to aquatic ecosystems. In this study, Al–Fe-pillared bentonite extrudates shaped into Raschig rings were used to catalyze the oxidation of the phenolic compounds in CWPW. The catalytic wet hydrogen peroxide oxidation was tested in a semi-batch basket reactor at 25 °C under atmospheric pressure. Al–Fe-pillared bentonite extrudates achieved a 62.4% total phenol conversion with a 67.5% selectivity toward CO_2 after 96 h. Catalytic performance of the Al–Fe-pillared bentonite extrudates in the oxidation of phenolic compounds shows the potential of applying this catalyst for the treatment wastewaters. The implementation of systems for wastewater treatment is essential to the conservation of natural resources and the preservation of Colombian biodiversity, therefore, this research is a contribution to the sustainable development of coffee growing.

Keywords: CWHPO; Coffee wastewater; Al–Fe-pillared clay; Extrudates; Phenolic compounds

1. Introduction

According to the International Coffee Organization (ICO), coffee is the most widely traded tropical agricultural commodity. Approximately 70 countries produce coffee, and the exporting members of the ICO generate over 97% of the global output. In 2010, the coffee sector employed an estimated 26 million people across 52 countries [1].

Coffee is grown in Africa, Asia, and Latin America. Brazil is the largest producer, followed by Vietnam, Indonesia, and Colombia. The two main species grown for coffee production are Arabica (*Coffea arabica*) and Robusta (*Coffea canephora*) [2]. Coffee beans must be removed from the fruit and dried before they can be roasted, and this step can be completed by either the dry method or the wet method. The wet method generates better coffee than the dry method.

The dry method, also called the natural method, involves drying the whole cherry. The coffee cherries are laid out in the sun and after the husk of the dried cherry is mechanically removed. The dry method is used to process approximately 90% of the Arabica

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coffee in Brazil, most of the coffee produced in Ethiopia, Haiti and Paraguay, and some Arabica coffees produced in India and Ecuador. Almost all Robusta coffees are processed using this method [1].

The wet method, also called the washed method, requires specific equipment and substantial quantities of water. After sorting and cleaning, the pulp is removed from the cherry. This operation is the key difference between the dry and the wet method because during the wet method, the pulp is separated from the beans before drying [1]. In Colombia, there are two types of wet processes: conventional and ecological. The conventional process uses water to de-pulp and wash the fermented coffee (removal of mucilage), consuming 40 L of water/kg of parchment coffee [3], and the ecological process developed by The National Coffee Research Center of Colombia—Cenicafé, which performs dry de-pulping and mechanical demucilaging, uses water in the washing stage at a rate of 5 L/kg of parchment coffee [4]. The Colombian Arabica coffee obtained using the wet method has a medium/high acidity and body, as well as a pronounced and complete aroma.

One disadvantage of wet coffee processing is the use of large volumes of water, generating equivalent amounts of wastewaters, and this wastewater contains a high content of suspended and dissolved organic matter. Coffee wet processing wastewater (CWPW) is rich in sugars and pectins, making it amenable to rapid biodegradation [3,5]. Consequently, Cenicafé has developed a modular anaerobic treatment system (SMTA, the Spanish acronym) using hydrolytic, acidogenic, and methanogenic reactors to treat the coffee processing wastewater before it is released, reducing the chemical oxygen demand (COD) by approximately 87% [6]. The remaining COD in the effluent is not easily degraded because it includes recalcitrant compounds, such as phenolic compounds [7]. Although anaerobic digestion has been applied with varying degrees of success while treating coffee processing wastewater [6,8–10], the effluent is still toxic to aquatic ecosystems [11,12]. Therefore, combining processing systems (biological and chemical) to treatment of the coffee wastewater may be a good strategy [13,14].

Among the advanced oxidation processes, the activation of hydrogen peroxide with a solid catalyst (catalytic wet hydrogen peroxide oxidation, CWHPO) is one of the most promising processes used to oxidize phenols [15] and phenol-like compounds during the treatment of wastewater [16,17]. Pillared clays containing Al–Fe (Al–Fe-PILCs) are promising catalysts for the CWHPO of phenol because they combine a porous support with active sites capable of degrading organic compounds. In general, Al–Fe-PILCs are efficient catalysts for phenol removal under mild conditions (atmospheric pressure and room temperature) without considerable leaching of metal ions [18–23]. The advantage of using extrudates based on pillared bentonites with Al–Fe is that these materials retain the properties of the pillared clay (high specific surface area and reactivity), exhibit good mechanical stability and do not disintegrate upon contact with water [24]. Moreover, when using a catalyst extrudates, a separation process (filtration or centrifugation) is not required for the reaction medium, unlike catalysts used in a powdered form. These aspects make catalyst extrudates an attractive alternative for treating wastewater.

This study is the first to propose an efficient solution for degrading the recalcitrant pollutants in the CWPW produced in Colombia. The Al–Fe-pillared bentonite extrudates were shaped into Raschig rings and used during the oxidation of the phenolic compounds in CWPW. Changes in the structure and texture of the catalyst extrudates were evaluated using X-ray diffraction (XRD), infrared spectroscopy (IR), and N_2 adsorption at 77 K before and after eight oxidation tests.

2. Materials and methods

2.1. Characterization of CWPW

The coffee wastewater generated during wet coffee (*Coffea arabica*) processing contains mechanically removed mucilage and leached of pulp. This CWPW was treated in a hydrolytic, acidogenic, and methanogenic reactor located in Hacienda Venecia in Manizales, Colombia for 38 days [25]. The effluent from this biological treatment system is the CWPW sample used for this study.

The physicochemical characterization of the CWPW was performed by an accredited laboratory according to the Standard Methods for the Examination of Water and Wastewater [26]. The CWPW samples for the oxidation tests were filtered and frozen at −18 °C until used. The total organic carbon content (TOC) in the filtered sample was determined with a Torch Analyzer (Teledyne Tekmar, Ohio, USA); this instrument uses sample combustion to generate CO_2, which is measured with a non-dispersive infrared detector. Measurements of TOC were carried out by triplicate and, in all tests, the relative error was lower than 4%. The total phenolic content was determined colorimetrically using the Folin–Ciocalteau reagent to test the phenolic compounds during phosphomolybdic–phosphotungstic reagent reduction [27,28]. For this purpose, a calibration curve of gallic acid in the concentration range of 0–100 ug/mL was prepared, with a correlation coefficient (r^2) of 0.999 and a detection limit of 1.05 ug/mL. Phenolic content was determined by duplicate, and the difference between the measurements was always less than 2%.

2.2. Extraction of phenolic compounds from the coffee wastewater and the chromatographic profiles

The extraction process for the phenolic compounds in the CWPW was conducted using a procedure similar to that used for olive mill wastewater [29]. First, 10 mL of CWPW was diluted fivefold and extracted with ethyl acetate (5 × 5 mL) while stirring. The organic extracts were mixed, treated with sodium sulfate and dried at 35 ℃ using a rotary evaporator. The residue was dissolved in 900 μL of methanol and purified via solid phase extraction with a copolymer of styrene and divinylbenzene (LiChrolut IN, Merck). The final extract was stored at −18 ℃ until analysis by high-performance liquid chromatography (HPLC).

The chromatographic profiles of the phenolic compounds in the coffee wastewater extract (before and after CWHPO treatment) were obtained using a Shimadzu Liquid Chromatograph with a Premier C_{18} column (150 × 4.6 mm i.d.), a deuterium lamp, and a UV–vis detector. Two mobile phases composed of water/formic acid/acetonitrile (A, 95:1:4% *v*/*v* and B, 39:1:60% *v*/*v*) were used at 0.4 mL/min. The gradient was applied according to the following proportions of mobile phase B: 0–2 min, 6%; 2–33 min, 50%; and 33–40 min, 6%. All the measurements were performed at 280 nm.

2.3. Catalyst characterization

The details for manufacturing the catalyst extrudates based on Al–Fe pillared bentonite and the results for the analyses of chemical stability, mechanical resistance, and EPR spectroscopy are described in the literature [24,30]. The final dimensions of the Raschig rings (catalyst extrudates) were $d_{\text{ext}} = 4.25$ mm, $d_{\text{int}} = 2.40$ mm, $h = 6.0$ mm, and a 31.9% void fraction.

The catalyst extrudates (labeled as Al–Fe-PILC extrudate) were characterized using XRD, IR, and the adsorption–desorption of N_2 at 77 K. The XRD patterns were collected with a LabX Shimadzu XRD-6000 diffractometer using Cu–Kα radiation (steps of 0.01 °2θ at 2 s/step). The infrared spectra were recorded from 4,000 to 400 cm^{-1} on a Perkin Elmer Spectrum BX spectrometer. The nitrogen adsorption–desorption isotherms were measured with a Micromeritics ASAP 2020 instrument at 77 K after outgassing the samples for 1 h at 90 ℃ and 3 h at 400 ℃ under vacuum. The above analyses were performed before and after the catalytic activity tests.

2.4. Catalytic wet peroxide oxidation of coffee wastewater

The activity of the catalyst extrudates was evaluated during the oxidation of the phenolic compounds in CWPW. A semi-batch glass basket reactor with the following characteristics was used: 400 mL capacity, open to the atmosphere, maintained at 25 ℃, constant magnetic agitation (700 rpm), and supplied with four plastic mesh baskets attached to a stainless steel shaft that was connected to a motor. This reactor is similar to that used during an oxidation test with phenol [24,30]. The tests were performed using 250 mL of coffee wastewater diluted fivefold with deionized water, 4.10 g of the catalyst extrudates (2.46 g of active phase), 0.17 M hydrogen peroxide solution (2 mL/h), bubbling air (2 L/h), and a continuously adjusted pH (3.7) using 0.1 M NaOH or HCl.

To analyze the oxidation capability of the coffee wastewater and the stability of the catalyst extrudates, successive tests in the basket reactor were performed. Once each test was completed (every 12 h), the catalyst extrudates was separated from the CWPW solution (removing the basket), washed with distilled water and dried for 2 h at 60 ℃ before being used again with the same CWPW for additional reaction cycles. Eight successive tests, totaling 96 h, were performed. The Fe ions that leached into the CWPW solution during the last test were analyzed. All catalytic experiments were performed in duplicate.

The total phenol conversion in CWPW was monitored using the Folin–Ciocalteu colorimetric method. The selectivity of the catalyst toward CO_2 and H_2O (grade of mineralization) was evaluated using the TOC data collected at the beginning and end of the reaction.

3. Results and discussion

Table 1 shows the results of the physicochemical characterization of the CWPW. In general, the effluent from the biological treatment system had a high organic load because the treatment achieved only a

Table 1
Physicochemical parameters of the coffee wastewater after biological treatment

Parameters	Value
pH (units)	4.2
BOD_5 (mg O_2/L)	22,330
COD (mg O_2)/L	38,416
Total phenolic content (μg/mL)	4,661
TOC (mg C/L)	9,038

50.8% reduction of chemical oxygen demand (COD before and after biological treatment of 78,094 and 38,416 mg O_2/L, respectively); this value is lower than that of the SMTA developed by Cenicafé [6]. The CWPW still contained biodegradable organic matter due to the high biochemical oxygen demand. However, the difference between the COD and BOD_5 suggests the existence of non-biodegradable organic matter represented primarily by phenolic compounds.

Considering the high organic load of CWPW, this sample was diluted five times with distilled water for the oxidation tests. Therefore, the diluted wastewater used in the catalytic tests contained 932 μg/mL of total phenolic compounds and 1808 mg/L of TOC.

Fig. 1 shows the XRD patterns of the catalyst extrudates before and after the CWHPO tests. The diffraction patterns of the Al–Fe-PILC extrudates showed the characteristic signal of pillared bentonite (d_{001} = 18.0 Å) and the natural clay used as a binder (d_{001} = 10.1 Å) [24,30]. The diffraction pattern of the catalyst extrudates after 96 h in the oxidation reaction differed from that of the fresh catalyst extrudates. The XRD signal corresponding to the d_{001} of pillared clay was shifted toward a minor basal spacing due to a partial collapse of the pillared bentonite structure after prolonged use.

The IR spectrum for the fresh catalyst extrudates is shown in Fig. 2. The bands in the infrared spectrum were identified by comparisons with data in the literature [31,32]. The bands at 3,438, 1,639, and 1,653 cm^{-1} are due to adsorbed water. The signals at 1,043 and 798 cm^{-1} are attributed to the Si–O bond stretches in the clay structure and quartz, respectively. The vibrations of the structural O–H bonds corresponding to the dioctahedral smectites characteristic of Al_2OH groups produced signals at 3,620 cm^{-1}. The band at 473 cm^{-1} is assigned to the Si–O–Si bending vibrations.

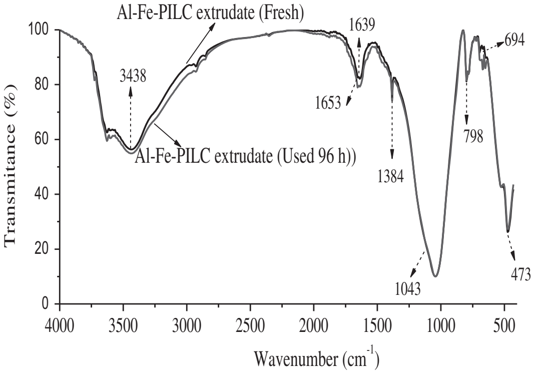

Fig. 2. IR spectra of catalyst extrudates before and after the catalytic tests.

In both cases (fresh and used), the catalyst showed the same IR spectrum, which was primarily attributed to the clay mineral (smectite), indicating that no significant structural change occurred at the molecular level after using the catalyst extrudates. No additional bands generated by the adsorption of the organic molecules present in the wastewater nor in those molecules generated during the oxidation reaction (by-products) were observed, evidencing that the reaction occurs only through the decomposition of hydrogen peroxide (to yield free radicals) at the active sites without any significant adsorption of organic molecules.

Fig. 3 shows the N_2 adsorption–desorption isotherms for the fresh and used catalyst extrudates. According to the IUPAC classifications, the adsorption isotherms and hysteresis cycles are type II (with a tendency toward type I) and H3, respectively. This type

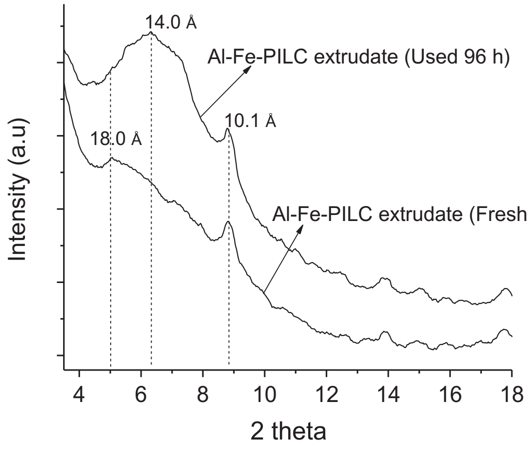

Fig. 1. XRD profiles of the catalyst extrudates before and after the catalytic tests.

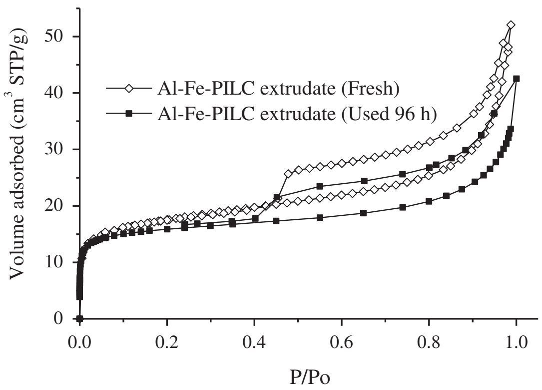

Fig. 3. Nitrogen adsorption–desorption isotherms of the catalyst extrudates before and after the catalytic tests.

Table 2
Textural characterization of the catalyst extrudates

Sample	$S_{\text{BET-Remy}}$ (m^2/g)	S_{External} (m^2/g)	$S_{\text{micropore}}$ (m^2/g)	$V_{\text{micropore}}$ (cm^3/g)
Al–Fe-PILC extrudate (fresh)	70	33	37	0.0131
Al–Fe-PILC extrudate (used 96 h)	64	28	36	0.0127

of isotherm is characteristic of solids with a mixed porosity (micropores/macropores) and a multilayer formation [33,34]. Type H3 hysteresis is usually displayed by the aggregates of plated particles or solids containing slit-shaped pores. To determine the specific surface area of the catalyst extrudates, a BET model corrected was used [35]. The micropore area and volume were determined using the *t* curves (statistical thickness between 3.5 and 5.0 Å using the Harkins–Jura equation) [34]. The texture analysis is summarized in Table 2. The specific surface area of the catalyst extrudates was smaller than that found for the pillared bentonite with Al–Fe ($S_{\text{BET-Remy}} = 138\ m^2/g$) due to the smaller specific surface area of the raw bentonite added as binder ($S_{\text{BET-Remy}} = 44\ m^2/g$) [24].

The catalytic activity of the Al–Fe-PILC extrudates was assessed during long-term experiments examining the oxidation of phenolic compounds in CWPW. Fig. 4 shows the consecutive tests of the CWHPO for the reduction of phenolic compounds from the coffee wastewater. The catalyst extrudates reached 62.4% total phenol conversion after 96 h. The TOC conversion was 67.5% for the same catalyst extrudates after 96 h. Once the reaction was complete (96 h), the catalyst extrudates was removed, and the aqueous medium was recovered and analyzed. The medium exhibited an iron concentration of 0.62 mg/L, demonstrating the high stability of the active phase in the reaction medium. Therefore, the catalytic activity of Al–Fe-PILC was successfully introduced in a tailored catalyst extrudates for both total phenol conversion and TOC abatement in real wastewater.

Catalytic activity of Al–Fe-pillared clay extrudates in the oxidation of CWPW was lower than that found for phenol (model molecule, 100% phenol conversion, and 42% TOC conversion after 8 h of reaction) [30]. This result is attributed to the complexity of coffee wastewater, in which a variety of phenolic compounds [7] and high organic matter content have been found.

The binding material (bentonite) did not significantly contribute to the catalytic activity of the catalyst extrudates because, after 96 h of reaction, the powdered binding material alone only achieved 8% total phenol conversion. This catalytic activity was attributed to the Fe in the bentonite (6.9 wt%). For the binding extrudates, the catalytic tests were not performed because this sample was not mechanically stable in the reaction medium, and it disintegrated after 6 h. If catalytic tests could be performed with the binding extrudates, the conversion of the phenolic compounds would be less than that found with the binder in powder form due to the intraparticle diffusion resistance generated by the agglomeration process.

The catalytic activity observed in this research differs from those obtained during the oxidation tests with coffee wastewater from Cenicafé in a previous study for several reasons [13]: (1) the catalyst used in previous study was powdered Al–Fe-PILC and not an extrudate, (2) the total phenolic content in the CWPW from Cenicafé was 165 µg/mL, which is lower than the CWPW from Hacienda Venecia (total phenol in the diluted sample of 932 µg/mL), and (3) the COD of the CWPW from Cenicafé was 551 mg O_2/L, while the CWPW from the Hacienda Venecia was 38,416 mg O_2/L. The difference in the organic loads of these two coffee wastewaters is attributed to their respective origins. The CWPW from Cenicafé was obtained from a pilot-scale bioreactor (SMTA) operating under optimal conditions; this system removes most of the biodegradable organic matter [6]. The CWPW from Hacienda Venecia is from a biological reactor that processes higher volumes of water with a COD of 78,094

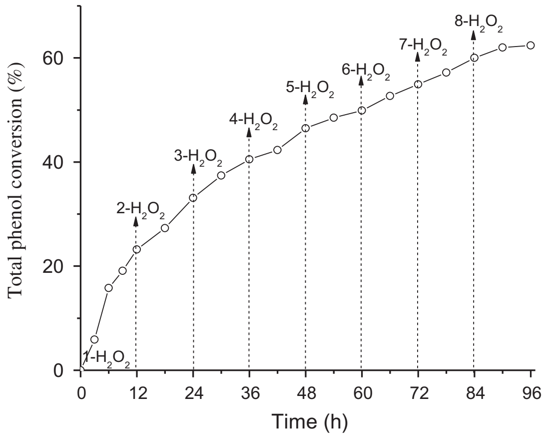

Fig. 4. Total phenol conversion in the CWPW. Each H_2O_2 dose corresponds to a CWHPO test using the Al–Fe-pillared bentonite extrudates.

mg O_2/L; this reactor only removes 50.8% of the initial organic load.

The performance of Al–Fe-PILC extrudates in the oxidation of phenolic compounds and the TOC abatement in coffee wastewater were higher than those found in the olive oil milling wastewater using iron-based pillared clays (powder catalyst). In this case, the TOC abatement was about 20%, but it should be taken into account that the initial value is quite high (TOC of 28,000 mg/L before filtration). The polyphenolic compounds conversion reached 45% (initial concentration of polyphenolic compounds of 780 mg/L) [40]. However, in the present research, the catalyst was used in shape of extrudates, which become an advantage for possible application in wastewater treatment.

The CWPW samples were analyzed using HPLC before and after catalytic oxidation, and two representative chromatograms are shown in Fig. 5. The different phenolic compounds are present in the original sample, but they do not appear in the chromatogram after 96 h of catalytic oxidation. This result is consistent with the elimination of phenolic compounds and TOC abatement observed during the catalytic tests.

In general, the catalyst extrudates based on the Al–Fe pillared bentonite retained its catalytic activity, preserving mechanical stability (no cracks) in the reaction medium over at least eight consecutive tests. After eight cycles, the partial collapse of the pillared bentonite structure was consistent with the slight decrease in the textural properties of the catalyst extrudates.

The COD was not measured after the oxidation tests because this parameter is vulnerable to interferents, such as ferrous ion [26], nitrites [36], chlorides [37], and hydrogen peroxide (added during the reaction) [38,39]; in addition, this analysis requires special treatments that are incompatible with the reaction conditions. The TOC is less vulnerable to interferents than the COD measurement, particularly with regard to nitrogenous matter; this method is also more rapid and reproducible. Additionally, TOC analysis is relatively free from matrix effects.

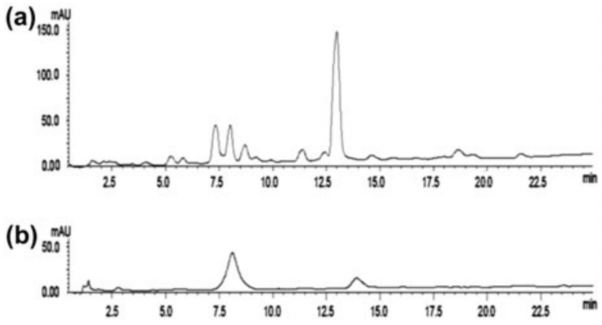

Fig. 5. Chromatographic profiles of the CWPW extracts: (a) untreated original sample and (b) sample after 96 h of CWHPO using the Al–Fe-pillared bentonite extrudates.

Therefore, the Al–Fe-PILC extrudates can be used to oxidize the phenolic compounds in coffee processing wastewater, becoming an efficient method for reducing the amount of organic material measured as TOC.

4. Conclusions

The Al–Fe-pillared bentonite extrudates were effective catalysts for the wet hydrogen peroxide oxidation of phenolic compounds and TOC abatement in CWPW, at mild operating conditions (temperature of 25 °C and atmospheric pressure). The catalyst extrudates achieved a 62.4% total phenol conversion and 67.5% selectivity toward CO_2 after 96 h. This extrudate showed catalytic activity during eight consecutive oxidation tests without considerable iron leaching. Catalytic performance of the Al–Fe-pillared bentonite extrudates in the oxidation of phenolic compounds shows the potential of applying this catalyst for the treatment of real wastewaters. The implementation of systems for wastewater treatment is essential to the conservation of natural resources and the preservation of Colombian biodiversity, therefore, this research is a contribution to the sustainable development of coffee growing.

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