Al/Cu-PILC as a Photo-Fenton Catalyst: Paracetamol Mineralization

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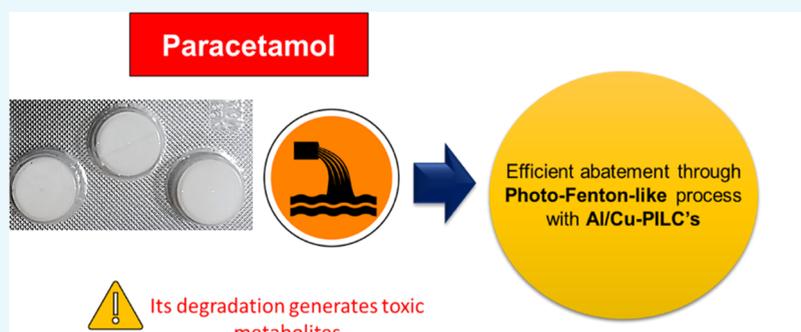
ABSTRACT: Pillared clays have shown to effectively catalyze the photo-Fenton process without the necessity of acidic conditions, which is a very attractive feature from the perspective of environmentally friendly processes, especially when high natural abundance of chemical elements are incorporated. In this work, the catalytic activity of Al/Cu interlayered pillared clays for the degradation and mineralization of paracetamol through a photo-Fenton-like process was investigated. Al/Cu-pillared clays were prepared by adding ane Al/Cu pillaring solution to a bentonite suspension. X-ray diffraction (XRD) confirmed the enlargement of the interlayer space of the clay provoked by the pillaring process and Al and Cu species in the prepared samples were verified by atomic absorption spectroscopy (AAS). The specific surface area of pure bentonite was 2-fold increased after the Al/Cu pillaring process. A synthetic paracetamol solution with an initial concentration of 100 ppm was prepared for the assessment of the activity of the prepared materials. Different catalyst concentrations were tested (0.2, 0.5, 0.75, and 1 g L^{-1}) and the complete removal of paracetamol was achieved in all cases, but the highest mineralization rate (69.8 mg total organic carbon (TOC) g$_{cat}^{-1}$ h^{-1}) corresponds to the catalyst loading of 0.5 g L^{-1}. An ultraviolet-C (UVC) light source was employed, and no adjustment of the pH to acidic conditions was needed to achieve these results. Liquid chromatography coupled to mass spectroscopy (LC-MS) was employed to identify the reaction intermediates of paracetamol degradation. A proposed pathway for the oxidation of paracetamol molecule is presented. The effect of Cu content in the pillared clay and the stability and reusability of the catalyst were also assessed. The kinetic constants of paracetamol removal were 0.2318 and 0.0698 min^{-1}, under photo-Fenton and UV + H$_2$O$_2$ processes, respectively.

1. INTRODUCTION

Paracetamol, also known as acetaminophen, is classified as a non-steroidal anti-inflammatory drug (NSAID) with wide use around the world due to its accessibility without prescription. Despite its benefits as painkiller, its extended use has received growing interest from the scientific community since its degradation is able to produce toxic metabolites that are released into the environment.[1,2] It has been reported that these toxic compounds are a potential source of cellular damage, inhibition of reproduction, or even, death of aquatic species.[3,4] The effective abatement of paracetamol by means of different water treatment procedures based on advanced oxidation processes (AOP's) has been reported in the literature[5−8] but among them, the photo-Fenton process has emerged as a promising alternative due to the utilization of widely accessible reagents (iron catalysts, H$_2$O$_2$, and a light source) in addition to the complete removal of the pollutant achieved under mild

reaction conditions.[9−11] The simplified chemical reactions involved in a photo-Fenton process are presented in eqs 1−3[12]

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO\bullet + H^+ \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \tag{2}$$

$$\bullet OH + \text{organic pollutants} \rightarrow \text{oxidized products} \tag{3}$$
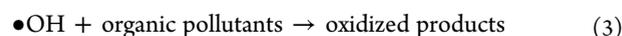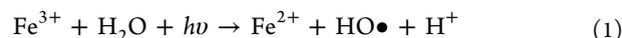
Although photo-Fenton has been demonstrated to be an effective alternative for water purification, this process exhibits as
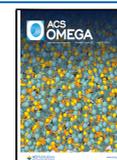
the main limitation the requirement of acidic reaction conditions to avoid iron precipitation.[13] In a previous work, we presented the utilization of Fe/Cu-pillared interlayered clays (PILC's) as alternative to overcome this issue.[14] The interest in employing clays as catalysts in photo-Fenton processes is given by their low cost, availability, and inexistent toxicity. During the last few years, extensive research has been conducted to develop materials with environmentally friendly properties for water purification, and they include metal−organic frameworks,[15,16] biochar-based catalysis,[17,18] and MXenes (transition metal nitrides, carbides, or carbonitrides).[19] Particularly, PILC's are composed of laminar solids with a permanent porous structure commonly obtained from natural clay minerals. These materials are synthesized through a cationic exchange process that involves the displacement of the cations from the natural material by hydroxyl-metal polycations. After thermal treatment, polycations become oxide species within the interlayer, keeping the layers separate and avoiding structure collapse, such oxides are the so-called pillars of the PILC.[20,21] Fe/Cu-PILC's were employed as the catalyst for the photo-Fenton process where paracetamol was completely removed under circumneutral pH conditions (5.8) although iron leaching was also reported. Thus, to decrease this problem, iron substitution would be desirable. In this context, alternative materials to iron compounds have been studied to conduct the pillaring process and among them, aluminum exhibits interesting properties like its high natural abundance (most abundant metal in earth's crust), low weight (three times lighter than Fe), and chemical stability in its oxidized form.[22] The presence of aluminum in the pillars produces a considerable increase in the specific surface area.

Since in Al-PILC's the only accessible oxidation state for aluminum (Al) is Al^{3+}, the electron transfer reaction between Al^{3+} and H_2O_2 to generate OH radicals is not possible[23] and, in this sense, the incorporation of chemical elements with multiple redox states is appropriate. A common alternative is copper since both, the monovalent (Cu^+) and divalent (Cu^{2+}) oxidation states directly decompose H_2O_2 into •OH through conventional Fenton-like pathways eqs 4−5[22,24]

$$Cu^{2+} + H_2O_2 \rightarrow Cu^+ + HO_2^\bullet + OH^- \quad (4)$$

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^\bullet + OH^- \quad (5)$$
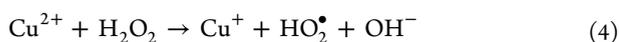
In this context, herein, the utilization of Al/Cu-PILC as a catalyst to achieve efficient abatement of the paracetamol molecule by a photo-Fenton-like process is proposed. Several authors have reported the utilization of this kind of materials in the catalytic wet peroxide oxidation (CWPO)[21,22,25] and the electro-oxidation[26] of organic compounds but the research related to the photo-Fenton-like process is inexistent to the best of our knowledge. Therefore, this work aimed, to assess the feasibility of using Al/Cu-PILC as a catalyst of a photo-Fenton-like process and to establish the Paracetamol oxidation and mineralization efficiency and pathway by the aforementioned process.

2. MATERIALS AND METHODS

2.1. Reagents. Pillared clays were prepared from bentonite (pure-grade) supplied by Fisher Scientific. Aluminum chloride hydrate ($AlCl_3 \cdot 6H_2O$) and copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) were provided by Fermont and J.T Baker respectively and NaOH from Fermont. Hydrogen peroxide (30%) supplied by Fermont was used to conduct the photo-Fenton-like process. Paracetamol ($C_8H_9NO_2$) was purchased

from Alfa Aesar. All reagents were of analytical grade and used without further purification.

2.2. Catalysts Synthesis. Al/Cu-pillared interlayered clay samples were prepared following the procedure reported by Galeano et al.[27] This consists in the direct introduction of the Al/Cu pillaring solution into the dilute bentonite suspension. Mixed-oxide pillars were prepared by the slow addition of a 0.2 M NaOH aqueous solution to Al and Cu chlorides (0.18 and 0.02 M, respectively) solutions at 65 °C under continuous stirring (ratio (OH/(Al + Cu) = 2.0)). To evaluate the effect of Cu content on paracetamol mineralization, other samples with different Cu chloride concentrations were prepared. Separately, the bentonite suspension (0.02% w/w) was prepared by incorporating the bentonite powder into the appropriate amount of deionized water.

After that, the pillaring solution was added dropwise to the bentonite suspension. The mixture was then kept under continuous vigorous stirring for over 12 h followed by the separation of the prepared catalyst powder by centrifugation for further chloride ion elimination through a washing process with deionized water until the conductivity of the liquid phase reached 5 μS cm^{-1}. The final sample was dried overnight at 70 °C and calcined at 400 °C for 2 h.

2.3. Catalyst Characterization. Characterization of the Al/Cu-PILC catalyst sample was carried out by X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and nitrogen physisorption. The XRD pattern was obtained in a Bruker Advance 8 instrument using Cu Kα radiation at 35 kV and 30 mA. Al and Cu content (wt %) was determined by AAS in an AA240FS VARIAN spectrometer. The analyzed samples were dissolved in hydrofluoric acid and diluted down to the interval of measurement. The specific surface area of the pillared clay was determined from data of N_2 physisorption carried out in an Autosorb-1 analyzer (Quantachrome instruments). Degasification of the sample (2 h) was required prior to adsorption measurements. The specific surface area of the pillared clay was calculated according to the Brunauer−Emmett−Teller (BET) method.

2.4. Paracetamol Degradation. Paracetamol degradation by photo-Fenton-like experiments was carried out in a Pyrex glass reactor (dimensions: 20 cm length, 2.5 cm diameter). Then, 0.1 L of aqueous solution of paracetamol (C_0 = 100 ppm) was loaded in the reactor in all experiments. The temperature of the reaction system (298 K) was controlled by a thermal bath. An UVP-Pen Ray Model 3SC-9 high-pressure mercury lamp (8W) was employed as the light source providing radiation at 254 nm. The lamp was placed inside the reactor in the central axis. In a typical experiment, 50 mg of the catalyst were dispersed in the paracetamol solution by magnetic stirring at 800 rpm followed by the incorporation of a stoichiometric amount of H_2O_2 (145 μL) into the system, and finally, illumination was turned on. Samples were periodically withdrawn from the reactor to determine paracetamol and by-product concentrations and total organic carbon (TOC) content at different times. For this purpose, liquid chromatography coupled to mass spectroscopy (LC-MS) and TOC analyses were conducted. Each sample was first filtered using polyethersulfone membrane filters (0.45 μm pore size) prior to analysis.

LC-MS analyses for the detection and quantification of paracetamol and its sub-products were carried out in an Agilent 1220 series high-performance liquid chromatography (HPLC) system (Agilent Technologies, Mississauga, ON, Canada) coupled with an Agilent 6530 LC/MS Q-TOF spectrometer

equipped with electrospray ionization (ESI) source (gas temperature, 350 °C; drying gas, 10 L min^{-1}; nebulizer, 13 psig; sheath gas temperature, 325 °C; sheath gas flow, 8 L min^{-1}; Vcap, 3500 V; fragmentor voltage, 60 V). Samples were analyzed in the positive ion mode, and mass spectra were collected between 30 and 500 m/z. During analysis, the injected sample volume was 2 μL, the flow rate of the mobile phase was 0.4 mL min^{-1} and the temperature column (100 mm × 2.1 mm, 1.8 μm, Eclipse Plus C18, Agilent) was kept at 35 °C. The mobile phase composition was composed of an aqueous phase (water, A) and an organic phase (acetonitrile, B) with 1% v/v formic acid. Additionally, the elution gradient presented in Table 1 was used.

Table 1. Elution Gradient for Mobile Phase Composition

time (min)	A (%)	B (%)
0.0	20	80
3.0	40	60
5.0	70	30
5.3	40	60
5.5	20	80
6.0	20	80

Total organic carbon (TOC) of each sample was measured with a Shimadzu TOC-V$_{CSH}$ instrument with an integrated Shimadzu ASI−V autosampler after acidification and sparging to remove inorganic carbon. For both analyses, LC-MS and TOC, the error was established to be lower than 2%.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Characterization.
X-ray diffraction patterns of raw clay (Bentonite) and Al/Cu-pillared clay are depicted in Figure 1. As can be seen, the XRD pattern of
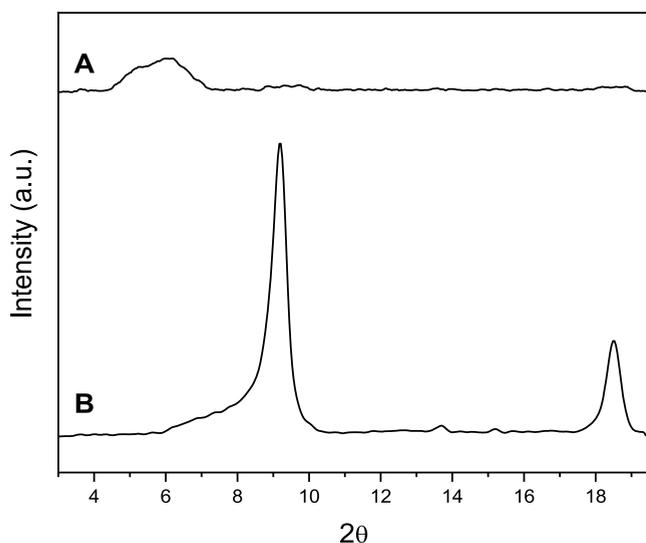
Figure 1. (A) XRD pattern of synthesized Al/Cu-pillared clay and (B) XRD pattern of bentonite.

bentonite exhibits crystallinity, and two main peaks are identified and located at 9 and 18° in the 2θ scale. The first peak is characteristic of raw clay and has been assigned to the basal (0 0 1) reflection (d$_{001}$) related to the distance between interlaminar layers of bentonite (9.8 Å). On the other hand, the XRD pattern of the Al/Cu-pillared clay shows a unique signal between 4 and 6°. It is expected that the introduction of Al and

Cu polycations into the interlayered spaces of the bentonite causes the sheets to separate and according to Dorado,[28] this reflection can be ascribed to the enlargement of the interlayer space provoked by the pillaring process. The interplanar distance estimated for this sample was 15.5 Å, confirming the enlargement of the distance between the layers of the pillared clay with respect to pure bentonite. Thus, by this means, the pillaring process was confirmed.

3.2. Textural and Physicochemical Properties.
It was found that Al/Cu-pillared clay sample possesses a mesoporous surface given by its average pore diameter of 3.83 nm. Textural properties of bentonite, Al-PILC and Al/Cu-PILC (specific surface area, pore volume) are summarized in Table 2. Regarding the metal content, the mixed Al/Cu-PILC sample contains 7.3% (wt) of Al in addition to 1.2% (wt) of Cu according to AAS analysis.

Table 2. Textural Properties of the Pillared Clays and Comparison with Pure Bentonite

material	specific surface area (m^2 g^{-1})	pore volume × 10^7 (m^3 g^{-1})
bentonite	35	0.58
Al-PILC	104	0.005
Al/Cu-PILC	89	1.24

The specific surface area of the starting clay was close to increasing 3-fold after the pillaring process with Al but it experimented a reduction when both cations, Al and Cu, were incorporated into the layered structure. This behavior has been reported for several mixed pillared clays[14,29,30] and the explanation is given by the less homogeneous intercalation of both cations in comparison to a unique metallic species to be intercalated to the layered clay structure. This fact is supported by the wide peak observed in the XRD pattern for the Al/Cu-PILC sample presented before where the crystalline structure is less predominant than in the case of pure bentonite. Bahranowski suggested that copper in the pillared matrix may be located at the following sites: (1) within the interlayer, with no strong bonds with either silicate sheets or pillars, (2) coordinated to the oxygens of the silicate layer, or (3) coordinated to a pillar.[31,32]

3.3. Paracetamol Degradation and Mineralization by the Photo-Fenton-Like Process.
In this work, Al/Cu-PILC was assessed as the catalyst for paracetamol oxidation by means of a photo-Fenton-like reaction, and the obtained results in terms of paracetamol degradation and percent of TOC removal are plotted in Figure 2. The catalyst concentration employed in these experiments was 0.5 g$_{cat}$ L^{-1} and for comparison purposes, some control experiments are also included.

It can be observed in Figure 2 (left) that complete degradation of paracetamol is achieved in about 20 min by means of a photo-Fenton-like experiment. The good performance of the Al/Cu-PILC catalyst studied in this work, can be explained as follows: According to Maekara et al.,[33] the higher solubility of copper in a wider pH range provides an opportunity for the Fenton-like operation under neutral pH conditions. The same authors found that, for phenol degradation through a Fenton process, the transformation of Cu^{2+} into Cu$^+$ with H$_2$O$_2$ via a Fenton-like reaction is a slow process ($k \sim 1\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at pH 7) but is followed by a fast regeneration of Cu^{2+} from Cu$^+$ with the generation of a strong oxidant, •OH radicals ($k = 4 \times 10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at pH 6−8). This mechanism allowed the efficient oxidation of organic compounds. On the other hand, Al-PILCs provide a larger
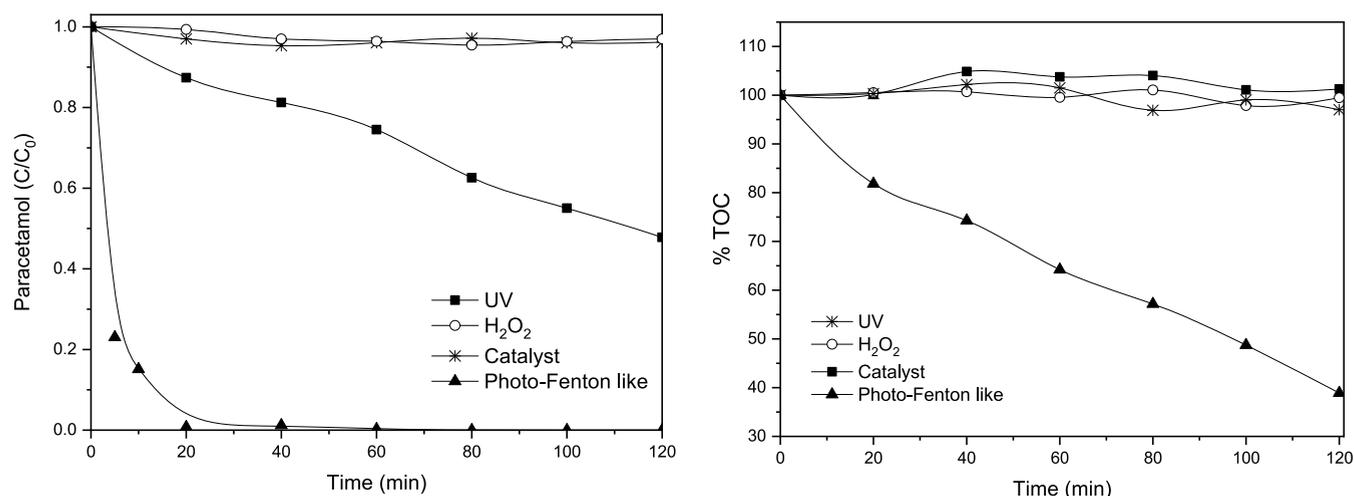
Figure 2. Paracetamol oxidation with an Al/Cu-PILC catalyst. Comparison of photo-Fenton-like process versus control experiments. Left panel: Normalized paracetamol degradation. Right panel: Percent of TOC. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8.

surface area and higher porosity which promote the higher dispersion of active phase[34] percent. It was found that complete mineralization of the organic molecules was not attained after 120 min but about 60% of the initial TOC was removed by the photo-Fenton-like process. An initial concentration of paracetamol of 100 ppm corresponds to a TOC concentration of 64 mg L^{-1} and the remaining TOC can be attributed to highly recalcitrant organic compounds derived from the degradation paracetamol molecule.

Nonetheless, from Figure 2, the efficiency of the photo-Fenton-like process is notorious since for the tested control experiments (UV, H$_2$O$_2$, and catalyst), the achieved paracetamol mineralization was negligible. About 50% of paracetamol was oxidized by means of the photolytic process (UV light). This has already been reported previously and ascribed to the photons in the radiation field being able to degrade the paracetamol molecule;[35] however, the original molecule was only decomposed into smaller compounds but not to CO$_2$. To extend our study to the oxidation of paracetamol, we performed additional experiments where the components of the photo-Fenton-like process were evaluated to elucidate their effect on the oxidation process. Figure 3 summarizes our findings concerning the degradation and mineralization of the pollutant molecule. Remarkably, all the experiments were performed at an initial pH of 5.8 avoiding the necessity of acidic reaction media for a successful Fenton-like process.

The oxidation of the paracetamol molecule exclusively by means of the PILC catalyst (1), H$_2$O$_2$ (2) or UV light (3), resulted in a negligible reduction of the TOC of the parent compound. On the other hand, the insignificant effect of the PILC catalyst on the paracetamol reduction, indicates low adsorption properties of this catalytic material. Furthermore, the combined effect of the PILC catalyst with peroxide and with UV light (4th and 5th bar) showed similar performance, about 50% of paracetamol was oxidized but less than 10% of the original TOC was removed.

Conversely, the combination of UV light and H$_2$O$_2$ leads to the complete removal of the paracetamol but the mineralization degree was about 20% lower than that attained with the photo-Fenton-like process. By doing this set of experiments we confirmed that the Al/Cu-PILC catalyst plays an important role in the generation of OH groups required for the oxidation of the
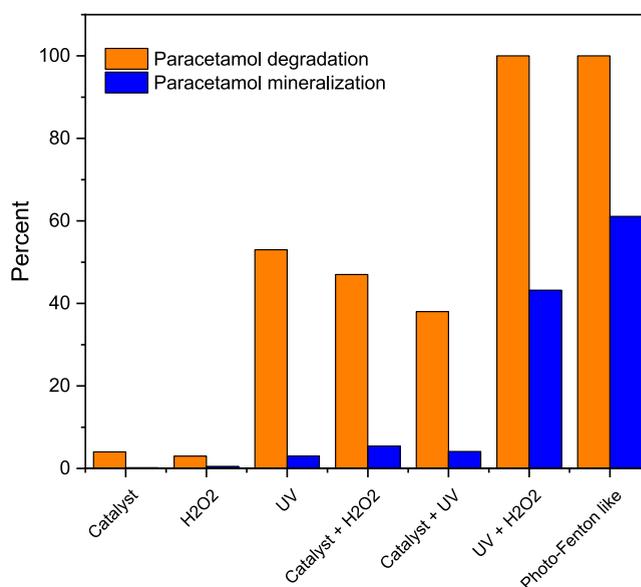
Figure 3. Summary of results of control experiments and photo-Fenton-like process for the oxidation of paracetamol after 120 min. Reaction conditions: Al/Cu-PILC catalyst concentration: 0.5 g$_{cat}$ L^{-1}; H$_2$O$_2$ volume: 145 μL; T = 298 K.

organic compound and this is attributed to the multiple oxidation states of the Cu that are continuously exchanging in a Fenton-like process and the generation of Lewis acid sites by means of the presence of Al that can contribute to the adsorption of organic molecules with a Lewis basic character.[22] Copper species have been recognized as photo-sensitive promising materials for environmental applications due to their low toxicity, low cost, and good environmental acceptability. Its use in photochemical reactions is highly motivated for its small band gap (∼2.0 eV in the case of Cu$_2$O), which makes it a suitable material to promote the utilization of visible light.[1,36]

The experimental data corresponding to UV, H$_2$O$_2$ + UV, and photo-Fenton-like reactions were adjusted to a pseudo-first-order kinetic model. A good fitting was obtained and the value of the apparent kinetic constants for these processes is given in Table 3 in addition to the determination coefficient (R^2). The

fitting of the model with the experimental points has been included as Supporting Information.

Table 3. Kinetic Parameters and Determination Coefficient of the Pseudo-First Order Kinetic Model

process	k (min^{-1})	R^2
Al/Cu-PILC + H$_2$O$_2$ + UV	0.2318	0.9892
H$_2$O$_2$ + UV	0.0698	0.9768
UV	0.0059	0.9956

3.4. Effect of Al/Cu Content. Samples with different content of Cu and with the same amount of Al (7.3 wt %) were prepared to evaluate the effect of Cu species on the TOC removal efficiency. A Cu percentage of 0, 0.58, and 1.2, was assessed. It was found that, in all the cases, TOC was reduced after 120 min and the degree of mineralization is related to the Cu content (see Figure 4). While almost 30% of the initial TOC
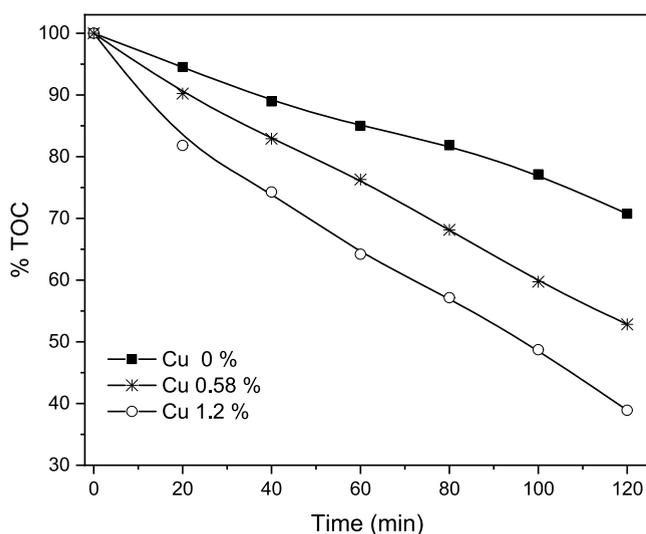
Figure 4. Effect of the Cu content of the Al/Cu-PILC on the TOC removal efficiency. Reaction conditions: Al/Cu-PILC catalyst concentration: 0.5 g$_{cat}$ L^{-1}; H$_2$O$_2$ volume: 145 μL; T = 298 K.

was removed exclusively by Al species, when Cu was incorporated into the sample, the removal of TOC was increased up to 60% (sample Cu 1.2%) after 120 min. This result demonstrates that the presence of Al and Cu facilitates the electron transfer required to generate OH radicals, which are responsible for the oxidation of the organic molecules in solution.

In the introduction section of this work, the chemical reactions involved in a Fenton-like process to produce the oxidant radicals are presented (eqs 4−5). In addition, when the reaction is conducted under illumination (Photo-Fenton-like), the generation of hydroxyl radicals occurs at a higher rate due to the photolysis of H$_2$O$_2$ (eq 6) and through eqs 7−9 (adapted from[37]) the generated hydroxyl radicals participate in the reduction of Cu^{2+} to Cu$^+$. The regeneration of Cu^{2+} species proceeds by eq 5.

$$H_2O_2 + h\upsilon \rightarrow 2HO^\bullet \tag{6}$$

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \tag{7}$$

$$HO_2^\bullet \rightarrow O_2^{\bullet -} + H^+ \tag{8}$$

$$Cu^{2+} + O_2^{\bullet -} \rightarrow Cu^+ + O_2 \tag{9}$$
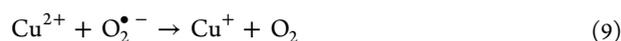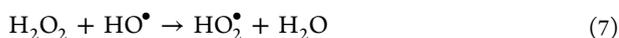
Although eqs 6 and 7 explain the degradation of paracetamol when Al/Cu-PILC is not added to the system (see Figure 1), the results in Figures 2 and 4 are evidence of the impact of Al/Cu-PILC addition. In this regard, Cu^{2+} and Cu$^+$ are the chemical species that importantly contribute to produce the oxidant species to degrade paracetamol and the generated products (acetamides and acids). The efficiency of the process varies according to the content of Cu in the sample as shown in Figure 4. Even though only three different percentages of Cu in the Al/Cu-PILC sample were assessed, it was found that a higher Cu content corresponds to higher removal of TOC and this can be related to the higher production rate of oxidant radicals via eqs 4−5.

3.5. Effect of the Catalyst Loading. The effect of the Al/Cu-PILC loading employed as the catalyst of the photo-Fenton process was also assessed. Four catalyst concentrations (0.2, 0.5, 0.75, and 1 g$_{cat}$ L^{-1}) were evaluated in the chemical reaction of interest. Complete paracetamol oxidation was observed in all the cases, but considerable differences rise from TOC analysis. Table 4 presents these results in addition to the initial mineralization rate normalized to the catalyst loading and per time unit.

Table 4. Paracetamol Mineralization Rate by the Photo-Fenton-Like Process: Effect of the Al/Cu-PILC Concentration

catalyst concentration (g$_{cat}$ L^{-1})	% TOC mineralization	paracetamol initial mineralization rate (mg TOC g$_{cat}$$^{-1}$ h^{-1})
1	65.0	24.3
0.75	57.5	40.6
0.5	61.0	69.8
0.2	48.0	60.3

The TOC removal percentage did not follow a linear trend with the amount of catalyst. The experiment with 0.5 g$_{cat}$ L^{-1} showed slightly superior performance in comparison to the loading of 0.75 g$_{cat}$ L^{-1}. In fact, this catalyst loading leads to the highest mineralization rate according to Table 4 (69.8 mg of TOC g$_{cat}$$^{-1}$ h^{-1}). The lower catalyst loadings showed better mineralization rates. The experiment with 0.5 g$_{cat}$ L^{-1} overperform almost 3-times, the mineralization attained with 1 g$_{cat}$ L^{-1}. The reasoning behind the higher mineralization rate achieved with lower catalyst concentrations is given by the effective utilization of the active sites on the surface of the catalyst in addition to the effective illumination of the catalyst particles well distributed inside the reactor. Likely, a higher concentration of catalyst limited the passage of light through the reactor by the "wall effect" originated from the excessive number of particles dispersed in the aqueous solution. In all cases, mass transfer limitations are discarded due to the uniform and vigorous stirring of the catalyst particles.

The concentration of the catalyst affected the pathway of the reaction according to the evolution of acetamide, a common by-product of paracetamol oxidation. In our case, acetamide was produced in all the experiments where the catalyst concentration was assessed, and individual trends were found (Figure 5). After 120 min a lower acetamide concentration was produced with the concentration of 0.5 g$_{cat}$ L^{-1} but the profile for 1.0 g$_{cat}$ L^{-1} showed a decreasing trend after it reached a production of acetamide as high as 25 ppm. Similar behavior was observed for
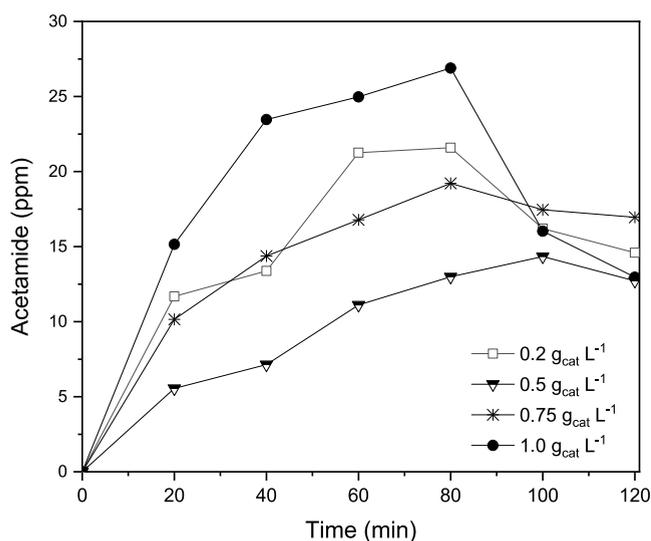
Figure 5. Acetamide formation at different catalyst loadings during the photo-Fenton-like process. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8.

the concentration of 0.2 g_{cat} L^{-1}. A more detailed study of the reaction intermediates of paracetamol degradation is presented in the following section.

3.6. Stability of the Al/Cu-PILC Catalyst. To establish the stability and reusability of Al/Cu-PILC with 1.2% of Cu content, four experiments were carried out with the catalyst recovered from the first use. The catalyst recovery was conducted by centrifugation. The results of these experiments are reported in Figure 6. It can be observed in this figure that after the first use ca. 13% less TOC removal than in the first use was achieved. It is worth noting, however, that this difference is much less in the subsequent uses (about 2% after each use). The difference in TOC removal values between the first and second use might be mainly due to three factors: a possible lixiviation of Cu

(observed in other works[14]), loss of the catalyst during the recovery step, and the inherent error of experiments and TOC measurement. Although the lixiviated amount of Cu was not quantified in this study, it can be presumed to occur mainly during the first use since the difference in TOC removal in subsequent uses was not as high as that after the first use. Therefore, after the second use, the change in the remaining TOC in solution might be only attributable to the loss of catalyst in the recovery step and/or to the experimental error.

3.7. pH of the Photo-Fenton-Like Reaction. After 120 min of reaction, the pH of the reaction mixture was measured in all cases. Acidic pH values of 4.14, 3.44, 3.55, and 3.28 were registered for the experiments catalyzed with loadings of 1, 0.75, 0.5, and 0.2 g_{cat} L^{-1}, respectively. The initial pH was determined to be 5.8. The more acidic conditions of the reaction media are given by the recalcitrant organic compounds with an acidic character that remain stable after 120 min. Moreover, an extended experiment up to 360 min was conducted with a catalyst loading of 0.5 g_{cat} L^{-1} and it showed that the pH turned from acidic to circumneutral (Figure 7).

The final products of the oxidation of paracetamol and the generated intermediates, are CO_2 and H_2O. Therefore, despite the recalcitrant organic compounds with acidic properties that remain in solution (even after long reaction periods), there is also dissolved CO_2 that can be present as CO_2 and as carbonates and bicarbonates (depending on the solution pH). It can be observed in Figure 7, that at 360 min a pH above 6.0 was registered. At this pH and according to a CO_2 speciation diagram,[38] the plausible species to be found are CO_2 and bicarbonate ions, which are produced according to Scheme 1. Carbonic acid is also formed but it is expected to decompose into bicarbonate ions. At this point, it is worth recalling that carbonic acid pK_{a1} = 6.35.

The basic character of bicarbonate ions is directly related to the observed increase in the pH of the solution in Figure 7. This is in concordance with previous reports on the degradation of organic compounds by AOP processes.[39] In another study,[40]
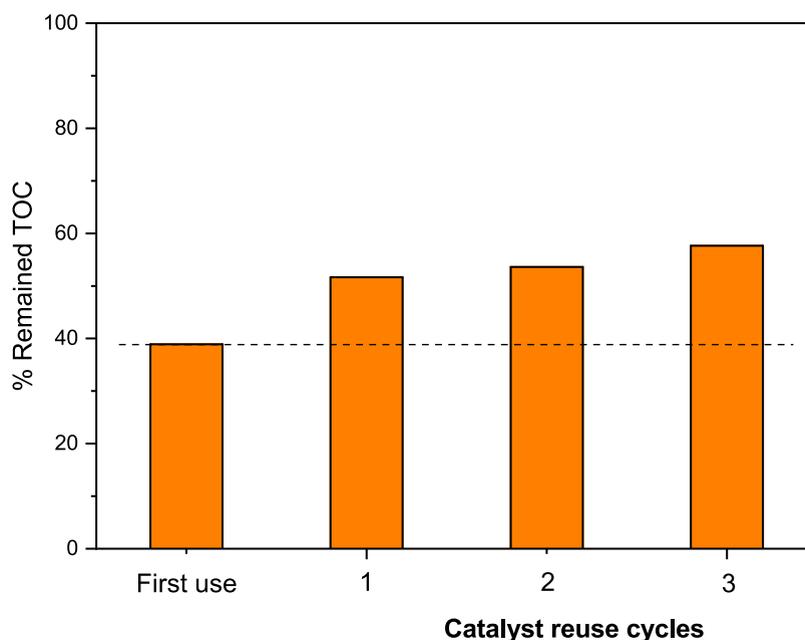
Figure 6. Comparison of the TOC removal efficiency: original catalyst and up to three reuse cycles. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8.
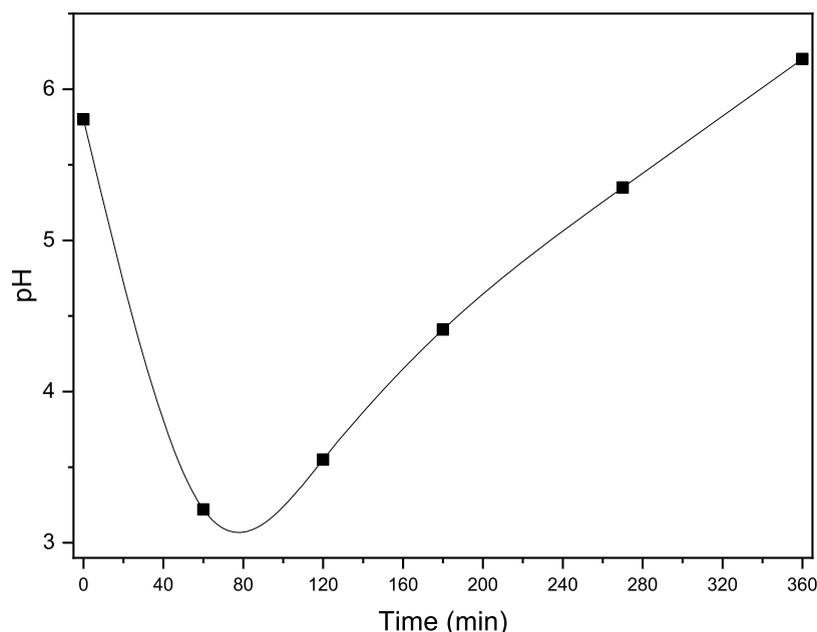
Figure 7. pH profile of the photo-Fenton-like process with a catalyst loading of 0.5 g_{cat} L^{-1}. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8.

Scheme 1. Bicarbonate Ions Generated from Dissolved CO_2 [a][38]

$$CO_{2\,(g)} \rightleftharpoons CO_{2\,(liq)} \xrightarrow{+H_2O} H_2CO_3 \xrightarrow{+H_2O} HCO_3^- + H_3O^+$$
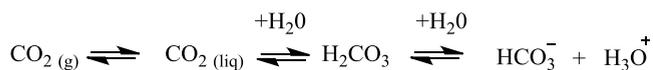
[a]Adapted from Ganesh.[38] Copyright (2016) with permission from Elsevier.

where pillared clays were applied in a photo-Fenton process, it was demonstrated that the toxicity of the solution after treatment was related to an acidic pH rather than to the mineralization extent. In such a study, although an almost complete mineralization degree was attained under acidic conditions, the toxicity of the resulting solution was higher than that at circumneutral pH where only partial mineralization was achieved. Thus, the increase in pH observed in Figure 7, can be considered as an advantage of this type of treatment for the safe discharge of treated wastewater to water bodies given the potential application of the present technology to treat real effluents.

3.8. Reaction Intermediates. Despite the complete removal of paracetamol attained by means of a Photo-Fenton-like process catalyzed by Al/Cu-PILC (Figure 2), the complete mineralization was not reached after 120 min. Thus, in this work, LC-MS was employed to identify the recalcitrant compounds responsible(s) for this behavior. Acetamide (C_2H_5NO), oxamic acid ($C_2H_3NO_3$), and hydroquinone ($C_6H_6O_2$) have been extensively reported as the main reaction intermediates in the
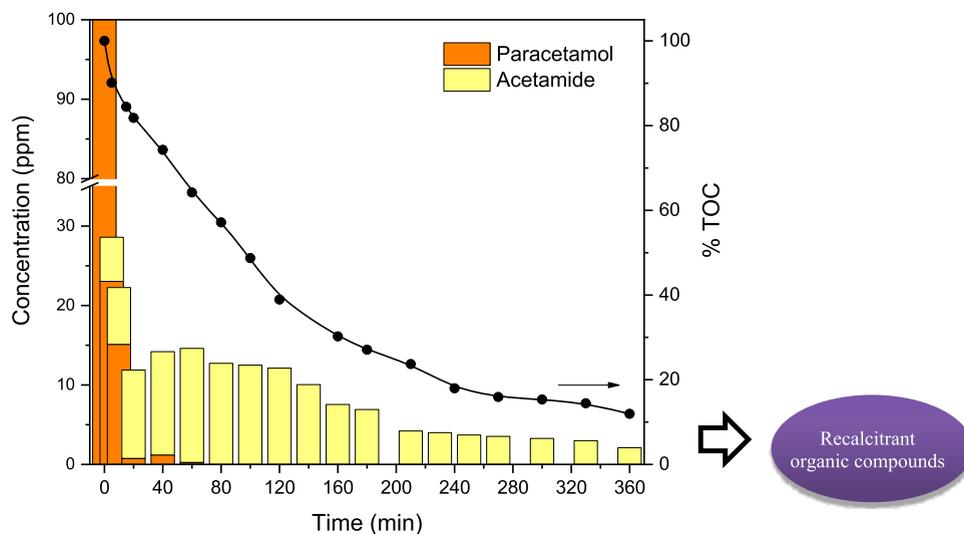
Figure 8. Cumulative organic compound concentration identified by LC-MS from the photo-Fenton process with the Al/Cu-PILC sample and percent of TOC evolution with time-profile. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8; catalyst loading: 0.5 g_{cat} L^{-1}.
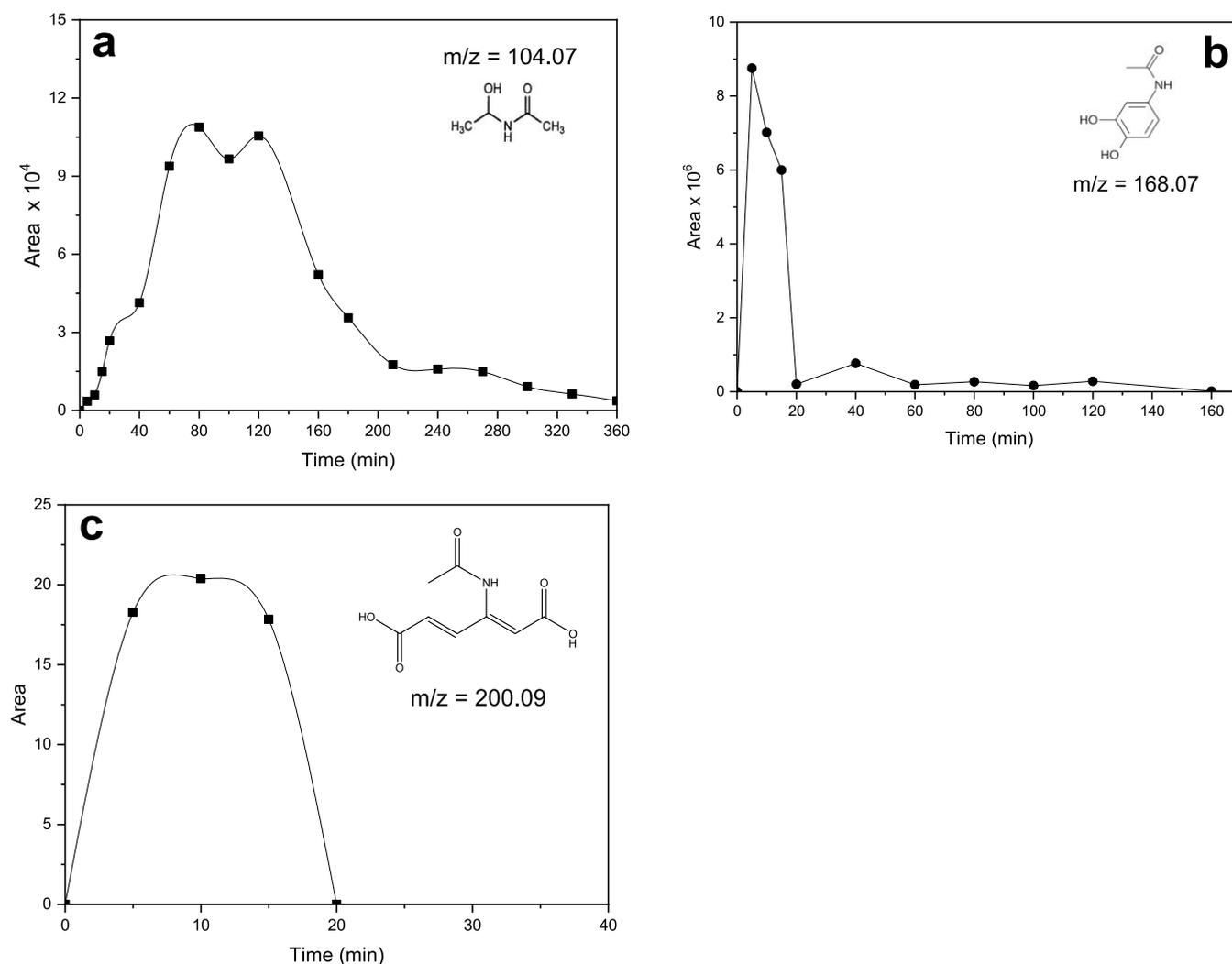
Figure 9. Time evolution of the sub-products of the oxidation of paracetamol through a photo-Fenton-like process: (a) *N*-(1-hydroxyethyl)acetamide, (b) *N*-(3,4-dihydroxyphenyl)acetamide, and (c) 3-acetamidohexa-2,4-dienedioic acid. Reaction conditions: V = 0.1 L; T = 298 K; C_0 = 100 ppm (paracetamol); initial pH = 5.8; catalyst loading: 0.5 g_{cat} L^{-1}.

paracetamol degradation through different AOP's[5,14,41] and they were also identified in this work. In addition, acetic, maleic, malonic, and succinic acids were also identified, as well as *N*-(1-hydroxyethyl)acetamide (m/z = 104.7), *N*-(3,4-dihydroxyphenyl)acetamide (m/z = 168.07), and -acetamido-hexa-2,4-dienedioic. Among the numerous by-products identified in the oxidation of paracetamol, only acetamide was quantified, given its higher abundance in our samples. Figure 8 depicts paracetamol and acetamide time-profile attained in a cumulative fashion at different times and paired with the degree of mineralization of the parent compound. The paracetamol molecule was completely degraded after 60 min and in contrast, acetamide was identified along the 360 min experiment. The highest acetamide concentration was attained between 50 and 70 min but its concentration after 360 min was reduced to about only 3 ppm. Likewise, it was found that after 360 min of performing the photo-Fenton reaction, 10% of the total organic carbon present in the fresh sample, still remained in the treated solution and this is attributed to the presence of compounds like the aforementioned acetamide, *N*-(1-hydroxyethyl)acetamide and a mixture of carboxylic acids (mainly oxamic and oxalic acids).

Carboxylic acids are known to be very stable organic compounds and their complete oxidation is difficult. Maleic acid was identified only in the early steps of the photo-Fenton reaction and after 110 min it was completely removed. In contrast, oxamic, acetic, malonic, and succinic acids reached their highest concentration between 50 and 100 min followed by their degradation to lower amounts but in all the cases, their complete disappearance was not achieved. The last group of identified sub-products included *N*-(1-hydroxyethyl)acetamide, *N*-(3,4-dihydroxyphenyl)acetamide, and 3-acetamidohexa-2,4-dienedioic acid, which were identified mostly at the beginning of the reaction but *N*-(1-hydroxyethyl)acetamide remained in a small amount even after 360 min (see Figure 9).

Even though 10% of the initial TOC in our process was not removed after 360 min, it is considered a low or inexistant threat to the environment since the concentrations of the remaining sub-products are minimal, and for example, concerning acetamide, its toxicity has been reported to be low for animal species and only in concentrations higher than 10,000 ppm acetamide could represent a danger for life.[42]

3.9. Paracetamol Oxidation Pathway. The photo-Fenton-like process starts with the generation of hydroxyl radicals (•OH) according to eq 5. Hydroxyl radicals are highly

Scheme 2. Production of *N*-(3,4-Dihydroxyphenyl)acetamide and 3-Acetamidohexa-2,4-dienedioic Acid by Paracetamol Oxidation through Hydroxyl Radical Attack

3-Acetamidohexa-2,4-Dienedioic Acid
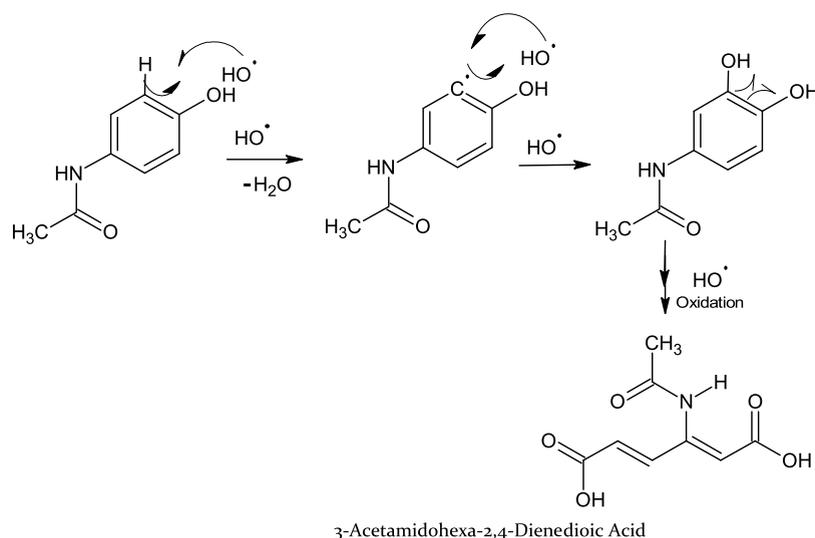
Scheme 3. Production of Acetamide by Paracetamol Oxidation through the Hydroxyl Radical Attack
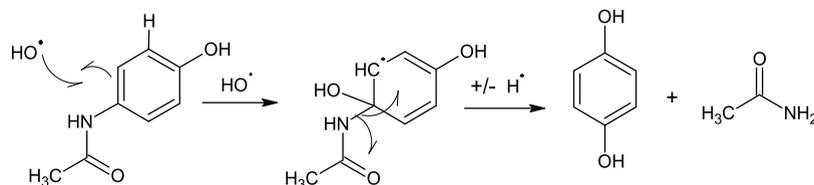
Scheme 4. Mechanistic Proposal for the Production of *N*-(1-Hydroxyethyl)acetamide with Concomitant Production of Acrylic Acid
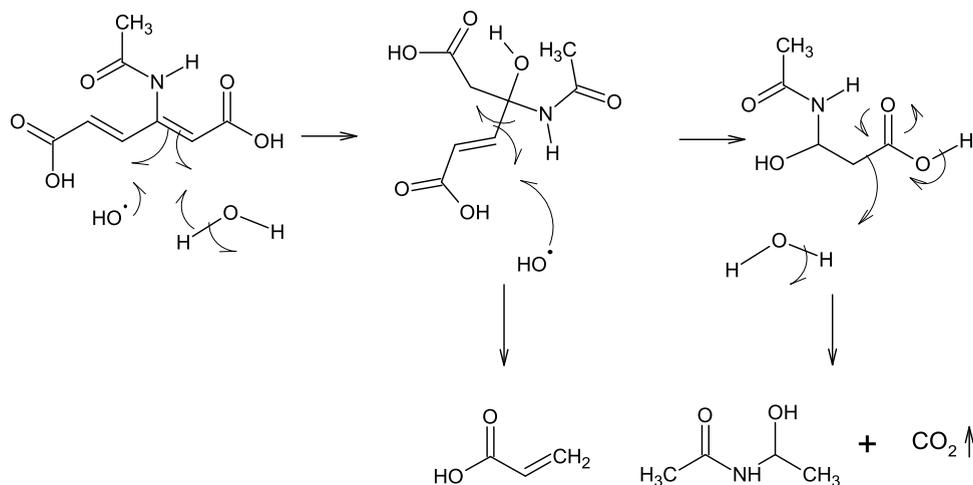
reactive, so they break paracetamol down by oxidation. The reaction continues with the hydrogen atom abstraction, generating the free radicals of the organic species, giving rise to compounds such as acetic acid, oxalic acid, oxamic acid, and maleic acid.

In the first 5 min of the reaction, where nearly 80% of initial paracetamol has been removed, four main compounds were identified, acetamide, *N*-(1-hydroxyethyl)acetamide, *N*-(3,4-dihydroxyphenyl)acetamide and 3-acetamidohexa-2,4-diene-dioic acid.

To obtain 3-acetamidohexa-2,4-dienedioic acid, the substitution of hydrogen by the hydroxyl radical (•OH) is proposed, generating *N*-(3,4-dihydroxyphenyl)acetamide which is oxidized by undergoing homolytic rupture in the catechol position (see reaction Scheme 2). Thus, according to this scheme, to obtain 3-acetamidohexa-2,4-dienedioic acid, *N*-(3,4-dihydroxyphenyl)acetamide should be first produced. This is in concordance with the results shown in Figure 9.

Concomitantly to reaction Scheme 2, the production of acetamide begins with the homolytic rupture of the double ligation of the aromatic ring in the paracetamol molecule (see Scheme 3). It continues with the rapid attack of the hydroxyl radical, breaking the aromaticity, which favors the acetamide

Scheme 5. General Oxidation Pathway Followed by the Paracetamol Molecule during A Photo-Fenton-Like Process Catalyzed with Al/Cu-PILC′s

radical fast exit, after which aromaticity is regenerated again. This explains the appearance of hydroquinone.

The mechanistic proposal for obtaining N-(1-hydroxyethyl)-acetamide involves the loss of acrylic acid with the subsequent decarboxylation of the 3-acetamidohexa-2,4-dienedioic acid, as observed in Scheme 4.

Oxamic acid, maleic acid, succinic acid, acetic acid, N-(1-hydroxyethyl)acetamide, malonic acid, and oxalic acid, are the result of the high oxidizing capacity of hydroxyl radicals. Hydrolysis reactions also occur in compounds with double

bonds. All the aforementioned are summarized in the proposed reaction pathway depicted in Scheme 5. At around 60 min, the mixture of carboxylic acids had a strong presence, and this is confirmed by the pH profile presented in Figure 7. In this interval of time, the reaction media possesses the most acidic conditions of the experiment. As the reaction evolves, the amounts of acidic compounds were reduced until total disappearance in the case of maleic acid or the reduction to tiny amounts (acetic and malonic). Among the carboxylic acids, oxamic and oxalic acids were found to present higher resistance

to conversion to CO_2 despite the highly oxidizing reaction conditions. These compounds, in addition to small amounts of acetamide and *N*-(1-hydroxyethyl)acetamide, were found to be the remaining products originated from the oxidation of paracetamol.

The obtained results presented here, in terms of mineralization and low-toxicity reaction intermediates, are promising within the context of providing environmentally friendly solutions for wastewater treatment employing accessible catalytic materials activated by light and operating under mild reaction conditions.

4. CONCLUSIONS

Al/Cu interlayered pillared clay was successfully prepared from bentonite and its photocatalytic activity was evaluated in a photo-Fenton-like process for the degradation of paracetamol. The use of this catalyst increases the paracetamol removal rate about five times with respect to the UV + H_2O_2 process and two orders of magnitude higher than the photolytic process. The complete removal of paracetamol was achieved after only 20 min of treatment and up to 90% of reduction of the initial total organic carbon was reached after 360 min. Notably, no adjustment of the pH to acidic conditions was needed to achieve these results. Acetamide was found to be the main reaction intermediate. The pH of the treated paracetamol solution by a photo-Fenton-like process after 360 min was determined to be 6.1 representing an important feature of our process aiming for the safe discharge of treated effluents to water bodies. After four uses of the same catalyst, the difference in remained TOC is only about 17% with respect to the use of the fresh catalyst. The findings in this work bode well for the development of strategies for water purification by means of safe, accessible, and effective chemical processes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02508.

Fitting of the experimental data corresponding to the UV, H_2O_2 + UV, and photo-Fenton-like reactions to a pseudo-first-order kinetic model (PDF)

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Author Contributions

L.H., R.N., and R.R. conceived and designed the experiments. O.A. carried out the synthesis and characterization of the materials and carried out the paracetamol degradation experiments. R.N. and R.R. funded the project. L.H., R.N., and O.A. wrote the paper. S.B., K.D., R.M.G.E., and O.A. provided significant contributions to the discussion. All the authors discussed the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

REFERENCES

(1) Kuo, C. Y.; Wu, C. H.; Wu, J. T.; Chen, Y. C. Preparation of Immobilized Cu_2O Using Microwave Irradiation and Its Catalytic Activity for Bisphenol A: Comparisons of Cu_2O/H_2O_2 and Visible-Light/Cu_2O/H_2O_2 Systems. *Water Sci. Technol.* **2014**, *70*, 1428.

(2) Taoufik, N.; Boumya, W.; Achak, M.; Sillanpää, M.; Barka, N. Comparative Overview of Advanced Oxidation Processes and Biological Approaches for the Removal Pharmaceuticals. *J. Environ. Manage.* **2021**, *288*, No. 112404.

(3) Novoa-Luna, K. A.; Mendoza-Zepeda, A.; Natividad, R.; Romero, R.; Galar-Martínez, M.; Gómez-Oliván, L. M. Biological Hazard Evaluation of a Pharmaceutical Effluent before and after a Photo-Fenton Treatment. *Sci. Total Environ.* **2016**, *569−570*, 830−840.

(4) Fatima, S.; Asif, N.; Ahmad, R.; Fatma, T. Toxicity of NSAID Drug (Paracetamol) to Nontarget Organism—Nostoc Muscorum. *Environ. Sci. Pollut. Res.* **2020**, *27*, 35208−35216.

(5) Trovó, A. G.; Pupo Nogueira, R. F.; Agüera, A.; Fernandez-Alba, A. R.; Malato, S. Paracetamol Degradation Intermediates and Toxicity during Photo-Fenton Treatment Using Different Iron Species. *Water Res.* **2012**, *46*, 5374−5380.

(6) De Laurentiis, E.; Prasse, C.; Ternes, T. A.; Minella, M.; Maurino, V.; Minero, C.; Sarakha, M.; Brigante, M.; Vione, D. Assessing the Photochemical Transformation Pathways of Acetaminophen Relevant to Surface Waters: Transformation Kinetics, Intermediates, and Modelling. *Water Res.* **2014**, *53*, 235−248.

(7) Leyva, E.; Moctezuma, E.; Baines, K. M.; Noriega, S.; Zarazua, E. A Review on Chemical Advanced Oxidation Processes for Pharmaceuticals with Paracetamol as a Model Compound. Reaction Conditions, Intermediates and Total Mechanism. *Curr. Org. Chem.* **2018**, *22*, 2−17.

(8) Velempini, T.; Prabakaran, E.; Pillay, K. Recent Developments in the Use of Metal Oxides for Photocatalytic Degradation of Pharmaceutical Pollutants in Water—a Review. *Mater. Today Chem.* **2021**, *19*, No. 100380.

(9) Rodríguez, M.; Bussi, J.; Andrea De León, M. Application of Pillared Raw Clay-Base Catalysts and Natural Solar Radiation for Water Decontamination by the Photo-Fenton Process. *Sep. Purif. Technol.* **2021**, *259*, No. 118167.

(10) Oller, I.; Malato, S. Photo-Fenton Applied to the Removal of Pharmaceutical and Other Pollutants of Emerging Concern. *Curr. Opin. Green Sustainable Chem.* **2021**, *29*, No. 100458.

(11) Brillas, E.; Garcia-Segura, S. Benchmarking Recent Advances and Innovative Technology Approaches of Fenton, Photo-Fenton, Electro-Fenton, and Related Processes: A Review on the Relevance of Phenol as Model Molecule. In *Separation and Purification Technology*; Elsevier B.V. April 15, 2020; p 116337 DOI: 10.1016/j.seppur.2019.116337.

(12) Minella, M.; Marchetti, G.; De Laurentiis, E.; Malandrino, M.; Maurino, V.; Minero, C.; Vione, D.; Hanna, K. Photo-Fenton Oxidation of Phenol with Magnetite as Iron Source. *Appl. Catal., B* **2014**, *154–155*, 102–109.

(13) Diya'uddeen, B. H.; Abdul Aziz, A. R.; Daud, W. M. A. W. On the Limitation of Fenton Oxidation Operational Parameters: A Review *Int. J. Chem. React. Eng.* 2012, *101* DOI: 10.1515/1542-6580.2913.

(14) Hurtado, L.; Romero, R.; Mendoza, A.; Brewer, S.; Donkor, K.; Gómez-Espinosa, R. M.; Natividad, R. Paracetamol Mineralization by Photo Fenton Process Catalyzed by a Cu/Fe-PILC under Circumneutral PH Conditions. *J. Photochem. Photobiol., A* **2019**, *373*, 162–170.

(15) Yu, S.; Pang, H.; Huang, S.; Tang, H.; Wang, S.; Qiu, M.; Chen, Z.; Yang, H.; Song, G.; Fu, D.; et al. Recent Advances in Metal-Organic Framework Membranes for Water Treatment: A Review. *Sci. Total Environ.* **2021**, *800*, No. 149662.

(16) Hao, M.; Qiu, M.; Yang, H.; Hu, B.; Wang, X. Recent Advances on Preparation and Environmental Applications of MOF-Derived Carbons in Catalysis. *Sci. Total Environ.* **2021**, *760*, No. 143333.

(17) Qiu, M.; Liu, L.; Ling, Q.; Cai, Y.; Yu, S.; Wang, S.; Fu, D.; Hu, B.; Wang, X. Biochar for the Removal of Contaminants from Soil and Water: A Review. *Biochar* **2022**, *4*, No. 19.

(18) Qiu, M.; Hu, B.; Chen, Z.; Yang, H.; Zhuang, L.; Wang, X. Challenges of Organic Pollutant Photocatalysis by Biochar-Based Catalysts. *Biochar* **2021**, *3*, 117–123.

(19) Yu, S.; Tang, H.; Zhang, D.; Wang, S.; Qiu, M.; Song, G.; Fu, D.; Hu, B.; Wang, X. MXenes as Emerging Nanomaterials in Water Purification and Environmental Remediation. *Sci. Total Environ.* **2022**, *811*, No. 152280.

(20) Herney-Ramirez, J.; Vicente, M. A.; Madeira, L. M. Heterogeneous Photo-Fenton Oxidation with Pillared Clay-Based Catalysts for Wastewater Treatment: A Review. *Appl. Catal., B* **2010**, *98*, 10–26.

(21) Gil, A.; Assis, F. C. C.; Albeniz, S.; Korili, S. A. Removal of Dyes from Wastewaters by Adsorption on Pillared Clays. *Chem. Eng. J.* **2011**, *168*, 1032–1040.

(22) Bokare, A. D.; Choi, W. Review of Iron-Free Fenton-like Systems for Activating H2O2 in Advanced Oxidation Processes. *J. Hazard. Mater.* **2014**, *275*, 121–135.

(23) Bokare, A. D.; Choi, W. Zero-Valent Aluminum for Oxidative Degradation of Aqueous Organic Pollutants. *Environ. Sci. Technol.* **2009**, *43*, 7130–7135.

(24) Salazar, R.; Brillas, E.; Sirés, I. Finding the Best Fe2+/Cu2+ Combination for the Solar Photoelectro-Fenton Treatment of Simulated Wastewater Containing the Industrial Textile Dye Disperse Blue 3. *Appl. Catal., B* **2012**, *115–116*, 107–116.

(25) Minz, S.; Garg, S.; Gupta, R. Catalytic Wet Peroxide Oxidation of 4-Nitrophenol Over Al–Fe, Al–Cu and Al–Cu–Fe Pillared Clays. *Indian Chem. Eng.* **2018**, *60*, 16–36.

(26) Mojović, Z.; Banković, P.; Milutinović-Nikolić, A.; Dostanić, J.; Jović-Jovičić, N.; Jovanović, D. Al,Cu-Pillared Clays as Catalysts in Environmental Protection. *Chem. Eng. J.* **2009**, *154*, 149–155.

(27) Galeano, L. A.; Gil, A.; Vicente, M. A. Effect of the Atomic Active Metal Ratio in Al/Fe-, Al/Cu- and Al/(Fe-Cu)-Intercalating Solutions on the Physicochemical Properties and Catalytic Activity of Pillared Clays in the CWPO of Methyl Orange. *Appl. Catal., B* **2010**, *100*, 271–281.

(28) Dorado, F.; de Lucas, A.; García, P. B.; Romero, A.; Valverde, J. L. Copper Ion-Exchanged and Impregnated Fe-Pillared Clays. Study of the Influence of the Synthesis Conditions on the Activity for the Selective Catalytic Reduction of NO with C3H6. *Appl. Catal., A* **2006**, *305*, 189–196.

(29) Luo, M.; Bowden, D.; Brimblecombe, P. Catalytic Property of Fe-Al Pillared Clay for Fenton Oxidation of Phenol by H2O2. *Appl. Catal., B* **2009**, *85*, 201–206.

(30) Mojović, Z.; Banković, P.; Milutinović-Nikolić, A.; Dostanić, J.; Jović-Jovičić, N.; Jovanović, D. Al,Cu-Pillared Clays as Catalysts in Environmental Protection. *Chem. Eng. J.* **2009**, *154*, 149–155.

(31) Bahranowski, K.; Dula, R.; Łabanowska, M.; Serwicka, E. M. ESR Study of Cu Centers Supported on Al-, Ti-, and Zr-Pillared Montmorillonite Clays. *Appl. Spectrosc.* **1996**, *50*, 1439–1445.

(32) Bahranowski, K.; Gąsior, M.; Kielski, A.; Podobiński, J.; Serwicka, E. M.; Vartikian, L. A.; Wodnicka, K. Copper-Doped Alumina-Pillared Montmorillonites as Catalysts for Oxidation of Toluene and Xylenes with Hydrogen Peroxide. *Clay Miner.* **1999**, *34*, 79–87.

(33) Maekawa, J.; Mae, K.; Nakagawa, H. Fenton-Cu2+ System for Phenol Mineralization. *J. Environ. Chem. Eng.* **2014**, *2*, 1275–1280.

(34) Pan, J.; Wang, C.; Guo, S.; Li, J.; Yang, Z. Cu Supported over Al-Pillared Interlayer Clays Catalysts for Direct Hydroxylation of Benzene to Phenol. *Catal. Commun.* **2008**, *9*, 176–181.

(35) Alvarado-Rolon, O.; Natividad, R.; Ramírez-García, J.; Orozco-Velazco, J.; Hernandez-Servin, J. A.; Ramírez-Serrano, A. Kinetic Modelling of Paracetamol Degradation by Photocatalysis: Incorporating the Competition for Photons by the Organic Molecule and the Photocatalyst. *J. Photochem. Photobiol., A* **2021**, *412*, No. 113252.

(36) Huang, L.; Peng, F.; Yu, H.; Wang, H. Preparation of Cuprous Oxides with Different Sizes and Their Behaviors of Adsorption, Visible-Light Driven Photocatalysis and Photocorrosion. *Solid State Sci.* **2009**, *11*, 129–138.

(37) Lee, H. J.; Lee, H.; Lee, C. Degradation of Diclofenac and Carbamazepine by the Copper(II)-Catalyzed Dark and Photo-Assisted Fenton-like Systems. *Chem. Eng. J.* **2014**, *245*, 258–264.

(38) Ganesh, I. Electrochemical Conversion of Carbon Dioxide into Renewable Fuel Chemicals – The Role of Nanomaterials and the Commercialization. *Renewable Sustainable Energy Rev.* **2016**, *59*, 1269–1297.

(39) Amado-Piña, D.; Roa-Morales, G.; Barrera-Díaz, C.; Balderas-Hernandez, P.; Romero, R.; Martín del Campo, E.; Natividad, R. Synergic Effect of Ozonation and Electrochemical Methods on Oxidation and Toxicity Reduction: Phenol Degradation. *Fuel* **2017**, *198*, 82–90.

(40) Natividad, R.; Mendoza, A.; Brewer, S. E.; Martínez-Vargas, S. L.; Pérez-Mazariego, J. L.; Novoa, K. A.; Gómez-Oliván, L. M.; Romero, R. Photo-Fenton Treatment of a Pharmaceutical Industrial Effluent Under Safe PH Conditions. In *Handbook of Environmental Chemistry*; Springer Science and Business Media Deutschland GmbH, 2020; Vol. *96*, pp 241–259 DOI: 10.1007/698_2020_551_COVER.

(41) Vogna, D.; Marotta, R.; Napolitano, A.; D'Ischia, M. Advanced Oxidation Chemistry of Paracetamol. UV/H2O2-Induced Hydroxylation/Degradation Pathways and 15N-Aided Inventory of Nitrogenous Breakdown Products. *J. Org. Chem.* **2002**, *67*, 6143–6151.

(42) Kennedy, G. L.; Short, R. D. Biological Effects of Acetamide, Formamide, and Their Monomethyl and Dimethyl Derivatives. *Crit. Rev. Toxicol.* **1986**, *17*, 129–182.