



Evaluation of copper slag to catalyze advanced oxidation processes for the removal of phenol in water

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ABSTRACT

The aim of this work was to evaluate the use of copper slag to catalyze phenol degradation in water by advanced oxidation processes (AOPs). Copper slag was tested in combination with H_2O_2 (slag/ H_2O_2) and H_2O_2 /UV (slag/ H_2O_2 /UV). The studied methods promoted the complete photocatalytic degradation of phenol. Besides, they were able to reduce about 50% the TOC content in the samples. Slag/ H_2O_2 /UV and slag/ H_2O_2 treatments have favored biodegradability increment along the reaction time. Nevertheless, the irradiated method achieved higher values of the biodegradability indicator (BOD_5 /TOC). The toxicity assessment indicated the formation of more toxic compounds in both treatments. However, the control of the reaction time would minimize the environmental impact of the effluents.

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1. Introduction

Copper slag is produced in the metallurgical industry as a result of smelting process of copper concentrate. Its production is calculated in millions of tons each year; 2.2 tons of slag is produced for every ton of copper fabrication [1]. Environmental problems related to its disposal create an increasing need to investigate alternative uses for copper slag as raw material of other processes. Based on its physical properties and composition (iron, alumina and calcium oxide) it can be used in the construction field as dry abrasive blasting material, to fabricate cement, ballast, fill, aggregate, glass, roofing granules and tiles [1,2]. There is no published research dealing with the use of copper slag in the environmental field.

Recently, it has been proposed the use of slag, different from copper slag, in the environmental field to catalyze the depletion of contaminants in water. Studies using high basic oxygen furnace steel slag/ H_2O_2 system have been performed for the depletion of 4-chlorophenol and reactive black 5,2-naphthalenesulfonate reaching in both cases removal of 69% COD, 51.2% TOC, 56% TOC [3,4]. Iron content in steel slag is used to catalyze H_2O_2 break down to $\bullet OH$ radicals. In one hand iron is leached from slag as Fe^{2+} and Fe^{3+} , in the other hand it can be present in its current solid phases such as

wuestite FeO and hematite Fe_2O_3 . The result is that iron breakdown catalysis of H_2O_2 is achieved as a combination of heterogeneous and homogeneous system following the Fenton's (H_2O_2 /Fe) and Fenton like reaction. Iron content in copper slag (35–45%, w/w, reported as Fe_2O_3 in X-ray fluorescence analysis) is even higher than any other type of slag, thus favoring catalytic oxidation reaction. However, none work of the use of copper slag/ H_2O_2 for the depletion of recalcitrant substances has been reported.

Fenton like reaction is an advanced oxidation process, known for its ability to treat recalcitrant substances. It is a non selective process based on $\bullet OH$ and $\bullet RO$ radical formation via H_2O_2 breakdown catalyzed by a transition metal (Fe, Mn, Mg, Cu) at acidic pH [5]. Once irradiated with UV light, the new system, called photo-Fenton, has the ability to produce higher quantities of $\bullet OH$ radicals and therefore increases its capacity to oxidize organic pollutants.

Phenol, a recalcitrant and widely used substance by pharmaceutical and painting industries, has been treated by the Fenton's reaction [6,7]. Because it is a simple well known molecule having medium toxicity and low biodegradability which makes it a proper target to be used as model compound in advance waste water processes evaluation such as AOPs [8,9]. TOC depletion is also admitted as plausible efficiency parameter for the assessment of the efficiency of waste water treatments. TOC decrease gives an acceptable view of the depletion efficiency of organic compounds, nevertheless further information such as acute toxicity and biodegradability of effluents are considered essential to protect the environment from the disposal of hazardous effluents. This represents a

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serious problem since recalcitrant molecule decomposition leads to a wide complexity of other molecules which sometimes can be more recalcitrant or even less biodegradable than the original molecule.

Since biological systems are not adequate to treat non-biodegradable molecules, then it is possible to use AOP as an alternative treatment method. Thus, AOP can be used to treat waters containing low concentration of phenol or when a high quality effluent is required such as in water reuse.

Research reporting the use of the Fenton's reagent to achieve organic chemical biodegradability, has found that the treatment can eliminate the toxic substances and increase biodegradability ratio (DBO₅/COD). The mineralization and biodegradability increase of by-products are a function of iron chemical form in the Fenton reaction and it varies for each pollutant [10].

Currently, there are no studies related to using copper slag/H₂O₂ and copper slag/H₂O₂/UV systems for the depletion of organic contaminants. And there are no reports of biodegradability and acute toxicity assessment of this kind of systems. Some studies assessing acute toxicity and biodegradability during AOPs systems [11,12] demonstrate that the obtained data give crucial information to understand precisely the potential capacity of a treated effluent to harm the environment.

This research is focused in evaluating the catalytic oxidation of phenol by means of the copper slag/H₂O₂ and copper slag/H₂O₂/UV systems. The evaluation is completed with biodegradability (DBO₅) and EC₅₀ acute toxicity assessment (Microtox[®]) to give an accurate evaluation of the system. The copper and iron leaching during the treatment is also matter of study.

2. Materials and methods

2.1. Materials

All reagents were used as received by Pancreac (Spain). The 50 mg L⁻¹ phenol solutions were prepared using bi-distilled water. Solutions of HCl (37%, v/v) 0.1 M, NaOH (>99%) 2.5 M were used for pH adjustment (pH = 3) at the beginning of experimental runs. To ensure the exactitude of the method, hydrogen peroxide (30 wt.%) was first validated through iodometric titration to rectify the bottle reagent concentration. Oxidation reaction was stopped with a thiosulfate 0.01 M solution together with raising pH to 9 using a NaOH 10 M solution. Experiments for biodegradability and acute toxicity assessment were quenched using catalase (Sigma, Spain) 200 mg L⁻¹ solution at pH adjusted to 7. Slag sample was provided by a Mexican metallurgical copper company located in northern Mexico. Sample was grinded and sieved to a grain size ranging from 44 μm to 149 μm and kept in a dry place for further use.

2.2. Oxidation experiments

Experimental setup for phenol depletion consisted of a 2 L capacity pyrex[®] glass reactor provided with a thermostatic jacket connected to a cooling system (Frigiterm Selecta, Spain), which kept constant temperature at 25 °C. Reactor was set with a magnetic stirrer and was provided with three UV 8 W lamps (Philips, Holland), emitting between a wavelength range of 350–400 nm, with a maximum wavelength peak in 365 nm and $6.2 \pm 0.6 \mu\text{Einstein s}^{-1}$ of photon emission (black blue light). Lamps were immersed inside the reactor and protected with a silica glass tube to ensure a good homogeneity of irradiation. It was isolated of day light by an aluminum paper cover. The experimental system is described elsewhere [13].

The slag/H₂O₂ experimental trials were carried out in heterogeneous phase using 1.5 L of a 50 mg L⁻¹ not buffered phenol solution

which was adjusted to pH 3 inside the reactor at the beginning of experimentation. Afterwards, [H₂O₂] = 160 mg L⁻¹ and 2.49 g of copper slag were added to the solution inside the reactor at the same time and then stirred at 300 rpm for 224 min. During slag/H₂O₂/UV runs, the system was constantly irradiated by UV black blue light. Experimental conditions were chosen considering previous experiments testing different slag concentrations and hydrogen peroxide doses.

Along the experiments, 5 mL of representative samples were extracted from the reactor at different reaction times. Samples were carefully filtered using a 0.45 μm (Millipore, Spain) filter and the reaction was immediately stopped using 0.1 mL of thiosulfate 0.01 M solution and raising pH to 9 using a NaOH 10 M solution. Final volume in the sample increases less than 1% due to thiosulfate and NaOH addition.

Samples were analyzed to determine Total Organic Carbon (TOC), [phenol], [H₂O₂], leached Fe and Cu, and acute toxicity along the reaction trial. pH was measured along the reaction with a pH meter (Crison, Spain) in a fresh sample at different times along the reaction. 500 mL samples for BOD₅ determination were obtained by running different experiments. For each experiment the reaction was stopped and the effluent was used to evaluate biodegradability at that time.

2.3. Chemical analysis

TOC was measured using a Shimadzu 5055 TOC analyzer (Japan). Phenol residual concentration was determined using the HPLC technique by means of a Waters chromatograph set provided with a Waters 996 Photodiode array detector and a Teknocrroma column. Mobile phase system was acetonitrile:water (50:50%, v/v) using an isocratic elution mode, a 20 μL sample injection and 1.5 mL min⁻¹ flow rate. Phenol was identified at 270 nm wavelength. Residual [H₂O₂] was determined through the iodometric titration technique. Cu and Fe leached from slag were verified by means of the atomic absorption technique (AA), using a Varian (model AA240 FS). BOD₅ was measured by means of a respirometric measuring system OxiTop[®] and following the Standard Methods (5120).

Acute toxicity was determined through commercially developed system mark Microtox[®] (AZUR Environmental, USA). This system uses *Vibrio Vischeri* as target bacterium. The test measures the decay on bacteria photoluminescence after 15 min of sample exposure. To facilitate the toxicity assessment, results are expressed as 1/EC₅₀. Samples were kept in a fridge 24 h at 0 °C, before toxicity measurement.

Characterization of copper slag was performed by several analytic techniques. The purpose was to combine chemical and mineralogical characterization in order to identify physicochemical characteristics useful to explain copper slag catalytic capacity. Measured physicochemical properties were copper and iron crystalline phases, specific surface area and total copper and iron content. Crystalline phases were identified using the X-ray diffraction technique (XRD). A Bruker D8 Advance diffractometer Bragg Brentano geometry with a θ - θ configuration, Cu K α radiation and a Bruker Lynxeye detector (silicon strips) were used for this analysis. The diffraction intensity was measured in a 2θ angle ranging from 10° to 70°. The identification of crystalline phases and minerals was carried out using the database Powder Diffraction File (PDF-2) of the International Centre for Diffraction Data (ICDD). The lower detection limit is 2.5% by weight for heavy compounds. The specific surface area was determined by the nitrogen physical adsorption technique (Brunauer–Emmett–Teller (BET) isotherm) using a BELSORP Mini II. The detection limit for this parameter is 0.01 m² g⁻¹.

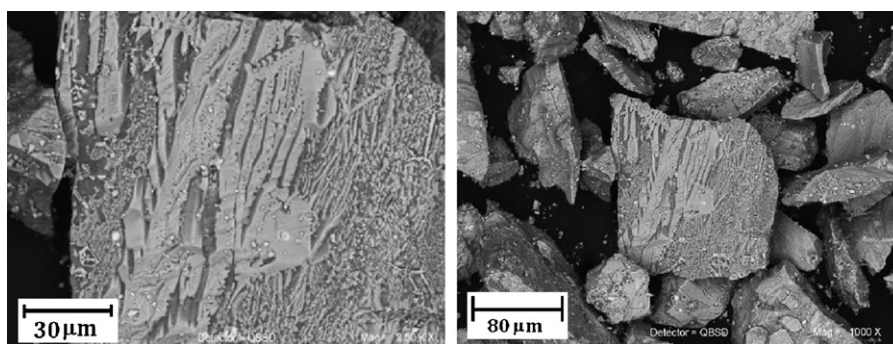


Fig. 1. SEM images of copper slag grains (20 kV, BSE).

3. Results and discussion

3.1. Slag characterization

Characterization revealed that surface copper slag grains have small crystalline formation, predominating over rough zones (Fig. 1). The presence of conglomerates of crystalline phases were indicated by XRD as Fe_2SiO_4 fayalite, MgFe_2O_4 magnesium ferrite; SiO_2 quartz was also detected. Ferrite has been reported to be active toward Fenton-type reaction in solid synthesized Fenton catalyst [14]. Thus, it is possible that superficial iron at slag, could act as a potential catalyst for phenol depletion. The specific surface area of slag determined by the nitrogen adsorption method (BET) shows a $14.9 \text{ m}^2 \text{ g}^{-1}$ which is similar to data reported for other copper slag samples ($<16 \text{ m}^2 \text{ g}^{-1}$). A high value of this parameter ($>100 \text{ m}^2 \text{ g}^{-1}$) is favorable for catalysis, thus slag shows a disadvantage in this matter.

Results for atomic absorption analysis (AA) show that copper slag has 36 wt.% of iron and 1.4 wt.% of copper in its composition. It is important to notice that not all iron and copper analyzed by AA is located at the surface of slag where it can be available for heterogeneous catalysis. It can only be estimated that 1% of total copper could be at the surface. While leached Cu and Fe are expected to participate on homogeneous catalysis.

3.2. Phenol and TOC removal

Phenol concentration was followed along the reaction time to evaluate the effect of the used AOPs on the oxidation of organic pollutants. In addition, TOC was monitored along the runs to assess the mineralization. Reaction was carried out at acidic pH = 3 because it is well known that Fenton's reaction has shown the best results at this pH value. However, at acidic pH, iron and copper are leached from the surface of slag grains. Iron species, which are leached from slag as Fe^{2+} and Fe^{3+} are known as catalysts to break down the H_2O_2 molecule. Moreover, copper specie Cu^{2+} has also been found to produce H_2O_2 break down to $\cdot\text{OH}$ radicals [15]. Thus, it can be assumed that a synergic catalysis between copper and iron species may occur in the experimental system. In this type of system, some authors demonstrated that homogeneous catalysis predominates at pH between 2 and 4.4 while heterogeneous catalysis prevails at pH between 4.4 and 7.0 [16,17]. Therefore, it is assumed that slag/ H_2O_2 and slag/ H_2O_2 /UV catalytic reaction takes place predominately in homogeneous phase.

Fig. 2 shows phenol depletion in terms of normalized concentration (C/C_0) of phenol versus time. Results show that copper slag/ H_2O_2 /UV was able to achieve total phenol depletion in 30 min while slag/ H_2O_2 system reached the same results at 90 min of treatment. Slag/UV and H_2O_2 /UV were used as controls to be certain that UV interaction with slag and/or H_2O_2 do not enhance phenol

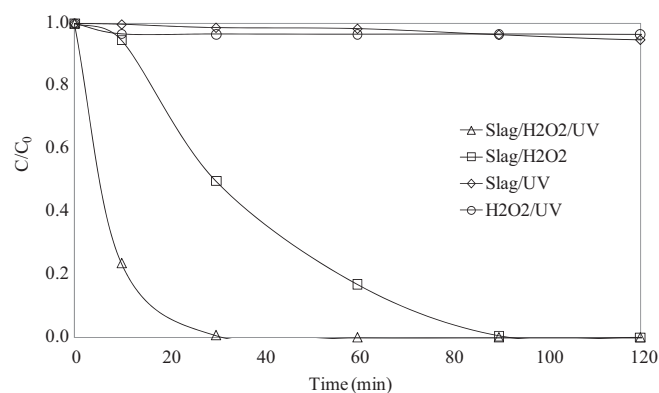


Fig. 2. Phenol oxidation as a function of reaction time, $[\text{H}_2\text{O}_2] = 160 \text{ mg L}^{-1}$, $[\text{slag}] = 2.48 \text{ g L}^{-1}$.

oxidation. These results indicate the capability of copper slag to catalyze H_2O_2 break down to $\cdot\text{OH}$ radicals and other oxidant species. Thus, it can be suggested that the iron and copper content in slag are responsible for the catalytic activity. Besides, the addition of UV light importantly accelerates phenol oxidation. Blank experiments only with the use of UV and slag alone were performed and no phenol removal was observed along 120 min of exposition, showing no significant contribution to phenol oxidation.

Regarding the mineralization of the organic content, Fig. 3 demonstrates that the system produces $\cdot\text{OH}$ radical in a quantity enough to promote a constant mineralization of the organic content. After 224 min of treatment, the system achieved 46% and 51% of TOC removal for slag/ H_2O_2 /UV and slag/ H_2O_2 , respectively. Although, slag/ H_2O_2 promoted a slight higher TOC removal than the irradiated system, it can be considered that the levels of mineralization are similar in both methods and the observed difference can

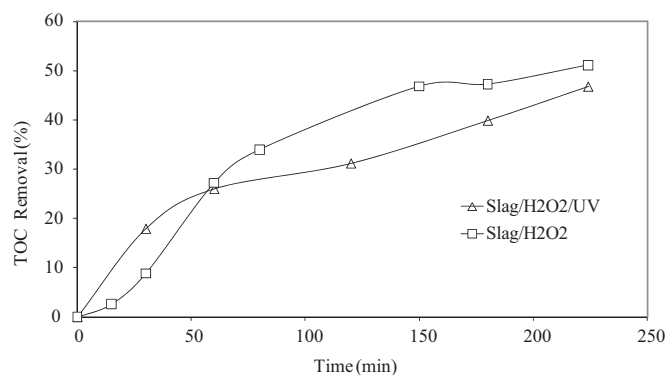


Fig. 3. Total organic carbon removal as a function of reaction time, $[\text{H}_2\text{O}_2] = 160 \text{ mg L}^{-1}$, $[\text{slag}] = 2.48 \text{ g L}^{-1}$.

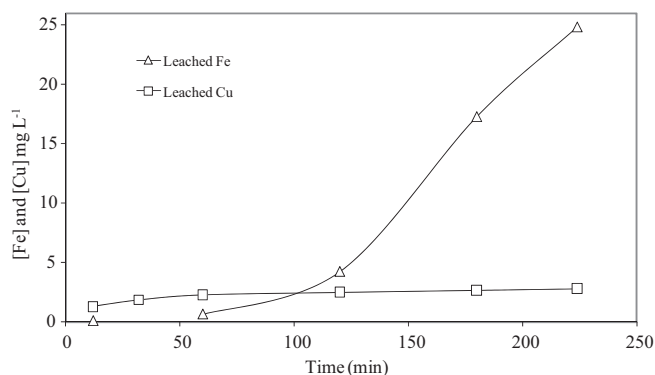


Fig. 4. Leached Fe and Cu from copper slag as a function of reaction time during slag/H₂O₂ treatment. Initial pH=3, slag concentration=2.49 g L⁻¹, H₂O₂ dosage=160 mg L⁻¹.

reside on experimental errors during TOC measurements. Therefore, it was observed a higher phenol oxidation rate in the irradiated system; nevertheless both methods reached a constant mineralization of the formed intermediates. The results achieved with the use of copper slag in terms of phenol removal and mineralization were similar to those achieved in previous investigation using homogeneous Fenton and photo-Fenton in presence of dissolved iron salts [8,18]. While phenol was used as a model target molecule as a first approach, no further studies regarding different concentrations were performed. Nevertheless, it is convenient to explore copper slag catalytic capacity for different phenol concentration.

As previously described, Fe and Cu leaching was monitored during the runs. Fe and Cu releasing along the reaction time are shown in Fig. 4 for slag/H₂O₂, the behavior of slag/H₂O₂/UV was similar. According to the graphic, leaching of copper and iron species from slag grain surface was made as a gradual process. The two metals leaching had different behavior. Although, Cu releasing is observed since the first minutes of reaction (10 min), its leaching rate was very slow, favoring a constant Cu concentration in the medium around 3 mg L⁻¹ during the whole treatment time. In the case of iron, its presence in the aqueous phase was only detected after 50 min of reaction. However, its higher releasing rate promoted the system reaches concentration near 25 mg L⁻¹ at the end of the treatment (224 min). Although the photo degradation of contaminants catalyzed by copper slag promotes an important Fe leaching, at the reaction time need for the contaminant removal (30 and 90 min for slag/H₂O₂/UV and slag/H₂O₂, respectively) its concentration is lower than the values reported in other studies using Fenton's reaction, where iron concentration is around 10–25 mg L⁻¹. However, the treatment time should be carefully controlled to avoid excessive Fe leaching in the effluent. On one hand, it is important to point out that as Fe was not detected during the first minutes of

treatment, Cu should be responsible for the catalytic activity on the slag/H₂O₂/UV system for the removal of phenol (30 min). On the other hand, slag/H₂O₂ system occurred with the participation of both metals as catalysts (90 min). When compared to regular homogeneous or heterogeneous Fenton/photo-Fenton, the advantages of using copper slag are the reuse of an industrial residue as catalyst, which can protect the environment and reduce the costs due to the large availability of this waste in mining areas.

In order to confirm the H₂O₂ consumption during the studied methods and ensure that phenol depletion is due to oxidation by radicals, the hydrogen peroxide concentration was measured along the reaction time. Fig. 5a shows H₂O₂ concentration during the runs. The graphic confirmed that no H₂O₂ consumption is observed by the single irradiation of H₂O₂ by black blue light, thus the sole irradiation was not able to promote the breakdown of H₂O₂ in •OH radicals. In presence of copper slag, H₂O₂ concentration decreased along the experimentation time, confirming that Fenton's and photo-Fenton like reactions take place. Slag/H₂O₂/UV system consumed higher quantity of oxidant, thus corroborating with the previous results which showed higher phenol degradation rate in this method. Since the pH of the medium is also an important factor to control in Fenton's and photo-Fenton reactions due to Fe precipitation at pH higher than 4, Fig. 5b presents pH evolution during the experiments. This figure allows observing that among the studied methods, only slag/H₂O₂/UV promoted the increase of the pH to values higher than 4. Nevertheless, this augment occurs after 150 min of experimentation. Considering that phenol was removed around 30 min of treatment, it would not constitute a serious problem if the objective is the removal of similar organic pollutants.

3.3. Biodegradability and acute toxicity

During an oxidation treatment, depending of the degradation pathway of the organic compound in study, more toxic compounds can be formed. To assess the effluent risk to environment, biodegradability and toxicity of samples were monitored along the experimental time. Biodegradability and toxicity tests were performed for slag/H₂O₂/UV and slag/H₂O₂. To better analyze the influence of both methods on the biodegradability of the samples, results are expressed as BOD₅/TOC. Toxicity results are also expressed as 1/EC50 in order to make the values directly proportional to toxicity. Fig. 6 shows the biodegradability and toxicity of the samples along the reaction time for the slag/H₂O₂/UV.

According to Fig. 6, phenol degradation by slag/H₂O₂/UV promotes the increment of the biodegradability indicator (BOD₅/TOC) from the first minutes of reaction to values higher than 0.6 after 50 min of treatment. Beyond this point the values show an important variation; however the treated sample achieved along the experimentation time higher biodegradability than the untreated

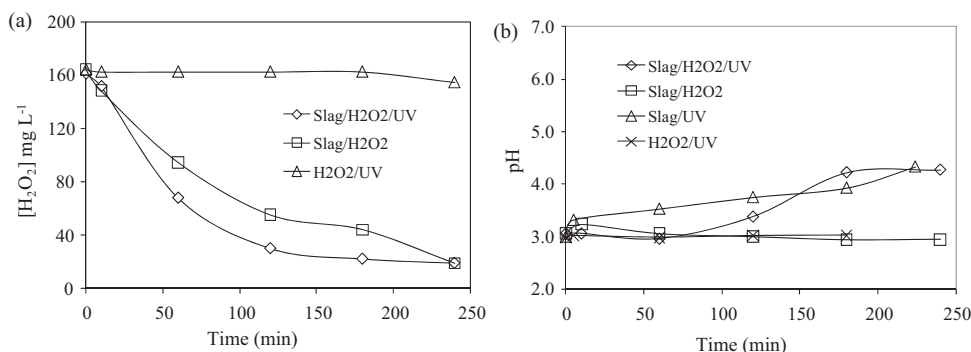


Fig. 5. (a) Hydrogen peroxide concentration and (b) pH evolution during experimentation as a function of reaction time.

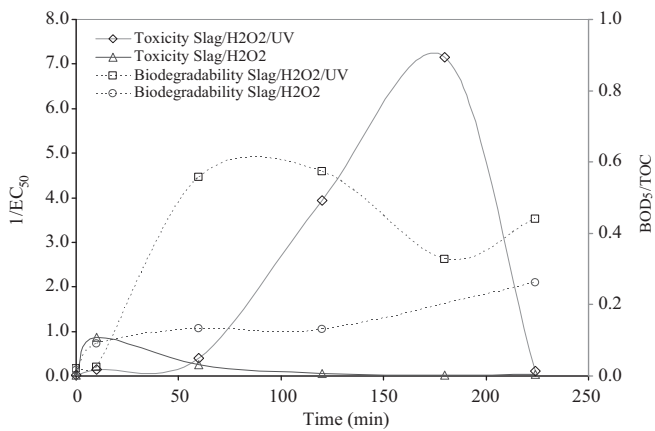


Fig. 6. Toxicity ($1/EC_{50}$) and biodegradability (BOD_5/TOC) measurements during phenol degradation.

solution. The toxicity measurements allowed observing that the first minutes of phenol oxidation did not promote any important change on sample toxicity; however, after 50 min of reaction toxicity increased to values much higher than the toxicity presented by the untreated solution. This system favors the increase of toxicity along all the reaction time, however, when all phenol was removed (30 min) the system did not promote any significant toxicity increment. This behavior indicated that the treatment time control is an important variable to be controlled to avoid the increment of the effluent toxicity. The same assessment was carried out for the slag/ H_2O_2 system. The results of toxicity and biodegradability measurements are also presented in Fig. 6. In this case, the process also favored a continuous biodegradability increment since the first minutes of treatment. However, the oxidation induced the augment of the biodegradability indicator to a lower extent when compared to the irradiated process. Concerning the toxicity of the formed intermediates, the first minutes of phenol degradation promoted slight increase of toxicity, which has a peak around 10 min of treatment. Nevertheless, in the course of the reaction time toxicity decreased to values near the toxicity observed to the untreated solution. At the reaction time needed to remove phenol from the solution (90 min), the toxicity curve allow to interpolate a values with indicates that when phenol is completely removed by slag/ H_2O_2 , the overall toxicity would be similar the initial one. Comparing the two proposed methods, one could observe that although slag/ H_2O_2/UV would suppose an increment on the treatment cost due to the need of UV light irradiation, this method present some advantages such as a fast phenol removal rate and higher biodegradability. Concerning the toxicity, it can be observed that slag/ H_2O_2 did not promote the increment of toxicity along the reaction time, while slag/ H_2O_2/UV formed after the phenol removal intermediates with high toxicity. The higher biodegradability achieved with the use of slag/ H_2O_2/UV can be explained by the higher OH radical formation rate in this method due to UV irradiation, promoting a higher transformation level of phenol in more biodegradable molecules such as aliphatic and hydroxylated structures i.e. catecol [19]. Concerning the difference on toxicity profiles, the properly assessment would be performed with the identification of all intermediates, which due to analytical limitation, unfortunately was not possible. In this study, catecol was the only intermediate identified by HPLC during the treatment, appearing just before the complete phenol removal. Moreover, the toxicity increment could not be related to the Fe and Cu leaching during experimentation time, since toxicity curves did not follow the trend of Cu and Fe leaching observed in Fig. 4.

4. Conclusions

The used slag presented acceptable capacity to act as catalyst to promote the photocatalytic degradation of organic compounds, represented by phenol degradation. During experimentation, Cu and Fe leaching were observed, with Fe concentration reaching about 25 mg L^{-1} at the end of the treatment time. However, its concentration was not high during the treatment time needed to remove phenol. The two proposed AOP system were able to reduce 50% the TOC in the samples. Slag/ H_2O_2/UV and slag/ H_2O_2 treatments promoted biodegradability increment during reaction time. Nevertheless the irradiated system achieved higher biodegradability indicator (BOD_5/TOC) increase. The toxicity assessment was accomplished with the observation of toxicity peaks, indicating the formation of more toxic compounds in both treatments. However, the control of the reaction time would minimize the environmental impact of the produced effluents.

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