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Integrated CWPO and Biological Treatment for the Removal of 4-Chlorophenol From Water

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Catalysts based on pillared clays with Al-Fe have been synthesized from a commercial bentonite and tested for catalytic wet peroxide oxidation (CWPO) of 4-chlorophenol (4-CP). Different H_2O_2 doses have been tested in order to find the lowest amount of that reagent needed for an efficient oxidation treatment since this is a main component of the economy of the process. Using a hydrogen peroxide dose of 150 mg/L, less than one-half the stoichiometric amount, complete conversion of 4-CP and the most toxic species of the oxidation pathway (aromatics, as 4-chlorocatechol and hydroquinone), was achieved. Short-chain carboxylic acids were the remaining products found after 4 h of reaction together with a small amount of unconverted hydrogen peroxide. The resulting effluents were submitted to a biological treatment for further removal of the remaining oxidation byproducts. Aerobic respirometric studies showed that a dose of hydrogen peroxide below one-half the stoichiometric is sufficient for obtaining an easily biodegradable effluent from the CWPO step.

Keywords 4-chlorophenol; Al-Fe pillared clays; biodegradability; CWPO; respirometry

INTRODUCTION

The efficient cleaning of a wide diversity of wastewaters containing highly toxic organic pollutants generated by different industrial processes is a topic of growing interest in the last decades. Among the numerous classes of pollutants, an increased concern is directed towards organic refractory compounds which are difficult to remove by means of conventional wastewater treatment technologies and their efficient treatment by inexpensive methods is still a challenge. Chlorophenols (CPs) are synthetic organic compounds of particular importance obtained on large industrial and commercial scales and extensively used as pesticides, herbicides, dyes, etc. They are highly toxic and hardly biodegradable and different methods have been tested to remove them from water. Among the processes used for the removal of these pollutants, advanced oxidation processes (AOP's) have been defined as those aqueous phase oxidation processes based on the use of hydroxyl radical as oxidant. This group of methods has attracted an increasing interest since they avoid the use of costly reactors (as other methods, like wet air oxidation) (1). One of the most promising AOP's is based on the use of Fenton's reagent. The Fenton process uses Fe^{+2} as catalyst to generate hydroxyl radicals from hydrogen peroxide. The main disadvantage of this process is the continuous loss of the catalyst in the effluent which furthermore has to be removed from it before discharge (2). Besides, this process requires acidification of the initial solution since the optimum operating pH is around 3 (3), corresponding to the maximum concentration of the active Fe^{+2} species and to the lowest rate of H_2O_2 parasitic decomposition. The use of solid Fenton-type catalysts using different Fe-bearing catalysts offers a promising solution due to its easier recovery after the oxidation treatment, the low contamination of the effluents with metals which could negatively influence on a possible subsequent biological treatment step, and a wider operative pH range (2). Heterogeneous catalysts for catalytic wet peroxide oxidation (CWPO) consist most commonly of transition-metal oxides and noble metals as active phases supported on zeolites (4) or activated carbon (5). Deactivation has been often observed together with leaching of the catalytically active elements. Clay-based catalysts pillared by Fe hydroxo complexes (6) or mixed Al-Cu^{+2} or Al-Fe^{+3} pillared clays have shown encouraging results for oxidizing organic compounds in aqueous media using hydrogen peroxide (7–12). These materials are based on layered silicate clays intercalated by pillaring polyoxocations and they have recently become an important class of new microporous materials with potential applications as catalysts due to their thermal and mechanical stability (13). These pillared clays have shown high oxidation rates, as well as a lower sensitivity to pH than iron ions in solution at the same reaction

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conditions, with marginal leaching of the cations, maintaining their activity during successive runs (9). Recent work has been reported on the successful use of pillared clays containing Cu as catalysts in the CWPO of real wastewaters from agro-food production (14) and Cu and Fe-pillared clays for olive oil mills effluents (15,16). Likewise Al-Fe pillared clays have been employed for the catalytic wet peroxide photo-oxidation of phenolic compounds bearing olive oil mill wastewaters (17).

Coupling of different techniques in order to improve the final removal of organic pollutants has received increasing attention in the last years. The use of advanced oxidation processes in conjunction with biological treatment is a strategy of growing interest (18–22). High removal efficiencies have been reported using this approach for textile wastewaters (23). These coupled treatments show a promising future but optimization of the oxidation pre-treatment and its consequent effect on the biological process has to be investigated more in depth. The consumption of the oxidant must be adjusted to the strictly necessary amount for that pre-treatment step since some of the oxidants, like hydrogen peroxide, negatively affect the microorganisms (24). Besides, a detailed knowledge of the oxidation byproducts is needed since some of them show a highly toxic effect on the biological treatment.

The main role of the chemical oxidation pre-treatment is the conversion of bioresistant species into biodegradable intermediates. The objective is not the complete oxidation of the pollutants which may involve an unnecessary expense of chemical oxidant and energy, increasing the operation cost. Regarding the biological step, the effect of the chemical pre-treatment on the characteristics of the effluents is usually assessed by means of biodegradability tests, toxicity tests (25), integrated studies with a biological post-treatment, or a combination of all of them (19).

In this work, 4-chlorophenol (4-CP) in aqueous solution was submitted to sequential CWPO and biological treatment using Al-Fe pillared clays as catalysts in the oxidation pre-treatment. The amount of hydrogen peroxide for the CWPO step was optimized in order to adjust it to the objective of decreasing the toxicity of the resulting effluent allowing an effective biological treatment. Respirometry tests were used to follow the biodegradability of the CWPO effluents.

MATERIALS AND METHODS

Preparation of the Pillared Clays

The Al-Fe pillared clays (AlFe-PILC) used as catalysts for the CWPO process were synthesized from a commercial purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, Oregon, USA). The chemical analysis (wt%) of this bentonite was: SiO_2, 52.22; Al_2O_3, 16.81; Fe_2O_3, 3.84; Na_2O, 1.26; MgO, 0.88; CaO, 0.74; K_2O, 0.80. The cation-exchange capacity (CEC) was 97 meq per 100 g of clay. A 0.2 M NaOH solution was slowly added to an Al-Fe solution (0.1 M $AlCl_3$ and 0.1 M $FeCl_3$). After aging, the pillaring solution obtained was added to a bentonite suspension (1 wt%). The pillaring stoichiometries employed were: 10 mmol of Al per gram of clay (26) and a molar ratio $Fe/(Al + Fe) = 0.10$. The interchange process was carried out at room temperature for 12 h under constant stirring. The resulting product was washed by centrifugation with deionized water until chloride free (conductivity lower than 10 μS). After air-drying, it was calcined at 400°C for 2 h.

Characterization Methods

X-ray diffractograms of the pillared clays were obtained with a Siemens model D5000 diffractometer using Cu$K\alpha$ radiation. To maximize the (001) reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass slides. BET surface area values were determined from 77 K N_2 adsorption in a Quantachrome Autosorb 1 apparatus. The samples were previously outgassed at 160°C and 5×10^{-3} Torr for 16 h. The metal content was measured by means of X-ray fluorescence with a TXRF EXTRA-II (Rich & Seifert, Germany) spectrometer after digestion of the samples with a nitric, chlorhidric and sulphuric acids mixture at 100°C.

CWPO Experiments

The CWPO experiments were performed in a glass jacketed batch stirred reactor (1 L) at 25°C and ambient pressure using 4-CP and catalyst initial concentrations of 100 mg/L and 1 g/L, respectively. Samples were withdrawn from the reactor at 15 min, 30 min, and each hour until completing 4 h of reaction time. The catalyst was separated by filtration. The pH was continuously controlled within the range of 3 to 3.5, which has been found as the optimum for Fenton oxidation (27) as well as for CWPO with Al-Fe pillared clays catalysts (28). The effect of the H_2O_2 initial concentration was studied in the range of 50 to 200 mg/L, in all cases lower than that corresponding to the stoichiometric amount required for 100 mg/L of 4-CP (344 mg/L, 4-CP/H_2O_2: 1/13 molar) was studied.

Analytical Methods

The oxidation process was followed from the evolution of the Total Organic Carbon (TOC), 4-CP and H_2O_2 concentrations. The amount of Fe leached from the pillared clay was also measured. 4-CP and the oxidation intermediates (4-chlorochatecol (4-CC), hydroquinone (HQ), p-benzoquinone (BQ), and catechol (Cat)) were analyzed by HPLC (Varian Pro-Start 240) with a diode array detector (at 210 nm wavelength) using a C_{18} column (Microsorb-MV, 15 cm length and 4.6 mm diameter). Two different mobile phases were used: 1 mL min^{-1} of 4 mM aqueous H_2SO_4 solution for HQ, Cat and BQ and

$0.8\,mL\,min^{-1}$ of a mixture of 30% (v/v) of acetonitrile and 70% (v/v) of a 75 mM aqueous acetic acid solution for 4-CP and 4-CC. Short-chain organic acids and chloride were quantified by means of anionic suppression Ionic Chromatography (Metrohm, mod. 761 Compact IC) with a conductivity detector using a Supp 5 column (25 cm long, 4 mm diameter) and a mixture of 1 mM $NaHCO_3$ and 3.2 mM Na_2CO_3 aqueous solution as mobile phase. The H_2O_2 concentration was determined by a colorimetric titration method based on the formation of a yellow coloured complex Ti(IV)-H_2O_2, using a UV-VIS spectrophotometer at 410 nm. Total Organic Carbon (TOC) was determined with a 1010 TOC Analyser. Analyses of Chemical Oxygen Demand (COD) were performed according to the APHA Standard Methods (29). The 5-day Biochemical Oxygen Demand (BOD_5) analyses were carried out by means of a BOD apparatus (STC90E, VELP Scientifical). Since synthetic water is sterile, a small amount of washed municipal activated sludge was inoculated. The Fe concentration in the reaction media was analyzed by a colorimetric method based on the formation of a reddish coloured complex of Fe with ortho-fenantroline analyzed in an UV-VIS spectrophotometer at 510 nm. Ecotoxicity of the samples from CWPO was measured by means of the Microtox Acute Toxicity Test (SCI 500 Analyzer) using a freeze-dried preparation of the marine bacterium *Vibrio fischeri* (*Photobacterium phosphoreum*).

Biodegradability Tests

Biological batch runs were carried out in a liquid-static-static respirometer® (Universidad de Córdoba) which operated simultaneously with two independent reactors to guarantee reproducibility. The specific oxygen uptake rate (SOUR) profiles were directly recorded. The temperature was controlled by means of a thermostatic bath within the 20–25°C range. An initial VSS concentration of 350 mg/L was used. The original innoculum comes from a municipal wastewater treatment plant and it was maintained with acetate and glucose as carbon sources. Prior to use in each experiment, the sludge was maintained overnight in starvation and aeration to ensure only endogenous activity. Nevertheless, before adding the effluent, the residual TOC and endogenous uptake rate were measured. Once the sample was added, the respirogram was recorded until the endogenous activity was reached again and a total degradation of TOC was achieved up to a maximum of 48 h. The chemical analysis of the samples was performed by the same methods described for the CWPO experiments.

RESULTS AND DISCUSSION

Characterization of the Pillared Clays

The oriented powder X-ray diffractogram of the Al-Fe pillared clay synthesized is shown in Fig. 1, which includes also those of the starting bentonite and Al pillared clay (Al-PILC) for comparison. Fairly sharp d_{001} peaks can be seen in the cases of both pillared clays, indicating a quite homogeneous pillaring process. However, the presence of a second peak at 2θ around 9°, which corresponds to the main peak found in the pattern of raw Fisher bentonite, seems to indicate the existence of a fraction of unpillared material. In the case of the pillared clays, the maximum of the (001) reflection peak is placed at similar 2θ values (around 5°), indicating a similar basal spacing in these samples.

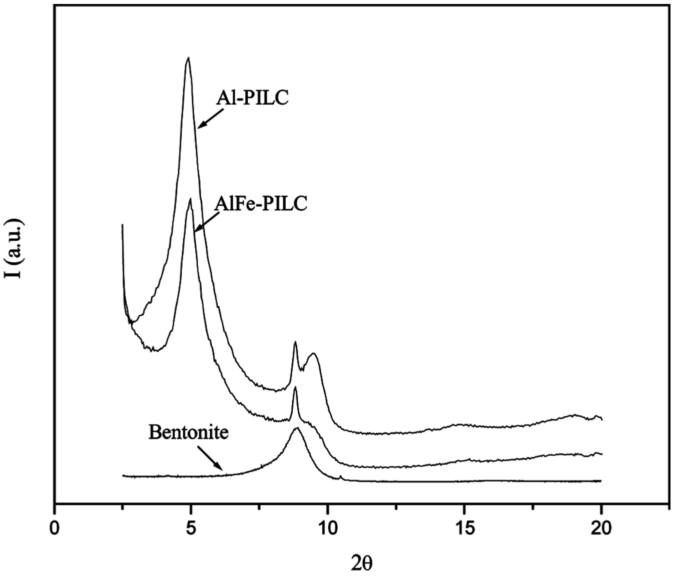


FIG. 1. X-ray diffractograms of the raw bentonite and the Al and Al-Fe pillared clays.

Table 1 reports the basal spacing d_{001} and textural properties of Al and Al-Fe pillared clays. The corresponding values of the starting bentonite are also included for comparison. The substantial increase of basal spacing and BET surface area indicate a successful pillaring process. The Al-Fe pillared clay shows a lower surface area due to the introduction of Fe in the structure. This decrease can be also observed in the micropore surface area and micropore volume values. The introduction of Fe in the structure of the pillared clay is confirmed by the Fe load measured by X-ray fluorescence given in Table 1.

CWPO Experiments

Preliminary tests were carried out in order to check any catalytic activity of the raw bentonite in the oxidation of 4-CP with H_2O_2. Very low 4-CP and TOC conversion values were observed, most probably due to adsorption rather than to oxidation. When the Al-PILC was used as catalyst an increased activity was found which can be explained by a higher accessibility of the iron present in the starting clay as a result of the opening of the porous

TABLE 1
Characterization of the raw bentonite and the pillared clays

Sample	Basal spacing d_{001} (nm)	BET surface area (m^2g^{-1})	External surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	Fe content (wt%)
Bentonite	0.98	35	11	0.005	3.5
Al-PILC	1.80	298	51	0.101	3.4
AlFe-PILC	1.78	236	82	0.081	7.2

structure which follows the pillaring process. The introduction of iron in the preparation of the Al-Fe pillared clays led to a dramatic increase of the catalytic activity for CWPO of 4-CP.

Figure 2 shows the evolution of the 4-CP and TOC conversion values upon reaction time at three different H_2O_2 initial concentrations. A significant improvement of 4-CP conversion can be observed when increasing the H_2O_2 dose from 50 to 100 mg/L. This last value becomes sufficient for complete 4-CP conversion at 4-hour reaction time. This complete conversion can be achieved in about half the time doubling the H_2O_2 dose up to 200 mg/L. TOC conversion is much lower than that of 4-CP, indicating that important amounts of oxidation byproducts are remaining in the liquid phase even at the highest reaction time tested. Now the effect of the H_2O_2 dose appears more linear within the range investigated.

Figure 3 shows the time-evolution of the species identified in the liquid phase in C units (TOC) grouped in two blocks, aromatics (including 4-CP) and organic acids. In addition to non-converted 4-CP hydroquinone, benzoquinone, catechol, and 4-chlorocatechol were identified among the aromatic byproducts. This group is the most concerning since it is integrated by highly toxic compounds. At H_2O_2 doses below 100 mg/L (around 30% of the stoichiometric) 4-chlorocatechol was the main component of this group. At that H_2O_2 dose complete removal of the aromatic species identified in the liquid phase requires about 4 hours reaction time.

Table 2 summarizes the concentrations of all the identified byproducts after that time at different H_2O_2 doses. Among the organic acids malonic and oxalic are the most abundant. This last is important given its negative effect in Fe leaching reported in the literature for other supported Fe catalysts (5). In this case, the Fe leaching was fairly low, as can be seen in Table 3, representing at the most around 3.5% of the initial Fe load in the catalyst after 4 h reaction time. A small increase with the oxalic acid concentration was observed (see Tables 2 and 3).

Adjusting the H_2O_2 dose is a critical feature in wet peroxide oxidation processes since H_2O_2 consumption is a determining component of the treatment cost. Moreover, the excess of this reagent needs to be removed before discharge since it represents an additional contribution to the toxicity of the effluent. The results from Table 3 shows that a H_2O_2 dose beyond 100 mg/L (around 30% of the

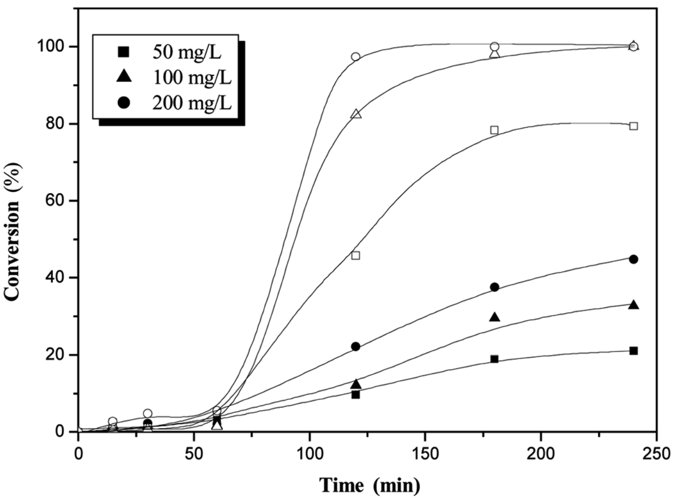


FIG. 2. Time-evolution of 4-CP (open symbols) and TOC (solid symbols) conversion values in the CWPO of 4-CP with Al-Fe pillared clays at different H_2O_2 initial concentrations.

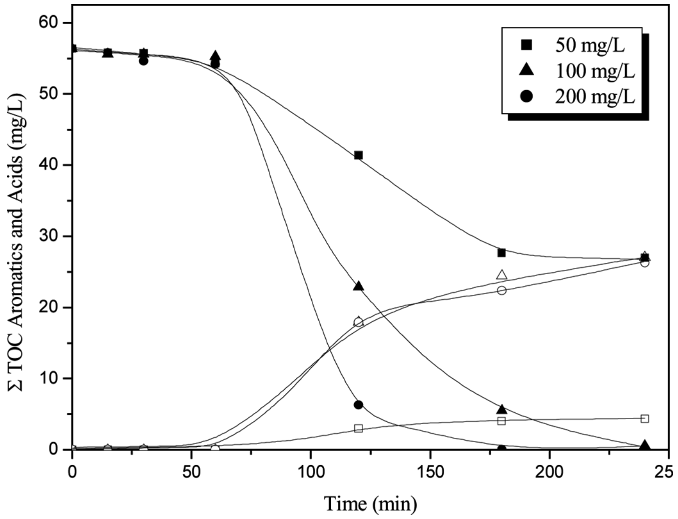


FIG. 3. Time-evolution of TOC corresponding to identified aromatics (solid symbols) and acids (open symbols) from CWPO of 4-CP with Al-Fe pillared clays at different H_2O_2 initial concentrations.

TABLE 2
Concentration of 4-CP and identified oxidation byproducts after 4 h of reaction at different H_2O_2 initial concentrations (mg/L)

$[H_2O_2]_0$	4-CP	4-CC	HQ	BQ	Cat	Acetic acid	Formic acid	Malonic acid	Maleic acid	Oxalic acid
50	20.7	20.0	2.6	0.5	8.9	1.6	4.6	7.1	0.0	0.2
75	3.2	11.1	1.4	0	1.7	2.7	6.7	54.9	1.7	0.9
100	0	1.1	0	0	0	3.3	6.8	62.4	2.9	5.9
150	0	0	0	0	0	2.3	5.9	49.4	4.6	32.8
200	0	0	0	0	0	4.4	7.1	41.6	5.2	32.2

TABLE 3
H_2O_2 and TOC residual concentrations, Fe leached and ecotoxicity values after 4 h of reaction at different H_2O_2 doses

Initial H_2O_2 concentration (mg/L)	H_2O_2 (mg/L)	Fe leached (mg/L)	Ecotoxicity (T.U.)	TOC (mg/L)	
				Measured	Calculated
50	4.6	1.4	59.9	44.2	33.3
75	6.1	1.8	7.4	40.8	31.7
100	4.1	2.3	4.5	38.7	27.2
150	15.3	2.5	1.7	34.2	27.4
200	56.7	2.6	5.6	32.3	26.0

stoichiometric) leads to a significant increase of the residual H_2O_2 concentration without a justified counterpart on the reduction of TOC neither of ecotoxicity. A comparison of the experimental TOC values and the calculated TOC from the carbon-containing compounds analyzed in the liquid phase reveal some differences derived from the existence of unidentified species. Nevertheless, the relative differences do not depend on the H_2O_2 dose and neither do they seem to represent a significant source of toxicity.

Biodegradability

Aerobic mixed liquor was used for the evaluation of the biodegradability of the samples resulting from the CWPO process investigated. In order to analyze more in depth the respirometric profiles, respirograms of all the individual compounds identified were obtained. A starting concentration equivalent to 35 mg/L TOC was used in all cases. The results obtained are summarized in Table 4.

Different groups of compounds can be recognized regarding their biodegradability. Thus, readily biodegradable compounds (acetic acid) can be distinguished from those that, although biodegradable, require an adaptation period (lag) of the sludge (malonic and maleic acids), and compounds which are hardly biodegradable except at very low concentrations, either because their biodegradation rate is very low (formic acid) or because they show a high inhibition by substrate (the case of oxalic acid, 4-CP and 4-CC). Finally, hydroquinone is a highly refractory compound, which oxidizes to *p*-benzoquinone without any reduction of TOC.

TABLE 4
Biodegradability of the individual compounds identified in CWPO of 4-CP with Al-Fe pillared clays

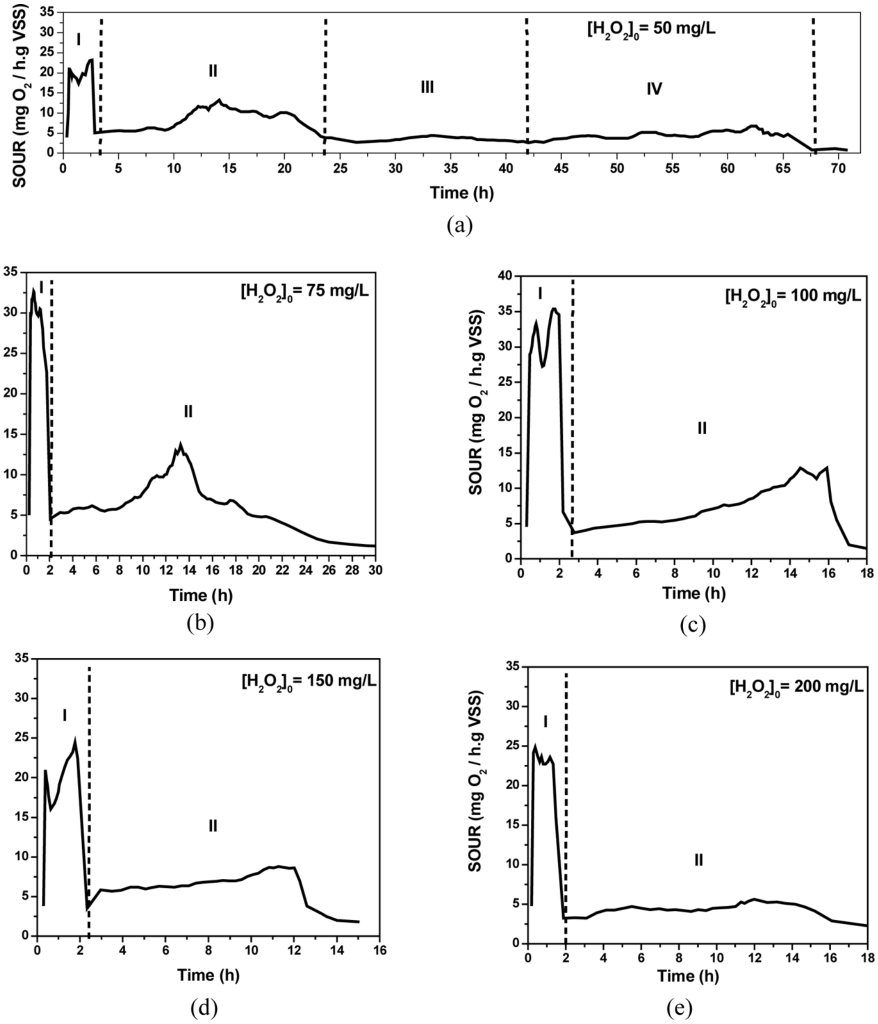
Compound	Acetic acid	Formic acid	Malonic acid	Maleic acid	Oxalic acid	4-CP	4-CC	HQ
Biodegradability	high	low	yes	yes	partial	partial	partial	no
Lag phase	no	no	30 h	20 h	20 h	*	*	*
X_{TOC}	93% (6 h)	32% (48 h)	100% (48 h)	82% (48 h)	100% (90 h)	–	–	–
Inhibition by substrate	no	no	no	yes	yes	yes	yes	center

*At the concentration of the test these compounds show a very high toxicity. Nevertheless, partial or even complete biodegradation has been observed at low concentrations (<20 mg/L).

An additional aspect to be considered in the respirometric study is the presence of hydrogen peroxide in the samples. At neutral pH and in the presence of catalase positive microorganisms, H_2O_2 decomposes generating additional oxygen which provokes disturbances of the SOUR measurements. Thus, an additional test was performed using a solution with the composition of that resulting from an initial H_2O_2 concentration of 100 mg/L. A similar evolution of both TOC and each compound concentration was found in the presence and absence of H_2O_2.

The respirometric profiles obtained for the samples from CWPO of 4-CP at 4 h reaction time and different H_2O_2 initial concentrations are shown in Fig. 4. For the sample from a dose of H_2O_2 of 50 mg/L four zones can be observed (Fig. 4a). The first one represents a TOC conversion of 50% due to the biodegradation of acetic and formic acids, the latter being in a very low concentration. The second zone corresponds to the degradation of malonic and maleic acids, reaching a final TOC conversion of 59%. The existence of high concentrations of 4-CP and 4-CC caused a delay in the biodegradation process up to 72 h. 4-CC was first converted along zone III and then 4-CP conversion occurred in zone IV. A refractory fraction of 7% TOC corresponding to the presence of a certain amount of hydroquinone was detected.

A higher biodegradability was observed when CWPO was conducted at a H_2O_2 initial concentration of 75 mg/L (Fig. 4b). A TOC conversion of 38% was achieved after 2 h, which greatly corresponds to the acetic acid biodegradation. After 16 h, TOC conversion was already of 85% and acids were not detected. The inhibition effect derived from the presence of 4-CP and 4-CC was significant even when these compounds were present at low concentrations. 30 h were needed in order to obtain a final TOC conversion of 99.8%.



(a)

(b) (c)

(d) (e)

FIG. 4. Respirometric profiles of the samples from CWPO of 4-CP with Al-Fe pillared clays after 4 h using different H_2O_2 initial concentrations.

The time required for almost complete mineralization of the sample from 100 mg/L initial concentration of H_2O_2 fairly decreased to 17 h, reaching a TOC conversion of 98% (Fig. 4c). Now a high fraction of TOC corresponds to organic acids. Although oxalic acid concentration suffered a slight increase when H_2O_2 was increased from 75 to 100 mg/L, its inhibitory effect was negligible at the concentrations detected in this work. Additionally, an H_2O_2 initial concentration of 100 mg/L ensures the absence of aromatics, allowing the increase of the BOD_5/COD ratio from 0.025 of the initial 4-CP solution up to 0.24 upon CWPO treatment.

As shown in Figs. 4d and 4e, the increase of the starting hydrogen peroxide concentration above 100 mg/L did not improve the biodegradability of the final samples from the CWPO treatment. Moreover, the increasing presence of an inhibitory compound as oxalic acid and the lower concentrations of acetic acid were detrimental for the biodegradability of the samples.

CONCLUSIONS

Coupled CWPO with Al-Fe pillared clays and biological treatment can be highly effective for 4-CP degradation with high mineralization. With around 30% of the stoichiometric amount of H_2O_2 a TOC removal of 30% was achieved upon CWPO, mainly affecting the most toxic compounds. The subsequent biological treatment reached 99.8% TOC removal after 18 h. Hydrogen peroxide doses below 100 mg/L reduce the biodegradability of the CWPO effluents due to the presence of remaining concentrations of inhibitory compounds such as 4-CP, 4-CC, and HQ.

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