Improved wet peroxide oxidation strategies for the treatment of chlorophenols

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HIGHLIGHTS

- CWPO of chlorophenols with Fe_xO_y/γ-Al_2O_3 catalysts is more efficient than Fenton oxidation.
- Increasing the temperature improves both the oxidation rate and mineralization degree.
- The Fe_xO_y/γ-Al_2O_3 catalysts are highly active and stable upon CWPO of chlorophenols.
- CWPO (Fe_3O_4/γ-Al_2O_3) at high temperature is the preferable strategy for chlorophenols oxidation.
- Fe_3O_4/γ-Al_2O_3 catalyst can be easily recovered from the liquid phase by a magnet.

GRAPHICAL ABSTRACT
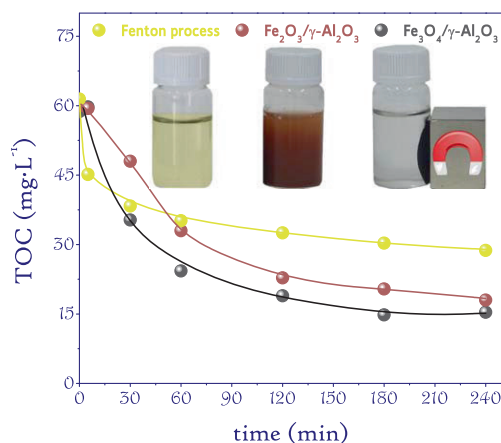
ABSTRACT

Different advanced oxidation strategies have been investigated for the treatment of chlorophenols in aqueous phase with the aim of improving the removal efficiency in terms of mineralization, remanent by-products and kinetics. Those strategies were homogeneous Fenton-like oxidation and CWPO with two different own-prepared Fe_xO_y/γ-Al_2O_3 catalysts. The intensification of the process by increasing the temperature has been also evaluated. CWPO of chlorophenols with those catalysts has proved to be more efficient than homogeneous Fenton-like oxidation due to a lower rate of H_2O_2 decomposition allowing a higher availability of hydroxyl radicals along the course of reaction. Increasing the temperature clearly improved the oxidation rate and mineralization degree of both homogeneous Fenton-like oxidation and CWPO, achieving almost 90% TOC reduction after 1 h at stoichiometric H_2O_2 dose, 100 mg L^{-1} initial chlorophenol concentration, 1 g L^{-1} Fe_3O_4/γ-Al_2O_3 catalyst, pH 3 and 90 °C temperature. Both Fe_xO_y/γ-Al_2O_3 catalysts suffered fairly low iron leaching (<5%) and a remarkable stability in a three-cycles test with 2,4,6-TCP. The use of the magnetic catalyst is preferable due to its easy separation and recovery from the liquid phase by a magnet. Its magnetic properties remained unchanged after use in CWPO.

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1. Introduction

Chlorophenols (CPs) are widely used in the production of herbicides, fungicides, insecticides, pharmaceuticals and dyes.

The wastewater from those industries commonly contains chlorophenols in significant amounts, and they have been detected in both surface and ground waters [1–4]. This fact involves a significant risk for the environment due to the high toxicity, persistence and low biodegradability of these compounds which have been listed as priority pollutants by the European Decision 2455/2001/EC and by the US EPA in the Clean Water Act.

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Biological processes are ineffective for the removal of such recalcitrant compounds from wastewater requiring long acclimation periods [5,6]. Although thermal destruction is effective for the breakdown of CPs this way suffers from serious drawbacks derived from energy consumption and the formation of even more toxic species [7,8]. Activated carbon adsorption has also been used for the treatment of chlorophenols [9,10], but it leaves spent carbon as a waste of hazardous character. Therefore, considering other destructive technologies for the treatment of CPs is of significant interest. In this sense, Advanced Oxidation Processes (AOPs) appear to be a promising solution, which has been reported to be effective for CPs breakdown even at near–ambient temperature and pressure.

The Fenton process is one of the most commonly used AOP for the removal of recalcitrant pollutants from wastewaters [11–14]. It has gained large attention due to the simplicity of design and setup, safe operation, high efficiency and the use of readily availability reagents. However, the efficiency of this process is marred by the sludge generation since the catalyst, Fe^{2+}/Fe^{3+} in solution, cannot be retained in the process requiring additional separation steps. Another drawback of the Fenton process is related to the costly consumption of H_2O_2. The possibility of lowering the H_2O_2 dose for the purpose of reducing costs is limited. In fact, it has been recently demonstrated that the use of substoichiometric amounts of H_2O_2 in the oxidation of CPs leads to the formation of highly toxic condensation by-products such as chlorinated diphenyl ethers, biphenyls, dibenzofurans or dioxins [15–17]. The intensification of the process by increasing the temperature has proved to allow a more efficient use of H_2O_2 upon enhanced generation of OH radicals at low iron concentrations [18]. However, the need of dealing with the sludge generated in the process is not avoided. In this sense, the use of solid catalysts by immobilization of iron over a convenient support, the so-called Catalytic Wet Peroxide Oxidation (CWPO), offers a potential solution. So far, activated carbon [19,20], silica [21], mesostructured materials [22–24], zeolites [25,26], pillared clays [27–30] and alumina [31,32] have been used as supports to prepare the catalysts. Among them, the one based on alumina has proved to be an excellent highly-stable catalyst for CWPO not only with phenol but with real wastewaters from the cosmetic industry [31,32].

Typically, CWPO is conducted in a suspension of powdered particles. Therefore, an additional separation step is required to recover the catalyst from the reaction medium. This poses a major drawback for the application of CWPO for wastewater treatment. One approach for overcoming this drawback is to develop a magnetic catalyst that can be easily separated by an external magnet, thereby simplifying its recovery. Moreover, the use of magnetite as active phase represents an important advantage with respect to the conventional catalysts, commonly based on Fe_2O_3, since it contains both Fe (II) and Fe (III) in its structure thus enhancing the rate of ·OH generation. In a previous contribution we focused on the preparation and characterization of a magnetic Fe_3O_4/γ-Al_2O_3 catalyst, which showed to be more active than the conventional Fe_2O_3/γ-Al_2O_3 catalyst and exhibited a high stability working under moderate conditions (50 °C) [33]. In this work, different oxidation strategies have been investigated for the treatment of chlorophenols with the aim of improving the treatment performance in terms of mineralization, remanent by-products and kinetics. Since the recalcitrant character of chlorophenols increases with the number of chlorine atoms in the phenolic ring, the oxidation of mono-, di- and tri- chlorophenols has been studied. Those strategies were homogeneous Fenton-like (Fe^{3+}) oxidation and CWPO with two different own-prepared Fe_xO_y/γ-Al_2O_3 catalysts. The intensification of these processes by increasing the temperature has been analyzed on the basis of kinetics and mineralization degree of the organic species, namely TOC reduction. Particular attention has been paid to the formation of condensation by-products and the reaction mechanism. The reusability of the own-prepared catalysts has been evaluated as well.

2. Materials and methods

2.1. Catalysts preparation and characterization

Two γ-alumina-supported iron catalysts (Fe_xO_y/γ-Al_2O_3) were prepared. They were synthesized by incipient wetness impregnation of powdered γ-Al_2O_3 ($d_p < 100\ \mu m$) supplied by Merck with a $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution. The Fe load was adjusted to a nominal 4% (w/w). After impregnation, the samples were left for 2 h at room temperature, dried for 12 h at 60 °C and calcined for 4 h at 300 °C. An additional reduction stage in H_2 atmosphere was carried out for 2 h at 350 °C in order to develop magnetic properties in one of the catalysts. Thus, the identification of the catalysts was Fe_2O_3/γ-Al_2O_3 and Fe_3O_4/γ-Al_2O_3 for the non-magnetic and the magnetic catalyst, respectively.

X-ray diffraction (XRD) and Mössbauer techniques were used to determine the crystalline phases in the catalysts. The Mössbauer analysis has been described in detail elsewhere [33] and the X-ray diffraction profiles were obtained using a Siemens model D-5000 diffractometer with Cu Kα radiation. These analyses allowed to confirm that iron were in the form of hematite in the Fe_2O_3/γ-Al_2O_3 catalyst and magnetite in the Fe_3O_4/γ-Al_2O_3 catalyst. Total iron content was analyzed by inductively coupled plasma (ICP-MS Elan 6000 Perkin-Elmer Sciex) and the porous structure of the fresh and used catalysts was characterized from the nitrogen adsorption–desorption isotherms at 77 K (Micromeritics Tristar 3020). Elemental analyses were carried out in a LECO CHNS-932 Elemental Analyzer. The chlorine content of the used catalysts was determined by total reflection X-ray fluorescence (TXRF), using a TXRF spectrometer 8030c. Magnetic measurements were performed in a Quantum Design MPMS XL-5 Superconducting Quantum Interference Device (SQUID). The magnetic moment M was measured as function of applied magnetic field H at room temperature.

2.2. Oxidation experiments

Oxidation runs were carried out in a 500 mL glass batch reactor equipped with a PTFE stirrer (700 rpm). All the experiments were performed adjusting the initial pH value of the reaction medium to 3 with nitric acid. Chlorophenols with different chlorine content (4-CP, 2,4-DCP and 2,4,6-TCP) were used as target pollutants. A 100 mg L^{-1} starting concentration of chlorophenol and the theoretical stoichiometric amount of H_2O_2 for complete oxidation up to CO_2, H_2O and HCl, were always used. Homogeneous Fenton-like experiments were conducted at 10 mg L^{-1} Fe^{3+}, while CWPO was always carried out with 1 g L^{-1} Fe_xO_y/γ-Al_2O_3 catalyst. Both established as the optimum values in previous works [18,33]. The temperature effect was tested within the 50–90 °C range.

A previous set of experiments with the three chlorophenols tested was conducted in absence of H_2O_2 within the range of temperatures studied (50–90 °C), confirming the very low adsorption of chlorophenols by the Fe_xO_y/γ-Al_2O_3 catalysts prepared in this work (<5%).

2.3. Analytical methods

The progress of the oxidation processes was followed by periodically withdrawing and analyzing liquid samples from the reactor. In the case of CWPO experiments, the catalyst was separated by filtration using a PTFE filter (pore size 0.45 μm). Chlorophenols were quantified by means of high-performance liquid chromatography (HPLC; Varian Pro-Start 325) equipped with a UV detector and a Microsorb C18 5 μm column (MV 100, 15 cm length, 4.6 mm diameter) as the stationary phase. The analyses were carried out at 270 nm using a 70/30, 55/45 and 45/55% v/v mixture of

acetonitrile/acetic acid aqueous solution (75 mM) as the mobile phase, for 4-CP, 2,4-DCP and 2,4,6-TCP, respectively. Quantification of chloride (Cl^-) as well as organic acids was performed by ion chromatography (Metrohm 790 Personal IC). A Metrosep A supp 5–250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a 3.2 mM Na_2CO_3 aqueous solution as the mobile phase. Total Organic Carbon (TOC) was measured using a TOC analyzer (Shimadzu, mod. TOC, VSCH) and the H_2O_2 concentration was determined by colorimetric titration by the titanium sulfate method [34] using an UV 1603 Shimazdu UV/Vis spectrophotometer. Fe leached to the reaction medium was measured by the *o*-phenantroline method [35].

3. Results and discussion

Fig. 1 shows the evolution of 4-CP, 2,4-DCP and 2,4,6-TCP concentration upon Fenton-like oxidation and CWPO with the own-prepared catalysts at 50 °C. As can be seen, the homogeneous Fenton-like process led to the highest conversion of the starting CP with the three chlorophenols tested. In fact, the chlorine content
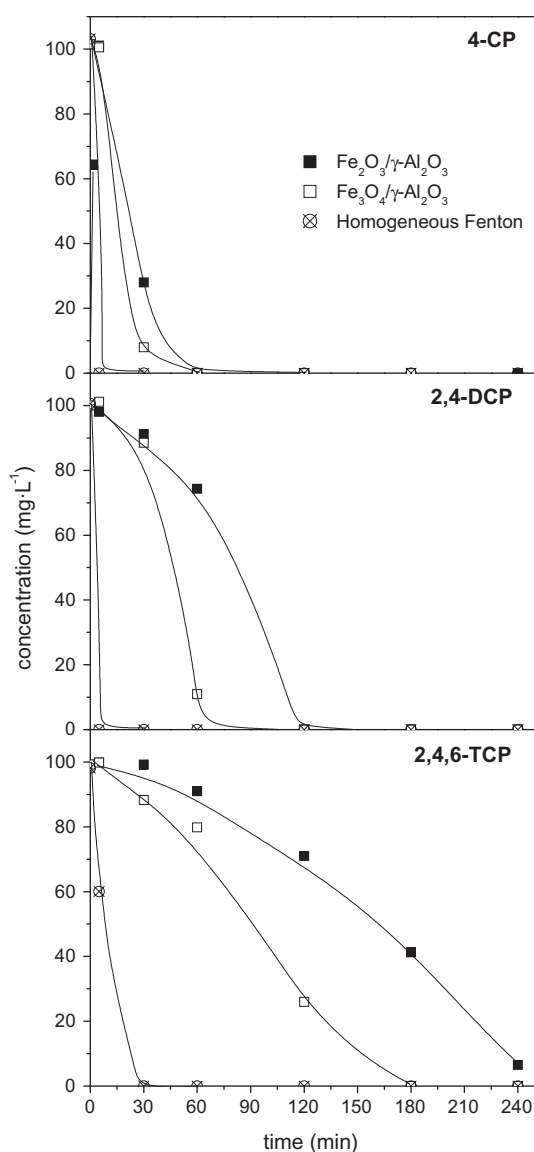
Fig. 1. Evolution of 4-CP, 2,4-DCP and 2,4,6-TCP upon homogeneous Fenton-like oxidation ([Fe^{3+}]$_0$ = 10 mg L^{-1}) and CWPO with Fe_xO_y/γ-Al$_2$O$_3$ (1 g L^{-1}); ([CP]$_0$ = 100 mg L^{-1}; [H_2O_2]$_0$ at stoichiometric dose; pH$_0$ = 3; *T* = 50 °C).

of the target pollutant did not influence significantly the conversion achieved upon Fenton-like oxidation which was complete for the three CPs although proceeded at a lower rate in the case of 2,4,6-TCP. On the opposite, CWPO with both Fe_xO_y/γ-Al$_2$O$_3$ catalysts was significantly affected by the number of chlorine atoms of the target CP molecule. In fact, the magnetic catalyst was the only leading to complete conversion of 2,4,6-TCP upon the 4 h reaction time of the experiment. The higher activity of the magnetic catalyst (Fe_3O_4/γ-Al$_2$O$_3$) can be related to the presence of both Fe (II) in addition to Fe (III). This allows a faster decomposition of H_2O_2 thus enhancing the oxidation process.

Fig. 2 shows the evolution of TOC and H_2O_2 conversion in the experiments of Fig. 1. As observed, the homogeneous process promotes a faster decomposition of H_2O_2 but with a lower TOC removal at the end of the 4 h-experiments. This indicates a fairly inefficient consumption of hydrogen peroxide due to a very fast decomposition, which provokes a high concentration of ·OH and ·OOH radicals in the initial stages favoring auto-scavenging reactions. On the opposite, the lower rate of H_2O_2 decomposition in the heterogeneous process allows higher availability of hydroxyl radicals along the reaction time, i.e. higher degrees of mineralization for the three chlorophenols tested. Fairly high mineralization percentages (75% and 70%, using the magnetic and the non-magnetic catalysts, respectively) were achieved at the end of the experiments (4 h), while the homogeneous Fenton-like process led to a degree of mineralization significantly lower (≈50%). It has to be pointed out that under these operating conditions complete decomposition of H_2O_2 was not achieved after 4 h of reaction where conversion values around 80% were observed for the three chlorophenols tested.

Short-chain organic acids were the only by-products detected beyond the first 5 min of reaction. The differences between the measured TOC and the amount of carbon in the identified compounds reveal the existence of unidentified by-products, which have been usually assessed to condensation species [15–17]. Fig. 3 shows the percentage of starting C remaining as organic acids and unidentified condensation by-products at the end of the 4 h-experiments at 50 and 90 °C. The chlorine balance was matched in more than 95% being that element as chloride ion except some small amounts of chloroacetic acid. Oxalic was by far the major organic acid in all the studied processes (see Figs. S1, S2 and S3 in Supplementary Material). As can be seen in Fig. 3, the use of the solid catalysts reduced significantly the amount of condensation by-products being that effect more pronounced at increasing temperature. At 90 °C the amount of those species was negligible with the two own-prepared catalysts both of them giving rise to a higher mineralization which indicates a more efficient consumption of H_2O_2. A similar effect of temperature has been reported by Zazo et al. [18] in homogeneous Fenton oxidation of phenol but those authors found that complete disappearance of condensation by-products required up to 110 °C.

The use of the stoichiometric dose of H_2O_2 allowed complete oxidation of the aromatic species upon the first 5 min of reaction. In previous contributions [16,17], we reported that the first by-products from homogeneous Fenton-like oxidation of CPs were chlorine-containing hydroxylated compounds, predominantly in *ortho* position. In addition to these compounds the oxidation of CPs under substoichiometric conditions can lead to the formation of condensation by-products (including chlorine-containing) by oxidative coupling reactions. Finally, ring opening of the aromatic and condensation intermediates leads to the formation of organic acids, which can be finally mineralized in varying extents. Fig. 4 shows the reaction scheme proposed as well as a comparison between homogeneous Fenton-like oxidation and CWPO with Fe_xO_y/γ-Al$_2$O$_3$ at high temperature, i.e. 90 °C. As it is shown, the use of the solid catalysts is more efficient than the homogeneous Fenton-like
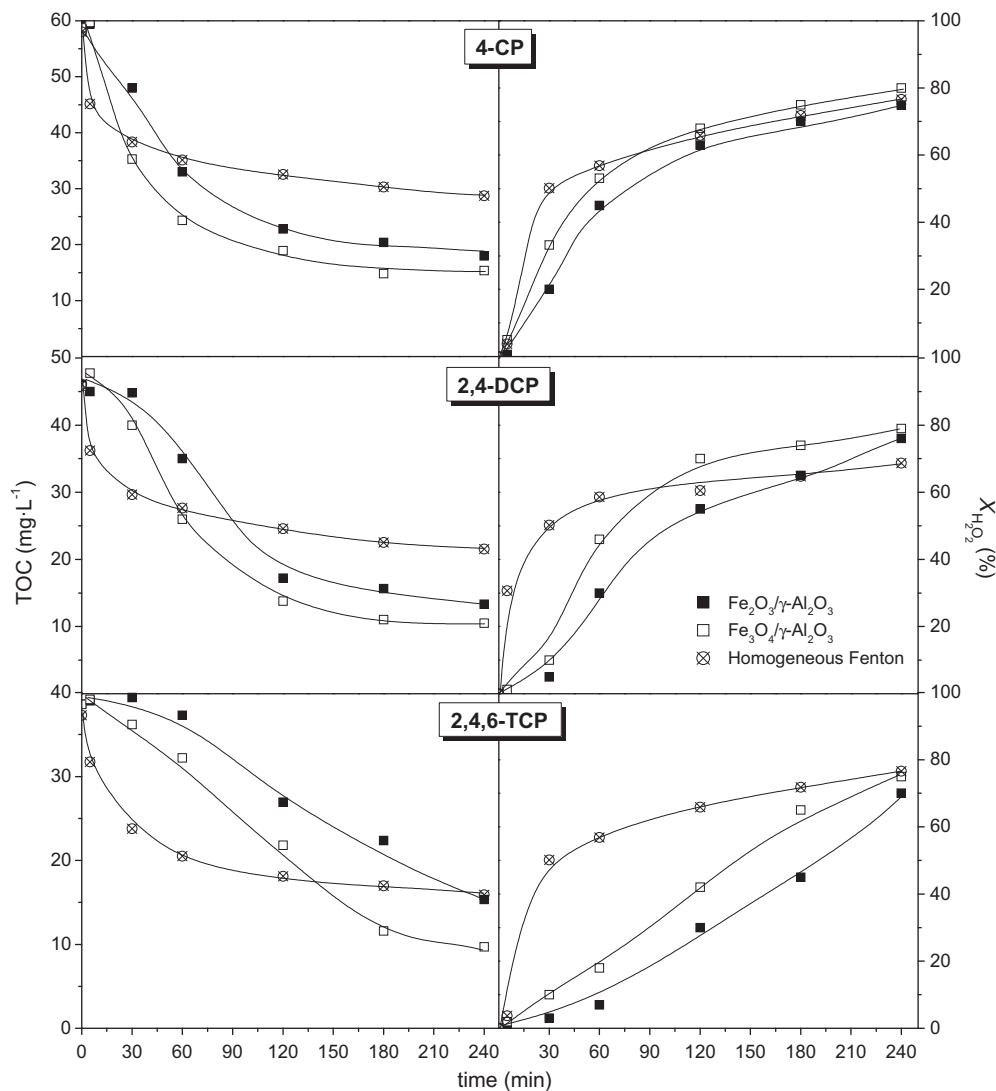
Fig. 2. Evolution of TOC and H_2O_2 upon homogeneous Fenton-like oxidation ($[Fe^{3+}]_0 = 10$ mg L^{-1}) and CWPO with Fe_xO_y/γ-Al_2O_3 (1 g L^{-1}); ($[CP]_0 = 100$ mg L^{-1}; $[H_2O_2]_0$ at stoichiometric dose; $pH_0 = 3$; $T = 50\ °C$).

process since, as stated above, significantly higher mineralization degrees are reached, reducing the formation of condensation by-products.

Increasing the temperature can be considered as a way of intensifying the Fenton process [18]. Fig. 5 shows the evolution of TOC upon oxidation of 4-CP by the homogeneous Fenton-like process and by CWPO with the own-prepared Fe_xO_y/γ-Al_2O_3 catalysts at different temperatures covering the range of 50–90 °C. The curves showing the decomposition of H_2O_2 are also included. The results clearly show that the rate and degree of TOC reduction increase with temperature, especially in the CWPO process. After 30 min reaction time the degree of mineralization of 4-CP by homogeneous Fenton-like oxidation was around 40% at 50 °C and 60% at 90 °C whereas the use of the Fe_3O_4/γ-Al_2O_3 catalysts allowed achieving significantly higher percentages (around 70% and 90% at 50 and 90 °C, respectively). Meanwhile, H_2O_2 decomposition shows a lower rate with the solid catalysts. Therefore, these results allow concluding a more efficient use of the oxidant with the own-prepared catalysts, especially in the case of the magnetic one whose better performance is more pronounced at lower temperatures within the range tested. It has to be pointed out that at 90 °C all the chlorophenols tested were completely converted after 60 min reaction time (see Fig. S4 in Supplementary Material).

The consumption of H_2O_2 is a critical issue of the Fenton and related oxidation processes since it represents by far the main contribution to the operating cost [18,36]. The efficiency on the use of hydrogen peroxide can be more clearly seen in Fig. 6. That efficiency, defined as the amount of TOC converted per unit mass of H_2O_2 decomposed does not decrease when increasing the temperature as should be expected if H_2O_2 would be degraded into O_2 and H_2O due to thermal breakdown. On the opposite, increasing temperature led to a higher mineralization per unit mass of H_2O_2 decomposed.

The efficiency on the use of H_2O_2 was almost 90% in CWPO with the own-prepared catalysts whereas in homogeneous Fenton-like oxidation was around 75% at the best. It is important to note that no residual H_2O_2 remained in the reaction medium after 1 h reaction time working at 90 °C so that it can be considered around the optimum from this point of view since H_2O_2, which cannot be recovered, needs to be eliminated before discharge due to its toxicity.

3.1. Catalysts stability and reusability

Stability is a main question with regard to the potential application of solid catalysts in practice. Iron concentration in the liquid
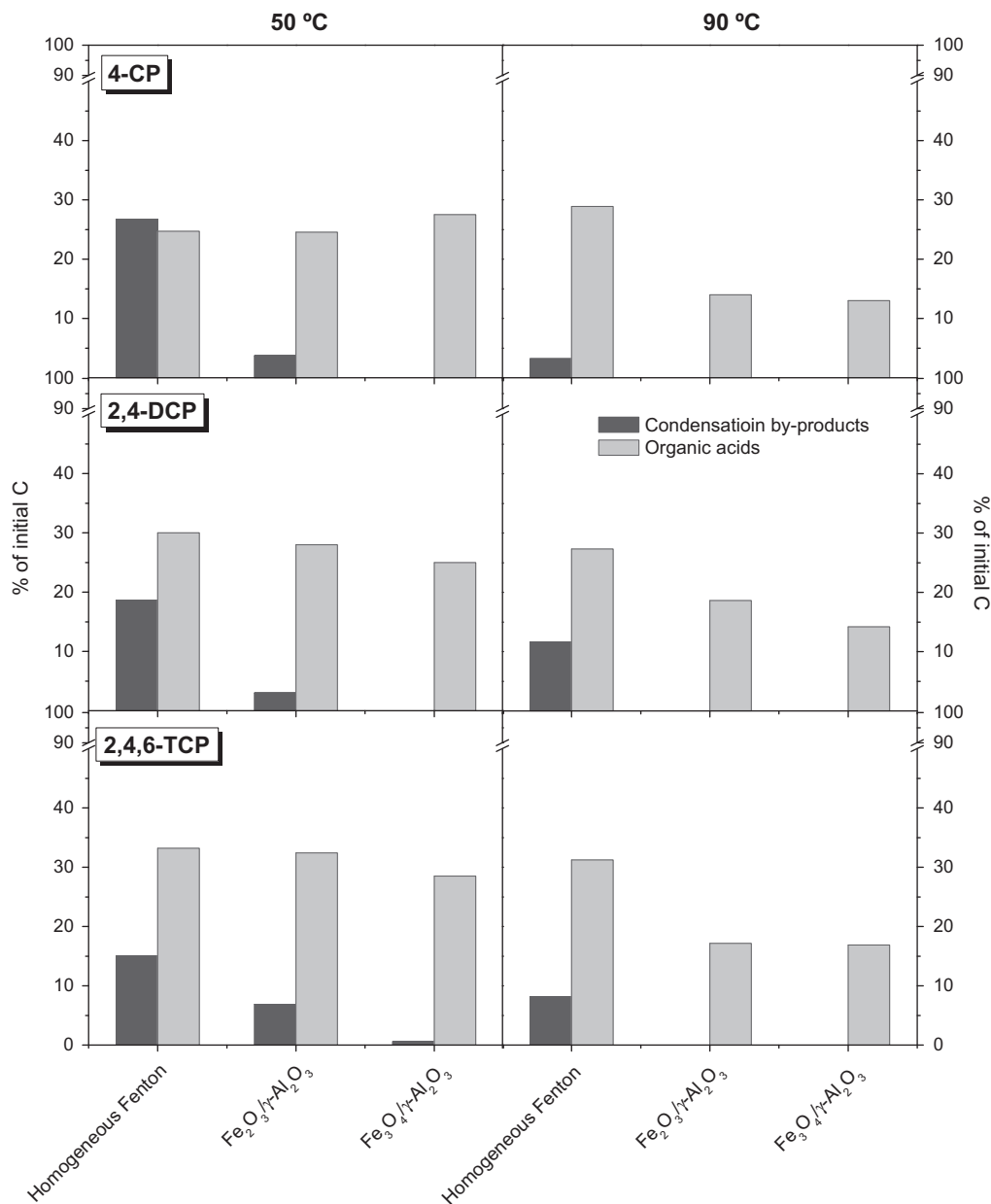
Fig. 3. Remaining by-products (4 h) from chlorophenols oxidation by homogneous Fenton-like ([Fe^{3+}]$_0$ = 10 mg L^{-1}) and by CWPO with Fe$_x$O$_y$/γ-Al$_2$O$_3$ catalysts (1 g L^{-1}) at 50 an 90 °C ([CP]$_0$ = 100 mg L^{-1}; [H$_2$O$_2$]$_0$ at stoichiometric dose; pH$_0$ = 3).

phase was measured in the CWPO experiments in order to evaluate possible leaching from the catalysts. The results obtained are depicted in Fig. 7, confirming the fairly good stability of the own-prepared Fe$_x$O$_y$/γ-Al$_2$O$_3$ catalysts used in this work. Iron leaching represented 6% of the initial iron content at the most. It is notice-able that increasing the temperature gave always rise to lower concentrations of Fe in solution. Therefore, the leaching of Fe from the catalyst must be mostly associated to the action of some oxidation by-product. According to a number of authors [19,20,37] the iron leaching from Fe-bearing catalysts upon CWPO of organic pollu-tants is directly related to the formation of oxalic acid. Zazo et al. [19] found a linear relationship between Fe leaching from Fe/AC catalysts and the concentration of oxalic acid in the liquid phase ([Fe] = 0.33·[oxalic acid]). These authors postulated that the action of oxalic acid could be the result of Fe complexation since the Fe to oxalate weight ratio in that expression is very close to a trivalent Fe-oxalate complex. Those findings are in good agreement with

the observed in this work, where both, the iron leached to the reac-tion medium and the oxalic acid concentration, decreased as the temperature and the chlorine content of the target chlorophenol increased. The last effect is due to the TOC associated to each start-ing target pollutant. In this sense, lower TOC values (2,4,6-TCP < 2,4-DCP < 4-CP) led to lower concentrations of oxalic acid as can be seen in Figs. S3, S5 and S6 of Supplementary Information.

The homogeneous contribution associated to Fe leaching in CWPO can be considered negligible since iron release occurred gradually and when the highest Fe concentration in solution (2–3 mg L^{-1} at the most) was achieved the remaining H$_2$O$_2$ con-centration was already fairly small and the oxidation process was almost completed.

The recovery and reusability of the catalyst represents a key is-sue regarding its potential application. Given the magnetic proper-ties of the Fe$_3$O$_4$/γ-Al$_2$O$_3$ catalyst it can be easily separated from the liquid phase by a magnet. The saturation magnetization (M_S)

Hydroxylated chlorobenzenediols and condensation by-products
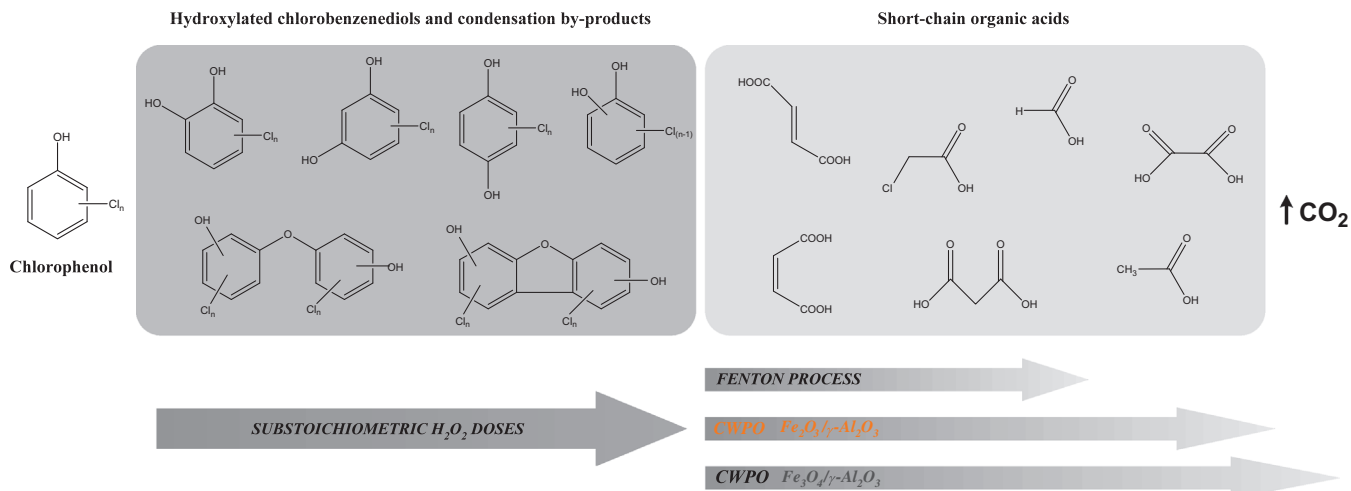
Short-chain organic acids

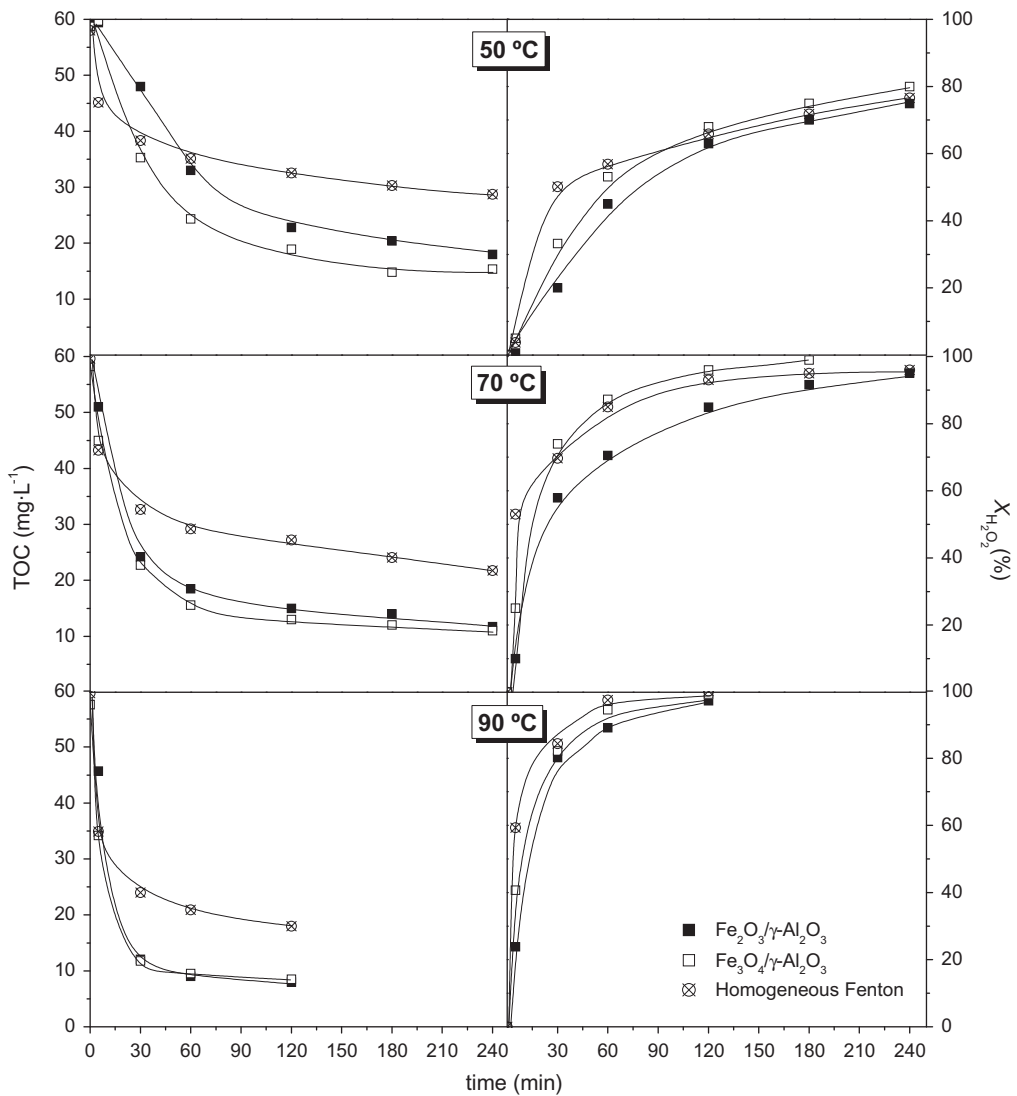**Fig. 4.** Enhanced oxidation strategies for an efficient degradation of chlorophenols.

Fig. 5. Effect of temperature on TOC reduction upon 4-CP breakdown by homogeneous Fenton-like oxidation ($[Fe^{3+}]_0 = 10$ mg L^{-1}) and CWPO with the Fe$_x$O$_y$/γ-Al$_2$O$_3$ at 1 g L^{-1}; ($[4\text{-CP}]_0 = 100$ mg L^{-1}; $[H_2O_2]_0 = 350$ mg L^{-1}; pH$_0 = 3$).
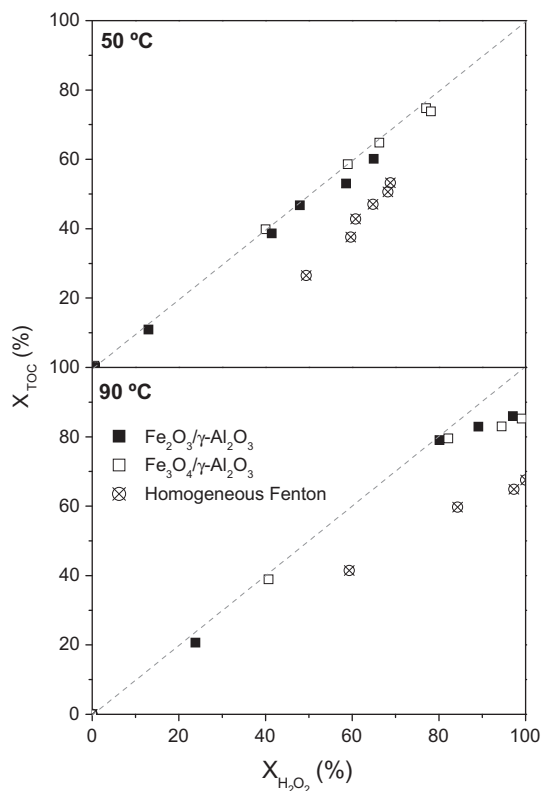
Fig. 6. Evolution of TOC vs. H_2O_2 conversion upon 4-CP breakdown by homogeneous Fenton-like oxidation ($[Fe^{3+}]_0 = 10$ mg L^{-1}) and CWPO with Fe_xO_y/γ-Al_2O_3 (1 g L^{-1}); ($[4$-CP$]_0 = 100$ mg L^{-1}; $[H_2O_2]_0 = 350$ mg L^{-1}; $pH_0 = 3$).

Fig. 8. Magnetization curves at room temperature of the Fe_3O_4/γ-Al_2O_3 catalyst before (red line) and after CWPO oxidation of 4-CP at different temperatures (grey lines). The inset shows a photograph of the used catalyst separated by a magnet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Saturation magnetization (M_S) of the Fe_3O_4/γ-Al_2O_3 catalyst before and after use in CWPO of CPs at different temperatures.

Sample	M_S (emu g^{-1})		
	50 °C	70 °C	90 °C
Fresh catalyst	2.23		
After 4-CP CWPO	2.11	2.17	2.21
After 2,4-DCP CWPO	2.18	2.19	2.21
After 2,4,6-TCP CWPO	2.21	2.22	2.23

of the fresh catalyst was found to be 2.23 emu g^{-1}. This value is somewhat higher than those previously reported in the literature [38,39]. This fact suggests that most of the iron incorporated to the catalyst is in form of magnetite. The magnetization curves of the catalyst before and after CWPO experiments with 4-CP at different temperatures are shown in Fig. 8. As can be seen, no significant changes occur upon use in CWPO. A photograph is included showing the effective separation of the used catalyst by applying an external magnetic field. Table 1 summarizes the values of saturation magnetization of the fresh and used Fe_3O_4/γ-Al_2O_3 catalyst. As can be seen, the M_S values slightly decreased upon use at lower temperatures with the less chlorinated phenols consistently with a higher iron leaching. Nevertheless, the magnetization values did
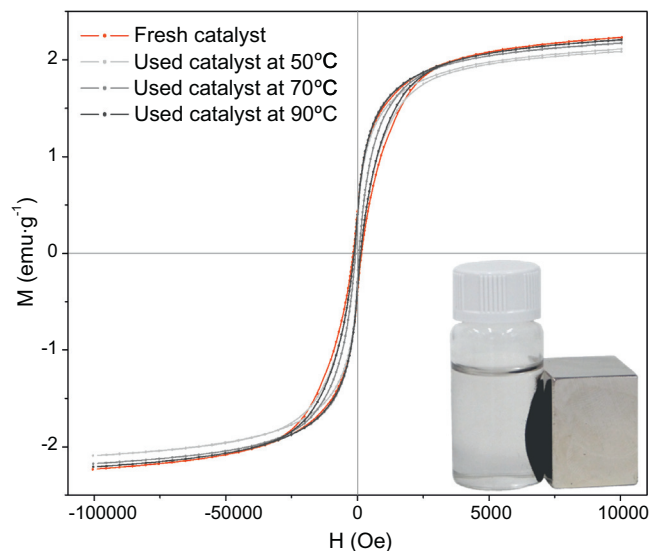
not decrease more than 5% at the most and the used catalyst was always easily separated from the liquid phase by a magnet.

To learn more on the stability of both catalysts, they were used in three successive runs at 90 °C after simply drying in vacuum at low temperature (60 °C). As can be seen in Fig. 9, the catalysts suffered a small decrease of activity after each successive application amounting about 10% based on TOC reduction after the third cycles. This loss of activity may be related with the deposition of residual carbon-containing matter over the surface of the catalysts
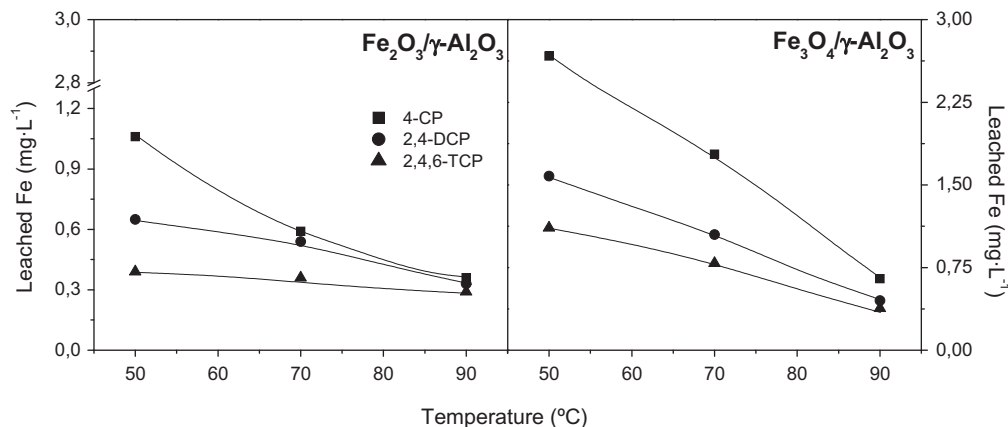

Fig. 7. Iron leaching from the Fe_xO_y/γ-Al_2O_3 catalysts upon CWPO of 4-CP, 2,4-DCP and 2,4,6-TCP at different temperatures after the 4 h reaction time.

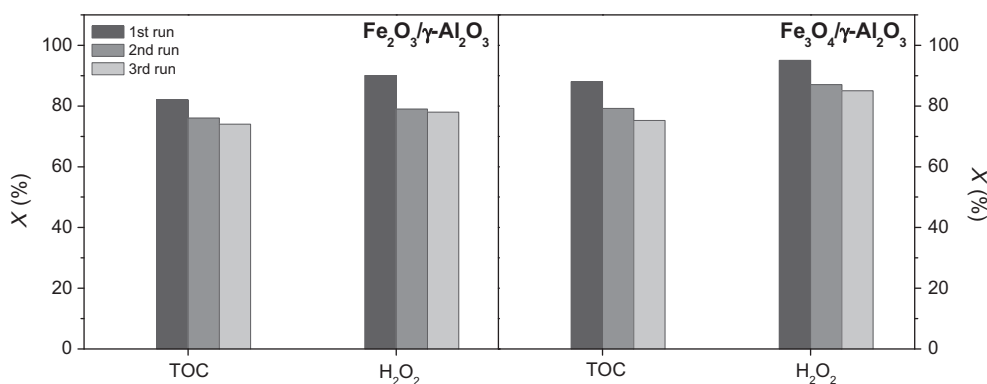**Fig. 9.** TOC and H_2O_2 conversion (4 h) upon CWPO of 2,4,6-TCP with the $Fe_xO_y/\gamma\text{-}Al_2O_3$ catalysts in successive applications ($[Fe_xO_y/\gamma\text{-}Al_2O_3] = 1 \text{ g L}^{-1}$). ($[2,4,6\text{-}TCP]_0 = 100 \text{ mg L}^{-1}$; $[H_2O_2]_0 = 190 \text{ mg L}^{-1}$; $T = 90\,°C$).

since Fe leaching was almost negligible in both cases (3% of initial Fe at the most). The C content of both catalysts varied from ≈0.5% after the first run to ≈0.7% after the third one. This may lead to a partial coverage of active sites. After use the BET surface area remained almost invariable and chlorine was not detected on the catalysts. On the other hand, the XRD of the fresh and used catalysts showed the same profile except for a new peak appearing in the used catalyst at 2θ around 18°, which may correspond to the aforementioned deposits (see Figs. S7 and S8 in Supplementary Material). Moreover very similar Mössbauer analyses were obtained for fresh and used catalysts. Then, it can be concluded that the active phase did not change significantly upon the CWPO process. This conclusion is also supported by the magnetic measurements in the used $Fe_3O_4/\gamma\text{-}Al_2O_3$ catalyst, which confirmed that the magnetic properties remained unchanged after CWPO. Bautista et al. [31] also observed carbonaceous deposits as well upon CWPO of cosmetic wastewater with a γ-alumina-supported Fe catalyst. These authors demonstrated that the deposits disappear upon calcination at 550 °C without significant reduction of the catalytic activity.

4. Conclusions

CWPO of CPs with own-prepared magnetic and non-magnetic Fe catalysts supported on γ-alumina has been proved to be more efficient than homogeneous Fenton-like oxidation. Although the Fenton-like process promotes a faster decomposition of H_2O_2 than CWPO, the own-prepared catalysts yielded higher mineralization percentages with the three chlorophenols tested. The lower rate of H_2O_2 decomposition in the heterogeneous process allows a higher availability of hydroxyl radicals along the course of reaction. Increasing the temperature clearly improved the oxidation rate and mineralization degree. The lower amount of remaining carboxylic acids, in particular oxalic, decreased iron leaching from the catalysts. Both $Fe_xO_y/\gamma\text{-}Al_2O_3$ catalysts synthesized in this work suffered fairly low iron leaching (below 5% of the initial content at the most) and a good stability upon successive applications in a three-cycles test with 2,4,6-TCP. The use of the magnetic $Fe_3O_4/\gamma\text{-}Al_2O_3$ catalyst is preferable due to its advantage of easy separation and recovery from the liquid phase by a magnet. Its ferromagnetic properties remained unchanged after use in CWPO.

According to our findings, the $Fe_3O_4/\gamma\text{-}Al_2O_3$ catalyst reported in this work could be feasibly used in CWPO as potential alternative to the homogeneous Fenton process which has been so far demonstrated for a diversity of effluents from different industries such as paper, chemical, pharmaceutical, textile and cosmetic at laboratory scale, and is currently used at industrial scale

(OHP®, MFC-Foret®). The optimum operating conditions used for homogeneous Fenton oxidation could be maintained since they are basically the same for both systems.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2013.05.057.

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