

Fe/C CATALYSTS FOR HETEROGENEOUS FENTON TREATMENT OF PHENOL IN AQUEOUS PHASE

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Introduction

The decontamination of aqueous effluents containing phenolic compounds is of main concern, since these compounds are toxic and resistant to natural biodegradation [1]. Wet air oxidation (WAO) and supercritical water oxidation (SCWAO) are some techniques that enable to obtain a high degree of mineralization of such hazardous substances. Nevertheless they require high temperatures (200°C-350°C) and pressures (70-230 atm) which severely affects the economy of these technologies [2]. Therefore, new effective options, such as chemical and catalytic processes are being investigated. Among these, the Fenton process has gained increasing interest [3]. It is based on the catalytic decomposition of H₂O₂ with iron salts in acidic media, The OH* radicals produced in these conditions present higher redox potential than hydrogen peroxide itself.

However, Fenton homogeneous treatment (H₂O₂ + Fe²⁺) presents some important disadvantages. First, it uses high H₂O₂ amounts, well above the stoichiometric ratio, to increase the reaction extension and to avoid intermediate oxidation products showing a higher toxicity than the primary pollutants [4]. Residual H₂O₂ itself gives rise to increased toxicity. On the other hand, high iron concentrations are required to enhance OH* production rate. This iron has to be removed to fulfil the discharge limits.

The main goal of this work consists on the development of a new heterogeneous Fenton oxidation system based on Fe/C catalyst. A series of iron-active carbon catalysts were prepared, characterized and tested in the oxidation reaction between H₂O₂ and phenol.

Experimental

Catalyst preparation

Fe/C catalysts were prepared by incipient wetness impregnation of a commercial active carbon supplied by Merck (1.5 mm particle size, code 1.02514.1000) with an aqueous solution of iron nitrate (Fe(NO₃)₃·9H₂O) at the concentration required to provide the desired amount of Fe on the activated carbon. The samples were pre-dried at room temperature for 2 h, subsequently at 60°C for 12 h and finally heat-treated at 200°C for 4 h in air atmosphere. Three catalysts with different nominal iron contents (1, 2 and 4% w/w) have been prepared.

Catalyst characterization

BET surface area (S_{BET}) values were obtained from N_2 adsorption-desorption isotherms at 77 K, in a Micromeritics Tristar apparatus. The samples were outgassed at 523 K and a pressure lower than 10^{-4} torr.

The amount of Fe on the catalysts was analyzed by ICP with a 3300DV model Perkin Elmer apparatus.

Catalytic activity tests

Homogeneous Fenton experiments were carried out in a 50 mL batch reactor at 50°C for 4 h and the following starting concentrations: 100 mg/L phenol, 500 mg/L H_2O_2 and 10 mg/L Fe^{2+} . The same reactor and operating conditions were used for heterogeneous Fenton experiments. Powdered iron-active carbon catalyst ($d_{\text{particle}} < 100 \mu\text{m}$) was added into the reactor at a concentration of 0.5 g/L of catalyst.

Phenol and aromatic intermediate compounds were followed by means of HPLC (Varian Pro-Start 240, Diode array detector) with a C-18 column at 50°C and 4mM H_2SO_4 in water as mobile phase. Short-chain organic acids were analyzed by Ion Chromatograph with chemical suppression (Metrohm 790 IC) using a Metrosep A supp 5-250 column with 3.2 mM/1 mM $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ as mobile phase. TOC was measured with an OI TOC Analyzer.

Results and Discussion

For the sake of comparison homogeneous Fenton experiments were performed as well as heterogeneous ones. Figures 1 and 2 show the results obtained upon homogeneous Fenton oxidation. As it can be seen, phenol is completely removed, but important amounts of oxidation intermediates are still remaining as reveal the TOC values. Several short-chain organic acids were identified as oxidation products (Figure 2). The significant difference observed between the experimental TOC values and those corresponding to the detected oxidation products, is attributable to unidentified intermediates. Moreover, aromatic intermediate compounds are not quantitatively detected because of they are rapidly oxidized to acids.

A series of iron-active carbon catalysts were prepared to carry out heterogeneous Fenton experiments. Table 1 reports the values of iron content and BET surface area of these catalysts.

Figure 3 reports the results obtained in the heterogeneous Fenton oxidation experiments conducted under the operating conditions already indicated for the homogeneous ones.

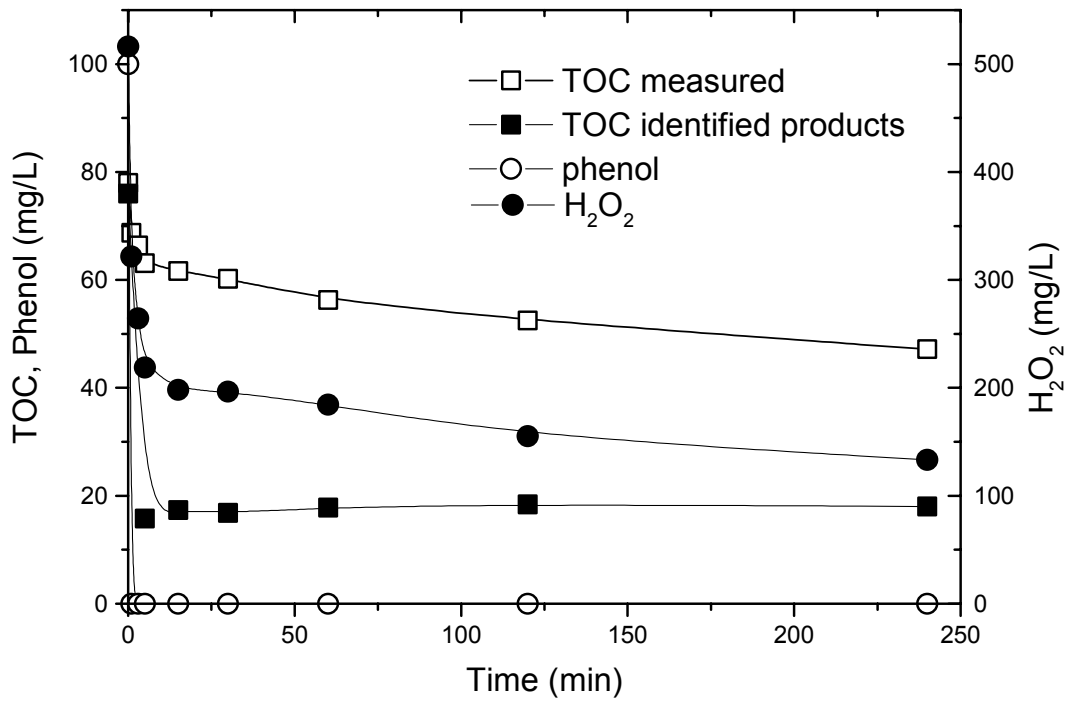


Figure 1. Evolution of phenol, TOC and H₂O₂ upon homogeneous Fenton oxidation.

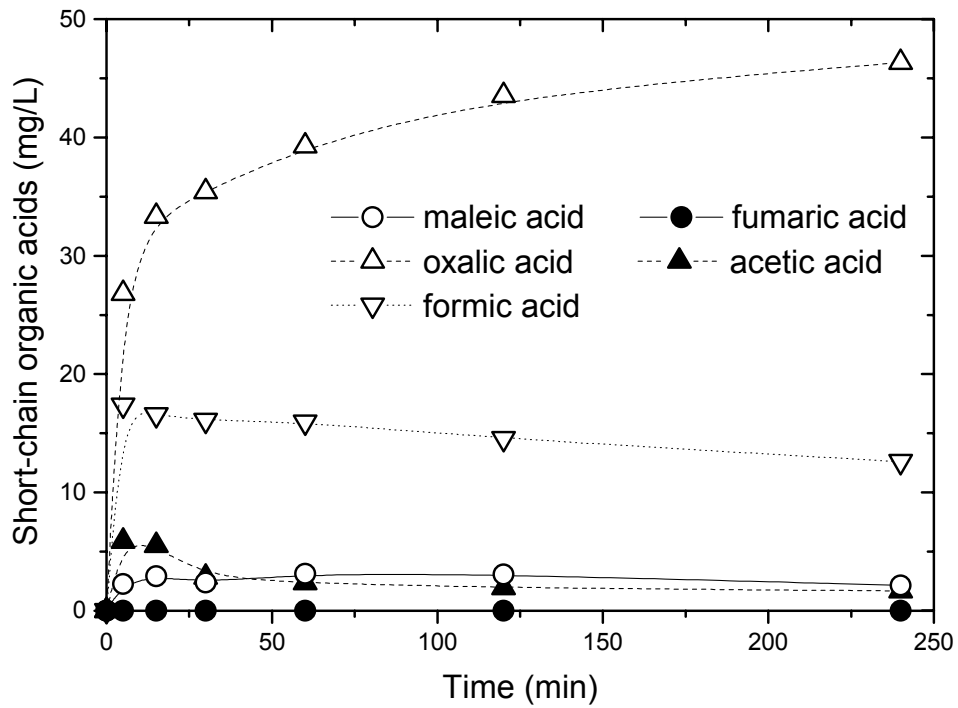


Figure 2. Evolution of short-chain organic acids produced upon homogeneous Fenton oxidation.

Table 1.- Prepared catalysts.

Catalyst	Iron (% wt.)	S _{BET} (m ² /g)
Active carbon support	-	974
Fe/C-1	1.2	733
Fe/C-2	2.2	784
Fe/C-4	4.3	703

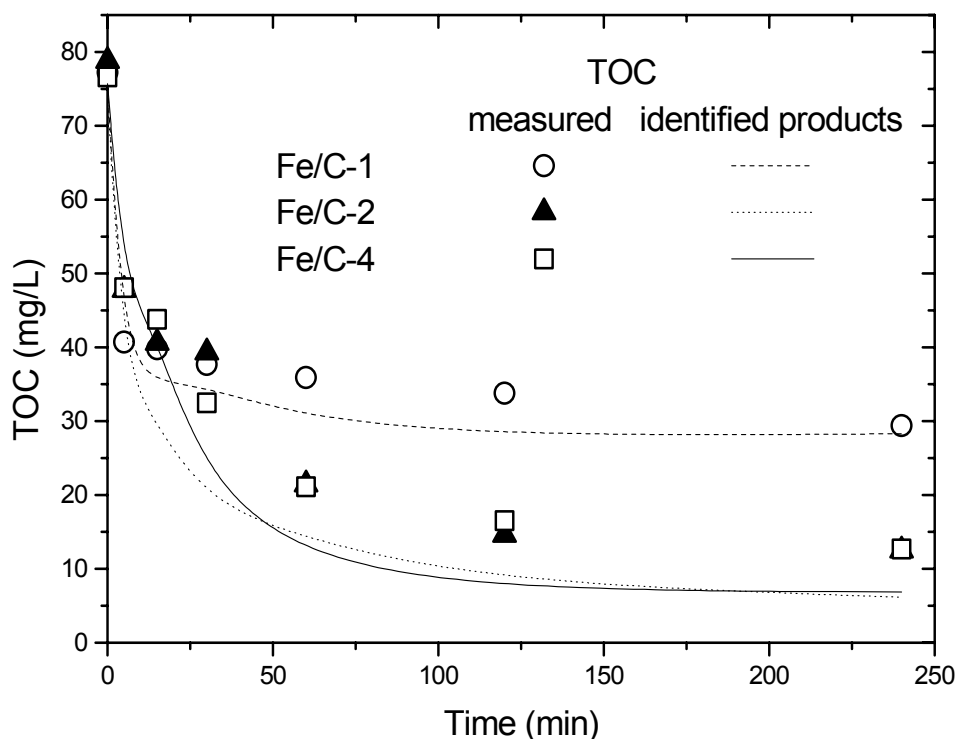


Figure 3.- Evolution of TOC upon heterogeneous Fenton oxidation with different Fe/C catalysts.

A 50% reduction of TOC was obtained with the Fe/C-1 catalyst which is around the value encountered in homogeneous operation. Increasing the Fe content of the catalyst increases the TOC reduction reaching a 80% for the Fe/C-4 catalyst. A significant difference of the heterogeneous Fenton process with respect to the homogeneous one is the much closer agreement between the measured TOC values and the corresponding to the detected oxidation products. This indicates that the unidentified products, corresponding mainly to polyaromatics, whether are formed in much lower extent or they are retained on the carbon surface.

Figure 4 shows the evolution of phenol and TOC upon heterogeneous Fenton oxidation using the Fe/C-4 catalyst. It is included the adsorption curve of phenol in the absence of H₂O₂. As it can be seen a significant difference is observed between the adsorption and reaction values. The evolution of intermediate oxidation products are reported in Figure 5 for aromatics and 6 for short-chain organic acids.

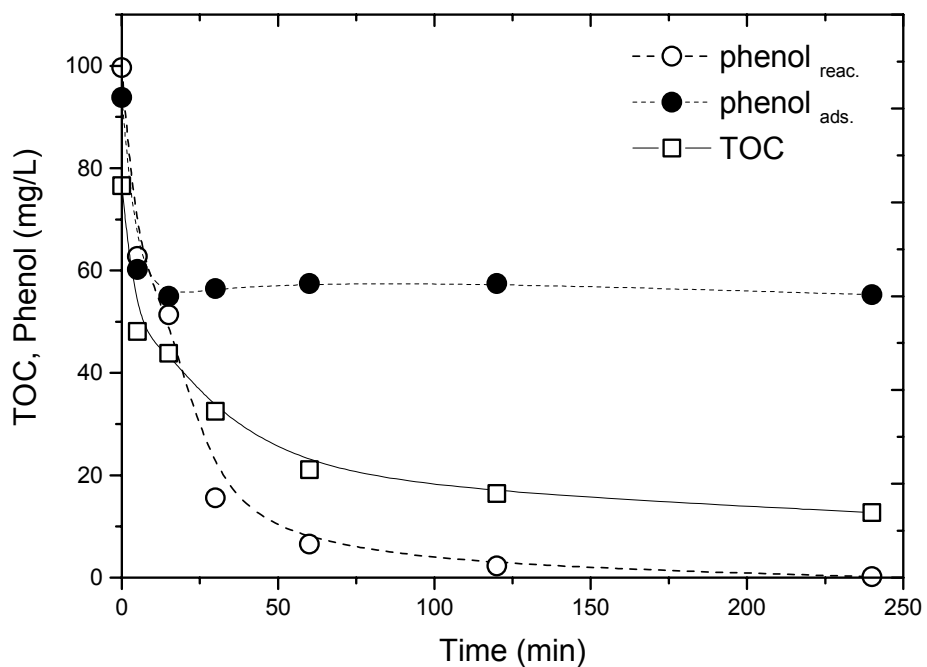


Figure 4. Evolution of phenol and TOC upon heterogeneous Fenton oxidation with Fe/C-4 catalyst.

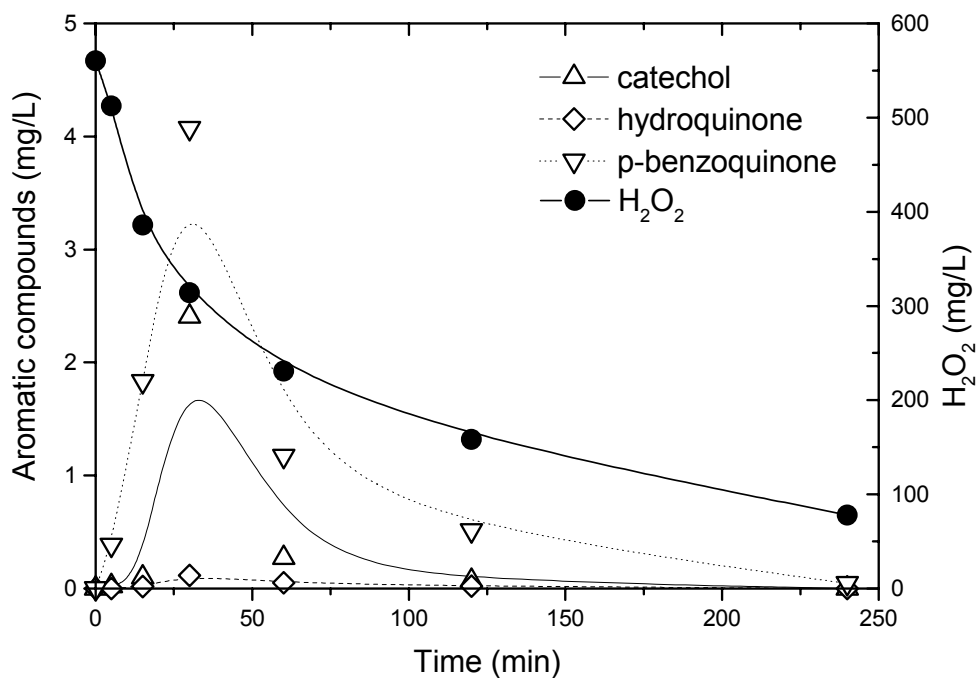


Figure 5. Evolution of aromatic intermediate compounds and H₂O₂ upon heterogeneous Fenton oxidation with Fe/C-4 catalyst.

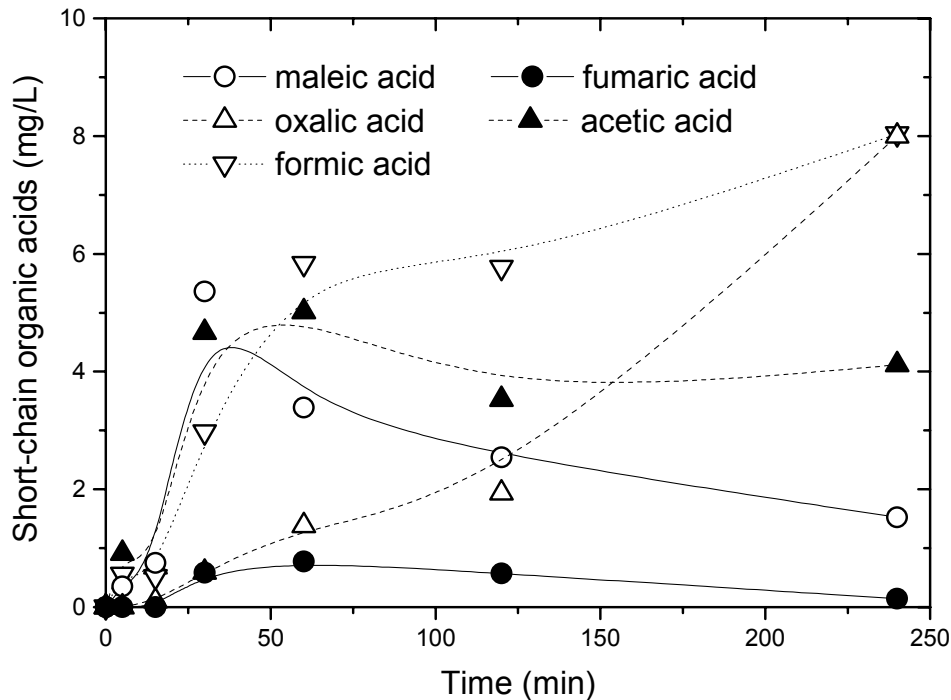


Figure 6. Evolution of short-chain organic acids upon heterogeneous Fenton oxidation with Fe/C-4 catalyst.

Conclusions

One important advantage of the heterogeneous Fenton oxidation investigated with respect to the homogeneous process arises from the significantly lower H_2O_2 consumption per unit TOC reduction. The catalyst decomposes the H_2O_2 leading to lower residual concentrations of this reagent and consequently lower toxicity values in the final effluent.

Very low amounts of Fe are leached from the catalyst and thus the heterogeneous process greatly reduces the problem of $Fe(OH)_3$ precipitation upon final neutralization.

Acknowledgements

Authors acknowledge financial support from the CAM and the Spanish MCYT through the contracts 07M/0039/2002 and PTR1995-0722-OP, respectively.

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