



## CATALYTIC WET HYDROGEN PEROXIDE OXIDATION OF 4-CHLOROPHENOL OVER IRON-EXCHANGED CLAYS

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### Abstract

Chlorophenols were selected for this study because most of them are toxic and difficult to biodegrade. They represent a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act and by the European Decision 2455/2001/EC. The efficiency of advanced oxidation processes for degradation of chlorophenols has been extensively documented. The catalytic wet hydrogen peroxide oxidation process, involving oxidation with H<sub>2</sub>O<sub>2</sub> and solid catalysts in mild reaction conditions, was found to be very attractive for different pollutants; however, data regarding the degradation of chlorophenols are very scarce. The aims of this paper were: (i) to prepare and characterize a series of iron-exchanged montmorillonites and (ii) to assess their catalytic performances in a Fenton-like process for the oxidation of para-chlorophenol. DR-UV-VIS spectroscopy was tentatively used to elucidate the structure of the iron oxo sites intervening in the reaction. This approach has been used previously for ion-exchanged zeolites and was able to distinguish between isolated Fe(III) species and Fe<sub>x</sub>O<sub>y</sub> clusters of different nuclearity. The catalytic tests, performed at room temperature, showed that all iron-containing clays were very active, leading to the complete oxidation of para-chlorophenol and a significant reduction of TOC values. 4-chlorocatechol was the major reaction intermediate found in the CWHPO of 4-CP, followed by hydroquinone and traces of benzoquinone, 5-chloro-1,2,4-benzenetriol, 1,2,4-benzenetriol and 3-chloro-muconic acid. The leaching test indicates that the catalytic activity is mainly due to leached iron ions, at least in the second part of the process.

*Key words:* 4- chlorophenol, catalytic wet peroxide oxidation, clay, hydrogen peroxide

### 1. Introduction

The sustainable approach for water and wastewater treatment as well as for water resources management represents a major concern worldwide. Issues such as: overexploitation and pollution of available water resources, changed and depleted natural vegetation, contamination of groundwater resources represent major problems nowadays (Perathoner and Centi, 2005; Teodosiu, 2007).

Removal of pollutants from industrial processes, either at the source of their production or by end of pipe treatments represent an important research area, as the amount and quality of freshwater available at global level continues to decrease due to

the growing water demand and long period of droughts.

Chemical and petroleum industries generate a wide variety of wastewater contaminated with inorganic and organic priority organic pollutants. Among organic pollutants, phenol and phenol derivatives, used as raw materials in chemical, petrochemical and pharmaceutical industries have received increased attention in the last years due their toxicity (Guo and Al-Dahlan, 2003; Liotta et al., 2009). Chlorophenols constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act and by the European Decision (EC Decision, 2001). Because of their broad-spectrum antimicrobial properties, chlorophenols have been used as preservative agents for wood, paints,

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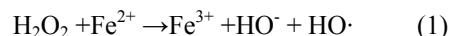
vegetable fibers, leather and as disinfectants. These pollutants can be produced by chlorination reactions which take place during disinfection of wastewater or drinking water sources (WHO, 2003). Phenol and their chlorinated derivatives represent one of the most abundant families of industrial toxic compounds which are resistant to biodegradation and persist in the environment for long period (Pera-Titus et al., 2004). Emissions are mainly due to the manufacture, storage, transportation and application of chlorophenols. The need to restore contaminated sites to avoid further risk to the environment has contributed in the last years to the development of effective methods for chlorophenol removal. The main goal of this process is to achieve a complete mineralization of chlorophenols to CO<sub>2</sub> and H<sub>2</sub>O in addition to smaller amounts of some ions, e.g. chloride anions, or at least to produce less harmful intermediates (Catrinescu and Teodosiu, 2007). These compounds cannot be removed by means of primary or secondary treatment processes, and even in low concentrations, they can cause special problems because of their toxicity to human and the aquatic environment, the depletion of oxygen resources from natural waters and the stimulation of the algal growth.

There are several technologies available for the removal of priority organic pollutants, such as biological, thermal and chemical treatments. Conventional biological processes requires a long residence time for microorganisms to degrade this type of pollutants, because they are affected by chlorophenol toxicity. Thermal treatments present many drawbacks, such as considerable emission of other hazardous compound.

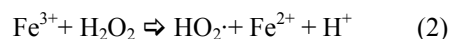
The chemical methods are additive, requiring high capital investment and creating problems of dissolved solid content in the effluent (Doong et al., 2000; Liotta et al., 2009). Alternative destructive technologies for pollutants removal are Advanced Oxidation Processes (AOPs), which have been reported to be effective for the near ambient degradation of soluble organic pollutants from wastewater and solids, because they can provide almost total degradation (Esplugas et al., 2002). AOPs are characterized by a common chemical feature: the capability of exploiting the high reactivity of HO• radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants (Catrinescu, 2008; Liotta et al., 2009). These processes include catalytic wet air oxidation, methods based on ultrasound, plasma and electrohydraulic discharge along with processes based on hydrogen peroxide, photolysis, photocatalysis and processes based on ozone.

Catalytic Wet Peroxide Oxidation (CWPO) is seen as a promising wastewater treatment technology because this process is efficient for the removal of priority organic pollutants from wastewater with medium to high organic load (Busca et al., 2008; Catrinescu and Teodosiu, 2007). CWPO is a liquid phase catalytic oxidation with hydrogen peroxide,

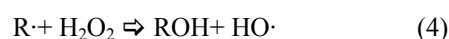
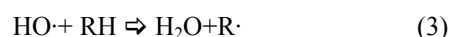
which does not form any harmful by-products, and it is a non-toxic and ecological reactant. In the classical version of this process, Fenton's reagent (Fe<sup>2+</sup>/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>) is used to generate highly reactive hydroxyl radicals from hydrogen peroxide, in mild reaction. To enhance the decomposition of hydrogen peroxide to hydroxyl radicals, the use of a catalytic system is very important. The system containing hydrogen peroxide and Fe(II) salts in water solution form hydroxyl radicals following the reaction (1):



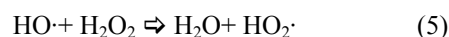
This is known as the Fenton's reagent, which finds wide application for wastewater treatment (Walling, 1998). The oxidizing efficiency of the Fenton reagent is the highest for pH ranging from 2 to 5 and for molar ratio 1:1. The formation of Fe (III) ions plays an important role, decompose H<sub>2</sub>O<sub>2</sub> and produce HO<sub>2</sub>• radicals (2):



In the solution of H<sub>2</sub>O<sub>2</sub> and Fe (II) salts, organics (RH) are oxidized by means of radical chain reactions. The main agents oxidizing and propagating the reactions are HO• radicals:



HO• radicals also decompose H<sub>2</sub>O<sub>2</sub> producing HO<sub>2</sub>• radicals:



The major drawbacks that limit the industrial application of these Fenton-type homogeneous catalytic systems are the tight pH control, as well as the production of additional toxic wastes, which need to be treated. For these reasons, there has been a considerable interest in the development of heterogeneous catalyst for this process. There are several heterogeneous catalysts which present interest in this field, such: metal-exchanged clays (Barrault et al., 2000; Carriazo et al., 2003, 2005; Catrinescu et al., 2002; Catrinescu et al., 2003; Catrinescu et al., 2007; Caudo et al., 2007) and resins (Liou et al., 2004, 2005), metal-exchanged zeolites (Calleja et al., 2005) and hydrotalcite-like compound (Barbosa et al., 2005). The use of clay as catalysts of Fenton-like reactions is a promising alternative for the industrial effluents treatment. The low cost, abundance, and environmentally friendly nature of clay minerals is an added advantage (Garrido-Ramirez et al., 2009).

The aims of this research were to prepare and characterize a series of iron-exchanged montmorillonites and to assess their catalytic activity in a Fenton-like process for the oxidation of 4-chlorophenol.

## 2. Experimental

4-chlorophenol of analytical reagent grade supplied by Aldrich was used for the preparation of the synthetic wastewater solutions.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  of analytical reagent grade supplied by Aldrich was used for the preparation of iron exchange clays.

Low-Fe montmorillonite type 'Cheto' SAZ-1 was received from The Clay Minerals Society Source Clay Repository (Purdue University, West Lafayette, Indiana).

The chemical composition, the cation exchange capacity (CEC) and surface area of this clay, provided by the supplier, are listed in Table 1.

Iron exchanged clays were prepared by a classical ion exchange method at room temperature, involving a 10 min interaction between the clay and the iron containing solution  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , followed by rapid filtration and washings with distilled water. The starting clay was treated with enough iron ions in order to cover 25, 50, 75 and 100% of the cationic exchange capacity.

The modified clays were characterized by DR UV-VIS. DR-UV-VIS spectroscopy was used to identify the nature of the iron species from the catalyst. This approach has been used previously for ion-exchanged zeolites and was able to distinguish between isolated Fe (III) species and  $\text{Fe}_x\text{O}_y$  clusters of different nuclearity. The DR UV-VIS spectra were recorded on a UV-2501 PC Shimadzu in the 190-600 nm range with a resolution of 2 nm.  $\text{BaSO}_4$  was used as standard. The reflectance was recalculated to Kubelka-Munk absorbance and the positions of the absorption maxima were estimated from the minima of the 2<sup>nd</sup> derivative of 50 point FFT smoothed spectra.

The 4-chlorophenol concentration was measured with a Dionex Ultimate 3000 high performance liquid chromatography (HPLC) coupled with a Thermo mass spectrometer and a electro-spray ionisation interface (ESI). Analytes were separated using a C18 column kept at 30 °C. The injection volume was 5  $\mu\text{l}$ . The pump was operated in isocratic mode. The mobile phase A was 0.1% acetic acid in water (60 %), phase B was methanol (40%) and the total flow rate was 0.2  $\text{mL min}^{-1}$ .

The instrument was operated in positive/negative ionization mode. The needle voltages were +/- 3000 V and the cone voltages were +/- 40 V, for positive/negative mode.

The probe temperature was 350 °C. The iron concentration was quantified by atomic absorption spectroscopy (GBC Avanta with system 3000 Graphite Furnace). Total organic carbon (TOC) values were analysed using a Total carbon analyser (TOC-VCSN from Shimadzu). The hydrogen peroxide concentrations were determined by a colorimetric titration method.

## 3. Results and discussions

### 3.1. Catalyst characterization. Assignment of UV-VIS DRS bands

UV/VIS-Diffuse reflectance Spectroscopy is an important technique which is able to distinguish between isolated Fe species of different structures and  $\text{Fe}_x\text{O}_y$  clusters of different nuclearity. This technique has been widely used to study Fe-zeolites (Zecchina et al., 2007). In principle, two different types of electron transitions can be detected, mainly crystal or ligand field transitions (d-d transitions, including electron pair transitions - EPT) and charge-transfer (CT) transitions. The single electron d-d transitions of  $\text{Fe}^{3+}$  ions, around 710 and 910 nm, are symmetry and spin forbidden. Hence, often d-d transitions are weak and/or not observed. However, medium-intense d-d electron pair transition bands, between 400-500 nm, are usually observed in the electron spectra of the iron oxides. On the other hand, CT transitions are allowed and result in usually intense absorption bands. CT bands are very sensitive, but they are neither are nor phase specific for different forms of iron oxides. The wavelength of  $\text{Fe}^{3+}$  CT bands depends on the coordination number and on the degree of aggregation (Bordiga et al., 1996; Brückner et al., 1996; Centi and Vazzana, 1999; Pérez-Ramírez et al., 2004). In principle, two ligand-to-metal charge-transfer (CT) transitions,  $t1 \rightarrow t2$  and  $t1 \rightarrow e$ , are to be expected for a  $\text{Fe}^{3+}$  ion (Tippins, 1970).

For isolated  $\text{Fe}^{3+}$  ions they fall in the high energy range of the spectrum, usually below 300 nm, whereby their particular position depends on the number of ligands. Thus, the CT bands of  $\text{Fe}^{3+}$  ions are red-shifted with increasing number of coordinating oxygen ligands. Based on these considerations, for zeolites it is accepted that subbands below 250 nm are assigned to isolated tetrahedral  $\text{Fe}^{3+}$  while those between 250 and 300 nm are attributed to isolated  $\text{Fe}^{3+}$  with a higher number of coordinating ligands.

**Table 1.** Chemical composition, surface area and cationic exchange capacity (CEC) of SAZ-1

Clay	Chemical composition (% oxide)									$A_{BET}$	CEC (mequiv./100g)
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Others		
SAZ-1	0.06	6.73	19.98	59.65	0.19	3.15	0.25	1.77	0.01	130	120

CT bands between 300 and 400 nm are assigned to octahedral  $\text{Fe}^{3+}$  in small oligomeric  $\text{Fe}_x\text{O}_y$  clusters (Bordiga et al., 1996). The bands above 450 nm are usually attributed to d-d electron pair transitions, and are considered to be enough phases specific for the characterization of admixtures of free iron oxides.

These EPT bands are used to distinguish between hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), with absorption above 520 nm, from all other iron oxides, including ( $\alpha\text{-FeOOH}$ ) and ferrihydrite, with bands below 500 nm.

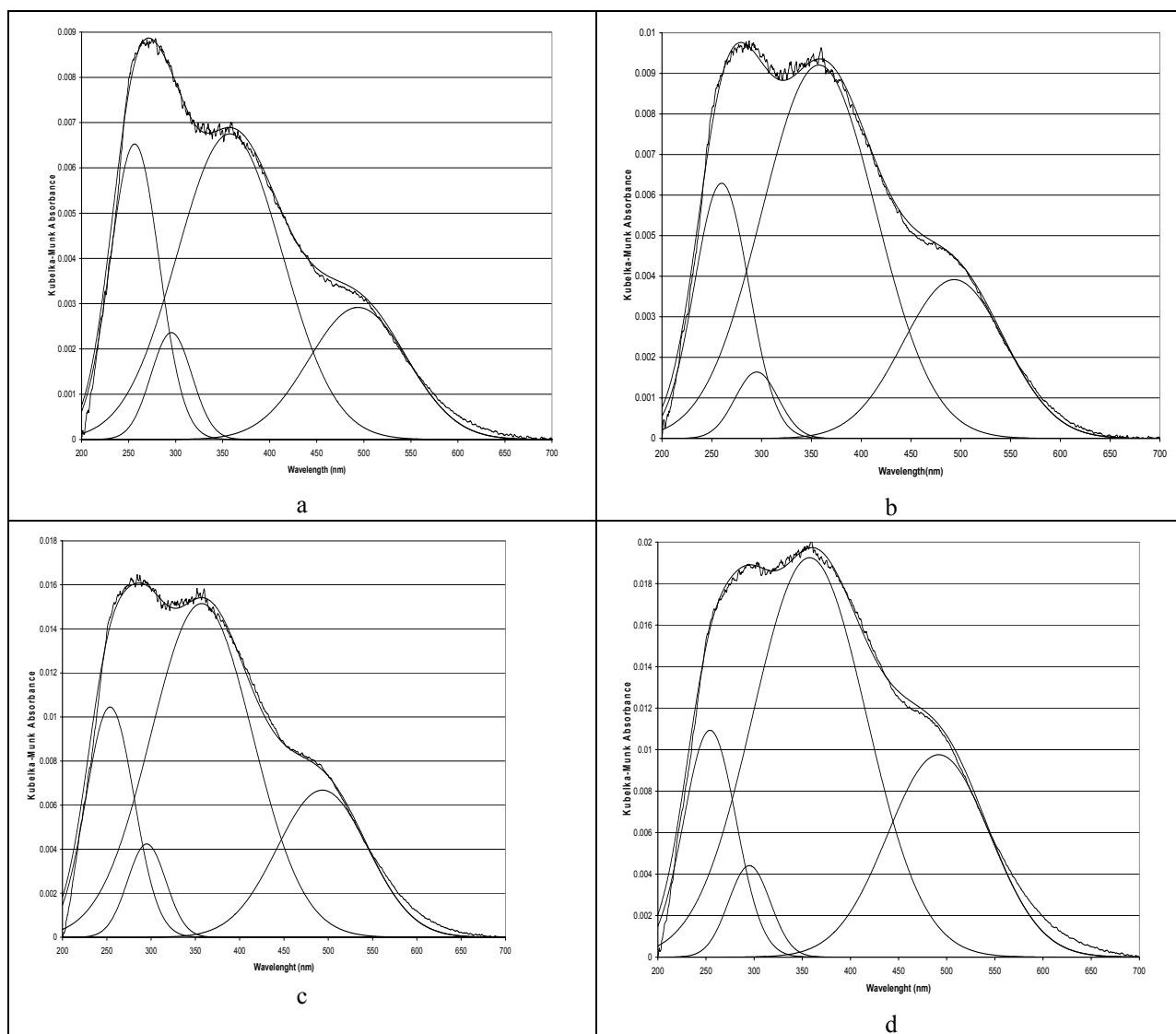
To facilitate band assignment, experimental spectra were deconvoluted into respective sub bands. For the deconvolution procedure, the lowest possible number of sub bands has been used.

Since the two CT transitions for the same  $\text{Fe}^{3+}$  species are experimentally not resolved, they have been fitted by one sub band only for each type of  $\text{Fe}^{3+}$  species (tetrahedral and octahedral coordination).

UV-VIS DRS spectra of  $\text{Fe}^{3+}$ -exchanged clays display two CT bands below 300 nm, more precisely at 255 and 295 nm.

For ion-exchanged zeolites, these bands are usually attributed to isolated  $\text{Fe}^{3+}$  species in octahedral coordination.

This is based on the fact that the most common forms of iron oxide (e.g.,  $\alpha\text{-Fe}_2\text{O}_3$ ) do not contribute much to the UV-VIS spectrum below 300 nm. However, some oxides, such as  $\gamma\text{-Fe}_2\text{O}_3$ , have an important contribution in this range of the spectrum. For this reason, for samples that contain different (unknown)  $\text{Fe}_x\text{O}_y$  clusters, the role of these phases in the wavelength region below 300 nm cannot be completely ruled out. The most intense band of the spectrum is centered at 357 nm, which is very close to dimers  $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$  (Lopes et al., 2002) and very weakly condensed  $\text{Fe}^{3+}$  ions (Capek, et al., 2005) in  $\text{Fe}^{3+}$ -exchanged zeolites.



**Fig.1.** Deconvolution spectra for iron-exchange clays: a) 25%Fe-SAZ-1; b) 50%Fe-SAZ-1; c) 75%Fe-SAZ-1; d) 100%Fe-SAZ-1

The band at 494 nm can be assigned to a d-d electron pair transition (EPT) of a structure with edge-sharing octahedra  $\text{Fe}(\text{O},\text{OH})_6$ , similar to that of  $\text{FeOOH}$  and ferrihydrite (Grygar et al., 2007).

However, in these iron oxides, the EPT band is almost as strong as the near-UV absorption, which is not the case in  $\text{Fe}^{3+}$ -exchanged clay. The ion-exchangeability of all the  $\text{Fe}^{3+}$  species allows us to deduce that  $\text{Fe}^{3+}$  bound to clay is mainly present in ion-exchange positions, as electrically charged monomeric, dimeric or small oligomeric hydrated species.

From the ratios between the maximum amount of  $\text{Fe}^{3+}$  bound to clay and the CEC of the clay, the formal charge of Fe ions in the gallery varies between 1.5 and 1.8. This partial effective charge is in good agreement with the existence of hydrated Fe species, such as  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ ,  $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{4+}$  etc. The lack of extended polymerization of  $\text{Fe}(\text{O},\text{OH})_6$  octahedra, as in  $\text{FeOOH}$  or ferrihydrite, can be assumed from the very low intensity of the EPT band, which is typical for highly condensed iron oxides.

### 3.2. Identification of the reaction intermediates

4-chlorocatechol was the major reaction intermediate found in the CWHPO of 4-CP, followed by hydroquinone and traces of benzoquinone, 5-chloro-1,2,4-benzenetriol, 1,2,4-benzenetriol and 3-chloro-muconic acid. A typical HPLC chromatogram, with an absorbance detector (280 nm), showing the main reaction products is presented in Fig. 2.

In ESI(-)-MS mode, mass spectra of phenols contain, in addition to phenoxide ions, other ions from the mobile phase, namely acetate ( $\text{AcO}^-$ ) with a

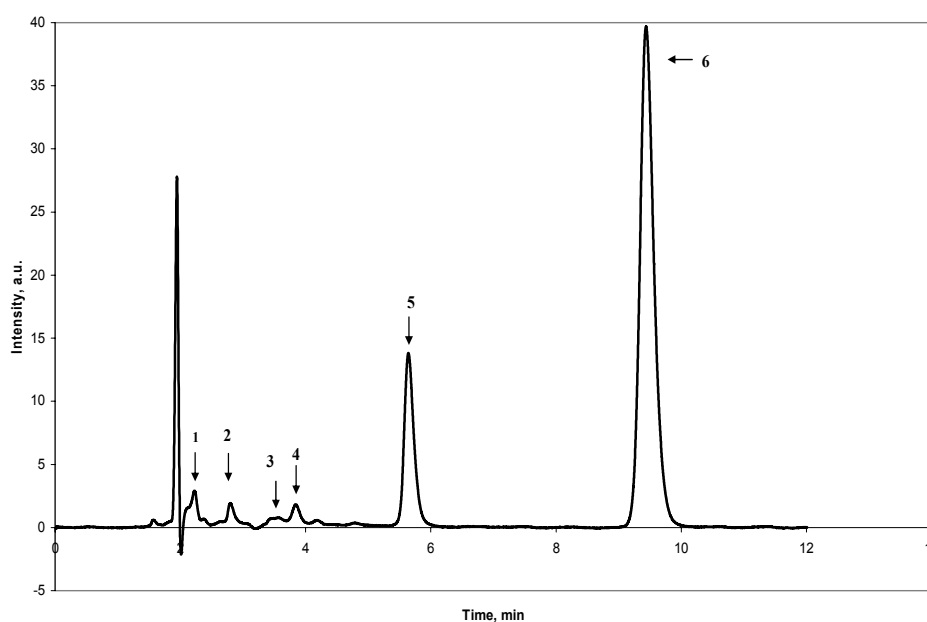
mass-to-charge ratio  $m/z=59$  and an adduct of acetate with acetic acid ( $\text{AcOH}\cdot\text{AcO}^-$ ) at  $m/z=119$ .

The mass spectra, extracted at the maximum of the chromatographic peak of each compound, contain different phenoxide-based ions, such as: phenoxide ( $\text{PO}^-$ ), a phenoxide adduct with acetic acid ( $\text{AcOH}\cdot\text{PO}^-$ ), a phenoxide adduct with the same phenol ( $\text{PO}\cdot\text{PO}^-$ ) and other adducts of phenoxide with different carboxylic acids. Mass spectra of the identified compounds are summarized in Table 2.

**Table 2.** Intermediate products from 4 CP oxidation

Compound	Detected ions, mass-to charge ratio $m/z$
4-chlorophenol	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 127.5 ( $\text{PO}^-$ ), 187.5 ( $\text{AcOH}\cdot\text{PO}^-$ ), 256 ( $\text{PO}\cdot\text{PO}^-$ )
4-chlorocatechol	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 143.5 ( $\text{PO}^-$ ), 203.5 ( $\text{AcOH}\cdot\text{PO}^-$ ), 288 ( $\text{PO}\cdot\text{PO}^-$ )
Hydroquinone	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 109 ( $\text{PO}^-$ ), 169.5 ( $\text{AcOH}\cdot\text{PO}^-$ ), 219 ( $\text{PO}\cdot\text{PO}^-$ )
5-chloro-1,2,4-benzenetriol	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 159.5 ( $\text{PO}^-$ )
1,2,4-benzenetriol	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 125 ( $\text{PO}^-$ )
3-chloro-muconic acid	59 ( $\text{AcO}^-$ ), 119 ( $\text{AcOH}\cdot\text{AcO}^-$ ), 175.5 ( $\text{ClMu}^-$ )

The ESI(-)-MS spectrum of the main reaction intermediate (4-chlorocatechol) is presented in Fig. 3.



**Fig. 2.** A representative HPLC chromatogram of the reaction mixture. 1- hydroquinone, 2-1,2,4-benzenetriol, 3-benzoquinone, 4-5-chloro-1,2,4-benzenetriol, 5-4-chlorocatechol, 6- 4-chlorophenol.

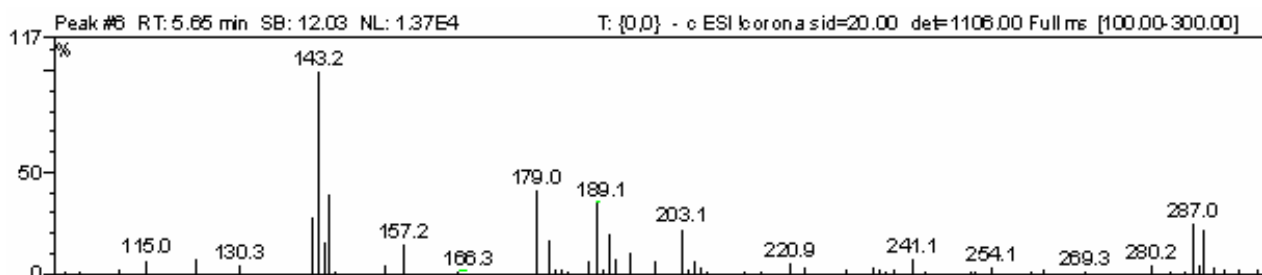


Fig. 3. ESI(-)-MS spectrum of the main reaction intermediate

The identification of quinone-like products was not possible in negative ion mode, because they contain no acidic hydrogen. They can be detected in positive ion mode ESI(+)-MS, as  $[Q+H]^+$  (protonation of the CO group), whereas ESI(-)-MS fails to detect the  $[Q-H]^-$  anion.

Based on the reaction intermediates presented above, two major pathways may be proposed (Fig. 4). In the first one, it can be supposed that the reaction starts with the hydroxyl radical ( $HO\bullet$ ) attack, directed by the position of the hydroxyl group, which is a stronger ortho-para director than chlorine. In the case of 4-chlorophenol the main reaction intermediate, 4-Chlorocatechol (4-CC), is the result of  $HO\bullet$  attack at ortho position to the hydroxyl group. The hydroxylation of 4-CC leads to 5-chloro-1,2,4-benzenetriol. Substitution to give 1,2,4-benzenetriol is observed as is oxidative cleavage of the C1-C2 bond to give the diacid.

The major products of all of the triols are those of oxidative cleavages, occurring mainly between ortho hydroxy-substituted carbons to give diacids, but also between one hydroxy and one unsubstituted carbon to give acid-aldehydes.

The formation of non chlorinated products (hydroquinone) indicates that the presence of a chlorine group did not prevent the  $HO\bullet$  attack at that particular position on the ring (second pathway). Hydroxyl radical attack did however take place more readily at ortho position that was not occupied by chlorine group, because dechlorination occurs via a different reaction mechanism, which is probably not as efficient as reactions without dechlorination. Further hydroxylation to form 1,2,4-benzenetriol followed by oxidative cleavage of either the C1-C2 or C3-C4 bond of 1,2,4-benzenetriol, lead to several acidic compounds. Benzoquinone is also formed from hydroquinone but in small amounts.

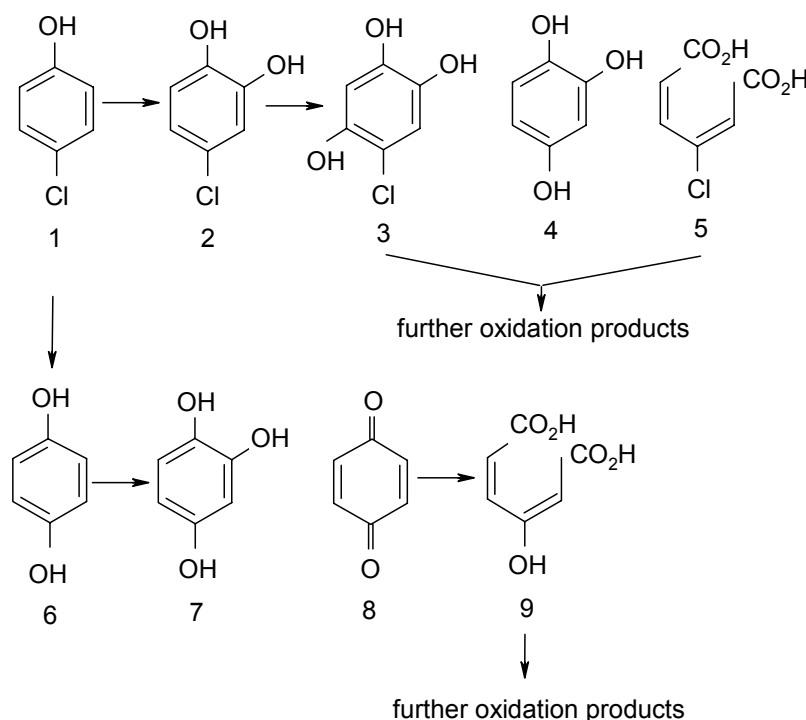


Fig. 4. Proposed reaction pathways for the CWHPO of 4-CP. Reaction intermediates 4-CP (1), 4-CC (2), 5-chloro-1,2,4-benzenetriol (3,7), 1,2,4-benzenetriol (4), 3-chloro-muconic acid (5), hydroquinone (6), benzoquinone (8), 3-hydroxy-muconic acid (8)

At the end of the reaction only carboxylic acids are present in the solution, all the aromatic intermediates being completely converted.

### 3.3. Catalytic activity tests

4-CP conversion curves, for catalysts with different  $\text{Fe}^{3+}$  content, show a sigmoidal profile, as seen in Fig. 5, which is typical for autocatalytic or radical reactions. There are two different regions: one for the initial part of the curve, which represents the induction period, and the other after the inflection point, which represents the steady-state. There is a significant difference in the induction period of oxidation, for different  $\text{Fe}^{3+}$  content of the catalyst; the time required to reach steady-state decreases as the  $\text{Fe}^{3+}$  content increases.

However, when the steady state is reached, the 4-CP conversion curves fall almost into the same line. It is evident that a catalyst with a higher  $\text{Fe}^{3+}$  content gives better results in terms of the reaction rate and removal efficiencies.

The steady state could be rapidly reached and the inflection point almost circumvented. Nevertheless, at the end of the reaction (no  $\text{H}_2\text{O}_2$  left in solution) all the catalysts displayed similar performances, as it can be observed in Fig. 6.

Total organic carbon (TOC) analysis is performed to characterize the degree of organic carbon mineralization in the liquid phase. The removal efficiencies (expressed as TOC), for the most active catalyst (100%Fe-SAz-1), is shown in Fig. 7.

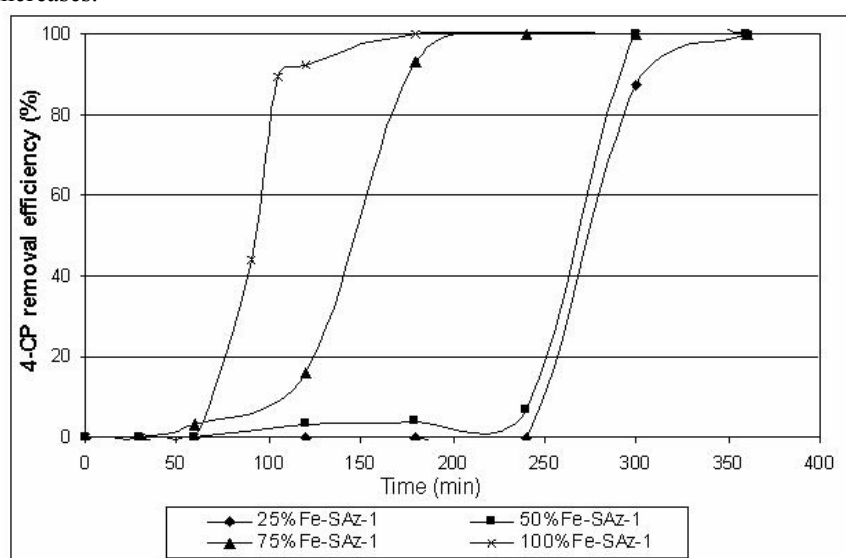


Fig. 5. 4-CP removal efficiency (%) during the reaction, for catalysts with different  $\text{Fe}^{3+}$  content

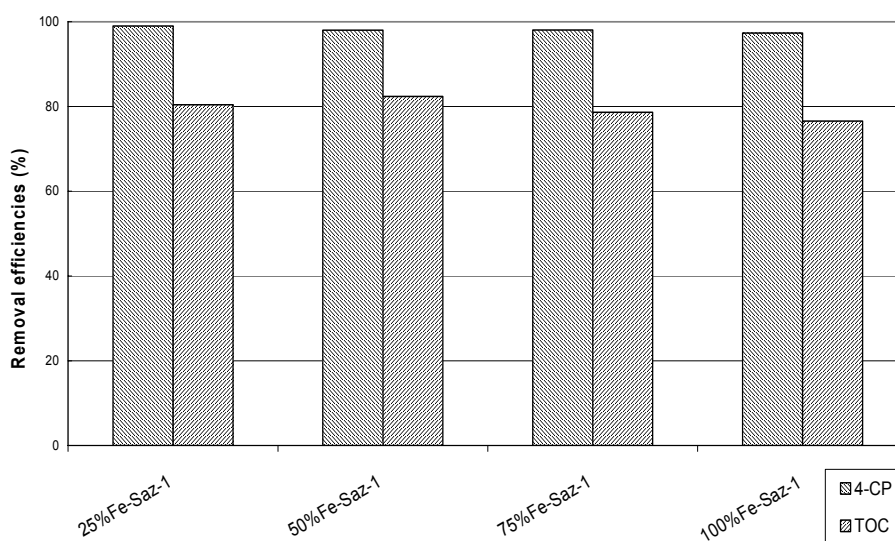


Fig. 6. 4-CP and TOC removal efficiency (%) at the end of the reaction, for catalysts with different  $\text{Fe}^{3+}$  content

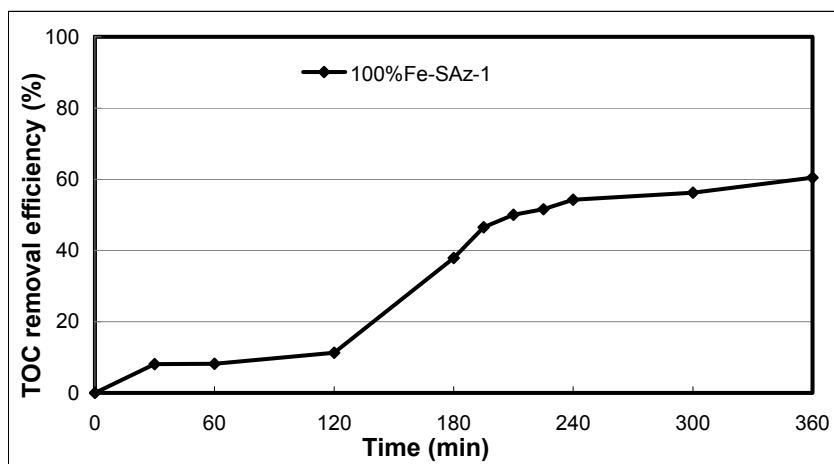


Fig. 7. Evolution of TOC removal efficiency in time

The removal efficiencies expressed as TOC is less than that for 4-CP, confirming that 4-CP oxidation occurs in multiple steps and results in several byproducts, which are more resistant to oxidation than the initial pollutant. The short-chain carboxylic compounds, formed during the oxidation process, are refractory to further oxidation into CO<sub>2</sub> and H<sub>2</sub>O. The enhancement of the aqueous solution acidity, as shown by the evolution of the pH value (Figure 8), can be regarded as an indirect prove for the generation of carboxylic acids, as final and stable reaction intermediates.

The performance of a solid catalyst cannot be assessed based only on the analysis of the organic pollutants removal. The stability of the catalyst against leaching is another important aspect that has to be taken into account. The concentration of the total iron ions in solution, during the whole oxidation process, as measured by Atomic Absorption Spectroscopy (AAS), is depicted in Fig. 8. The amount of leached iron could be related to the pH of the solution.

Data shown in Fig. 8 suggest that the leaching of Fe ions is a process secondary to the catalytic reaction and strongly related to the amount of carboxylic acids produced during the oxidation. A similar behavior was observed by Perathoner and Centi (2005) in the CWHPO of p-cumaric acid, where the amount of leached iron was related to the concentration of the oxalic acid in solution. This differs from what was observed for Cu-based catalysts where the leaching of the metal is the first step of the process, followed by the degradation of the organic pollutant.

The leaching test indicates that, at least in the second part of the process, the catalytic activity is mainly due to leached iron ions. The high concentration of the Fe ions (> 10 mg/L) is enough to efficiently catalyze the oxidation process. In addition, the similar values obtained for TOC removal efficiency, for all the catalysts (Figure 6), can be explained by the operation of a homogeneous catalytic process.

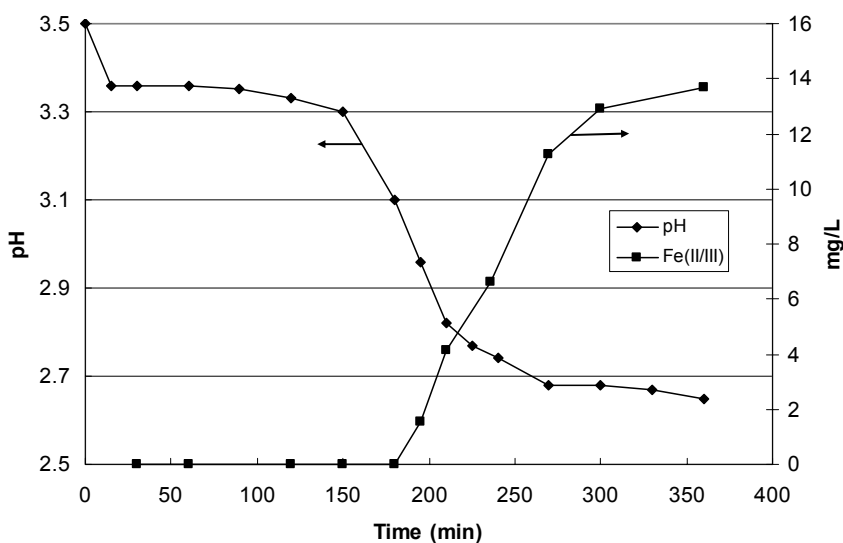
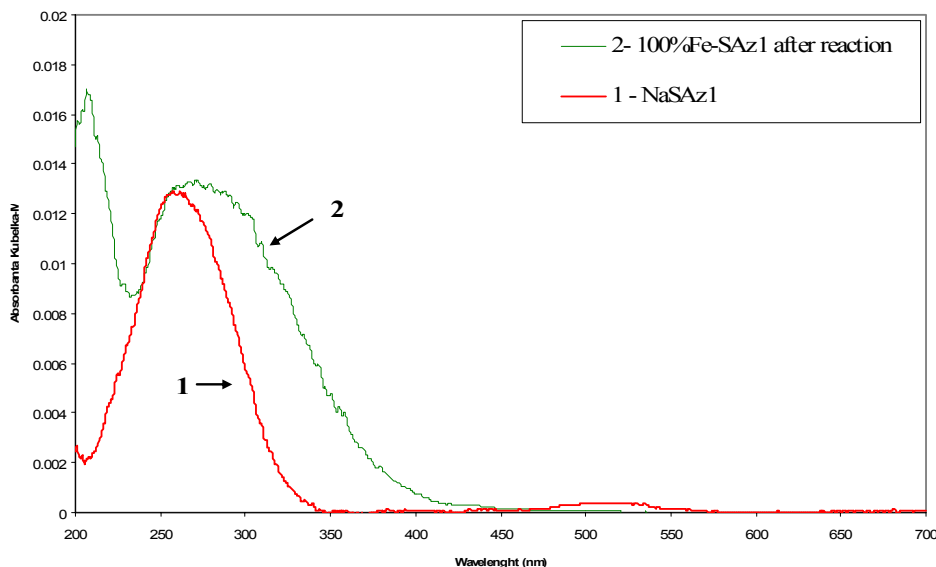


Fig. 8. pH evolution and iron concentration





**Fig.9.** DR UV-VIS spectra for 100% Fe-SAz-1 after reaction as compared to Na-SAz-1

The UV-VIS diffuse reflectance spectrum of the spent catalyst, shown in Fig. 9, confirms the almost complete leaching of the Fe ions.

#### 4. Conclusions

This study presents the results obtained during the catalytic oxidation with hydrogen peroxide of an aqueous solution of 4-chlorophenol on clay-based catalysts containing iron.

According to DR UV-VIS spectroscopic data, it can be deduced that  $\text{Fe}^{3+}$  bound to clay is mainly present in ion-exchange positions, as electrically charged monomeric, dimeric or small oligomeric hydrated species. The lack of extended polymerization of  $\text{Fe}^{3+}$  can also be assumed from the very low intensity of the EPT band.

The major reaction intermediates in the catalytic wet peroxide oxidation of 4-chlorophenol are: 4-chlorocatechol, hydroquinone, benzoquinone, 5-chloro-1,2,4-benzenetriol, 1,2,4-benzenetriol and 3-chloro-muconic acid. At the end of the reaction only carboxylic acids are present in the solution, all the aromatic intermediates being completely converted.

The catalytic tests, performed at room temperature, showed that all iron-containing clays were very active, leading to the complete oxidation of para-chlorophenol and a significant reduction of TOC values. The 4-CP conversion curves have a sigmoidal profile, with an initial induction period followed by a steady-state. The time required to reach steady-state decreases as the  $\text{Fe}^{3+}$  content increases.

A strong decrease in the solution pH was observed for all the catalysts and was attributed to the generation of carboxylic acids as stable and refractory to oxidation reaction products. The leaching of Fe

ions was considered a process secondary to the catalytic reaction and strongly related to the amount of carboxylic acids produced during the oxidation.

The leaching test indicates that, at least in the second part of the process, the catalytic activity is mainly due to leached iron ions.

The high concentration of the Fe ions ( $> 10$  mg/L) is enough to efficiently catalyze the oxidation process. The similar values obtained for TOC removal efficiency, for all the catalysts, can be explained by the operation of a homogeneous catalytic process.

The results presented will be included in a more complex study in which a comparison between several advanced processes for wastewater treatment will be performed.

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