Cold Incineration of Chlorophenols in Aqueous Solution by Advanced Electrochemical Process Electro-Fenton. Effect of Number and Position of Chlorine Atoms on the Degradation Kinetics

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Received: July 22, 2009; Revised Manuscript Received: September 1, 2009

This study reports the kinetics of the degradation of several chlorophenols (CPs), such as monochlorophenols (2-chlorophenol and 4-chlorophenol), dichlorophenols (2,4-dichlorophenol and 2,6- dichlorophenol), trichlorophenols (2,3,5- trichlorophenol and 2,4,5-trichlorophenol), 2,3,5,6-tetrachlorophenol, and pentachlorophenol, by the electro-Fenton process using a carbon felt cathode and a Pt anode. The effect of number and the position of the chlorine atoms in the aromatic ring on the oxidative degradation rate was evaluated and discussed. The oxidation reaction of all the CPs with hydroxyl radicals evidenced a pseudo-first-order kinetics and the rate constant decreased with increasing the number of chlorine atoms. The absolute rate constant of second-order reaction kinetics between CPs and $^{\bullet}OH$ was determined by the competition kinetics method in the range of $(3.56-7.75) \times 10^9\ M^{-1}\ s^{-1}$ and follows the same sequence of the apparent rate constants. The mineralization of several CPs and of a mixture of all CPs under study was monitored by the total organic carbon (TOC) removal and the chlorine release during mineralization was followed by ion chromatography. Our results demonstrated that more chlorinated phenols are more difficult to mineralize; however for all the tested CPs, almost quantitative release of chloride ions was obtained after 6 h of treatment.

1. Introduction

Chlorinated organic compounds have received increased interest in recent years because of their environmental significance as potentially hazardous substances.[1,2] Cholorophenols (CPs) constitute a particular group of chlorinated organic compounds that are widely used.[3] Monochlorophenols (MCP) and dichlorophenols (DCP) have been widely employed in many industrial processes, for example as synthesis intermediates or as raw materials in the manufacturing of herbicides, fungicides, pesticides, insecticides, pharmaceutical products, and synthetic dyes. Pentachlorophenol (PCP), tetrachlorophenol (TeCP), and trichlorophenol (TCP) have been used as fungicides, herbicides, and defoliants since the early 1930s. Chlorophenols can be found not only in industrial wastewaters but also in soils and surface waters and groundwaters, as a consequence of agricultural runoff, breakdown of herbicides, and spontaneous formation following chlorination of water for disinfection.[4] CPs have bacteridicidal activities, phototoxicity, and bioaccumulation ability in organisms.[5−7] Because of the low biodegradability of CPs, their widespread use caused pollution of soils and groundwater.[8] Consequently, CPs have been designated as priority toxic pollutants by the US EPA[9] and by the European Parliament decision.[10] Therefore, in order to protect the aquatic environment and soils, it is necessary to develop highly efficient and reliable technologies for their removal.

The conventional organic pollutant destructive methods may be thermal, biological, and physical/chemical treatment processes. Thermal treatments can lead to the production of the hazardous compounds, in particular dioxins in the case of chloroorganics. Biological treatment requires a long residence time for micro-organisms to destroy CPs due to the toxic nature of these compounds, which tended to increase as the number of chlorine substituents on the phenol ring increased.[11] Physical/chemical treatments such as flocculation, precipitation, adsorption on activated carbon, air stripping, or reverse osmosis require a post-treatment to remove the pollutants from the newly contaminated environment. Therefore, some alternative methods to degrade toxic and persistent organic pollutants are utilized for rehabilitation of the contaminated sites to avoid further risks to the environment. These alternative treatment processes include the advanced oxidation processes (AOPs)[12−16] that can provide an almost total degradation of organic pollutants. AOPs include all methods in which the highly oxidizing species hydroxyl radicals ($^{\bullet}OH$) is produced by chemical, photochemical, and photocatalytic systems such as ozone (O_3), ultraviolet light (UV), ozone and ultraviolet light (O_3/UV), hydrogen peroxide (H_2O_2), hydrogen peroxide and ultraviolet light (H_2O_2/UV), ultrasound, Fenton's reagent (H_2O_2/Fe^{2+}), homogeneous photocatalysis (H_2O_2/Fe^{2+}/UV), and heterogeneous photocatalysis (TiO_2/UV).[17−19] The main problem of these technologies relies on the economy of the process.

Recently, a new AOP induced by electrochemistry, the so-called electro-Fenton, was proposed as an alternative method for organic removal.[20−24] It is based on hydroxyl radical production taking place from Fenton's reagent (a mixture of H_2O_2 and ferrous ion), where hydrogen peroxide is generated in situ from the two-electron reduction of O_2 at RVC, carbon-felt, or gas-diffusion cathodes

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10.1021/jp9069674 CCC: $40.75

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + {}^{\bullet}OH \quad (2)$$

Fenton's reaction (eq 2) which provides $^{\bullet}OH$ is catalyzed by electroreduction of $Fe(OH)^{2+}$ at the cathode (eq 3) at the reduction potential of O_2

$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + OH^- \quad (3)$$

Thus, no chemicals were introduced into the wastewater to be treated since the reagents of the Fenton's reaction are in situ electrogenerated (H_2O_2) or electroregenerated (Fe^{2+}) in a controlled and continuous way.

The electro-Fenton process has been efficiently applied for the treatment of many pollutants including phenols,[20,25−29] synthetic dyes,[30−37] herbicides and pesticides,[38−52] drugs,[53] and real wastewaters.[54] The degradation of chlorophenols was also investigated by several authors in literature. In an early study, Brillas et al.[25] demonstrated that 4-chlorophenol can be completely removed in acidic solution by electro-Fenton and photoelectro-Fenton using a gas diffusion electrode (GDE) as cathode. In both methods, the initial hydroxylated intermediate is 4-chloro-1,2-dihydroxybenzene, which is further oxidized with loss of chloride ion to yield maleic and fumaric acids. More recently, Agladze et al.[55] obtained a 90−98% destruction of 4-chlorophenol where hydrogen peroxide was electrogenerated at a GDE in the cathodic chamber of a cell separated by a proton-exchange membrane both in ex-cell and in-cell Fenton treatment, but higher rates of decomposition were achieved in the former process.

In our previous studies[23,56] we showed that the electro-Fenton process using a carbon felt cathode enables the total degradation of pentachlorophenol (PCP) with a quantitative release of chloride ions in solution.

Few studies have also reported on the relationship between chlorine content and the degradation rate of CPs, but the results are contradictory and no final conclusions have so far been drawn. For example, the electrochemical degradation of different chlorophenols (phenol, 4-CP, and 2,4-DCP) was studied by Wang and Wang[57] in a diaphragm electrolysis device with Ti/IrO_2/RuO_2 anode and GDE cathode. The removal efficiency for organic compounds reached about 90% after 120 min, conforming to the sequence of phenol, 4-CP, and 2,4-DCP, which suggested that with the increase of the number of chlorine atoms in the aromatic ring, the organics became more difficult to be oxidized. On the contrary, Song-hu and Xiao-hua,[58] comparing the degradation of various CPs by electro-Fenton methods, have found that the pseudo-first-order degradation rate constants gave the following sequence: 2,4-DCP > 2,4,6-TCP > PCP > 4-CP.

In the present paper we present a detailed study on the effect of chlorine content on the oxidation kinetic of different CPs and also of a mixture of CPs during their electro-Fenton treatment. Monochlorophenols (2-CP, 4-CP), dichlorophenols (2,4-DCP, 2,6-DCP), trichlorophenols (2,3,5-TCP, 2,4,5-TCP), tetrachlorophenol (2,3,5,6-TeCP), and pentachlorophenol (PCP) were degraded by the electro-Fenton method on a carbon felt cathode, and solution mineralization efficiency was measured in each case. The absolute rate constants between the hydroxyl radicals and the CPs were also determined using this competitive method.

2. Experimental Section

2.1. Chemicals. Chloropenols (CPs) 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, 2,3,5-TCP, 2,4,5-TCP, and PCP from Sigma-Aldrich and 2,3,5,6-TeCP from Riedel de Haën were reagent grade and were used as received. Acetic and sulfuric acids, anhydrous sodium sulfate, and heptahydrated ferrous sulfate as well as pentahydrated ferric sulfate used as iron ions (catalyst) sources were analytical grade from Fluka, Merck, and Acros Organics. All solutions were prepared with ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at room temperature. Acetonitrile used as organic solvent for the liquid chromatography mobile phase was HPLC grade from Across Organics.

2.2. Electrochemical System. Constant current electrolyses were performed with a laboratory power supply (HAMEG International), model HM8040-3 Triple Power Supply. Bulk electrolyses were carried out at room temperature in an open, cylindrical, and undivided glass cell of 6 cm diameter and 250 mL capacity and equipped with two electrodes. The cathode was a 60 cm^2 (15 cm × 4 cm) carbon felt piece (Carbone Loraine) and the anode was a 4.5 cm height cylindrical grid (3.1 cm i.d.). The anode was centered in the electrolytic cell, surrounded by the cathode, which covered the inner wall of the cell. H_2O_2 was produced from reduction of O_2 dissolved in the solution, from reaction 1. Continuous saturation of the solution by O_2 at atmospheric pressure was ensured by bubbling of compressed air having passed through a frit at about 1 L min^{-1}, starting 10 min before electrolysis. Solutions were vigorously stirred with a magnetic bar to allow mass transfer.

The pH of solutions was adjusted to 3 by sulfuric acid (H_2SO_4). This value was selected as the optimum one to carry out Fenton's reaction (eq 2), according to several studies on the electro-Fenton process.[46,59] It is maintained about 2.8−3 during the treatment (H^+ consumed by eq 1 being compensated by oxidation of water at the anode

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

Solutions were prepared in aqueous medium by using ultrapure water, and stability was ascertained by measuring their initial concentration given by comparison with HPLC calibration curves. Solutions of 220 mL containing appropriate concentration of CP(s) with 0.05 M Na_2SO_4 as background electrolyte and 0.2 mM ferric iron salt as catalyst at pH 3.0 adjusted with H_2SO_4 have been degraded at constant current from 50 to 300 mA.

2.3. Analytical Procedures. Evolution of CP concentrations during electrolyses was monitored by a Merck-Hitachi Lachrom high-performance liquid chromatography (HPLC) system equipped with a L-7100 pump and a L-7455 photodiode array detector and fitted with a Purospher RP-18, 5 μm, 25 cm × 4.6 mm (i.d.) column at 40 °C. The column was eluted at isocratic mode with a mobile phase composed of water/methanol/acetic acid (34.5/64.5/1 v/v) at a flow rate of 0.8 mL min^{-1}. The column was placed in an oven which was thermostated at 40 °C. Detection was performed at 280 nm. The system was controlled through EZChrom Elite 3.1 software. Under these analytic conditions, CPs under study exhibit well-defined chromatographic peaks at retention times of 5.4, 6.0, 7.6, 10.0, 18.6, 20.07, 22.6, and 25.5 min for 2-CP, 4-CP, 2,6-DCP, 2,4-DCP, 2,4,5-TCP, 2,3,5-TCP, 2,3,5,6-TeCP, and PCP, respectively.

Chloride ion released in treated solutions was analyzed by Dionex ICS-1000 ion chromatography equipped with a DS 56

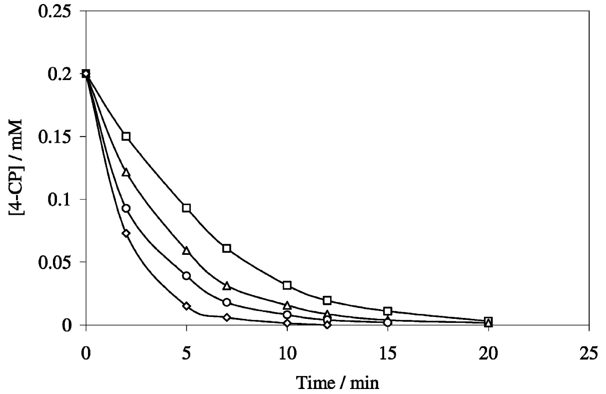

Figure 1. Influence of applied current on the decay of 4-CP during electro-Fenton treatment. Conditions: [4-CP] = 0.2 mM; V = 220 mL; [Fe^{3+}] = 0.2 mM; I = (□) 50 mA, (Δ) 100 mA, (○) 200 mA, (◇) 300 mA.

conductivity detector containing a cell heated at 35 °C under control through Chromeleon SE software, using an Ion Pac AS4A-SC, 4 mm × 250 mm anion-exchange column linked to an IonPac AG4A-SC, 5 cm × 4 mm (i.d.), column guard. The mobile phases were a solution of 1.7 mM sodium bicarbonate and 1.8 mM potassium carbonate circulating at 1.0 mL min^{-1} flow rate. The sensitivity of this detector was improved from electrochemical suppression using a SRS-ULTRA II self-regenerating suppressor.

The mineralization of CP aqueous solutions was monitored by the abatement of the total organic carbon (TOC) measurements using a Shimadzu VCSH TOC analyzer according to the thermal catalytic oxidation principle. Samples were acidified with HCl (1% HCl 2 mM). The injection volumes were 50 μL. The carrying gas was oxygen with a flow rate of 150 mL min^{-1}. TOC measurements were based on the combustion of organics and detection of CO_2 formed by infrared gas analysis method. The combustion reaction was carried out in the oven at 680 °C on a Pt catalyst. Calibration of the analyzer was achieved with potassium hydrogen phthalate standards.

3. Results

3.1. Influence of Applied Current on the Oxidation of 4-CP. Aqueous solutions of 4-CP have been initially treated by electro-Fenton under current controlled electrolysis conditions in the presence of 0.2 mM Fe^{3+} as catalyst. The oxidative degradation of the 4-CP was followed by HPLC, where it displayed a well-defined peak at a retention time $t_R = 6.0$ min. The effect of applied current on the decay kinetics of 4-CP was investigated by electrolysis at different current values, i.e., 50, 100, 200, and 300 mA. It can be seen from Figure 1 that the concentration of 4-CP decreases to zero for all current values and that the oxidation rate gradually increased with raising applied current value. In fact, the time needed for complete destruction of 4-CP in aqueous solution decreased from 25 min at 50 mA to 12 min at 300 mA applied current. This enhancement can be explained by increase of the production of H_2O_2 from reaction 1 leading to the generation of higher amount of hydroxyl radicals from Fenton's reaction (eq 2).

The decay of 4-CP concentration exhibits an exponential behavior with all the applied current indicating a first-order reaction kinetic for its oxidation by $^{\bullet}$OH

$$\text{4-CP} + {}^{\bullet}\text{OH} \rightarrow \text{oxidation products} \qquad (5)$$

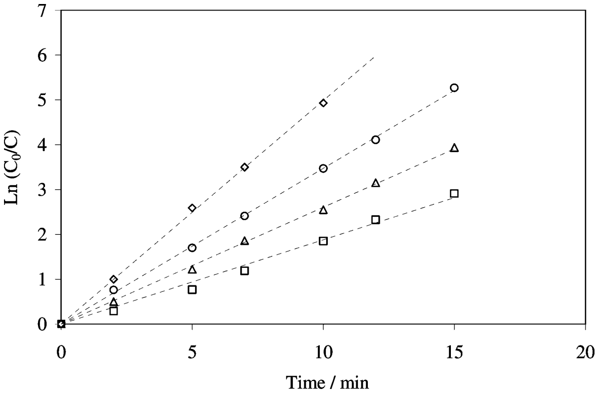

Figure 2. Kinetic analysis for the pseudo-first order reaction between 4-CP and $^{\bullet}$OH at different applied current during electro-Fenton treatment. Conditions: [4-CP] = 0.2 mM; V = 220 mL; [Fe^{3+}] = 0.2 mM; I = (□) 50 mA, (Δ) 100 mA, (○) 200 mA, (◇) 300 mA.

TABLE 1: Kinetic Rate Constant (k_{app}) and Half-Life Times ($t_{1/2}$) for the Oxidation of 4-CP by $^{\bullet}$OH at Different Applied Current under Operating Conditions of Figure 2

applied current (A)	k_{app} (min^{-1})	R^2	$t_{1/2}$ (min)
50	0.187 ± 0.011	0.9902	3.7
100	0.261 ± 0.012	0.9989	2.65
200	0.347 ± 0.009	0.9994	2
300	0.498 ± 0.010	0.9992	1.4

Considering the steady-state approximation for $^{\bullet}$OH in the electro-Fenton treatment, the 4-CP oxidation rate expression can be written as follows

$$-\frac{d[\text{4-CP}]}{dt} = k[{}^{\bullet}\text{OH}][\text{4-CP}] = k_{app}[\text{4-CP}] \qquad (6)$$

which can be integrated to give the following expression

$$\text{Ln}\,\frac{[\text{4-CP}]_0}{[\text{4-CP}]_t} = k_{app}t \qquad (7)$$

where $[\text{4-CP}]_0$ and $[\text{4-CP}]_t$ are the concentrations of 4-CP at the beginning and at time t and k_{app} is the apparent (observed) pseudo-first-order rate constant.

Apparent rate constants for the oxidative degradation of 4-CP were determined by plotting Ln($[\text{4-CP}]_0$/[4-CP]) against time at different applied current (Figure 2). After linear regression analysis the first-order rate constant were determined and showed in Table 1 together with half-life times $t_{1/2}$ or times necessary to reduce the initial concentration of the 4-CP in solution by a factor of 2. Obviously, the rate constant increased with increasing the applied current, but it is interesting to note that when then applied current is doubled (e.g., from 50 to 100 mA) the apparent rate constant value did not increased 2-fold. This indicates that increasing the current intensity favored not only the electrogeneration of hydrogen peroxide but also the secondary reaction of hydrogen evolution

$$2H^+ + 2e^- \rightarrow H_2 \qquad (8)$$

3.2. Influence of the Number and Position of Cl Atoms on the Oxidative Degradation Kinetic of Chlorophenols. The oxidative degradation of several CPs (i.e., 2-CP, 4-CP, 2,4-DCP, 2,6-DCP, 2,3,5-TCP, 2,4,5-TCP, 2,3,5,6 TeCP, and PCP) by

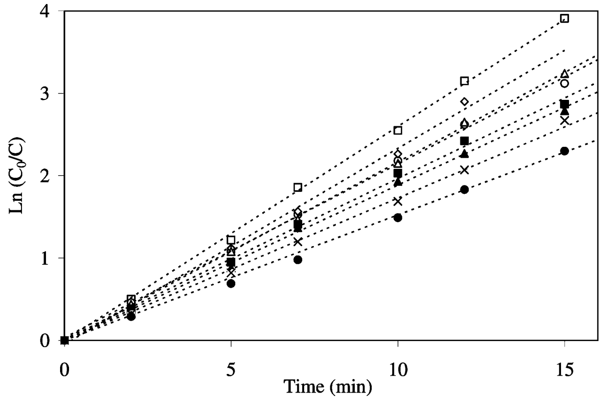

Figure 3. Kinetic analysis for the pseudo-first-order degradation plot of different CPs during electro-Fenton treatment. Conditions: [CP] = 0.2 mM; V = 220 mL; I = 100 mA; [Fe^{3+}] = 0.2 mM; CP = (□) 4-CP, (◇) 2-CP, (△) 2,4-DCP, (○) 2,6-DCP, (■) 2,3,5-TCP, (▲) 2,4,5-TCP, (×) 2,3,5,6-TeCP, (●) PCP.

TABLE 2: Apparent Kinetic Rate Constant (k_{app}) and Half-Life Times ($t_{1/2}$) for the Degradation of Different CPs at I = 100 mA under Conditions of Figure 3

chlorophenol	k_{app} (min^{-1})	$t_{1/2}$ (min)
2-CP	0.23 ± 0.04	3.05
4-CP	0.261 ± 0.06	2.65
2,4-DCP	0.217 ± 0.05	3.15
2,6-DCP	0.214 ± 0.06	3.21
2,3,5-TCP	0.196 ± 0.07	3.47
2,4,5-TCP	0.188 ± 0.06	3.68
2,3,5,6-TeCP	0.172 ± 0.07	4.02
PCP	0.155 ± 0.06	4.55

electro-Fenton was performed applying a constant current of 100 mA. For all the CPs an exponential trend of the degradation curves was obtained versus time and this again suggests that a pseudo-first-order kinetic perfectly approaches the oxidation mechanism. In fact, in the plot Ln(CP_0/CP) versus reaction time for all the CPs points lie satisfactorily around straight lines (Figure 3). After regression analysis, the results obtained for k_{app} and for the half-life times are reported in Table 2.

On the basis of the above experimental results, the oxidation rates follow the sequence 4-CP > 2-CP > 2,4-DCP > 2,6-DCP > 2,3,5-TCP > 2,4,5-TCP > 2,3,5,6-TeCP > PCP. In general it is observed that the degradation kinetic decreases with the increase of the number of chlorine atom in the aromatic ring. Our results are in agreement with those reported by Wang and Wang[57] during the electro-Fenton degradation of 4-CP and 2,4-CP and also with those reported by other authors during the degradation of various CPs using other AOPs.[60] For example Benitez et al.[11] observed that the both photocatalysis and Fenton-s reagent gave the same sequence of oxidation rate: 4-CP > 2,4-DCP > 2,4,6-TCP > 2,3,4,6-TeCP, and Tang and Huang[61] reported that the sequences were 2-CP > 2,4-DCP > 2,4,6-TCP during oxidation by Fenton's reagent.

In fact, $^{\bullet}OH$ generated during electro-Fenton or other AOPs usually attack the aromatic ring at the sites which are not occupied by chlorine atoms, and therefore, the increase in the chlorine atom number in the aromatic ring decreases the reactivity toward the hydroxyl radicals, and subsequently, the trend in the $t_{1/2}$ values is inverse: they increase when the substituent chlorine atoms also increase (Table 2).

In order to explain the differences of reactivity toward $^{\bullet}OH$ between CPs of the same number of chlorine atoms, it must be taken into consideration that the −OH group is both an ortho and para director with activation while −Cl is an ortho and para director with deactivation. Thus it is expected that the $^{\bullet}OH$, in attacking CPs, be directed to the electron-rich positions and cause faster oxidation of these substrates. Moreover, when the chlorine is in the ortho position, close to the hydroxyl group, it is subject to more steric strain than other congeners and therefore, hydroxylation at the ortho position will experience more steric strain than that at the meta or para position.[62]

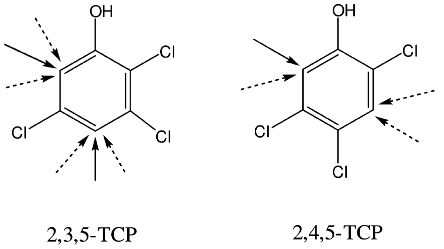

Figure 4. Effect of the position and nature of the substituents in the reaction of TCPs with $^{\bullet}OH$ radicals. Solid arrows represent the activation imposed by the hydroxyl group, whereas dashed arrows represent the deactivation effect of chlorine atoms.

In the case of 4-CP and 2-CP, no position is enhanced by both −OH and −Cl directors, but 2-CP will have some steric hindrance effect due to the closer location between −OH and −Cl groups on the aromatic ring than that on 4-CP. As a result, 2-CP will be more difficult to oxidize than 4-CP. Similarly 2,4-DCP and 2,6-DCP has no position enhanced by both −OH and −Cl directors, but 2,6-DCP has two chlorine atoms in ortho position and therefore is more difficult to oxidize than 2,4-DCP.

In the case of the three substituted CPs, the 2,3,5-TCP has ortho and para positions strongly activated by −OH and −Cl directors (Figure 4) and therefore it is more reactive than 2,4,5-TCP. In the above diagram, the solid arrow represents the stronger directory effect by the hydroxyl group than that by the chlorine group, which is represented by the dashed arrow.

Regarding the 2,3,4,6-TeCP, the molecule possess only one free site for $^{\bullet}OH$ addition between two −Cl substituents with desactivation which can explain the weak value of its k_{app} compared to DCPs or TCPs. The PCP presents a specific case with no free site for electophilic addition of $^{\bullet}OH$. However its oxidation takes place through ipso attack of $^{\bullet}OH$ on ortho and para chlorine positions leading to formation of tetrachloro-*o*- and -*p*-hydroquinones/benzoquinones before mineralization aromatic ring opening and mineralization reactions.[23]

3.3. Determination of the Absolute Rate Constant for the Oxidation of CPs. The second-order or absolute rate constant for the reaction between differently substituted CPs and $^{\bullet}OH$ was then determined by means of the competitive kinetics method, taking *p*-hydroxybenzoic acid (BA) as standard competition substrate whose absolute rate constant with $^{\bullet}OH$ is well established ($k_{BA} = 4.30 \times 10^9\ M^{-1}\ s^{-1}$).[63,64] Briefly, for each tested CP, solutions containing 0.124 mM BA and 0.124 mM of the different CPs (i.e., 4-CP, 2,6-DCP, 2,4,5-TCP, 2,3,5,6-TeCP) with 0.2 mM Fe^{2+} as catalyst were electrolyzed at 50 mA, and the evolution of the corresponding peaks was followed for short reaction times by reversed-phase HPLC. Concerning the poorly soluble PCP, trials were carried out with 0.05 mM. In all cases, both BA and CPs decreased exponentially, so it was possible to determine simultaneously the apparent rate constants for the pseudo-first-order reactions of BA ($k'_{app(BA)}$) and of each CP ($k'_{app(CP)}$) with $^{\bullet}OH$. Figure 5 shows for example the good linear straight lines found for the pseudo-first-order decays obtained during the oxidation of 4-CP, but similar results were obtained for all the tested CPs. These values along with relation 7 were used to calculate the absolute rate constants for each CP (k_{CP}) according to the relation

$$k_{\mathrm{CP}} = k_{\mathrm{BA}} \frac{k'_{\mathrm{app(CP)}}}{k'_{\mathrm{app(BA)}}} \qquad (9)$$

Results obtained are given in Table 3. Absolute rate constant values decreased in the order 4-CP > 2,6-DCP > 2,4,5-TCP > 2,3,5,6-TeCP > PCP, and these values agree with the order already observed in Table 2. Note that these values are found within the range 10^9 M^{-1} s^{-1} reported for many authors for the reaction between aromatic compounds and a hydroxyl radical.[59,63] In particular, the rate constant value of 4-CP is close to that determined by Shetiya et al.[65] (i.e., 7.6 × 10^9 M^{-1} s^{-1}) using a γ-radiolysis method and that of PCP determined by Oturan et al.[23] (i.e., 3.59 × 10^9 M^{-1} s^{-1}). These values are also comparable with the oxidation rate constants between $^{\bullet}OH$ and 2,4-DCP and 2,4,6-TCP determined by Tang and Huang[61] (i.e., 7.2 × 10^9 and 6.3 × 10^9 M^{-1} s^{-1}, respectively).

3.4. Mineralization of CPs: TOC Removal and Chloride Release. In order to verify the effect of the number of chlorine atoms on the mineralization (transformation to CO_2 and water) of CPs, aqueous solutions containing different CPs (i.e., 4-CP, 2,6-DCP, 2,4,5-TCP, 2,3,5,6-TeCP, and PCP) and also their mixture were electrolyzed at 300 mA, with 0.2 mM Fe^{2+} for 6 h. During the electro-Fenton process the TOC evolution was monitored and is reported in Figure 6. In agreement with the values of the rate constants found above, the results suggest that the mineralization efficiency (in terms of TOC abatement) decreases with the increase of the number of chlorine atoms in the aromatic ring; the organic became more difficult to mineralize. Mineralization of aqueous 4-CP is complete (99%) after 6 h of treatment while degree of mineralization is weakest for PCP solution (87%). It is also interesting to observe that a mixture of CPs is also mineralized with a rate between tri- and tetrachlorophenols with a TOC abatement of 91%. It is worthy to note that at mineralization degrees around 90%, the treated solution does not contain any more toxic aromatics, the remaining TOC being related to some short-chain carboxylic acids, in particular oxalic acid, which presents low reactivity toward $^{\bullet}OH$.

On the other hand, the ion chromatography analysis allowed the monitoring of the dechlorination of CPs during electrolysis. The release of the chloride ions during the treatment is reported in Figure 7. For all the compounds, almost complete release of chloride ions (represented by the dotted line in Figure 7) was obtained after 6 h of treatment, meaning that no chlorinated intermediates were present in treated solution. In addition from Figure 7 it is also possible to observe that the rate of chloride ion release is almost independent of CPs treated. These results show almost mineralization of CPs in addition to TOC abatement values.

TABLE 3: Absolute Rate Constants (k_{abs}) of the Oxidation of CPs by $^{\bullet}OH$ under Electro-Fenton Conditions of Figure 5

chlorophenol	k_{abs} (10^9 M^{-1} s^{-1})
4-CP	7.75 ± 0.07
2,6-DCP	6.13 ± 0.05
2,4,5-TCP	5.72 ± 0.05
2,3,5,6-TeCP	4.95 ± 0.07
PCP	3.56 ± 0.06

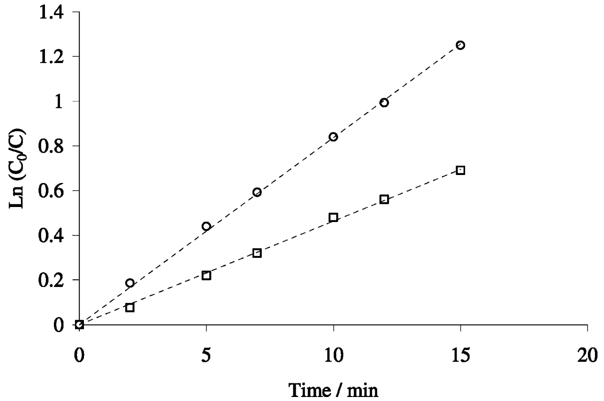

Figure 5. Kinetic analysis for the pseudo-first-order reaction of (○) 4-CP and (□) benzoic acid with $^{\bullet}OH$. Electro-Fenton experiments were carried out with 0.124 mM for 4-CP and benzoic acid, 50 mM Na_2SO_4, and 0.2 mM Fe^{3+} at pH 3.0 and I = 50 mA.

4. Conclusions

The kinetics of the oxidative degradation of several CPs by $^{\bullet}OH$ during the electro-Fenton process has been investigated using a carbon felt cathode. It was demonstrated that the number and the position of the chlorine atoms in the aromatic ring influences significantly the oxidation of CPs. For all the tested CPs, the degradation followed a pseudo-first-order kinetics and the apparent rate constant follows the sequence 4-CP > 2-CP > 2,4-DCP > 2,6-DCP > 2,3,5-TCP > 2,4,5-TCP > 2,3,5,6-TeCP > PCP. With the competition kinetic method, a higher absolute rate constant between CPs and $^{\bullet}OH$ was found as 7.75 × 10^9 M^{-1} s^{-1} for 4-CP and it decreased with the same sequence of

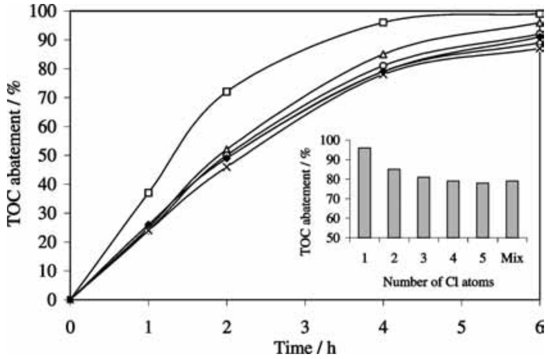

Figure 6. TOC decay during the electro-Fenton process of different CP aqueous solutions. Conditions: [CP] = 0.2 mM; V = 220 mL; I = 50 mA; [Fe^{3+}] = 0.2 mM; CP = (□) 4-CP, (Δ) 2,6-DCP, (○) 2,4,5-TCP, (◇) 2,3,5,6-TeCP, (×) PCP, (◆) mixture of CPs. The inset shows the TOC abatement after 4 h of electrolysis as a function of Cl atoms.

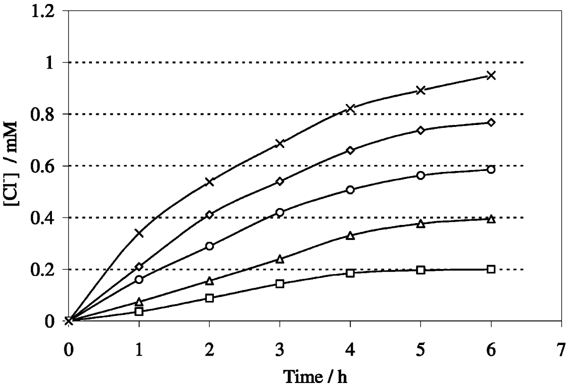

Figure 7. Time course of chloride ions release in solution during the electro-Fenton process of different CPs. Conditions: [CP] = 0.2 mM; V = 220 dm^3; I = 50 mA; [Fe^{3+}] = 0.2 mM; CP = (□) 4-CP, (Δ) 2,6-DCP, (○) 2,4,5-TCP, (◇) 2,3,5,6-TeCP, (×) PCP. The dotted lines represent the complete release of chloride ions.

the apparent rate constant taking the value of 3.56×10^9 M^{-1} s^{-1} for PCP.

It was also observed that the mineralization rate of CPs decreased with increasing the number of chlorine atoms in the aromatic ring, confirming that more chlorinated phenols are more difficult to mineralize. However, after 6 h of electrolysis for all the tested CPs, almost quantitative mineralization degree in terms of TOC abatement and chloride ions released were obtained.

Acknowledgment. Dr. M. Panizza acknowledges the financial support of the Université Paris-Est Marne-la-Vallée for the "Invited Professor" position in Laboratoire Géomatériaux et Environnement during his research stay in Paris.

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JP9069674