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Mechanism for the oxidation of phenol by sulfatoferrate(VI): Comparison with various oxidants

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ABSTRACT

The oxidative action of a solid and stable potassium sulfatoferrate(VI) material on phenol was studied in aqueous solution under different stoichiometries. The performance towards phenol and the total organic carbon is compared to that of potassium permanganate and calcium hypochlorite. The total mineralization of phenol is not completely achieved by the studied chemical oxidants, and some oxidation products have been identified by gas chromatography-mass spectrometry and gas chromatography-flame ionization detector analysis. A radical reaction pathway, involving the formation of oxidation intermediates or by-products such as benzoquinone, phenoxyphenol and ring opening products, is proposed for the decomposition of phenol by ferrate(VI). Phenoxyphenol is also involved in the oxidation mechanism for permanganate whereas chlorinated phenols are produced by hypochlorite. The role of the chloride anion impurity of the potassium sulfatoferrate(VI) material has been highlighted in this study; no negative impact on the removal of phenol and its mineralization is observed compared to the use of a pure commercial ferrate(VI). The efficiency of sulfatoferrate(VI) for the oxidative removal of phenol from industrial wastewater is also confirmed.

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1. Introduction

In water and wastewater treatment, specialists are currently working to find less hazardous and more broadly applicable innovative processes, to meet more stringent discharge standards. The removal of environmental pollutants through oxidation processes is attractive but total mineralization has rarely been observed and some harmful by-products can be generated with the oxidants currently used in water treatment processes. Indeed, chlorinated oxidants, including hypochlorite, are widely criticized because they create hazardous disinfectant by-products (DBP) after treatment. Ozone leads to the formation of carcinogenic bromate in the presence of bromide (Gunten, 2003) and the implementation of this technology is not cost-effective. Potassium permanganate can be a good oxidant candidate but its cost is high and the discharge standards for manganese are very strict. Nevertheless, the oxidation processes are still interesting and one oxidant has been the subject of increasing interest in recent decades: the ferrate(VI)

FeO_4^{2-}. Its oxidizing power is important throughout the entire pH range, with potentials of 2.20 V under acidic conditions and 0.72 V in alkaline solutions (Wood, 1958). After its use, Fe(VI) is reduced to nontoxic ferric hydroxide $Fe(OH)_3$ and can be considered to be an environmentally friendly treatment chemical. Its efficiency has been demonstrated widely on both organic and inorganic contaminants, such as pharmaceuticals, metals, cyanides, nitrogen- and sulfur-containing compounds (Sharma, 2013, 2011; Sharma et al., 2015; Yu et al., 2013). Coagulation and disinfection of sewage are efficient by decreasing turbidity, color and biological species (Jiang et al., 2006). Because of its multifunctional properties as an oxidant/disinfectant and coagulant, Fe(VI) can meet the new challenges confronting the water industry.

Among the existing salts $MFeO_4$ (M = Ca, Sr, Ba) or M'_2FeO_4 (M' = Li, Na, K, Rb, Cs, Ag), the Fe(VI) salts of calcium, sodium and potassium are of interest in the field of water treatment because the associated cation is nontoxic. The synthesis of calcium ferrate is complex and the product obtained is too unstable to be interesting (Xu et al., 2007). Sodium ferrate is primarily known in solution or is isolated in the solid state with significant amounts of impurities. In contrast, potassium ferrate is easier to obtain as a solid product (Jiang and Lloyd, 2002). Three main approaches exist for the synthesis of ferrate salts. The electrochemical methods produce

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iron(VI) in an alkaline solution from a sacrificial iron(0) anode or an inert electrode immerged in an iron(III) solution (Mácová et al., 2009). The wet synthesis consists of oxidation of ferric ions in aqueous solution under strongly alkaline conditions (Li et al., 2005). Solutions of Fe(VI) formed electrochemically or by wet methods quickly decompose. The production and use of ferrate in situ with an electrochemical method is of great interest (Alsheyab et al., 2009). But to obtain a stable solid product, further precipitation, washing and drying steps must be conducted (Schreyer and Ockerman, 1951). Dry thermal syntheses have been developed to avoid the reaction of ferrate with water (Thompson, 1985); however, processes at temperatures higher than 230 °C are not convincing because of the low thermal stability of Fe(VI) (Machala et al., 2007).

Since 1990, synthetic processes at room temperature have been developed and the inclusion of a sulfate salt in the composition of the potassium ferrate stabilizes it (Ninane et al., 2008). Sulfur atoms substitute for some of the iron atoms to stabilize the FeO_4^{2-} group and form the double salt potassium sulfatoferrate(VI) $K_2(Fe,S)O_4$. The potassium sulfatoferrate prepared for this study is obtained according to patent FR 2908128 (Castetbon et al., 2008). This solid phase synthesis requires a mixture of ferric sulfate, potassium hydroxide and calcium hypochlorite. The product of the reaction exists in the form of solid pellets for which no further purification is performed because the impurities do not alter the quality of the treated water. This method is faster and easier than other production methods leading to pure potassium ferrate.

This study focuses on the chemical oxidation of phenol, chemical present in the wastewater of various industries. In spite of the biodegradability of this compound, its mineralization requires a long time and chemical oxidants are often used to accelerate its transformation. Moreover, a goal of studying the oxidation of such a simple molecule is improving the understanding of the oxidation mechanisms of various oxidants. In particular, the action of ferrate on phenol has been studied by few workers (Graham et al., 2004; Huang et al., 2001; Lee et al., 2005; Waite and Gilbert, 1978); all the cited studies have been performed in buffered solutions, mainly with phosphate. A phosphate buffer is used to perform kinetic studies of Fe(VI) in solution because phosphate reacts very slowly with Fe(VI) and prevents formation of the precipitate generated by the decomposition of Fe(VI) into ferric hydroxide (Schreyer and Ockerman, 1951); by stopping this precipitation, the equilibrium reaction is disturbed and stabilizes the ferrate ion (Mills and Smith, 1956). In industrial treatment conditions, no buffering can be established; only pH adjustment is economically viable. To simulate these conditions, the treatments have been performed on phenol solutions with a preliminary adjustment to pH 9. The aim of this work is to estimate the efficiency of the transformation of phenol by several oxidants under similar pH conditions. Mechanisms are proposed for each oxidant. Another aspect of this study is to evaluate the impact of the impurities of the potassium sulfatoferrate material synthesized by the dry method. Its action on phenol is compared to the action of a pure potassium ferrate. A concrete example of the oxidation of phenol by sulfatoferrate in a complex matrix is shown.

2. Materials and methods

2.1. Chemicals

Potassium sulfatoferrate(VI) was obtained according to the patent FR 2908128, filed in 2006 by STRADIA (Castetbon et al., 2008). The composition of the resulting pellets is 15–18% K_2FeO_4, 20–26% KOH, and 2–3% $Fe(OH)_3$. The balance is composed of excess chemicals from the synthesis reaction: Cl^-, SO_4^{2-}, Ca^{2+}, K^+, Na^+, and CO_3^{2-}. The price of this iron(VI) matter is estimated at 20 $/kg with the actual process (including reactants and their preparation, conditioning of the pellets, workforce and energy consumption) but the optimization of the synthesis is still studied. Pure potassium ferrate(VI) (90%) was obtained from Sigma–Aldrich; the price of the commercial product is more than 2000 $/kg.

Solutions of phenol were obtained from a standard solution of phenol of 1 g/L C_6H_5OH in 0.4% NaOH from Chem-Lab. Granules of calcium hypochlorite (72%) were purchased from Barcelonesa. Potassium permanganate (>99.5%) was obtained from Prolabo. Dichloromethane stabilized with amylene (25 mg/L) was purchased as the Pestanal® grade chemical (>99.8%, Fluka Analyticals). Orthophosphoric acid (>95%) and nitric acid (70%) were from Fisher Chemical. Sodium hydroxide R.P. Normapur was from Prolabo. Dried ferrous sulfate $FeSO_4 \cdot xH_2O$ (88%) was purchased from Univar. Acetic acid (>99%) and methanol (>98%) from Fisher Scientific, acetone Pestanal® (>99.9%) and ethanol (>99.9%) from Fluka Analyticals, and 1-propanol (>99.5%), 2-propanol Chromasolv® (>99.9%), butyric acid (>99%) formic acid (>98%) and propionic acid (>99.5%) from Sigma–Aldrich were used as standards for the gas chromatography-flame ionization detector (GC-FID) analyses.

2.2. Methods

2.2.1. Experimental procedures

In the oxidation of phenol, pH is very influential because it determines the distribution of species for each reactant. Fe(VI) can have four different states in aqueous solutions, i.e. $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$ and FeO_4^{2-} with pKas of 1.6 ± 0.2, 3.5 and 7.3 ± 0.1 (Rush et al., 1996). Potassium permanganate and calcium hypochlorite exist in dissociated and undissociated forms (HClO, ClO^-, $HMnO_4$ and MnO_4^-). Phenol is found as PhOH and PhO^-. The corresponding equilibrium constants are $pKa_{(HClO/ClO^-)} = 7.5$, $pKa_{(HMnO_4/MnO_4^-)} = -2.25$ and $pKa_{(PhOH/PhO^-)} = 9.99$. The pH also affects the redox potential of the oxidants. In alkaline media, Fe(VI) is relatively stable whereas it degrades immediately in acidic media (Wagner et al., 1952). The oxidizing power of ferrate increases as the pH decreases (Wood, 1958). A pH value of 9 is a good compromise to have both powerful and stable ion ferrate (Li et al., 2005).

A solution of phenol 30 mg/L (0.319 mM) is prepared by diluting the phenol standard. The pH is adjusted to 9.0 ± 0.1 by addition of H_3PO_4. Each oxidant is injected in a solid form in the phenol solution and stirred for 1 h (the pellets of impure sulfatoferrate are grounded before injection). Different molar ratios of oxidant to phenol are used to be close to the theoretical mineralization of phenol (Table 1) or to have excess oxidant or excess phenol.

The degradation of Fe(VI) in water leads to the formation of hydroxide anions (Eq. (1)) (Goff and Murmann, 1971). Thus, after the ferrate reaction, the final pH values of the solutions have been measured to be between 9.5 and 10 depending on the ratio (modifying the proportion of dissociated and undissociated forms of phenol).

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe^{3+} + 3/2O_2 + 10OH^- \tag{1}$$
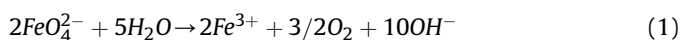
To study the evolution of the reaction, solutions of phenol and oxidant are quenched at different times. Ferrous sulfate is used to stop the action of permanganate and hypochlorite by their reduction to MnO_2 and Cl^-, respectively. To stop the action of ferrate, the solutions are acidified with H_3PO_4 to a pH of approximately 2 because protonated Fe(VI) species are unstable in aqueous media and decompose very quickly. No filtration is performed before

Table 1
Theoretical reactions of total mineralization of phenol by the oxidants studied.

Equation of total mineralization of phenol (pH 9–12)	Masses of oxidant introduced for ratio 1:1
$C_6H_5OH + 28/3FeO_4^{2-} + 61/3H_2O \rightarrow 6CO_2 + 28/3Fe(OH)_3 + 56/3OH^-$	63 mg/L K_2FeO_4
$C_6H_5OH + 28/3MnO_4^- + 5/3H_2O \rightarrow 6CO_2 + 28/3MnO_2 + 28/3OH^-$	50 mg/L $KMnO_4$
$C_6H_5OH + 14ClO^- \rightarrow 6CO_2 + 14Cl^- + 3H_2O$	22.8 mg/L $Ca(ClO)_2$

acidification so only the oxidation properties of the ferrate anion are observed. Indeed, the chemical reduction of Fe(VI) through its action on phenol led to the formation of insoluble Fe(III) species, which might have the ability to adsorb organic compounds and thereby remove them from solution. In acidic media, the Fe(III) particles are solubilized and the coagulant effect on the phenol is avoided. Solutions of permanganate and hypochlorite are also acidified to a pH of approximately 2 after quenching to avoid coagulation by the Fe(III) formed from the action of ferrous sulfate on the oxidants.

2.2.2. Analytical methods

The concentration of ferrate(VI) in solution was monitored through measurement of the absorbance at 510 nm (Jiang and Lloyd, 2002) by the spectrophotometer Shimadzu UV-1800.

The chemical oxygen demand (COD) was measured using pre-measured Lange tubes (method ISO 15705), as the total organic carbon (TOC). The accuracy of the concentrations obtained from the COD and TOC pre-measured tubes was checked with a standard solution of potassium hydrogen phthalate. The COD measured by this method (y) is related to the theoretical COD (x) by the equation $y = 1.148x$ ($R^2 = 0.998$). The TOC measured by this method (y′) is related to the theoretical TOC (x′) by the equation $y' = 1.058x'$ ($R^2 = 0.999$).

The organic compounds were extracted with dichloromethane and gas chromatography has been chosen to analyze the phenol and its transformation products due to their volatility. The concentration of phenol was determined by gas chromatography-mass spectrometry (GC−MS) with a calibration curve. The limit of detection is 0.1 mg/L of phenol. Qualitative analyses of the studied oxidation products were performed by GC−MS and gas chromatography-flame ionization detector (GC-FID) measurements. The evolution of the products identified by GC−MS was studied by determining the quotient of the peak area of the by-product divided by the peak area of the phenol 30 mg/L. This study is not quantitative; it only gives information about the oxidation mechanisms of phenol by showing the appearance or destruction of any product (arbitrary unit AU). GC-FID was used to observe acetone, methanol, ethanol, 1-propanol, 2-propanol, formic acid, acetic acid, propionic acid and butyric acid in the samples. The GC−MS used is a Varian CP-3800 GC equipped with a capillary column (30 m × 0.25 mm, and a 0.25 μm thick film composed of 5% phenyl- and 95% methyl-siloxane). The GC conditions were as follows: a sample volume of 1 μL was injected in the splitless mode at 250 °C and the oven temperature was programmed from 40 °C (0.5 min) to 120 °C at 20 °C/min, followed by an increase at 2 °C/min to 170 °C (5 min) and finally an increase at 25 °C/min to 270 °C (10 min). Helium was used as the carrier gas at a flow rate of 1 mL/min. The mass spectrometer used is a Varian Saturn 2200 GC/MS. The ionization source is electronic, and the separated compounds are analyzed in ion trap mode with a mass scan range of m/z 35 to 449. The Varian MS Workstation version 6.8 is used to pilot the GC−MS and identify the molecules. The GC-FID is a Varian CP-3900 GC equipped with a capillary column (10 m × 0.53 mm, 1 μm film thickness composed of 100% dimethylpolysiloxane). A sample volume of 5 μL was injected in splitless mode at 280 °C and the

oven temperature was programmed from 50 °C to 80 °C at 50 °C/min followed by an increase at 30 °C/min to 320 °C. The helium carrier gas was used at a flow rate of 15 mL/min; for the flame analysis, the hydrogen flow was 30 mL/min. A flame ionization detector placed at the outlet of the gas chromatograph detected the molecules.

Two real wastewater effluents containing phenol have been provided by local industries. The composition of both effluents is mainly organic matter (COD 3350 mg(O_2)/L and 7017 mg(O_2)/L), the initial pH is close to neutrality. The phenol index, expressed in milligrams per liter of phenol (C_6H_5OH), was determined according to the procedure NF ISO 6439.

3. Results

The theoretical TOC and COD for a 30 mg/L solution of phenol are 23.0 mg(C)/L and 71.4 mg(O_2)/L, respectively. The results are expressed as normalized concentrations C/C_0 (C_0 corresponds to 30 mg/L of phenol). Phenol in the operating conditions is present under its protonated and unprotonated forms. The experiments were conducted three times to define the uncertainty in the measurement. The uncertainty associated with the quantification of phenol by GC−MS is approximately 1% for concentrations of phenol higher than 1 mg/L. As the concentration decreases below 1 mg/L, the error increases. For the TOC and COD measurements, the results are expressed with a precision of 5%.

The stoichiometric ratios were calculated according to the oxidation reaction for phenol with the different oxidants studied (Table 1). To mineralize 1 mol of phenol in CO_2, 28/3 mol of FeO_4^{2-} (a factor of 10 was preferred in the experiments) or MnO_4^- and 14 mol of ClO^- are needed. These molar ratios are called the stoichiometric ratios in the present study.

3.1. Action of ferrate on phenol

Before studying the reaction of ferrate with a compound P, the pH-dependent rate of autodecomposition of Fe(VI) (reaction of a molecule of Fe(VI) with a molecule of water or another molecule of Fe(VI) (Carr, 2008; Lee et al., 2014)) must be determined. Few studies deal with this topic and different authors indicate different orders of reaction (Lee and Gai, 1993; Li et al., 2005; Rush et al., 1996). A second-order reaction has been observed over a large range of pH values (Rush et al., 1996) whereas Lee and Gai showed second-order kinetics at pH values below 9 and first-order kinetics at pH values above 10 (Lee and Gai, 1993). A more recent study showed first-order kinetics from pH 7 to 12 (Li et al., 2005). In addition, the decomposition depends on other factors beyond pH, such as the presence of coexisting ions and their concentrations. For each study with ferrate, the decomposition of Fe(VI) should be monitored under the treatment conditions; in the present study, Fe(VI) concentration in solution prepared with sulfatoferrate has been monitored over time through measurement of the absorbance at 510 nm. The evolution of the Fe(VI) concentration shows second-order kinetics in the pH range 8–10.5 and first-order kinetics for pH higher than 11 (see Figure A in the Supplementary material).

All reactions of Fe(VI) with phenol or other organic compounds

have been estimated to be first order with respect to both reactants. This result was also reported by Sharma et al. (Sharma, 2013, 2011).

Finally, two pathways can be described: the reaction of auto-decomposition of Fe(VI) (second-order kinetic in the operating conditions of the present study) and reactions with solutes [P] (Eq. (2)). The solutes are phenol and the salts initially present in the pellets of sulfatoferrate.

$$-\frac{d[Fe(VI)]}{dt} = k1[Fe(VI)][Fe(VI)] + k2[Fe(VI)][P] \qquad (2)$$

The reaction of Fe(VI) with the compounds [P] in aqueous solution dominates the reaction of autodecomposition when $k2[P] > k1[Fe(VI)]$, i.e. when $[Fe(VI)] < (k2/k1)[P]$. Hence, when the concentration of Fe(VI) is higher than $(k2/k1)[P]$, the reaction with water or another molecule of Fe(VI) prevails (Ciabatti et al., 2010).

3.1.1. Comparison of pure potassium ferrate with impure potassium sulfatoferrate

The action of pellets of potassium sulfatoferrate obtained according to patent FR 2908128 is compared to pure potassium ferrate. This study is important because it has been shown that some coexisting ions influence the stability of ferrate in water (Schreyer and Ockerman, 1951) and the efficiency of removal of a molecule (Han et al., 2013).

Both forms of ferrate were introduced in stoichiometric molar ratios of FeO_4^{2-} to phenol = 10:1. The performances toward phenol, COD and TOC achieved with both forms are similar (Fig. 1). The reaction of Fe(VI) with phenol is confirmed to be first-order with respect to both reactant. The apparent second-order rate constants (k_{app}) for the reactions of pure Fe(VI) and impure sulfatoferrate on phenol are respectively 78 M^{-1} s^{-1} and 80 M^{-1} s^{-1}. A similar reactivity of phenol with pure ferrate has been observed in the literature (Lee et al., 2005). Impurities in the pellets do not have a negative impact on the removal of phenol and its mineralization in the stoichiometric ratio.

3.1.2. Treatment with potassium sulfatoferrate: phenol, COD, and TOC abatement

Several molar ratios of FeO_4^{2-} to phenol were applied. The concentration of phenol (Fig. 2(a)), COD (Fig. 2(b)) and TOC (Fig. 2(c)) were monitored during the treatments. When Fe(VI) is the limiting reactant (molar ratio 1:1), its action on the phenol is low (10% abatement of phenol, no action on TOC and COD). Total transformation of the phenol is achieved in approximately 30 min when Fe(VI) is introduced in stoichiometric amounts (10:1) and in excess (15:1). The observed reduction of the TOC and COD shows that there is partial mineralization of the phenol and formation of by-products.

The addition of an excess of ferrate is also observed to give lower TOC and COD abatements. At a molar ratio of 10:1, the TOC decreases by 57% and the COD decreases by 82% whereas the decreases are 49% for TOC and 52% for COD when ferrate is introduced in excess. An excess of ferrate could decrease the efficiency of the treatment in the oxidative mechanism through the kinetics of the reactions of the ferrate ion in aqueous solutions. As shown previously in Eq. 2, when the concentration of Fe(VI) is higher than $(k2/k1)[P]$, the reaction of autodecomposition of ferrate in water prevails on its action on phenol. Less oxidant is available for the mineralization so an excess of ferrate causes a lower efficiency for the TOC and COD abatements.

3.1.3. Study of intermediates and by-products/mechanisms

Analyses by GC–MS permit us to follow the evolution of some of the reaction intermediates (Fig. 3), identified by comparison to the bank of mass spectrums of the software (see Figure B in the Supplementary material).

When Fe(VI) is the limiting reactant (Fig. 3(a)), only 10% of the phenol is transformed and no mineralization to CO_2 occurs (the

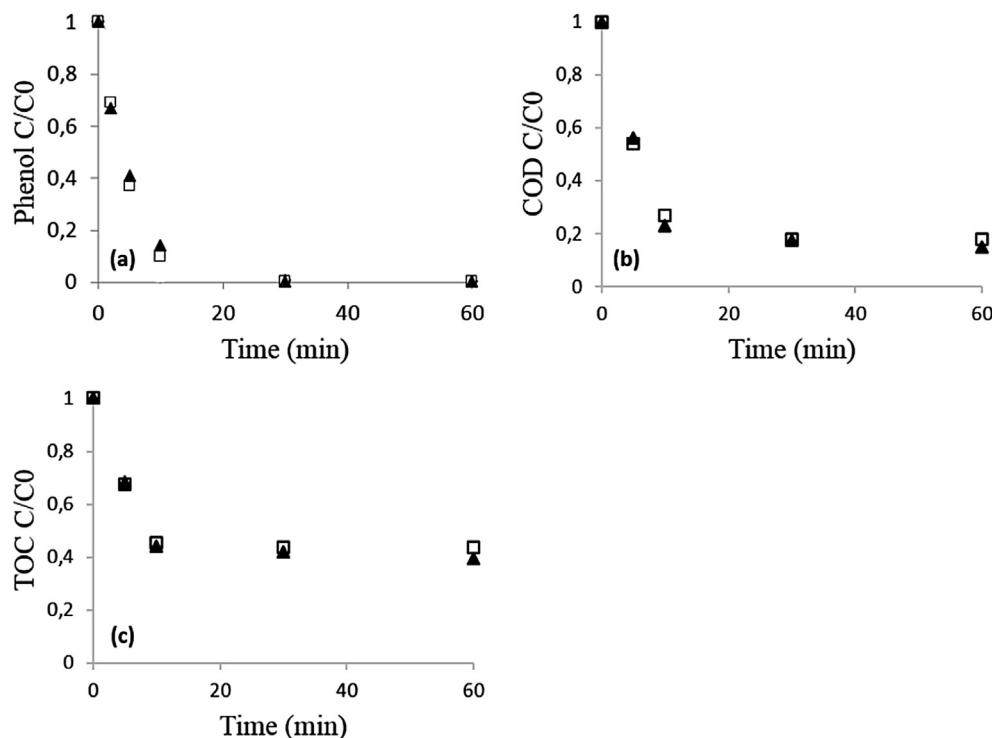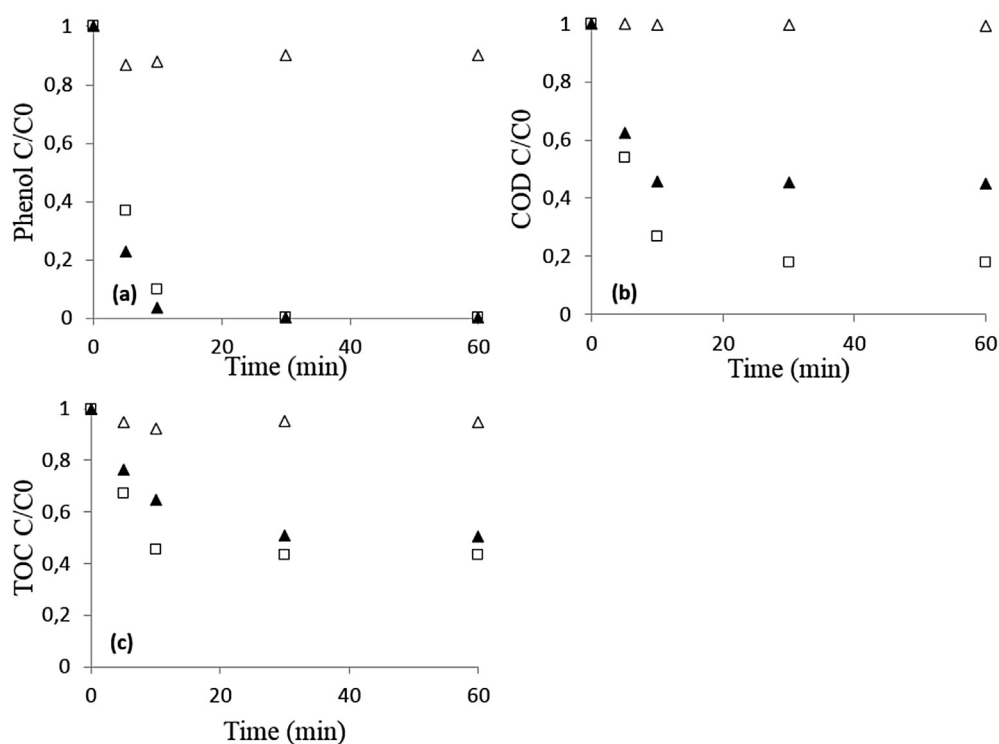**Fig. 1.** Evolution of (a) phenol, (b) COD, (c) TOC during the treatment by ferrate introduced in molar ratios of FeO_4^{2-} to phenol 10:1 in the form of (▲) powder of pure potassium ferrate; (□) powder of impure potassium sulfatoferrate.

Fig. 2. Evolution of (a) phenol, (b) COD, (c) TOC during the treatment by impure potassium sulfatoferrate for the molar ratios FeO_4^{2-}:phenol (Δ) 1:1; (□) 10:1 (stoichiometry); (▲) 15:1.

TOC is constant). Benzoquinone is a reaction intermediate because it disappears in less than 30 min; it is also oxidized to form species not identified by GC−MS. These species are proposed to result from the cleavage of the aromatic ring. The presence of butyric acid,

acetic acid, formic acid, ethanol and 1-propanol has been confirmed by GC-FID analyses. Benzoquinone has also been observed by Huang and coworkers during their kinetic studies of the oxidation of phenol by Fe(VI) under stoichiometric conditions (Huang et al.,
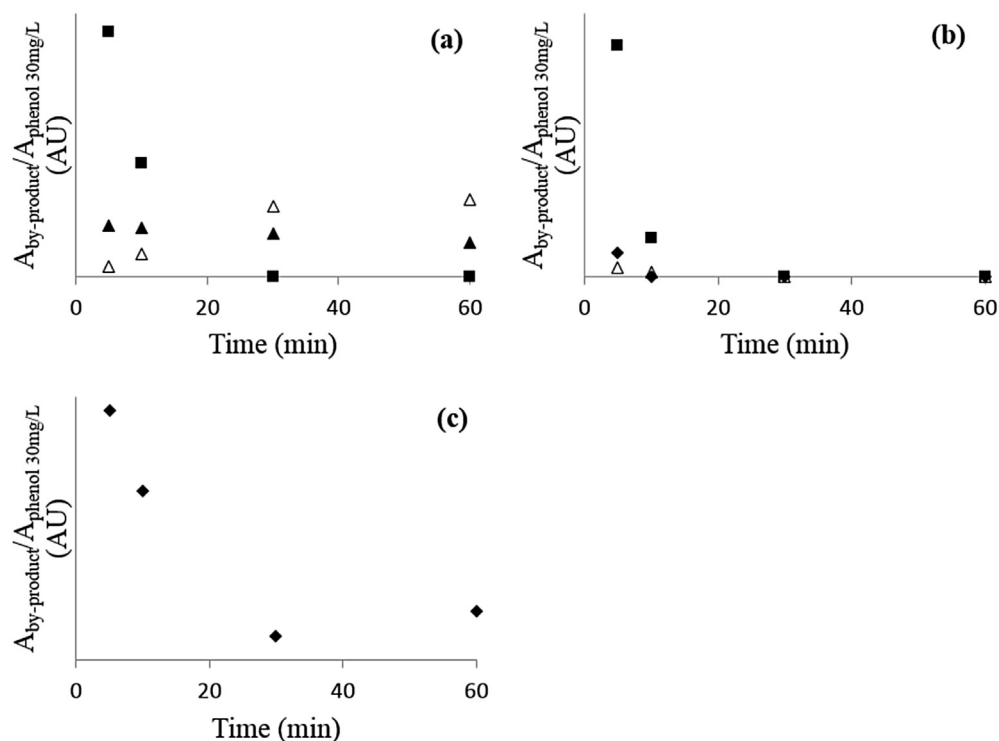
Fig. 3. Evolution of by-products of treatment of phenol by impure potassium sulfatoferrate: (■) benzoquinone; (Δ) 2-cyclohexene-1-one; (♦) parachlorophenol; (▲) 2-phenoxyphenol; for the molar ratios FeO_4^{2-}:phenol (a) 1:1; (b) 10:1(stoichiometry); (c) 15:1.

2001). A radical reaction pathway was demonstrated in their study by spin-trapping analysis and electron paramagnetic resonance (EPR) spectroscopy. Although no detailed information about the radical adduct has been obtained, this adduct is suspected to be the phenoxy radical. The reaction scheme proposed by Huang and co-workers shows that benzoquinone is the product of the reaction of Fe(V) with the phenoxy radical. The formation of the phenoxy radical during the action of ferrate on phenol can be confirmed in the present study because of the presence of 2-phenoxyphenol throughout the reaction. The 2-phenoxyphenol seems to be the product of the dimerization of phenoxy radicals. The presence of the cyclohexenone is difficult to explain because cyclohexenone seems to be the result of a reduction, so its presence can be questioned.

Under stoichiometric molar ratios (Fig. 3(b)), the benzoquinone intermediate appears and is oxidized as when Fe(VI) is the limiting reactant. During the first minutes, cyclohexenone is also detected as an intermediate. Phenoxyphenol is not observed, so even if it is formed, it is removed in the first 5 min. A novel intermediate appears, parachlorophenol, which may result from the reaction of a phenoxy radical with a chlorine radical. The chlorine free radical is proposed to result from the oxidation of the chloride ion Cl^- that is present in the salts of the sulfatoferrate pellets (from 40 to 600 mg(Cl^-)/L depending on the ratio of FeO_4^{2-} to phenol). Cl^- is a weak reducing agent but it appears to be the only plausible source of formation of the free radical, while no hypochlorite anion or dichlore are present in solution. The chlorine radical is thus proposed to be the product of the reaction of the reactive species Fe(VI), Fe(V) or phenoxy radical with the chloride anion. The ortho form of chlorophenol was not observed by GC–MS but its formation can be postulated. Chlorophenol disappears before the first 10 min of treatment and this disappearance shows that the high oxidation states of iron (Fe(VI) or Fe(V)) can also oxidize chlorophenol. Finally, the oxidation under stoichiometric conditions leads only to the formation of ring opening products and carbon dioxide, as shown by the GC-FID analysis and the TOC abatement.

The excess of potassium sulfatoferrate is responsible for the persistent presence of parachlorophenol during the treatment (Fig. 3(c)). Ferrate has been shown to be more reactive with chlorophenol than with phenol at pH between 7 and 9 (Graham et al., 2004; Lee et al., 2005). The remaining chlorophenol is due to the prevailing reaction of autodecomposition of ferrate in water at high concentrations (§3.1.2). The excess of ferrate implies lower abatements of the concentrations of TOC and COD. The presence of other impurities seems to not interfere in the oxidation mechanism. Carbonate anions are present in very small concentration (from 5 to 100 mg/L depending on the ratio of FeO_4^{2-} to phenol). No influence on the reaction has been observed. No reaction between Fe(VI) and sulfate has been reported in the literature, as the sulfate anion is a very weak reducing agent.

3.2. Action of other oxidants on phenol

3.2.1. Action of potassium permanganate

When permanganate is the limiting reactant with regard to phenol (molar ratio of MnO_4^- to phenol of 1:10), only 33% of the phenol is removed and 28% of the TOC is mineralized. The oxidation by-products were identified by GC–MS. The phenoxyphenol seems to be produced by the dimerization of the phenoxy radical. Previous studies have indicated that the oxidation of phenol by permanganate is initiated by a transfer of one electron from the phenolate ion to permanganate; this transfer leads to the formation of phenoxy radical and manganate(VI) ion MnO_4^{2-} (Doré et al., 1975). Some of the phenoxyphenol formed by this way is eventually removed by permanganate over time. Phenoxybenzaldehyde remained

constant throughout the experiment; its presence is difficult to explain; it might be a product from the reaction of a byproduct not identified in this study on the phenoxyphenol. Of the 33% of phenol removed, some was transformed to carbon dioxide, as shown by the TOC abatement, and to short-chain products, such as the propionic acid, acetic acid and 1-propanol identified by GC-FID.

The total removal of phenol is observed beyond the stoichiometric amounts, and TOC decreases by 70% and 77%, respectively, for ratios of 10:1 and 15:1. The transformation of phenol was completed very quickly, in less than 5 min. No by-products were identified by GC–MS, but analysis by GC-FID confirmed that ring opening products remain in the solution. In view of the TOC abatement, carbon dioxide is the major product of the oxidation.

3.3. Action of calcium hypochlorite

Two cases with limiting quantities of hypochlorite were studied with molar ratios of ClO^- to phenol of 1:10 and 10:1. For a significant excess of phenol (ClO^-:phenol of 1:10), the degradation of phenol was 8% and no mineralization occurs (the TOC is constant). Several chlorophenols formed were identified by GC–MS (Fig. 4(a) and (a′)). The same byproducts are identified at the ratio of 10:1 (Fig. 4(b) and (b′)). The hypochlorous acid present in solution reacts with the phenolate or chlorinated phenolate to form the different chlorophenols observed. This chlorination proceeds through an electrophilic substitution pathway (Michałowicz et al., 2007). The major chlorophenols formed in each case are clearly different. For the 1:10 ratio, the by-products, listed in order of decreasing concentration, are chlorophenol > dichlorophenol > trichlorophenol > trichloroanisole. For the 10:1 ratio, the concentrations of by-products decrease in the order: trichlorophenol > trichloroanisole > dichlorophenol > chlorophenol. In conclusion, when the concentration of hypochlorite increases relative to that of phenol, more substitution occurs. Finally, the presence of the observed trichloroanisole is not explained in this study.

Beyond the stoichiometric amount, total removal of phenol is observed and the TOC decreases by 61% and 75%, respectively, for the ClO^-:phenol ratios of 14:1 (stoichiometric ratio) and 20:1. The transformation of phenol by calcium hypochlorite occurs in less than 5 min. The concentration of the formed chlorophenols is lower than when excess phenol is present. For the stoichiometric ratio of 14:1 (Fig. 4(c)), chlorophenol, dichlorophenol, trichlorophenol and trichloroanisole are still present but are at trace levels. Only trichlorophenol and trichloroanisole were observed for the ratio 20:1 (Fig. 4(d)).

The decrease in the TOC proves that partial mineralization has occurred. ClO^- cleaves the phenolic aromatic ring of the chlorinated phenols to form oxidized linear molecules and carbon dioxide. Several products of the cleavage have been identified by GC-FID, such as butyric acid, propionic acid, acetic acid, formic acid, 1-propanol and ethanol. A previous study also reported the detection of carboxylic acids, primarily acetic and formic acids, from the degradation of the aromatic ring of phenol (Michałowicz et al., 2007).

3.4. Action of ferrate on phenol in real wastewater

The previous results (§3.1 and 3.2) show that powder of impure sulfatoferrate is very reactive with phenol and has the same efficiency as pure ferrate. The yields of the transformation are similar for the three oxidants studied, but ferrate presents the advantage of being a less harmful oxidant by avoiding the formation of hazardous organic or metallic by-products.

To confirm the efficiency of the impure sulfatoferrate in reducing water pollution, the treatment of phenol in a complex
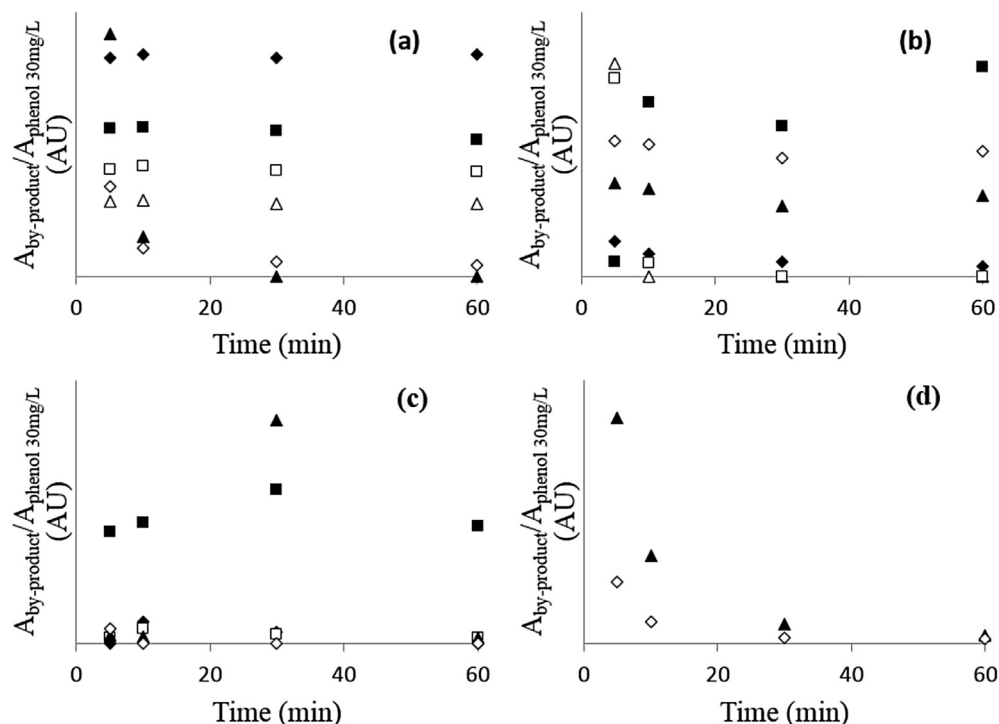
Fig. 4. Evolution of by-products of treatment of phenol by Ca(ClO)$_2$: (■) 2-chlorophenol; (Δ) 2,4-dichlorophenol; (◆) parachlorophenol; (□) 2,6-dichlorophenol; (▲) 2,4,6-trichlorophenol; (◊) 2,4,6-trichloroanisole; for the molar ratios ClO$^-$:phenol: (a) and (a′) 1:10; (b) and (b′) 10:1; (c) 14:1(stoichiometry); (d) 20:1.

matrix was studied. Two different industrial effluents were treated with synthesized sulfatoferrate (containing 13% K$_2$FeO$_4$). The concentrations of ferrate were increased relative to those of the previous experiments because of the presence of various organic substrates in the wastewaters. The phenol index was measured according to the norm NF ISO 6439. The first effluent contained 4.175 mg/L of phenol (corresponding to 9.94 mg(O$_2$)/L) and had a COD of 3350 mg(O$_2$)/L. This effluent was treated with 0.5 g/L and 2 g/L of impure ferrate matter. The molar ratios of FeO$_4^{2-}$ to phenol applied in these two cases are 7:1 and 30:1. The second effluent contained 1.884 mg/L of phenol (corresponding to 4.48 mg(O$_2$)/L) and had a COD of approximately 7017 mg(O$_2$)/L. This second effluent was treated with 1 g/L and 2 g/L of impure ferrate. The associated molar ratios of FeO$_4^{2-}$ to phenol are 33:1 and 66:1.

For effluent 1, 0.5 g/L and 2 g/L of impure ferrate remove 57% of the phenol and 52% of the COD, and 99% of the phenol and 64% of the COD, respectively. For effluent 2, 1 g/L and 2 g/L of impure ferrate remove 87% of the phenol and 81% of the COD and 96% of the phenol and 88% of the COD, respectively (Fig. 5). The efficiency of

sulfatoferrate(VI) for the oxidative removal of phenol is confirmed in industrial wastewater. The action of sulfatoferrate(VI) on other organic molecules is also observed. Although effluent 1 contains less COD than effluent 2, the ferrate is less efficient for this effluent. The nature of the organic compounds responsible for the COD must be different and be more difficult to oxidize in effluent 1. Finally, small quantities of potassium sulfatoferrate are sufficient to oxidize a wide range of molecules.

4. Discussion

All the oxidants studied completely transform the phenol when used in greater than stoichiometric amounts. The TOC analyses show that partial mineralization occurs and that by-products are formed during the reaction. Under stoichiometric conditions, KMnO$_4$ has the highest mineralization (70%), followed by Ca(ClO)$_2$ (61%) and K$_2$FeO$_4$ (57%). The apparent standard potential (E′^{0}) of each oxidant as a function of pH is determined from the Nernst equation (Table 2). At pH 9, the strongest oxidant is FeO$_4^{2-}$, followed
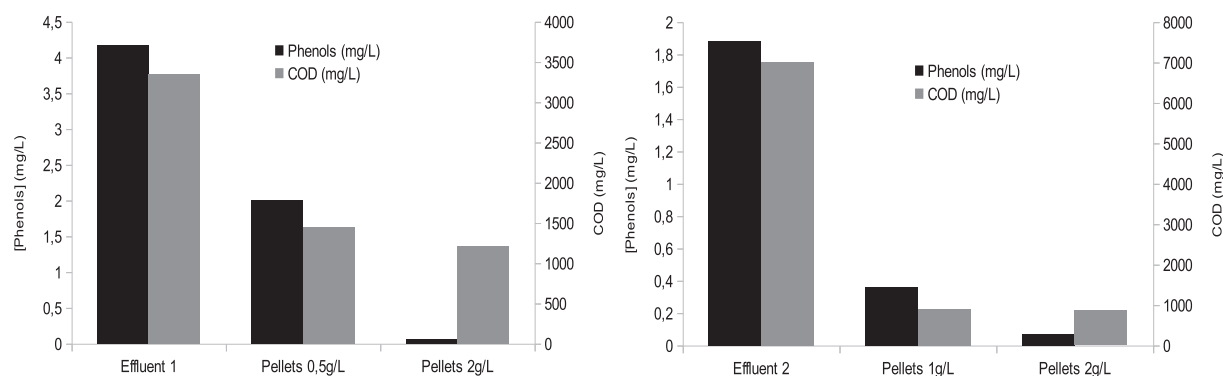
Fig. 5. Evolution of phenol index and COD under treatment by powder of impure potassium sulfatoferrate in two real effluents.

Table 2
Standard potential (E^0) and apparent standard potential (E'^0) at pH 9.

Redox couple	Half-reaction	E^0 (V)	E'^0 (pH 9)
$MnO_{4(aq)}^-/MnO_{2(s}$	$MnO_4^- + 4H^+ + 3\bar{e} \rightarrow MnO_2 + 2H_2O$	1.68	0.96
$ClO_{(aq)}^-/Cl_{(aq}^-$	$ClO^- + 2H^+ + 2\bar{e} \rightarrow Cl^- + H_2O$	1.72	1.18
FeO_4^{2-}/Fe^{3+}	$FeO_4^{2-} + 8H^+ + 3\bar{e} \rightarrow Fe^{3+} + 4H_2O$	2.2	1.22

by ClO^- and MnO_4^-. The TOC abatements do not follow this trend, showing that the efficiency of each oxidant is not only the result of the redox potential. The reactivities of the oxidants depend on their affinity to phenol and on their reactions with water or themselves. Many factors ultimately influence the reactivity of an oxidant. Among the significant factors, the discussion of this study focuses on the oxidation mechanisms.

Mechanisms are proposed for the oxidation of phenol by impure sulfatoferrate (Fig. 6). Mixing of Fe(VI) and phenol results in the formation of the phenoxy radical and the Fe(V) anion FeO_4^{3-}. These species indicate that a 1-e⁻ reduction of Fe(VI) occurs (Fig. 6(1)) (Huang et al., 2001). The phenoxy radical has different resonance structures (Fig. 6(2)). Fe(V) was not detected because it reacts 2–3 orders of magnitude faster than Fe(VI) (Rush et al., 1995). The observed benzoquinone and Fe(III) are the products of the reaction of Fe(V) with the phenoxy radical through a 2-e⁻ oxidation process (Fig. 6(3)). Ferric hydroxide is observed as a precipitate. The formation of chlorine radical is proposed to result preferably from the action of the Fe(VI) anion FeO_4^{2-} on the chloride anion. This formation occurs through a 1-e⁻ reduction of Fe(VI) to Fe(V) (Fig. 6(4)). Parachlorophenol may be the product of the reaction between the chlorine radical and the phenoxy radical (Fig. 6(5)). Phenoxyphenol

is the product of the dimerization of two resonance structures of the phenoxy radical (Fig. 6(6)). In previous studies, high performance liquid chromatography (HPLC) analyses have indicated the additional presence of biphenoquinone and biphenols, identified when phenol is present in great excess with regard to ferrate concentration (Huang et al., 2001; Rush et al., 1995). This compound has not been identified in our study because ferrate has been introduced in stoichiometric quantities. Unlike the previous studies, the further oxidation of benzoquinone is observed in the present study (Fig. 3). The TOC is reduced, and products such as acids and alcohols are observed. The oxidation mechanism cleaves the aromatic rings of benzoquinone, chlorophenol and phenoxyphenol, and partially leads to mineralization to CO_2 and H_2O. The impurities affect the mechanism, the role of chloride anion has been highlighted in this study. Anyway, chlorophenol and phenol have a similar reactivity with ferrate (Graham et al., 2004; Lee et al., 2005), thus the generated parachlorophenol is not persistent in the final reaction solution. It has only been observed when the doses of ferrate are not correctly adjusted, promoting the reaction of autodecomposition of Fe(VI). When phenol is treated with the impure sulfatoferrate in stoichiometric conditions, no persistent byproducts other than organic acids and alcohols are identified, and the same performance is achieved compared to the pure ferrate. The efficiency of the sulfatoferrate(VI) for the oxidative removal of phenol is confirmed in real industrial wastewater. The optimal pH has to be adjusted between 8 and 9 after the injection of ferrate (best compromise between the oxidizing power of ferrate in its stability field in solution), but if a high concentration of ferrate is required the pH could be higher (the ferrate synthesized contains potassium hydroxide and the reaction of degradation of Fe(VI)
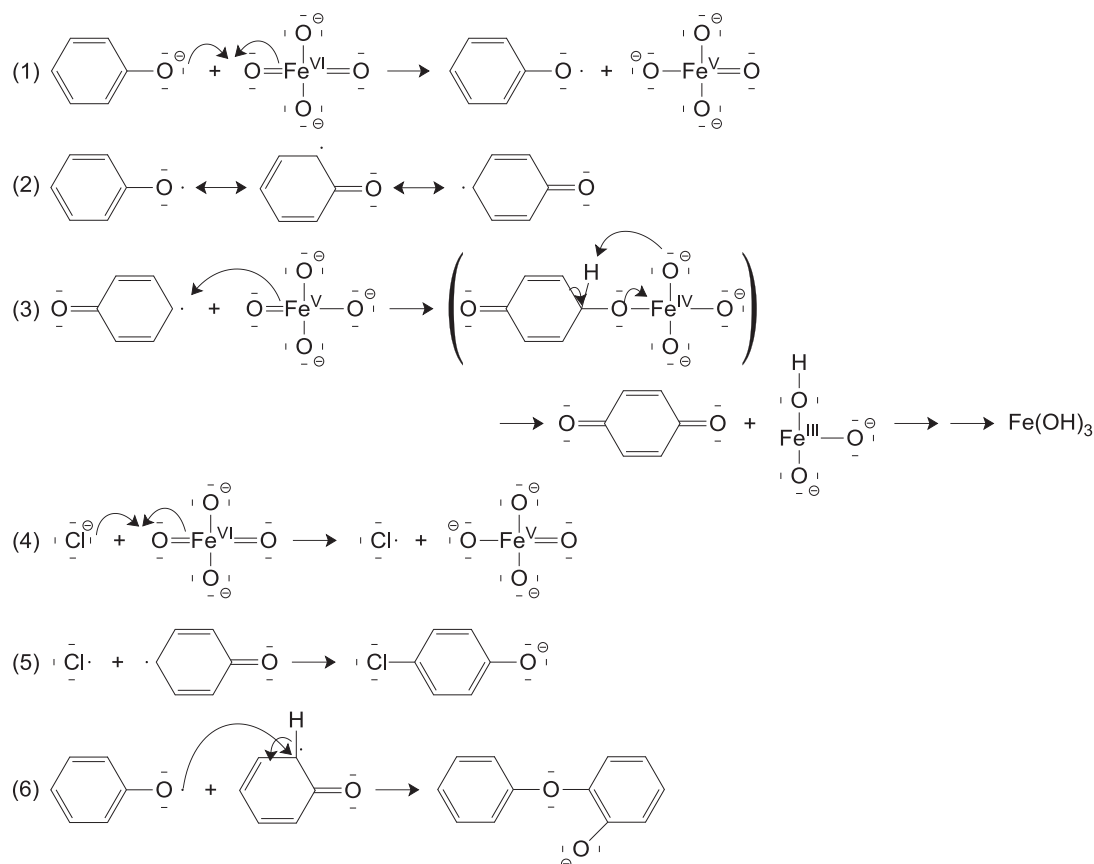
Fig. 6. Proposed reaction scheme for the action of impure potassium sulfatoferrate on phenol.

releases hydroxide anion (Eq. (1)). The pH of the solution may have to be adjusted depending on the discharge standards. After the treatment, iron is present under the precipitated form $Fe(OH)_3$. This compound is not very soluble ($Ks = 10^{-39}$ (Smith and Martell, 1976)) and can easily be removed by filtration (eventually after a flocculation step), making potassium ferrate an environmentally friendly oxidant.

The reaction of permanganate with phenol produces phenoxyphenol, phenoxybenzaldehyde and ring opening products such as propionic acid and propanol. The phenolic compounds remain in solution only when phenol is in excess. A hydroxybenzoic acid-type by-product has been observed in previous studies. Dimerization of phenoxy radicals leads to the formation of dihydroxyphenyl, which further decomposes to hydroxybenzoic acids (Doré et al., 1975). These unsaturated compounds are attacked by permanganate, and this attack leads partially to the formation of CO_2 and H_2O (TOC abatement). These reactions are rapid because we could not observe these by-products in our study (no analysis before 5 min of reaction); however, their presence can be postulated. Finally, under optimal conditions, where phenol is totally removed and no phenolic compounds persist, the concentration of remaining manganese in solution must be controlled and is expected to be less than 0.05 mg/L for drinking water (Council Directive 98/83/EC) or on the order of mg/L for wastewater discharge (concentrations from 1.75 to 262.50 mg (Mn)/L were applied in this study to remove phenol and the TOC). These norms impose to add very small doses of permanganate, limiting its domain of application.

Chlorinated phenols are formed during the treatment by hypochlorite, but they are further oxidized when the concentration of the oxidant is sufficiently high. A greater oxidation degree is observed for several chlorinated phenols. In the present study, trichlorophenol seems to be the last step before the cleavage of aromatic ring. Pentachlorophenol, observed by Michałowicz et al. (2007), is not observed in the present study, but its presence can be postulated. According to the literature, the formation of the chlorinated phenol compounds by the action of hypochlorite on phenol is lower under alkaline conditions (Michałowicz et al., 2007). Finally, it is important to ensure that the dose of hypochlorite is correct because chlorinated phenols are mutagenic and carcinogenic.

5. Conclusions

The impure potassium sulfatoferrate(VI) synthesized according to patent FR 2908128 is as efficient as pure commercial potassium ferrate in the removal of phenol. The apparent second-order rate constants (k_{app}) for the reactions of pure Fe(VI) and impure sulfatoferrate on phenol in the ratio FeO_4^{2-}:phenol 10:1 are respectively 78 $M^{-1}.s^{-1}$ and 80 $M^{-1}.s^{-1}$. An important excess of ferrate can be detrimental to the mineralization efficiency by promoting the reaction of autodecomposition of FeO_4^{2-}.

The cleavage of the phenolic aromatic ring is observed with the use of ferrate, permanganate and hypochlorite, leading to the formation of organic acids, alcohols, and carbon dioxide. The use of permanganate is limited by the attention paid to the manganese concentration in water. Treatments by hypochlorite are not encouraged because of the formation of several chlorinated by-products. The advantage of using ferrate(VI) is that the formation of hazardous organic or metallic by-products is avoided.

The efficiency of sulfatoferrate(VI) for the oxidative removal of phenol and other organics is confirmed in industrial wastewater. The use of a cheapest material than pure ferrate and in a non-buffered effluent is encouraging regarding a large application.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.04.004.

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