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Degradation of chlorinated phenols in water in the presence of H_2O_2 and water-soluble μ-nitrido diiron phthalocyanine

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ABSTRACT

Efficient disposal of pollutants is a key problem in the environmental context. In particular, chlorinated aromatic compounds are recalcitrant to biodegradation and conventional treatment methods. Iron phthalocyanines were previously shown to be efficient catalysts for the oxidative degradation of chlorinated phenols considered as priority pollutants. We have recently discovered μ-nitrido diiron phthalocyanines as powerful oxidation catalysts. Herein, we evaluate these emerging catalysts in the oxidation of chlorinated phenols in comparison with conventional mononuclear complex. Catalytic performance of iron tetrasulfophthalocyanine (FePcS) and corresponding μ-nitrido dimer $[(FePcS)_2N]$ have been compared in the oxidation of chlorinated phenols by hydrogen peroxide in water. The oxidative degradation of 2,6-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) has been studied. The $(FePcS)_2N$ exhibited better catalytic properties than mononuclear FePcS in terms of conversion and mineralization (transformation of organic chlorine to Cl^- and decrease of total organic carbon due to the formation of CO_2). Kinetics of the DCP oxidation indicated that different reaction mechanisms are involved in the presence of FePcS and $(FePcS)_2N$. The high catalytic activity of $(FePcS)_2N$ in the degradation and mineralization of chlorinated phenols make μ-nitrido diiron phthalocyanines promising catalyst to apply also in environmental remediation.

1. Introduction

Contamination of the environment by chlorinated aromatic compounds is a severe problem because of their large-scale applications as biocides, lubricants, solvents, etc. and their high stability to bio-degradation. Energy-efficient and low-cost elimination of toxic organic pollutants from the environment has therefore been a long-standing challenge. One of the promising approaches is the application of metal complexes in combination with hydrogen peroxide operating at ambient conditions [1]. Metal phthalocyanine complexes have received a great attention as the catalysts for many reactions [2] including selective oxidations and bleaching [3]. In particular, iron 2,9(10),16(17),23(24)-tetrasulfophthalocyanine (FePcS) was shown to be a very active catalyst for the oxidative degradation of 2,4,6-trichlorophenol (TCP) and other chlorinated phenols, recalcitrant priority pollutants [4–13]. This topic has been developed by many researchers toward degradation of different pollutants using different metallophthalocyanine complexes [14–23].

It should be noted that the FePcS–H_2O_2 system was the most efficient in the presence of an organic solvent (CH_3CN, 25 vol.%) added to facilitate the dissolution of poorly water-soluble substrates and phosphate buffer [4–8]. A careful mechanistic study disclosed a non-innocent role of the phosphate buffer for the degradation of chlorinated phenols, dichloroanilines and catechols suggesting the intermediate formation of a peroxyphosphate–FePcS complex [13]. The involvement of the organic solvent and phosphate buffer limits a potential for the practical application of this approach. In this context, the catalytic system operating in pure water would be advantageous from practical point of view and might provide a deeper insight into reactivity. For instance, although the formation of CO_2 was evidenced using ^{14}C-TCP substrate [6], the evaluation of mineralization efficiency of the catalytic system by determination of total organic carbon (TOC) cannot be performed in the presence of the organic solvent. Hence, the development of the catalytic system capable of oxidizing chlorinated phenols in water would be of great mechanistic and practical interest.

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Recent development of iron phthalocyanine-based catalysts led to the discovery of the remarkable catalytic properties of μ-nitrido diiron phthalocyanines in the oxidation of organic compounds, formation of C—C bonds and oxidative dehalogenation [24–33]. The structure of these bio-inspired catalysts reflects the structural features of two the most powerful monooxygenase enzymes: an active site containing two iron ions like in soluble methane monooxygenase but in the macrocyclic ligand environment similarly to iron porphyrin active site in cytochrome P-450. Such a construction provides better possibilities for stabilization of high oxidation states of the catalyst developed during catalytic oxidation cycle [2]. The Fe(μ-N)Fe structural unit is also essential for the improved catalytic properties. Using tetraphenylporphyrin platform we have shown that a μ-nitrido high-valent diiron oxo complex was much stronger oxidant in the oxidation of alkanes including methane compared to its mononuclear counterpart [34]. Thus, a distinctive feature of μ-nitrido diiron complexes is their powerful catalytic properties in oxidation. It is therefore of interest to evaluate them in the oxidation of difficult-to-oxidize chlorinated phenols. On the other hand, the development of μ-nitrido diiron complexes via modification of the structure of the macrocyclic ligand(s) is a tool which should open new possibilities for catalytic applications. The complexes with electron-withdrawing [35] and electron-donating substituents [36] have been prepared. In this context, the preparation of the first water-soluble μ-nitrido diiron tetrasulfophthalocyanine [37] was particularly important since it provides the possibility to apply these promising catalysts in water. Up to now, no direct comparison of the catalytic behavior of mononuclear iron pthalocyanines and their respective μ-nitrido dimers has been reported.

In the present work, we assessed and compared catalytic properties of FePcS and $(FePcS)_2N$ (see Fig. 1 for their structures) in the oxidation of 2,6-dichlorophenol (DCP) and TCP by H_2O_2 in water. The important requirements for the degradation of chlorinated aromatics are the cleavage of the aromatic cycle and the transformation of the organic chlorine substituents to inorganic chloride ions without formation of more dangerous products like chlorinated dibenzodioxins and dibenzofurans. To compare conventional FePcS and its μ-nitrido dimer and to evaluate the efficiency in the oxidative degradation of the chlorinated phenols we have determined the conversions, the dechlorination degree (amount of Cl^- formed per converted substrate) and decrease in the total organic carbon (TOC) as well as the products of their degradation.

2. Experimental

2.1. Materials

Iron 2,9(10),16(17),23(24)-tetrasulfophthalocyanine was synthesized by Weber-Busch method [38]. μ-Nitrido diiron tetrasulfophthalocyanine was prepared according to the published protocol [37]. 2,6-dichlorophenol (99%) and 2,4,6-trichlorophenol (99%) were purchased from Sigma-Aldrich and used without additional purification. All other reactants were obtained commercially and used as received. Hydrogen peroxide (35% aqueous solution) was obtained from Sigma–Aldrich.

2.2. Catalytic tests and product analyses

Reaction vessel was charged with 4 mL H_2O containing 2,6-dichlorophenol (5 mM) or 2,4,6-trichlorophenol (1 mM), H_2O_2 (typically 0.1 M in the case of DCP and 0.02 M in the case of TCP) and catalyst (0.05 mM or 0.025 mM in the case of DCP and 0.01 mM in the case of TCP). The large excess of H_2O_2 was intentionally used to avoid the lack of the oxidant for complete degradation and mineralization of the chlorinated phenols. The reaction mixture was kept at the desired temperature (25 or 60 °C) with magnetic stirring for 3 or 6 h. After cooling to room temperature, the reaction mixtures were analyzed by HPLC to follow the substrate conversions and chloride ion concentrations were measured by the mercury thiocyanate method [39]. Total organic carbon content was determined using the final reaction mixtures.

2.3. Identification of the reaction products

The oxidation of DCP was performed in water (5 mM, 25 mL scale) in the presence of $(FePcS)_2N$ (0.05 mM) and H_2O_2 (0.1 M) at 60 °C for 3 h. The reaction mixture was saturated with NaCl and extracted with diethyl ether (3 × 15 mL). The combined ether extracts were dried with anhydrous sodium sulfate, filtered and the ether was evaporated under vacuum. The yellow residue was either dissolved in DMSO-d_6 and examined by ^{1}H-NMR or dissolved in acetonitrile and directly analyzed by LC–MS method. The ^{1}H-NMR spectrum of the extracted reaction mixture showed the signals of the vinylic protons of maleic acid (δ 6.37, 2H), chloromaleic acid (δ 6.66, 1H), and fumaric acid (δ 6.72, 2H). LC–MS analyses confirmed the identification of these products. Chloromaleic acid: *m*/*z* (%) = 151 (40) $[(M+2\text{-}H)^-]$, 149 (100) $[(M-H)^-]$. Maleic acid: *m*/*z* (%) = 115 (100) $[(M-H)^-]$. The 3,5-dichloro-2-hydroxy-1,4-benzoquinone (**2**) was identified by LC-MS. *m*/*z* (%) = 193 (69) $[(M+2\text{-}H)^-]$, 191 (100) $[(M-H)^-]$, 165 (38.5) $[(M+2\text{-}H\text{-}CO)^-]$, 163 (32) $[(M-H\text{-}CO)^-]$.

2.4. Instrumentation.

HPLC analyses of the oxidation of chlorinated phenols were carried out using an Agilent 1100 liquid chromatograph equipped with a 20 μL injection loop and Coregel-87H3 column with detection at 280 nm. Acetonitrile-water mixture (1/1, v/v, 0.8 mL min^{-1}) was used as the eluent. LC–MS analyses were conducted on a Shimadzu LCMS-2020 instrument equipped with SPD M20A photodiode array detector using Luna Phenyl-Hexyl column (5 μm, 250 × 3.0 mm, Phenomenex). Conditions: 40 °C column oven temperature, 10 μL injection volume, photodiode array (PDA) response at 254 nm, mobile phase: solvent B (acetonitrile) from 30 to 80% in 30 min and solvent A: water without any additive, flow rate, 0.5 mL min^{-1}. Samples were analyzed using LC–electrospray ionization (ESI)–MS in the negative ionization mode. Under these conditions, the products were identified as their $[M-H]^-$ ions.

Liquid-state ^{1}H NMR spectra were obtained using a AM 250 Bruker spectrometer. The UV–vis spectra of solutions were obtained with Agilent 8453 diode-array spectrophotometer. Total organic carbon analyses were performed on a Shimadzu TOC-5050A spectrometer.

3. Results and discussion

3.1. Oxidative degradation of 2,6-dichlorophenol

Two complexes were first examined in the oxidative degradation of DCP using 0.5 mol% and 1 mol% catalyst loadings. Both complexes exhibited a good catalytic activity toward this pollutant, but their oxidation kinetics were very different. In course of the reaction with $(FePcS)_2N$, a rapid disappearance of DCP was observed and the blue color of the reaction mixture was retained during all reaction time indicating the high stability of the complex. This conclusion was supported by UV–vis study of the evolution of the reaction mixture during the reaction (Fig. 2). After 1 h reaction only ~6% decrease of the catalyst concentration was observed. More than 80% of the $(FePcS)_2N$ catalyst was still present in the

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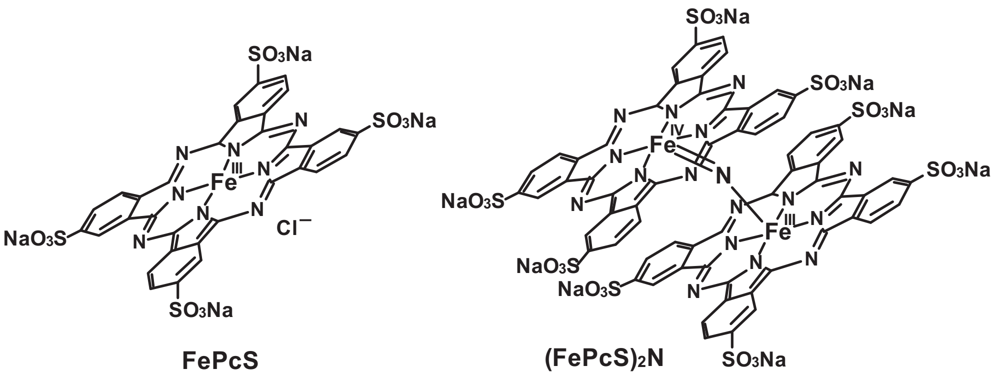

Fig. 1. Structures of iron 2,9(10),16(17),23(24)-tetrasulfophthalocyanine (FePcS) and μ-nitrido diiron 2,9(10),16(17),23(24)-tetrasulfophthalocyanine [$(FePcS)_2N$] complexes. Only one of possible position isomers is depicted for monomeric and dimeric structures.

Table 1
Comparison of the catalytic activity of $(FePcS)_2N$ and FePcS in the oxidative degradation of 2,6-dichlorophenol in water at 60 °C.

Catalyst	Reaction time (h)	Conversion (%)		Dechlorination degree		Total organic carbon removal (%)	
		1 mol% catalyst	0.5 mol% catalyst	1 mol% catalyst	0.5 mol% catalyst	1 mol% catalyst	0.5 mol% catalyst
$(FePcS)_2N$	1	80	70	0.81	0.36	–	–
	2	94	81	0.92	0.7	–	–
	3	94	92	1.00	0.91	43	33
FePcS	1	0	0	0	0	–	–
	2	61	49	1.16	0.57	–	–
	3	86	81	1.04	0.81	31	27

reaction mixture after the reaction (3 h). With 1 mol% catalyst loading the DCP conversion was 80% after 1 h (Table 1). After 3 h of the reaction the conversion reached 94% and one of two chlorine substituents was converted to chloride anion. In contrast to $(FePcS)_2N$, a blue color of FePcS disappeared within 1 h owing to its degradation. UV–vis study indicated that the Q band of FePcS core almost disappeared after 15 min reaction (Fig. 3). Noteworthy, no DCP conversion was detected during first hour of the reaction. When FePcS was completely bleached, the consumption of the DCP started (Table 1) to reach a 86% DCP conversion and dechlorination degree of 1.04 after 3 h. Similarly, $(FePcS)_2N$ was more efficient than FePcS with 0.5 mol% catalyst loading providing conversion of 92% vs. 81% and dechlorination degree of 0.91 vs. 0.81, respectively. The reaction can also be performed at 25 °C, though the rate of oxidation of DCP was slower. After 5 h of the reaction, 6% and 27% DCP conversions were obtained with FePcS and $(FePcS)_2N$, respectively. The reactions were allowed to react for 15 h to achieve 65–75% conversion and 0.9–0.95 dechlorination degree.

The efficiency of degradation was further evaluated by the measurements of total organic carbon (TOC) after 3 h reactions. In the presence of 1 and 0.5 mol% of $(FePcS)_2N$ the TOC removal was 43% and 33%, respectively, indicating that up to 2.74 carbon atoms of substrate from six were mineralized. When FePcS was used as the catalyst, the TOC removal was lower: 31% and 27% for 1 and 0.5 mol% catalyst loading, respectively (Table 1). In principle, a degradation of the catalysts could contribute to observed TOC values. The UV–vis study showed that more than 80% of $(FePcS)_2N$ was unchanged after the reaction. Thus, a maximal possible contribution to TOC values due to the degradation of the catalyst can be estimated as 2% and 1% with 1 mol% and 0.5 mol% catalyst loadings, respectively. These maximal values could be obtained if all

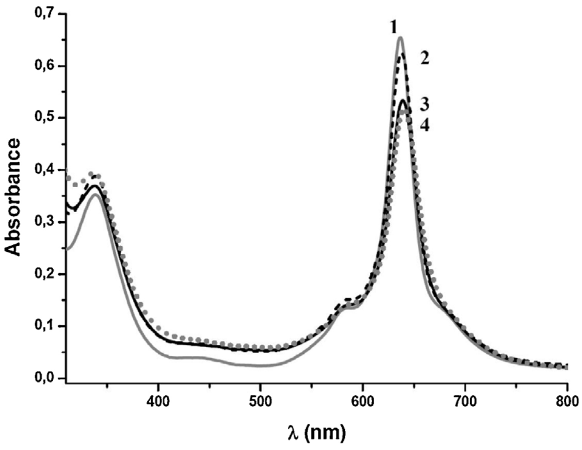

Fig. 2. Evolution of UV–vis spectrum of $(FePcS)_2N$ (0.05 mM) in water in the presence of 2,6-DCP (5 mM) and H_2O_2 (0.1 M) at 60 °C: before H_2O_2 addition (**1**, solid line), after 1 h (**2**, dashed line), 2 h (**3**, solid line) and 3 h (**4**, dotted line) of reaction.

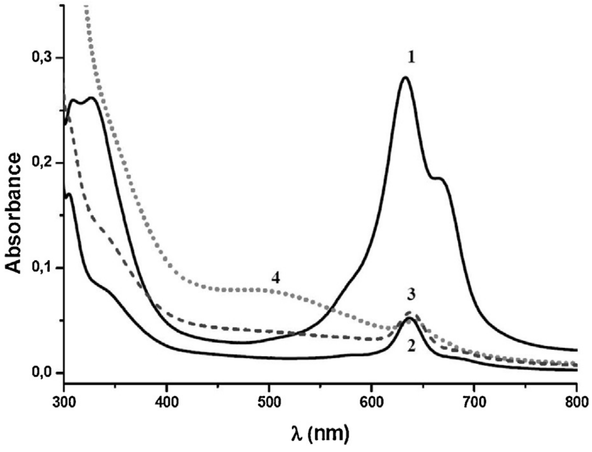

Fig. 3. Evolution of UV–vis spectrum of FePcS (0.05 mM) in water in the presence of 2,6-DCP (5 mM) and H_2O_2 (0.1 M) at 60 °C: before H_2O_2 addition (**1**, solid line) and after 15 min (**2**, solid line), 45 min (**3**, dashed line), and 1 h (**4**, dotted line) of reaction.

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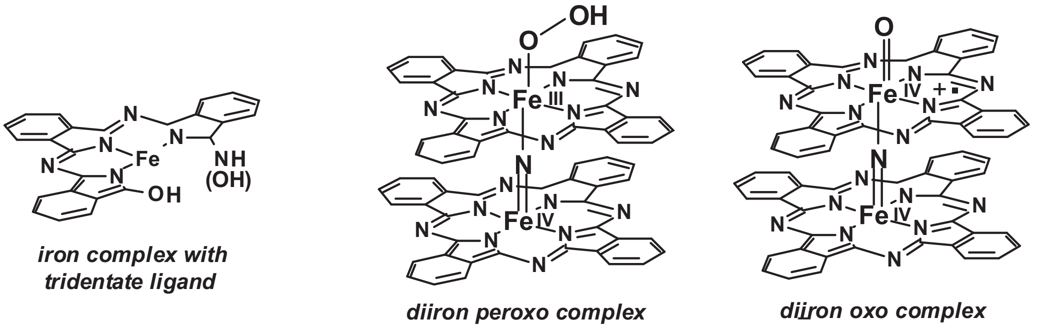

Fig. 4. Proposed iron and diiron active species involved in the oxidation of chlorinated phenols in the presence of FePcS and $(FePcS)_2N$, respectively. The structure of iron complex with tridentate ligand was proposed by N. d'Alessandro et al. (Ref. [42]). SO_3Na substutuents are omitted for clarity.

degraded catalyst molecules would be mineralized to CO_2 that is certainly not the case. d'Alessandro and co-workers showed that major degradation products of phthalocyanine core were sulfonated isoindole and tridentate sulfoindole ligand [40–42]. Consequently, the contribution to TOC values due to degradation of $(FePcS)_2N$ should be negligible. The same considerations should be valid for FePcS case.

The products of DCP mineralization in the presence of $(FePcS)_2N$ were identified by microGC-MS analysis of gas phase. To this aim the reaction was performed under argon. Importantly, the DCP conversions and TOC losses obtained under air and under argon were the same with $(FePcS)_2N$ suggesting that O_2 was not involved in the reaction. After 3 h reaction the gas phase contained 4.7% CO_2 and 0.5% of CO. This result corroborates with the TOC analysis and confirms the significant mineralization of DCP mediated by $(FePcS)_2N$. In contrast to $(FePcS)_2N$, the oxidation of DCP in the presence of 1 mol% FePcS was less efficient under Ar. Only 39% DCP conversion was observed after 3 h compared with 86% conversion obtained under air. The TOC removal dropped from 31% (under air) to 12% (under Ar). This strong influence of O_2 on the reaction in the presence of FePcS suggests the possible involvement of free radical chemistry.

3.2. Oxidative degradation of 2,4,6-trichlorophenol

The solubility of TCP in pure water is significantly lower than solubility of DCP. For this reason the experiments were performed with 0.001 M TCP solution compared with 0.005 M in the DCP case. In these conditions, the oxidation of TCP in water was less efficient compared with DCP. Using 1 mol% $(FePcS)_2N$ loading, a 12% TCP conversion was observed after 4 h. In the next set of the experiments the initial 0.001 M TCP solution was adjusted to pH 7 with NaOH and loading of $(FePcS)_2N$ catalyst was increased to 2 mol%. After 6 h reaction, a 46% conversion of TCP and 11% TOC removal were obtained. Noteworthy, no TCP conversion (<1.5%) was detected when $(FePcS)_2N$ was replaced with FePcS, other conditions being the same. Thus, $(FePcS)_2N$ showed a higher catalytic activity and stability compared with FePcS.

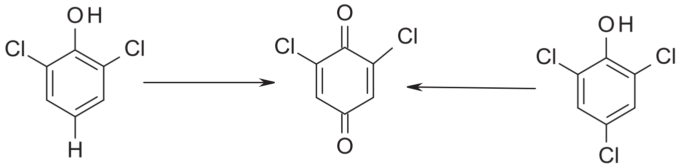

Fig. 5. Proposed first step of the oxidation of chlorinated phenols: formation of the quinone.

3.3. Mechanistic considerations

Different kinetics of DCP conversion found for FePcS and $(FePcS)_2N$ imply that different reaction pathways should be involved. In the case of FePcS, the oxidation of DCP started only after bleaching of the complex. This observation can be explained by the involvement of free-radical Fenton chemistry initiated by iron ions liberated during degradation of FePcS. Strong dependence of the efficiency of the oxidation on the presence of O_2 in this case is in agreement with this suggestion. However, efficient Fenton reaction needs a significant iron loading and operates in the narrow acidic pH range (typically pH 2.5–3.5). Alternatively, the products of degradation of metallophthalocyanines can also show some catalytic activity [40,41]. This catalytic activity was associated with the formation of meso-nitrogen oxide derivatives and metal-biliverdin-like compounds formed from RuPcS and FePcS in the presence of H_2O_2 or $KHSO_5$ [42]. These compounds were identified by ESI-MS and NMR techniques at short reaction times. Although

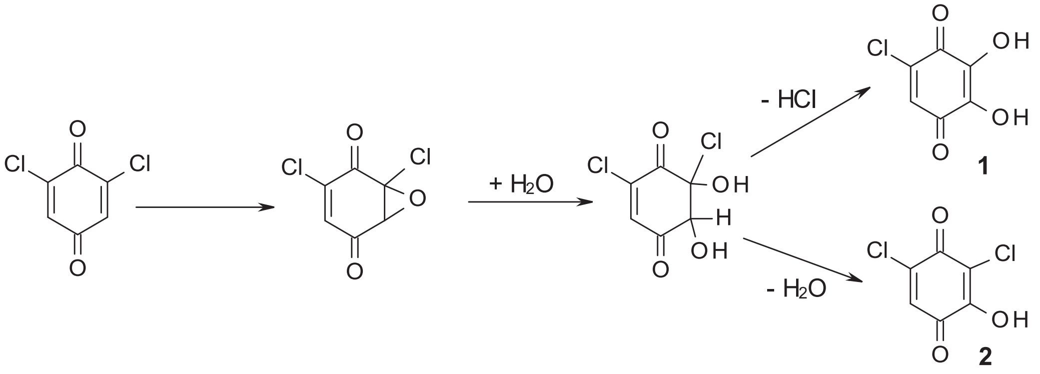

Fig. 6. Proposed second step of the oxidation of chlorinated phenols: epoxidation of 2,6-dichlorobenzoquinone.

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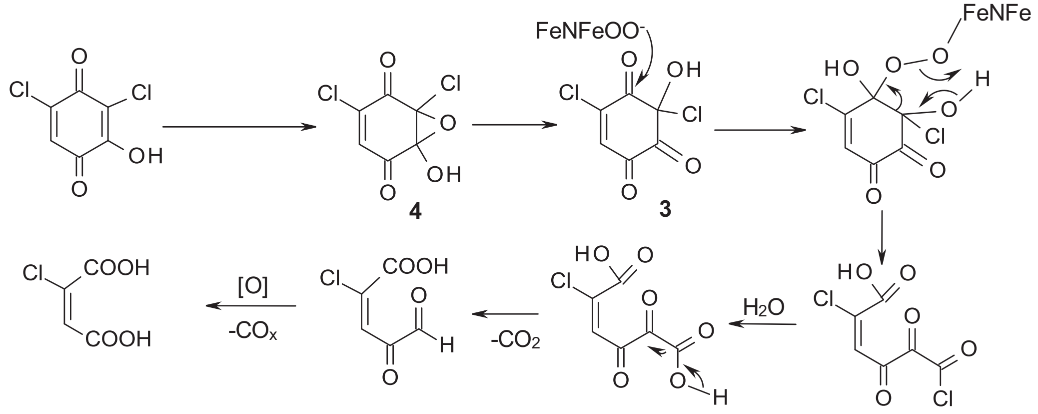

Fig. 7. Proposed mechanism of the cleavage of the aromatic cycle of chlorinated phenols.

some involvement of Fenton chemistry cannot be excluded, the latter mechanism involving an iron complex with a tridentant ligand could also be responsible for the DCP degradation.

In the presence of $(FePcS)_2N$ the oxidation of DCP shows no induction period and not sensitive to the presence of O_2. Both observations are more compatible with the involvement of oxo- and hydroperoxo diiron-centered species rather than with free-radical Fenton chemistry. The $(FePcS)_2N$ is also quite stable under reaction conditions (Fig. 2). The preparation and characterization of both high-valent iron [43] and diiron [29] oxo species supported by phthalocyanine ligand in organic solvents have previously been published. The results of this study suggest that with mononuclear FePcS in aqueous medium the oxo pathway is probably less favored than in organic solvents. In contrast, μ-nitrido diiron construction is more suitable for obtaining oxo and peroxo diiron species and their involvement in the oxidation which is in accordance with previous results [24,26,29,34]. The structures of the proposed iron and diiron active species are depicted in Figure 4. Iron complex with tridentate ligand proposed by N. d'Alessandro et al. [42] might activate H_2O_2 and form active species capable of oxidizing DCP. Recently, iron complexes with modified phthalocyanine core were shown to catalyze the oxidation of alkanes [44] and epoxidation of olefins [45] with H_2O_2.

Based on the results obtained in this study and our previous studies on TCP oxidation [4–7] we propose the following mechanism. The first step includes the oxidation of both DCP and TCP to 2,6-dichlorobenzoquinone which involve the cleavages of C—H and C—Cl bonds in the *para*-position to phenolic group, respectively (Fig. 5). A diiron oxo species should be competent to perform this oxidation. The higher reactivity of DCP compared with TCP can be explained by an easier cleavage of the *para*-C—H bond of DCP with respect to *para*-C—Cl bond of TCP. The further key step of the reaction is the epoxidation of the electron-deficient double bond of 2,6-dichlorobenzoquinone (Fig. 5). This step can be performed either by nucleophilic diiron peroxo complex or electrophilic diiron oxo species. Hydrolysis of the epoxide to diol followed by HCl or H_2O elimination gives violet quinones **1** and **2**, respectively (Fig. 6). These quinones were isolated and characterized in our previous work [5]. A violet color of the reaction mixture observed at short reaction times in the present work suggests that these intermediates are also formed during the oxidation of DCP [5]. This suggestion was confirmed by identification of 3,5-dichloro-2-hydroxy-1,4-benzoquinone (**2**) using LC–MS technique. Second epoxidation step provides intermediate **3** via **4** (Fig. 7). Another key step is the cleavage of the aromatic cycle according to the mechanism proposed in Fig. 7. A nucleophilic attack of peroxo complex on the quinone carbonyl group of **3** having Cl and OH substituents in the orto-position leads to the C-C bond cleavage via six-membered transition state. Decarboxylation and decarbonylation of different intermediates formed after the cleavage of the aromatic cycle should provide CO_2 and CO detected by microGC–MS method as well as chloromaleic acid identified by LC–MS and ^{1}H-NMR analyses (Fig. 8). The proposed intermediate **1** undergoes the second dechlorination according to the same reaction sequence to provide maleic and fumaric (isomerization product) acids which were also detected by LC–MS and ^{1}H-NMR analyses (see Section 2 for details).

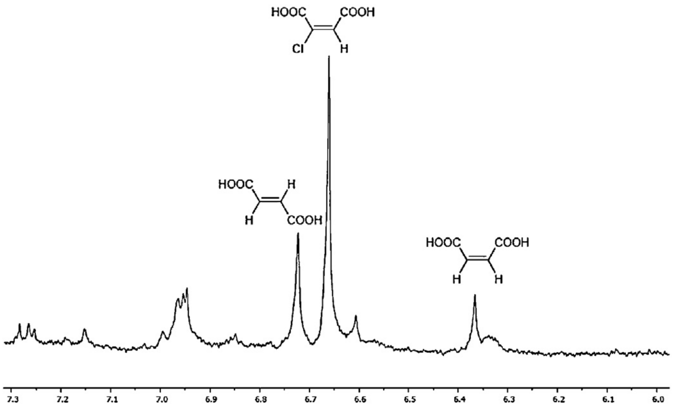

Fig. 8. ^{1}H-NMR spectrum of the products of DCP oxidation isolated as described in Section 2 showing the presence of vinylic protons of maleic, fumaric and chloromalein acids. Solvent: DMSO-d_6.

4. Conclusions

We have shown that water-soluble μ-nitrido diiron phthalocyanine is an efficient catalyst for the oxidative degradation of chlorinated phenols in water with hydrogen peroxide, cheap and clean industrial oxidant. Almost complete conversion of 2,6-dichlorophenol has been achieved using 0.5–1 mol% catalyst amounts with the total organic carbon removal up to 43% to form CO_2 and CO in ~10:1 ratio. The $(FePcS)_2N$–H_2O_2 catalytic system is more efficient than mononuclear FePcS–H_2O_2 system in terms of conversion and mineralization of chlorinated phenols. In addition, mechanistic studies indicate that $(FePcS)_2N$–H_2O_2 system operates via diiron-centered oxo and peroxo species while FePcS itself was not active in the oxidation of chlorinated phenols in pure water. The mononuclear FePcS complex was not stable under reaction conditions giving rise to iron ions and iron complex with tridentate sulfoisoindole ligand, previously proposed by d'Alessandro et al. [42]. These species are responsible for the oxidation of DCP occurring after degradation of FePcS.

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N-Bridged diiron phthalocyanine complex is non-expensive and non-toxic, and can be readily available on a large scale. The hydrogen peroxide is green and cheap industrial oxidant. The catalytic system operates in water with no need for organic co-solvent and/or buffered solution. The $(FePcS)_2N$ is quite stable and can be readily immobilized onto different supports via covalent anchoring or electrostatic interaction [2]. For all these reasons we believe that this novel approach might be useful for the development of disposal methods for the recalcitrant pollutants.

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