Sequential addition of H_2O_2, pH and solvent effects as key factors in the oxidation of 2,4,6-trichlorophenol catalyzed by iron tetrasulfophthalocyanine

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The efficiency of the H_2O_2 oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by iron tetrasulfophthalocyanine (FePcS) is highly dependent on the pH value of the reaction mixture, the local hydrogen peroxide concentration and the organization of FePcS molecules in solution. Among the several forms of FePcS in aqueous solutions (dimer or monomer), monomeric FePcS is proposed to be the catalytically active complex. The key role of the organic co-solvent (acetonitrile, acetone, alcohol, . . .) is to shift the dimer/monomer equilibrium toward monomeric FePcS, the efficient catalyst precursor. A stepwise addition of hydrogen peroxide significantly improves the conversion of TCP and allows a low catalyst loading, below 1% with respect to the pollutant, to be used.

Facteurs clés dans l'oxydation du 2,4,6-trichlorophénol catalysée par la tétrasulfophtalocyanine de fer: ajout séquentiel d'eau oxygénée, effets du pH et du solvant. L'efficacité de l'oxydation du 2,4,6-trichlorophénol (TCP) catalysée par la tétrasulfophtalocyanine de fer (FePcS) est très dépendante de la valeur du pH du milieu réactionnel, de la concentration locale en eau oxygénée et de l'organisation des molécules de FePcS en solution. Parmi les différentes formes possibles de FePcS en solution aqueuse (dimère ou monomère), la forme monomérique de FePcS est probablement la forme active du catalyseur. Le rôle clé du co-solvant organique (acétonitrile, acétone, alcool, . . .) est de déplacer l'équilibre dimère/monomère vers la forme monomérique de FePcS, le précurseur catalytique efficace. Une addition fractionnée d'eau oxygénée améliore de manière significative la conversion du TCP et permet d'utiliser moins de 1% de catalyseur par rapport au polluant.

Degradation of chlorinated aromatics is an important environmental research field since these compounds are among the most recalcitrant pollutants.[1] Recently we found an efficient catalytic oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by iron tetrasulfophthalocyanine (FePcS, see Fig. 1 for the structure).[2–4]

With hydrogen peroxide ('the clean peroxide'), FePcS has been shown to catalyze aromatic ring cleavage of trichlorophenol and pentachlorophenol.[2–4] Chloromaleic acid has been demonstrated to be the main product of this aromatic ring cleavage, with chlorofumaric, maleic and fumaric acids being minor products.[2] The proposed mechanism of this aromatic ring degradation involves a nucleophilic iron(III) peroxo complex, $PcSFe^{III}OOH$, as the key active species responsible for the epoxidation of intermediate quinones and for the attack of carbonyl groups of the oxidized quinones to explain the aromatic C—C cleavage *via* a Grob-type fragmentation.[4] By using ^{14}C-labeled TCP substrate, carbon dioxide was demonstrated to be the ultimate degradation product in this catalytic oxidative degradation of such a recalcitrant compound.[3] In this catalytic oxidation of TCP two out of the three chlorine substituents of the starting material were recovered as chloride ions, one carbon out of the six carbon atoms ended as carbon oxides and four other carbon atoms finished as water-soluble diacids.[3] The final goal of this approach is not to burn the recalcitrant molecule to carbon dioxide, as in incineration processes, but to initiate a degradation of the pollutant to more biodegradable products. Here we wish to report new data on the key factors controlling the catalytic activity of the FePcS–H_2O_2 system in the oxidation of TCP: the sequential addition of H_2O_2 and the pH and solvent effects on the monomer/dimer equilibria of the catalyst precursor(s).

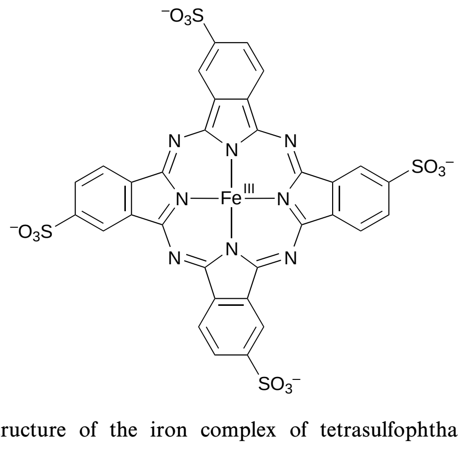


Fig. 1 Structure of the iron complex of tetrasulfophthalocyanine (FePcS)

Results and Discussion

Sequential addition of H_2O_2

A typical reaction mixture (final volume of 2 mL) contained the following final concentrations: 10^{-2} M of substrate (corresponding to 2000 ppm of TCP), 3.7×10^{-4} or 10^{-4} M of catalyst (corresponding to 3.7 or 1% [FePcS]-to-[TCP] ratios, respectively) and 5×10^{-2} M of oxidant (H_2O_2). All oxidations, performed in an acetonitrile-buffered water mixture ($v/v = 1:3$) to dissolve the hydrophobic 2,4,6-trichlorophenol, were initiated by a single addition of 5 equiv. of H_2O_2. In homogeneous conditions, a relatively high catalyst-to-substrate ratio of 3.7% was necessary to obtain a full conversion of the pollutant within a few minutes. In the early stage of reaction we observed a gas release. GC analyses of the gas phase over the reaction mixture before and after reaction showed a slight increase in the dioxygen concentration, indicating a catalase-like dismutation of H_2O_2. Consequently, two main reactions, namely the substrate oxidation and the H_2O_2 dismutation, are competing. Previously, iron and manganese porphyrin complexes have been shown to be catalase models.[5] Because of the second reaction order in hydrogen peroxide in catalase-type dismutation (two molecules of H_2O_2 are required to produce one molecule of O_2) a decrease of the local H_2O_2 concentration should strongly disfavor the dismutation reaction with respect to the catalytic oxidation. In fact, we observed a reduction of the gas release when reducing the rate of the oxidant addition. Therefore we decided to add the oxidant sequentially: five 20 μL aliquots of an aqueous 3.5% H_2O_2 solution were added every 5 min to the reaction mixture (initial volume: 2 mL). The results obtained with this method at different catalyst : substrate ratios are reported in Table 1.

The two important criteria for optimal degradation of the pollutant are fast conversion of the substrate and a high number of chloride ions released per converted TCP molecule; the latter is expected for an advanced degree of oxidation of the substrate. Complete substrate conversions were obtained with only 1% and 0.5% FePcS (runs 2 and 3) and the final conversion in the presence of only 0.1% FePcS was still 50% (run 5). These results show that fast and complete substrate conversion with a high dechlorination (2 Cl^- per converted TCP) was obtained using 1% of catalyst (run 2). Sequential addition of the H_2O_2 solution remarkably improved the substrate conversion at low FePcS-to-TCP ratios and led to complete substrate conversion and a higher number of released Cl^- with only *one-fourth* of the catalyst, as compared to an addition of H_2O_2 all at once. High oxidant concentrations favor the dismutation reaction; H_2O_2 is thus consumed and no longer available for the substrate oxidation. Furthermore, we noted that a very large excess of hydrogen peroxide (1 M H_2O_2 final concentration; *i.e.*, a $[H_2O_2]:[TCP]$ ratio of 100 : 1) inhibited both TCP conversion and H_2O_2 dismutation, although the green-blue color of the reaction mixture remained, indicating no FePcS degradation (the blue color of the starting iron phthalocyanine changes to blue-green after addition of the oxidant and gradually to a deep purple when quinone derivatives are generated).

Table 1 Oxidation of 2,4,6-trichlorophenol by FePcS–H_2O_2

Run	Catalyst : substrate ratio (%)	TCP conversion at 14 min (%)[b]	TCP conversion at 60 min (%)	Dechlorination[a] at 60 min
1	3.7	100 (27)	100	1.9
2	1.0	100 (100)	100	2.0
3	0.5	83 (166)	100	1.8
4	0.25	64 (256)	84	n.d.
5	0.1	44 (440)[c]	50	n.d.
6	3.7	100 (27)	100	1.7
7	1.0	38 (38)	38	n.d.

Runs 1–5: sequential addition of H_2O_2 (5 aliquots), runs 6–7: one-portion addition of H_2O_2

[a] Cl^- ions released per converted TCP molecule. n.d. = not determined. [b] Number of catalytic cycles. For very fast reactions (run 1 and run 6), the number of catalytic cycles cannot be compared with the other runs, since full conversion was achieved before 14 min. [c] Based on 14 min, the turnover rate corresponds to 31 cycles min^{-1}.

Table 2 Quantitative analysis of oxidation products[a]

Run	Chloromaleic acid **1**	Chlorofumaric acid **2**	Maleic acid **3**	Fumaric acid **4**	Coupling products
1[b]	10	<1	<1	<1	20
2[c]	21	3	1	2	24
3[c]	13	2	1	2	37
4[c]	7	4	1	2	25

Run 1: 1% FePcS, one-portion addition of H_2O_2; run 2: 1% FePcS, 5 aliquots of H_2O_2; run 3: 3.7% FePcS, one-portion addition of H_2O_2; run 4: 3.7% FePcS, 5 aliquots of H_2O_2.

[a] Products were quantified by integration of the vinylic proton signals at 6.67 ppm (for **1**), 7.30 ppm (for **2**), 6.39 ppm (for **3**), 6.75 ppm (for **4**) and of the aromatic protons at 7.9–8.1 ppm for coupling products. All these data are yields in % with respect to TCP. [b] TCP conversion was only 80% in this run. [c] TCP conversion was 100% in runs 2–4.

Quantitative analysis of the oxidation products formed by the different H_2O_2 addition methods allowed us to compare the efficiency of the catalytic system to oxidize TCP. The products were quantified by NMR and the results are reported in Table 2. The catalytic TCP oxidations were performed using 1 and 3.7% catalyst-to-substrate ratios with different modes of H_2O_2 addition. With a 1% catalyst-to-substrate ratio the sequential addition of H_2O_2 gave a significant increase in the yields of generated acids, from 11% in the case of a one-portion addition of H_2O_2 (run 1, Table 2) up to 27% (run 2, Table 2) indicating a more complete TCP degradation. It should be noted that only the sequential-addition method allowed full substrate conversion at low catalyst loading to be reached. In the case of a 3.7% catalyst-to-substrate ratio, we observed a significant decrease in the yield of coupling products, from 37% in the case of the one-portion addition of H_2O_2 (run 3, Table 2) to 25% (run 4, Table 2), suggesting again that the sequential addition of the H_2O_2 solution favored the formation of ring-cleavage products in this catalytic TCP oxidation. The lower yields of dicarboxylic acids could be explained by their further oxidation in the reaction mixture because of a higher catalyst concentration compared to run 2, Table 2.

Influence of the pH value

We also studied the influence of pH value of the buffered reaction mixture on the conversion of TCP at 60 min; the data are reported in Fig. 2. The catalytic reaction is strongly dependent on the pH value of the solution. No catalytic activity was detected at pH 4 after 60 min, but for the same reaction time the substrate conversion at pH 5 and pH 6 increased to 24 and 66%, respectively. Full conversion of TCP was obtained at pH 7 and pH 8, which correspond to the optimal pH values of the catalytic reaction mixture. At pH 9 we observed a dramatic loss of catalytic activity.

The first step of the TCP oxidation is the one-electron oxidation of the phenolate anion.[3,4] Since the pK_a value of TCP is 6.2,[6] only small amounts of TCP are present in the reaction mixture as phenolate (a more oxidizable form compared to the phenol itself) at pH 5 and 6, leading to poor substrate conversions. At pH 7 and pH 8, 100% of the TCP is present as phenolate, thus explaining the full substrate conversions as well as the better oxidation rates. The absence of catalytic activity at pH 9 can probably be explained by the base-favored formation of μ-oxo dimeric species of FePcS.

It should be noted that the buffer concentration influenced the substrate conversion as well. Final buffer concentrations of 0.125 M or 0.25 M were necessary to keep the catalyst in an

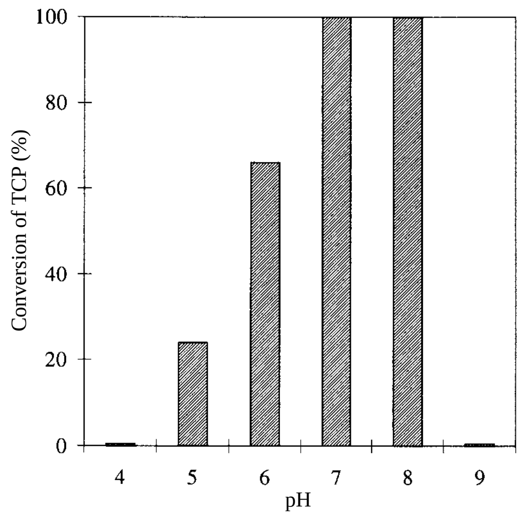


Fig. 2 Influence of the reaction mixture pH on the oxidation of 2,4,6-trichlorophenol (TCP) by the FePcS–H_2O_2 system

active form and to neutralize the acids formed during TCP oxidation.

Influence of the solvent on the catalytic oxidation reaction

In order to have a homogeneous solution when we worked with a reaction mixture containing 10 mM of TCP (2000 ppm), we used acetonitrile as a co-solvent to dissolve the hydrophobic TCP (acetonitrile : buffered water ratio of 1 : 3). Keeping in mind the possible development of the FePcS–H_2O_2 system for the oxidative depollution of aqueous effluents, we decided to study the influence of acetonitrile content using 1 mM TCP (200 ppm) and a 3.7% FePcS-to-TCP molar ratio. Increasing the acetonitrile : water ratio leads to an increase in the substrate conversions (Table 3). The conversions of TCP after one hour were 13, 54, 96 and 100% in reaction mixtures containing 2.5, 10, 25 and 50% acetonitrile, respectively.

Several hypotheses can be proposed to explain the strong influence of the acetonitrile content on this catalytic oxidation: (i) MeCN might act as an axial ligand on the iron center of FePcS to enhance its catalytic activity; (ii) H_2O_2 might react with MeCN to form a new peroxide able to react quickly with FePcS to give a highly active species. (Alkali-catalyzed epoxidations by H_2O_2 using nitriles as co-reactant have been published[7,8] and peroxycarboximidic acid generated by addition of H_2O_2 to acetonitrile has been proposed as an active species in olefin epoxidations.); and (iii) acetonitrile might be able to dissociate an inactive dimer of FePcS to a monomeric complex, which is catalytically active.

Table 3 Oxidation of TCP by FePcS–H_2O_2. Influence of the acetonitrile : buffered water ratio over the substrate conversion[a]

Run	Acetonitrile content (%)	TCP conversion at 60 min (%)	Dechlorination[b] at 60 min
1	2.5	13	0.2 (1.5)
1[c]	2.5	17	n.d.
2	10	54	1.2 (2.2)
3	25	96	2.0 (2.1)
4	50	100	2.4 (2.4)

[a] [TCP] = 1 mM, [FePcS] = 0.037 mM, [phosphate buffer] = 50 mM (pH 7), [H_2O_2] = 5 mM, one-portion addition. [b] Cl^- ions released per initial TCP molecule; the data in parentheses correspond to the number of Cl^- ions released per converted TCP molecule. [c] Addition of 3-cyanobenzoic acid; 3-cyanobenzoic acid : FePcS ratio of 100 : 1.

Table 4 Solvent influence on TCP conversion[a]

Co-solvent	Conversion of TCP at 60 min (%)	Polarity $E_T(30)$[b]
Acetone	100	42.2
Acetonitrile	96	45.6
Ethanol	86	51.9
Formamide	69	56.6
Water[c]	13	63.1

[a] [TCP] = 1 mM, [FePcS] = 0.037 mM, [phosphate buffer] = 50 mM (pH 7), [H_2O_2] = 5 mM, one-portion addition, solvent : buffer ratio = 1 : 3. [b] Solvent parameter developed by Dimroth and Reichardt,[9a] see ref. 9(*b*) for a recent review article on solvent properties. [c] We used 2.5% acetonitrile in this reaction mixture to completely solubilize TCP.

To check the role of acetonitrile, we replaced it by different solvents. The conversions obtained after one hour in the presence of acetone, acetonitrile, ethanol and formamide were 100, 96, 86 and 69%, respectively (solvent : buffered water ratio of 1 : 3) (Table 4). The total dechlorination values decreased in the same order. The data in Table 4 also indicate that TCP conversions decrease when the solvent polarity[9] increases, suggesting that these organic solvents might have a strong influence on the dissociation of inactive dimeric forms of the catalyst precursors.

To verify the hypothesis of an organic solvent molecule acting as axial ligand to FePcS, we added 100 equivalents of 3-cyanobenzoic acid, a potentially good axial ligand, to 1 equivalent of FePcS (Table 3, run 1[c]). We did not observe a significant difference in the substrate conversions in the presence or in the absence of 3-cyanobenzoic acid (17% and 13%, respectively). This lack of influence of the 3-cyanobenzoic acid suggests that the effect of the different organic solvents is not related to their possible coordination on the axial position of FePcS.

The possible formation of a reactive intermediate between acetonitrile or formamide and H_2O_2 by analogy to the Payne reaction[8] was excluded, since a solvent unable to form this kind of peroxidic intermediate, such as ethanol, also gave a high conversion (86% within 60 min, Table 4). In addition, this experiment confirmed that free hydroxyl radicals (usually trapped by ethanol) do not play a key role in this H_2O_2 oxidation reaction catalyzed by iron sulfophthalocyanine.

Influence of the solvent on the catalyst precursor(s)

The organic solvents caused a noticeable change in the UV-vis spectrum of FePcS. In pure water, we observed only one absorption maximum in the visible range at 632 nm. When adding an aqueous solution of this complex to a solvent mixture with a final organic solvent : water ratio of 1 : 3, we observe a decrease of the absorption maximum at 632 nm and the appearance of two absorption bands at 636 and 668 nm within 30 min (the co-solvents used were the same as in the catalytic reaction : acetonitrile, acetone or ethanol). The changes observed in the UV-vis spectra in the presence of acetonitrile with isobestic points at 554, 644 and 714 nm might be due to the dissociation of a dimer of FePcS to a monomeric complex. The dependence of the spectrum of FePcS on acetonitrile content is shown in Fig. 3.

The nature of the FePcS structure in aqueous solutions has already been the subject of many different studies.[10–18] There is a general agreement that FePcS exists in a dimeric form in aqueous solutions with an absorption maximum near 630 nm, whereas a monomeric form exhibits a peak in the region of 670 nm.[10,13,14] FePcS obtained from different preparations,

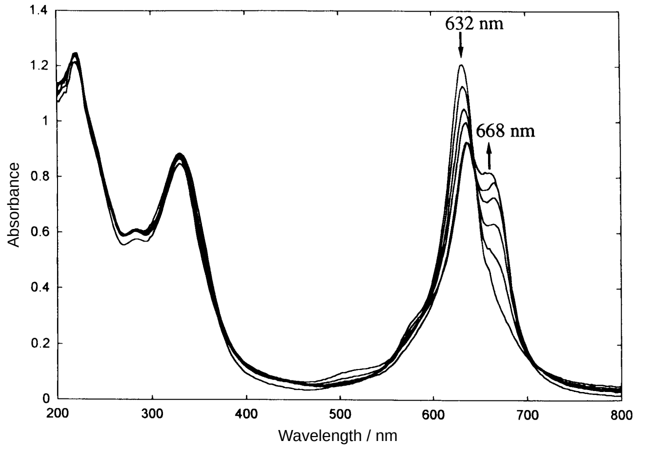


Fig. 3 Modification of the UV-vis spectrum of FePcS in water by addition of acetonitrile

by the Weber–Busch method[19] using iron(II) or iron(III) template compounds, or by the insertion of an iron(II) salt with H_2PcS in the presence of air, can be separated on Sephadex G10 into two main fractions.[18] The first fraction, a dark green product, showed a strong peak at 670 nm with minimal absorption at *ca.* 630 nm. The second fraction, containing a Fe^{III} low-spin product, was dark blue with a strong absorption at 632 nm and minimal absorption at 670 nm. The ratio between these two components was dependent on the preparation method. Materials prepared by these different methods gave the same complex in the presence of imidazole. The exact nature of these green and blue products is still not available in the literature on metallophthalocyanine chemistry.

The magnetic moments of the solid FePcS obtained from the Weber–Busch preparation were in the low-spin d^5 region and Mössbauer parameters were consistent with a mixture of ferric $S = 1/2, 3/2, 5/2$ spin states, with the low-spin species being the major component.[12] FePcS has been prepared by the Weber–Busch method in different forms (H^+, Na^+, K^+, Cs^+) and studied by different spectroscopic methods.[17] The authors concluded that FePcS contained a wide range of iron complexes with ratios depending on each preparation. The sodium salt of FePcS was a low-spin Fe^{III} species in the solid state, whereas high-spin Fe^{III} compounds were detected in buffer solutions (pH 2.5–12.0). Fanning *et al.* found no evidence for μ-oxo complexes in the solid state or in solution.[17] One or two molecules of water were proposed to be axial ligands susceptible to be bound to the stacked high-spin Fe^{III} complexes at high ionic strengths. By lowering the ionic strength and increasing the concentration a strong water interaction can occur to form a low-spin Fe^{III} complex.[17] However, the preparation and characterization of μ-oxobis-[tetraalkylsulfonamidophthalocyanine iron(III)] complexes have been reported by Lever *et al.*[11] The identity of this μ-oxo dimer has been confirmed by UV-vis spectroscopy, magnetism and FTIR (the band at 810 cm^{-1} being attributed to the Fe—O—Fe antisymmetric deformation). Gupta *et al.* published a FTIR spectrum for the solid FePcS complex in a KBr matrix having a band at 837 cm^{-1}, in the typical frequency region of the Fe—O—Fe deformation mode (800–900 cm^{-1}).[10] However, a similar band is also present in the FTIR spectra of CoPcS (831 cm^{-1}) and H_2PcS (850 cm^{-1}), indicating that the identification of the FePcS μ-oxo dimer by IR is still a matter of debate.

Using the hydrophobic FePc complex, Ercolani *et al.* published the preparation and a well-documented characterization of two interchangeable μ-oxo dimers.[15] The first μ-oxo dimer showed two antisymmetric Fe—O—Fe frequencies at 852 and 824 cm^{-1}, which can be shifted to 806 cm^{-1} upon $^{18}O_2$ treatment, while the second μ-oxo dimer did not show any band for the Fe—O—Fe vibration. These authors proposed a bent Fe—O—Fe structure for the first μ-oxo species and a quasi-linear one for the second μ-oxo dimer. In fact, the proposed bent μ-oxo dimer might be a hydroxo bridge, as recently proposed by Scheidt and co-workers for iron and manganese porphyrin complexes.[20,21] Hanack and co-workers have also prepared and characterized by UV-vis, FD mass, Mössbauer, NMR and EPR spectroscopy two isomeric μ-oxo compounds for various substituted iron phthalocyanines.[16] However, the nature of these two isomeric μ-oxo compounds remains unknown.[16] One can conclude that despite a large number of studies the chemistry of μ-oxo complexes of iron phthalocyanines, and in particular of FePcS, in aqueous solutions and the solid state is not presently fully understood.

We tried to evidence a μ-oxo dimer structure of FePcS by using FTIR spectroscopy. We observed a band at 833 cm^{-1}, which can be attributed to the Fe—O—Fe deformation mode. Previously, a Fe—O—Fe band at 810 cm^{-1} has been evidenced for the iron(III) complex of μ-oxo-bis-tetra(dodecylsulfonamido)phthalocyanine.[11] In order to check the hypothesis that the band at 833 cm^{-1} is the signature of a μ-oxo dimer, we incubated FePcS in $H_2{}^{18}O$ in the presence of 0.1 M acid in order to cleave the μ-oxo dimer; then the solution was neutralized with KOH to generate a Fe—^{18}O—Fe μ-oxo dimer. We obtained practically the same IR spectrum to that of the starting FePcS with only a small shift of the 833 cm^{-1} band to 839 cm^{-1}, which cannot be attributed to an isotopic shift. However, this disappointing experiment should not be taken as proof of the definitive absence of a μ-oxo dimer for the FePcS material that we are using as a catalytic precursor in the FePcS-mediated oxidation of TCP because of the complex nature of water-soluble metallophthalocyanines.

Nevertheless, the formation of strongly associated FePcS dimers in water is highly favorable since this process should reduce the unfavorable contacts between water and the apolar core of this aromatic macrocyclic molecule. In contrast, less polar organic solvents should disfavor the hydrophobic interactions between two different planes of phthalocyanines, which is a driving force for dimer formation. Consequently, the presence of an organic solvent should diminish the tendency of dimerization. So co-solvents with a low polarity should strongly contribute to shift the dimer/monomer equilibrium towards monomer formation. In fact, this correlation was observed in the oxidation of TCP catalyzed by FePcS: acetone > acetonitrile > ethanol > formamide > water (see data in Table 4).

Modifications of FePcS spectra in the presence of TCP, acids or bases

Addition of TCP to a water solution of FePcS resulted in the same changes in the UV-vis spectra as observed after an organic solvent addition (see above) with isobestic points at 552, 650 and 714 nm, suggesting the formation of a FePcS monomer.[4] Spectrophotometric titration of a 20 μM FePcS aqueous solution with 50 mM HCl revealed a decrease of the band at 632 nm and the appearance of two new absorbances at 636 and 680 nm with quasi-isobestic points at 340, 564 and 650 nm (Fig. 4). Thus spectral changes (positions of new bands and isobestic points) are similar in all three cases: addition of acid, acetonitrile or TCP to a water solution of FePcS.

These data strongly suggest the formation of (a) monomeric form(s) of FePcS under all these conditions. We also noted a significant difference of 12 nm between the absorption bands in the presence of acetonitrile and TCP (668 nm) and HCl (680 nm). Upon HCl titration the spectrum reached a saturation level with maxima at 636 and 680 nm when the acid concentration was 2.5 mM. A further increase in acid

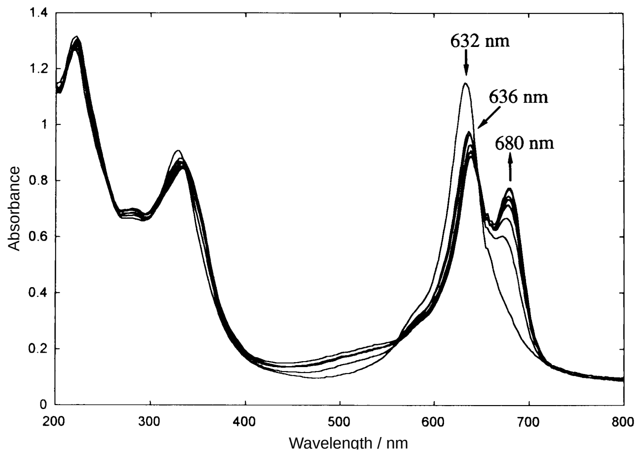


Fig. 4 Modification of the UV-vis spectrum of FePcS in water by addition of an HCl solution

concentration up to 250 mM did not change the UV-vis spectrum. When hydrochloric acid was replaced by sulfuric or phosphoric acid, the same phenomenon was observed. Therefore we concluded that the presence of different anions of these acids, chloride, sulfate or phosphate, were not at the origin of the changes observed in the visible spectra of FePcS. To check the reversibility of an equilibrium between different forms of FePcS, a FePcS solution previously acidified by H_2SO_4, was titrated with NaOH. In the beginning we observed the regular disappearance of the maximum at 680 nm without an increase of the absorption bands at 636 and 632 nm. At pH 6, the maximum at 680 nm nearly disappeared and further addition of NaOH produced a spontaneous reappearance of the initial maximum at 632 nm (Fig. 5). Further titration with NaOH up to pH 9 provoked the appearance of a shoulder at approximately 670 nm.

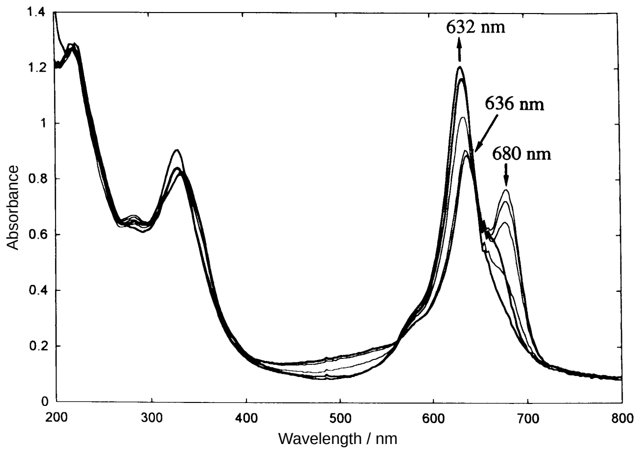
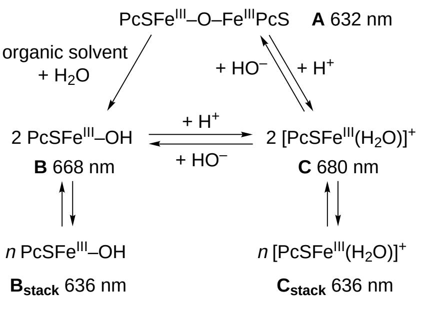


Fig. 5 Modification of the UV-vis spectrum of an acidic aqueous solution of FePcS by addition of an NaOH solution



Scheme 1 Schematic representation of the different forms of FePcS in aqueous solution. All these different proposed structures must be considered as working hypotheses (see text). The four negative charges of the sulfonato groups have been omitted for clarity

The hypothesis that a dimeric form of FePcS is transformed into a single monomer is not sufficient to explain all these different experimental results. In the presence of a co-solvent or TCP, we propose that the μ-oxo dimer (632 nm, compound **A** in Scheme 1) can be cleaved to a FePcS monomer with a hydroxide or phenolate residue as an axial ligand (668 nm, compound **B** in Scheme 1). Titration of $Fe^{III}(PcS)OH$ with an acid leads to another monomer {compound **C**, $[Fe^{III}(PcS)H_2O]^+$}, probably with a water axial ligand as previously observed for sulfonated iron porphyrin complexes.[22] The absorption band at 636 nm, observed with all the different acids, can be attributed to the corresponding stacked monomers (compounds $\mathbf{B_{stack}}$ and $\mathbf{C_{stack}}$).

When a 20 μM FePcS solution is titrated with acid, the ratio between the absorption bands at 680 and 636 nm is always equal to 0.8 and does not change when adding more acid. But when we titrate a 4 μM FePcS solution under the same conditions, the ratio between the two absorption maxima changes and is equal to 1.0. The higher monomer content at lower FePcS concentration supports the hypothesis of an equilibrium between the monomer form **C** and the corresponding stacked monomer $\mathbf{C_{stack}}$. Finally, the formation of a monomeric FePcS is a prerequisite for catalytic activity of the metallophthalocyanine in TCP oxidations and the key role of an organic solvent is to shift the dimer/monomer equilibrium towards a monomeric FePcS complex, the true catalyst precursor.

Lifetime of the FePcS catalyst in the H_2O_2 oxidation of TCP

One of the key questions in homogeneous catalytic oxidations is the lifetime of the catalyst. In order to answer this question we decided to monitor the catalytic activity in batch reactions after addition of new portions of pollutant and oxidant (in a one-portion addition or five-aliquot addition fashion, see Fig. 6).

These experiments were performed under the conditions of run 4 of Table 3. To our surprise, we found that the TCP conversion was still 90% within 10 min in the third run [see Fig. 6(*a*)]. The half-conversion time of the third run was 3 min, very close to that measured for the first two runs (2 min) and the total dechlorination was 5.0 Cl^- for 2.9 converted TCP molecules or an average value of 1.7 Cl^- per TCP. The kinetics were slightly different in the case of the five-aliquot addition of hydrogen peroxide (half-conversion times were 9, 5 and 7 min for runs 1, 2 and 3, respectively), but the total dechlorination was 5.2 Cl^- for 2.9 converted TCP molecules or an average value of 1.8 Cl^- per TCP [see Fig. 6(*b*)]. It must be noted that the initial blue color of FePcS changed to green or violet after addition of hydrogen peroxide by aliquots or by the one-portion mode, respectively. But the color turned to brown during the second and third runs due to the formation of quinone derivatives, making the monitoring of the catalyst concentration by UV-visible spectrophotometry more difficult. Finally, these data are highly encouraging for a catalyst that is easily accessible and cheap.

Conclusion

Gradual addition of H_2O_2 to the reaction mixture in oxidations of trichlorophenol, catalyzed by FePcS, results in a more "economic" consumption of the oxidant due to a decrease of the wasteful dismutation of H_2O_2. As a consequence, higher conversions occurred with more advanced TCP oxidations using a smaller charge of catalyst. The catalyst precursor is probably a non-stacked monomeric iron sulfophthalocyanine able to react with hydrogen peroxide to generate an iron-peroxo complex, previously proposed as the active species in the oxidative degradation of chlorophenols. The key role of

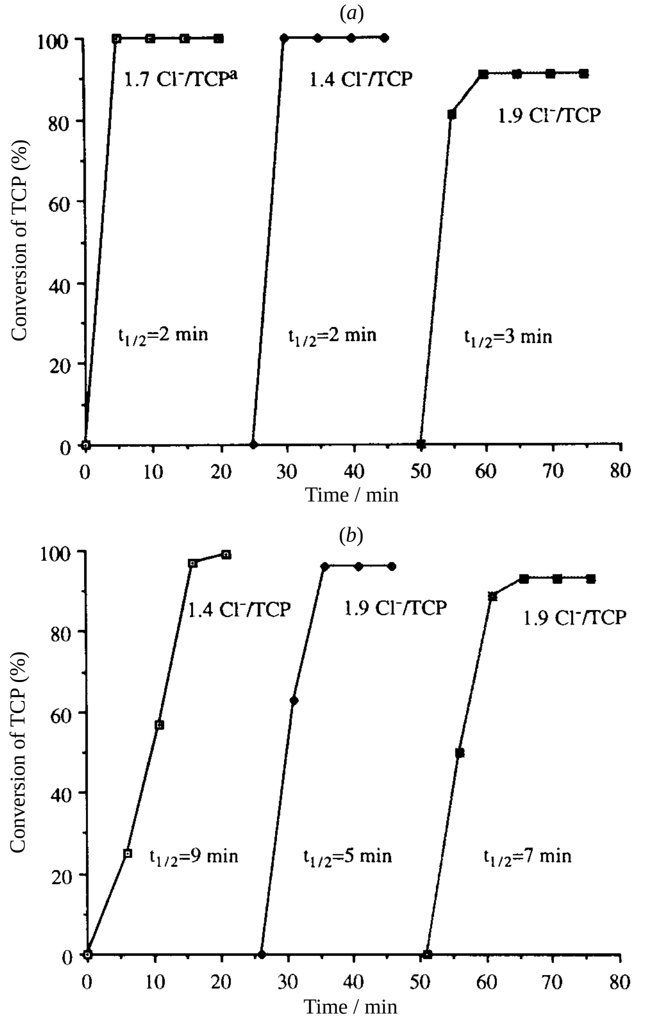


Fig. 6 Conversion of TCP in three consecutive oxidation reactions by FePcS–H_2O_2 in the same batch; (*a*) one-portion addition of the oxidant, (*b*) five-aliquot addition

the miscible organic solvent used in these aqueous catalytic mixtures is related to the shift of the dimer/monomer equilibrium towards a non-stacked monomeric form of FePcS. At the present stage of development, this catalytic system requires an organic co-solvent to be efficient. This fact makes the FePcS–H_2O_2 system more adapted for the treatment of process waters still containing 10 to 20% of organic solvents than for the final treatment of aqueous effluents. Repetitive batch experiments confirmed that the catalyst is not destroyed at the end of substrate conversion, making this catalytic system based on a "green oxidant" and a low cost catalyst very attractive.

A further step in the development of the FePcS–H_2O_2 system would be to prepare a phthalocyanine complex that would exist in a monomeric form in water solution without addition of miscible organic solvents and to support this catalyst on materials compatible with water treatments. We are currently working in this direction.

Experimental

Materials

The conversion of TCP was monitored by HPLC (Waters 510 pump, Waters 486 detector) equipped with a μ-Bondapak C18 column, a methanol : water mixture (7 : 3, v/v) as the eluent at 1 mL min^{-1} and detection at 294 nm. The UV-visible absorption spectra were recorded on a Hewlett Packard 8452 A spectrophotometer. ^{1}H NMR spectra were obtained on a Bruker AM 250 MHz spectrometer. All solvents used were of analytical grade. 2,4,6-Trichlorophenol was purchased from Janssen. Hydrogen peroxide was obtained from Acros as a 35 wt.% solution. 3-Cyanobenzoic acid was purchased from Aldrich. The concentrations of Cl$^-$ were determined by the mercuric thiocyanate method.[23]

Preparation of the iron tetrasulfophthalocyanine FePcS

Iron tetrasulfophthalocyanine (FePcS) was prepared according to the method of Weber and Busch.[19] We found that the yield is highly dependent on the addition rate of the solid reagent mixture to the hot nitrobenzene solution. Thus the well-ground mixture of the monosodium salt of 4-sulfophthalic acid (17.28 g, 64.8 mmol), ammonium chloride (1.88 g, 36 mmol), urea (23.2 g, 388 mmol), ammonium molybdate (272 mg, 0.24 mmol) and $FeSO_4 \cdot 1.5H_2O$ (3.44 g, 19.2 mmol) was added to 24 mL of nitrobenzene at 180 °C over a period of 1 h. The resulting mixture was then heated for 7 h. The isolation and purification of FePcS was performed according to the published protocol. Yield 68%. Anal. calcd for $C_{32}H_{12}N_8O_{12}S_4Na_4Fe \cdot 8H_2O$: C 33.78; H 2.57; N 9.85; Fe 4.91. Found: C 33.52; H 2.49; N 9.82; Fe 5.05%. UV-vis (water), λ_{max}/nm (ε/mol L^{-1} cm^{-1}): 328 (55 700), 632 (65 200). IR (KBr pellet), ν_{max}/cm^{-1}: 1717, 1634, 1511, 1399, 1330, 1192, 1146, 1110, 1074, 1056, 1030, 930, 833, 761, 747, 698, 649, 636, 594.

Treatment of FePcS in the presence of $H_2{}^{18}O$

Two milligrams of FePcS were dissolved in 200 μL of $H_2{}^{18}O$ (97 atom%, Eurisotop, Gif-sur-Yvette) and 2.3 μL of 48% HBr were added (final HBr concentration of 0.1 M). The resulting mixture was stirred for 1 h. Then HBr was neutralized with 2.3 μL of 8.84 M KOH and the reaction mixture was again stirred for 1 h. The sample was dried in vacuum. The IR spectrum of a KBr pellet showed the same bands as the initial FePcS material except that the 833 cm^{-1} band shifted to 839 cm^{-1}.

Oxidation of TCP by FePcS and H_2O_2

Different concentrations of FePcS (Table 1). The reaction mixture of 2 mL contained 20 μmol of 2,4,6-trichlorophenol (500 μL of a 40 mM stock solution in acetonitrile), phosphate buffer (1 mL of a 500 mM stock solution at pH 7) and different catalyst concentrations: 740, 200, 100, 50, 20 nmol of FePcS for a 3.7, 1.0, 0.5, 0.25, 0.1% catalyst-to-substrate ratio (*i.e.*, 500 μL of a 1.48, 0.4, 0.2, 0.1, 0.04 mM stock solution of FePcS in water, respectively). H_2O_2 (5 × 20 μL or 1 × 100 μL of a 3.5% H_2O_2 solution in water, which was prepared by ten fold dilution of a commercial 35 wt.% H_2O_2 solution) was added to the reaction medium and stirred at 18 °C. Aliquots of the reaction mixture were taken at defined times, diluted with an acetonitrile–water mixture to stop the oxidation reaction and analyzed by HPLC.

Quantitative analysis of the oxidation products by NMR (Table 2). The NMR analysis of the oxidation products was performed as for runs 1, 2 and runs 6, 7 of Table 1; the scale was 50 times larger (100 mL reaction volume). Acetonitrile and water were evaporated under vacuum at 50 °C and the residue was dried for 1 h at room temperature. Seven milliliters of 1 M HCl saturated with NaCl were added to the residue; the solution was adjusted to pH 2 by dropwise addition of 12 M HCl. The products were extracted with diethyl ether (8 × 60 mL). After evaporation of ether, the dark brown residue was dried under vacuum for 2 h at room temperature and dissolved in deuterated dimethyl sulfoxide for NMR analysis. We added 6 μL of $CHCl_3$ (75 μmol) as an internal standard to quantify the oxidation products. The total yields of coupling products were based on two protons per aromatic ring.

Different pH values. The reaction mixture of 2 mL contained 20 μmol of 2,4,6-trichlorophenol (500 μL of a 40 mM stock solution in acetonitrile), 0.2 μmol of FePcS (500 μL of a 0.4 mM stock solution in water) and 500 μmol of buffer (1 mL of the respective stock buffer solution: pH 4 (0.25 M citric acid–0.5 M disodium hydrogen phosphate); pH 5, 6, 7, 8 (0.5 M phosphate buffer); pH 9 (0.5 M boric acid–sodium hydroxide). H_2O_2 (5 × 20 μL of a 3.5% H_2O_2 solution in water) was added to the reaction mixture and stirred at 18 °C.

Variation of the acetonitrile : water ratio (Table 3). The reaction mixture of 10 mL contained 10 μmol of 2,4,6-trichlorophenol (250 μL of a 40 mM stock solution in acetonitrile), 0.37 μmol FePcS (250 μL of a 1.48 mM aqueous stock solution) and 500 μmol of phosphate buffer (1 mL of a 500 mM stock solution at pH 7). This solution was adjusted with the required volumes of acetonitrile and water to obtain the desired ratio (*e.g.*, 4.75 mL of acetonitrile and 3.75 mL of water to obtain an acetonitrile : water ratio equal to 1 : 1). H_2O_2 (50 μL of a 3.5% H_2O_2 solution) was added and the reaction mixture stirred at 18 °C.

In the presence of different co-solvents (Table 4). The concentrations used were the same as given above for Table 3. The stock solutions of TCP were prepared in the respective co-solvents. To obtain a co-solvent : water ratio of 1 : 3, the reaction mixture was adjusted with 2.25 mL of a co-solvent (acetone, acetonitrile, ethanol, formamide) and 6.25 mL of water.

Titration of FePcS

With different co-solvents. A solvent mixture of 730 μL of water and 250 μL of co-solvent (*e.g.*, acetone, acetonitrile, ethanol or formamide) was prepared in a cuvette with a volume of 1 mL. Twenty microliters of a 1.48 mM stock solution of FePcS in water were added and the mixture was quickly shaken. The first UV-vis spectrum was recorded immediately; further spectra were recorded every 2 min.

With TCP. One milliliter of a 20 μM FePcS solution in water was titrated every 5 min with 10 μL of a 40 mM TCP solution in acetonitrile. The UV-vis spectra were recorded 4 min after every addition. To control the effect of acetonitrile, the TCP stock solution was replaced by acetonitrile.

With acetonitrile. Different samples of acetonitrile–water mixtures with 0, 5, 10, 15, 20, 25, 30 or 35% of acetonitrile containing 20 μmol of FePcS were prepared and the spectra recorded 10 min after preparation.

With HCl, H_2SO_4 or H_3PO_4. One hundred microliters of a 0.2 mM FePcS stock solution in water were added to a mixture of 5 μL of 0.05 M HCl (H_2SO_4 or H_3PO_4) and 895 μL of H_2O. To obtain different acid concentrations, we changed the 0.05 M HCl : water ratio to 10 : 890, 15 : 885, 20 : 880, 25 : 875, 30 : 870, 50 : 850. The spectra were recorded 15 min after preparation.

Titration of an acidic solution of FePcS with NaOH. One hundred microliters of a 0.2 mM FePcS stock solution in water were added to a solution of 850 μL H_2O and 50 μL of 0.05 M HCl (or H_2SO_4) in a cuvette of 1 mL and the spectrum was recorded after 15 min. The acidified FePcS solution was then titrated every 5 min with 10 μL of 0.05 M NaOH solution. The UV-vis spectra were recorded 4 min after every addition.

Lifetime of the FePcS catalyst in the H_2O_2 oxidation of TCP

Batch experiments were performed under the conditions used for run 4 in Table 3 (*i.e.*, 3.7% FePcS *vs.* TCP and 50% acetonitrile). The preparation of the reaction mixture is the same as mentioned above in the experimental part of Table 3 (the total volume being equal to 10 mL). New 10 μmol portions of 2,4,6-trichlorophenol (250 μL of a 40 mM stock solution in acetonitrile) were added at 24 and 49 min. In the case of a one-portion addition of H_2O_2 corresponding to Fig. 6(*a*), 50 μL of a 3.5% H_2O_2 solution (*i.e.*, 3 aliquots of 50 μmol of H_2O_2) were added at 0, 25 and 50 min. In the case of a sequential addition of the oxidant corresponding to Fig. 6(*b*), 15 × 10 μL of a 3.5% H_2O_2 solution (*i.e.*, 15 aliquots of 10 μmol of H_2O_2) were added every 5 min. In both cases, the dechlorination values were determined at 22, 47 and 90 min.

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