# Efficient $H_2O_2$ Oxidation of Chlorinated Phenols catalysed by Supported Iron Phthalocyanines

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Amberlite-supported iron and manganese sulfonated phthalocyanines are efficient catalysts for the oxidation of chlorinated phenols by $H_2O_2$; these support catalysts can be recycled several times without important loss of catalytic activity.

Contamination of the environment by chlorinated aromatic compounds is a severe problem, despite their useful applications as biocides, lubricants and solvents. Accumulation of chloroaromatics in the environment is a result of their slow biotransformation to non-damaging and/or more biodegradable chemicals.[1-3] Two different pathways have been identified in the biotransformation of polychlorinated aromatic or ethylenic derivatives by microorganisms: (*i*) a reductive dehalogenation route in anaerobic conditions[4,5] or (*ii*) an oxidative pathway catalysed by a peroxidase like ligninase[6] or monooxygenases like methane monooxygenase[7] or cytochrome P-450.[8] For example, *rhodococcus chlorophenolians* PCP-1 is known to dechlorinate aerobically several polyhalogenated phenols *via* an oxidative process catalysed by a cytochrome P-450[8] (but the enzyme-mediated degradation is slow: pentachlorophenol is converted by this enzyme at a turnover rate of 2.26 nmol of pentachlorophenol per mg of protein per h, *i.e.* one catalytic cycle every 8–9 h). So, there is an obvious need for efficient chemical catalysts for the oxidative degradation of halogenated phenols. We have previously described the oxidation of 2,4,6-trichlorophenol to 2,6-dichloro-1,4-benzoquinone catalysed by water-soluble metalloporphyrins,[9] but the two main limitations of this catalytic system were the rather low activity when using hydrogen peroxide (a 'clean oxidant', water being the only released byproduct after oxidation) and the current absence of large-scale manufacturing of these biomimetic catalysts. Since phthalocyanines (Pc) derivatives are important industrial dyes, metallophthalocyanines are an attractive alternative as cheap and readily available oxidation catalysts. Up to now iron or manganese phthalocyanine catalysts were reported as being less active in oxidation reactions compared to metalloporphyrin complexes.[10]

Here we report the efficient oxidative degradation of polychlorinated phenols catalysed by supported iron and manganese complexes of 2,9,16,23-tetrasulfophthalocyanine {[Fe(PcS)] and [Mn(PcS)] were prepared according to ref. 11}. 2,4,6-Trichlorophenol (TCP, one of the main pollutants in paper mill effluents when wood pulp is delignified by chlorine bleaching) was used as paradigm pollutant.

We first assayed the catalytic activities of the soluble complexes [Fe(PcS)] and [Mn(PcS)] in the oxidation of TCP by potassium monopersulfate or hydrogen peroxide [see Table 1 and footnote (*a*) for the experimental conditions]. In the $KHSO_5$ oxidation of TCP, at pH 7, both [Fe(PcS)] and [Mn(PcS)] are highly efficient catalysts: full substrate conversion is observed within few minutes with only 0.1% of catalyst/TCP (runs 1 and 2 of Table 1; turnover rates, based on substrate converson, being 16 and >30 cycles per second, respectively). It should be noted that high turnover rates were obtained with $KHSO_5$, but it is also possible to use an environment-compatible oxidant such as $H_2O_2$ (runs 3 to 5).

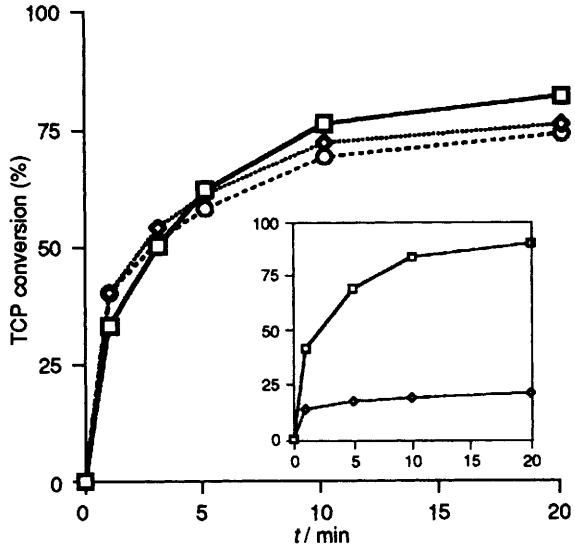


**Fig. 1** Catalyst recycling in repetitive oxidations of 2,4,6-trichlorophenol by [Fe(PcS)]–Amb–$H_2O_2$ (1% catalyst/substrate molar ratio, reagent concentrations as for run 3 of Table 2, but with a final volume of 8 ml instead of 2 ml. In these conditions, substrate conversions are slightly below that ones observed with a final volume of 2 ml, suggesting that mass transport is an important parameter in these heterogeneous catalytic reactions) and [Fe(PcS)]–Amb–$KHSO_5$ (see inset. Experimental conditions as for run 1 of Table 2); (□) 1st, (◇) 2nd, (○) 3rd run.

**Table 1** Oxidation of 2,4,6-trichlorophenol by $KHSO_5$ and $H_2O_2$ mediated by iron and manganese phthalocyanine complexes, [Fe(PcS)] and [Mn(PcS)][a]

| Run | Catalyst | % Cat./sub. | pH | Oxidant | Conversion (%) 1 | Conversion (%) 5 min | Initial rate (cycles $s^{-1}$)[b] |
|---|---|---|---|---|---|---|---|
| 1 | [Fe(PcS)] | 0.1 | 7 | $KHSO_5$ | 97 | 98 | 16 |
| 2 | [Mn(PcS)] | 0.1 | 7 | $KHSO_5$ | 100 | — | n.d. |
| 3 | [Fe(PcS)] | 1 | 7 | $H_2O_2$ | 6 | 38 | 0.1 |
| 4 | [Fe(PcS)] | 3.7[c] | 7 | $H_2O_2$ | 68 | 100 | 0.3 |
| 5 | [Mn(PcS)] | 1 | 8.5 | $H_2O_2$ | 8 | 25 | 0.13 |

[a] Typical procedure: A mixture of 20 μmol of 2,4,6-trichlorophenol (500 μl of a 40 mmol $dm^{-3}$ stock solution), catalyst solution {200 or 20 nmol of [Fe(PcS)] or [Mn(PcS)] for 1 or 0.1% catalyst/substrate ratio; *i.e.* 500 or 50 μl of 0.4 mmol $dm^{-3}$ solution in water, respectively} and a buffered solution of the oxidant [100 μmol of oxidant in 500 μl of buffer (30.7 mg of $KHSO_5$ or 10 μl of 35% $H_2O_2$ solution in water)] was adjusted to a final volume of 2 ml with water and stirred at 20 °C. Reactions were monitored by HPLC [μ-Bondapak C18 column, eluent: methanol–water (1/1 v/v) 1 ml $min^{-1}$, detection at 280 nm]. For very fast reactions, *e.g.* full conversion within 1 min, initial rates can not be accurately determined by HPLC methods (n.d.). Phosphate (pH 7), citrate (pH 3) or borate buffers (pH 8.5) were used. [b] Based on 1 min reaction time. [c] In this case,740 nmol of [Fe(PcS)] were used (500 μl of a 1.48 mmol $dm^{-3}$ stock solution).

**Table 2** Oxidation of polychlorinated phenols by supported iron or manganese phthalocyanine catalysts.[a] Runs 1–12: substrate trichlorophenol; 13, 14: pentachlorophenol. Runs 1,2 oxidant: $KHSO_5$; 3–14: $H_2O_2$. Run 1, pH 2; Runs 2–10, 12–14: 7; Run 11 8.5

| Run | Catalyst | % Cat./sub | Conversion (%) 1 | 5 | 60 min |
|---|---|---|---|---|---|
| 1 | [Fe(PcS)]–Amb | 1 | 43 | 71 | 98 |
| 2 | [Fe(PcS)]–Amb | 1 | 44 | 80 | 90 |
| 3 | [Fe(PcS)]–Amb | 1 | 65 | 80 | 93 |
| 4 | [Fe(PcS)]–Amb | 3.7 | 63 | 93 | 100 |
| 5 | [Mn(PcS)]–Amb | 1 | 38 | 45 | 63 |
| 6 | [Fe(PcS)]–PVP (25%) | 1 | 73 | 87 | — |
| 7 | [Fe(PcS)]–PVP (2%) | 1 | 41 | 53 | 59 |
| 8 | [Fe(PcS)]–PVPMe$^+$ (25%) | 1 | 81 | 84 | 89 |
| 9 | [Fe(PcS)]–PVPMe$^+$ (2%) | 1 | 33 | 40 | 40 |
| 10 | [Mn(PcS)]–PVP (2%) | 1 | 60 | 60 | 60 |
| 11 | [Mn(PcS)]–PVP (2%) | 1 | 85 | 86 | 87 |
| 12 | [Mn(PcS)]–PVPMe$^+$ (2%) | 1 | 41 | 47 | 53 |
| 13 | [Fe(PcS)]–Amb | 1 | 27 | 36 | 65 |
| 14 | [Fe(PcS)]–Amb | 3.7 | 57 | 67 | 88 |

[a] Catalysts supported on poly(vinylpyridine) polymers cross-linked with 2 or 25% of divinylbenzene [PVP (2%) or PVP (25%)] or on poly-(vinyl-4-methylpyridinium) polymers (PVPMe$^+$) have been prepared according to ref. 13(*b*), using water–acetonitrile (1 : 1) as medium during the impregnation step (all PVP polymers were from Fluka). [Fe(PcS)]–Amb and [Mn(PcS)]–Amb were prepared by addition of 1 g of Amberlite IRA 900 (from EGA-Chemie or Aldrich) to a solution of 10 mg of [Fe(PcS)] or [Mn(PcS)] in water–acetonitrile (40 ml, 1 : 1). After 48 hours of gentle magnetic stirring, the material was isolated by filtration, washed with water–acetonitrile (40 ml, 3 : 1), no metallophthalocyanine could be detected in the washing solution. During the impregnation step the concentration of metallophthalocyanine in the solution was monitored by UV–VIS spectroscopy indicating the amount of complex fixed on the polymer. The material was dried in air at room temperature and then at 65 °C for 65 hours. Amounts of catalyst fixed by 1 g of resin: [Fe(PcS)]–Amb = 6.75 μmol, 7.7 mg; [Mn(PcS)]–Amb = 15.3 μmol, 17.5 mg; [Fe(PcS)]–PVP (25%) = 1.25 μmol, 1.4 mg; [Fe(PcS)]–PVPMe$^+$ (25%) = 1.06 μmol, 1.2 mg; [Fe(PcS)]–PVP (2%) = 6.20 μmol, 7.1 mg; [Mn(PcS)]–PVP (2%) = 6.70 μmol, 7.6 mg; [Mn(PcS)]–PVPMe$^+$ (2%) = 3.60 μmol, 4.1 mg.

However, the bleaching of these soluble catalysts is always competing with the substrate oxidation. This is noticeable in runs 3 and 5. 2,6-Dichloro-1,4-benzoquinone is the initial oxidation product of TCP. But this quinone is only detected in the first 3 min of the catalytic reaction, as it then undergoes further catalytic transformations to more dechlorinated molecules. At low substrate concentration (2.5 mmol dm$^{-3}$) high dechlorination can be achieved with up to 2.1 $Cl^-$ ions per oxidized TCP molecule being released during its oxidation catalysed by $3.7 \times 10^{-4}$ mol dm$^{-3}$ FePcS (free $Cl^-$ was determined by the mercuric thiocyanate method).[12]

Even more attractive are the performances (Table 2) of [Fe(PcS)] and [Mn(PcS)] catalysts when they are fixed onto an insoluble support like a cationic ion-exchange resin (see ref. 13 for recent articles on ion-exchange supported metalloporphyrins). We used poly(vinylbenzene) resins having ammonium groups able to strongly interact with the sulfonato groups of the metallophthalocyanine catalyst by electrostatic interactions (Amberlite IRA 900 in the case of [Fe(PcS)]–Amb and [Mn(PcS)]–Amb. Both supported catalysts exhibit a strong green colour). The same catalysts [Fe(PcS)] and [Mn(PcS)] have also been impregnated onto differently reticulated poly(vinylbenzene) polymers, reticulation with 2 or 25% of divinylbenzene, PVP(2%) or PVP(25%). PVPMe$^+$ corresponds to the cationic polymer poly(vinyl-4-methylpyridinium) [see ref. 13(*b*) for preparation of these methylated PVP polymers]. [M(PcS)]–PVP and [M(PcS)]–PVPMe$^+$ show a turquoise and a green–brown colour, respectively. No phthalocyanine complexes were removed from the impregnated amberlite or PVP-based resins by washing them with different solvents (water, methanol or acetone). As expected, supported metallophthalocyanine catalysts are less efficient than the corresponding soluble catalysts in $KHSO_5$ oxidations. Full conversion of TCP mediated by [Fe(PcS)]–Amb is observed within 1 hour (runs 1, 2 of Table 2) as compared to 1 min for soluble [Fe(PcS)].

The important feature though, is the better efficiency of these supported metallophthalocyanines in $H_2O_2$ oxidations when *fixed onto amberlite*. With the 'clean oxidant' and 1% of [Fe(PcS)]–Amb catalyst, nearly full conversion of TCP is obtained in 1 h at pH 7 (run 3, Table 2). In the same experimental conditions, the soluble catalyst gave only 38% of substrate conversion in 5 min (run 3, Table 1) compared to 80% for [Fe(PcS)]–Amb. [Mn(PcS)]–Amb, is slightly less efficient (run 5) than [Fe(PcS)]–Amb (run 3). When [Fe(PcS)] and [Mn(PcS)] are supported onto PVP polymers, full conversion is not observed in $H_2O_2$ oxidation of TCP (runs 6–12), despite a good catalytic activity in the first few minutes of the reaction before the catalyst bleaching. Pentachlorophenol is also successfully oxidized with the [Fe(PcS)]–Amb–$H_2O_2$ system (runs 13 and 14, Table 2). Runs 6 to 12 indicate that PVP-supported catalysts are quickly bleached after an efficient catalytic activity in the early stage of the substrate oxidation.

Furthermore, the [Fe(PcS)]–Amb catalyst can be easily recycled by filtration and re-engaged in new $H_2O_2$ oxidations of TCP. High conversions of TCP are observed in three successive TCP oxidations with [Fe(PcS)]–Amb as catalyst (the catalytic activity in the second and third run is 92 and 90% of that of the 1st run), confirming that this supported Fe(PcS) complex is not degraded significantly during the catalytic oxidation of the pollutant molecule (see Fig. 1). The same catalyst is not as stable when using potassium monopersulfate: 70% of the catalytic activity of the first run is lost in the second run (inset of Fig. 1).

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