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# Oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by iron tetrasulfophthalocyanine (FePcS) supported on a cationic ion-exchange resin

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**Summary** — The oxidation of 2,4,6-trichlorophenol (TCP) with $H_2O_2$ or $KHSO_5$ catalyzed by iron(III) tetrasulfophthalocyanine (FePcS) supported on a cationic ion-exchange resin (Amberlite IRA 900) is reported. In order to obtain the catalytic oxidative degradation of the aromatic ring of TCP, the supported catalyst FePcS–Amberlite should be pre-saturated with the substrate since the phenolate form of TCP is strongly adsorbed by the cationic resin. In these conditions, the oxidation of TCP is observed even when the aqueous phase is deprived of acetonitrile, an organic solvent able to enhance the activity with the soluble catalyst by displacement of the dimer–monomer equilibrium towards momeric active species. The dispersion of FePcS monomers onto the support is a way to avoid the formation of inactive dimers.

**catalytic pollutant oxidation / iron tetrasulfophthalocyanine / 2,4,6-trichlorophenol / heterogeneous catalysis / cationic ion-exchange resin**

**Résumé — Oxydation du 2,4,6-trichlorophénol (TCP)catalysée par une tétrasulfophtalocyanine de fer (FePcS) supportée sur une résine cationique échangeuse d'ions.** L'oxydation du 2,4,6-trichlorophénol (TCP) avec $H_2O_2$ ou $KHSO_5$ catalysée par le complexe du fer(III) de la tétrasulfophtalocyanine (FePcS) supporté sur une résine cationique échangeuse d'ions est décrite. Afin d'obtenir la dégradation catalytique du cycle aromatique du TCP, le catalyseur supporté FePcS–Amberlite doit être pré-saturé avec le substrat étant donné que la forme phénolate du TCP est fortement adsorbée par la résine cationique. Dans ces conditions, l'oxydation du TCP est observée même lorsque le milieu réactionnel est privé d'acétonitrile, un solvant organique permettant d'améliorer l'activité du catalyseur en solution par déplacement de l'équilibre dimère–monomère en faveur d'espèces monomères actives. La dispersion des monomères FePcS sur le support est un moyen d'éviter la formation des dimères inactifs en catalyse.

**oxydation catalytique de polluant / tétrasulfophtalocyanine de fer / 2,4,6-trichlorophénol / catalyse hétérogène / résine cationique échangeuse d'ions**

## Introduction

Chlorinated aromatics are persistent molecules in the environment, since they are not easily degraded by microorganisms via oxidative pathways. Only perhalogenated aromatic compounds, in contrast to those having a low halide-content, can be easily reduced by the low-valent oxidation states of different metalloenzymes [1, 2]. We recently developed a catalytic system able to oxidize 2,4,6-trichlorophenol, a classical phenolic substrate known for being resistant to oxidative or hydrolytic degradation processes, by using hydrogen peroxide and iron tetrasulfophthalocyanine (FePcS, see scheme 1 for structure) as water-soluble catalyst [3]. This catalytic reaction is able to cleave the aromatic ring to C4-diacids (mainly chloromaleic acid), oxalic acid and carbon dioxide with the release of two free chloride ions per converted TCP molecule [3]. The only limitation of this catalytic method is the presence of a small amount of an organic solvent (5–10% vol) miscible with water: ethanol, acetone, acetonitrile, ... [4]. The organic co-solvent is necessary to displace the catalyst dimer–monomer equilibrium towards the monomeric active species [4]. One way to avoid the formation of inactive FePcS dimers would be to disperse the catalyst molecules onto a support. We have previously used this method with sulfonated metalloporphyrin catalysts by using ion-exchange resins usually based on modified polystyrene or polyvinylpyridine polymers [5]. In addition these supported catalysts will be easy to recycle by simple filtration of the reaction mixture. Here we report the results concerning the oxidative degradation of 2,4,6-trichlorophenol by $H_2O_2$ or $KHSO_5$ by using a cationic polystyrene-based resin Amberlite IRA 900 to immobilize the tetrasulfonated iron(III)phthalocyanine catalyst via strong electrostatic interactions.

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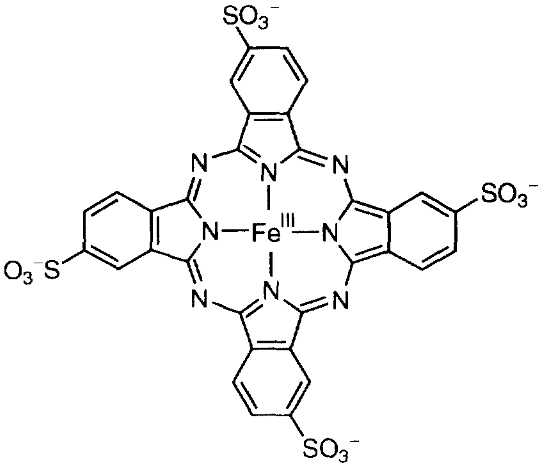


**Scheme 1.** Structure of the iron(III)-tetrasulfophthalocyanine (FePcS); only one of the four possible regioisomers is depicted here.

## Results and discussion

### *Catalytic behavior of FePcS–Amberlite in relation with the substrate adsorption*

Amberlite IRA 900 is a classical cationic ion-exchange resin with ammonium groups, which are able to interact with any anionic species present in solution. We previously used this type of resin for the immobilization of polysulfonated metalloporphyrins in the catalytic oxidations of diketones or hydrocarbons [5a,b]. However, in order to monitor the release of chloride ions during the catalytic degradation of TCP, an easy way to check its oxidative aromatic ring cleavage [3a], we decided to exchange the chloride ions of Amberlite IRA 900 for sulfate ions. Then, FePcS was immobilized onto this sulfate-Amberlite resin by shaking the polymeric material with a metallophthalocyanine solution (an acetonitrile/water mixture, 1:1, v/v) for 48 h at room temperature. The FePcS concentration of the solution was monitored by UV-vis spectroscopy and the amount of fixed catalyst (9 $\mu$mol of FePcS per g of sulfate-Amberlite) was indirectly calculated.

In order to check the catalytic activity of the supported catalyst, the following final concentrations were used (reaction volume = 8 mL): TCP = 10 mM (80 $\mu$mol), 182 mg of FePcS-Amberlite (1.6 $\mu$mol of FePcS, catalyst/substrate molar ratio = 2%), $H_2O_2$ or $KHSO_5 \cong 50$ mM, phosphate buffer (pH 7) = 125 mM. The supported catalyst and the oxidant were added to the acetonitrile/water mixture (1:3, v/v) containing the phenolic substrate. The consumption of TCP was monitored by HPLC and is depicted in figure 1 (table I, runs 1–3).

The consumptions of TCP after 4 min at room temperature were 87% and 65% with $KHSO_5$ and $H_2O_2$, respectively. The final substrate consumptions reached within 60 min were 94% with $KHSO_5$ (table I, run 1) and 96% with $H_2O_2$ (table I, run 2), the dechlorination values corresponded to 0.9 $Cl^-$ and 0.4 $Cl^-$ per disappeared TCP molecule, respectively. The third curve describes the control reaction without oxidant. 53% and 88% of the pollutant were adsorbed onto the ion-exchange resin within 4 min and 60 min, respectively (table I, run 3) and no free chloride ions were detected (indicating that all chloride ions were exchanged after the treatment with sulfate ions). The disappearance of TCP is probably due to the adsorption of the phenolate anion onto the cationic resin ($pK_a$ of TCP = 6.2 [6]).

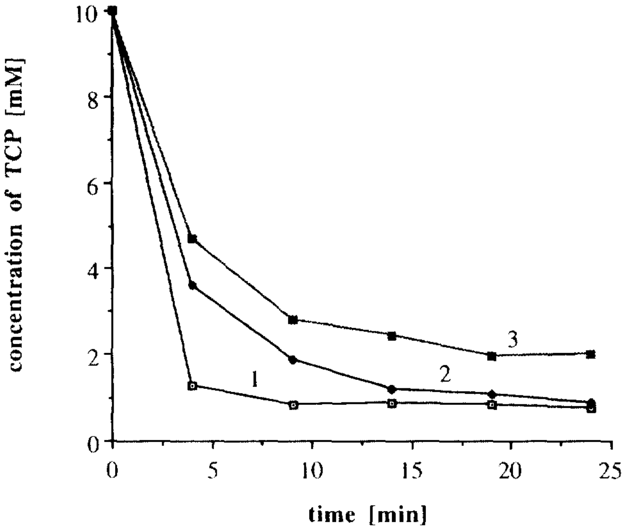


**Fig 1.** Oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by FePcS–Amberlite with $KHSO_5$ (**1**), $H_2O_2$ (**2**), control reaction without oxidant (**3**).

**Table I.** Oxidation of TCP catalyzed by FePcS–Amberlite at room temperature[a].

| *Run* | *Oxidant* | *Consumption of TCP after* | | | *Dechlorination*[b] |
|---|---|---|---|---|---|
| | | *4 min [%]* | *24 min [%]* | *60 min [%]* | |
| 1 | $KHSO_5$[c] | 87 | 93 | 94 | 0.8 (0.9) |
| 2 | $H_2O_2$[d] | 65 | 91 | 96 | 0.3 (0.4) |
| 3 | –[e] | 53 | 80 | 88 | 0 |
| 4 | $KHSO_5$[c,f] | 62 | 90 | 94 | 1.0 (1.1) |
| 5 | $H_2O_2$[d,f] | 44 | 76 | 83 | 0.2 (0.3) |
| 6 | –[e,f] | 44 | 74 | 82 | 0.2 (0.3) |

[a] The following final concentrations were used: [TCP] = 10 mM, [FePcS] = 0.2 mM, [phosphate buffer] = 125 mM (pH 7). [b] $Cl^-$ ions released after 60 min per initial TCP molecule; the data in parentheses correspond to the number of $Cl^-$ ions released per consumed TCP molecule. [c] $[KHSO_5]$ = 50 mM. [d] $[H_2O_2]$ = 57 mM. [e] Control reaction without oxidant. [f] The recycled catalyst was used.

The higher consumption of the pollutant in the presence of an oxidant and the detected amount of released chloride ions proved that the supported catalyst FePcS–Amberlite was able to oxidize TCP. Furthermore, the oxidation of the pollutant was significantly faster with $KHSO_5$ than with $H_2O_2$. However, the adsorption of the substrate competed with its catalytic oxidation and contributed to the disappearance of TCP from the liquid phase. The quantity of the adsorbed substrate during the catalytic reaction can not be easily determined, since the adsorption kinetics depend on the initial TCP concentration, which decreases during the catalytic oxidation reaction, but remains constant in the blank reaction.

Then we checked the activity of the recycled supported catalyst. After the first oxidations corresponding to runs 1 and 2 of table I, FePcS–Amberlite was removed by filtration, washed and dried overnight at room temperature. The catalyst was re-employed in a second reaction and the consumption of TCP was monitored (fig 2 and table I, runs 4–6).

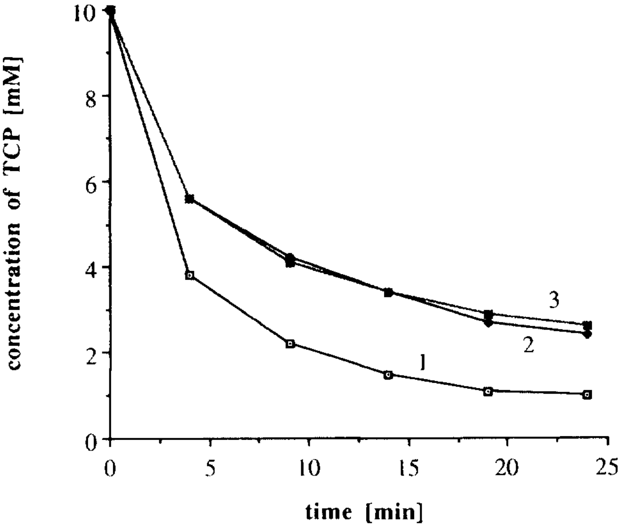


**Fig 2.** Oxidation of TCP catalyzed by recycled FePcS–Amberlite with $KHSO_5$ (**1**), $H_2O_2$ (**2**), control reaction without oxidant (**3**).

With $KHSO_5$ as oxidant, 62% of TCP were consumed within 4 min after the addition of oxidant (table I, run 4). The final consumption of 94% was reached within 60 min and the dechlorination value was 1.1 $Cl^-$ per consumed TCP molecule. As shown in figure 2 (curves 2 and 3), no difference was observed between the consumption of TCP in the presence of $H_2O_2$ and without oxidant, respectively (table I, runs 5 and 6). The amount of chloride ions per consumed TCP molecule was 0.3 in both cases and is probably due to an exchange of chloride ions for phenolate ions onto the resin. The chloride ions have been adsorbed during the first oxidation reaction. *All these data clearly indicate that the catalytic activity is mainly masked by the easy adsorption of the phenolate form of TCP onto the cationic sites of the resin.*

In control experiments, both oxidants $H_2O_2$ and $KHSO_5$ were unable to convert TCP without soluble catalyst under homogeneous conditions. Also, the Amberlite resin without impregnated FePcS, which was previously saturated with TCP, did not catalyze the oxidation of the pollutant with $H_2O_2$, the TCP concentration was unchanged after 60 min and no chloride ions were detected. When using $KHSO_5$, a low conversion was observed: 20% within 60 min and 1.9 $Cl^-$ were released per converted TCP molecule. This slow conversion might be attributed to a small amount of transition metal ions present in the resin. Furthermore, we found that FePcS–Amberlite did not release chloride ions in the presence of $KHSO_5$, after chloride ions of the commercial resin have been exchanged for sulfate ions.

### *Catalytic oxidations of TCP using a TCP-saturated FePcS–Amberlite*

In order to avoid the adsorption problem during the catalytic reaction, we decided to saturate the free adsorption sites of the remaining cationic sites of FePcS–Amberlite. The order of affinity of mono- and divalent anions for cationic ion-exchange resins is as follows: phenolate > sulfate, hydrogenosulfate > chloride. This order is strongly supporting the saturation phenomenon of the resin by 2,4,6-trichlorophenolate (TCPA). Consequently, we performed the saturation of cationic sites of FePcS–Amberlite by treating this modified resin with an aqueous solution of TCP ([TCP] = 80 mM) at pH 8 obtained by a dropwise addition of a 10 M NaOH solution. The adsorption process was monitored by UV-vis spectroscopy of TCPA remaining in solution. The characteristic TCPA absorption band at 312 nm allowed us to determine the fixed amount of TCP as being equal to 1.3 mmol/g FePcS–Amberlite–TCP (ie, 250 mg of TCP per g of modified resin). Therefore in catalytic conditions when using 243 mg of FePcS–Amberlite–TCP, the amount of adsorbed TCP is 316 μmol and represents the 4-fold initial quantity of TCP used in a catalytic reaction (80 μmol). Before using the FePcS–Amberlite–TCP in a catalytic reaction, this modified resin was equilibrated with a 10 mM TCP solution identical to that one used in a catalytic reaction (see Experimental section).

The catalytic reactions were carried out under the same conditions as that ones described in table I. Considering the lower mass-content of FePcS after the saturation of the resin with TCP (6.8 μmol FePcS/g FePcS–Amberlite–TCP). 243 mg of FePcS–Amberlite–TCP were used for each catalytic run to obtain a 2% catalyst/substrate molar ratio.

- *Reactions with $KHSO_5$*

The disappearance of TCP in a catalytic reaction using $KHSO_5$ as oxidant was very fast, 84% of the pollutant were consumed within 4 min (table II, run 1). But the concentration of TCP increased in the liquid phase after 4 min and was 4 mM at 24 min and 6 mM at 60 min ('conversions' of 60% and 40%, respectively). This surprising result can be explained by the desorption of TCP from the resin during the catalytic reaction (fig 3, curve 1). The supported catalyst has been saturated to be in an equilibrium with a 10 mM TCP solution corresponding to the initial concentration of a catalytic reaction. But after 4 min of reaction time, the concentration of TCP in the reaction mixture was only 1.6 mM (corresponding to 84% of conversion) leading to the desorption of TCP from the resin. To verify this hypothesis, 243 mg of the supported catalyst impregnated with TCP by using a 10 mM TCP solution were added to a 1.5 mM TCP solution in the absence of oxidant in order to simulate the desorption phenomenon observed in run 1 (table II). The increase of TCP concentration in the liquid phase is illustrated by curve 2 of figure 3. The

**Table II.** Oxidation of TCP catalyzed by FePcS–Amberlite at room temperature[a].

| *Run* | *Oxidant* | *Disappearance of TCP after* | | | *Dechlorination*[b] |
|---|---|---|---|---|---|
| | | *4 min [%]* | *24 min [%]* | *60 min [%]* | |
| 1 | $KHSO_5$[c] | 84 | 60 | 40 | 3.1 (‘7.8’) |
| 2 | $H_2O_2$[d] | 9 | 22 | 27 | 0.5 (1.8) |
| 3 | $KHSO_5$[c,e] | 17 | 34 | 38 | 2.1 (‘5.4’) |
| 4 | $H_2O_2$[d,e] | 3 | 6 | 10 | 0 |
| 5 | –[f] | 2 | 28 | 44 | 0.8 (1.8) |
| 6 | –[g] | 17 | 22 | 22 | 0.1 (0.6) |

[a] The following final concentrations were used: [TCP] = 10 mM, [FePcS] = 0.2 mM, [phosphate buffer] = 125 mM (pH 7). [b] $Cl^-$ ions released after 60 min per initial TCP molecule; the data in parentheses correspond to the number of $Cl^-$ ions released per ‘consumed’ TCP molecule based on TCP ‘conversion’ after 60 min (see text for explanations for these nonsense values). [c] $[KHSO_5] = 50$ mM. [d] $[H_2O_2] = 57$ mM, addition in five aliquots at 0, 5, 10, 15 and 20 min of reaction time. [e] The recycled, resaturated catalyst was used. [f] Control reaction without oxidant using the recycled catalyst after a reaction with $KHSO_5$ (run 1). [g] Control reaction without oxidant using the recycled catalyst after a reaction with $H_2O_2$ (run 2).

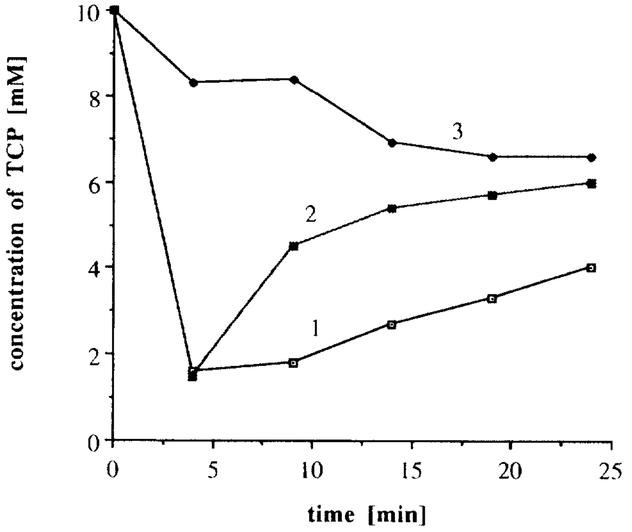


**Fig 3.** Oxidation of TCP catalyzed by TCP-saturated FePcS–Amberlite with $KHSO_5$: first reaction (**1**), control experiment (**2**), reaction with the recycled catalyst (**3**). Control reaction to monitor the desorption of TCP from a FePcS–Amberlite resin saturated with TCP similar to that used for run 1 of table II in the presence of a 1.5 mM TCP solution without oxidant.

slower increase in the presence of $KHSO_5$ (fig 3, curve 1) was due to the oxidation of desorbed TCP. The dechlorination value based on 40% of TCP conversion corresponded to ‘7.8’ released chloride ions per converted TCP molecule (table II, run 1), a nonsense value, which confirmed the hypothesis of TCP desorption being promoted by the rapid decrease in TCP concentration in the reaction mixture (in the case of $H_2O_2$, a negligeable desorption was observed, since the catalytic oxidation of TCP with this oxidant was slower). As already noted, the adsorption–desorption equilibrium is influenced by the TCP concentration *and* the solvent mixture of the solution. The desorption is favoured at low TCP concentrations and at a high acetonitrile content. Therefore different reaction mixtures required special presaturated resins. Another additional parameter of the TCP adsorption–desorption equilibrium is the ionic strength of the solution. With a 50 mM $KHSO_5$ concentration in a 125 mM buffered solution, persulfate itself contributes to modify the ionic strength, which is not the case with hydrogen peroxide.

The adsorption–desorption status of the recycled catalyst after the reaction with $KHSO_5$ was checked in a 10 mM TCP solution before using it for the second oxidation reaction: 44% of the substrate were adsorbed within 1 h (table II, run 5). Therefore, the recycled catalyst was saturated again with a 10 mM TCP solution and the catalytic oxidation was repeated as described for run 1 (table II). Using the recycled and re-TCP-saturated catalyst (table II, run 3), 17% of TCP were consumed within 4 min and the final conversion of 38% was reached within 60 min (fig 3, curve 3). The dechlorination value based on 38% of converted substrate corresponded to ‘5.4’ $Cl^-$ per consumed TCP molecule, again a nonsense value, confirming that the authentic conversion of TCP should be higher than 38%, without being able to precise this value in the present experimental conditions. The use of a continous-flow reactor should be necessary to overcome this problem, but this is presently beyond the scope of the present study.

- *Reactions with $H_2O_2$*

In the presence of $H_2O_2$, 9% of TCP were converted within 4 min and the final TCP consumption of 27% was reached within 60 min at room temperature (table II, run 2). The dechlorination value of 1.8 chloride ions per consumed TCP molecule is in agreement with the observed conversion. The recycled catalyst after the reaction with $H_2O_2$ adsorbed 22% of TCP in a 10 mM TCP solution within 1 h (table II, run 6). Therefore, it was saturated again with a 10 mM TCP solution and the catalytic oxidation was repeated. The reaction catalyzed by a recycled FePcS–Amberlite–TCP led to 10% of conversion within 1 h, the amount of chloride ions released is lower than the detection limit of the analytical method (<0.15 $Cl^-$ per initial TCP molecule). It must be noted that higher substrate conversions were observed with monopersulfate compared to hydrogen peroxide, at least in the initial step of TCP oxidation, which involves an electron abstraction from the phenolate anion by a high-valent iron(V)-oxo species in the case of $KHSO_5$ or by an iron(IV)-oxo species (or an iron(III)-OOH) in the case of $H_2O_2$ [3a, d].

### *Oxidation products of TCP*

The main ring-cleavage product of the homogeneous oxidation of TCP catalyzed by FePcS has been previously identified as being chloromaleic acid [3a, b]. The oxidation products of heterogeneous catalysis with FePcS–Amberlite and hydrogen peroxide were analyzed and compared to the distribution of the products generated under homogeneous conditions.

In the first attempts, the reaction mixture was separated of the catalyst by filtration and treated with an organic solvent under acidic conditions to extract

**Table III.** Influence of the acetonitrile content on the oxidation of TCP with $H_2O_2$ catalyzed by FePcS–Amberlite–TCP of by FePcS in solution[a].

| *Run* | *Conditions* | *Content of acetonitrile [%]* | *Conversion*[b] *[%]* | *Concentration of chloride ions*[b] *[mM]* | *$Cl^-$ released per converted TCP molecule* |
|---|---|---|---|---|---|
| 1 | heterogeneous | 25 | 28 | 0.5 | (1.8) |
| 2 | heterogeneous | 0 | 28 | 0.4 | (1.4) |
| 3 | heterogeneous | 25 | 100 | 2.0 | (2.0) |
| 4 | homogeneous | 0 | 32 | 0.6 | (1.9) |

[a] The following final concentrations were used: [TCP] = 1 mM, [FePcS] = 0.02 mM, [$H_2O_2$] = 5 mM, [phosphate buffer] = 50 mM (pH 7). [b] Conversion and concentration of chloride ions after 60 min at room temperature.

the products (see [3a] for the initial report on this analytical method). Under these conditions, only traces of products and TCP were detected by NMR analysis, the major part of the TCP oxidation products being adsorbed on the resin. Therefore, we included the supported catalyst in the work-up. Consequently, the acidification was carried out using 6 M sulfuric acid saturated with $Na_2SO_4$. Since the sulfate ions have a high affinity for the cationic Amberlite, they should be able to replace the anionic adsorbed products (eg, carboxylic acids). Using this modified work-up, the oxidation products of TCP were analyzed after a heterogeneous catalytic reaction performed under the particular conditions described in the Experimental section. The catalyst FePcS–Amberlite was not pre-saturated by TCP to avoid the presence of a large excesss of TCP, which would have disturbed the NMR analyses of the TCP degradation products. After 1 h at room temperature, the $^1H$ NMR analysis of the reaction mixture indicated that 31% of the initial amount of TCP were identified as oxidation products: 23% of starting TCP were converted into coupling products and 8% into dicarboxylic acids (4% of chloromaleic, 2% of maleic and 2% of fumaric acid). 15% of the initial substrate were also detected. We checked in a control experiment that the yield of the extraction method was very high (90%) for the three $C_4$ diacids mentioned above. However the fact, that 54% of the engaged TCP were not recovered in this experiment, indicated that oxidation products other than the diacids were not removed from the resin during the extraction process.

The amount of ring-cleavage products is lower than that observed with FePcS under homogeneous conditions, but the presence of these $C_4$ diacids is a definitive evidence on the capacity of this supported catalytic system to cleave the aromatic ring of TCP, a pollutant recalcitrant towards oxidative degradation.

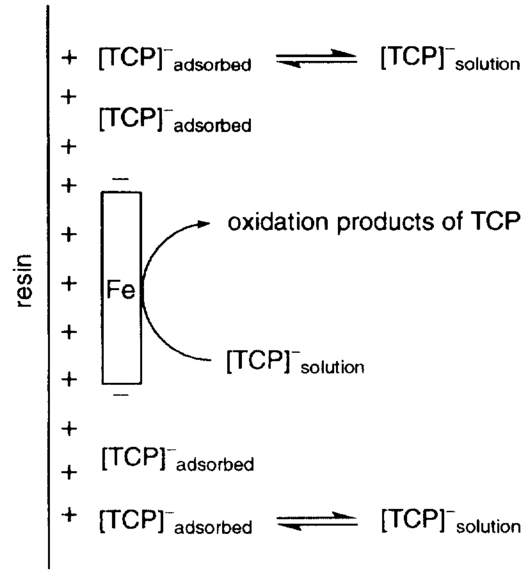
### *Influence of the acetonitrile content of the reaction mixture*

In a previous article [4], we reported the strong influence of different co-solvents in the reaction mixture on the conversion of TCP. An increased volume of acetonitrile in solution improved the catalytic oxidation of the pollutant. The key role of the organic co-solvent is to shift the dimers/monomers equilibria of the catalyst towards monomeric FePcS species, which are the efficient catalyst precursors. According to the working hypothesis, the co-solvent of the reaction mixture should not influence the conversion of TCP if monomeric species of the catalyst have been fixed onto the resin. In order to study the influence of the acetonitrile content, FePcS was fixed on the Amberlite resin using an acetonitrile/water mixture (1:1, v/v), since the absorption band at 668 nm showed the formation of monomeric FePcS species under these conditions [4].

The reaction mixture of a total volume of 8 mL contained the following final concentrations: 1 mM of TCP (8 $\mu$mol), 24 mg FePcS–Amberlite–TCP (0.16 $\mu$mol FePcS, catalyst/substrate molar ratio = 2%) and 5 mM of $H_2O_2$. As explained above, FePcS–Amberlite resins must be saturated by TCP before working with 1 mM TCP solutions. The supported catalysts were saturated with 1 mM aqueous TCP solutions containing 0% or 25% of acetonitrile (an increased acetonitrile content shifts the adsorption–desorption equilibrium towards desorption).

These two supported catalysts were used to oxidize TCP under two different conditions: with 25% of acetonitrile (table III, run 1) and without acetonitrile (table III, run 2) and the conversion of TCP was 28% within 60 min in both cases. The corresponding chloride ion concentrations of the final solutions were 0.5 and 0.4 mM, corresponding to 1.8 and 1.4 released chloride ions per converted TCP molecule. For comparison, two reactions were carried out under homogeneous conditions (table III, runs 3 and 4). The polychlorinated phenol was degraded completely within 60 min using 25% of acetonitrile (table III, run 3), but the conversion decreased to 32% without acetonitrile (table III, run 4). The final $Cl^-$ concentrations were 2 mM and 0.6 mM, respectively.

Whereas the content of acetonitrile has a crucial influence on the catalytic activity of FePcS under homogeneous conditions, it must be noted that the presence of acetonitrile does not influence the catalytic oxidation of TCP when using the supported catalyst. The oxidation of TCP was slower under heterogeneous conditions, since kinetics of the substrate oxidation are lowered by mass transport effects and interface interactions. In addition kinetics will be complicated during the catalytic reaction by exchanges of substrate molecules and oxidation products in solution for TCP molecules adsorbed on the support (scheme 2).



**Scheme 2.** Interface interactions of TCP molecules in solution with the TCP-saturated supported catalyst (FePcS–Amberlite–TCP). 2,4,6-Trichlorophenol is present as phenolate at pH 7.

## Conclusion

The use of cationic ion-exchange resins to support the tetrasulfonated iron-phthalocyanine is leading to a somewhat complicated system with a strong dependence of the TCP adsorption–desorption phenomenon competing with the heterogeneous catalytic reaction. Consequently the data published in a preliminary communication must be considered as reflecting mainly the adsorption of the substrate onto the resin and a limited oxidative degradation of TCP, which has been proved when using the supported catalyst and a $C^{14}$-labeled molecule [5d, 3b]. However, the present results obtained with a supported catalyst pre-impregnated with TCP demonstrated that FePcS is able to catalyze the oxidation and the ring cleavage of TCP. This result is encouraging and confort the fact that immobilization of FePcS onto a support is the route to create a new generation of iron-phthalocyanine catalysts able to catalyze the oxidation of recalcitrant molecules in water solution without any addition of an organic solvent to avoid the formation of inactive dimeric complexes.

## Experimental section

The conversion of TCP was monitored by HPLC (Waters) equipped with a μ-Bondapak C18 column, a methanol/phosphate buffer mixture (7:3, v/v; 50 mM phosphate buffer at pH 5 acidified to pH 4 with orthophosphoric acid) and detection at 294 nm. The UV-vis absorption spectra were recorded on a Hewlett Packard 8452A spectrophotometer. $^1H$ NMR spectra were obtained on a Bruker AM 250 MHz spectrometer. The ion-exchange resin Amberlite IRA 900 was purchased from Aldrich (Lot-No 02420JV). 2,4,6-Trichlorophenol was obtained from Janssen and hydrogen peroxide was supplied from Acros as a 35 wt% solution. Curox® ($2\,KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$) was a gift from Peroxid Chemie GmbH. All solvents used were of analytical grade and milliQ-water was always used to prepare aqueous solutions. Iron tetrasulfophthalocyanine (FePcS) was prepared according to previously published modifications of the method of Weber and Busch [4, 7] and chloride ion concentrations were determined by the mercuric thiocyanate method [8]. All catalytic reactions were performed at room temperature.

### *Catalytic behavior of FePcS–Amberlite in relation with the substrate adsorption*

- *Exchange of chloride ions of Amberlite for sulfate ions*

31 mmol (10 g) of $Na_2SO_4 \cdot 10\,H_2O$ (Prolabo) were dissolved in 50 mL of water. After addition of 5 g Amberlite, the solution was shaked for 7 h. The resin was filtered and washed twice with 20 mL of water. This process was repeated four times and the resin was then dried at 54 °C for 48 h. To check the completeness of the anion exchange, 20–30 mg of Amberlite were added to 1 mL of a solution prepared according to the reaction mixture for run 2 of table I, no release of chloride ions was detected within 1 h.

- *Immobilization of FePcS*

9 μmol (10 mg, $M_{FePcS} = 1101$, calculated for $C_{32}H_{13}N_8FeNa_4O_{13}S_4 \cdot 4\,H_2O$) of FePcS were dissolved in 20 mL of water. 20 mL of acetonitrile were added and the solution was shaked for 1 h to adjust the equilibria of different FePcS species. Before adding 1 g of anion-exchanged resin, the UV-vis spectrum of the initial FePcS solution was recorded ($A_{636\,nm} = 1.2$, $A_{668\,nm} = 1.0$ for a 10-fold dilution). The mixture was shaked carefully for four days to fix FePcS onto the Amberlite resin. The adsorption was monitored by UV-vis spectroscopy and the fixed amount of FePcS calculated indirectly. The supported catalyst was filtered, washed four times with 5 mL of an acetonitrile/water mixture (1:1, v/v) and dried at 54 °C for 48 h. The content of FePcS on the resin was calculated to be 9 μmol FePcS per g of FePcS–Amberlite (10 mg FePcS per g of FePcS–Amberlite).

- *Oxidations catalyzed by FePcS–Amberlite (table I)*

The reaction mixtures consisted of 80 μmol of 2,4,6-trichlorophenol (2 mL of a 40 mM stock solution in acetonitrile) and 1 mmol of phosphate buffer (2 mL of a 500 mM aqueous stock solution at pH 7).

When using $KHSO_5$ as oxidant (run 1), 2 mL of water were added to obtain a volume of 6 mL before the addition of $KHSO_5$. 400 μmol (123 mg) of Curox® were dissolved in 2 mL of water and added to the reaction mixture immediately after the addition of 1.6 μmol (182 mg) of FePcS–Amberlite.

When using $H_2O_2$ as oxidant (run 2), 4 mL of water were added to adjust the final volume to 8 mL. 460 μmol (40 μL of a 35 wt% $H_2O_2$ solution) of $H_2O_2$ were added immediately after the addition of 1.6 μmol (182 mg) of FePcS–Amberlite. In both cases, the reaction mixtures were stirred at room temperature, the catalyst was filtered at 60 min of reaction time, washed with water and dried overnight at room temperature. The experimental procedures of the oxidations using the recycled catalysts (runs 4 and 5) were the same as for runs 1 and 2. Aliquots of the reaction mixture were taken at defined time, diluted with a methanol/buffer mixture (eluent) to stop the oxidation reaction and analyzed by HPLC.

- *Control reactions*

To carry out the blank reactions without catalyst under homogeneous conditions, the reaction mixtures consisted of 80 μmol of 2,4,6-trichlorophenol (2 mL of a 40 mM stock solution in acetonitrile) and 1 mmol of phosphate buffer (2 mL of a 500 mM aqueous stock solution at pH 7).

When using $KHSO_5$ as oxidant, 2 mL of water were added to obtain a volume of 6 mL before the addition of $KHSO_5$. 400 $\mu$mol (123 mg) of Curox® were dissolved in 2 mL of water and added to the reaction mixture. When using $H_2O_2$ as oxidant, 4 mL of water were added to adjust the final volume to 8 mL. 460 $\mu$mol (40 $\mu$L of a 35 wt% $H_2O_2$ solution) of $H_2O_2$ were added to the reaction mixture.

In order to prepare the TCP-saturated Amberlite for blank reactions without catalyst in heterogeneous conditions, 2.7 mmol (530 mg) of TCP were dissolved in 20 mL of acetonitrile. 20 mL of water were added and the resulting solution ([TCP] = 67 mM) basified to pH 8 with a 10 M NaOH solution. 511 mg of Amberlite resin, the chloride ions of which have been previously exchanged for sulfate ions, were added to the TCP solution and the mixture shaked carefully. The adsorption was monitored by UV-vis spectroscopy and the characteristic absorption band of 2,4,6-trichlorophenolate at 312 nm allowed us to calculate the fixed amount of TCP. The adsorption–desorption equilibrium was reached within 14 h, afterwards the saturated resin was filtered, washed four times with an acetonitrile/water mixture (1:1, v/v) to leave the excess of TCP and dried for 3 days at room temperature. 900 $\mu$mol (178 mg) of TCP were adsorbed onto Amberlite corresponding to 1.3 mmol TCP/g Amberlite-TCP (257 mg TCP/g Amberlite-TCP). The TCP content has been calculated for 690 mg of saturated resin at the end of the work-up. The reaction procedures for the blank reactions were the same as for runs 1 and 2 (table I) described above, 240 mg of TCP–Amberlite were added to the reaction mixture before the addition of $H_2O_2$ or $KHSO_5$.

### *Catalytic oxidations of TCP using a TCP-saturated FePcS–Amberlite*

- *Preparation of FePcS–Amberlite–TCP*

3.2 mmol (630 mg) of TCP were dissolved in 20 mL of acetonitrile and 20 mL of water were added. The resulting solution ([TCP] = 80 mM) was basified to pH 8 with a 10 M NaOH solution before the addition of 600 mg FePcS–Amberlite. The work-up corresponded to that of the preparation of Amberlite–TCP described above. One mmole (197.5 mg) of TCP was adsorbed on FePcS–Amberlite corresponding to 1.3 mmol TCP/g FePcS–Amberlite–TCP (257 mg TCP/g FePcS–Amberlite–TCP). The content of FePcS on the resin was 6.8 $\mu$mol FePcS/g FePcS–Amberlite–TCP (7.5 mg FePcS/g FePcS–Amberlite–TCP) after the saturation by TCP. The contents given were based on 790 mg of the supported saturated catalyst at the end of preparation.

The adsorption–desorption behaviour in experimental conditions was tested before using FePcS–Amberlite–TCP. 240 mg of FePcS–Amberlite–TCP (1.6 $\mu$mol FePcS) were added to the reaction mixture prepared according to run 2 of table I and stirred at room temperature. The increase in TCP concentration of the solution was 4% ([TCP] = 10.4 mM) at 60 min. The increase or decrease in TCP concentration is highly dependent on the fixed amount of TCP on the supported catalyst and varied from one preparation to another. When the increase was higher and could not be ignored, the supported catalyst was filtered and the control reaction repeated to attain an adsorption–desorption equilibrium of TCP in a 10 mM TCP solution.

- *Oxidations catalyzed by FePcS–Amberlite–TCP (table II)*

The reaction procedures for runs 1 and 2 (table II) were the same as for runs 1 and 2 (table I) described above. Instead of 182 mg FePcS–Amberlite, 240 mg of FePcS–Amberlite–TCP (corresponding to 1.6 $\mu$mol FePcS) were added. The experimental conditions of oxidations catalyzed by recycled FePcS–Amberlite–TCP (runs 3 and 4) corresponded to those of runs 1 and 2.

- *Control reactions (table II)*

To check the desorption of TCP from FePcS–Amberlite–TCP in a 1.5 mM solution of TCP, the reaction mixture was prepared as described above for run 2 of table I. Instead of 80 $\mu$mol of TCP (2 mL of a 40 mM stock solution in acetonitrile), 12 $\mu$mol of TCP (300 $\mu$L of a 40 mM stock solution in acetonitrile) and 1.7 mL of acetonitrile were added to give a final mixture being 1.5 mM of TCP.

The control experiments were carried out with the recycled catalysts (runs 5 and 6). The reaction mixtures were prepared according to run 2 of table I, no oxidant was added. The re-saturation of the recycled catalyst by TCP was repeated as described above until the adsorption–desorption equilibrium of TCP was reached in a 10 mM TCP solution.

### *Oxidation products of TCP*

100 mL of reaction mixture consisted of 1 mmol (198 mg) of TCP (25 mL of a 40 mM stock solution in acetonitrile), 1.2 g of FePcS–Amberlite (30 $\mu$mol FePcS/g FePcS–Amberlite) and 250 mmol of phosphate buffer (50 mL of a 500 mM stock solution at pH 7). 5 × 1 mmol of $H_2O_2$ (corresponding to 5 × 100 $\mu$L of a 35 wt% aqueous solution) were added to the reaction medium within 20 min and the solution was stirred for 1 h at room temperature. The acetonitrile/water ratio of the reaction mixture was equal to 1:3 (v/v). Acetonitrile (at room temperature) and the residual water (by heating to 60 °C) were evaporated under vacuum, afterwards the residue was dried under vacuum for 1 h at room temperature. 14 mL of 6 M sulfuric acid, which was previously saturated by 20 g of $Na_2SO_4 \cdot 10\ H_2O$, were added to the residue and the acidic solution was stirred for 1 h to exchange the oxidation products adsorbed onto the resin for sulfate ions. 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 (DMSO-$d_6$) for $^1$H NMR analysis. We added 12 $\mu$L of $CHCl_3$ (149 $\mu$mol) as internal standard to quantify the oxidation products. The total yields of coupling products were based on two protons per aromatic ring.

### *Influence of the acetonitrile content of the reaction mixture (table III)*

The reaction mixture for run 1 (supported catalyst, 25% of acetonitrile) with a final volume of 8 mL contained 8 $\mu$mol of TCP (200 $\mu$L of a 40 mM stock solution in acetonitrile) and 400 $\mu$mol of phosphate buffer (800 $\mu$L of a 500 mM stock solution at pH 7). 1.8 mL of acetonitrile and 5.2 mL of water were added to obtain an acetonitrile/water ratio equal to 1:3 (v/v). 0.16 $\mu$mol of FePcS (corresponding to 24 mg FePcS–Amberlite–TCP) and 40 $\mu$mol of $H_2O_2$ corresponding to 40 $\mu$L of a 3.5 wt% $H_2O_2$ solution, which was prepared by 10-fold dilution of a commercial 35 wt% solution, were added to the reaction medium and stirred for 1 h at room temperature.

The reaction mixture for run 3 (homogeneous catalyst, 25% of acetonitrile) was prepared as for run 1 described above, the supported catalyst was replaced by 0.16 $\mu$mol of FePcS (400 $\mu$L of a 0.4 mM aqueous stock solution) and 4.8 mL of water were added (instead of 5.2 mL) to obtain the final reaction volume of 8 mL.

With respect to the low solubility of TCP in $H_2O$, 0.1 mmol (20 mg) of TCP were dissolved in 100 mL of a solution containing 5 mmol of phosphate buffer (pH 7) within 5–6 h in an ultrasound bath. To carry out the oxidation (run 2: heterogeneous catalyst, 0% of acetonitrile), 0.16 $\mu$mol of FePcS (corresponding to 24 mg FePcS–Amberlite–TCP) and 40 $\mu$mol of $H_2O_2$ (corresponding to 40 $\mu$L of a 3.5 wt% $H_2O_2$) solution were added to 8 mL of this solution and stirred for 1 h at room temperature. The reaction mixture for run 4 (homogeneous catalyst, 0% of acetonitrile) was prepared in the same way, 0.1 mmol (20 mg) of TCP were dissolved in 100 mL of a solution containing 2 $\mu$mol of FePcS and 5 mmol of phosphate buffer (pH 7) within 5–6 h in an ultrasound bath. 40 $\mu$mol of $H_2O_2$ (corresponding to 40 $\mu$L of a 3.5 wt% $H_2O_2$) solution were added to 8 mL of this solution and stirred for 1 h at room temperature.

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