Hydrogen peroxide oxidation of 2-chlorophenol and 2,4,5-trichlorophenol catalyzed by monomeric and aggregated cobalt tetrasulfophthalocyanine

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Abstract

Cobalt tetrasulfophthalocyanine (CoTSPc) was used to catalyze the oxidation of 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (TCP) using hydrogen peroxide (H_2O_2) as the oxidant. This CoTSPc catalyzed hydrogen peroxide oxidation of chlorophenols resulted in the formation of different types of oxidation products depending on the solvent conditions. In water/methanol conditions (where CoTSPc is mainly monomeric, and unionized forms of the phenols), phenol and hydroquinone were the main oxidation products, while in phosphate buffer solutions (pH 7 and 10 for TCP and 2-CP, respectively, where CoTSPc is mainly aggregated, and ionized forms of the phenols), benzoquinone was the main product. In contrast to CoTSPc, other MTSPc complexes studied (AlTSPc, CuTSPc and NiTSPc) exhibited no detectable catalytic effect on the oxidation of chlorophenols under the experimental conditions employed, thus proving the effect of the central metal ions on efficient catalysis of chlorophenol. Reaction pathways are proposed based on the relative time of oxidation products formation.
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1. Introduction

Chlorinated organic compounds such as 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (TCP) are well known recalcitrant pollutants, despite their useful applications as pesticides, lubricants and solvents [1]. Polychlorinated aromatics in particular are resistant to biotransformation in the environment to less harmful analogues, and the toxicity and resistance to degradation of chlorinated organic compounds increases with the number of halogen substituents [2–5]. Efficient chemical catalysts are needed to convert chlorinated phenols to more biodegradable molecules. Complete degradation to carbon dioxide (CO_2) is desirable. It is also desirable that the catalyst is active but does not completely self-destruct through oxidation.

Some metallophthalocyanine (MPc) complexes are important industrial dyes hence readily available. MPc complexes containing electroactive central metals are preferred catalysts

for the oxidation of chlorophenols since these complexes have a wide range of readily available oxidation states. Iron and manganese tetrasulfophthalocyanines complexes have been extensively studied as biomimetic catalysts for the oxidation of chlorophenols in the presence of an environmentally clean hydrogen peroxide (H_2O_2) oxidant [6–12]. Cobalt tetrasulfophthalocyanine (CoTSPc) has however, not been explored for the catalytic oxidation of chlorophenols, even though it is produced industrially in large amounts as a catalyst for the oxidation of mercaptans in gasoline fraction [13–16]. CoPc complexes have rich redox chemistry and, because of their high catalytic activities, have been more widely employed in electrocatalytic reactions than their FePc or MnPc counterparts. It is surprising therefore that, up to date, there have been no detailed literature reports on the catalytic oxidation of chlorinated phenols by any CoPc complex. FeTSPc and MnTSPc catalysts exist as μ-oxo dimers, which have to undergo cleavage before the formation of the active form of the catalysts. CoTSPc on the other hand does not form μ-oxo dimers. For MPc catalyzed reactions, the nature of the catalyst would be dependent on the nature of the
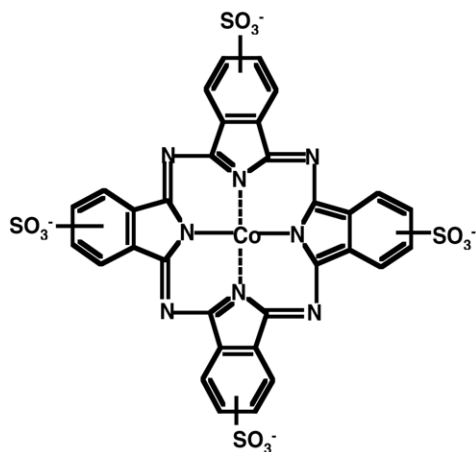

Fig. 1. Molecular structure of cobalt tetrasulfophthalocyanine.

central metal, since the catalytic process is mediated by axial ligation of the substrate or oxidation intermediates. This work thus reports on the use of CoTSPc (Fig. 1) catalyst for the hydrogen peroxide oxidation of 2-chlorophenol (2-CP) and 2,4,5-trichlorophenol (TCP). Since tetrasulfometallophthalocyanine (MTSPc) complexes readily form inactive aggregates it is necessary to add an organic solvent to the reaction mixture or to disperse the catalysts onto supports [9]. The addition of organic co-solvent would seriously limit MPc application in water treatment, thus it is necessary to work in water as a sole solvent. However, for a good understanding of the reactivities of CoTSPc in water and water with organic co-solvent, this work employed a mixture of water and methanol as well as water as sole solvent for the catalytic processes. The fate of the CoTSPc catalyst was monitored by ultraviolet-visible (UV–vis) spectroscopy.

2. Experimental

2.1. Materials

Cobalt (CoTSPc), aluminium (AlTSPc), copper (CuT-SPc) and nickel (NiTSPc) tetrasulfophthalocyanine complexes were synthesized, purified and characterized according to the procedure of Weber and Busch [17].

Phenol, dichlorobenzoquinone (DCBQ, Aldrich), benzoquinone (BQ, Aldrich), hydroquinone (HQ, May and Baker), phenol (PH, SAARChem) and maleic acid (MA, SAARChem), were of reagent grade and were used as standards for high performance liquid chromatography (HPLC) studies. The oxidant, hydrogen peroxide, and the substrates: 2,4,5-trichlorophenol (TCP) and 2-chlorophenol (2-CP) were obtained from Aldrich and used as received. Millipore water was used to prepare all the solutions. Water containing 60% methanol (v/v) (pH 3.4) or phosphate buffers (pH = 7 and pH = 10) were used to prepare all the solutions.

2.2. Catalytic studies

The reaction mixtures containing 1.0×10^{-2} mol/l of substrate (2-CP or TCP), 1.0×10^{-2} mol/l of the oxidant (hydrogen peroxide) and the catalyst was employed. Various amounts of the CoTSPc catalyst (0.1–2.5% of the total mixture) were employed in order to determine the optimal catalyst loading. Substrates conversions were monitored by HPLC, using the Quad-Gradient HPLC system, Agilent 1100 series fitted with an analytical column, μ Bondapak C18 (390 × 3.00 mm) and connected to a variable wavelength UV–vis detector (set at λ = 280 nm). The mobile phase comprised of 70:30 methanol:water mixture, with a flow rate of 1 ml/min. The sample injection volume was 20 μl. The separation of the substrates and the products was achieved within 9 min for TCP and 4 min for 2-CP. The oxidation products were identified by spiking using standards and by retention times in HPLC traces. The nature of some of the products was further confirmed by mass to charge ratios of molecular ion peaks and fragmentation patterns as obtained from a liquid chromatograph connected to a mass spectrometer (LC–MS). Mass spectra were recorded with Finnigan LCQ–MS coupled with μ Bondapak C18 (390 × 3.00 mm diameter). The UV–vis absorption spectra of the catalyst were monitored at regular intervals during the reaction. Electronic absorption spectra were recorded with a Cary 500 UV/Vis/NIR spectrophotometer. For the purpose of studying the effect of the central metal of the catalyst, AlTSPc, CuT-SPc and NiTSPc were also employed as catalysts, using 1% catalyst loading. The degradation reactions were monitored for 5 h.

3. Result and discussion

3.1. Catalyst: loading and spectral characterization

MTSPc complexes are in general known to exist as dimers in equilibrium with monomers in aqueous solutions. Their UV–vis spectra thus consists of two peaks in the Q band region. The lower energy absorption band near 670 nm is associated with the monomeric species while the high-energy absorption band near 620 nm is due to the dimeric species. In the presence of organic solvents, MTSPc complexes show monomeric behaviour. Fig. 2 shows the spectra of CoTSPc in water/methanol, pH 7 and pH 10 solutions. The presence of aggregates is evident under pH 7 and pH 10 conditions, as seen by a clear split in the Q band in the former and a broadened Q band in the latter. Thus Fig. 2 shows that aggregation of the CoTSPc decreases as follows: water/methanol > pH 10 buffer > pH 7 buffer. The catalytic behaviour of CoTSPc towards the oxidation of TCP and 2-CP was studied in water/methanol and also under the different pH conditions. pHs 7 (for TCP) and 10 (for 2-CP) were so chosen because the pK_a values of 2-CP and TCP are 8.55 and 6.23, respectively [18].
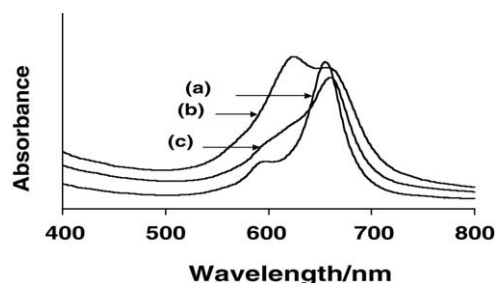
Fig. 2. Electronic absorption spectra of CoTSPc in (a) water/methanol; (b) pH 7; and (c) pH 10. [CoTSPc] $\sim 1 \times 10^{-6}$ mol/l.

The concentration of the oxidant chosen in this work (1×10^{-2} mol/l) was found to effect the least destruction of the catalyst. The optimum amount of catalyst needed for the maximum conversion of the substrates was determined in water/methanol solvent mixture, after 5 h reaction time, Fig. 3. The results indicate that the catalytic conversion of the chlorophenols, under the experimental conditions employed here, is highly dependent on the CoTSPc loading. Fig. 3 shows that the maximum conversion of the 2-CP and TCP to products in water/methanol conditions were approximately 81 and 67%, respectively, at 1% CoTSPc loading. Hence, all subsequent experiments were performed at 1% CoTSPc loading. As stated in the introduction, it is well established that the chlorophenols resist oxidative degradation and this resistance increases with the number of halogen substituents [2–4,18,19]. The lower conversion rate of the TCP, compared to the 2-CP, could therefore be attributed to the difficulty in catalytic oxidation of polychlorinated phenols compared to their unchlorinated and monochlorinated derivatives.

3.2. Effects of pH

Changes in the HPLC peak area of the substrates during the oxidative catalysis were monitored at the three different experimental conditions for a 5 h period. Fig. 4 shows the variation of substrate concentrations, 2-CP and TCP with time, in the absence and presence of the CoTSPc catalyst (0.5% catalyst loading was employed in this case), using the water/methanol solvent mixture. In the absence of the catalyst
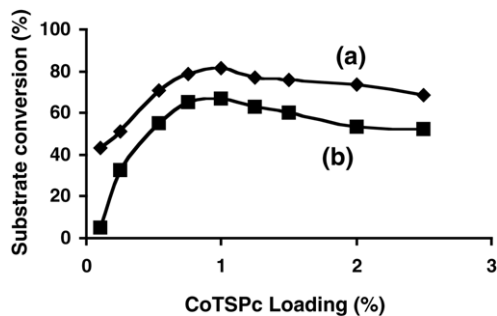

Fig. 3. Effect of catalyst loading on the conversion of (a) 2-CP and (b) TCP water/methanol. [Hydrogen peroxide] = 1×10^{-2} mol/l. Starting concentration of the phenols = 1×10^{-2} mol/l.
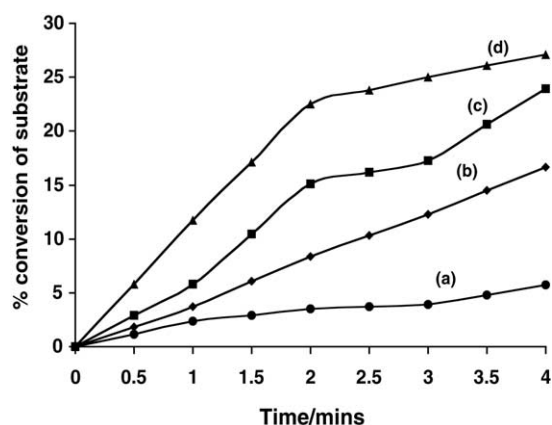

Fig. 4. Percent conversion of substrate vs. time for the H_2O_2 oxidized and CoTSPc catalyzed oxidation of TCP (a) and 2-CP (b) without catalyst, and TCP (c) and CP (d) with CoTSPc catalyst. [CoTSPc] = 0.5% loading; $H_2O_2 = 10^{-2}$ mol/l. Solvent = water/methanol. Starting concentration of the phenols = 1×10^{-2} mol/l.

(Fig. 4a and b), oxidative transformation of the chlorophenols was observed, but much less than in the presence (Fig. 4c and d) of the catalyst. The kinetic plots in Fig. 4 show that the ratio of the slopes (2-CP:TCP) in the first two hours was 1.5 in the presence of the CoTSPc catalyst. This result once again shows the difficulty in the oxidation of polychlorophenols compared to the monochlorophenols. Kinetic curves that are similar to those shown in Fig. 4, were also observed at pH 7 for TCP and pH 10 for 2-CP. Comparative kinetic plots of the conversion of the substrates at different pH conditions (water/methanol (pH 3.4), and pH 7 and 10 for TCP and 2-CP, respectively) at 1% catalyst loading are shown in Fig. 5. The percent conversion is lower in water/methanol for both 2-CP and TCP. From the pK_a values of the chorophenols, there are two species with different properties, which are in equilibrium in 2-CP or TCP solutions; these are the undissociated phenol (PhOH; below their pK_a values) and phenoxide ion (PhO⁻ above their pK_a values [18]. Since the equilibrium between these two forms is pH dependent, chemical transformations involving these compounds should be pH-dependent as well. The enhanced catalytic conversion of the substrates at pH 7 and pH 10, clearly reflect the significant contribution of the ionized forms of chlorophenols. It is interesting to see an appreciable degree of catalysis under the acid water/methanol conditions, Fig. 5a and b, curves (ii). For TCP (Fig. 5b, curve i), while catalysis is completed within the first one hour at pH 7.0 buffer solution, catalysis continues for several hours (>5 h) in water/methanol mixture (Fig. 5b, curve ii). This behaviour is possibly due to the enhanced solubility of the chlorophenols in co-organic solvent environment as well as the less aggregated conditions of the catalyst as shown in Fig. 2.

Fig. 6 shows the HPLC traces obtained for the catalysis of 2-CP and TCP by H_2O_2 in the presence of CoTSPc catalyst under water/methanol conditions and after 5 h reaction time. New peaks started to emerge after about 60 min of reaction
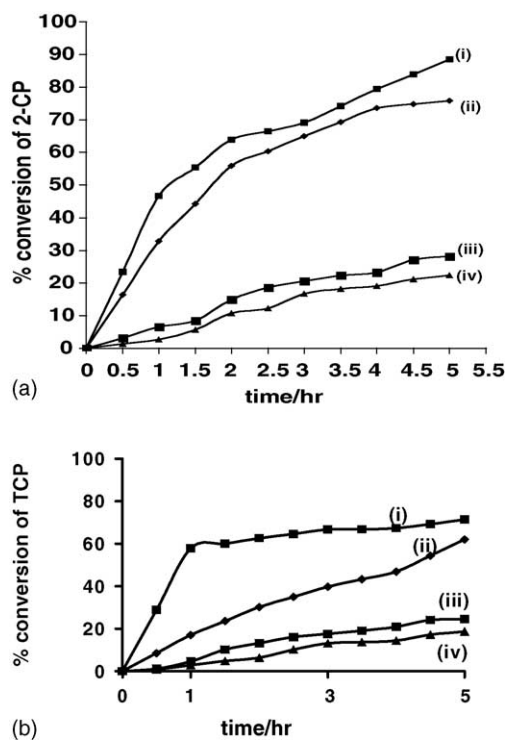
Fig. 5. (a) Effect of pH on the rate of oxidative degradation of 2-CP in pH 10 (curve i) and water/methanol (curve ii) in the presence of CoTSPc. Curves iii (pH 10) and curve iv (water/methanol) are in the absence of the CoT-SPc catalyst (1% loading). Starting concentration of 2-CP = 1×10^{-2} mol/l. [H_2O_2] = 1×10^{-2} mol/l. (b) Effect of pH on the rate of oxidative degradation of TCP in pH 7 (curve i) and water/methanol (curve ii) in the presence of CoTSPc. Curves iii (pH 7) and curve iv (water/methanol) are in the absence of the CoTSPc catalyst. Starting concentration of TCP = 1×10^{-2} mol/l. [H_2O_2] = 1×10^{-2} mol/l.
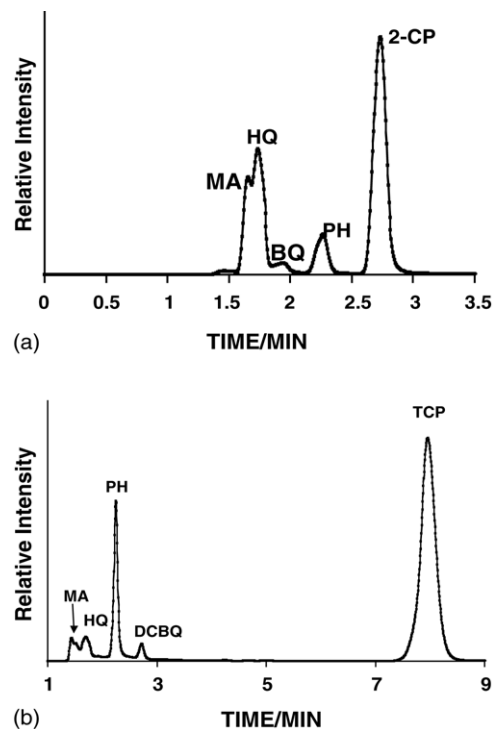

Fig. 6. (a) HPLC traces obtained after 5 h of transformation of 2-chlorophenol in water/methanol mixture. Starting concentration of 2-CP = 1×10^{-2} mol/l. [H_2O_2] = 1×10^{-2} mol/l. Catalyst: CoTSPc (2%). (b) HPLC traces obtained after 5 h of transformation of 2,4,5-trichlorophenol in water/methanol mixture. Starting concentration of TCP = 1×10^{-2} mol/l. [H_2O_2] = 1×10^{-2} mol/l. Catalyst: CoTSPc (2%).

for both 2-CP and TCP. The peaks were clearly identified using HPLC by spiking with pure compounds and with LC-MS. For 2-CP the products are hydroquinone (HQ), phenol (PH), benzoquinone (BQ) and maleic acid (MA), Fig. 6(a). The intensity of the product peaks increased with time while that of the parent 2-CP peak decreased. The formation of maleic acid is an indication that the catalytic oxidative degradation of these substrates included ring cleavages. For TCP, peaks due to dichlorobenzoquinone (DCBQ), hydroquinone (HQ), phenol (PH) and maleic acid (MA) were observed, Fig. 6(b). The first step when FeTSPc [8] and iron octacarboxyphthalo-cyanine [20] were employed as catalysts for hydrogen peroxide oxidation of TCP was reported to be the formation of dichlorobenzoquinone, which subsequently transformed to the formic acid, oxalic acid, 3-chloro-2-propenoic acid, dichloroacetate, and a small amount of oxidative coupling products [20]. In this work, however, it was observed that for TCP, after about 180 min of reaction, the phenol (PH) peak was formed and increased in intensity accompanied by a reduction in the peak intensity of the dichlorobenzo-quinone. We attribute this behaviour to the transformation of dichlorobenzoquinone to mostly phenol and possibly other oxidative products.

Fig. 7 shows the chromatograms of the 2-CP and TCP degradation respectively after 5 h, under pH 10 and 7 conditions, respectively. The products formed under pH 7 and 10 conditions were different from those formed when methanol/water solvent mixture was employed. The main products of oxidation were benzoquinone (for 2-CP at pH 10, Fig. 7a) and 2,5-dichlorobenzoquinone (for TCP at pH 7, Fig. 7b). In both cases smaller amounts of maleic acid were formed. The formation of benzoquinone or dichlorobenzo-quinone is desirable since these molecules are readily degraded. Thus fewer products were formed under pH 7 and 10 conditions in contrast to a wider variety of products formed in water/methanol solvent mixture. In particular, phenol is not formed at high pH. This proves that the use of different solvents and/or solution pH (hence the presence of either ionized or unionized forms of the phenols) is a determining factor in the type of oxidation products obtained during MPc catalyzed oxidation of chlorophenols. The aggregated nature of CoTSPc under pH 7 and 10 conditions may also contribute to the different products compared to when the monomeric form in water/methanol is employed. However, addition of hydrogen peroxide to CoTSPc solutions in pH 7, resulted in the decrease in the intensity of the dimeric peak and the increase and shifting of the monomeric peak (Fig. 8a) showing that the aggregated form of CoTSPc is monomerised by hydrogen peroxide oxidant.
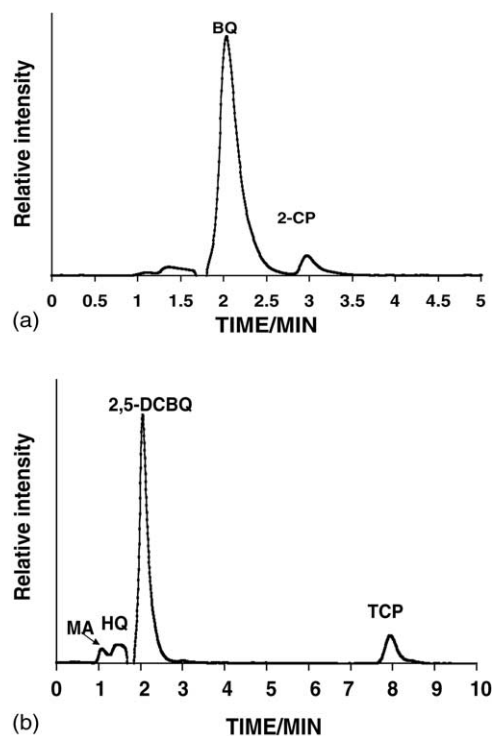
Fig. 7. (a) HPLC traces obtained after 5 h of transformation of 2,4,5-trichlorophenol in pH 7.0 buffer solution. Starting concentration of TCP $= 1 \times 10^{-2}$ mol/l. $[H_2O_2] = 1 \times 10^{-2}$ mol/l. Catalyst: CoTSPc (2%). (b) HPLC traces obtained after 5 h of transformation of 2-chlorophenol in pH 10.0 buffer solution. Starting concentration of 2-CP $= 1 \times 10^{-2}$ mol/l. $[H_2O_2] = 1 \times 10^{-2}$ mol/l. Catalyst: CoTSPc (2%).

Spectral studies on the fate of the CoTSPc catalyst during the catalytic reaction were undertaken in water/methanol solvent mixture. Addition of hydrogen peroxide to solutions of CoTSPc, resulted in spectral changes shown in Fig. 8b. There was a shift in the Q band from 660 to 665 nm, an increase in absorption in the 480 nm area, as well as decrease in the intensity of the Q band. The shift in the Q band is consistent with metal oxidation of Co^{II}TSPc to Co^{III}TSPc [21]. The broad peak around 480 nm suggests ring oxidation. Thus addition of hydrogen peroxide to solutions of CoTSPc resulted in both metal and ring oxidation of CoTSPc, accompanied by degradation of the ring. Addition of reducing agents (NaBH$_4$) to solution of Fig. 8b, (following oxidation with hydrogen peroxide) resulted in the decrease in 480 nm peak and a shift of the Q band back to 660 nm. Under pH 7 or pH 10 conditions as explained above, the monomer is formed first on addition of hydrogen peroxide, followed by a shift to longer wavelengths (662 to 666 nm, Fig. 8a) due to the oxidation of the central metal and the formation of the Co^{III}TSPc species. In the presence of CP or TCP, spectral changes shown in Fig. 8c were observed when using either methanol/water (Fig. 8b) or pH 7 (TCP) or pH 10 (2-CP) solutions. As catalysis progressed there was a gradual decrease in the intensity of the Q band of the CoTSPc catalyst, Fig. 8c, suggesting catalyst degradation as is typical [22] of MPc catalysts in homogeneous catalysis. There was an increase in background between 400 and
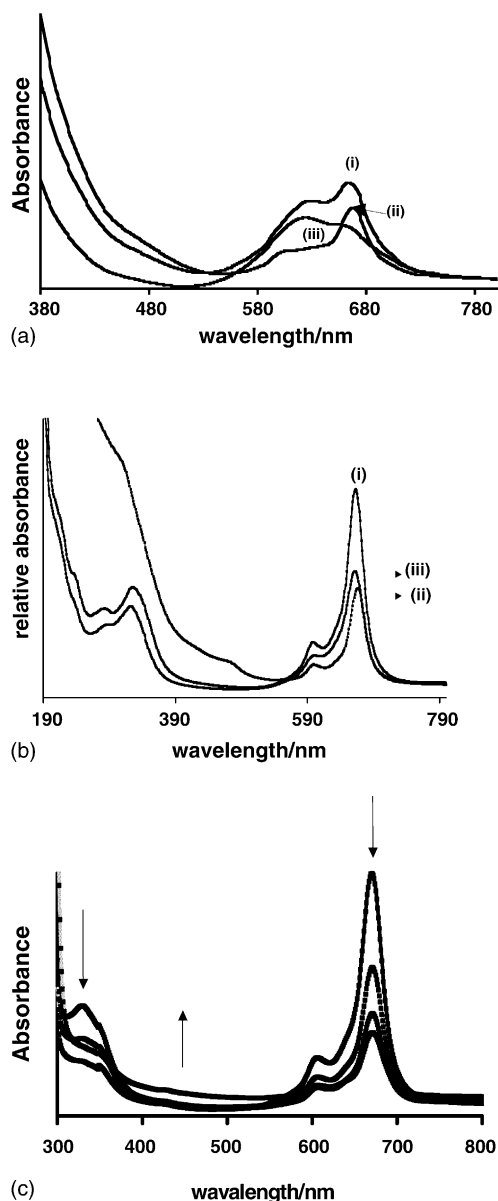

Fig. 8. (a) Electronic absorption spectra of CoTSPc in pH 7 (i) before, (ii) after addition of 0.02 M hydrogen peroxide, (iii) spectrum obtained on addition of NaBH$_4$ to (ii). (b) Electronic absorption spectra of CoTSPc in water/methanol solvent mixture (i) before, (ii) after addition of 0.02 M hydrogen peroxide, (iii) spectrum obtained on addition of NaBH$_4$ to (ii). (c) Electronic absorption spectral changes observed for CoTSPc in water/methanol solvent mixture as catalysis proceeds. Starting concentration of 2-CP $= 1 \times 10^{-2}$ mol/l. $[H_2O_2] = 1 \times 10^{-2}$ mol/l. Catalyst: CoTSPc (1%).

500 nm, which suggests the involvement ring-based oxidation of the phthalocyanine ring during the catalytic oxidation of the phenols. However the shift in the Q band observed in the presence of hydrogen peroxide alone was not observed when both hydrogen peroxide and the phenols were present. This suggests that the Co^{III}TSPc species is readily reduced back to the Co^{II}TSPc species through oxidation of the phenols. There was also a small increase in absorption in 350 nm region in Fig. 8c, due to the oxidation products of the phe-
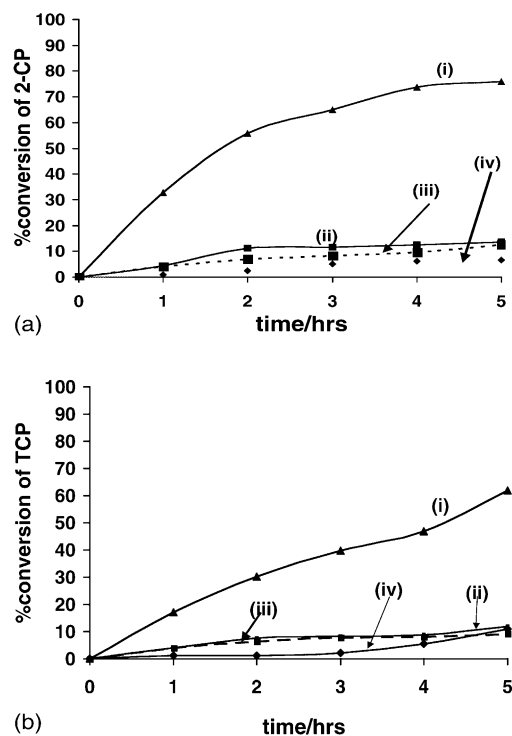
Fig. 9. (a) Comparative plots of percentage conversion of the 2-CP vs. time using (i) CoTSPc, (ii) NiTSPc (iii) CuTSPc and (iv) AlTSPc. MTSPc = ~10^{-4} mol/l; $H_2O_2 = 1 \times 10^{-2}$ mol/l. Starting concentration of 2-CP = 1×10^{-2} mol/l. (b) Comparative plots of percentage conversion of the TCP vs. time using (i) CoTSPc, (ii) NiTSPc (iii) AlTSPc and (iv) CuTSPc. MTSPc = ~10^{-4} mol/l; $H_2O_2 = 1 \times 10^{-2}$ mol/l. Starting concentration of TCP = 1×10^{-2} mol/l.

nols. The colour of the solution changed from blue to green to colourless as catalysis progressed. However, the reaction products continued to form even after the catalyst had turned colourless, suggesting that once reaction intermediates are formed, the reaction can still proceed in the presence or absence of the original form of the catalyst.

3.3. The effect of the central metal in MTSPc

It is known that the central metal ion of the MPc catalyst has significant influence on the catalytic activities. We carried out studies on other tetrasulfophthalocyanine complexes: NiTSPc, AlTSPc and CuTSPc, using similar experimental conditions as for CoTSPc. In contrast to CoTSPc, NiTSPc, CuTSPc and AlTSPc exhibited no measurable oxidative catalytic conversion of the chlorophenols investigated in this work (Fig. 9). The central Al and Cu metal ions in both AlTSPc and CuTSPc exist in only one oxidation state and hence cannot be oxidized. Surprisingly however, Seelan and Sinha [23] recently reported that when CuPc and CoPc were encapsulated in zeolite-Y, CuPc exhibited higher phenol hydroxylation activity with H_2O_2 than CoPc. The authors attributed this observation to the changes in molecular and electronic structures of the MPc complexes on encapsulation. We may
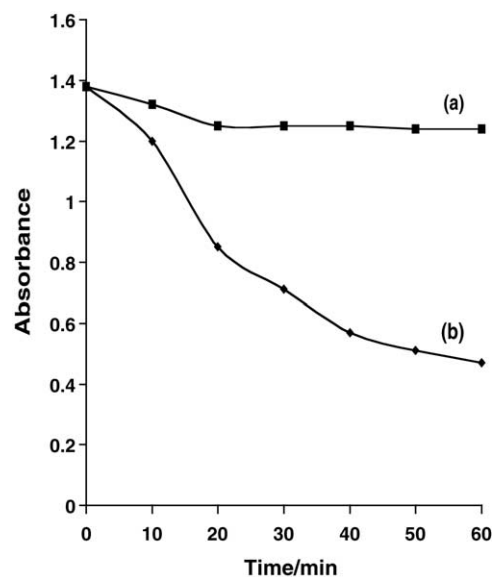

Fig. 10. Changes in the Q band absorption for (a) NiTSPc and (b) CoTSPc during catalysis for TCP oxidation by hydrogen peroxide. MTSPc = 1% loading; $H_2O_2 = 1 \times 10^{-2}$ mol/l. Starting concentration of TCP = 1×10^{-2} mol/l.

therefore conclude that the enhanced catalytic activity observed in this present work for CoTSPc over CuTSPc could partly be associated with the retention of the molecular and electronic structures of the MPc complexes in homogeneous catalysis for the former. There was no significant change in the intensity of the Q band for NiTSPc, CuTSPc and AlTSPc, contrary to the observation for CoTSPc, where the Q band decreased in intensity as the reactions proceeded (Fig. 8c). Fig. 10 compares the changes in absorbance of the CoTSPc and NiTSPc during the reaction.

The Ni central metal ion in NiTSPc could be oxidized from +2 to +3, although this has been a subject of some controversy [24–27]. Recent reports have shown that NiTSPc has electrocatalytic activity towards 2-CP [25] and hydrazine [24] in the solid state, when adsorbed onto the electrode. The Ni(III)/Ni(II) redox couple has however not been observed electrochemically in solution. The lack of catalytic activity for the hydrogen peroxide oxidation of chlorophenols could be due to the absence of Ni(III)/Ni(II) couple in solution. As with nickel porphyrin complexes [28], the Ni(III)/Ni(II) couple may occur in the solid state for NiPc complexes. NiPc complexes, like the main group MPcs (such as ZnPc and MgPc) whose metal ions have no accessible d-orbital levels lying in the HOMO–LUMO (LUMO = lowest unoccupied molecular orbital and HOMO = highest unoccupied molecular orbital) gap are redox-inactive with respect to their metal centers [29], this situation is probably different for adsorbed NiPc complexes.

3.4. Possible mechanism

Scheme 1a and b show the possible reaction pathways of transformation of 2-CP and TCP, respectively, under

$$Co^{II}TSPc \xrightarrow{H_2O_2} Co^{III}TSPc^1\text{-OOH} \qquad\qquad (1)$$
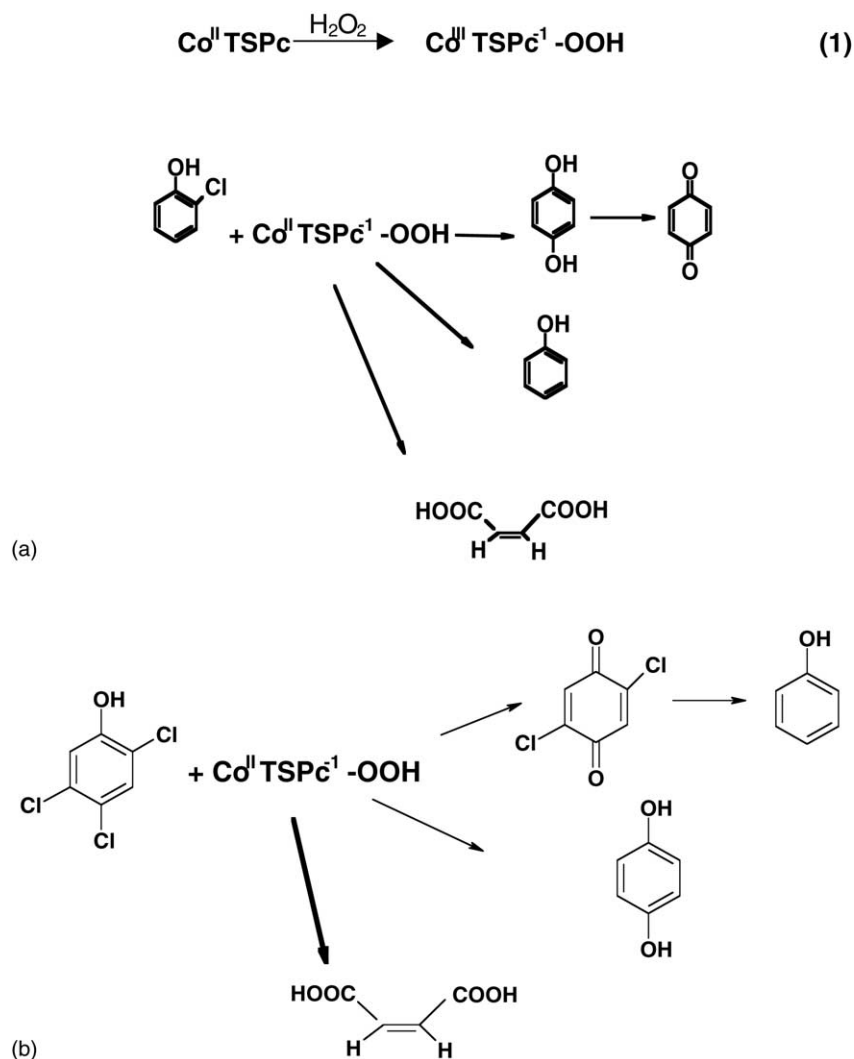
Scheme 1. (a) Proposed reaction pathways for the CoTSPc-catalyzed transformation of 2-chlorophenol using H_2O_2 oxidant; (b) proposed reaction pathways for the CoTSPc-catalyzed transformation of 2,4,5-trichlorophenol using H_2O_2 as oxidant.

methanol/water solvent conditions. Under these acidic conditions, the undissociated PhOH species is being oxidized, resulting in a wide variety of products. When pH 7 or 10 (for TCP and 2-CPh, respectively) are employed, the PhO⁻ is the reactive species, and phenol is not formed. The involvement of radicals in the mechanism was excluded by adding a radical scavenger (sodium azide) into the reaction mixture, the formation of products was not affected by the presence of sodium azide. The first step of the mechanism if the oxidation of CoTSPc by hydrogen peroxide (as proved by UV–vis spectroscopy) to form $Co^{III}TSPc$-OOH species, Eq. (1), which then reacts with the phenols to give the various species shown in Scheme 1.

4. Conclusion

We have shown in this work that the oxidation of 2-CP and TCP using CoTSPc catalyst and hydrogen peroxide ox-

idant, in different solvent conditions gives different products. In water/methanol mixture (low pH 3.4), the products are phenol, benzoquinone, hydroquinone and maleic acid for 2-CP. And for TCP, the products are phenol, dichlorobenzoquinone, hydroquinone and maleic acid. In water (pH 7 or pH 10) the main products are the dichlorobenzoquinone and benzoquinone respectively for TCP and 2-CP. There is spectroscopic evidence for the involvement of both the metal and phthalocyanine ring oxidized species in the mechanism.

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