



First observation of tetranitro iron (II) phthalocyanine catalyzed oxidation of phenolic pollutant assisted with 4-aminoantipyrine using dioxygen as oxidant

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ABSTRACT

A novel system for catalytic oxidation of phenol and chlorophenol pollutant in water by tetranitro iron (II) phthalocyanine (TNFe(II)Pc) is reported for the first time. In this system, several phenolic substrates (phenol, 2-chlorophenol, 4-chlorophenol and 2,4-dichlorophenol) could be easily oxidized by naturally dissolved oxygen in the presence of TNFe(II)Pc, and then rapidly combined with 4-aminoantipyrine to generate the pink dye. The catalytic oxidation process and resulting products were monitored by UV–Vis spectroscopy and high performance liquid chromatography–mass spectrometer (HPLC–MS) technique. Control experiments demonstrated that the generation of superoxide anion radical was crucial for the dye formation, and a possible mechanism involved a successive single electron transfer from phenolic substrates to O₂ via the axis of TNFe(II)Pc was proposed. Potentially, this system is promising for application in chromogenic identification of phenolic pollutant.

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1. Introduction

Phenol and chlorophenol compounds such as 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4-dichlorophenol (DCP) are common environmental pollutants produced from fungicide, herbicide, pesticide and paper manufacturing industry [1–5]. Most of these contaminants exist in industrial wastewater and even drinking water, which are extremely dangerous to the environment for their toxicity and resistance to natural degradation [6,7]. Nowadays, various methods have been explored on the detection of phenolic pollutants in water or soil. Among them, catalytic oxidation of phenol assisted with 4-aminoantipyrine (4-AAP) to generate the pink antipyrilquinoneimine dye is the representative technique for chromogenic measurement of phenols and their derivatives [8–14]. In general, the catalytic efficiency is closely related to the properties of catalyst and oxidant [15]. The structure of catalyst and its working conditions would have significant influence on the precision and sensibility of the measurement. Moreover, from the environmental and economic point of view, molecular oxygen is a preferred oxidant favorable for the current development of green chemistry.

In nature, microorganisms such as *Phanerochaete chrysosporium* can catalyze oxidation of lignin (natural polyphenolic compounds) by means of a manganese peroxidase and H₂O₂. This natural

catalytic oxidation system was utilized with 4-AAP for detecting phenols and their derivatives [12]. However, for the instability and easy inactivation of these natural enzymes in some rigorous conditions, biomimetic catalysts, such as porphyrin and phthalocyanine metal complexes that could mimic active sites of natural enzymes and reproduce their catalytic activity, have become the attractive candidates to replace some natural enzymes [15]. Early investigations had proved that iron and manganese porphyrins and their derivatives exhibited excellent biomimetic oxidation activity of natural cytochrome P-450 system [16,17]. Recently, Rezzano's group reported that mono and bimetallic polymeric porphyrin (polyCoCuPP and polyFeCuPP) on Au support could catalyze H₂O₂ oxidation of phenols assisted with 4-AAP in aqueous solution [13]. In spite of these advancements in their catalytic performance, the application of metal porphyrins still suffers from their high cost. Therefore, some cheap and readily available phthalocyanine metal complex, especially, the functionalized metalphthalocyanine with tetra-substituted sulfonic groups had received much attention [7]. Meunier's group firstly reported that water-soluble tetrasulfophthalocyanine Fe(III) or Mn complexes (FePcTS, MnPcTS) could efficiently catalyze H₂O₂ oxidation of polychlorophenols and degrade them into various products with different oxidation degrees [6,7,18,19]. Later, the catalytic co-oxidation of phenols with 4-AAP performed by different metal tetrasulfophthalocyanines in the presence of H₂O₂ was observed by Santhanalakshmi [14]. However, compared with metal porphyrin, the deficient development of metal phthalocyanine catalysis is far from satisfying [15]. Moreover, additional oxidant was necessary (such as corrosive H₂O₂, KHSO₅, or toxic ^tBuOOH (tert-butyl hydroperoxide)) in most of the

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documented oxidation reaction catalyzed by MPcTS. Therefore, the exploration of novel phthalocyanine metal system with green oxidant for catalytic oxidation of phenolic pollutant remains an active topic. Furthermore, understanding the details of reaction mechanism is important for the development of phthalocyanine catalysis.

In this work we show that tetranitro iron (II) phthalocyanine (TNFe(II)Pc) could efficiently catalyze oxidation of phenols and chlorophenols (2-CP, 4-CP and DCP) assisted with 4-AAP in aqueous medium. The dissolved molecular oxygen as oxidant was sufficient for the catalytic oxidation reaction. Although TNFe(II)Pc is not a novel phthalocyanine metal complex [20], we found for the first time that TNFe(II)Pc was an efficient heterogeneous catalyst for oxidation of phenolic substrates in aqueous medium. Control experiments demonstrated that superoxide anion radical ($O_2^{\bullet-}$) was the active species involved in catalytic oxidation process and the resulting pink dye was considered to be generated from radical coupling. Moreover, we analyzed the resultant dye and proposed a catalytic mechanism for the chromogenic reaction.

2. Experimental

2.1. Instrumental

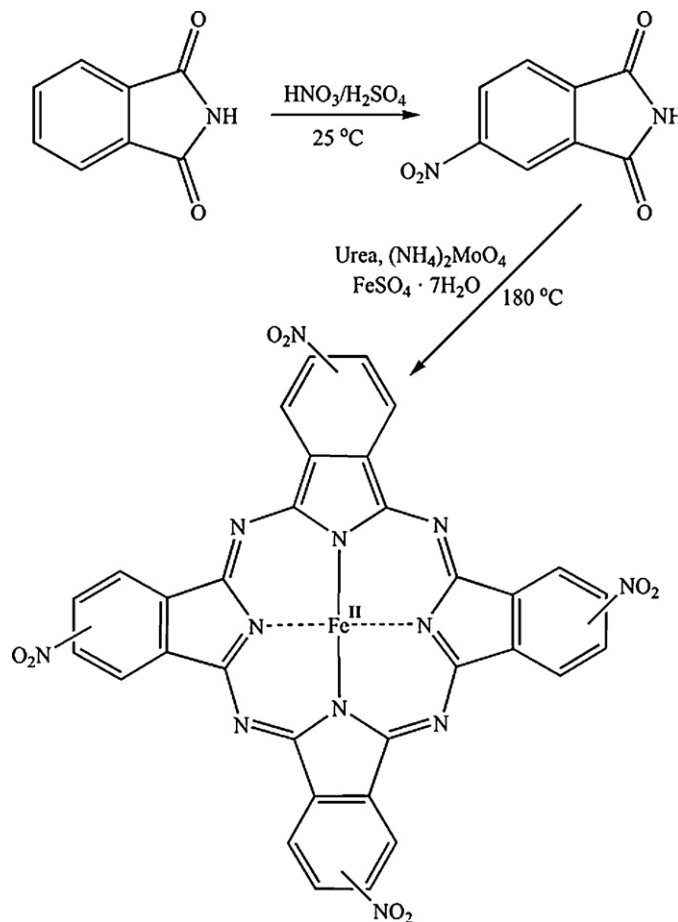
UV-Vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. IR spectra were recorded on a Thermo Nicolet Nexus FT-IR spectrometer with the standard KBr pellet method. Elemental analyses were performed on a Elementar Vario EL III Elemental Analyzer. 1H NMR spectra were recorded on a Varian NMR System 600 MHz Spectrometer. Nitrogen adsorption-desorption isotherms were collected on a Micromeritics Gemini V2380 surface area and porosity analyzer at 77 K after the reaction had been degassed in the flow of N_2 at 200 °C. Catalytic reaction was monitored by high performance liquid chromatography (HPLC, Dalian Elite P230 series). The reaction products were identified by HPLC-MS. HPLC analyses were carried out using Agilent 1100 instrument equipped with a SGE μ .C18 column (150 mm \times 4.6 mm). The mobile phase consisted of acetonitrile-methanol-water mixture (4:1:5, v/v) with a flow rate of 1.0 mL/min. The column temperature was set at 25 °C. Mass spectrometry (MS) analyses were performed using Applied Biosystems API2000 instrument. Electrospray ionization (ESI) source of MS was set at the positive ionization mode.

2.2. Materials and reagents

Phenol, 2-chlorophenol, 4-chlorophenol, 2, 4-dichlorophenol and 4-aminoantipyrine are of analytical reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The raw materials used for the synthesis of tetranitro iron (II) phthalocyanine are phthalimide, urea, ammonium molybdate (VI) tetrahydrate, iron (II) sulfate heptahydrate, concentrated H_2SO_4 and fuming HNO_3 . All these reagents are analytical pure and used without further purification. Boric acid-borax buffer solution (0.2 M, pH 7.4 and 9.0) and $Na_2HPO_4-KH_2PO_4$ buffer solution (0.2 M, pH 5.5) were used as catalytic reaction medium. Deionized water was used in all the experiments. Methanol and acetonitrile (HPLC grade, Sinopharm Chemical Reagent Co., Ltd.) was used as elution solution for HPLC study.

2.3. Preparation and characterization of TNFe(II)Pc

There are two steps in our synthesis of TNFe(II)Pc catalyst: (I) the nitration reaction of phthalimide to 4-nitrophthalimide; (II) the formation of TNFe(II)Pc via the reaction of 4-nitrophthalimide, urea, $FeSO_4$ and ammonium molybdate. The synthetic procedure for TNFe(II)Pc is described in Scheme 1.



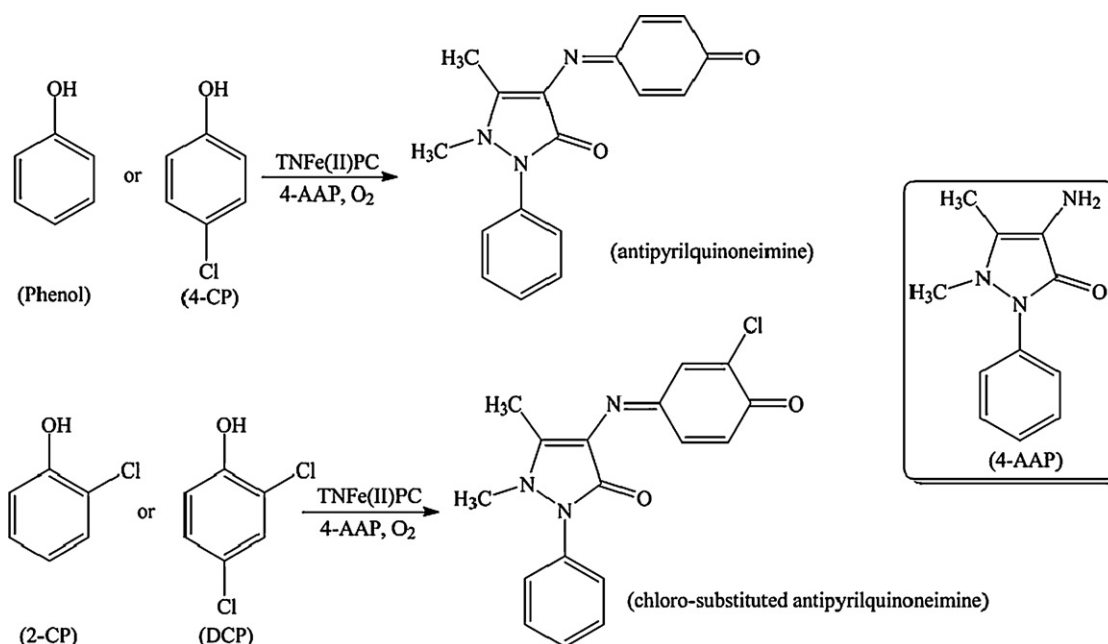
Scheme 1. Synthesis of 4-nitrophthalimide and tetranitro iron (II) phthalocyanine complex.

2.3.1. 4-Nitrophthalimide

The synthesis of 4-nitrophthalimide was adopted according to Young's method [21]. Yield: 66%. FT-IR (KBr pellets) 3328(s), 3077(w), 3043(w), 1791(m), 1705(s), 1622(m), 1546(s), 1349(s), 1307(s), 1110(s), 1075(s), 720(s) cm^{-1} ; 1H NMR (600 MHz, d_6 -DMSO): δ 8.07 (d, 1H, $J=2.4$ Hz, Ph-H), 8.43 (s, 1H, Ph-H), 8.61 (d, 1H, $J=2.4$ Hz, Ph-H), 11.84 (s, 1H, =NH).

2.3.2. Tetranitro iron (II) phthalocyanine

TNFe(II)Pc was prepared by a reported method [22], but with some modifications. 3.84 g 4-Nitrophthalimide, 1.4 g $FeSO_4 \cdot 7H_2O$, 0.05 g ammonium molybdate, and excess 12 g urea were added into a 100 mL three-necked flask containing 20 mL nitrobenzene under magnetic stirring. Then the mixture was heated slowly to 130 °C to completely dissolve all the organic solid under the protection of N_2 , and subsequently the temperature was raised to reflux for 3 h. Thereafter, the mixture was cooled to room temperature and dark blue product was obtained. The product solution was poured into ethanol, stirred and collected by vacuum filtration to afford the crude product. Then the crude product was added into 400 mL of 1 M HCl solution, boiled for about 30 min and then filtered, washed with deionized water for several times, followed by the further treatment with 400 mL of 1 M NaOH solution by the similar treatment mentioned above. Finally, the TNFe(II)Pc solid was washed with ethanol by Soxhlet extraction to remove the residual nitrobenzene, then the dark blue solid was collected and dried at 100 °C overnight in vacuum. Yield: 56%. FT-IR (KBr pellets) 733(m), 760(m), 808(w), 852(w), 1097(m), 1142(m), 1254(w), 1335(s), 1517(s), 1614(w) cm^{-1} . UV-Vis (DMSO) $\lambda_{max} = 284, 682$ nm. Anal.



Scheme 2. Catalytic oxidation of 2-CP, DCP, 4-CP and phenol to corresponding dyes by O_2 in the presence of TNFe(II)Pc catalyst and 4-AAP. The chloro-substituted antipyrilquinoneimine is one possible isomer.

Calcd. for $\text{C}_{32}\text{H}_{12}\text{FeN}_{12}\text{O}_8$: C, 51.36; H, 1.62; N, 22.46. Found: C, 51.62; H, 1.89; N, 22.67.

2.4. Catalytic oxidation experiment

The typical catalytic oxidation of phenolic substrates with 4-AAP by TNFe(II)Pc catalyst was performed under the following experimental procedure (see Scheme 2). A 40 mL of deionized water, 5 mL of 4-AAP aqueous solution (1×10^{-3} mol/L), and 5 mL of substrate solution (phenol or chlorophenol, 1×10^{-3} mol/L) were added into a 50 mL glass beaker. The catalytic reaction was initiated by addition of 0.015 mmol of TNFe(II)Pc powder into the above solution, followed by the ultrasonic treatment for 1 min and continuous magnetic stirring at 20°C . The suspension was filtered with a membrane ($0.22 \mu\text{m}$) to remove TNFe(II)Pc particles at the regular intervals. The filtrate was detected with UV-Vis spectrophotometer and HPLC for process monitoring. (HPLC, Dalian Elite P230 series fitted with a C 18 reverse column ($200 \text{ mm} \times 4.6 \text{ mm}$) and connected to a variable wavelength UV-Vis detector (set at $\lambda = 220 \text{ nm}$). The mobile phase was composed of acetonitrile–methanol–water mixture (4:1:5, v/v), with a flow rate of 1.0 mL/min. The sample inject volume was $50 \mu\text{L}$.) The phenolic substrates and 4-AAP were identified by spiking using standards via comparison of retention times in HPLC trace.

The recycling experiments of TNFe(II)Pc were performed under the typical conditions. After each catalytic experiment, the TNFe(II)Pc powder was separated by centrifugation and washed with deionized water until the pink color was disappeared. Then the resulting TNFe(II)Pc powder was added into boiled water for 60 min to make the catalyst free from the possible residual organic compounds. Finally, the TNFe(II)Pc powder was collected and dried at 100°C in vacuum for the next catalytic experiment.

3. Results and discussion

3.1. Chromogenic reaction of phenols and chlorophenols catalyzed by TNFe(II)Pc

Previous reports had documented that oxidation of various phenolic compounds could be catalyzed by phthalocyanine metal

complex [6,19,23,24], herein four types of phenolic substrate were chosen to investigate the catalytic activity of TNFe(II)Pc in aqueous solution. For this purpose, the absorbance increased at 510 nm during catalytic oxidation was followed due to the formation of (chloro-substituted) antipyrilquinoneimine dyes [14]. Fig. 1 shows the UV-Vis absorption spectra for chromogenic reaction of 2-CP, DCP, 4-CP and phenol with 4-AAP in the presence of TNFe(II)Pc at regular intervals, respectively (Fig. 1a–d). Obviously, the intensities of characteristic peak of dye at 510 nm gradually increased along with the gradually decreased intensities of substrates and 4-AAP in the range of 200–300 nm within 90 min, suggesting the continuous transformation of phenols or chlorophenols with 4-AAP to dyes in the presence of TNFe(II)Pc, while the auto-oxidation reaction without TNFe(II)Pc was negligible (see Fig. S1 in supplementary data). The UV-Vis spectra of these four systems exhibited no obvious change after 90 min, which meant the completion of catalytic reaction. Compared with the absorption intensities of dye at 510 nm, the catalytic reactivity trend for different phenolic substrates was in the following order: 2-CP > DCP > phenol > 4-CP. The above results indicated that the oxidation reaction of all these four kinds of phenolic substrate with 4-AAP were successfully catalyzed by TNFe(II)Pc, which was promising for chromogenic identification as well as environmental decontamination.

3.2. Effect of pH on catalytic oxidation of 2-CP and DCP

For the obvious chromogenic indication in 2-CP and DCP system, we chose them to further study the activity of TNFe(II)Pc under different pH conditions. It is known that the dominating species of chlorophenol varied with pH of aqueous solution due to the existence of equilibrium between undissociated chlorophenols (below their pK_a values) and corresponding chlorophenolates (above their pK_a values), thus the catalytic oxidation of chlorophenols assisted with 4-AAP was considered to be closely related to pH [25]. Since the pK_a for the deprotonation of 2-CP and DCP OH-group are 8.48 and 7.85, respectively, therefore, boric acid–borax buffer solution (BBS, pH 7.4, 9.0) and Na_2HPO_4 – KH_2PO_4 buffer solution (PBS, pH 5.5) as well as deionized water were used to investigate the effect of pH on catalytic reaction.

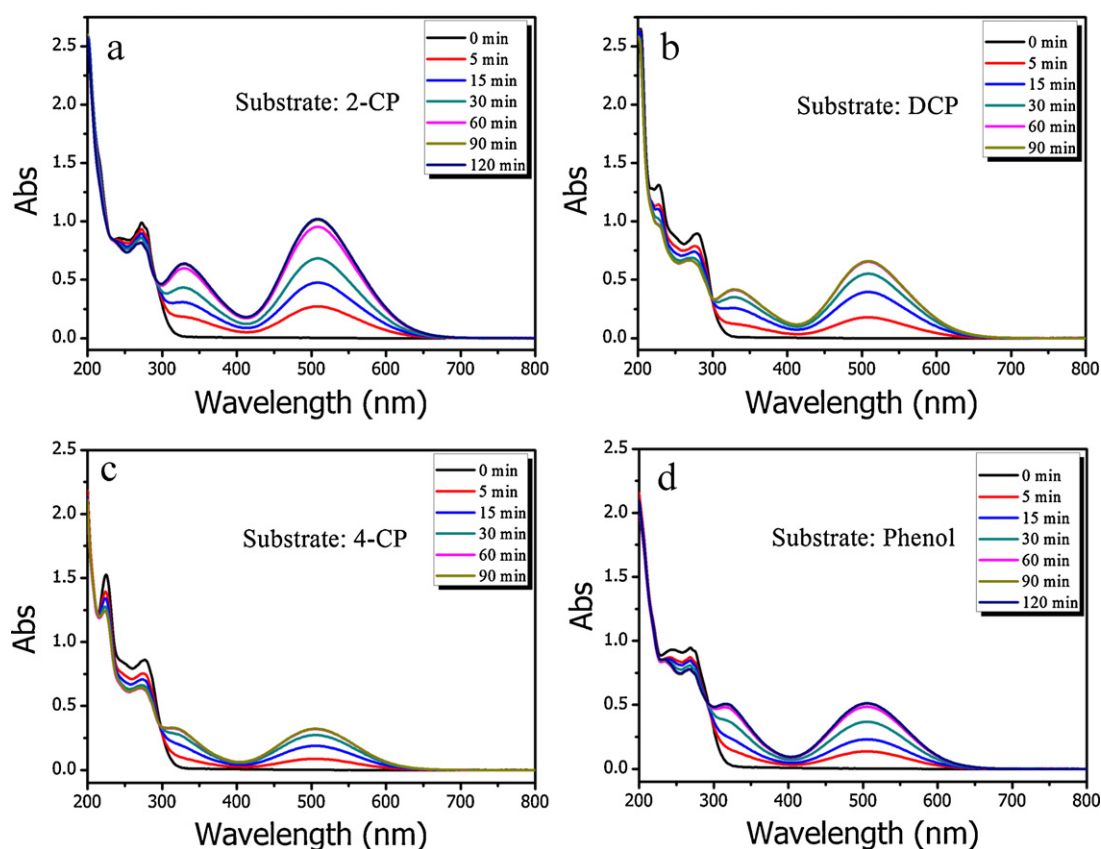


Fig. 1. Stacked UV-Vis absorption spectra of catalytic oxidation of various phenolic substrates with 4-AAP at regular intervals. The initial concentration of phenolic substrates and 4-AAP was 1.0×10^{-4} M, and the dosage of TNFe(II)Pc powder was 11.3 mg.

Fig. 2 records the dye formation process in 2-CP and DCP system at different pH on the plot of UV-Vis absorption ($\lambda = 510$ nm) versus reaction time. For 2-CP system (Fig. 2a), the catalytic reaction was completed after 3 h at pH 7.4 and 5.5, while the catalytic reaction still proceeded after 5 h at pH 9.0. Compared with the catalytic oxidation of 2-CP in deionized water, more dyes were formed at pH 7.4 although longer reaction time (≥ 180 min) was required. However, the concentrations of dye at pH 5.5 and pH 9.0 after 300 min were still lower than that in deionized water at 60 min. For comparison, the reaction trend of DCP at selected pH was similar to that of 2-CP system except for the small difference at pH 5.5 and 9.0. Although the chromogenic reaction was faster in deionized water at the early stage, the maximal conversion of chlorophenol

to dye could be achieved in buffer solution at pH 7.4, both of which reflected the significant contribution of the molecular chlorophenol rather than chlorophenolate. The detailed reasons for different rates of dye formation and their final yields would be discussed later.

3.3. Determination of active oxygen species

Because the solution was exposed to air and there were no other oxidants employed in it, dissolved O_2 was considered to be the possible oxidant for the chlorophenol oxidation. To investigate the effect of dissolved O_2 on the catalytic oxidation, the reaction was firstly carried out with continuous nitrogen-bubbling to eliminate

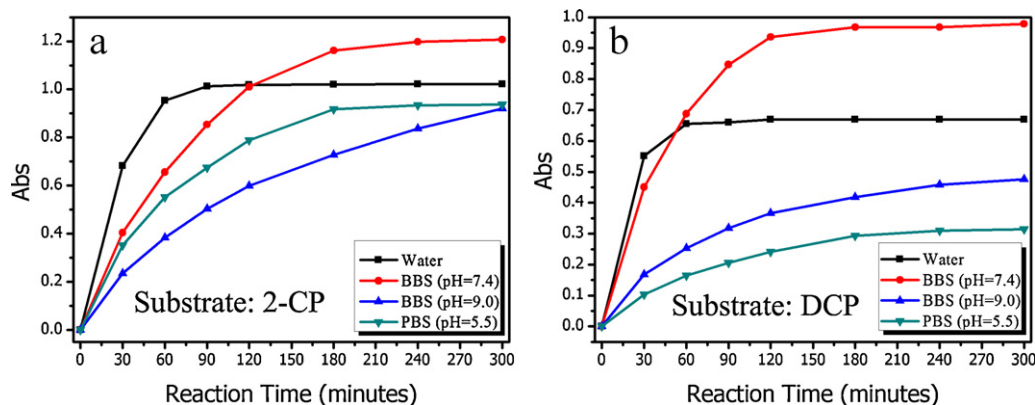


Fig. 2. Dye formation process in 2-CP and DCP system under different pH conditions in the presence of TNFe(II)Pc. ($\lambda_{\text{abs}} = 510$ nm) (■) in deionized water; (●) in boric acid–borax buffer solution, 0.2 mol/L, pH 7.4; (▲) in boric acid–borax buffer solution, 0.2 mol/L, pH 9.0; (▼) in Na_2HPO_4 – KH_2PO_4 buffer solution, 0.2 mol/L, pH 5.5. The initial concentration of 2-CP and DCP is 1.0×10^{-4} M and the dosage of TNFe(II)Pc is 11.3 mg.

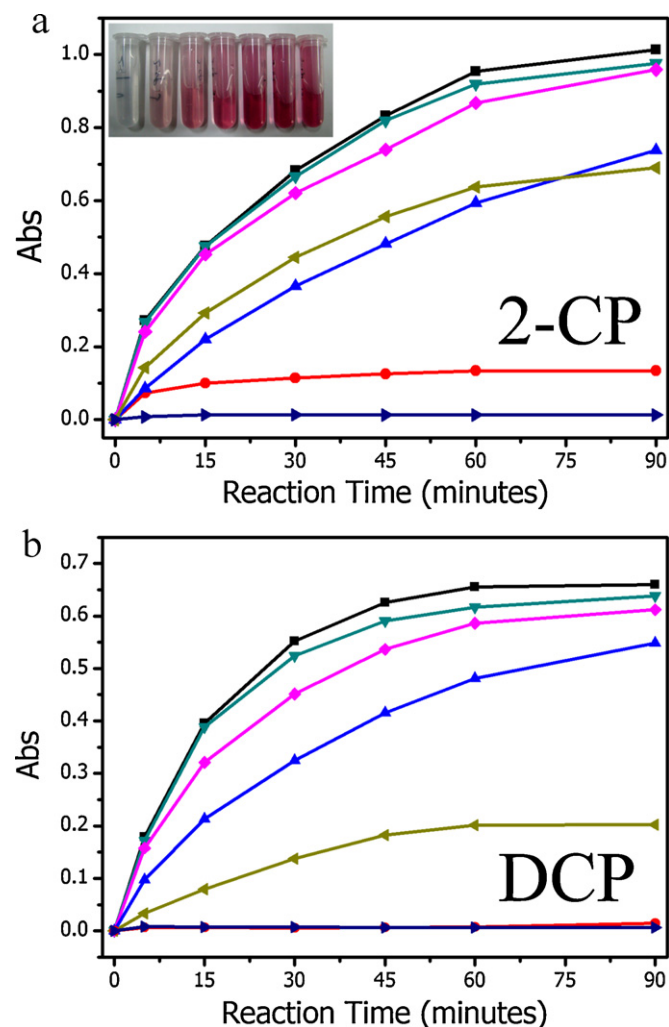


Fig. 3. Dye formation process in 2-CP (a) and DCP (b) system versus reaction time under different conditions. ($\lambda_{\text{abs}} = 510 \text{ nm}$) (a, ■) Typical catalytic reaction; (b, ▼) iso-propanol 0.01 M; (c, ◆) in the dark; (d, ◀) $\text{K}_2\text{Cr}_2\text{O}_7$ 0.1 mM; (e, ▲) NaN_3 0.01 M; (f, ●) N_2 bubbled; (g, ▶) $\text{K}_2\text{Cr}_2\text{O}_7$ 1 mM. The inset picture shows the color deepening in 2-CP system of typical catalytic reaction (a, ■).

the dissolved oxygen in solution. Time courses for the dye formation process in 2-CP (a) and DCP (b) system is shown in Fig. 3. Under anaerobic conditions (curve f), the dye formation rate was largely prohibited compared to the typical catalysis (curve a), suggesting that oxygen was crucial for the oxidation of chlorophenol. Generally, O_2 molecule can trap electron to produce active oxygen radicals ($\text{O}_2^{\bullet-}$ and OH^{\bullet}) that could initiate oxidation reaction [26]. To further confirm the existence of specific reactive species, several scavengers (iso-propanol for OH^{\bullet} , $\text{K}_2\text{Cr}_2\text{O}_7$ and NaN_3 for $\text{O}_2^{\bullet-}$) were employed. The addition of iso-propanol exhibited little influence on the dye generation compared with the typical catalysis (curve b versus curve a), suggesting that OH^{\bullet} unlikely takes part in the catalytic oxidation reaction. However, when $\text{K}_2\text{Cr}_2\text{O}_7$ or NaN_3 was added into the reaction solution, the generation of dye was significantly inhibited (curves d, g and e). Especially, when the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ was increased to 0.001 M, the catalytic reaction could hardly proceed (curve g). Therefore, the generation of $\text{O}_2^{\bullet-}$ was crucial for the chromogenic reaction and a $\text{O}_2^{\bullet-}$ mediated mechanism of TNFe(II)Pc catalysis is confirmed. Moreover, the typical catalysis could also proceed efficiently in the dark (curve a versus curve c), which indicates that sunlight is not essential for chlorophenol oxidation in the presence of TNFe(II)Pc catalyst.

3.4. Catalytic process monitoring and products identification by HPLC–MS

The produced pink dyes in 2-CP/DCP system had good stability and low volatility, thus HPLC–MS was considered to be a suitable analytical approach for the determination of the possible reaction products. We firstly identified 2-CP, DCP and 4-AAP by comparison of their retention time with that of standards ($\lambda = 220 \text{ nm}$), while the determination of the resulting dye products was realized by tuning the wavelength of UV–Vis detector to 510 nm and only one chromatogram peak was found (see Fig S2 in supplementary data), and the corresponding retention time (9.84 min) was same to that of P1 and P3 in Fig. 4a and c. Obviously, the concentration of dye increased fast in the initial 60 min, which was consistent with the corresponding UV–Vis results (Fig. 1a and b). Besides the dyes, one byproduct and at least three intermediate products were observed in 2-CP/DCP system, for the concentrations of P2 and P4 (byproducts) gradually increased in the whole catalytic reaction, while the contents of the intermediate products increased at the first 15 min or so and then decreased. Fig. 4b and d indicates that the 4-AAP disappeared completely after 90 min of reaction, while 2-CP/DCP remained less than 50%. For this reason, excess 4-AAP was needed for complete removal of chlorophenols. On the basis of HPLC analyses (conversion of chlorophenols and selectivity of dye in total oxidation products), we evaluate the final yields of dye by using normalization method, 38% for 2-CP system and 25% for DCP system (yield = conversion \times selectivity/100). Furthermore, we chose the reaction solution obtained at 30 min to further identify all the products by ESI–MS, unfortunately, the obvious molecular ion signal of the unknown byproducts and intermediate products could not be obtained for the difficulty of ionization (see Fig. S3 in supplementary data), only the dye products of P1 and P3 were identified according to the corresponding m/z values ($m/z = 328.0$ and 329.9) in Fig. S3b and e of Supplementary data. Both of the resultant $(\text{M}+\text{H})^+$ signals of P1/P3 resulted from the existence of isotopic element of chlorine (^{35}Cl and ^{37}Cl) in dye molecule. Moreover, the retention times of these unknown products were also different from those of commercial 1,4-benzoquinone and 2-chloro-benzoquinone (Fig. S2 in supplementary data). Therefore, in 2-CP and DCP system, the same dye of chloro-substituted antipyrilquinoneimine was determined.

3.5. Proposed mechanism for catalytic oxidation of phenolic substrates

Compared with the dye formation rate in the presence and absence of TNFe(II)Pc (Fig. 1 versus Fig. S1 in supplementary data), it is clear that TNFe(II)Pc catalyst is crucial for the fast formation of dye, and the oxidation catalysis was considered to be closely related to the generation of $\text{O}_2^{\bullet-}$ species. Therefore, understanding the catalytic mechanism as well as the effect of active reaction species is of guidance for practical application of phenolic oxidation chemistry. Until now, the well-developed catalysis system was the water-soluble MPcTS ($\text{M} = \text{Fe(III)}, \text{Mn}$) with H_2O_2 as oxidant, which was used as bleaching catalysts for oxidative degradation of chlorophenol [15]. Especially, for oxidation of 2,4,6-trichlorophenol (TCP) catalyzed by $\text{FePcTS-H}_2\text{O}_2$ system [6,7], Meunier and Sorokin proposed three different models of active iron-centered oxidizing species including $(\text{X})\text{PcSFe}^{\text{V}} = \text{O}$, $(\text{L})\text{PcSFe}^{\text{IV}} = \text{O}$ and $(\text{L})\text{PcSFe}^{\text{III}}\text{-OOH}$, which depended on the nature of oxidant, the axial ligand and the macrocycle ($\text{L} = \text{neutral ligand}$ and $\text{X} = \text{anionic ligand}$). The proper active iron–oxygen species could further abstract electrons from TCP and achieve the initial oxidation of TCP to DCQ (2,6-dichloro-1,4-benzoquinone).

From the point of Meunier and Sorokin, the proposed active iron–oxygen species was responsible for TCP oxidation, which

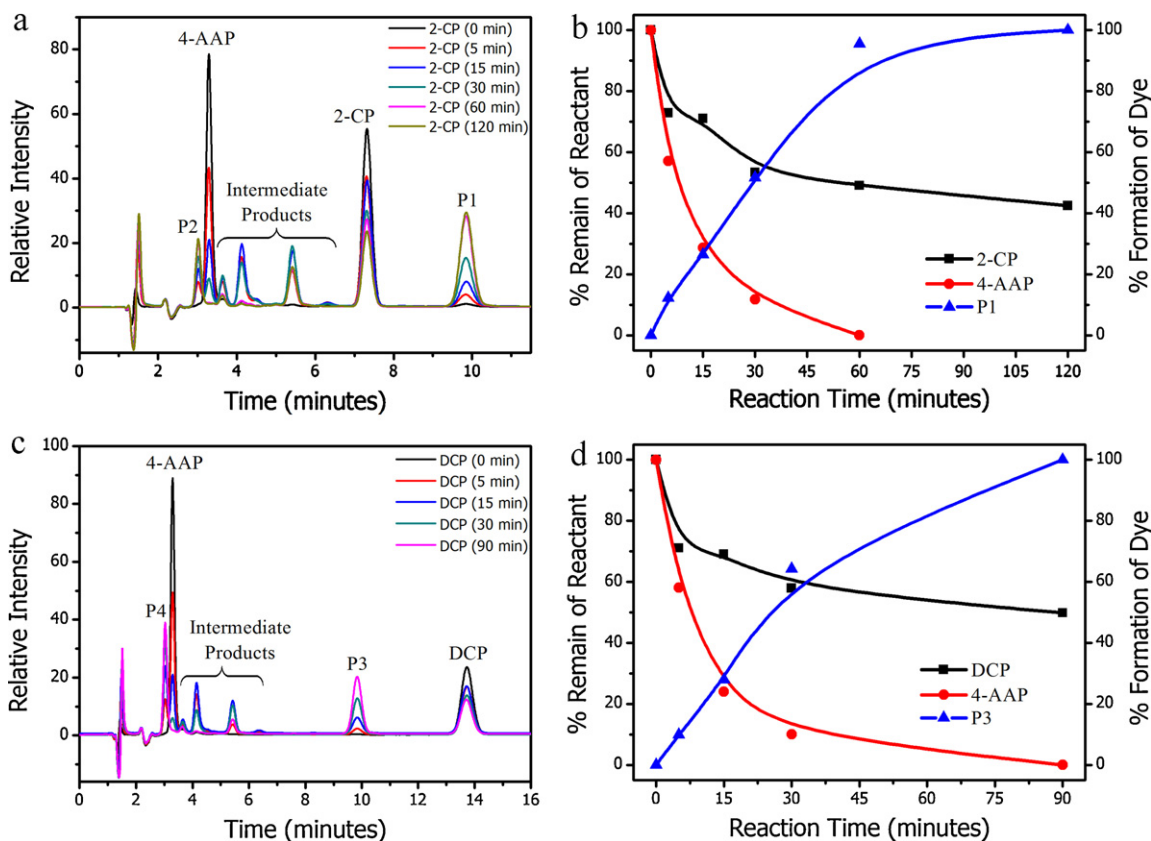


Fig. 4. HPLC chromatogram of 2-CP (a) and DCP (c) system obtained after regular intervals of catalytic reaction. P1 and P3 were dye products in 2-CP and DCP system, respectively, byproducts (p2 and P4) and several intermediate products were observed after 5 min of catalytic reaction. (b) and (d) Record the percentage data of substrate, 4-AAP and resulting dyes during catalytic reaction according to the corresponding peak areas of HPLC chromatogram.

also illuminated the donor–acceptor interactions existed in substrate, catalyst and oxidant [7,27,28]. Herein, in the TNFe(II)PC catalytic reaction system, the interactions among substrate, catalyst and O_2 should result in the coordination structures of chlorophenol–TNFe(II)PC– O_2 . Then the successive single electron transfer from hydroxyl oxygen (donor) of chlorophenol to O_2 (acceptor) via the axis of TNFe(II)PC macrocycle realized the fast oxidation of chlorophenol (see Scheme 3, a case of 2-CP), which was responsible for the succeeding generation of *p*-quinoid radical (possible chlorophenol oxidation product) and $O_2^{\bullet-}$ (step I). In turn, the resulting $O_2^{\bullet-}$ could further oxidize the amino group of 4-AAP to produce the Antipyrene-NH $^{\bullet}$ (radical form of 4-AAP) (step II). Immediately, *p*-quinoid radical and Antipyrene-NH $^{\bullet}$ could combine to generate the final products of pink chloro-substituted antipyrilquinoneimine dye (step III). This is the possible mechanism for the generation of $O_2^{\bullet-}$ and dye formation via radical coupling. For the phenol or 4-CP oxidation, the resulting pink dye should be antipyrilquinoneimine (see Scheme 2).

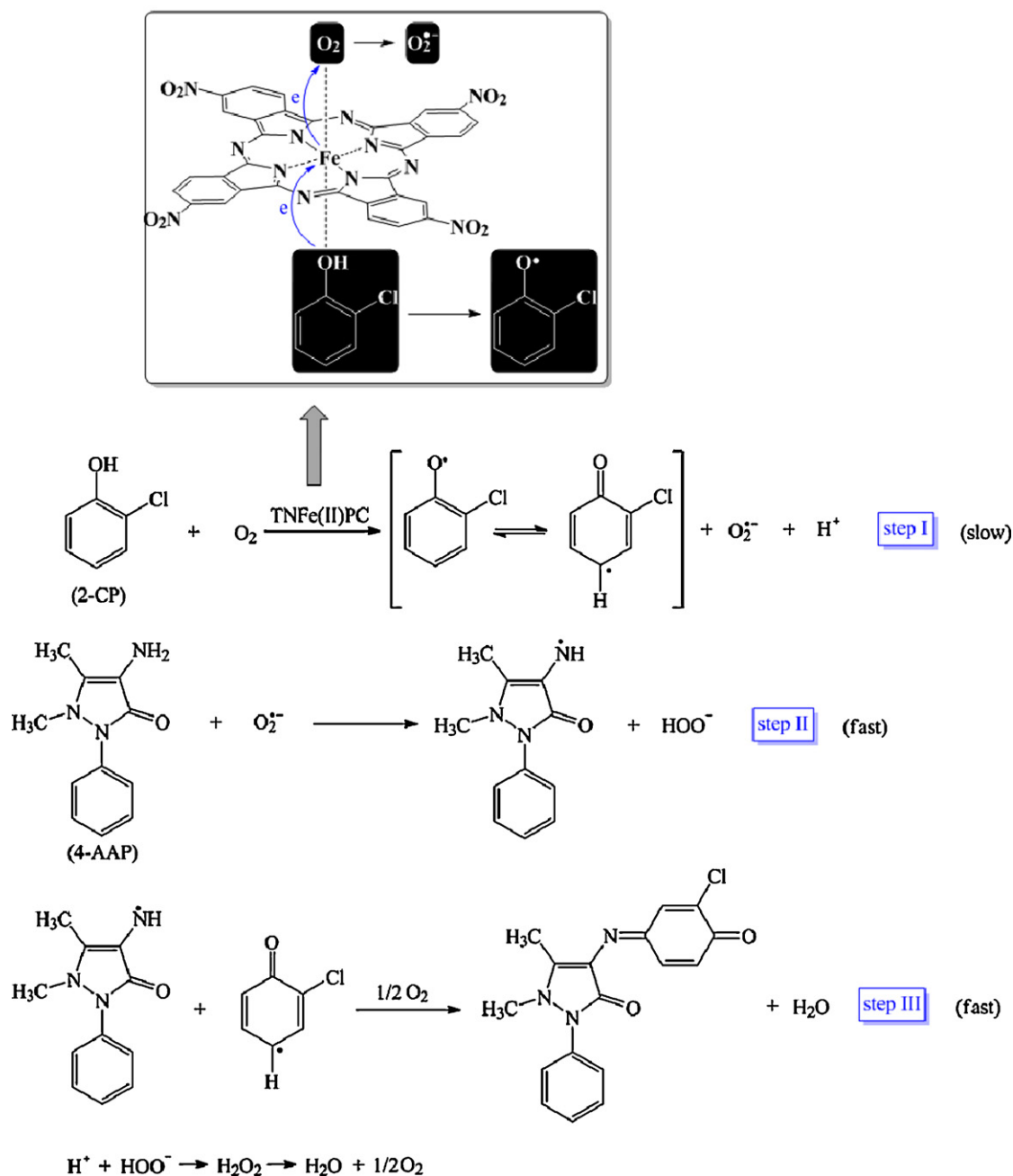
Furthermore, following the discussion of the effect of pH on catalysis, we found that lower pH was not suitable for dye formation (see Fig. 2). It is possible that the combination of $O_2^{\bullet-}$ with excess H^+ would be accelerated at lower pH, which would decrease the quantity of Antipyrene-NH $^{\bullet}$ radicals (see Scheme 3, step II) and thus resulted in the decreased yield of dye. In addition, the initial rate of dye formation in deionized water was the highest in contrast to that in buffer solution (see Fig. 2), which meant the fast generation of abundant radicals of *p*-quinoid and Antipyrene-NH $^{\bullet}$, the interaction of these active radicals might result in some byproduct or intermediate products (see Fig. 4), and thus the final dye with relatively small quantity in deionized water could be explained. In contrast,

the low initial concentration of chlorophenol molecules at pH 7.4 buffer solution and the possibility of greater number of collisions between radical reactants and phosphate ions in PBS contributed to the low rate of dye formation, while the durative transformation of chlorophenolate to chlorophenol molecule was responsible for the high yield of dye in the end. Therefore, pH is an important parameter that determines the dominating species of chlorophenol and influences the rate of dye formation in aqueous solution (see Scheme 4, a case of 2-CP).

We also found that the initial rate of dye formation in 2-CP system at higher temperature (40 °C) was enhanced, while less dyes were formed at the end of catalytic oxidation (Fig. 5a). The pseudo-first-order model was introduced to illuminate the reaction kinetic of dye formation at different temperature [14]. It is found that the reaction rate constant reached $110.83 \times 10^{-3} \text{ min}^{-1}$ at 40 °C, much higher than that ($53.38 \times 10^{-3} \text{ min}^{-1}$) of RT reaction (Fig. 5b). The fast formation of dye at 40 °C was considered to be closely related to the fast collision of radical reactants according to Arrhenius principle, while the acceleration of side reactions could be responsible for the final low yield of dye. Furthermore, detailed HPLC results confirmed the low conversion of 2-CP and low selectivity of dye, which contributed to the less amount of dye formed at 40 °C compared to that at RT (see Table 1).

3.6. Recycling experiments of TNFe(II)PC catalyst

The stability and reuse of catalyst is important for its practical application. To examine the catalytic effectiveness of the reused catalyst, a three-cycle experiment for catalytic oxidation of 2-CP was performed under typical conditions. It was interesting to find



Scheme 3. Proposed mechanism for O_2 oxidation of 2-CP and dye generation via radical coupling in the presence of TNFe(II)Pc.

the catalyst only exhibited slight deactivation after three cycles of repeated experiments for 2-CP system (Fig. 6). According to the general explanation, the possible permanent adsorption of some species on catalyst surface could result in the deactivation of some

active sites, which should be responsible for the reduction of catalyst's activity [29]. Moreover, the loss of catalyst should be another possible reason for the gradual reduction of activity, for it is difficult to collect total TNFe(II)Pc powder after several cycling experiments.

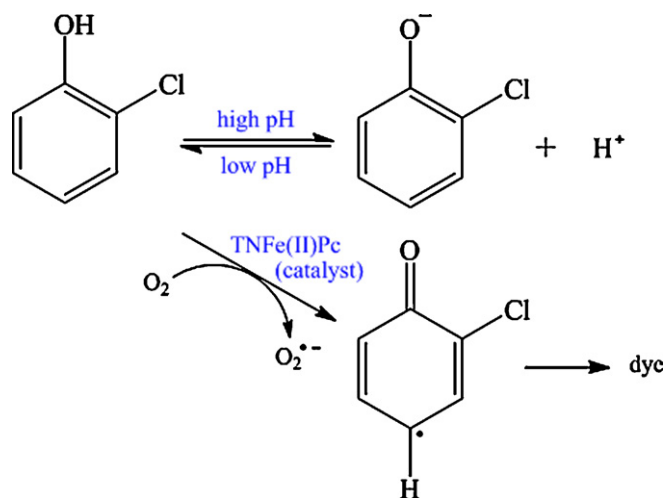
Table 1
The conversion, selectivity, yield and rate constant calculated for 2-CP system and textural parameters of TNFe(II)Pc catalyst.

System	Conversion/selectivity	Yield (%) ^a	$k \times 10^{-3} \text{ (min}^{-1}\text{)}^b$	BET surface area (m^2/g) ^c	Pore diameter (nm) ^c
2-CP (RT)	58/66	38	53.38	9.60	36.46
2-CP (40 °C)	50/60	30	110.83		

^a Yield calculated on the basis of HPLC analysis (yield = conversion \times selectivity/100).

^b The rate constants of dye formation at RT and 40 °C.

^c The data of TNFe(II)Pc catalyst.



Scheme 4. The ionization equilibrium between molecular chlorophenols and chlorophenolates, and their transformation to dyes during catalytic oxidation reaction.

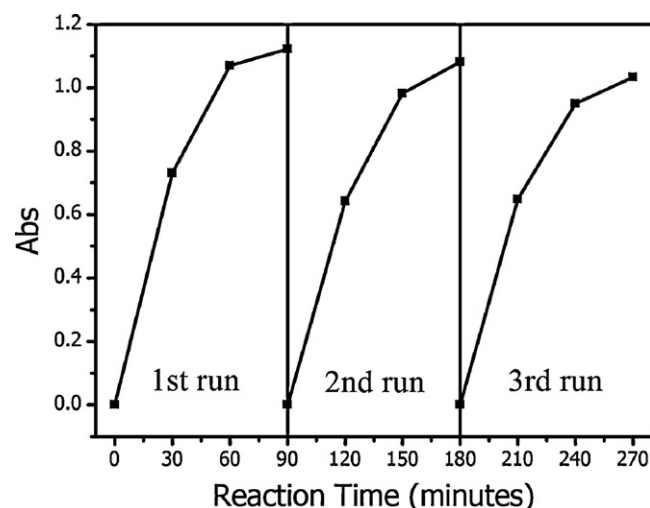


Fig. 6. Recycling runs in the catalytic oxidation of 2-CP in the presence of TNFe(II)Pc catalyst under same conditions. The UV-Vis absorption was recorded at the wavelength of 510 nm.

4. Conclusion

In summary, this study demonstrates that heterogeneous TNFe(II)Pc could efficiently catalyze O_2 oxidation of several phenolic substrates assisted with 4-AAP for fast chromogenic indication of phenolic pollutants. Control experiments testified that the generation of $O_2^{\bullet-}$ is the key step for initial chlorophenol oxidation and subsequent formation of dyes. This low-cost catalytic system consists of an easily accessible TNFe(II)Pc catalyst, clean and green oxidant of oxygen from air, and common 4-AAP, which provides an economical route for detective analysis and removal of harmful phenolic pollutants. It is notable that the oxidation of 2-CP and DCP would cause the consumption of O_2 and result in a quantitative relationship between the concentration of chlorophenol and O_2 , which would provide the basis for the development of fiber optic sensor based on oxygen sensing and biomimetic catalysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.06.002.

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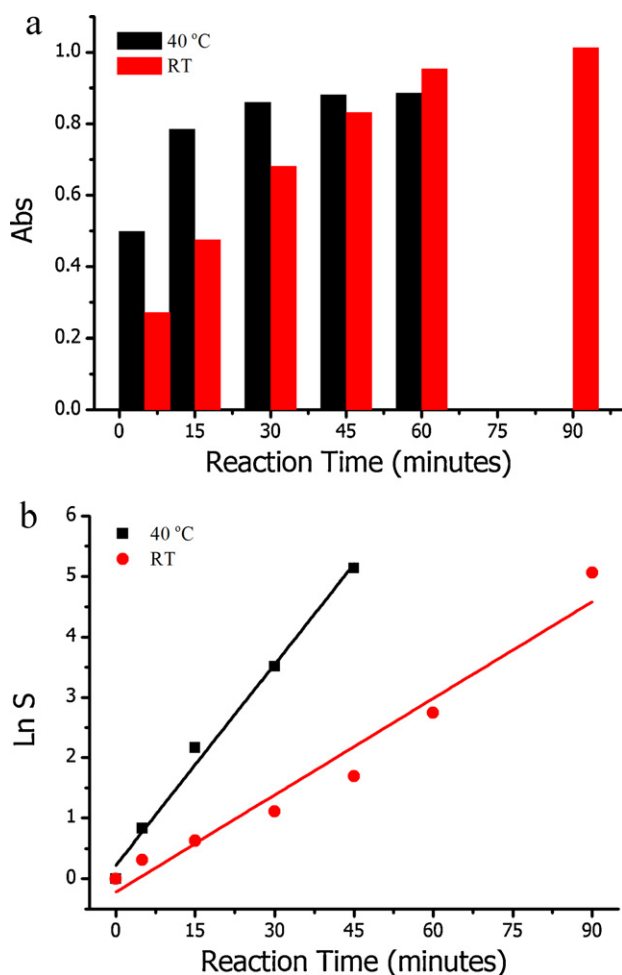


Fig. 5. (a) Comparison of dye formation process in 2-CP system at room temperature (RT) and 40 °C. ($\lambda_{\text{abs}} = 510 \text{ nm}$) (b) Kinetic plots of dye formation at RT and 40 °C on the basis of UV-Vis spectra. The correlation coefficients (R^2) for fit of experimental data are 0.9540 and 0.9893, respectively. (The kinetic parameter $\text{Ln } S$, where $S = \text{Abs}_\infty / (\text{Abs}_\infty - \text{Abs}_t)$ are calculated from absorbance versus reaction time).

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