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# Highly Efficient Decomposition of Organic Dyes by Aqueous-Fiber Phase Transfer and in Situ Catalytic Oxidation Using Fiber-Supported Cobalt Phthalocyanine

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A novel metallophthalocyanine derivative, cobalt tetra (2,4-dichloro-1,3,5-triazine) aminophthalocyanine (Co-TDTAPc), was prepared and immobilized on cellulosic fiber by covalent bond to obtain a supported oxidation catalyst (Co-TDTAPc-F). Co-TDTAPc-F/H<sub>2</sub>O<sub>2</sub> system based on phase-transfer catalytic oxidation for decomposing dyes, including acid, reactive, and direct dyes, has been investigated thoroughly. Compared to traditional adsorption technologies and advanced oxidation processes (AOPs) for dye treatment, Co-TDTAPc-F/H<sub>2</sub>O<sub>2</sub> combines the advantages of both and is more efficient and more effective. Azo dyes such as C. I. Acid Red 1 (AR1) can be quickly adsorbed onto/into the fiber from aqueous solution and decomposed in situ simultaneously in the presence of Co-TDTAPc-F and H<sub>2</sub>O<sub>2</sub>. It has been found that the reaction process is not affected by the visible light. Furthermore, it turns the negative effect of NaCl normally observed in homogeneous catalysis into positive one. The catalytic reaction can proceed at a wide pH range from acidic to alkaline. In 60 min, more than 98% of AR1 was eliminated at initial pH 2. In 90 min, about 40% of the carbon was found mineralized as determined by the analysis of the residual total organic carbon. The high-performance liquid chromatography result indicated that a substantial amount of the starting AR1 was converted to other organic products, while gas chromatography/mass spectrometry analysis showed the rest of the carbon existed mainly as small molecular biodegradable aliphatic carboxylic compounds such as oxalic acid, malonic acid, and maleic acid, etc. Co-TDTAPc-F is stable, causes no secondary pollution, and remains efficient in repetitive test cycles with no obvious degradation of catalytic activity.

## Introduction

Dye pollutants from dyestuffs and the textile industry are a dangerous source of environment contamination in many countries (1), particularly in developing countries. The conventional treatment technologies for eliminating dyes include physical chemistry methods such as flocculation, activated carbon adsorption, and biotreatment (2). However,

flocculation and adsorption treatments often generate a large amount of hazardous solid and liquid wastes (3, 4). Biotreatment utilizes the abilities of various microorganisms to scavenge organic dyes. However, some dyes are resistant to aerobic biodegradation, furthermore, under anaerobic conditions, the azo linkage is reduced to aromatic amines that are colorless but can also be toxic and potentially carcinogenic (5–7). In addition, the application of biotreatment is limited to some extent due to the complexity of the biological process.

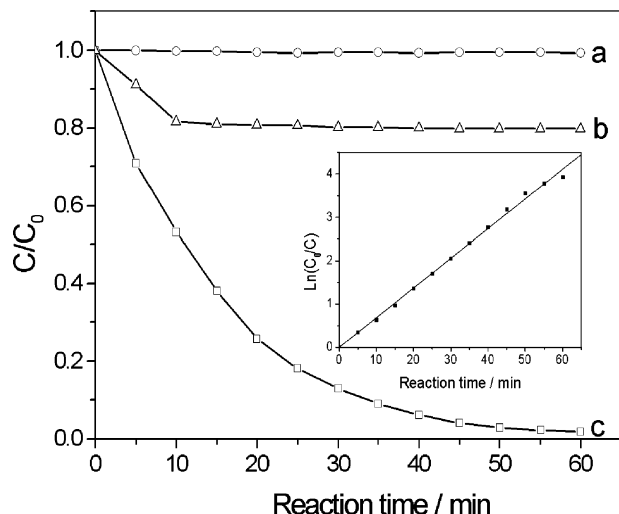
Recently, advanced oxidation processes (AOPs), which have high degradation rates, have received increasing attention as a promising technology for the destruction of organic pollutants (8–15). Hydrogen peroxide as the oxidant has potential in green chemical technology. Fenton's reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) and Fenton-like reagent (Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub>, Co<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> and ferrioxalate-photo-Fenton, etc.) can be employed to treat dye wastewater (16–18). It should be noted that the ions sludge generated in large quantity after reaction is a big drawback and the removal of the ions at the end of treatment is a rather costly process.

Some methods based on H<sub>2</sub>O<sub>2</sub> have been developed in recent years. Meunier and co-workers reported an iron(III) phthalocyanines/H<sub>2</sub>O<sub>2</sub> system for catalytic oxidation of aromatic pollutants in the presence of different organic solvents (19, 20). Collins, et al. recently showed a higher valency iron species, Fe-TAML (tetra-amido macrocyclic ligand) activators, which is responsible for selective oxidation of various pollutants, such as polychlorinated phenols and other aromatics (21, 22). Lente and Espenson summarized different iron-based catalysts using H<sub>2</sub>O<sub>2</sub> as a sole oxidant, which have 4 N donor atoms in a planar arrangement surrounding the metal center (23). It should be emphasized that above-mentioned catalysts were mostly used in a homogeneous reaction, which is likely to produce a secondary pollutant and be decelerated by some compounds existing in the effluents.

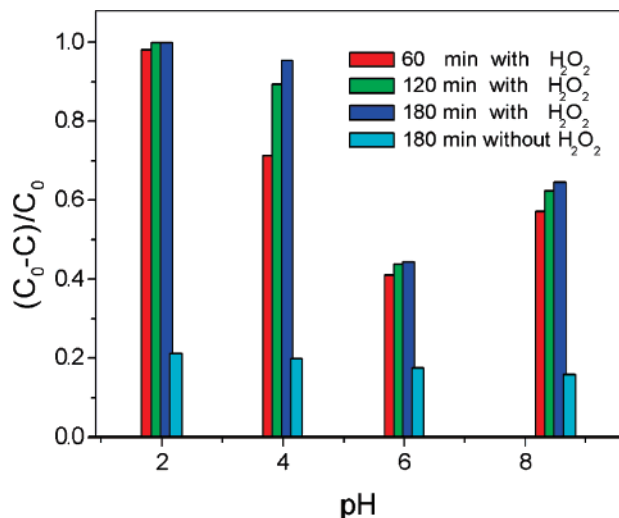
Considering the effectiveness of adsorption methods and these ground-breaking results of AOPs, we designed an efficient phase-transfer AOPs system, which combines adsorbent material supported catalyst and oxidant together. First, we chose an appropriate and efficient catalytic active site, cobalt phthalocyanine (CoPc) derivatives, which are widely used in many industries as pigments and new photoelectric materials, etc. (24–26), and have been studied as catalyzers for a variety of organic reactions (27, 28). Compared to the similar structural iron phthalocyanine (FePc), CoPc derivatives are more affordable, simpler to prepare in large scale, and more chemically stable. Second, cellulosic fiber is chosen as the support of CoPc, because it has a high natural affinity to dyes by physical and chemical interaction. Furthermore, cellulose is the most abundant organic polymer, which is produced at an annual rate of 10<sup>11</sup>–10<sup>12</sup> tons and has some prominent advantages such as good mechanical properties, nontoxicity, and most importantly biodegradability (29).

In this study, we report a highly efficient phase-transfer AOPs system, Co-TDTAPc-F/H<sub>2</sub>O<sub>2</sub>, for decomposing dyes. The supported catalyst (Co-TDTAPc-F) was obtained by immobilizing a novel catalyst, cobalt tetra (2,4-dichloro-1,3,5-triazine) aminophthalocyanine (Co-TDTAPc), on the cellulosic fiber by covalent bond. Several model dyes, as well as the factors that may influence the reaction process such as NaCl and visible irradiation were investigated. To the best of our knowledge, this is the first report on the application of cellulosic fiber bonding covalently with CoPc derivatives to increase the catalytic activity of metallophthalocyanine.

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**FIGURE 1.** Concentration changes of AR1 (50  $\mu\text{M}$ ) under different conditions: (a)  $\text{H}_2\text{O}_2$  (6 mM); (b) Co-TDTAPc-F (2 g); (c) Co-TDTAPc-F (2 g) and  $\text{H}_2\text{O}_2$  (6 mM). Inset shows the apparent first-order linear transform  $\ln(C_0/C) = f(t)$  for initial oxidation of AR1.



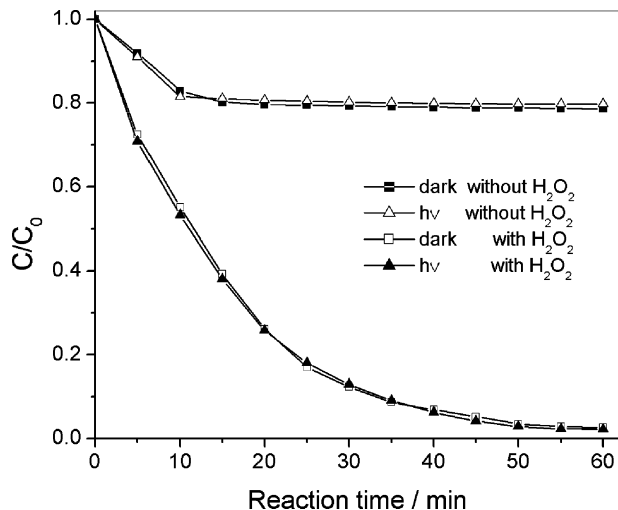
**FIGURE 2.** Effect of initial pH on adsorption and/or catalytic oxidation of AR1 at different reaction times in the presence of Co-TDTAPc-F (2 g) with  $\text{H}_2\text{O}_2$  (6 mM) or without  $\text{H}_2\text{O}_2$ .

This research provides a new practical approach for use of phase-transfer AOPs in the efficient treatment of dye effluent.

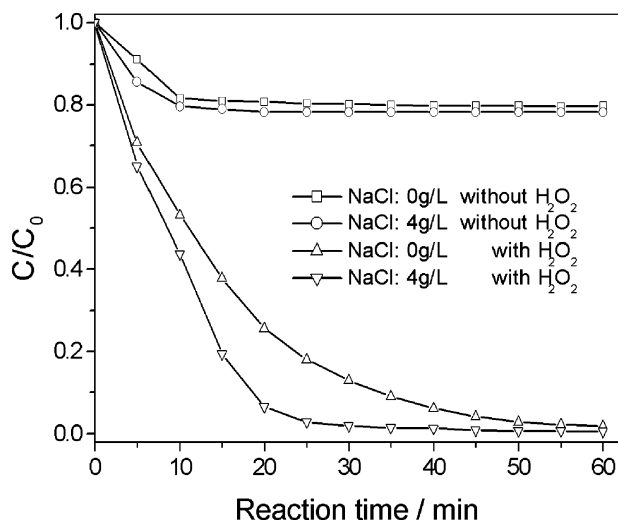
## Experimental Section

**Materials and Reagents.** Viscose fibers were obtained from Yuyao Chemical Fiber Co., Ltd (Zhejiang, China). Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) was industrial grade (>99.3%), while cobalt chloride hexahydrate, urea, and ammonium molybdate were analytical reagents, and hydrogen peroxide (9.7 M, Sinopharm Chemical Reagent Co., Ltd) was of laboratory reagent grade. All were employed without further purification. All dyes (Scheme S1, Supporting Information), including C. I. Acid Red 1 (AR1), C. I. Reactive Red 2 (RR2), C. I. Reactive Red 24 (RR24), C. I. Reactive Red 195 (RR195), C. I. Reactive Yellow 145 (RY145), C. I. Reactive Blue 221 (RB221), and C. I. Direct Red 31 (DR31), are commercial compounds and were purified three times by *N,N'*-dimethylformamide and acetone method (illustrated in the Supporting Information). Doubly distilled water was used throughout the dye decomposition process. All other solvents were of spectrometric grade.

**Catalyst Preparation.** Cobalt tetraaminophthalocyanine (Co-APc) was synthesized from 4-nitrophthalic acid, cobalt



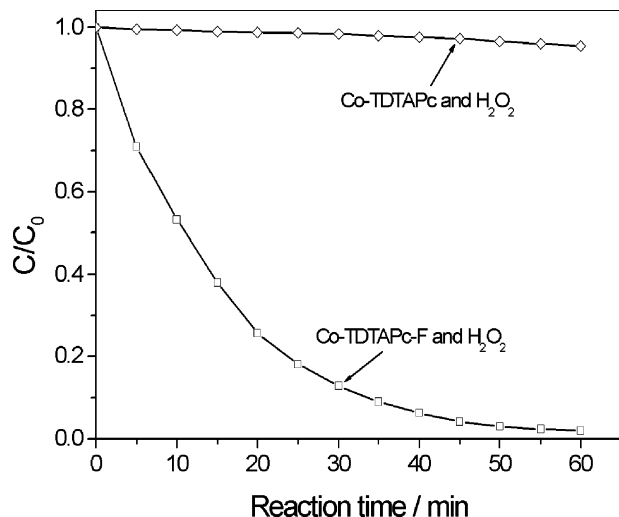
**FIGURE 3.** Effect of visible light irradiation on adsorption and catalytic oxidation of AR1 in the presence of Co-TDTAPc-F (2 g) with (6 mM) or without  $\text{H}_2\text{O}_2$ .



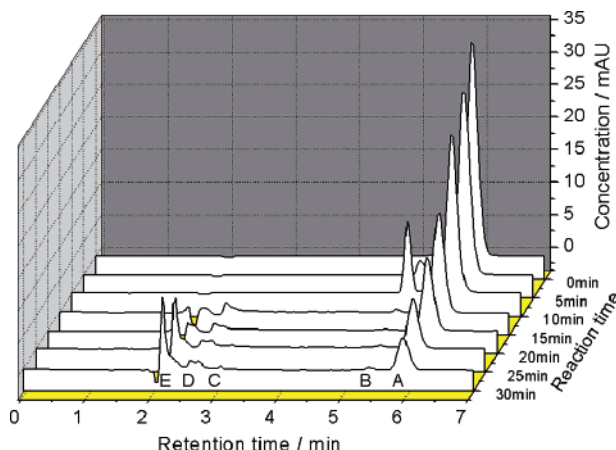
**FIGURE 4.** Effect of NaCl on adsorption and catalytic oxidation of AR1 in the presence of Co-TDTAPc-F (2 g) with (6 mM) or without  $\text{H}_2\text{O}_2$ .

chloride hexahydrate, and urea according to a method described in reference 30. The novel supported oxidation catalyst (Co-TDTAPc-F) was prepared by immobilizing cobalt tetra (2,4-dichloro-1,3,5-triazine) aminophthalocyanine (Co-TDTAPc) on the cellulosic fiber by covalent bond (Scheme S2).

**Oxidation Procedures and Analysis.** The catalytic oxidation of these different dyes was carried out in a 300-mL glass beaker. The temperature was controlled at 50  $^{\circ}\text{C}$  by a constant temperature shaker waterbath (DSHZ-300A, Taicang Laboratorial Equipment Factory, China). A typical reaction mixture contained the following initial concentrations or amount: (a) dye AR1 (50  $\mu\text{M}$ , 100 mL) or other dyes (50  $\mu\text{M}$ , 100 mL); (b) supported catalyst Co-TDTAPc-F (2 g, containing 4.56  $\mu\text{mol}$  CoPc) or Co-TDTAPc (45.6  $\mu\text{M}$ ); and (c) oxidant  $\text{H}_2\text{O}_2$  (6 mM). It was followed by the addition of NaCl (0.4 g/L). The reactions were allowed to proceed for various times and then quenched by a method appropriate to the analysis. For every run in the cyclic reaction, Co-TDTAPc-F was taken out, rinsed with distilled water, and dried for 60 min. For the control experiment in the visible light irradiation and in the dark, the irradiation source was a 500 W halogen lamp with a circulating water jacket. Light passed through a UV cutoff filter ( $\lambda > 400$  nm, Shanghai Seagull Coloured Optical Glass



**FIGURE 5.** Comparison between homogeneous and heterogeneous catalytic oxidation of AR1 in the presence of Co-TDTAPc (45.6  $\mu\text{M}$ ) or Co-TDTAPc-F (2 g, containing 4.56  $\mu\text{mol}$  CoPc) and with  $\text{H}_2\text{O}_2$  (6 mM).



**FIGURE 6.** Temporal HPLC spectra profiles during the adsorption and catalytic oxidation of AR1.

Co., Ltd) and then was focused onto the reaction beaker (illumination  $54000 \pm 1000$  lux). At given time intervals, the samples were analyzed immediately on a UV–visible spectrometer and a small part of the sample was determined by high-performance liquid chromatography (HPLC).

## Results and Discussion

**Kinetic Study of AR1 Catalytic Decomposition.** Figure 1 shows the catalytic oxidation process of a target dye AR1 under various conditions. AR1 was very stable and hardly decomposed in the presence of  $\text{H}_2\text{O}_2$  (curve a). When the supported catalyst Co-TDTAPc-F was present, adsorption took place quickly. The process of adsorption reached the dynamic equilibrium in 10 min, and about 20% of AR1 was adsorbed from aqueous phase to fiber phase (curve b). When both the supported catalyst Co-TDTAPc-F and the oxidant  $\text{H}_2\text{O}_2$  were present, the concentration of AR1 declined quickly and more than 98% of AR1 was eliminated in 60 min (curve c). As shown in the inset of Figure 1, a plot of  $\ln(C_0/C)$  versus reaction time represents a straight line, showing that the catalytic oxidation belongs to the first-order reaction with an initial rate constant of  $0.06858 \text{ min}^{-1}$ . The result indicated that the amount of dyes consumed by catalytic oxidation was continuously replenished from the aqueous solution.

**Effect of pH, Temperature, and  $\text{H}_2\text{O}_2$  Concentration.** The effect of solution pH on the rate of dye decomposition

has been investigated in a set of experiments where the pH of the solution was adjusted to 2, 4, 6, and 8.5, and the results of the rates of conversion are summarized in Figure 2. Clearly, the reaction can proceed at a wide pH range from acidic to alkaline in the Co-TDTAPc-F/ $\text{H}_2\text{O}_2$  catalytic system, although lower pH resulted in higher oxidation rate. This result is distinct from the traditional Fenton system where the oxidation can only take place at pH lower than 3. With or without  $\text{H}_2\text{O}_2$ , the amount of AR1 adsorbed and/or oxidized on Co-TDTAPc-F decreased with the increase of initial pH value. The rate of conversion increased with the reaction time, especially at pH 4, where about 95% of AR1 was eliminated in 180 min. The effect of temperature and  $\text{H}_2\text{O}_2$  concentration on catalytic oxidation has been studied and discussed as well. The results are presented in the Supporting Information (Figures S1 and S2). As expected, the dye degradation can be accelerated by the increase of temperature and  $\text{H}_2\text{O}_2$  concentration.

**Effect of Visible Light Irradiation.** Recently, visible light radiation has been introduced to the treatment of dyes, following the finding that it can accelerate the oxidation of dyes (31, 32). The activity of some Fe-based catalysts is dependent upon the radiation of visible light (33). So we designed a control experiment in the dark and in visible light radiation (500 W halogen lamp) to see whether this has the same effect on the novel system. Figure 3 shows that the concentration of AR1 declined quickly with time in visible light, as well as in the dark. This indicates that the visible light has negligible effect on the oxidation of AR1 involving Co-TDTAPc-F, in sharp contrast to the result observed by Zhao and co-workers who found that the photooxidative degradation in the presence of iron tetrasulfophthalocyanine or iron bipyridine complex occurs only under visible light (33–35). The ability of catalytic oxidation in the dark overcomes the drawback of low reaction efficiency normally found in the light sensitive system where some of the active sites are hidden inside the solid support and not accessible by the light.

**Effect of NaCl.** NaCl is a prevailing accelerant widely used in the textile dyeing industry for accelerating dye transfer from aqueous solution to fiber phase. It is important to evaluate the impact of NaCl on the catalytic oxidation for the novel system to be practical in dye effluent treatment. Figure 4 shows that when NaCl was present without  $\text{H}_2\text{O}_2$ , the adsorption of AR1 increased evidently in 10 min, and reached a dynamic equilibrium after then. However, the speed of dye decomposition increased significantly in the Co-TDTAPc-F catalytic system in the presence of NaCl and  $\text{H}_2\text{O}_2$ . This result is not in agreement with that reported in common AOPs technologies (36, 37), which claimed that  $\text{Cl}^-$  likely scavenges partial free hydroxyl radicals, thus, negatively affecting the treatment of dye effluent. We believe that the presence of  $\text{Na}^+$  increases the Zeta ( $\zeta$ ) electric potential which makes the transfer of these electronegative dyes more easily from aqueous phase to fiber phase (38), thus facilitating the catalytic oxidation. Therefore, it is an additional advantage for our system to be used practically.

**Comparison with Homogeneous Catalysis.** To explain whether the presence of fiber matrix affects the catalytic activity of CoPc derivatives, the homogeneous catalysis of Co-TDTAPc in the presence of  $\text{H}_2\text{O}_2$  was carried out (Figure 5). The molar content of CoPc in the Co-TDTAPc was the same as that in the fiber supported Co-TDTAPc-F/ $\text{H}_2\text{O}_2$  system. It can be seen that only 5% of AR1 disappeared in 60 min of reaction. This can be explained by the fact that the presence of AR1 in the Co-TDTAPc solution causes the molecule aggregation of Co-TDTAPc, which weakens the catalytic activity dramatically. However, in our novel system, the immobilization of Co-TDTAPc on cellulosic fiber prevents phthalocyanine aggregation and provides many more cata-



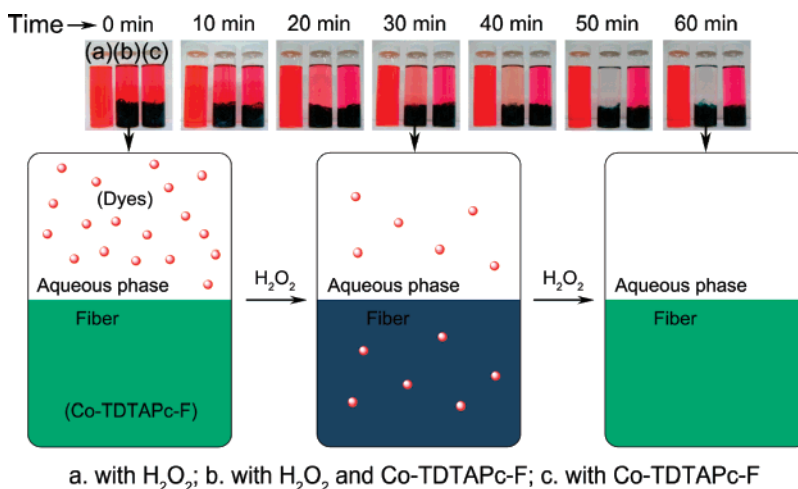


FIGURE 7. Aqueous-fiber phase transfer and/or simultaneous in situ catalytic oxidation of AR1 under different conditions.

lytic active sites. Despite the fact that this reaction process belongs to a heterogeneous reaction, the system maintains a high catalytic rate. Therefore, the fiber phase plays an important role in the whole catalytic oxidation process and improves the decomposition rate of dyes by concentrating dyes and catalytic active sites in the reaction system. The fiber matrix also provides a microenvironment that is prosperous to the catalytic reaction (39, 40). Similar results demonstrating that support materials can improve the catalytic activity of catalysts have been reported (41–43).

**Identification of Intermediates.** The concentration change of AR1 in the Co-TDTAPc-F/ $H_2O_2$  system and the intermediates generated during the oxidation process were examined by HPLC, as shown in Figure 6. The initial solution showed only one large peak due to AR1 (A) with the UV–vis spectrum, as shown in Figure S3. This peak diminished once the reaction took place, and a new peak attributed to degradation intermediate (B) appeared in 5 min, as shown in Figure S4. As the reaction progressed, the peaks of AR1 and B dramatically decreased and some new intermediates (C, D, and E) were identified. The UV–vis spectrum of C (Figure S5) with a characteristic absorption at about 310 nm indicates some naphthalene ring structures during the oxidation of AR1. In 30 min, D and E dominated over the products. According to the UV–vis spectra of D and E (Figure S6), no or little benzene ring and naphthalene ring structures were produced. The results indicate that the catalytic oxidation in the Co-TDTAPc-F/ $H_2O_2$  system leads to a deeper oxidation than decolorization.

In addition, the removal of total organic carbon (TOC) of AR1 accounted for about 40% in 90 min of reaction. This indicates that a substantial amount of AR1 was converted to other organic products, besides inorganic carbon such as  $CO_2$ . The intermediates from AR1 decomposition (curve c in Figure 1) were identified by gas chromatography/mass spectrometry (GC–MS). In Figure S7, five main residual organic acids from AR1 decomposition have been identified: oxalic acid, malonic acid, maleic acid, succinic acid, and malic acid. The result of these organic acid products is similar to the reaction catalyzed by some iron-based catalysts, which have 4 N donor atoms in a planar arrangement surrounding the metal center (19, 21).

**Discussion on Phase-Transfer Catalysis Process and Mechanism.** Figure 7 is the proposed process of phase transfer and/or simultaneous in situ catalytic oxidation. When  $H_2O_2$  existed alone in the AR1 solution (a in Figure 7), the color of the reaction solution did not change with reaction time. When Co-TDTAPc-F was added into the red AR1 dye solution

with  $H_2O_2$ , it turned from grass green to gray green, indicating the adsorption of the red AR1 dye on the catalyst (b in Figure 7). Finally, since the red dye on the catalyst was decomposed eventually over time, Co-TDTAPc-F turned back to its original color (grass green). We believe that the high affinity of cellulosic fiber to dyes involving Van der Waals forces and hydrogen bonds results in an anchor effect of dye molecule onto/into the fiber (44). On the other hand, the dyes anchored onto/into the fiber can therefore be oxidized rapidly and effectively in situ at the surface and interior of Co-TDTAPc-F. Due to the high affinity of the fiber matrix toward dyes and the concentration difference between these two phases, the decomposed dyes can be replenished continuously with dyes in aqueous phase until complete depletion. However, in the absence of  $H_2O_2$  in the dye solution (c in Figure 7), Co-TDTAPc-F kept its gray green color, indicating that the adsorption took place, but the oxidation did not.

**Cyclic Catalytic Oxidation Effect.** The reuse and stability of catalyst are two major concerns for a catalyst to be in practical application. The catalytic activity of Co-TDTAPc-F in cyclic utilizations was carried out and has been found not impaired by six repetitive experiments (Figure S13). No phthalocyanine derivatives absorbance peak in the range from 620 to 800 nm was observed by UV–vis spectrometer (Figure S14). In addition, no free cobalt ions were detected in the aqueous phase by using atomic absorption spectrometer after the reaction. This means that the catalyst remains intact in repetitive utilizations.

**Decomposition of Other Organic Dyes.** We further investigated the Co-TDTAPc-F/ $H_2O_2$  catalytic system for the oxidation degradation of other organic dyes. Some control experiments were carried out in the presence of Co-TDTAPc-F with or without  $H_2O_2$ , as shown in Table 1. Without  $H_2O_2$ , the single adsorption of dyes occurred in the presence of Co-TDTAPc-F. With the prolonged time, the adsorption process to dyes reached a dynamic equilibrium (entries 1–12), except DR31 which has a higher adsorption to cellulosic fiber (entries 13–15). When Co-TDTAPc-F and  $H_2O_2$  were co-present, the phase transfer of dyes and in situ catalytic oxidation occurred simultaneously. As the time increased, the rate of dye destruction increased correspondingly. The results indicate that these azo dyes can be quickly and effectively decomposed in this system as well. As to the direct dye DR31, it has higher affinity to Co-TDTAPc-F and more than 99% of the dye was eliminated from the dye solution within 10 min with  $H_2O_2$  (entries 13–15).

In conclusion, the novel Co-TDTAPc-F/ $H_2O_2$  system, based on the phase-transfer catalytic oxidation, offers

**TABLE 1. Phase Transfer Process and Catalytic Oxidation of Different Dyes<sup>a</sup>**

entry	dye	reaction time (min)	C/C <sub>0</sub> (%) <sup>b</sup>	
			without H <sub>2</sub> O <sub>2</sub> <sup>c</sup>	with H <sub>2</sub> O <sub>2</sub> <sup>d</sup>
1	RR2	30	79.86	22.65
2	RR2	60	79.15	2.79
3	RR24	30	82.70	35.34
4	RR24	60	81.39	12.27
5	RR24	120	80.96	1.56
6	RR195	30	79.52	22.44
7	RR195	60	78.78	13.30
8	RR195	120	78.27	1.75
9	RY145	30	77.48	10.13
10	RY145	60	76.40	0.48
11	RB221	30	80.88	0.81
12	RB221	60	80.14	0.20
13	DR31	3	50.52	16.54
14	DR31	10	38.62	0.98
15	DR31	60	8.65	0.01

<sup>a</sup> Standard conditions: the dye solution (50  $\mu$ M) was treated in the presence of Co-TDTAPc-F (2 g) without or with H<sub>2</sub>O<sub>2</sub> (6 mM). <sup>b</sup> The remaining rate (C/C<sub>0</sub>) of dyes in aqueous solution was measured by UV-visible spectrometer and HPLC. <sup>c</sup> Adsorption at various reaction times occurred in the presence of Co-TDTAPc-F without H<sub>2</sub>O<sub>2</sub>. <sup>d</sup> Adsorption and simultaneous catalytic oxidation occurred in the presence of Co-TDTAPc-F and H<sub>2</sub>O<sub>2</sub>.

capabilities and advantages of (1) efficiently oxidizing the organic dyes in aqueous solution into small molecular biodegradable compounds, such as oxalic acid, malonic acid, and maleic acid; (2) causing no secondary pollution due to the stability of this supported catalyst; (3) being recuperated easily from dye solution for reuse with no obvious degradation of catalytic activity; (4) being efficient without any lamp-house; and (5) having no negative effect caused by NaCl as encountered in other systems; instead, NaCl is an accelerant for the current catalytic oxidation. The fiber matrix plays an important role in the overall phase-transfer catalytic oxidation process and improves the catalytic oxidation rate of dyes dramatically by concentrating the dyes and catalytic active sites. Therefore, this research provides a new practical approach of phase-transfer AOPs to the efficient treatment of dye effluent.

## Acknowledgments

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## Supporting Information Available

Structures of the employed dyes, preparation of the phthalocyanine derivative and fiber supported cobalt phthalocyanine, effect of temperature and H<sub>2</sub>O<sub>2</sub> concentration on catalytic activity of Co-TDTAPc-F/H<sub>2</sub>O<sub>2</sub> system, UV-vis spectra of intermediates, and GC-MS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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