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Photocatalytic Degradation of Acid Orange II Using Activated Carbon Fiber-Supported Cobalt Phthalocyanine Coupled with Hydrogen Peroxide

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Abstract Activated carbon fiber-supported cobalt phthalocyanine photocatalyst (Co-TDTAPc-F) was prepared in this study, and its performance for dye wastewater decoloration was investigated, and Acid Orange II (AO7) was selected as the target pollutant. The morphology analysis of Co-TDTAPc-F was conducted, and the effects of catalyst loading, H_2O_2 addition, solution pH, and catalyst reuse on AO7 decoloration efficiency were evaluated. The results showed that AO7 decoloration efficiency increased by 23.2% during the Co-TDTAPc-F photocatalytic process as compared with solely Co-TDTAPc-F adsorption, and the decoloration process was fitted by pseudo first-order reaction. The increase of catalyst loading and H_2O_2 content both benefitted AO7 decoloration. Strong photocatalytic activities were observed at both acidic and alkaline conditions; however, total organic carbon (TOC) removal efficiency decreased with the increase of solution pH. Strong photocatalytic activity was still observed after four times reuse. The mechanisms of AO7 photocatalytic decomposition by Co-TDTAPc-F were proposed.

Keywords Cobalt phthalocyanine · Activated carbon fiber · Photocatalysis · Dyes · Decoloration · H_2O_2

1 Introduction

A variety of synthetic organic dyes has been widely used in modern textile industries, and most of these dyes present strong biologic toxicity and visibility in water, causing serious pollution (Li et al. 2011; Wang et al. 2014); and thus, complete removal of these dyes from effluents has become a major and urgent environmental problem of the textile industries. However, due to a number of aromatic rings in the dye molecules, traditional biological and physical treatment methods were ineffective for dye degradation (Eskandarloo et al. 2014). New approaches, called advanced oxidation processes (AOPs), have aroused considerable interest for degradation of toxic compounds in water (Li et al. 2011; Eskandarloo et al. 2014; Wang et al. 2014). Heterogeneous photocatalysis was one of the most promising AOPs developed in the past 20 years as an alternative to dye-containing wastewater treatment (Eskandarloo et al. 2014). The basic mechanism of heterogeneous photocatalysis has been well investigated, and the main oxidative species, •OH radicals, was strong enough to degrade most contaminants effectively in wastewater

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(Turchi and Ollis 1990). Nano-TiO_2 is one of the most widely utilized photocatalyst in wastewater treatment; however, the photocatalytic oxidation process for nano-TiO_2 photocatalyst actually had low efficiency, because of its band gap of 3.2 eV which limited the photo adsorption, and thus it usually took quite a long time to treat wastewater (Zanjanchi et al. 2010).

Metal phthalocyanines were porphyrin derivatives consisting of a central metallic atom bound to a π-conjugated ligand, characterized by high symmetry, planarity, and electron delocalization (Mele et al. 2015). Considerable attention has been focused on nanosized phthalocyanine owing to its unique properties and promising applications in photocatalysis (Mackintosh et al. 2008; Palmisano et al. 2008; Makhseed et al. 2009; Wang et al. 2016). Metal phthalocyanines and their derivatives possessed an intensive absorption in the blue-green region and therefore could be used in both homogeneous and heterogeneous photocatalytic processes (Guo et al. 2010). Phthalocyanines could produce highly active oxygen in the form of singlet oxygen or various reactive oxygen species such as the superoxide radicals, which could rapidly react with organic pollutants (Nensala and Nyokong 2000; Ozoemena et al. 2001).

Recently, the homogeneous photocatalytic activities of different phthalocyanine complex for organic pollutants degradation have been examined, such as chlorophenol (Kluson et al. 2008), bisphenol (Tai et al. 2005), and nitrophenol (Marais et al. 2007). Compared with the homogeneous catalysis, the heterogeneous catalysis had some advantages such as long life time of the catalyst, facile recovery, and easy separation from wastewater (Titinchi et al. 2015). Therefore, supported metallophthalocyanine has received much more interest in dealing with organic pollutants in wastewater (Wang et al. 2006; Khoza and Nyokong 2014; Li et al. 2015).

Activated carbon fiber (ACF) was profusely used as an efficient and versatile adsorbent in decontamination processes because of its extended surface area, high adsorption capacity, developed porous structure, and special surface reactivity (Teng et al. 2015). ACF has also been widely selected as the supporter of photocatalysts (Guo et al. 2008; Oh et al. 2009); on the one hand, the strong adsorption of ACF could condense organic pollutants around the photocatalyst, and then the reactions of pollutants with active species in the photocatalytic process would be accelerated; on the other hand, ACF surface functional groups could also participate in some catalytic reactions. However, little research has been conducted on photocatalytic activities of ACF-supported metal phthalocyanine for dye-containing wastewater treatment.

In the present research, ACF-supported cobalt phthalocyanine photocatalyst (Co-TDTAPc-F) was prepared, and the resulting solid photocatalyst was characterized and was tested for photocatalytic decomposition of Acid OrangeII (AO7). The influences of the amount of Co-TDTAPc-F, solution pH, H_2O_2 concentration, and the Co-TDTAPc-F reuse on AO7 decoloration efficiency were evaluated. The proposed mechanism for AO7 decomposition was also discussed.

2 Materials and Methods

2.1 Materials

ACF was purchased from Shenzhen Lvchuang Chemical Co. Ltd., AO7 was obtained from Shanghai Chemical Reagent Co. Ltd., and 4-nitro phthalates formyl amine, ammonium molybdate, $CoCl_2$, urea, N,N dimethyl formamide, cyanuric chloride, and other chemical reagents were all commercially available and used without further purification.

2.2 Preparation of Co-TDTAPc-F

Original ACF was firstly cut into some fragments with 5 mm × 5 mm, and boiled in deionized water for 60 min, and then dried in the oven at 90 °C. The dried ACF was immersed into HNO_3 solutions ($V/V = 1:1$) for 24 h, and washed with deionized water to neutral, and then dried before use. The obtained ACF was called as O-ACF.

Co-TDTAPc was synthesized from cobalt teraaminophthalocyanine and cyanuric chloride according to the method described by Chen et al. (2007). The preparation processes of Co-TDTAPc-F were as follows: firstly, some amounts of O-ACF were immersed into Co-TDTAPc solutions, and shaked for 60 min at 40 °C; secondly, the solution temperature was warmed up to 55 °C, and then some amounts of the Na_2CO_3 solution was added, and it was further shaked for 60 min at 55 °C; thirdly, the supported O-ACF was washed with deionized water until the washing liquid was not green; finally, the supported O-ACF was dried and Co-TDTAPc-F was obtained. Scanning electron microscope (SEM, S-4800, Hitachi) was used to characterize the morphology and structure of the Co-TDTAPc-F photocatalyst.

2.3 Photocatalytic Test

The photocatalytic system consisted of an UV lamp (365 nm, 250 W), quartz glass reactor (180 mm length, 45 mm width), and cooling system, as shown in Fig. 1. The UV lamp was surrounded by a water-cooling quartz jacket to cool the lamp. For the photocatalytic test, 400 mL AO7 solution with an initial concentration of 50 mg L^{-1} was treated. The AO7 solution was stirred and circulated via a circulating pump with a rate of 80 mL min^{-1}, and it was cooled via the ice-water bath method. The UV lamp and quartz glass reactor were both in the dark during the photocatalytic process. The stable light intensity was 0.496 W cm^{-2}. Decrease in the concentration of AO7 was analyzed by UV-vis spectrophotometer (UV-1901, Shanghai Youke). The AO7 mineralization efficiency was analyzed by total organic carbon (TOC). At given intervals of illumination, the samples of the reaction solutions were taken out and analyzed.

3 Results and Discussion

3.1 Morphology Analysis of Photocatalyst

The SEM micrographs of O-ACF and Co-TDTAPc-F with the same magnification were shown in Fig. 2. As could be seen from the micrographs, the surface of O-ACF was quite smooth, while obvious hot spots were observed on the surface of Co-TDTAPc-F; this result suggested that some amounts of cobalt phthalocyanine were supported on the O-ACF. In order to further confirm this point, Co-TDTAPc-F and O-ACF were both calcinated at 800 °C for 8 h, and the appearance was shown in Fig. 3. After being calcinated, O-ACF was converted into some agminated white particles, while Co-TDTAPc-F photocatalyst was converted into some dispersive blue particles; this phenomenon also suggested that cobalt phthalocyanine was supported on the O-ACF surface.

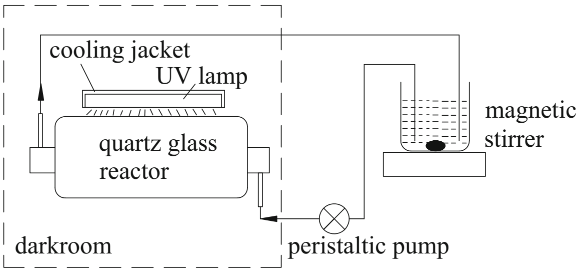


Fig. 1 Schematic diagram of photocatalytic reaction system

3.2 Adsorption Potentials Measurement

The adsorption potential of Co-TDTAPc-F was tested with AO7 as the target pollutant, and the adsorption potential of O-ACF was also evaluated, and the results were shown in Fig. 4. Herein, AO7 initial concentration was 50 mg L^{-1}, treatment volume was 400 mL, and O-ACF dosage was 0.75 g L^{-1}. As could be seen in Fig. 4, the adsorption potential of O-ACF was stronger than that of Co-TDTAPc-F; about 23.6% of AO7 was adsorbed on the surface of O-ACF within 120 min, while only 9.8% was adsorbed on the surface of Co-TDTAPc-F. This phenomenon suggested that some active sites on the O-ACF surface were occupied by Co-TDTAPc, and then the specific surface area of Co-TDTAPc-F would decrease, and thus inhibiting its adsorption potentials. Similar results were also observed by Huang et al. (2014), in whose research the adsorption potential of activated carbon fiber-supported cobalt phthalocyanine was weaker than that of activated carbon fiber.

3.3 Photocatalytic Activity

An experiment was carried out to test the photocatalytic activity of the Co-TDTAPc-F for the decomposition of AO7 under UV irradiation. For a better explanation of the photocatalytic efficiency of the sample, further comparative experiments were carried out in the decomposition of AO7 by O-ACF in the same experimental conditions. The detailed results on AO7 decomposition were shown in Fig. 5. Herein, the AO7 initial concentration was 50 mg L^{-1}, treatment volume was 400 mL, and the O-ACF dosage was 0.75 g L^{-1}. Obviously, AO7 removal efficiency was enhanced significantly during the Co-TDTAPc-F photocatalytic process as compared with adsorption experiments, and there was about 23.2% enhancement in AO7 removal efficiency within 120 min treatment. However, there was not any increase in AO7 removal efficiency by O-ACF under UV irradiation as compared with its adsorption experiments. These results suggested that the enhancement of AO7

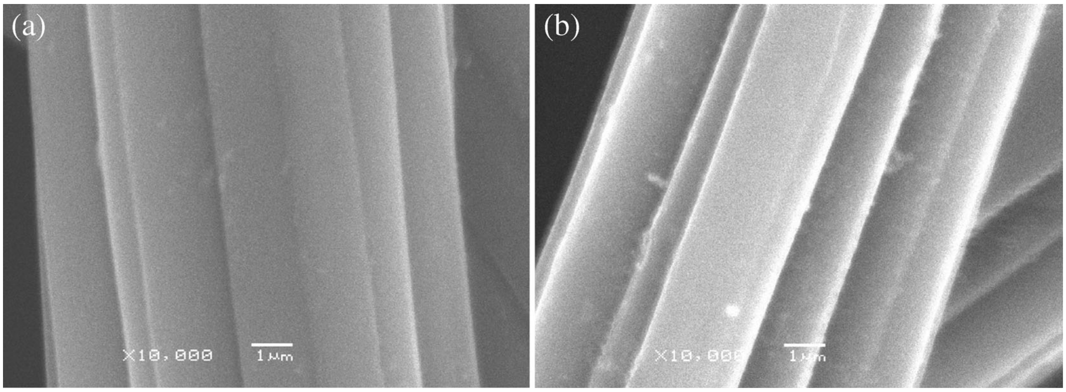


Fig. 2 The SEM micrographs of O-ACF and Co-TDTAPc-F (**a**: O-ACF; **b**: Co-TDTAPc-F)

removal efficiency by Co-TDTAPc-F under UV irradiation was attributed to its photocatalytic roles.

The photocatalytic decomposition of AO7 was fitted by pseudo first-order reaction, and its kinetics may be expressed as $\ln(C_0/C_t) = kt$, as shown in Fig. 5 (the inset). In this equation, k (min^{-1}) is the apparent rate constant; C_0 and C_t are the initial concentration and concentration at reaction time t of AO7, respectively. The results showed that the AO7 decomposition process by Co-TDTAPc-F photocatalyst under UV irradiation was suitable for the first-order kinetic reaction, and the reaction rate constant was 0.00273 min^{-1}.

3.4 Effect of Catalyst Loading

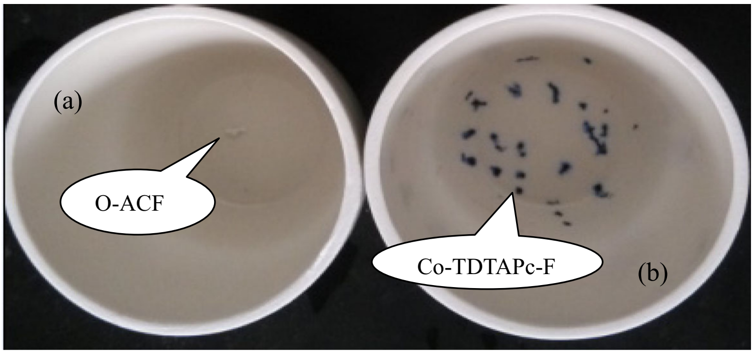
At low photocatalyst loading, the removal of the organic compounds increased with the catalyst loading; however, the presence of the excess photocatalyst in the aqueous solutions could cause a shielding effect in penetration of light (Wu et al. 2007). Therefore, the effect of Co-TDTAPc-F loading on AO7 removal was evaluated, and the results were shown in Fig. 6. Herein, the AO7 initial concentration was 50 mg L^{-1}, and the treatment volume was 400 mL. AO7 removal efficiency increased with the amount of Co-TDTAPc-F increased from 0.25 to 2 g L^{-1}, and about 47% of AO7 was removed within 120 min treatment by Co-TDTAPc-F photocatalytic reaction with the catalyst loading of 2 g L^{-1}.

3.5 Effect of H_2O_2 Addition

H_2O_2 is one kind of oxidant, and it is usually used to enhance organic pollutant removal in photocatalytic reaction. An important role of H_2O_2 addition is to generate ·OH radicals; ·OH radicals can be generated by direct photolysis of H_2O_2, or by reaction of H_2O_2 with superoxide radical (Cornish et al. 2000; Poulios et al. 2003). In our research, a source of UV-A was employed, emitting near-UV radiation, and it was unlikely that direct photolysis of H_2O_2 was significant.

The effect of H_2O_2 addition on AO7 removal by Co-TDTAPc-F photocatalytic reaction was evaluated, as shown in Fig. 7. Herein, the AO7 initial concentration was 50 mg L^{-1}, the treatment volume was 400 mL, and the catalyst dosage was 0.75 g L^{-1}. As control experiments, direct H_2O_2 oxidation without UV irradiation for

Fig. 3 ACF morphology after calcination at 800 °C (**a**: O-ACF; **b**: Co-TDTAPc-F)



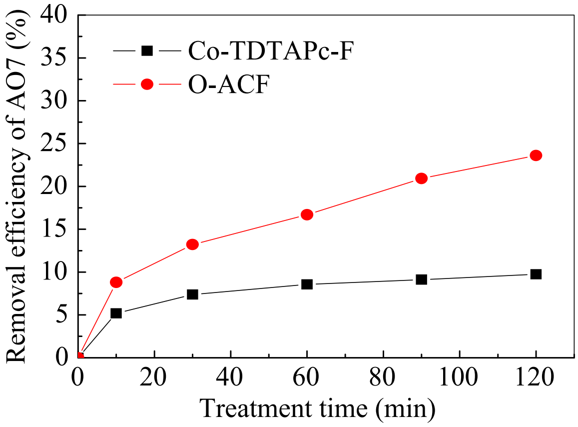


Fig. 4 Adsorption characteristics of Co-TDTAPc-F and O-ACF

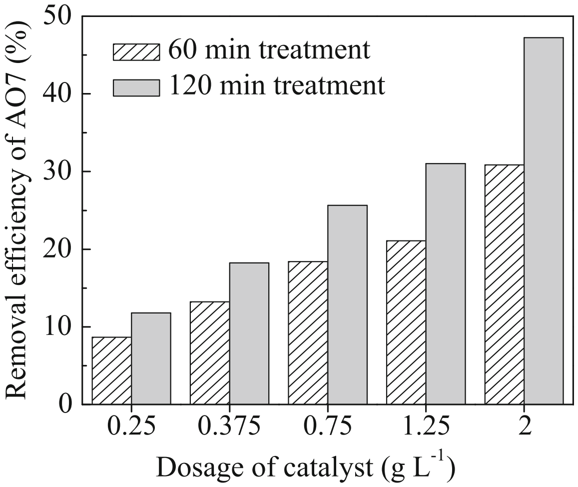


Fig. 6 Effect of catalyst loading on AO7 removal

AO7 removal was also carried out, and only 15% of AO7 was removed within 120 min treatment. As could be seen in Fig. 7, the AO7 removal efficiency increased with the increase of H_2O_2 concentration to a certain extent. For example, AO7 removal efficiency increased from 75 to 99% within 60 min treatment with H_2O_2 concentration increased from 1.25 to 12.5 mmol L^{-1}; however, no obvious enhancement in AO7 removal was observed with further increasing H_2O_2 concentration to 125 mmol L^{-1}. Generally, there existed an optimum H_2O_2 concentration to enhance pollutant removal, and large amounts of H_2O_2 would diminish the removal process. In a relatively lower H_2O_2 amount, H_2O_2 could absorb light energy from UV irradiation to produce ·OH radicals (Zangeneh et al. 2015); whereas at a higher concentration, the H_2O_2 could also react with the ·OH radicals to generate $HO_2\cdot$ (see reactions 1–2), which was less reactive than the ·OH, and thus relatively higher amount of H_2O_2 had a diminishing return on the removal process (Daneshvar et al. 2003). A similar phenomenon was also observed by Touati et al. (2016), in whose research there existed an optimum H_2O_2 concentration to gain relative higher wastewater treatment efficiency by photocatalytic degradation. In the present research, the optimum H_2O_2 concentration was found to be 12.5 mmol L^{-1} for AO7 removal, and the addition of H_2O_2 enhanced the generation of ·OH radicals by reaction of H_2O_2 with superoxide radicals.

$$H_2O_2 + \bullet\mathrm{OH} \rightarrow HO_2\bullet + H_2O \tag{1}$$

$$\mathrm{HO_2}\bullet + \bullet OH \rightarrow H_2O + O_2 \tag{2}$$

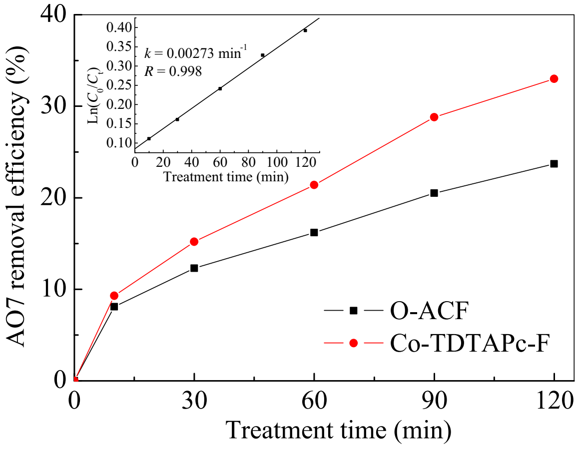


Fig. 5 Photocatalytic decomposition of AO7 by Co-TDTAPc-F

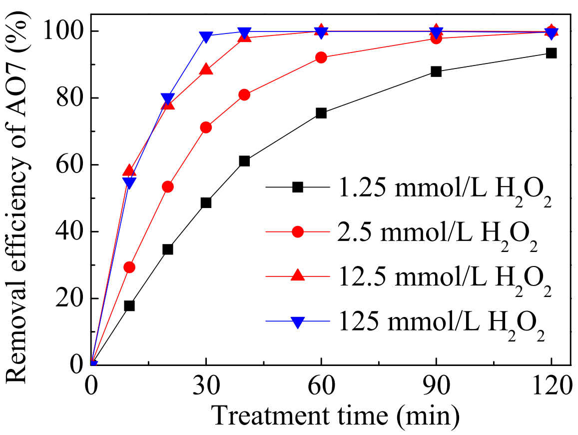


Fig. 7 Effect of H_2O_2 addition on AO7 removal

3.6 Effect of Solution pH

The solution pH of dye-containing wastewater is usually fluctuant with the changes of the manufacturing process and pollutant varieties, and solution pH value also affects the activity of photocatalyst. Therefore, it is significant to evaluate the effect of solution pH on AO7 removal by Co-TDTAPc-F photocatalytic degradation.

The effect of solution pH on AO7 removal was shown in Fig. 8. Herein, the AO7 initial concentration was 50 mg L^{-1}, the treatment volume was 400 mL, the catalyst dosage was 0.75 g L^{-1}, H_2O_2 concentration was 12.5 mmol L^{-1}, and the treatment time was 60 min. As could be seen in Fig. 8, the effect of solution pH on AO7 removal was not very significant; within 60 min photocatalytic treatment, AO7 removal efficiency was 98, 91, 93, 87, and 93% at solution pH value of 2.0, 4.0, 7.0, 10.0, and 11.0, respectively. These results indicated that Co-TDTAPc-F/H_2O_2 had strong photocatalytic activities at both acidic and alkaline conditions, and thus the application scope of Co-TDTAPc-F/H_2O_2 covered a wide solution pH range.

On the other hand, the mineralization of AO7 (TOC removal) was quite different from AO7 removal, as shown in Fig. 8. TOC removal efficiency decreased with the increase of solution pH value. TOC removal efficiency decreased from 70 to 42% as solution pH increased from 2.0 to 11.0. These results might be due to the fact that it was much easier for cobalt phthalocyanine to lose electrons under acidic conditions, and thus its photocatalytic activity would enhance. Furthermore, under acidic conditions, more H_2O_2 would be generated under the participation of H^+ (see reaction 3).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{3}$$

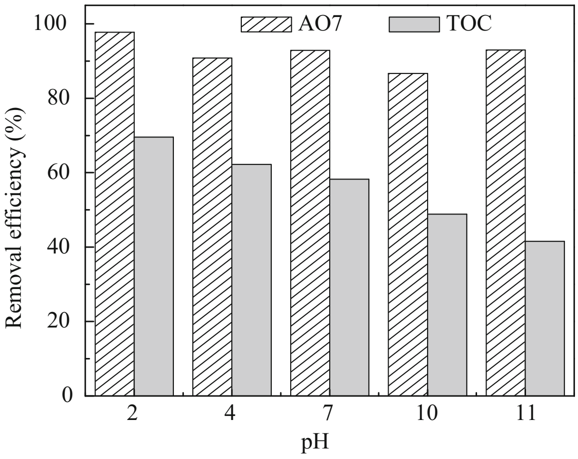


Fig. 8 Effect of solution pH value on AO7 removal

3.7 Catalyst Reuse

The stability of the photocatalyst is quite important for its application in environment pollution control. Therefore, the effectiveness of Co-TDTAPc-F reuse was examined for AO7 removal during a four cycle experiment. Each experiment was carried out under the same conditions. The AO7 initial concentration was 50 mg L^{-1}, the treatment volume was 400 mL, the catalyst dosage was 0.75 g L^{-1}, H_2O_2 concentration was 12.5 mmol L^{-1}, and the treatment time was 60 min. After each experiment, the AO7 solution residue from photocatalytic degradation was firstly filtered, and then the obtained Co-TDTAPc-F photocatalyst was washed with deionized water for several times, and dried; the dried Co-TDTAPc-F photocatalyst samples were used again for AO7 photocatalytic decomposition.

The effectiveness of the Co-TDTAPc-F reuse for AO7 removal was shown in Fig. 9. Recycling experiments showed that great performance of the Co-TDTAPc-F photocatalyst for AO7 removal after four catalytic cycles was still observed, and AO7 removal efficiency was still above 92% for four catalytic recycling experiments. These results suggested that the

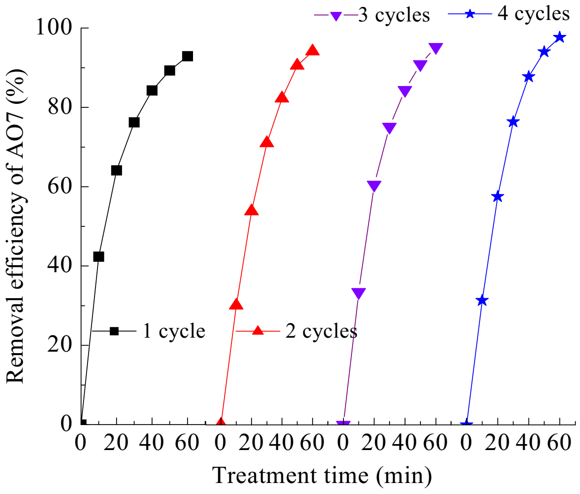


Fig. 9 Reuse of the Co-TDTAPc-F catalyst for AO7 removal for four successive cycles

photocatalysis activity of Co-TDTAPc-F was not decreased after several reuse, and it was still quite stable. More importantly, no external energy was involved in regenerating Co-TDTAPc-F during recycle use in the present research, since it was an oxidation regeneration process, and it represented a “real” removal of the substrate, but not simply its transfer from solution to adsorbent or from adsorbent to another environment. Similar results were also reported by Lu et al. (2009), in whose research great performance for 4-nitrophenol degradation by activated carbon fiber-supported metallophthalocyanine photocatalysis was still observed within six times reuse of the catalyst.

The proposed mechanism for the decomposition of AO7 by H_2O_2-assisted Co-TDTAPc-F photocatalysis might be as follows (Zhang et al. 2003; Sehlotho and Nyokong 2004; Marais et al. 2007; Chauke and Nyokong 2008):

$$\mathrm{MPc} \overset{hv}{\rightarrow} MPc^{*} \tag{4}$$

$$MPc^{*} + O_2 \rightarrow MPc^{\cdot +} + O_2^{\bullet -} \tag{5}$$

$$O_2^{\bullet -} + H^{+} \rightarrow HO_2^{\bullet} \tag{6}$$

$$O_2^{\bullet -} + H_2\mathrm{O} \rightarrow HO_2^{\bullet} + \mathrm{OH}^{-} \tag{7}$$

$$HO_2^{\bullet} + H_2\mathrm{O} \rightarrow \mathrm{H_2O_2} + \cdot\mathrm{OH} \tag{8}$$

$$H_2\mathrm{O}_2 + hv \rightarrow \cdot OH + \cdot OH \tag{9}$$

$$MPc^{\bullet +} + AO7 \rightarrow MPc + AO7^{\bullet +} \tag{10}$$

$$\mathrm{AO7}, AO7^{\bullet +} \overset{\cdot OH, H_2O_2, HO_2\cdot}{\rightarrow} products \tag{11}$$

where MPc represented the Co-TDTAPc-F. When Co-TDTAPc-F was irradiated by UV light, it converted into the excited state (MPc^{*}). The excited MPc^{*} would react with the ground state molecular oxygen to generate super-oxygen radical ions ($O_2^{\cdot -}$) and the MPc radical cations ($MPc^{\cdot +}$). The super-oxygen radical ions would on protonation generate the hydroperoxy radicals ($HO_2\cdot$), and then some ·OH radicals was formed, which was a powerful oxidizing agent to decompose AO7. ·OH radicals could also be generated by catalytic decomposition of H_2O_2 under UV irradiation. Moreover, $MPc^{\cdot +}$ had certain redox potentials, and it could oxidize the target pollutant AO7 into radical cations ($AO7^{\cdot +}$), together with recovery of the original MPc. Finally, the AO7 molecules and its radical cations further oxidized under the oxidation of ·OH radicals, H_2O_2, and $HO_2\cdot$.

4 Conclusions

Co-TDTAPc-F was prepared and its photocatalytic activity for AO7 decoloration was studied in the present research. SEM analysis showed that cobalt phthalocyanine was supported on the O-ACF surface. Great performance for AO7 decoloration was observed by Co-TDTAPc-F photocatalysis. Under the studied conditions, increasing catalyst loading and H_2O_2 additions both resulted in higher AO7 decoloration efficiency. Co-TDTAPc-F/H_2O_2 had strong photocatalytic activities at both acidic and alkaline conditions, and thus the application scope of Co-TDTAPc-F/H_2O_2 covered a wide solution pH range. The photocatalytic activity of Co-TDTAPc-F was not decreased after four times reuse, and it was still quite stable. Co-TDTAPc-F could be excited by UV light and converted into MPc^{*}, and then it reacted with O_2 to generate $O_2^{\cdot -}$, $MPc^{\cdot +}$, $HO_2\cdot$, and ·OH radicals, which could all oxidize AO7.

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