

Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2012, Article ID 121239, 8 pages
doi:10.1155/2012/121239

Research Article

Preparation of a Modified PTFE Fibrous Photo-Fenton Catalyst and Its Optimization towards the Degradation of Organic Dye

Zhizhong Ding,¹ Yongchun Dong,^{1,2} and Bing Li¹

¹Division of Textile Chemistry & Ecology, School of Textiles, Tianjin Polytechnic University, 399 Binshui Western Road, Xiqing District, Tianjin 300387, China

²State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou 350002, China

Correspondence should be addressed to Yongchun Dong, dyefib@yahoo.com.cn

Received 22 May 2012; Accepted 30 July 2012

Academic Editor: Meenakshisundaram Swaminathan

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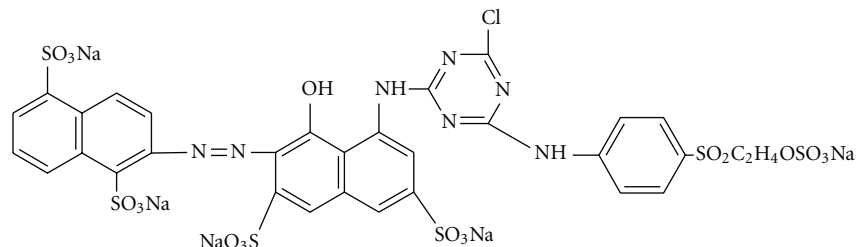
Polytetrafluoroethylene (PTFE) fiber was grafted with acrylic acid to impart the carboxyl groups onto the fiber surface, which were used to coordinate with both transition metal ions Fe(III) and Cu(II) and a rare metal ion Ce(III) to prepare the metal grafted PTFE fiber complexes as the novel heterogeneous Fenton catalysts for the degradation of the azo dye in water under visible irradiation. Some factors affecting the preparation process, such as nature and concentration of metal ions in the coordination solution, grafting degree of PTFE and reaction temperature were optimized with respect to the content and strength of metal fixation on the fiber and dye degradation efficiency. The results indicated that increasing metal ion concentrations in solution and grafting degree of PTFE fiber as well as higher coordination temperature led to a significant increase in metal content, especially Fe(III) and Cu(II) content of the complexes. Fe(III) ions fixed on the fiber showed the better catalytic performance than Cu(II) and Ce(III) ions fixed when three different complexes with similar metal content being employed, respectively. Moreover, increasing Fe content or incorporation of Cu(II) ions could significantly improve the catalytic activity of the complexes.

1. Introduction

Dye-containing wastewater from different industrial fields is a principal source of environmental contamination. And these dyes are known to be largely nonbiodegradable and toxic to aquatic plants and animals. In recent years, heterogeneous Fenton process has become a research focus in the treatment of these dyes in water because of its application over a wide pH range and easy separation of the catalyst after the reaction. The modified polyacrylonitrile (PAN) fiber Fe complexes have been regarded as the attractive heterogeneous Fenton catalysts with low cost and high effectiveness [1–5]. However, it was reported that the modifications, especially amidoximation can lead to a significant decrease in the mechanical performance of PAN fiber. Moreover, the tensile strength of the amidoximated PAN fiber was found to be further lower after coordinating with Fe ions in our previous work [2, 6]. This may limit its commercial applications in the future because good

mechanical performance is necessary for effective using of the fibers as the catalysts for Fenton system.

Polytetrafluoroethylene (PTFE) fiber has received more and more attention in the past decades because of their outstanding thermal, chemical stability, and mechanical properties even under very harsh conditions [7–9]. In recent years, there have been many reports of using modified PTFE fibers and films containing functional groups for the concentration and separation of metal ions from aqueous media [10–12]. However, little attention has been paid to the heterogeneous Fenton catalyst produced by PTFE modification and metal coordination and its catalytic property for degradation of organic dye. Therefore, our investigations have been directed to the preparation of a fibrous PTFE catalyst with both good catalytic activity and mechanical strength. In this work, the influence of grafting degree of PTFE fiber, nature, and concentration of metal ion in the coordination solution and reaction temperature was optimized with respect to the content and strength of metal



SCHEME 1: Chemical structure of RR 195.

fixation on the fiber and decomposition efficiency of organic dye in aqueous solutions.

2. Experimental

2.1. Materials and Reagents. PTFE fibers were commercially available and provided by Fuxin Sengfuli Polymer Materials Co., China. Acrylic acid, hydrogen peroxide (30%, w/w), and ammonium ferrous sulphate were of analytical grade. $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were used as the metal ions sources, respectively. Horseradish peroxidase (POD), N,N-diethyl-p-phenylene-deamine (DPD) and Reactive Red 195 (abbr. RR 195) was of laboratory agent grade and used without further purification. RR 195 was a typical azo dye and its molecular structure is presented in Scheme 1. Double distilled and deionized water was used throughout the study.

2.2. Preparation of Metallic Modified PTFE Fiber Complexes

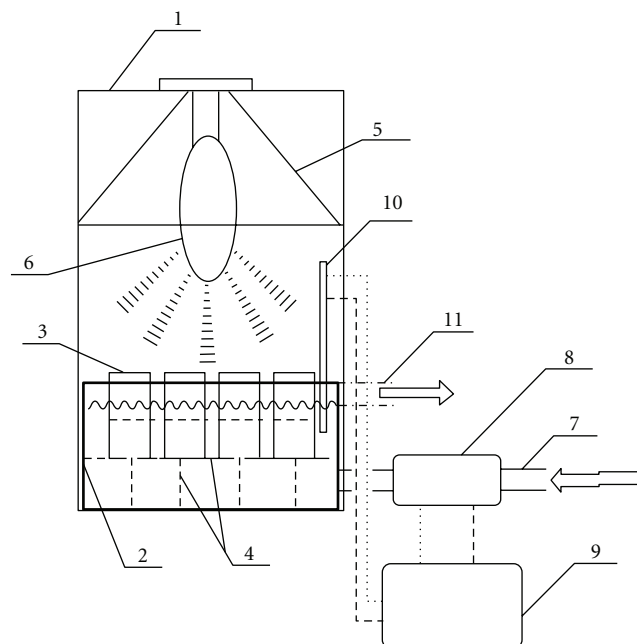
2.2.1. Graft Polymerization of PTFE Fibers. Before modification, PTFE fibers were treated with acetone at room temperature for 30 min, and then dried in a vacuum oven at 50°C for 48 h. 10.0 g of the dried fibers was immersed into the monomer solution containing 100 mL acrylic acid and 200 mL deionized water in a 500 mL flask. 3.0 wt% ammonium ferrous sulphate was also used in the monomer solution to minimize the homopolymerization of acrylic acid during the reaction. The flask containing the monomer solution and fibers was bubbled with nitrogen for 20 min to remove oxygen and sealed. The mixture in the flask was directly subjected to gamma-rays of irradiation from a ^{60}Co source at a dose rate of 0.5 kGy h^{-1} for a given time. After irradiation, the grafted PTFE fibers (denoted as PAA-g-PTFE) were took out and washed with hot water, and acetone repeatedly to remove the residual monomer, homopolymers adhered to the fiber surface. Finally, the obtained grafted fibers were dried in a vacuum oven at 50°C for 24 h and weighed. The grafting degree was obtained using the following formula: $G_f\% = (W_g/W_o - 1) \times 100\%$, where W_o and W_g are the weights of the original and grafted fibers, respectively. It was noticed that the breaking strength of the original PTFE fiber was measured to be 93.35 CN, and little decrease in its breaking strength was observed after the polymerization.

2.2.2. Transition Metal PAA-g-PTFE Complexes. 5.0 g of PAA-g-PTFE was immersed in 150 mL of FeCl_3 or CuSO_4 aqueous solution, and then the mixture was treated at 50°C and pH 2.0-3.0 for a given time under continuous agitation. The resulting fibrous metal complexes were filtered, washed with deionized water and dried under vacuum at 60°C for 4.0 h to obtain Fe(III-) grafted PTFE fiber complexes (denoted as Fe-PAA-g-PTFE) or Cu(II-) grafted PTFE fiber complexes (denoted as Cu-PAA-g-PTFE). The residual concentrations of Fe(III) or Cu(II) ions in the solutions after coordination were determined by using a WXF120 atomic absorption spectrometry (Beijing Rayleigh Analytical Instrument Corp., China) for calculating the Fe content ($Q_{\text{Fe-PTFE}}$) or Cu content ($Q_{\text{Cu-PTFE}}$) of the complexes.

2.2.3. Rare Metal PAA-g-PTFE Complexes. The complexes were prepared similarly to the transition metal PAA-g-PTFE complexes by using CeCl_3 in the coordination solution. And the final complexes were denoted as Ce-PAA-g-PTFE. The Ce content ($Q_{\text{Ce-PTFE}}$) of the complexes was measured and calculated by determining the residual Ce(III) ions in solution after coordination through a $\text{Na}_2\text{-EDTA}$ -based titrimetric method.

2.2.4. Cu-Fe Bimetallic PAA-g-PTFE Complexes. These complexes were also synthesized similarly to monometallic PAA-g-PTFE complexes by using the mixed coordination solutions containing different concentration of Fe(III) and Cu(II) ions during the coordination processes. Cu-Fe bimetallic PAA-g-PTFE complexes (denoted as Cu-Fe-PAA-g-PTFE) with different molar ratios of Fe(III) to Cu(II) ion (abbr. Cu/Fe molar ratio) were produced by adjusting the concentrations of the metal ions in coordination solution, and in which the concentrations of total metal ions were kept constant at 0.10 mol L^{-1} .

2.3. Catalytic Activity of the Complex towards H_2O_2 Decomposition. The decomposition of H_2O_2 was carried out at the 150 mL Pyrex vessels inside the photoreaction reaction system. A 400 W high pressure mercury lamp (Foshan Osram Illumination Co., China) was used as the illuminating source for photocatalytic reaction. A cutoff filter was used to ensure irradiation only by visible light ($\lambda > 420 \text{ nm}$) for the high pressure mercury lamp. The intensity of visible light irradiation over the surface of test solution inside photoreaction system was measured to be 9.65 W cm^{-2} using



- | | |
|------------------|---------------------------|
| (1) Chamber | (7) Water in |
| (2) Water bath | (8) Electromagnetic valve |
| (3) Glass vessel | (9) Relay |
| (4) Support | (10) Thermometer |
| (5) Lamp-chimney | (11) Water out |
| (6) Mercury lamp | |

FIGURE 1: The schematic diagram of photoreaction system.

FZ-A radiometer (BNU Light and Electronic Instrumental Co., China), respectively. The diagram of the photoreaction system was presented in Figure 1.

1.0 g of the complex was placed into the vessels containing 100 mL H_2O_2 solution of concentration 10.0 mmol L^{-1} at 25°C . The residual concentration of H_2O_2 in the solution during the reaction was determined through the spectrophotometric DPD method, in which the DPD was oxidized by H_2O_2 based on the POD catalyzed reaction [13]. The analysis of the residual concentration of H_2O_2 was repeated three times for each sample and the results averaged.

2.4. Dye Degradation Procedure. The dye degradation was performed in the photoreaction reaction system mentioned above under visible irradiation. 0.40 g of metal PAA-g-PTFE complex was added into 100 mL of test solution containing 0.04 mmol L^{-1} RR 195 and 6.0 mmol L^{-1} H_2O_2 . The reaction temperature was kept at $25 \pm 1^\circ\text{C}$, and the pH of the solution was adjusted with 0.10 mmol L^{-1} HNO_3 and/or NaOH aqueous solution and measured using DHS-25C digital pH meter (Shanghai Jingmi Instrumental Co., China). The degradation of the dye was initialized after the adsorption/desorption equilibrium of the dye on the complex was reached in the dark for 2.0 h. At given irradiation time intervals, 1-2 mL of the test solution was sampled from the reaction vessel and analyzed immediately by recording the UV-vis spectrum

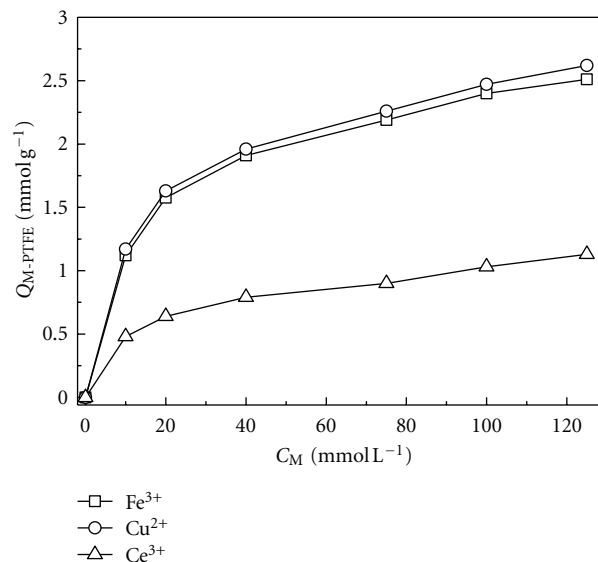


FIGURE 2: Effect of C_M on Q_{M-PTFE} of the complexes during the preparation.

of the dye at the λ_{max} (523 nm) with a UV-2401 Shimadzu spectrophotometer. The decoloration percentage of the dye was expressed as $D\% = (1 - C_d/C_{d,0}) \times 100\%$, where $C_{d,0}$ and C_d are the initial and residual concentrations of the dye (mmol L^{-1}), respectively. Moreover, total organic carbon (TOC) was assayed in the dye degradation process by using a Phoenix 8000 TOC analyzer (Tekmar-Dehrmann Inc., USA) and TOC removal percentage of the dye was calculated as follows: $\text{TOC removal \%} = (1 - \text{TOC}_t/\text{TOC}_0) \times 100\%$, where TOC_0 and TOC_t are the TOC values (mg L^{-1}) at reaction times 0 and t , respectively.

2.5. Metal Ions Leaching from the Complex. 0.40 g of metal PTFE fiber complex was placed into in 100 mL solution containing 6.0 mmol L^{-1} H_2O_2 . The leaching of Fe(III) or/and Cu(II) ions from the complex in solution at room temperature and under visible light irradiation was carried out for 300 min. And the concentrations of Fe(III) or Cu(II) ions in solution at intervals of time were measured using atomic absorption spectrometry method, respectively.

3. Results and Discussion

3.1. Optimization of Coordination Parameters with respect to Metal Contents on PAA-g-PTFE

3.1.1. Metal Ion Concentration in Coordination Solution. In order to investigate the effect of metal ion concentration in coordination solution (C_M) on metal content on PAA-g-PTFE (Q_{M-PTFE}), three metal ions including Fe(III), Cu(II), and Ce(III) ions were selected to react with PAA-g-PTFE with $G_f\%$ of 34.53 at 50°C , and results were shown in Figure 2.

It is seen from Figure 2 that all the Q_{M-PTFE} values significantly increase with increasing C_M , and the increasing tendency gradually declines when C_M being above

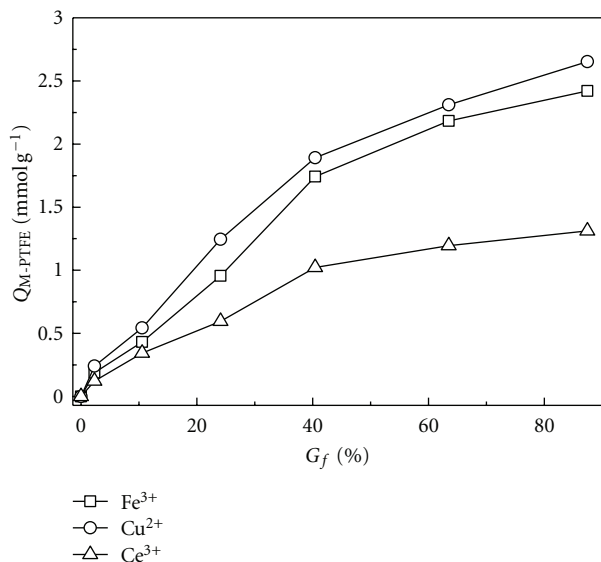


FIGURE 3: Q_{M-PTFE} of the complexes as a function of graft degree of PAA-g-PTFE.

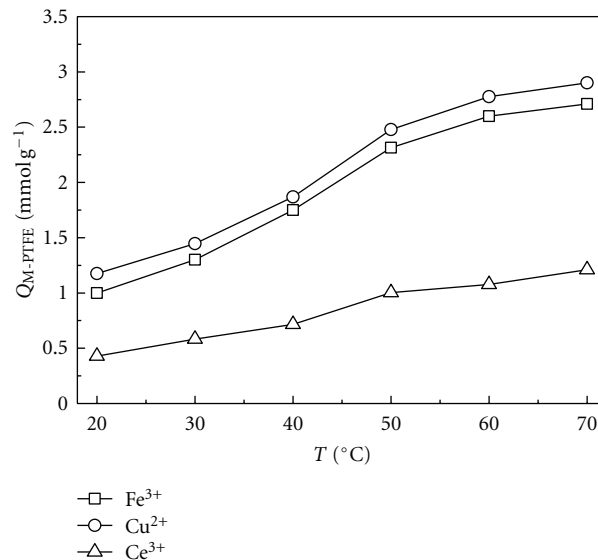


FIGURE 4: Q_{M-PTFE} of the complexes at different reaction temperatures.

40.0 mmol L⁻¹, especially for Ce(III) ions. This suggests that higher C_M can enhance the coordination of PAA-g-PTFE with metal ions, particularly two transition metal ions. The previous works [11, 12, 14] have found that the carboxyl groups on PAA-g-PTFE are the main coordinating sites with metal ions. Furthermore, it has been proposed that the oxygen of the carboxyl group has a pair of electrons that can add themselves to a proton or a metal ion to form a complex through a coordinated covalent bond. The metal ions with empty orbitals act as a Lewis acid capable of accepting electron pairs. In contrast, the carboxyl groups that have nonshared electron pairs function as Lewis bases donating their electrons pair [15, 16]. Moreover, transition metal contents ($Q_{Fe-PTFE}$ and $Q_{Cu-PTFE}$) on the fiber are much more than Ce content ($Q_{Ce-PTFE}$) on the fiber, especially at higher metal concentration in solution. This is because the 4f electrons of rare earth metal ion are in the inner orbital of the atomic structure, so that the ligand field has less effect on them and the rare earth metal ions have much lower LFSE values (4.18 kJ mol⁻¹) than d-transition metal ions (≥ 418 kJ mol⁻¹) [5, 17].

3.1.2. Graft Degree of PAA-g-PTFE. To determine the dependence of Q_{M-PTFE} value on graft degree of PAA-g-PTFE, the complexes were produced by the coordination of PAA-g-PTFE with different $G_f\%$ in 0.10 mol L⁻¹ metal ion aqueous solution at 50°C, and relationship between $G_f\%$ and Q_{M-PTFE} values was presented in Figure 3.

Figure 3 shows that the Q_{M-PTFE} value of metal PAA-g-PTFE complexes was greatly enhanced with $G_f\%$ of PAA-g-PTFE, particularly when Fe(III) and Cu(II) ion being used. This indicates that increasing $G_f\%$ value can benefit the fixation of three metal ions on the surface of PAA-g-PTFE and form the metal PAA-g-PTFE complexes with high Q_{M-PTFE} because PAA-g-PTFE with high $G_f\%$ values has

much more carboxyl groups on their surface than those with low $G_f\%$ values, thus more easily react with metal ions in solution.

3.1.3. Temperature. PAA-g-PTFE with $G_f\%$ of 34.53 was employed to coordinate with three metal ions, respectively, in the solution, for investigating the impact of reaction temperature on Q_{M-PTFE} value of the resulting metal PAA-g-PTFE complexes, and results were shown in Figure 4.

Figure 4 shows that Q_{M-PTFE} value of the complexes is increased with elevation of reaction temperature from 20 to 70°C. This obviously demonstrates that it is favorable for the coordination with the temperature rising, which implies that the coordination process is an endothermic process [11]. A possible reason is that higher temperature increases mobility of the polymer chains and the swelling of the fiber in the reaction medium, thus improving the interactions between metal ion and the fiber and resulting in more metal ions fixed on them.

3.2. Comparison of Metal Ions toward H₂O₂ Decomposition.

The catalytic activity of three metal PAA-g-PTFE complexes with similar Q_{M-PTFE} value (approximately 1.30 mmol L⁻¹) was examined with respect to the decomposition of H₂O₂, respectively, and the decay ratios of H₂O₂ as the function of irradiation time were shown in Figure 5.

It is observed from Figure 5 that the decay ratios of H₂O₂ gradually decline with the increasing irradiation time and vary with the nature of metal ions. The decay ratio of H₂O₂ is the lowest for Fe-PAA-g-PTFE, followed by Cu-PAA-g-PTFE, and the highest for Ce-PAA-g-PTFE. This indicates that Fe-PAA-g-PTFE has a stronger catalytic activity than the other complexes at the same conditions. Additionally, from the viewpoint of the toxicity and cost of three metal ions,

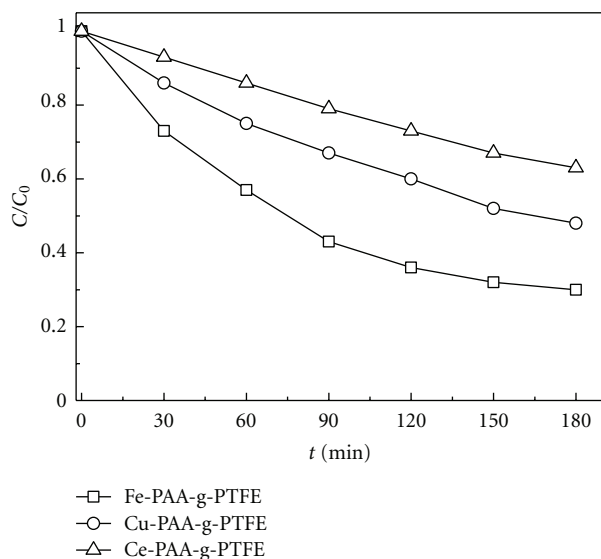


FIGURE 5: Decomposition of H₂O₂ in the presence of the different catalysts.

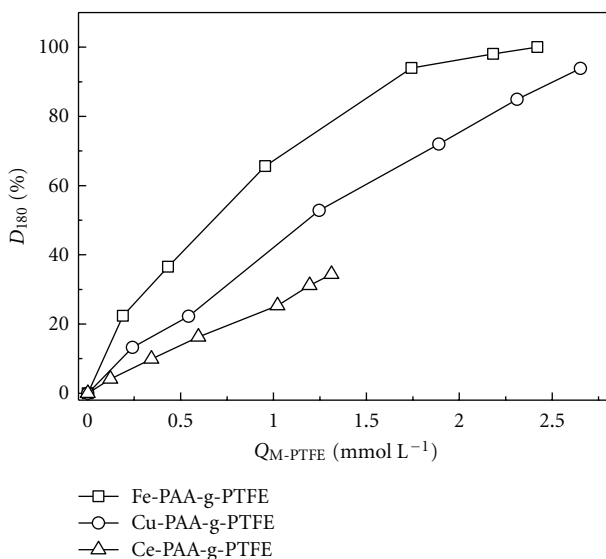


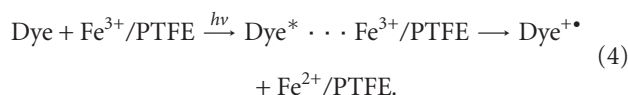
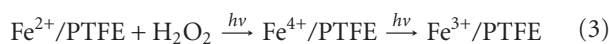
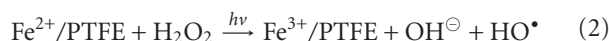
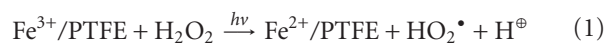
FIGURE 6: Relationship between Q_{M-PTFE} and D₁₈₀%.

Fe(III) ions should be selected to prepare the catalyst for the majority of the future research and practical application.

3.3. Effect of Metal Ion on Dye Degradation. The dye degradations were conducted in the presence of three metal PAA-g-PTFE complexes with different Q_{M-PTFE} values as the heterogeneous Fenton catalysts, respectively, and the influence of Q_{M-PTFE} value on decoloration percentage of the dye within 180 min (D₁₈₀%) was presented in Figure 6.

Figure 6 shows that increasing Q_{M-PTFE} value can remarkably enhance the dye degradation for all the complexes, particularly Fe-PAA-g-PTFE. Moreover, comparing three metal PAA-g-PTFE complexes with similar Q_{M-PTFE} values, the highest D₁₈₀% is achieved when Fe-PAA-g-PTF is used.

This means that Fe-PAA-g-PTFE exhibits the strongest catalytic activity for dye degradation, of three complexes. The main reason is that Fe-PAA-g-PTFE leads to the enhanced decomposition of H₂O₂ in solution indicated in Figure 5, thus possibly producing more hydroxyl radicals, which is responsible for the dye degradation. This reaction process is described by (1) and (2). On the other hand, the formed Fe(II) ions on Fe-PAA-g-PTFE may be oxidized to Fe(IV) ions in this work, which are regarded as another reactive intermediate from the photo-Fenton reaction which can decompose dye molecules. A possible formation of Fe(IV) ions was expressed by (3)



Additionally, the photosensitization of the azo dyes can promote a conversion of Fe(III) to Fe(II) ions during photo-assisted Fenton reaction [12]. In this work, it is believed that RR 195 could act as the sensitizer of Fe-PAA-g-PTFE to lead to a charge transfer with the concomitant quenching of the excited dye* and the formation of dye⁺. This process was suggested by (4).

It is well known the hydroxyl radicals is a powerful oxidant and can ultimately cause mineralization of textile dyes. Consequently, the mineralization of the dye was examined by measuring the TOC values of test solutions during the degradation when three complexes with the similar Q_{M-PTFE} values were employed, respectively.

Figure 7 shows that TOC removal % of the dye is as a function of irradiation time. It is found that TOC removal % gradually increases with the prolongation of irradiation time. Specifically, TOC removal % for Fe-PAA-g-PTF is much higher than those for the other complexes at the same time. These results demonstrate that three metal PAA-g-PTFE complexes as the photocatalysts can result in a drastic breakdown of dye molecules, and then convert them into water, carbon dioxide, and inorganic compounds. It should also be pointed out that TOC removal % is mainly determined by nature of metal ions, which is well consistent with the impact of nature of metal ions on the degradation mentioned above.

In order to study the catalytic activity of the complexes in a wide pH range, the dye degradation was carried out at different solution pH within 180 min of reaction time. The catalytic activity of the complexes was determined with respect to the dye degradation with the results presented in Figure 8.

Figure 8 shows that the dye degradation can be operated in the presence of the complex over a wide pH 3–9 range, indicating that a significant breakdown of the dye occur, especially at acidic media. Moreover, the catalytic activity

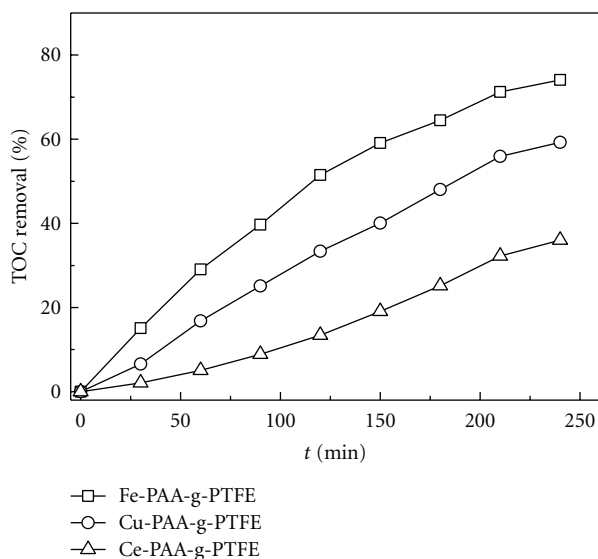


FIGURE 7: Mineralization of the dye with different catalysts.

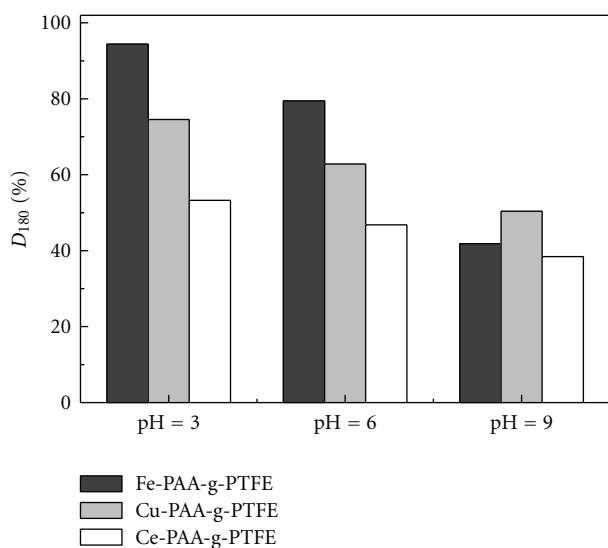
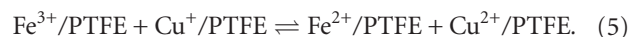


FIGURE 8: Dye degradation at different pH levels for three catalysts.

of three complexes at acid and neutral medium is ranked in this order: Fe-PAA-g-PTFE > Cu-PAA-g-PTFE > Ce-PAA-g-PTFE. However, higher pH range, especially alkaline pH medium dramatically decreases the catalytic activity of three complexes. It is worth noticing that Cu-PAA-g-PTFE shows a stronger activity than Fe-PAA-g-PTFE at pH 9. This is similar to the performance of Cu/MCM-41 as a highly stable and pH-insensitive heterogeneous photo-Fenton-like Fenton catalyst [18]. Some researches [18, 19] suggested that an advantage of Cu^{2+} ion as a Fenton-like catalyst is its characteristics of a wide-working pH range compared to the conventional Fenton catalyst. Therefore it is believed that Cu-PAA-g-PTFE behaves similarly to Fe-PAA-g-PTFE, and it has a higher catalytic activity over a wide pH range.

3.4. Role of Cu(II) Ion as an Assisted Metal Ion. It has been suggested that the performance of supported Fe catalysts is often improved by adding certain metals. And copper ion has a role as an assistant in photocatalysis [5]. Moreover, it has been presented that the outstanding catalytic activity of bimetal catalysts may be generally ascribed to synergistic effects between copper and iron redox couples. In order to meet the demands for rapid and stable dye degradation in future commercial application, a series of Cu-Fe bimetal PAA-g-PTFE complexes with different Cu/Fe molar ratios were prepared and used in the dye degradation at pH 9 in this work. And Cu/Fe molar ratio of metal PAA-g-PTFE complexes was observed to have a significant impact on the decomposition efficiency of the dye, and the results are given in Table 1.

The data in Table 1 indicate that higher concentration of Cu(II) ions in the solutions increased their Cu/Fe molar ratio. When the molar concentration of Cu(II) ions equals to that of Fe(III) ions in the solution, the Cu/Fe molar ratio of Cu-Fe-PAA-g-PTF is 2.87, much more than 1.0, suggesting that PAA-g-PTF has much higher affinity for Cu(II) ions than Fe(III) ions at the same conditions. More importantly, $D_{180}\%$ and TOC removal % of dye degradation in the presence of the bimetal PAA-g-PTFE complexes is much higher than those in the presence of the monometal PAA-g-PTFE complexes, and the maximum $D_{180}\%$ and TOC removal % was achieved for Cu-Fe-PAA-g-PTFE (ii). These results confirm that catalytic activity of metal PAA-g-PTFE complexes depends highly upon their Cu/Fe molar ratio, and Cu-Fe-PAA-g-PTFE (ii) with a Cu/Fe molar ratio of 2.87 shows the best catalytic activity at alkaline pH medium. This demonstrates the existence of synergetic effect between loaded Fe(III) and Cu(II) ions in the bimetal PAA-g-PTFE complexes, which improved their catalytic activity to a great extent. The main reason may be that the H_2O_2 molecules absorbed on the surface of Cu-Fe-PAA-g-PTFE can reduce Fe(III) to Fe(II) ions through the Fenton-like process under visible light irradiation, and the generated Fe(II) ions are then oxidized by H_2O_2 to complete the Fe(III)/Fe(II) ions cycle and produce hydroxyl radicals. Meanwhile, the formed Fe(II) ions can also react with the loaded Cu(II) ions to form the Cu(I) and Fe(III) ions (5) to accelerate the transformation of Fe(III)/Fe(II) ions and Cu(II)/Cu(I) ions in Cu-Fe-PAA-g-PTFE, thus giving rise to additional hydroxyl radicals during the degradation:



3.5. Metal Ions Leaching from the Catalyst. One problem with the heterogeneous photocatalysts is metal leaching from the catalyst that causes secondary contamination to wastewater in pilot-scale application. The leaching concentrations of metal ions from metal PAA-g-PTFE complexes in solution were measured. The results indicated that metal ions were continuously leached out from the complexes after the reaction started, and the final measured concentrations of both metal ions in the solution within 300 min at different pH levels were shown in Tables 2 and 3.

TABLE 1: Effect of Cu/Fe molar ratio of the catalysts on dye decomposition.

Samples	C_M (mol L ⁻¹)		Q_{M-PTFE} (mmol L ⁻¹)			Cu/Fe	$D_{180}\%$	TOC Removal %
	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Total			
Fe-PAA-g-PTFE	0.100	0.000	1.89	0.00	1.89	0	47.3	37.3
Cu-Fe-PAA-g-PTFE (i)	0.075	0.025	1.13	0.75	1.88	0.66	61.2	54.6
Cu-Fe-PAA-g-PTFE (ii)	0.050	0.050	0.54	1.55	2.09	2.87	84.6	72.7
Cu-Fe-PAA-g-PTFE (iii)	0.025	0.075	0.31	1.75	2.06	5.65	78.4	56.7
Cu-PAA-g-PTFE	0.000	0.100	0.00	1.98	1.98	/	51.9	45.1

TABLE 2: Leaching of Fe ions from Fe-PAA-g-PTFE with different Q_{Fe} values.

Fe-PAA-g-PTFE	Fe(III) ions concentration in solution (mg L ⁻¹)		
	pH = 3	pH = 7	pH = 9
$Q_{Fe} = 0.432$ mmol L ⁻¹	0.49	0.37	0.07
$Q_{Fe} = 0.955$ mmol L ⁻¹	0.72	0.57	0.15
$Q_{Fe} = 1.743$ mmol L ⁻¹	0.95	0.73	0.22
$Q_{Fe} = 2.183$ mmol L ⁻¹	1.22	0.94	0.43
$Q_{Fe} = 2.421$ mmol L ⁻¹	1.53	1.23	0.57

TABLE 3: Impact of Cu/Fe molar ratio on leaching of metal ions from Cu-Fe bimetallic PTFE fiber complexes.

Samples	Metal ions concentration in solution (mg L ⁻¹)					
	pH = 3		pH = 7		pH = 9	
	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Fe(III)	Cu(II)
Fe-PAA-g-PTFE	0.93	0.00	0.82	0.00	0.29	0.00
Cu-Fe-PAA-g-PTFE (i)	0.63	0.35	0.53	0.29	0.19	0.12
Cu-Fe-PAA-g-PTFE (ii)	0.21	0.76	0.13	0.49	0.06	0.24
Cu-Fe-PAA-g-PTFE (iii)	0.17	0.92	0.10	0.45	0.08	0.19
Cu-PAA-g-PTFE	0.00	1.25	0.00	0.89	0.00	0.31

It can be noticed from Table 2 that increasing Q_{Fe} value is accompanied by increasing Fe ion concentration in solution at three investigated pH levels. This means that Fe-PAA-g-PTFE with higher Q_{Fe} value can leach more Fe(III) ions than that with lower Q_{Fe} value. It is obvious from the results shown in Table 3 that Fe(III) and Cu(II) ion concentrations in solution are much affected by Cu/Fe molar ratio of the complexes. On the other hand, higher pH level caused a gradual decrease in leached Fe(III) or Cu(II) ion concentration in solution, revealing that metal ions leaching from the complexes is dependent on the solution pH. Moreover, it should be pointed out that the final leached concentration of Fe(III) or Cu(II) ions is lower than 1.0 mg L⁻¹ for both complexes, especially at pH 7 and 9. This result implies that both metal ions were attached on the surface of the modified PTFE via the hydroxyl group. Thus, these complexes can be regarded as the effective and stable heterogeneous photocatalysts for the dye degradation over a broad pH range due to a minimal threshold concentration

of 3–15 mg L⁻¹ Fe which allows the homogeneous Fenton reaction to proceed within a reasonable period of time. Additionally, it is well known that Cu ion is hazardous to both marine animals and humans. The discharge standard was suggested by the Environmental Protection Agency is 1.0 mg L⁻¹ [18], which is higher than the final leached concentration of Cu(II) ions for Cu-Fe bimetallic PTFE fiber complexes except Cu-Fe-PAA-g-PTFE (iii) and Cu-PAA-g-PTFE.

4. Conclusions

The novel heterogeneous photo-Fenton catalysts were produced by a modification of PTFE fibers through graft polymerization of acrylic acid to introduce the carboxyl groups onto the fiber surface, which were used to coordinate with transition metal ions (Fe(III) and Cu(II)) or rare metal ion (Ce(III)). Increasing metal ion concentrations in solution and grafting degree of PTFE fiber as well as higher coordination temperature could lead to a significant increase in metal content, especially Fe(III) and Cu(II) content of the catalysts. Moreover, Fe(III) and Cu(II) ions reacted with the modified PTFE fibers more easily than Ce(III) ion at the same conditions to form the complexes with higher metal content. Fe(III) ions fixed on the fiber showed a much powerful catalytic performance for the decomposition of H₂O₂ and the oxidative degradation of the dye than Cu(II) and Ce(III) ions fixed when three different complexes with similar metal content being employed as the catalysts, respectively. Also, taking into the toxicity of Cu (II) and Ce(III) ions and the cheapness of iron salt, thus, Fe(III) modified PTFE fiber complex was proposed to act as an effective catalyst for the dye degradation under visible irradiation. And increasing Fe content could remarkably improve the catalytic activity of the complex. Comparing with the three monometallic complexes, Cu-Fe bimetallic modified PTFE fiber complexes exhibited the excellent catalytic activity because of the existence of synergetic effect between Fe(III) and Cu(II) ions. Their catalytic activity depended highly on Cu/Fe molar ratio. 2.87 is the optimum Cu/Fe molar ratio to obtain the best catalytic activity for the bimetallic complexes. However, increasing the amount of Fe(III) or/and Cu(II) ions fixed on the fibers resulted in the relatively higher concentrations of both ions leaching from them, especially at low pH ranges. To sum up, the highest dye degradation efficiency and the accepted concentrations of metal ions leaching from the complexes were found when it was prepared with a mixture

of 0.05 mol L⁻¹ Fe(III) and 0.05 mol L⁻¹ Cu(II) ions at 50°C by poly acrylic acid grafted PTFE fiber as the supported material using a simple exhausting method.

Acknowledgments

The authors thank the Tianjin Municipal Science and Technology Committee for a Research Program of Application Foundation and Advanced Technology (11JCZDJ24600). This research was also supported in part by a Grant from the Natural Science Foundation of China (20773093).

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