



# Copper–iron bimetal modified PAN fiber complexes as novel heterogeneous Fenton catalysts for degradation of organic dye under visible light irradiation

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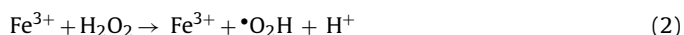
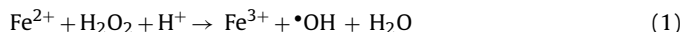
## ABSTRACT

A series of Cu–Fe bimetal amidoximated polyacrylonitrile (PAN) fiber complexes with different molar ratios of Cu<sup>2+</sup> to Fe<sup>3+</sup> ions was prepared using a simple exhaustion method, and characterized using FTIR, DRS and XPS, respectively. Then they were tested as the heterogeneous Fenton catalysts for Rhodamine B degradation with H<sub>2</sub>O<sub>2</sub> in the dark and under visible light irradiation. The results indicated that Cu–Fe bimetal amidoximated PAN fiber complexes could more effectively catalyze the dye degradation in water than Fe amidoximated PAN fiber complex, especially in the dark. And introduction of Cu<sup>2+</sup> ions significantly increased their catalytic performance. 0.56 was the optimum molar ratio of Cu<sup>2+</sup> to Fe<sup>3+</sup> ions to achieve the best catalytic activity and stability. This was mainly due to the synergistic effect in the bimetal complexes. Visible light irradiation improved the catalytic activity of the complexes, especially with a low molar ratio of Cu<sup>2+</sup> to Fe<sup>3+</sup> ions.

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## 1. Introduction

Dye-containing wastewater from the textile industry is a principal source of environmental contamination because over 15% of the dyes are lost in wastewater without treatment during their synthesis and dyeing processes [1,2]. And these dyes are known to be largely non-biodegradable and toxic to aquatic plants and animals. For the treatment of these dyes, Fenton process as an important advanced oxidation processes (AOP) technology has been attracting growing interest. It is well known that •OH radicals can be produced by Fenton reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> and Fe<sup>3+</sup> salts as presented in Eqs. (1)–(3) [3,4].



The generated •OH radical is a powerful oxidant and starts a cascade of oxidation reactions that can convert the organic matter in solution completely into water, carbon dioxide, and inorganic com-

pounds. But drawbacks in the use of Fenton reactions are found to be the limitation of pH value and the problem of separation and regeneration at the end of the reaction. Therefore, some attempts have been made to develop the heterogenization of homogeneous Fenton catalysts. In recent years, metal coordination has been used as an effective method to immobilize Fe<sup>3+</sup> ions on the materials such as zeolite [5], Nafion membrane [6], alginate microcapsules [7] and the modified polyacrylonitrile (PAN) fiber [8,9] for preparing heterogeneous Fenton catalysts. Fe modified PAN fiber complex may be one of promising heterogeneous catalysts because of its unique advantages, such as lower cost and easy separation of the catalyst after the reaction, and suitable chemical and mechanical stability [8,10]. It has been known that PAN fiber can be easily introduced into various functional groups through the transformation of its nitrile groups. Therefore, the modified PAN fibers have been used to prepare the heterogeneous Fenton catalysts through their coordination with Fe<sup>3+</sup> ions. Ishtchenko et al. [8] have prepared a heterogeneous Fenton catalyst by ligating the Fe<sup>3+</sup> ions onto the surface of the modified PAN fiber with a mixture of hydrazine and hydroxylamine for the decomposition of real dyeing effluent. Our recent study [11] found that the Fe amidoximated PAN fiber complex could also be served as a heterogeneous Fenton photocatalyst for the dye degradation, and higher visible light irradiation significantly enhanced its catalytic performance. Clearly, Fe amidoximated PAN fiber complex has a higher catalytic activity than the heterogeneous Fenton catalysts mentioned above, however it

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cannot meet the demands for rapid and stable degradation in future commercial application. Therefore it must be improved to obtain excellent catalytic activity and good stability. 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. Guimaraes et al. [12] reported that doping the copper ions into the goethite led to strong increase in its catalytic activity. Fe and Cu salen complexes simultaneously encapsulated zeolite Y were found to be higher activity than the Cu (salen)Y and Fe (salen)Y in the oxidation of cyclohexane [13]. It has been presented that the outstanding catalytic activity of bimetal catalysts may be generally ascribed to synergistic effects in relation with creation of defects, novel active sites and facile redox interplay between copper and iron redox couples. Moreover, the addition of certain metals to catalyst may stabilise the activity for the oxidation of organic pollutants in comparison with monometallic catalyst. In the present study, a series of Cu–Fe bimetal amidoximated PAN fiber complexes with different copper content were prepared using a simple exhaustion method at low temperature, and used as the novel heterogeneous Fenton catalysts in the degradation of Rhodamine B in the dark and under visible irradiation. FTIR, DRS, XPS, ESR and cyclic voltammetry techniques were used to elucidate the difference in catalytic activity and structure of these complexes. The primary objective of this study is to examine the catalytic degradation of dye over a range of Cu–Fe bimetal amidoximated PAN fiber complexes with different molar ratios. Activity and the ability to maintain stable dye degradation were evaluated for the various complexes. It is very important to explore the role of copper ions in the Cu–Fe bimetal amidoximated PAN fiber complexes for the effective treatment of organic pollutants. And a proposed mechanism of photocatalysis of Cu–Fe bimetal amidoximated PAN fiber complexes is also discussed.

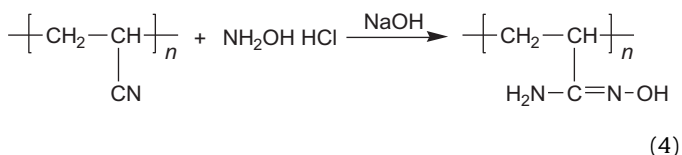
## 2. Materials and methods

### 2.1. Materials and reagents

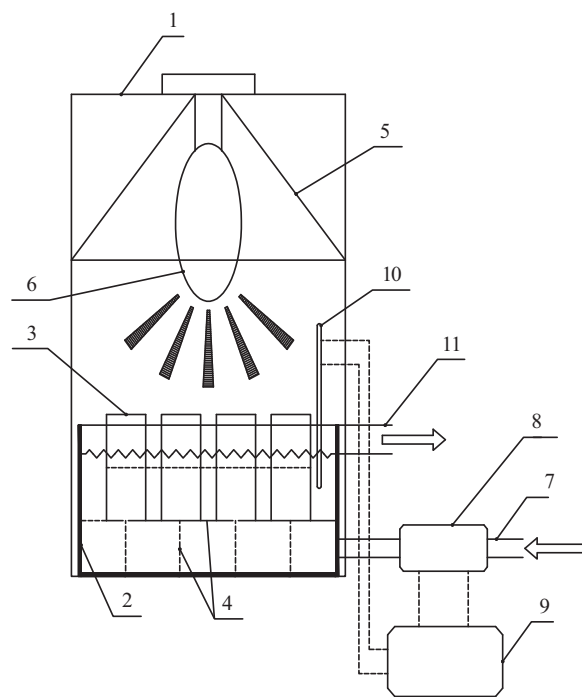
The commercial PAN knitting bulky yarns (PAN yarn) that consist of twisted PAN fibers (the content of acrylonitrile: 86.96%) were purchased from Shanghai Shilin Spinning Co., China. Hydroxylamine hydrochloride, ferric chloride, copper sulfate, hydrogen peroxide (30%, w/w), sodium hydroxide and Rhodamine B (RhB) were of laboratory grade. Double distilled and deionized water was used throughout the study.

### 2.2. Preparation of metal AO-PAN complexes

According to our previous study [11], PAN yarns were modified with hydroxylamine hydrochloride to prepare the amidoximated PAN yarns (denoted as AO-PAN). The degree of conversion from nitrile groups to amidoxime groups of the obtained AO-PAN was calculated to be 60.09%. The amidoximation of PAN yarns is described by Eq. (4).



5.0 g of AO-PAN was immersed in 150 ml of mixed metal salt aqueous solutions of ferric chloride and copper sulfate. In all cases, the concentrations of the total metal ions were kept constant at 0.10 mol L<sup>-1</sup>. The mixture was kept at 50 °C for 5 h under continuous agitation. And the resulting fibrous metal complexes were then filtered, washed with deionized water and dried under vac-



**Fig. 1.** The diagram of photoreaction system: (1) chamber, (2) water bath, (3) glass vessel, (4) support, (5) lamp-chimney, (6) mercury lamp, (7) water in, (8) electromagnetic valve, (9) relay, (10) thermometer, (11) water out.

uum at 60 °C for 4.0 h to obtain Fe amidoximated PAN fiber complex (denoted as Fe-AO-PAN), Cu amidoximated PAN fiber complex (denoted as Cu-AO-PAN), and Cu–Fe bimetal amidoximated PAN fiber complexes (denoted as Cu–Fe-AO-PAN). The residual concentrations of Fe<sup>3+</sup> and Cu<sup>2+</sup> ions in the solutions after coordination were determined by using a WXF120 atomic absorption spectrometry (Beijing Rayleigh Analytical Instrument Corp.), for calculating the Fe content ( $C_{\text{Fe-PAN}}$ ) and Cu content ( $C_{\text{Cu-PAN}}$ ) of the complexes. By adjusting the relative amounts of ferric chloride and copper sulfate in the solutions, a series of Cu–Fe-AO-PAN samples with different molar ratios of Cu<sup>2+</sup> to Fe<sup>3+</sup> (Cu/Fe molar ratios) were then produced.

### 2.3. Characterization of metal AO-PAN complexes

Fourier transform infrared (FTIR) spectra of the complexes were measured by a Nicolet Magna-560 Fourier transform spectrometer (Nicolet Inc., USA) using the conventional KBr pellet method. Diffuse reflectance UV–vis spectra (DRS) in the range of 200–800 nm of the complexes were recorded on a Varian Cary 500 UV–vis-NIR spectrometer (Varian Inc., USA) with BaSO<sub>4</sub> as the reflectance standard. X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out on a PHI 5600 X-ray photoelectron spectrometer (PekinElmer Inc., USA), and binding energy of C 1s was shifted to 284.6 eV as the reference.

### 2.4. Catalytic procedure and analysis

The RhB degradation was performed in a photoreaction system, which consisted mainly of polished aluminum chamber, lamps, electromagnetic valve, relay and water bath and the diagram of the photoreaction system was presented in Fig. 1.

The chamber was made of polished aluminum because it is highly reflective in the visible light range. Ten open Pyrex vessels of 150 ml capacity were used as reaction receivers in water bath. An electromagnetic valve was operated by relay and used to

**Table 1**  
Metal AO-PAN complexes with different Cu/Fe molar ratios.

Designation of samples	Concentration of metal ions in solution (mol L <sup>-1</sup> )		Metal contents in the complexes (mmol g <sup>-1</sup> )			Cu/Fe molar ratio
	Fe <sup>3+</sup>	Cu <sup>2+</sup>	C <sub>Fe-PAN</sub>	C <sub>Cu-PAN</sub>	Total	
Fe-AO-PAN	0.100	0.000	2.52	0.00	2.52	0.00
Cu-Fe-AO-PAN (I)	0.075	0.025	2.02	0.39	2.40	0.19
Cu-Fe-AO-PAN (II)	0.050	0.050	1.54	0.88	2.43	0.56
Cu-Fe-AO-PAN (III)	0.025	0.075	1.10	1.21	2.31	1.10
Cu-AO-PAN	0.000	0.100	0.00	2.39	2.39	–

control temperature in water bath. A 400 W high pressure mercury lamp (Foshan Osram Illumination Co., China) was used as the visible light source for photocatalytic reaction, which has prominent emission bands at 365.0 nm, 404.7 nm, 435.8 nm, 546.1 nm and 577.0–579.0 nm. A cut-off filter was employed to ensure irradiation only by visible light ( $\lambda > 420$  nm). The intensity of visible light irradiation over the surface of test solution inside photoreaction system was measured to be 9.11 mW cm<sup>-2</sup> using FZ-A radiometer (BNU Light and Electronic Instrumental Co., China), and the temperature in reaction vessel was kept at 25 ± 1 °C. Dye degradation was initialized after the adsorption/desorption equilibrium of the dye on AO-PAN metal complex was reached in the dark for 2.0 h. 0.50 g of AO-PAN metal complexes was first fixed on a small glass rack, and then placed into 100 ml of test solution containing 0.02 mmol L<sup>-1</sup> dye and 3.0 mmol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> at an initial pH of 6.0. The test solution was put under the irradiation of lamps in photoreaction system. At given time intervals, 1–2 ml of the test solution was withdrawn from the reaction vessel; the dye concentration was then determined by measuring the absorbance at the  $\lambda_{\max}$  (550 nm) of the solution using a UV-2401 spectrophotometer (Shimadzu Co., Japan). ESR (Electron spin resonance) signals of the radical spin-trapped by DMPO (5,5-dimethyl-1-pyrroline N-oxide) were examined on a Bruker ESP 300E spectrometer with an irradiation source of Quanta-Ray Nd:YAG pulsed laser system ( $\lambda = 532$  nm). Cyclic voltammetric measurement of AO-PAN metal complexes was performed on a LK3100 electrochemical workstation (Tianjin Lanlike Co., China).

### 3. Results and discussion

#### 3.1. Preparation of metal AO-PAN complexes

The previous studies [11,14] have found that either of Fe<sup>3+</sup> and Cu<sup>2+</sup> ions in aqueous solution prefer to react with both amino and hydroxyl groups of AO-PAN to form Fe or Cu monometal AO-PAN complex through coordination bonds. Moreover, the Fe<sup>3+</sup> ion of Fe-AO-PAN was coordinated with three amino nitrogen atoms and three hydroxyl oxygen atoms of three amidoxime units on the surface of AO-PAN, and the coordination number was six [15]. Therefore, it is quite possible that when both metal ions and AO-PAN coexist in a single solution during the reaction, they can simultaneously coordinate with the functional groups of AO-PAN by a similar bind mode to produce a Cu-Fe bimetal AO-PAN complex. In this present work, a series of Cu-Fe bimetal AO-PAN complexes with different Cu/Fe molar ratios were prepared. And the initial concentrations of the two metal ions in aqueous solution were observed to have a significant impact on the metal contents in metal AO-PAN complexes, and the results are given in Table 1.

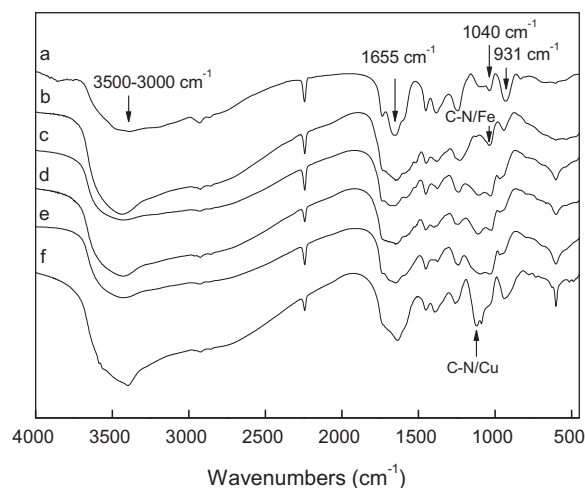
It is found from Table 1 that three Cu-Fe bimetal AO-PAN complexes were accomplished by co-impregnation of Fe<sup>3+</sup> and Cu<sup>2+</sup> ions. Moreover, higher concentration of Cu<sup>2+</sup> ions in the solutions increased their Cu/Fe molar ratio. However, when the molar concentration of Cu<sup>2+</sup> ions equals to that of Fe<sup>3+</sup> ions in the solution, the Cu/Fe molar ratio of Cu-Fe-AO-PAN (II) is 0.56, much less than 1.0, suggesting that AO-PAN has much higher affinity for Fe<sup>3+</sup>

ions than Cu<sup>2+</sup> ions at the same conditions. This may be because AO-PAN with amino and hydroxyl groups has the structural characteristics of hard base [16], thus prefer to react with Fe<sup>3+</sup> ions that served as the hard acid to form a stable complex. Additionally, the stronger polarity of Fe<sup>3+</sup> ions [8] was also responsible for the higher coordination ability of Fe<sup>3+</sup> ions with AO-PAN.

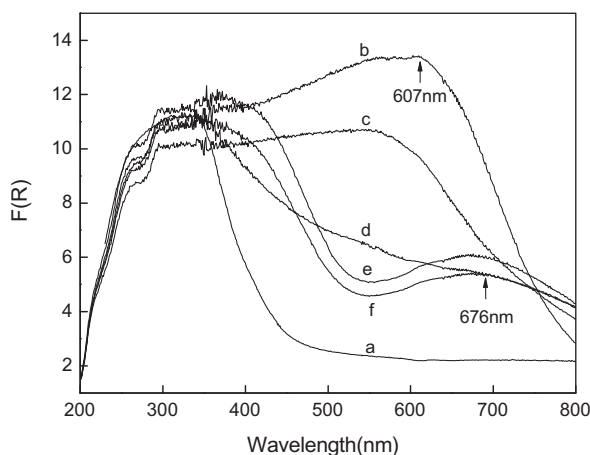
#### 3.2. Characterization of metal AO-PAN complexes

##### 3.2.1. FTIR analysis

The IR spectra of AO-PAN and its metal complexes are presented in Fig. 2. The spectrum of AO-PAN showed the characteristic bands including 3500–3000 cm<sup>-1</sup>, 1655 cm<sup>-1</sup>, 1040 cm<sup>-1</sup> and 931 cm<sup>-1</sup> of the amidoxime group. The broad adsorption at 3500–3000 cm<sup>-1</sup> was attributed to both N–H and O–H group vibrations, while the other three adsorptions were due to the stretching of C=N, C–N and N–O, respectively [17–19]. The N–O bands adsorption (931 cm<sup>-1</sup>) was less intensive and shift to higher frequencies, and the adsorption due to O–H bands became broader in the spectra of the complexes, implying that the O–H groups have been coordinated with Fe<sup>3+</sup> and/or Cu<sup>2+</sup> ions. Compared with AO-PAN, 10 cm<sup>-1</sup> and 8 cm<sup>-1</sup> shift of N–O bands was observed in the spectra of Fe-AO-PAN and Cu-AO-PAN, respectively. While corresponding shift was over 37 cm<sup>-1</sup> for the bimetal AO-PAN complexes, demonstrating that there may exist a significant interaction between the adjacent Fe<sup>3+</sup> and Cu<sup>2+</sup> ions through the hydroxyl oxygen atom on the fiber surface. On the other hand, the C–N bands of Fe-AO-PAN and Cu-AO-PAN are located at 1038 cm<sup>-1</sup> (denoted as C–N/Fe) and 1120 cm<sup>-1</sup> (denoted as C–N/Cu), respectively. Both bands were also present in the spectra of three bimetal AO-PAN complexes, and their shapes, positions and intensities varied with the Cu/Fe molar ratio, revealing that both metal ions have participated in the coordination with amino groups. It should be noticed that both C–N/Fe and C–N/Cu bands exhibited more significant variation in the spec-



**Fig. 2.** IR spectra of (a) AO-PAN, (b) Fe-AO-PAN, (c) Cu-Fe-AO-PAN (I), (d) Cu-Fe-AO-PAN (II), (e) Cu-Fe-AO-PAN (III) and (f) Cu-AO-PAN.



**Fig. 3.** UV-vis diffuse reflectance spectra of (a) AO-PAN, (b) Fe-AO-PAN, (c) Cu-AO-PAN (I), (d) Cu-AO-PAN (II), (e) Cu-AO-PAN (III) and (f) Cu-AO-PAN.

tra of Cu-Fe-AO-PAN (II) than the other bimetal AO-PAN complexes, suggesting that the Cu/Fe molar ratio in Cu-Fe-AO-PAN (II) may be the optimum ratio to give the most intensive interaction between  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions.

### 3.2.2. DRS analysis

The light adsorption properties of AO-PAN and its metal complexes were studied using diffuse reflectance UV-vis spectroscopy, and the results are shown in Fig. 3.

AO-PAN showed a characteristic broad band centered at 332 nm in the UV region due to its transitions of  $\pi$  electrons to the  $\pi^*$  excited state. A significantly broad and strong absorption band centered at 607 nm was observed in the UV and visible region after coordination of AO-PAN with  $\text{Fe}^{3+}$  ions (Fe-AO-PAN). The absorption band in the visible region may be attributed to the d-d transitions of the metal ions and the ligand-to-metal charge transfer (LMCT) transitions from AO-PAN toward metal ion in the complexes. This is because the d-orbital symmetry of the metal ions may be broken by the coordination effect of the ligands and their forbidden d-d transition is allowed [20], thus often leading to the adsorption in the visible region. And LMCT transitions can cause a significant absorption in the visible region, especially for the O-donor ligand complexes [21,22]. The incorporation of  $\text{Cu}^{2+}$  ion in Fe-AO-PAN leads to a less intensive and narrow absorption of light in the visible region and a characteristic band at 676 nm is found for Cu-AO-PAN. It should be noticed that Cu-Fe-AO-PAN (II) shows a significantly different spectrum from those of the other AO-PAN bimetal complexes, and no characteristic bands for

**Table 2**  
XPS analysis of AO-PAN and its metal complexes.

XPS peaks	Binding energy (eV)			
	AO-PAN	Fe-AO-PAN	Cu-AO-PAN	Cu-Fe-AO-PAN (II)
O 1s	531.2	531.5	531.5	531.7
N 1s	399.2	399.3	399.3	399.5
Fe 2p	–	711.1	–	710.0
Cu 2p	–	–	934.2	933.3

$\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  ions coordinated with AO-PAN is observed, which may be owing to a more dramatic interaction of  $\text{Fe}^{3+}$  with  $\text{Cu}^{2+}$  ions in Cu-Fe-AO-PAN (II) than the other two bimetal AO-PAN complexes.

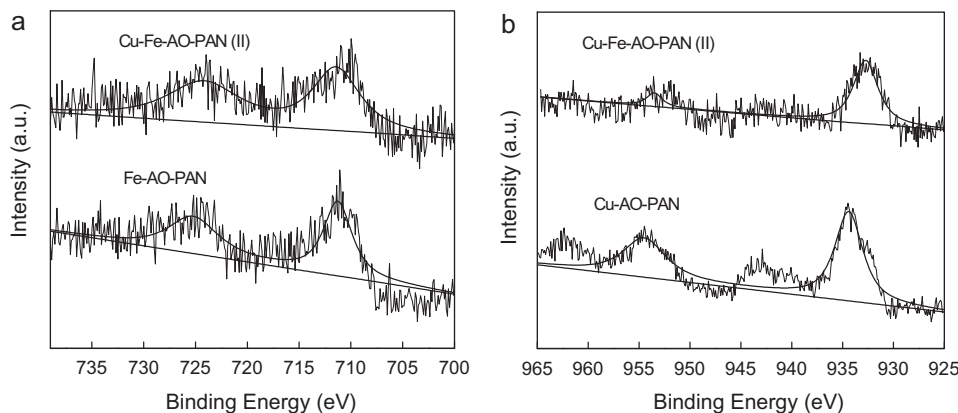
### 3.2.3. XPS analysis

AO-PAN and its three metal complexes were measured using XPS technique and the Fe 2p and Cu 2p core-level spectra of three complexes were compared in Fig. 4, and the binding energy of the main elements detected was also presented in Table 2.

As can be seen from Fig. 4 and Table 2, the binding energy values at 711.1 eV for the Fe 2p in Fe-AO-PAN and at 934.2 eV for the Cu 2p in Cu-AO-PAN are lower than those at 711.3 eV of the Fe 2p in  $\text{FeCl}_3$  and at 935.1 eV of the Cu 2p in  $\text{CuSO}_4$ , respectively. Meanwhile, the increase in binding energy of the O 1s and N 1s in Fe-AO-PAN and Cu-AO-PAN compared to AO-PAN is clearly found from Table 2. This indicates that oxygen and nitrogen atoms in the amidoxime groups of AO-PAN can coordinate with  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$  ions as the electron donors when Fe-AO-PAN or Cu-AO-PAN is prepared. It is also found that from Fig. 4 that the Fe 2p peak for Cu-Fe-AO-PAN (II) is broad. Moreover, the binding energy values for the Fe 2p and the Cu 2p in Cu-Fe-AO-PAN (II) are lower than those in Fe-AO-PAN and Cu-AO-PAN. And the binding energy of the O 1s and N 1s in Cu-Fe-AO-PAN (II) also shows the similar change to those in the monometal AO-PAN complexes mentioned above. This suggests that  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions have simultaneously ligated with the amidoxime groups of AO-PAN to produce Cu-Fe-AO-PAN (II) in the solution.

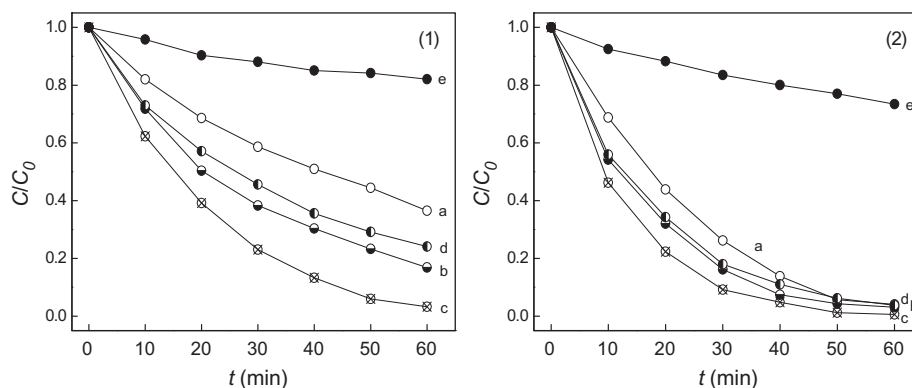
### 3.3. Catalytic tests

The metal AO-PAN complexes with different Cu/Fe molar ratios in Table 1 were used as the heterogeneous Fenton catalysts for the degradation of RhB in aqueous solution, respectively for investigating their catalytic activity. And the pseudo-first order rate constants,  $k_d$  (in the dark) and  $k_i$  (under visible irradiation) of RhB degradation within 40 min of reaction time were calculated. The experimental results were presented in Fig. 5 and Table 3.



**Fig. 4.** XPS spectra of metal AO-PAN complexes: (a) for Fe 2p and (b) for Cu 2p.





**Fig. 5.** Degradation profile of RhB at initial pH 6.0 and 25 °C (1) in the dark and (2) under visible irradiation in the presence of H<sub>2</sub>O<sub>2</sub> and different complexes: (a) Fe-AO-PAN, (b) Cu-Fe-AO-PAN (I), (c) Cu-Fe-AO-PAN (II), (d) Cu-Fe-AO-PAN (III) and (e) Cu-AO-PAN.

**Table 3**

The pseudo-first-order rate constants of RhB degradation with different complexes.

Catalyst	$k_d$ (min <sup>-1</sup> )	$R_d^a$	$k_i$ (min <sup>-1</sup> )	$R_i^b$
Fe-AO-PAN	0.015	0.9965	0.049	0.9948
Cu-Fe-AO-PAN (I)	0.030	0.9966	0.064	0.9973
Cu-Fe-AO-PAN (II)	0.050	0.9993	0.077	0.9992
Cu-Fe-AO-PAN (III)	0.025	0.9980	0.056	0.9992
Cu-AO-PAN	0.004	0.9907	0.006	0.9936

<sup>a</sup> The regression coefficient in the dark.

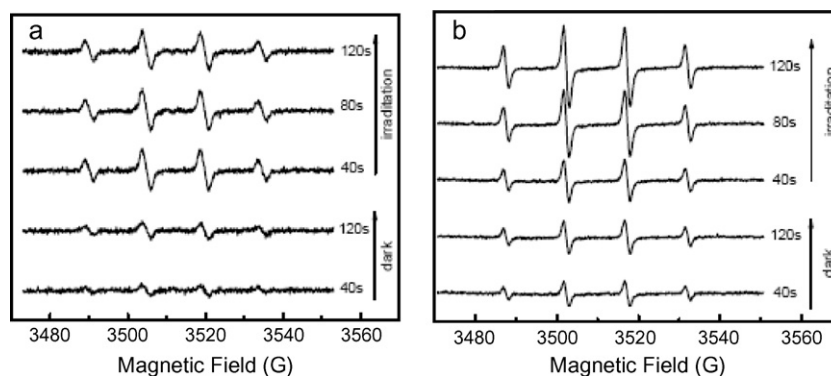
<sup>b</sup> The regression coefficient under visible irradiation.

Fig. 5 shows that the concentration of RhB decreases especially under visible irradiation in the presence of Fe-AO-PAN (curve a). While RhB decolorized very slowly in the case of Cu-AO-PAN (curve e). This implies that Fe<sup>3+</sup> ions exhibit much better catalytic activity than Cu<sup>2+</sup> ions loaded on AO-PAN at the same conditions. It is found from Table 3 that  $k_d$  and  $k_i$  values of dye degradation in the presence of the bimetal AO-PAN complexes are much higher than those in the presence of the monometal AO-PAN complex, and the maximum  $k_d$  and  $k_i$  values were achieved for Cu-Fe-AO-PAN (II). These results confirm that catalytic activity of metal AO-PAN complexes depends highly upon the Cu/Fe molar ratio, and Cu-Fe-AO-PAN (II) with a Cu/Fe molar ratio of 0.56 shows the best catalytic activity. This indicates the existence of synergetic effect between loaded Fe<sup>3+</sup> and Cu<sup>2+</sup> ions in the bimetal AO-PAN complexes, which improved their catalytic activity to a great extent. Consequently, Cu-Fe-AO-PAN (II) was chosen as a model for investigating the origin of synergetic effect in the bimetal AO-PAN complexes. Firstly, the specific surface area of Cu-Fe-AO-PAN (II) was measured to be 0.619 m<sup>2</sup> g<sup>-1</sup>, a little larger than that of Fe-AO-PAN (0.352 m<sup>2</sup> g<sup>-1</sup>) [11]. Therefore it is not believed that slight improvement in the specific surface area is the main reason for the higher catalytic ability of Cu-Fe-AO-PAN

(II). Secondly, some researches have reported that the activity of the heterogeneous Fenton catalysts is dependent on the amount of •OH radicals produced from H<sub>2</sub>O<sub>2</sub> decomposition during the degradation of the organic pollutants [23–25]. In this work, Fe-AO-PAN and Cu-Fe-AO-PAN (II) were used as the catalysts and the •OH radicals involved were determined by DMPO-trapping ESR technique.

Fig. 6 shows that the signals with intensity of 1:2:2:1 corresponding to the characteristic peaks of DMPO•OH adducts were observed during the reaction process both in the dark and under visible irradiation, and the intensity gradually increased with the prolongation of reaction time. This confirms that the •OH radicals have been formed in the presence of the complex during the dye degradation. The peak intensity of DMPO•OH adducts in the case of Cu-Fe-AO-PAN (II) is higher than that in the case of Fe-AO-PAN at the same conditions, demonstrating that Cu-Fe-AO-PAN (II) can enhance the H<sub>2</sub>O<sub>2</sub> decomposition to produce the higher concentration of •OH radicals during the degradation because of its synergetic effect coming from introduction of Cu<sup>2+</sup> ions into the metal AO-PAN complexes. Thirdly, the catalytic performance of the catalysts is related closely to their redox potentials. And cyclic voltammetry is a strong tool to investigate catalytic reactions in heterogeneous catalysis by testing the changes of their redox potentials. In this work, a big difference in the redox potentials measured using the cyclic voltammetry method between Cu-Fe-AO-PAN (II) and Fe-AO-PAN or Cu-AO-PAN was found, and the results were shown in Fig. 7 and Table 4.

As can be seen in Fig. 7 and Table 4, a quasi-reversible couple with two relatively weak peaks (reductive potential at –0.54 V and oxidative potential at –0.40 V) is observed for Fe-AO-PAN, which can be assigned to the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox. By contrast, the two redox peaks (reductive potential at 0.23 V and oxidative potential at 0.28 V) were obviously intensified in the case of Cu-Fe-AO-



**Fig. 6.** The ESR signals of the DMPO•OH adducts for (a) RhB/Fe-AO-PAN/H<sub>2</sub>O<sub>2</sub> and (b) RhB/Cu-Fe-AO-PAN (II)/H<sub>2</sub>O<sub>2</sub>.

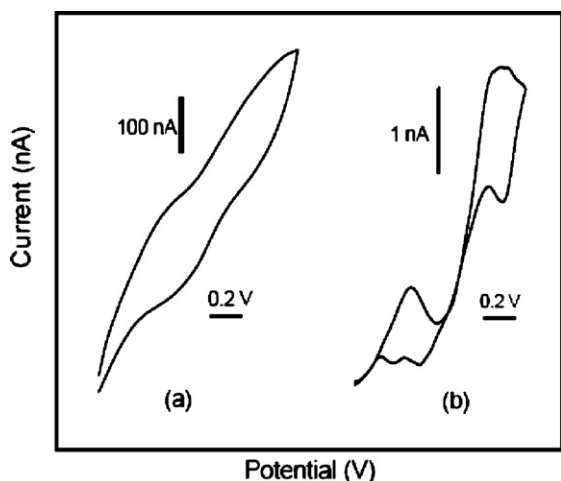


Fig. 7. Cyclic voltammograms of (a) Fe-AO-PAN and (b) Cu-Fe-AO-PAN (II).

PAN (II), although the electric current was relatively lower. An increase in the intensity of redox peaks indicates that there are more electrochemically accessible sites on the surface of Cu-Fe-AO-PAN (II) than on that of Fe-AO-PAN [13]. Specially, a new couple was found between 0.85 V (reductive potential) and 0.88 V (oxidative potential) for Cu-Fe-AO-PAN (II), which may be designated as the  $\text{Cu}^{2+}/\text{Cu}^+$  redox process. This can give the valuable information about the interaction between two metal ions and their coordination with AO-PAN. However, no redox peaks were observed for Cu-AO-PAN sample, implying that the  $\text{Cu}^{2+}/\text{Cu}^+$  redox process could hardly occur in Cu-AO-PAN. This may be a reason for its poor catalytic activity. Another remarkable difference in cyclic voltammogram between Fe-AO-PAN and Cu-Fe-AO-PAN (II) is their  $\Delta E$  value. It is clear that  $\Delta E$  value for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox of Cu-Fe-AO-PAN (II) is much lower than that of Fe-AO-PAN, suggesting that the redox potentials of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in Cu-Fe-AO-PAN (II) are more symmetric than that of Fe-AO-PAN. This may be the result of rapid transformation of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in Cu-Fe-AO-PAN (II). Moreover, Cu-Fe-AO-PAN (II) has a  $\Delta E$  value for  $\text{Cu}^{2+}/\text{Cu}^+$  redox lower than that for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox. This makes it possible that the redox process of  $\text{Cu}^{2+}/\text{Cu}^+$  ions became much easier in Cu-Fe-AO-PAN (II), thus causing a faster cycle of  $\text{Cu}^{2+}/\text{Cu}^+$  redox. These results indicated that an enhanced running of catalytic recycle may be obtained over Cu-Fe-AO-PAN (II), which give rise to the better catalytic ability. In addition, according to the method described by Silbey et al. [26], the equilibrium constant of the reaction process between the two metal ions expressed by Eq. (5) can be calculated from its redox potentials of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  listed in Table 4 to be  $10^{0.338}$ , which thus is regarded as an important evidence for the interaction of iron ions with copper ions as the origin of synergetic effect in the bimetal AO-PAN complexes.



On the other hand, both ratios of  $k_i$  to  $k_d$  were calculated from the data listed in Table 3 to be 3.27 and 1.54 for Fe-AO-PAN and Cu-Fe-AO-PAN (II), respectively. The remarkable difference between two

**Table 4**  
Electrochemical properties of the AO-PAN metal complexes.

Catalysts	Redox	Reductive potential (V)	Oxidative potential (V)	$\Delta E^a$ (V)
Fe-AO-PAN	$\text{Fe}^{3+}/\text{Fe}^{2+}$	-0.54	-0.40	0.14
Cu-Fe-AO-PAN (II)	$\text{Fe}^{3+}/\text{Fe}^{2+}$	0.23	0.28	0.05
	$\text{Cu}^{2+}/\text{Cu}^+$	0.85	0.88	0.03

<sup>a</sup>  $\Delta E$ : The difference between oxidative and reductive potentials.

ratios reveals that the photocatalytic degradation of the dye in the presence of Fe-AO-PAN shows the higher process photoreaction efficiency. Photo efficiency is often proposed to compare the process photoreaction efficiency. Generally, photo efficiency describes the number or moles of reactant molecules transformed or product molecules formed divided by the numbers of photons at a given wavelength incident on the reactor cell [27,28]. At this study, photo efficiency ( $\xi$ ) of the dye degradation is defined as the ratio of the difference between moles of dye molecules degraded under light irradiation and in the dark to the total incident light flux from the source within 60 min of degradation time, and expressed as follows:

$$\xi = \frac{(C_d - C_i) \times V}{A \times W \times I_v \times t} \quad (6)$$

where  $C_d$  and  $C_i$  are the residual concentrations of the dye within 60 min in the dark and under light irradiation ( $\text{mmol L}^{-1}$ ), respectively.  $V$  is the volume of solution in reactor cell (0.10 L).  $I_v$  is the total incident light intensity from the source ( $91.1 \text{ J s}^{-1} \text{ m}^{-2}$ ).  $A$  is the specific surface area of the catalyst ( $0.352 \text{ m}^2 \text{ g}^{-1}$  for Fe-AO-PAN and  $0.619 \text{ m}^2 \text{ g}^{-1}$  for Cu-Fe-AO-PAN (II)).  $W$  is the weight of catalyst (0.50 g).  $t$  is the degradation time (3600 s).  $C_d$  and  $C_i$  values in the case of both catalysts were obtained from the data in Fig. 5, and  $\xi$  value of the dye degradation with Fe-AO-PAN or Cu-Fe-AO-PAN was calculated to be  $1.11 \times 10^{-8} \text{ mmol J}^{-1}$  or  $5.29 \times 10^{-10} \text{ mmol J}^{-1}$ .

The recycling capability of Fe-AO-PAN and Cu-Fe-AO-PAN (II) as the catalysts was also examined by the additional degradation process of fresh RhB solution with the used catalysts from the previous runs. The used catalysts were thoroughly washed with distilled water after each run, and RhB and  $\text{H}_2\text{O}_2$  were added before the next run. Both complexes were reused up to five times, and the results were shown in Fig. 8.

Fig. 8 shows that the catalytic activity of Fe-AO-PAN lost significantly after each cycle, suggesting that Fe-AO-PAN as a heterogeneous Fenton catalyst was not stable using  $\text{H}_2\text{O}_2$  as oxidant. By contrast, no obvious deactivation of Cu-Fe-AO-PAN (II) in three successive runs was found when compared with the first run, and its catalytic activity slightly declined in the fifth run, but still much higher than that of Fe-AO-PAN at the same run. Besides, one problem with the heterogeneous photocatalysts is metal ions leaching from the catalyst that causes secondary contamination to wastewater in pilot-scale application. Therefore, the total concentration of metal ions leaching from 3.0 g in 100 ml solution at pH 6.0 after 180 min was measured by atomic absorption spectrometry method to be not higher than 3.0 ppm. The results confirm that the high catalytic activity of Cu-Fe-AO-PAN (II) can remain in reuse.

#### 3.4. A proposed reaction mechanism

On the basis of all the above experimental results, we proposed a possible mechanism for the cooperation between the photocatalytic cycles of the two metal ions in Cu-Fe-AO-PAN (II)/ $\text{H}_2\text{O}_2$  system in the dye degradation illustrated in Fig. 9.

Fig. 9 shows that the  $\text{H}_2\text{O}_2$  molecules adsorbed on the surface of Cu-Fe-AO-PAN (II) can reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions on the loaded state through the Fenton-like process in the dark or under visible irradiation, and the generated  $\text{Fe}^{2+}$  ions on the fiber are then oxidized immediately by  $\text{H}_2\text{O}_2$  to complete the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle and produce  $\bullet\text{OH}$  radicals. It is noted that this heterogeneous reaction may be not as fast as in a homogeneous solution. Meanwhile, the formed  $\text{Fe}^{2+}$  ions can also react with the  $\text{Cu}^{2+}$  ions loaded on the fiber to form the  $\text{Cu}^+$  and  $\text{Fe}^{3+}$  ions by Eq. (5) to accelerate the transformation of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{2+}/\text{Cu}^+$  in Cu-Fe-AO-PAN (II), thus giving rise to additional  $\bullet\text{OH}$  radicals during the degradation. The slow regeneration of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions by  $\text{H}_2\text{O}_2$  is the rate-determining step of the

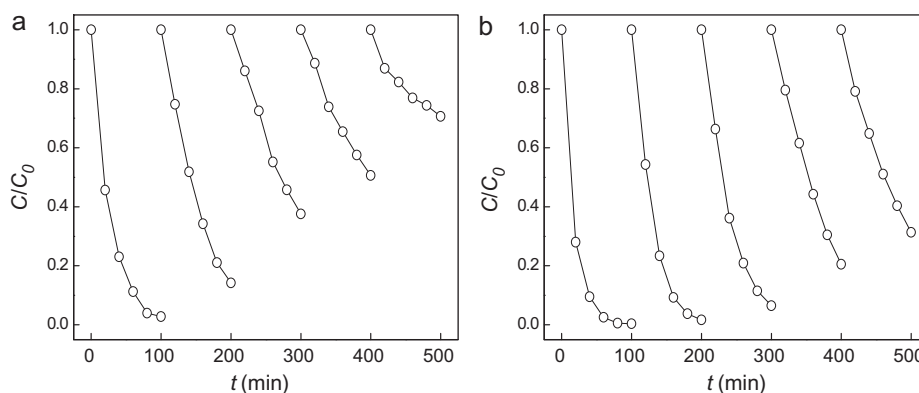


Fig. 8. Catalytic recycling of (a) Fe-AO-PAN and (b) Cu-Fe-AO-PAN (II) at initial pH 6.0 and 25 °C under visible light irradiation during repetitive degradation of RhB.

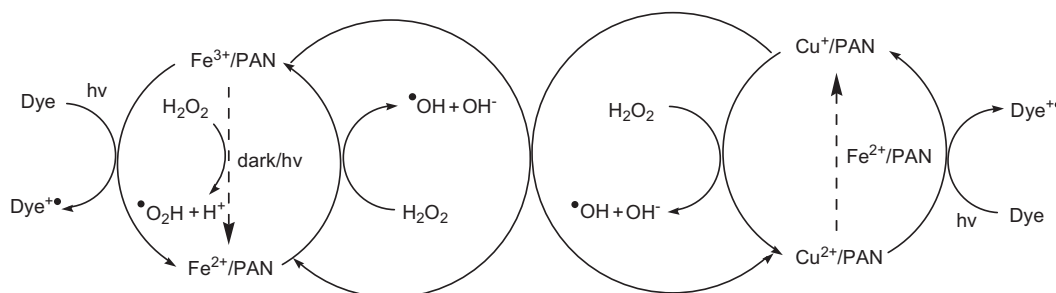


Fig. 9. Bimetal photoredox cycle of Cu-Fe bimetal AO-PAN complex as a heterogeneous Fenton photocatalyst during the dye degradation.

overall reaction. However, the rate of  $\text{Fe}^{2+}$  regeneration is dramatically driven by the interaction of light and complexes to decompose  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  radicals under visible light irradiation. Besides, our previous study Dong et al. [11] have found that the photosensitization of the dye molecules adsorbed on the catalysts may lead to a conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions during the photoassisted Fenton reaction by the excitation of the dye molecules, which is regarded as an additional way for the cycle of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  ions, enhancing the generation of the  $\cdot\text{OH}$  radicals detected by the spin-trapping ESR measurements of the DMPO- $\cdot\text{OH}$  adducts during the degradation. Also, the transformation of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  ions, similar to the iron ones, may also be promoted by the photosensitization of dye molecules. Consequently, the higher photocatalytic performance of the bimetal AO-PAN complex should be originated from a significant interaction between the two metal ions on the loaded state with the aid of both the dye and visible light irradiation, and the oxidative degradation of dye with metal AO-PAN complex that can absorb strongly visible light can be greatly accelerated by visible light irradiation. This provides possibly another better approach to the purification of dyeing wastewaters using visible light or sunlight.

### 3.5. Cost analysis

Cost is actually an important parameter for comparing the catalysts. PAN fiber is one of the commonly used man-made fibers in modern textile industry throughout the world. Moreover, it is available commercially at a low-cost. More importantly, PAN fiber is easily modified with hydroxylamine at alkaline solution by partial conversion of its nitrile groups into amidoxime groups, and which is then used to react with  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions to prepare Cu-Fe bimetal AO-PAN complex using a simple exhaustion method at low temperature. The regeneration of the used complex using alcohol is also inexpensive, and results in little loss of its activity as the catalyst. Due to scarcity of consistent cost information in the literature data, cost comparisons are difficult to make. However, the relative

cost of the catalysts used in this study is supposed much lower than that of some common catalysts such as Fe/Nafion catalyst, because the price of Nafion is more than 2000 USD  $\text{kg}^{-1}$  [25]. Besides, comparing with some heterogeneous Fenton catalyst such as Nafion membrane [6], Fe alginate gel bead [7] and other modified PAN fibrous catalyst [8], the bimetal AO-PAN complexes have a prime advantage of catalyzing the oxidative decomposition of organic dye in water more effectively, especially at approximately neutral pH and under visible light irradiation because of their unique coordination structure and strong light adsorption feature. Consequently, it is believed that Cu-Fe bimetal AO-PAN complexes are of practical importance in an industrial scale.

## 4. Conclusion

Cu-Fe bimetal AO-PAN complexes have been prepared by the simultaneous coordination of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions with AO-PAN, and then used as the new heterogeneous Fenton catalysts for the degradation of the dye in water under visible irradiation. Compared to Fe or Cu monometal AO-PAN complex, Cu-Fe bimetal complexes exhibited the higher activity and stability for the oxidative decomposition of the dye because of the existence of synergetic effect. The catalytic activity of Cu-Fe bimetal AO-PAN complexes is dependent greatly upon their Cu/Fe molar ratio. 0.56 is the optimum Cu/Fe molar ratio to achieve the best catalytic activity. Based on XPS, cyclic voltammograms and ESR measurements, the important origin of synergetic effect in Cu-Fe bimetal AO-PAN complexes is considered as the joint action of copper and iron species facilitating the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle and exciting the  $\text{Cu}^{2+}/\text{Cu}^+$  redox, followed by the increase in the  $\cdot\text{OH}$  radicals generation. DRS analysis indicates that the adsorption features of metal AO-PAN complexes are also determined by their Cu/Fe molar ratios. Visible irradiation can lead to an obvious increase in catalytic activity of metal AO-PAN complexes, especially with a low Cu/Fe molar ratio. Because of their advantages such as low cost, easy preparation and good regenerative property,

Cu–Fe bimetal AO-PAN complexes have great potential to be ideal Fenton catalysts for the practical treatment of industrial colorants at large scale.

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