

# Biomimetic preparation of ternary heterogeneous catalyst derived from biopolymer in biological sludge and synergistic effects in Fenton process

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**Abstract.** Biopolymer (BioP) was extracted from waste activated sludge and the ternary catalyst BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> was prepared by biomimetic method. Control experiments proved the synergistic effects of the components in BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>. The degradation of high concentration of model pollutant proved its good performance as the heterogeneous Fenton catalyst. The high utilization efficiency of H<sub>2</sub>O<sub>2</sub> and wide operational pH range showed the promising application of BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> in the oxidative degradation of organic pollutants. The possible reaction mechanism on the surface of BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> lies in that PANI provide the acidic condition and the initially generated ≡Fe(II) species react with H<sub>2</sub>O<sub>2</sub> to generate •OH, which destroy the organic dyes adsorbed onto catalyst surface. The redox process Fe(III)→Fe(II) take place easily due to convenient electro transfer in PANI and reduction power of functional groups in BioP.

## 1 Introduction

Fenton processes were invested to destruct organic pollutants widely since the Fenton was discovered[1] and they performed high degradation efficiency. However, the traditional Fenton systems have some drawbacks, which limit their application. For Fenton reactions, the optimum pH usually fall in 2.5~3.5[2-4]. However, most wastewater containing dyes is highly alkaline[5] and some environmental media may possess a high buffer capacity[6]. Therefore, the necessity to acidify the reaction medium limits the applicability in the dyeing wastewater treatment. Another inhibition lies in the iron sludge generated during the reaction, which is dangerous solids waste and may cause secondary pollution[3, 7]. Recently, some new types of heterogeneous catalyst were prepared in order to break through the bottlenecks. Georgi et al.[6] found that humic acid (HA) could extend the optimum pH of the Fenton process toward neutral conditions because of chelation. HA coated Fe<sub>3</sub>O<sub>4</sub> exhibited high Fenton-like catalytic ability during the mineralization of sulfathiazole[2]. These works indicated that the introduction of biopolymer into nanocomposites can improve their performance. Our previous study showed that composite of polyaniline (PANI) and nano Fe<sub>3</sub>O<sub>4</sub> have some advantages such as wide operational pH range, high catalytic activity, high utilization efficiency of H<sub>2</sub>O<sub>2</sub> and low iron concentration in water as the heterogeneous Fenton catalyst[8].

Waste activated sludge (WAS) is the major byproduct of wastewater treatment process and the subsequent

sludge processing, stabilization and disposal incur the high costs. This WAS problem become more and more pressing because of the current legal constrains, the rising costs and public sensitivity over the past decades[9, 10]. At the same time, the inherent properties of biopolymer elicited interest on developing composite materials that could render these molecular useful[11]. WAS contain over 60~75% organic components, mainly the mixture of microbial cells and secretion. The biological components, such as polysaccharide, proteins, lipid, nucleic acid, uronic acid and humic substances, are rich in carboxyl, hydroxyl, amino and other functional groups[12-14]. So, "we should expect more" out of sludge[10] and new resource recovery-based approach is possible to be developed.

Here, biopolymer (BioP) was extracted from WAS and successfully used for preparing the ternary BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> catalyst for the first time. This application of BioP provided a new resource recovery and effective reduction way for large quality of WAS. The catalytic activity and synergistic effects were evaluated using the model dyes and the possible synergistic mechanisms of the components were analyzed in this study.

## 2 Materials and methods

### 2.1 WAS and BioP extraction

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WAS from the secondary setting tank in a municipal sewage treatment plant was collected and cultivated in our lab for extraction of BioP. Thermal-alkaline extraction was carried out at pH 12.5, temperature 90°C for 60 min. The extracted supernatant was freeze-dried and finely ground to get the BioP power.

## 2.2 Biomimetic Preparation of ternary heterogeneous Catalyst

For biomimetic preparation of BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>, 0.5 g BioP power was dissolved in 100 mL citrate-citric acid buffer solution (pH = 4.00) and 0.25 g Fe<sub>3</sub>O<sub>4</sub> nanoparticles was added into the solution. After homogenizing by shaking for 10 min, 0.05 M of aniline, 0.05 g/L of hemin was added. Polymerization of aniline was initiated by injecting 0.2 mL 2.0 M H<sub>2</sub>O<sub>2</sub> solution at 10 min interval. After total 1.0 mL H<sub>2</sub>O<sub>2</sub> solution was used, the polymerization proceeded for 0.5 h at room temperature. Then 0.09 M HCl was added and the mixture was kept stirring for 0.5 h, and allowed to proceed with 12 h. The formed solid was collected via centrifugation at 3500 rpm, washed sequentially with ethanol and water. The final catalyst BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> was obtained by drying at 50°C.

## 2.3 Degradation experiments of dyes

Because Methyl orange (MO) and Rhodamine B (RhB) are typical anionic and cationic azo dyes and often present in wastewater, they were chosen as the target model pollutant in this study. MO and RhB degradation experiments using the ternary catalyst of BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> during heterogeneous Fenton-like reactions were preformed, and the optimal parameters were determined upon the basis of degradation efficiency. The effects of reaction condition including catalyst dosage, concentration of dyes, concentration of H<sub>2</sub>O<sub>2</sub> and pH value was investigated. The produced catalyst was dosed in 100 mL of dye aqueous solution at certain initial pH values and H<sub>2</sub>O<sub>2</sub> was added to initiate the degradation reaction. All experiments were conducted under constant shaking at 150 rpm, 25°C for 30 min. As control, different systems were tested to verify the synergistic effects of the components of catalyst. Sampling was carried out periodically. The collected suspension was filtered through 0.2 μm filters, and the filtrate were then immediately by measuring the absorbance of the solution at 464 nm for MO and 552 nm for RhB, corresponding to the maximum absorption wavelength of dyes.

## 2.4 Analytical method

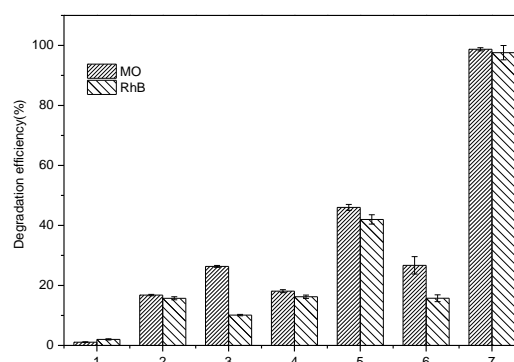
The chemical phase structure of the biomimetic products was characterized by X-ray diffraction (XRD). The morphology was characterized by scanning electron microscopy (SEM). The specific surface area

and pore diameter distribution was determined using N<sub>2</sub> adsorption-desorption isotherms.

## 3 Results and discussion

### 3.1 Synergistic effects of ternary catalyst

Control experiments were conducted to compare the removal efficiency of MO (800 mg/L) and RhB (600 mg/L) without pH adjusting in different systems, and the results were shown in Figure 1.



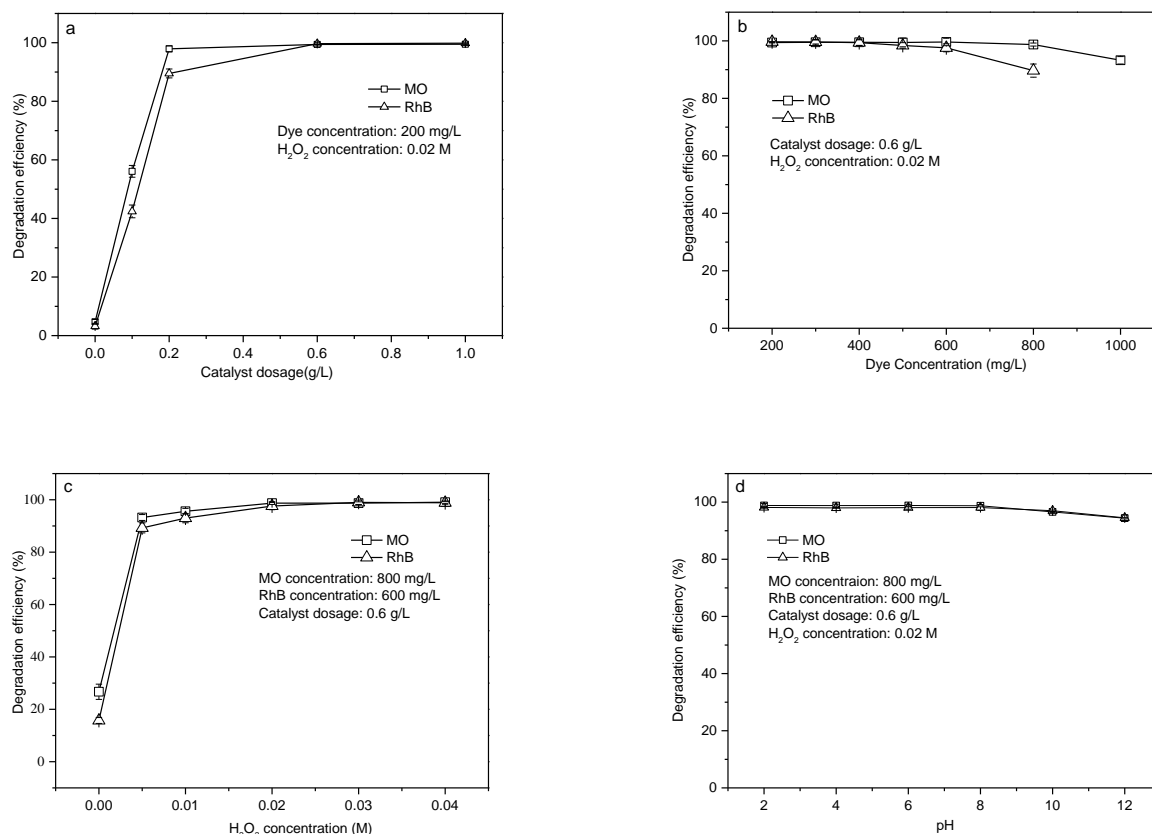
**Figure 1** Degradation efficiency of MO (800 mg/L) and RhB (600 mg/L) in different systems. (1) 0.02 M H<sub>2</sub>O<sub>2</sub>; (2) 0.6 g/L Fe<sub>3</sub>O<sub>4</sub>+0.02 M H<sub>2</sub>O<sub>2</sub>; (3) 0.6 g/L PANI+0.02 M H<sub>2</sub>O<sub>2</sub>; (4) 0.6 g/L BioP@PANI +0.02M H<sub>2</sub>O<sub>2</sub>; (5) 0.6 g/L PANI@Fe<sub>3</sub>O<sub>4</sub>+0.02 M H<sub>2</sub>O<sub>2</sub>; (6) 0.6 g/L BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>; (7) 0.6 g/L BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> +0.02 M H<sub>2</sub>O<sub>2</sub>.

As shown in Figure 1, 0.02 M H<sub>2</sub>O<sub>2</sub> only led to a very slight removal of dyes within 30 min. The small amount of dyes diminished in Fe<sub>3</sub>O<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>, PANI/H<sub>2</sub>O<sub>2</sub> and BioP@PANI/H<sub>2</sub>O<sub>2</sub> system is ascribed to the catalytic activity of nano-Fe<sub>3</sub>O<sub>4</sub> and PANI for H<sub>2</sub>O<sub>2</sub>[2, 15, 16]. About 26.7% MO and 15.8% RhB removal were observed mainly due to adsorption of 0.6 g/L BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>. In the presence of H<sub>2</sub>O<sub>2</sub>, the composite of PANI@Fe<sub>3</sub>O<sub>4</sub> shows higher catalytic activity than pure PANI and Fe<sub>3</sub>O<sub>4</sub>. While the removal of dyes using BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> was notably higher than that for PANI@Fe<sub>3</sub>O<sub>4</sub>, implying that the activity was enhanced by the introduction of BioP. These data indicated BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> performance well beyond those of its components and there are obvious synergistic effects in the ternary composite. The high activity makes it an efficient heterogeneous Fenton-like catalyst. The similar enhancement of catalytic activity was also found in the catalyst Fe<sub>3</sub>O<sub>4</sub>/HA due to the electron transfer between the complexed Fe(II)-HA or Fe(III)-HA[2].

### 3.2 Affecting factors of dyes degradation in heterogeneous Fenton process catalyzed by BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>

In heterogeneous Fenton-like processes, the reaction between  $H_2O_2$  with active sites of  $\equiv Fe(II)$  take place on

the surface of catalyst and active radicals generate[17, 18],



**Figure 2** Degradation of MO and RhB by catalyst under different a) catalyst dosage ; b) dye original concentration ; c)  $H_2O_2$  concentration ; d) pH value

so the suitable dosage of catalyst is essential for the degradation of dyes. As shown in the Figure 2a, when the catalyst dosage increased from 0.1 g/L to 0.6 g/L in 200 mg/L dyes solution, the degradation efficiency of MO and RhB increased from 56.09% and 42.41% to both above 99% after 30 min reaction. When catalyst dosage and  $H_2O_2$  were fixed at 0.6 g/L and 0.02 M respectively, the maximum initial concentration of MO and RhB should be lower than 800 mg/L and 600 mg/L respectively if above 99% degradation efficiencies were obtained (Figure 2b). This can be attributed to the inductive effects caused by high dyes concentration, as available active sites were predominantly covered by the dye molecules[3]. Figure 2c depicts the relationship between dyes degradation and  $H_2O_2$  concentrations. The presence of  $H_2O_2$  increased dramatically the degradation of dyes. When the concentration increased to 0.02 M, the degradation efficiency got to about 99% for both MO and RhB. These results suggest that  $H_2O_2$  plays the very important role in the degradation of dyes, and more active radicals are formed when  $H_2O_2$  concentration increased. However, the optimized  $H_2O_2$  concentration is relatively low, which showed that the  $H_2O_2$  can be used efficiently in the ternary catalyzed system. It should be pointed out that the catalyst showed very wide operational pH range as shown in Figure 2d. For the original pH 2~8 in MO and RhB solution, the degradation efficiency all kept over

98%. Even at pH 10 and 12, the efficiency also maintained about 97% and 95%. The results proved this ternary BioP@PANI@ $Fe_3O_4$  can overcome the drawback of narrow pH range of traditional Fenton catalyst, which makes it a promising candidate as the high efficient catalyst for treatment of various dyes-containing wastewater.

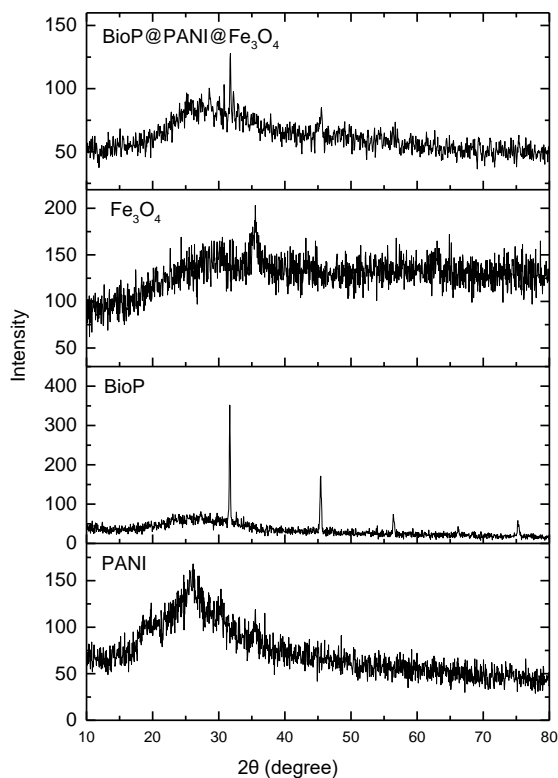
### 3.3 Catalyst characterization

Figure 3 shows the XRD patterns of BioP@PANI@ $Fe_3O_4$  and the three components,  $Fe_3O_4$ , BioP and PANI. The main characteristic peaks of PANI centered at  $2\theta = 20^\circ$  and  $25^\circ$ [19, 20], the peaks of  $Fe_3O_4$  at  $2\theta = 35.7^\circ$ [21] and the peaks of BioP at  $2\theta = 31.7^\circ$  and  $45.3^\circ$  are remained in the produced catalyst with weaker summit and broader range. The changes indicate that the main structure of PANI,  $Fe_3O_4$  and BioP retains in the composite, but their crystalline is distorted during the prepare.

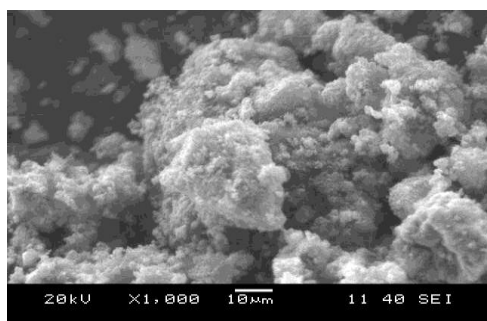
The SEM image of catalyst showed that the particles about tens of microns aggregate into porous lumps and the fine granules with diameter ranging from 100 nm to a few microns are well dispersed throughout the surface of larger particles. The presence of BioP

effectively prevented the aggregation of PANI and  $\text{Fe}_3\text{O}_4$ . The surfaces of the composite are very rough, which provide good possibilities to trap and adsorb the pollutants in water.

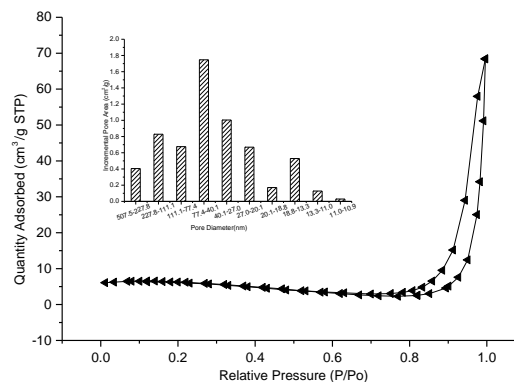
The specific surface area and pore diameter distribution were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, using  $\text{N}_2$  adsorption-desorption isotherms.



**Figure 3** XRD patterns of catalyst and three components



**Figure 4** SEM image of catalyst

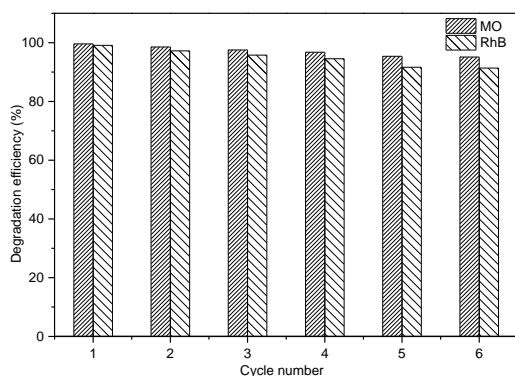


**Figure 5** Nitrogen adsorption-desorption isotherms (Insert : Pore area distribution)

As shown in Figure 5, the nitrogen adsorption-desorption isotherm exhibited multi-layer adsorption (Type IV and V isotherms) and hysteresis loops type H1 according to the Brunauer-Emmett-Teller classification, which indicates that  $\text{BioP@PANI@Fe}_3\text{O}_4$  is agglomerates (assemblages of rigidly joint particles) and relatively high pore size uniformity and facile pore connectivity[22]. The pore size distribution indicates that the catalyst contains macro- and meso-porous and the pore diameter of 77.4-40.1 nm provide the maximal pore area. The BET surface area of this composite are 19.89  $\text{m}^2/\text{g}$ , which much smaller than that reported for iron-loaded activated carbon used as adsorbent with BET surface area over 300  $\text{m}^2/\text{g}$ [23, 24]. This result indicated that the absorption might not be the most important removal reason of dyes, which is consistent with the results in Figure 1. It is speculated that degradation of dyes was due to catalysis instead of adsorption.

### 3.3 Reusability and stability of catalyst

Reusability and stability are vital for a catalyst used in pollutant degradation, so the repeated MO and RhB degradation tests were performed using the ternary catalyst in the Fenton-like reaction. As illustrated in Figure 6,  $\text{BioP@PANI@Fe}_3\text{O}_4$  was stable and maintained high catalytic efficiency in the six rounds with above 90% degradation efficiency. Additionally, the leaching test of iron indicated that the leached iron in the first and sixth runs were about 7 mg/L and less than 0.4 mg/L. Low iron dissolution means that heterogeneous catalysis was mainly responsible for the fast dye degradation[25, 26]. Meanwhile, the released low iron concentration can greatly reduce the treatment cost of subsequent iron sludge, which is one of the bottlenecks of application of Fenton process for the treatment of wastewater. These results demonstrate that this catalyst has a strong potential for wastewater treatment because of its excellent stability, reusability and safety.

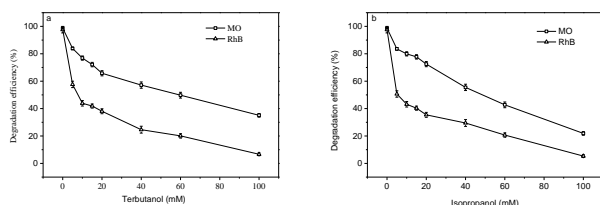


**Figure 6** Reusability of catalyst for the degradation of dyes

### 3.4 Possible mechanism

#### 3.4.1 Verification of $\cdot\text{OH}$

Radical  $\cdot\text{OH}$  are thought the main active oxidant in the Fenton reaction and tertbutanol[27] and isopropanol[28] are known as  $\cdot\text{OH}$  scavengers. In our experiments, varying concentrations of tertbutanol and isopropanol were added to the system in order to verification the roles of  $\cdot\text{OH}$ . The results summarized in Figure 7 clearly showed that the degradation of dyes was dramatically influenced by  $\cdot\text{OH}$  radical scavengers and were almost completely inhibited in the presence of 100 mM tertbutanol or isopropanol. So it is obvious that  $\cdot\text{OH}$  radicals are the oxidant that initiates the degradation of dyes.

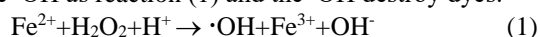


**Figure 7** Effects of  $\cdot\text{OH}$  scavengers on the degradation of dyes (MO 800mg/L, RhB 600mg/L, Catalyst 0.6 g/L,  $\text{H}_2\text{O}_2$  0.02 M)

#### 3.4.2 Possible synergistic effects in the degradation reaction

The ternary catalyst  $\text{BioP@PANI@Fe}_3\text{O}_4$  exhibit high activity for degradation of organic dyes and there are obvious synergistic effects among the three components. The possible interaction is schemed in Figure 8.

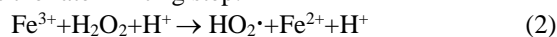
Nano- $\text{Fe}_3\text{O}_4$  in the  $\text{BioP@PANI@Fe}_3\text{O}_4$  plays the main role in the production of  $\cdot\text{OH}$ . As reported[18, 21], the initially generated  $\equiv\text{Fe(II)}$  species react with  $\text{H}_2\text{O}_2$  to generate  $\cdot\text{OH}$  as reaction (1) and the  $\cdot\text{OH}$  destroy dyes:



The introduction of PANI and biopolymer can protect iron from leaching, which was proved by the low leaching iron concentration. Just as shown in Figure 8, the nitrogen-containing functional groups in PANI and

BioP, the carboxyl in BioP act as active sites[6, 29] for forming complexes with  $\equiv\text{Fe(II, III)}$ . The ligand and the net-like structure influence the leaching of iron and resulting in the low dissolution into bulk solution.

In the traditional Fenton reactions, the reduction of  $\text{Fe}^{3+}$  is the rate-limiting step:



$\text{Fe}^{3+}$  easily form insoluble precipitates, which lead to the turbidity and color of the solution. In the  $\text{BioP@PANI@Fe}_3\text{O}_4/\text{H}_2\text{O}_2$  system, this redox process  $\text{Fe(III)} \leftrightarrow \text{Fe(II)}$  on the catalyst surface can take place when an excess of  $\text{H}_2\text{O}_2$  is added into the reaction solution. However, the iron redox cycle can be easily accomplished even without  $\text{H}_2\text{O}_2$ . The redox process  $\text{Fe(III)} \leftrightarrow \text{Fe(II)}$  is facilitated at the solid-water interface in  $\text{Fe}_3\text{O}_4$ [30, 31] and the electron transfer between the complexed  $\text{Fe(II)}$  or  $\text{Fe(III)}$  can lead to more rapid regeneration of  $\text{Fe(II)}$  species. Moreover, PANI is like an "electron pool"[21] and then improve the electron transfer on the interface of catalyst. At the same time, there are plenty of hydroxyl and carboxyl groups in the polysaccharide and protein in BioP. These organic matters can also exhibit reducing power to produce  $\text{Fe(II)}$ . Based on the analysis, the high catalytic ability of  $\text{BioP@PANI@Fe}_3\text{O}_4$  may be caused by the electron transfer, leading to rapid regeneration of  $\text{Fe(II)}$  active sites and the production of  $\cdot\text{OH}$  radicals at low  $\text{H}_2\text{O}_2$  concentration.

Usually reaction (1) is considered as the pH-independent below pH 3[32]. However, the  $\text{BioP@PANI@Fe}_3\text{O}_4$  shows wide work pH range from 2 to 12 for removal of dyes, which should be attributed to PANI. The PANI in the catalyst is the semi-oxidized state of PANI (Emeraldine form), and the number of protons can be varied depending on the medium[33]. In the reaction system with higher pH, de-doping process of PANI leads to the release of protons and decreases pH values. On the other hand, the  $\text{Fe(II)}$ -complex with BioP may change the optimum pH for its reaction with  $\text{H}_2\text{O}_2$  towards neutral conditions[6, 34].

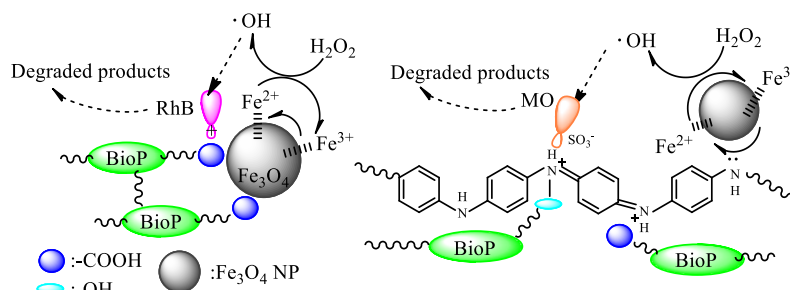
Based on the above discussion, the possible reaction mechanism on the surface of  $\text{BioP@PANI@Fe}_3\text{O}_4$  is proposed as follows: PANI provide the acidic condition in the reaction system and the initially generated  $\equiv\text{Fe(II)}$  species react with  $\text{H}_2\text{O}_2$  to generated  $\cdot\text{OH}$  on the catalyst surface. The organic dyes adsorbed onto the  $\text{BioP@PANI@Fe}_3\text{O}_4$  surface are destroyed by  $\cdot\text{OH}$  radicals. The redox process  $\text{Fe(III)} \rightarrow \text{Fe(II)}$  take place either in the presence of excess  $\text{H}_2\text{O}_2$  (Reaction 2) or by electro transfer. A small amount of dissolved iron and  $\cdot\text{OH}$  disperse into bulk solution and the chain reactions same as in homogeneous Fenton system occur[32] and organic dyes are destroyed.

### 3.5 Application in synthetic dyeing wastewater

It was proved that  $\text{BioP@PANI@Fe}_3\text{O}_4$  was an effective catalyst in the degradation of the model pollutant MO and RhB. However, verifying its promise as a degradation catalyst for wastewater treatment is

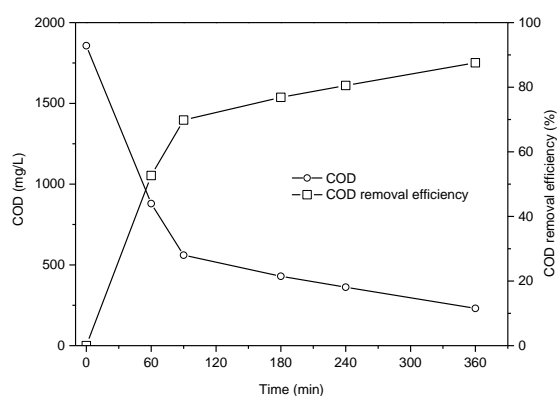
more important. Thus, more complex synthetic dyeing wastewater containing 100 mg/L MO, RhB, Methyl

Blue (MB) and Coomassie Brilliant Blue (CCB) respectively were treated.



**Figure 8** Possible mechanism on the surface of BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> composite

As shown in Figure 9, a decrease of 52.7% in COD achieved after treating for 60 min and the COD removal increased to 87.6% after 360 min. The results showed the high oxidation degree of organic dyes can be obtained catalyzed by BioP@PANI@Fe<sub>3</sub>O<sub>4</sub>.



**Figure 9** Profile of COD and COD removal of synthetic dyeing effluent (Catalyst 0.6 g/L, H<sub>2</sub>O<sub>2</sub> 0.02 M)

## 4 Conclusion

A new kind of ternary heterogeneous catalyst derived from activated sludge was prepared by biomimetic method and showed outstanding catalytic performance on the degradation of high concentration dyes in Fenton reaction. The components in the catalyst have obvious synergistic effects and the possible mechanism was postulated. The excellent results provide a new way of resource recovery and mass reduction for WAS, and BioP@PANI@Fe<sub>3</sub>O<sub>4</sub> is a potential synergic heterogeneous catalyst for oxidative degradation of organic pollutants in the presence of low concentration H<sub>2</sub>O<sub>2</sub>.

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