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Biological preparation and application of poly-ferric sulfate flocculant

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Abstract: A novel inorganic polymer flocculant, poly-ferric sulfate (BPFS) was prepared by oxidation of ferrous sulfate using domestic *Thiobacillus ferrooxidans* (*T.f*) under acid condition. The optimal conditions for the preparation were pH value of 1.5, $(NH_4)_2SO_4$ dosage of 0.5 g/L, initial Fe^{2+} concentration of 45g/L, inoculum 10%, rotating speed of 120 r/min, reaction time of 5−6 d and reaction temperature of 30 °C. Under the optimal conditions, the BPFS product with pH value of 1.5−2.2, basicity of 17.5%−22.7% and total iron content of 43.87−45.24 g/L was obtained. The application of the BPFS to three wastewaters was carried out, and the removal efficiencies of COD, decolorization and Zn^{2+} by BPFS can be reached 70%, 90% and 99%, respectively. The result suggests that the BPFS is an excellent flocculant for water treatment.

Key words: ferrite; poly-ferric sulfate; flocculant

1 Introduction

Flocculation sedimentation is one of the most widely used and lowest cost techniques for water treatment [1−2], and flocculant is the key in application of flocculation sedimentation technique. Recently, a novel inorganic polymer flocculant, poly-ferric sulfate(PFS) has received much attention because it has many advantages in comparison with conventional flocculant, such as low sample consumption, high efficiency, wide pH application range, low residual iron concentration, hydrolysate with high efficiently dehydration, non-toxicity, low-priced and fast settling rate [3−6].

At present, PFS is mostly prepared by direct oxidation of ferrous sulfate using strong oxidant such as H_2O_2, $KClO_3$, NaClO, HNO_3 or by catalytic oxidation of ferrous sulfate using $NaNO_2$ or NaI as a catalyst in acid media. However, the methods mentioned above have many limitations such as extremely slow reaction, unstable product, low yield, large consumption of catalyst, high cost and emissions of nitrogen oxides causing environmental pollution, so it is difficult to be applied to the industrial production [7−10].

The objective of this study is to develop a new preparation technique for PFS using the microbes and organic waste, and to gain the BPFS product with low cost, low energy consumption, high-quality and high stability [11−14]; the influencing factors in the preparation process of BPFS and its application in water treatment were also investigated.

2 Experimental

2.1 Microbial adaptation

9K culture medium containing 9 g/L Fe^{2+} was added into conical flask，then 10% (volume fraction) inoculum was innoculated and cultivated on a thermostatic waterbath at 30 °C with agitation of 120 r/min. The conversion rate of Fe^{2+} was determined at selected time until it reached 85%. After the reaction, the reaction mixture was used to initiate the next one, and the above-mentioned steps were replicated until the reaction time basically remained stable. With the repeated inoculation and cultivation, *T.f* bacteria gradually adapted to the new environment, and the reaction time gradually became stable. The *T.f* bacteria adaptation results are listed in Table 1.

As the *T.f* bacteria were in a new environment, their growth and oxidability were influenced to a certain extent. The reaction time to meet the oxidation rate

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Table 1 Adaptation results of *T.f* bacteria

Reaction times	Reaction time required/h
1	72
2	65
3	55
4	50
5	48

above 85% was 72 h. However, the more reaction times conducted, the less time was required. After 4 times repeated cultivation, the reaction time requried for oxidation rate above 85% was stabilized to be about 50 h, as listed in Table 1.

2.2 Preparation of BPFS

Based on breeding selection and domestication, eosinophilic aerobic autotrophic bacteria *T.f* were selected as biocatalyst to prepare BPFS with $FeSO_4{\cdot}7H_2O$ as raw materials. Ferrous sulfate solution was prepared by dissolving a certain amount of $FeSO_4{\cdot}7H_2O$ in deionized water, the pH value of the solution was adjusted with sulfuric acid. After the addition of essential nutrients, strains were introduced and cultivated in thermostatic waterbath at 30 °C. Under the catalysis of microbes, reddish-brown BPFS was synthesized through a series of oxidation, hydrolysis and polymerization reactions.

2.3 Flocculation experiments

To evaluate the flocculation effect of the prepared BPFS, flocculation experiments were carried out in a jar test apparatus. A lake water with high chemical oxygen demand (COD), a dye wastewater and a zinc containing wastewater were tested. Selected properties of the tested solutions were summarized in Table 2. The experimental procedurzes were as follows: 5 mL BPFS was added to the jar and then filled with 400 mL tested solution. Afterwards, the suspension was agitated at speed of 40−60 r/min for 10 min, then it was left undisturbed for over 30 min, and the supernatant sample (200−300 mL) was collected for further analysis.

Table 2 Selected properties for tested solutions

Solution	pH	COD/ $(mg{\cdot}L^{-1})$	Absorbance (methylene blue)	$\rho(Zn^{2+})$/ $(mg{\cdot}L^{-1})$
Lake water	6.72−7.02	330	−	−
Dye wastewater	8.0	−	0.143	−
Zinc containing wastewater	5−6	−	−	200

2.4 Analytical methods

COD was measured by fast digestion-spectrophotometric method and the content of dyes expressed as visible light absorbance at 665 nm was measured by a visible spectrophotometer; the Zn concentration in solution was measured by flame atomic absorption spectrophotometry. Fourier transform infrared spectroscopy (FTIR) was carried out on Nicolet Magna 550 to obtain the structural information of the BPFS composite.

3 Results and discussion

3.1 Preparation influence factors

3.1.1 Effect of temperature

Temperature is very important for microbial growth and activity of microbial enzymes. To investigate the effect of temperature on BPFS preparation, experiments were conducted at four different temperatures (20, 30, 35 and 40 °C) with 10% inoculum at pH 2.0. The results are shown in Fig. 1.

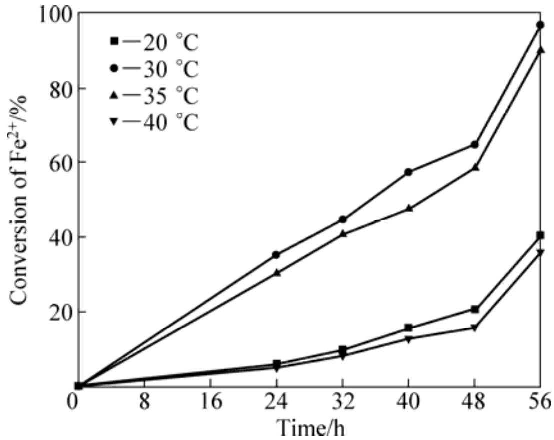

Fig. 1 Impact of reaction temperature on conversion of Fe^{2+}

It is shown that the conversion of Fe^{2+} at 30 and 35 °C is much stronger than that at 20 and 40 °C, illustrating that too high or low temperature is likely to result in significant decrease of Fe^{2+} oxidation rate, moreover, high temperature increases the amount of sediment. Thus, the optimum temperature is 30 °C for the preparation of BPFS.

3.1.2 Effect of pH

pH is critical to the preparation process, as pH increases, the oxidation of Fe^{2+} gets weak and more precipitation is generated, lowering the basicity of the product. However, too low pH is also unfavorable for the oxidation of Fe^{2+} due to the inhibition of bacteria growth, and it tends to make the prepared product has strong corrosivity, therefore, the pH value of the reaction solution should be well-controlled.

The effect of pH is studied at various pH (2.0, 1.8 and 1.5) with other experimental conditions constant.

Figure 2 shows the conversion of Fe^{2+} versus time at pH value of 2.0, 1.8 and 1.5. The conversion of Fe^{2+} is stronger at pH 2.0 than that at pH 1.8 and pH=1.5 in the initial stages; however, it is not different at the end of the experiment (after 100 h) with conversion of about 90% at pH=2.0, 1.8 and 1.5. It is found that the precipitation of jarosite [$MFe_3(SO)(OH)_6$] can be easily generated at initial pH value of about 2.0, especially with high iron concentration, resulting in inhibition occurring in the oxidation of Fe^{2+}. Therefore, initial pH value of 1.5 is considered to be appropriate for the preparation of BPFS.

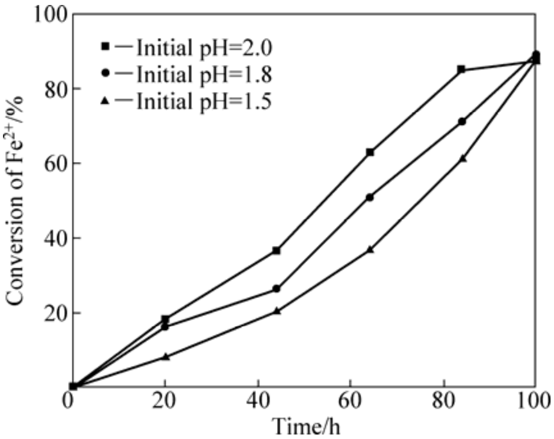

Fig. 2 Impact of initial pH on conversion of Fe^{2+}

3.1.3 Effect of inoculation amount

To investigate the effect of inoculation amount on the BPFS preparation, experiments were conducted with 5%, 10%, 15% and 20% inoculum. The results are shown in Fig. 3.

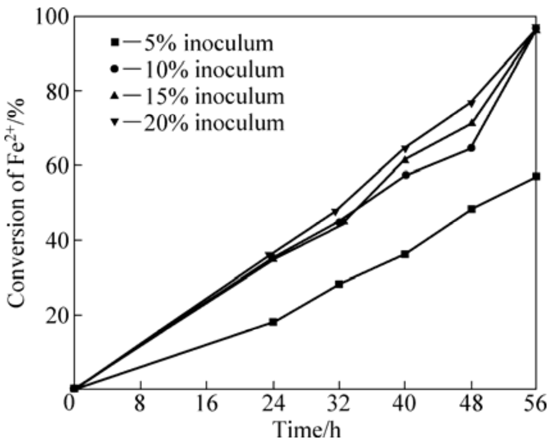

Fig. 3 Impact of inoculum on conversion of Fe^{2+}

Clearly, the conversion of Fe^{2+} is much lower with 5% inoculum, and the conversion of Fe^{2+} is only 55% after 56 h. However, with the addition of 10% to 20% inoculum, the conversions of Fe^{2+} are not significantly different and the conversion of about 98% is obtained after 56 h. It is illustrated that with 10% or more inoculum, the amount of inoculum does not have much impact on the conversion of Fe^{2+}. Thus, 10% inoculum for the preparation of BPFS is chosen.

3.1.4 Effect of initial iron concentration

The effect of the initial Fe^{2+} concentration on the BPFS preparation was studied by changing the Fe^{2+} concentration from 35 to 45 g/L. As shown in Fig. 4, with the increase of Fe^{2+} concentration, the average oxidation rate of Fe^{2+} decreases, and the color of BPFS gets darker because the growth of bacteria requires proper amount of Fe^{2+}. Low Fe^{2+} concentration cannot provide sufficient energy to the growth of bacteria and causes the prepared BPFS to be low in iron content and less useful in application. However, too much Fe^{2+} can inhibit the growth of bacteria. Based on the comparison of the growth of bacteria under different Fe^{2+} concentration conditions, it is concluded that with the initial Fe^{2+} concentration of 40 g/L, Fe^{2+} oxidation rate is more stable and BPFS with good performance can be obtained.

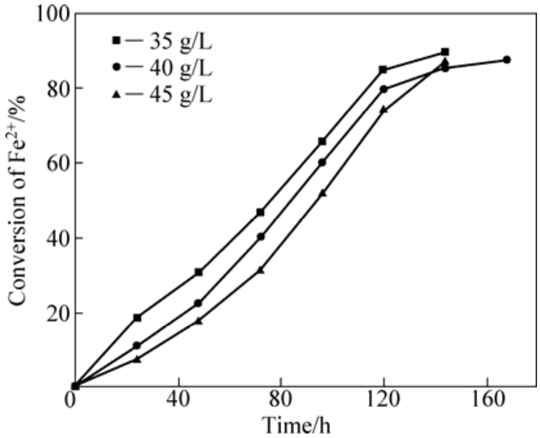

Fig. 4 Impact of different initial Fe^{2+} concentration on conversion of Fe^{2+}

3.1.5 Effect of reaction solution composition on preparation of BPFS

A certain amount of precipitation can be generated during the preparation of BPFS by microbes. Based on the analysis of X-ray diffraction (XRD), the precipitation is identified as pyrite vanadium with formula $MFe_3(SO_4)(OH)$. However, the precipitate produced during the preparation of BPFS is undesirable because it can cause the scale in bioreactor and affect the transmit between substrate and metabolites, resulting in deficiencies of the nutrients such as O_2, CO_2 and substrate Fe^{2+} and a decrease in the reaction rate. Thus, it is very important to obtain a suitable culture medium with good oxidative activity of bacteria as well as less precipitation [15−18].

As the chemical formula for jarosite precipitation is $MFe_3(SO_4)(OH)$, where M may be K^+, Na^+, NH_4^+ or H_3O^+, so the precipitation generation is related to the medium pH, cation species and concentration. Usually,

NH_4^+ makes great contribution to jarosite precipitation and its concentration has a large influence on the amount of precipitation. Ammonium sulfate [$(NH_4)_2SO_4$] concentration can be set at 0.5 and 3.0 g/L respectively in medium with pH=1.5 while other ingredients remain constant. The amounts of precipitation that change over time are acquired. The result is shown in Fig. 5.

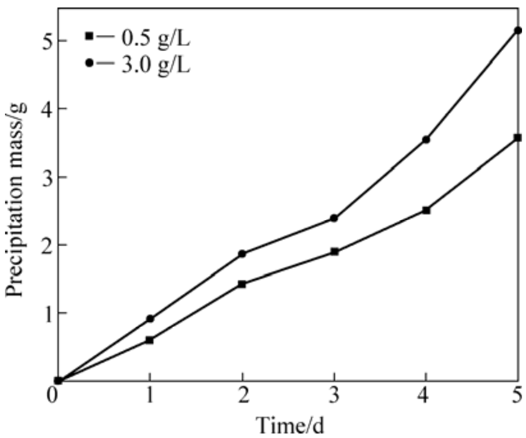

Fig. 5 Effect of $(NH_4)_2SO_4$ concentration on precipitation

As the concentration of $(NH_4)_2SO_4$ decreases from 3.0 to 0.5 g/L, the amount of precipitation is significantly reduced while the oxidation rate of Fe^{2+} is not changed. In addition, considering reagent usages and production costs, $(NH_4)_2SO_4$ concentration of 0.5 g/L is more favorable for the preparation of BPFS.

3.2 Characterization of prepared BPFS

The BPFS prepared under the optimum condition is characterized. pH of the BPFS ranges from 1.5 to 2.2, which is higher than that of the PFS prepared by conventional methods and can reduce corrosion for the reactor. The total iron content of the BPFS is 43.87−45.24 g/L and the basicity is 17.5%−22.7% which is higher than that of the most PFS previously reported, resulting in better flocculability.

Moreover, it is suggested that the BPFS coagulants consist of species containing both Fe and —OH by the analysis of FT-IR spectroscopy (Fig. 6). In particular, peak at 821 cm^{-1} corresponds to Fe—OH—Fe symmetrical stretching vibrations, peaks at 1 020 and 639 cm^{-1} are associated with a Fe—O—H bond, peaks at 3 460 and 1 640 cm^{-1} are related to H—O—H stretching vibrations and peak at around 1 100 cm^{-1} is the characteristic absorption peak of SO_4^{2-} [19−23].

3.3 Application of BPFS

The removal efficiencies of COD, decolorization and Zn^{2+} by the BPFS were investigated at different pH, the results are shown in Fig. 7.

Generally, the treatment effect of the PFS on contaminated water varies with pH. As the BPFS is

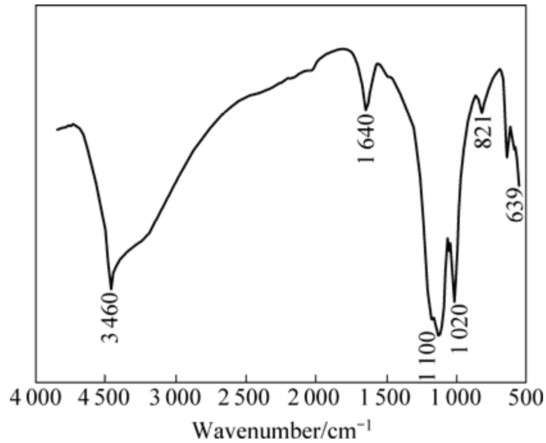

Fig. 6 FTIR spectrum of BPFS

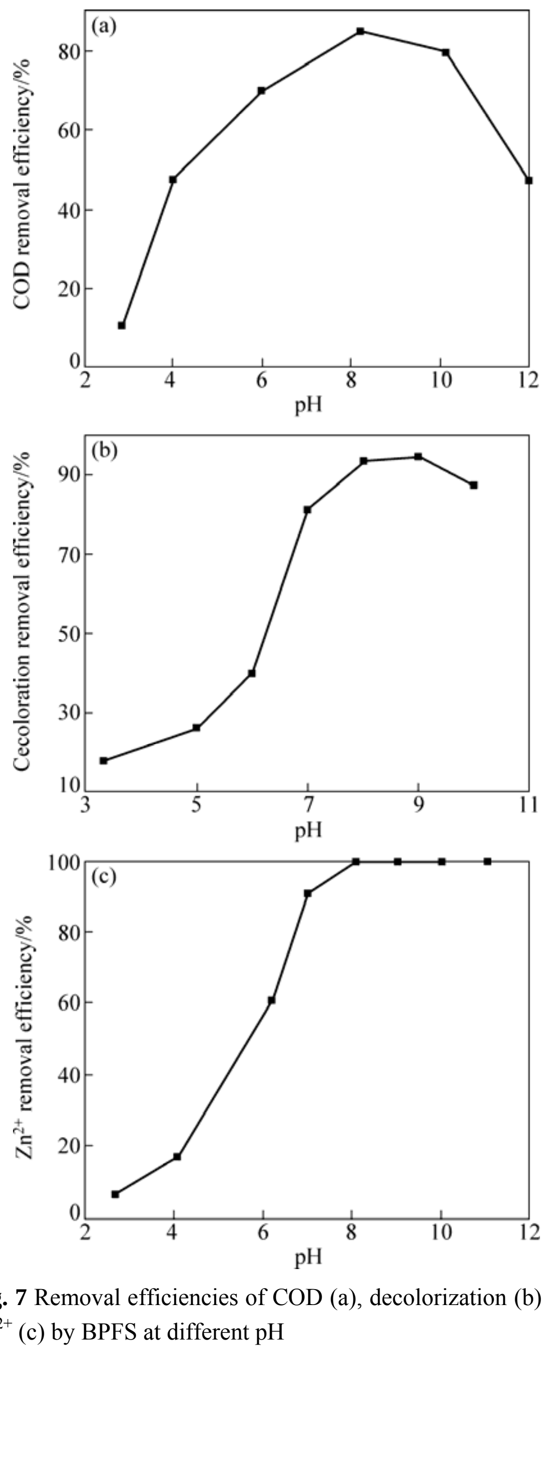

Fig. 7 Removal efficiencies of COD (a), decolorization (b) and Zn^{2+} (c) by BPFS at different pH

applied to treat the lake water, significant COD removal efficiency (above 70%) is found in the pH range of 6.0−10.0 as shown in Fig. 7(a).

For the treatment of the dye wastewater, the decolorization efficiency increases with increasing pH value. At pH above 8, the decolorization efficiency could be up to 90% (see Fig. 7(b)). Considering PFS is a metal ion containing polymer, it contains various high valence polynuclear complex ions and hydroxyl group —OH. Polymers can be generated by the bridging of —OH which interacts with negative charged materials. By controlling pH, the number hydroxyl complexes, distribution, electrical charge and molecular mass can be adjusted to achieve satisfactory results.

The results of the zinc removal efficiency at different pH using the BPFS are shown in Fig. 7(c). As pH increases, the zinc removal efficiency is enhanced. At pH above 8.0, the zinc removal efficiency reaches over 99%.

At the same time, the flocculating effect of BPFS and PFS is compared. The results are shown in Fig. 8.

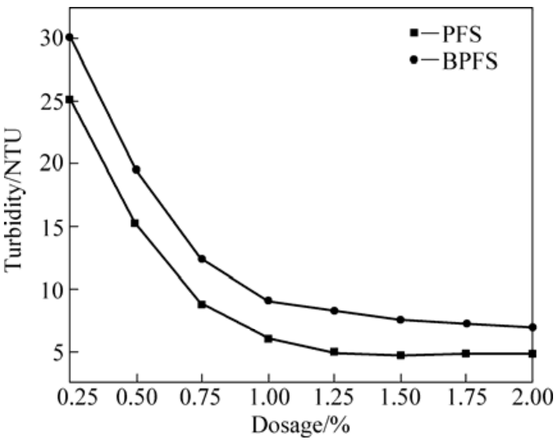

Fig. 8 Comparison of flocculation between PFS and BPFS

It is shown that compared with the PFS prepared by conventional methods, the BPFS prepared in this study is superior with respect to the turbidity removal and the subsidence effect. This is because BPFS not only has a high degree of polymerization, but also contains microorganisms，which can catalyze the oxidation of organic matter as a condensation nucleus during the flocculating-deposition process. Thus, it is sticky and can improve the coagulation efficiency, resulting in the adsorption of big molecular organic matter.

4 Conclusions

1) A new preparation method of PFS using *T.f* bacteria as biocatalyst is developed. The BPFS prepared under the optimum conditions has many advantages over the PFS prepared by conventional methods with high pH of 1.5−2.2, high basicity of 17.5%−22.7% and total iron content of 43.87−45.24 g/L, which can provides high flocculability and weak corrosivity to the reactor.

2) The BPFS is an effective flocculant for water treatment and the removal efficiencies of COD, decolorization and Zn^{2+} by the BPFS reach above 70%, 90% and 99%, respectively.

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生物法制备聚合硫酸铁及其应用研究

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摘　要：研究生物法制备铁系絮凝剂及其影响因素。以 $FeSO_4\cdot 7H_2O$ 为原料，利用驯化后的氧化亚铁硫杆菌(*T.f*)在酸性条件下的催化氧化作用制备生物聚合硫酸铁(PFS)，并确定最佳制备条件。实验表明：在反应液初始 pH 值 1.5、硫酸铵用量 0.5 g/L、初始 Fe^{2+}浓度 45 g/L、接种量 10%、温度 30 °C 时，在转速为 120 r/min 的恒温水浴摇床中连续培养 5~6 d、可以制出 pH 1.5~2.2、盐基度 17.5%~22.7%、全铁含量 43.87~45.24 g/L 的产品。实验通过处理 3 种废水来考察其絮凝性能，结果表明：当 PFS 投加量一定时，COD 去除率可达 70%以上，脱色率达 90%，Zn^{2+}去除率达 99%，说明 PFS 是一种絮凝效果优异的水处理剂。

关键词：铁系；生物聚合铁；絮凝剂

(Edited by FANG Jing-hua)