Preparation of solid composite polyferric sulfate and its flocculation behavior for wastewater containing high concentration organic compounds

R. M. Wang, Y. Wang, Y. F. He, F. Y. Li, Y. Zhou and N. P. He

ABSTRACT

A new kind of inorganic polymer flocculant, the solid composite polyferric sulfate (SPFS) was prepared using ferrous sulfate and Na-Bentonite. The obtained SPFS was characterized by FT-IR spectra, thermogravimetric analysis (TG), scanning electron microscope (SEM) and X-ray Diffraction (XRD). It showed that SPFS was a kind of composite inorganic polymer, which was the complex of PFS and Na-Bent, not only a simple mixture of raw materials. The synthetic mechanism and surface structure of SPFS were also discussed. Acting as a kind of environment-friendly flocculating agent, the solid composite polyferric sulfate (SPFS) was applied in pretreatment of potato starch industry wastewater, a typical wastewater containing high concentration organic compounds, which COD was above 6,000 mg/L. The results showed that the COD removal value reached 4,070 mg/L with COD removal rates being 46.6%. Based on these results, it is suggested that the SPFS can be attractive pretreatment agent for the starch industry wastewater.

Key words | highly concentrated organic wastewater, Na-Bentonite, polyferric sulfate, solid composite flocculant, starch industry wastewater

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INTRODUCTION

Surface water pollution is a serious problem for many developing countries. As industrial and domestic wastewater containing excessive concentrations of organic pollutants is discharged into natural waters, such as rivers and lakes (Wang *et al.* 2005). Potato is one of the world's most important staple food crops, and numerous potato starch products are used in industrial production. Wastewater in the potato processing industry contains high concentrations of biodegradable components such as starch and proteins. This wastewater can be considered as complex wastewater because of a rather high concentration of suspended solids, a high content of COD and significant quantities of potential foaming substances, such as proteins and fats (Barampouti *et al.* 2005). The characteristics of such wastewater were different with potato processing industry. However, there common characteristics are high COD (4,800–9,025 mg/L) and neutral environment (pH = 6.14–6.9) (Kalyuzhnyi *et al.* 1998). Water pollution caused by starch production has been reported to be a serious problem in many Asian countries, particularly in China (Wang *et al.* 2007), Thailand (Rajbhandari & Annachhatre 2004), Korea (Lee *et al.* 2004) and India (Pangasmy *et al.* 2007; Rajasimman & Karthikeyan 2007). This problem is greater in the region with being lack of water resources due to the higher concentrations of organic materials and ammonia discharged in the wastewater. The high COD results in the consumption of the majority of dissolved oxygen (DO) thus converting the water into an anoxic or even an anaerobic state, which is fatal to many aquatic species (Wang *et al.* 2009). Therefore, the treatment and reutilization of wastewater is of prime importance, and many types of technologies have been developed.

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Anaerobic treatment is a kind of effective technique for organic wastewater, which has been progressed rapidly during recent decade (Papadopoulos *et al.* 2003; Colin *et al.* 2007). However, in order to keep the anaerobic biological reactor running normally, the COD concentration of wastewater should be lower than 5,000 mg/L. For the highly concentrated organic wastewater, the pretreatment is necessary, such as flocculating, adsorption, membrane separation and so on.

Flocculation is a kind of effective manner to treat high concentration organic wastewater. The typical flocculants are organic polymer flocculants (OPF) (Shirzad-Semsar *et al.* 2007; Yue *et al.* 2008), inorganic polymer flocculants (IPF) (Cheng 2002; Domínguez *et al.* 2007; Shi *et al.* 2007) and composite polymer flocculants (CPF) (Fu & Yu 2007; Cheng *et al.* 2008). In general, the method for preparing composite flocculants is adding additive components into inorganic polymer flocculants (Yang *et al.* 2004) or mixing two kinds of flocculants (Gao *et al.* 2007), which enhance the aggregating power of flocculants. However, the simple mixture of different flocculants can not largely increase their flocculating ability. In this paper, Na-Bent was used as core in preparation of inorganic polymer flocculants, and a new kind of solid composite polyferric sulfate (SPFS) was afforded. It was applied to pretreatment the potato starch wastewater, which contains high concentration organic compounds.

In the west of China, a region with being lack of water resources, potato starch wastewater is an important source of water pollution as it contains high concentration organic contaminants. When this wastewater is discharged into natural waters, such as rivers and lakes, it could cause odor of water body and pollution of water sources, lead to the lack of water resources more serious. So, the treatment and reutilization of wastewater is very important. Because most starch processing factories are located in towns and the countryside dispersedly, it is very difficult to collect and treat all wastewater together. Therefore, we had designed and manufactured simply mobile equipment for the treatment of the potato starch wastewater (Wang *et al.* 2009). It was a kind of effective bioreactor when COD value was lower than 4,500 mg/L. If the COD value was more than 5,000 mg/L, the pretreatment was necessary. Here, a new kind of environment-friendly flocculant, the solid composite polyferric sulfate was used as highly efficient pretreatment agent.

MATERIALS AND METHODS

Materials

The Ca-bentonite (Ca-bent) is obtained from the Xinjiang of China. $FeSO_4{\cdot}7H_2O$ (from Shenyang Chemical Reagent Factory), H_2O_2 (30%) (from Shanghai Zhongqin Chemical Co., Ltd.), H_2SO_4 (98%) (from Baiyin Liangyou Chemical Co., Ltd.), sodium carbonate (from Tianjin Yatai Longxing Chemical Co., Ltd.) and other reagents used in the experiments were of analytical grade and used without further purification.

The Na-Bentonite (Na-Bent) was prepared by removing impurities from Ca-bent, such as coarse bentonite, and further being treated by sodium carbonate.

The raw potato starch wastewater was obtained from a Potato Starch Mill in Tianshui of Gansu Province located in western of China. The characteristics of the raw potato starch wastewater containing soluble starch and proteins were as follows: COD = 6,500–9,000 mg/L; pH = 5.0–7.5. And the wastewater was highly colored.

The polyferric sulfate (PFS) was prepared in our laboratory by catalytic oxidation of a solution containing concentrated sulfuric acid and ferrous sulfate. The typical procedure was as following: A certain amount of $FeSO_4{\cdot}7H_2O$ were quickly mixed with distilled water under intensely stirring. Then, 5 mL of 98% H_2SO_4 solution was slowly added in 5 min under stirring. And 23.5 mL of 30% H_2O_2 solution was slowly added in 20 min under strong stirring. The reddish-brown of pre-product was obtained after reacting 1 hr and depositing about 24 h. The pre-product was condensed for half the original volume. Finally, the PFS was obtained with an aging period of 15 d at room temperature. PFS was a yellow viscous material.

The typical procedure for preparation of the solid composite polyferric sulfate (SPFS) was as following: The Na-Bent suspensions were prepared by 2.0 g of Na-Bent and 25 mL of water, and quickly mixed with a certain amount of $FeSO_4{\cdot}7H_2O$ under stirring. 5 mL of 98% H_2SO_4 solution was slowly added in 5 min under stirring. Then, 23.5 mL of 30% H_2O_2 solution was slowly added in 20 min under strong stirring. The reddish-brown of pre-product was obtained after reacting 1 hr and depositing about 24 h. The pre-product was condensed for half the original volume.

Finally, the SPFS was obtained with an aging period of 15 d at room temperature, which is a kind of yellow moist loose solid (SPFS).

IR spectra

The samples of Na-Bent, PFS and SPFS as KBr pellets were subjected to IR spectral analysis by infrared spectrophotometry (DigiLAB Merlin, US).

TG measurement

All the samples (10.0 mg) used had been freeze-dried in vacuum at subzero 30°C. The thermal degradation test was conducted on TG/DTA (Pyris Diamond, PerkinElmer) at heating rate of 10°C/min under nitrogen. The change in the weigh differential difference with temperature was recorded.

X-ray diffraction

The Na-Bent, PFS and SPFS were freeze-dried at subzero 30°C. The X-ray diffraction of powder samples was analyzed by D/max-2400 X-ray Diffractionmeter (Japan) under the following conditions: graphite monochromatized Cu K? radiation; voltage 40 kV; electric currrent 100 mV; scanning ratio: 2θ = 5°/min.

Measurement of the particle size and zeta potential

The Zetasizer analyzer (nano series, UK, Malvern Instruments Ltd.) was used to measure the particle size and zeta potential of Na-Bent, PFS and SPFS. These substances suspensions were prepared by mixing above inorganic polymer in distilled water under ultrasonic vibration. The samples were analyzed and the data were recorded.

SEM measurement

The surface morphology of Na-Bent, PFS and SPFS were observed and pictured by a JSM-5600LV scanning electron microscope (JEOL, Japan). After freeze-drying for more than 10 hrs, the particles were coated with gold powder and attached to the microscope support with silver glue. SEM photographs were taken under accelerating voltage 20 kV and magnified 2000 times.

Determination of COD concentration and decoloration rate

COD was measured colorimetrically using the dichromate reflux method (Standard Methods for Analysis of Water and Wastewater). The appropriate amount of sample was introduced into the digestion solution in the range 0–180 mg/L containing potassium dichromate, sulfuric acid and mercuric sulfate and the mixture was then incubated for 10 min at 165°C in a COD reactor. COD concentration was measured colorimetrically at 610 nm using a 5B-3 COD Rapid Detector (Lanzhou Lianhua Sci. Co., China).

After flocculation, supernatant of the treated water samples were taken out. The absorbance (A) was measured at 610 nm with a TU-1901 double-beam UV-spectrophotometer. The decoloration rate was calculated by the following equation:

$$\text{Decoloration rate } (\%) = \frac{(A_0 - A)}{A} \quad (1)$$

The absorbance of the raw wastewater was expressed by A_0.

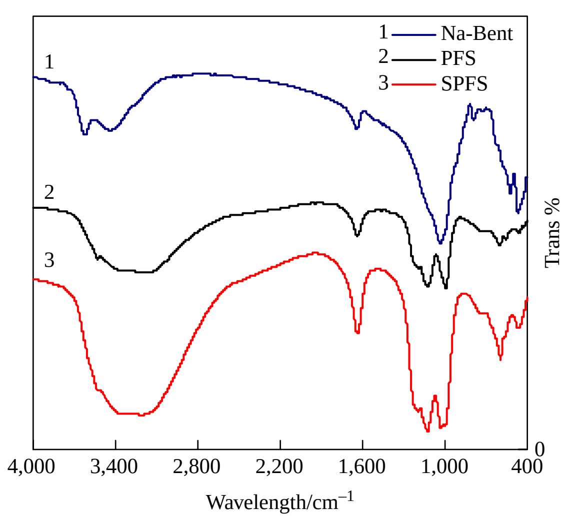


Figure 1 | IR spectra of SPFS and its materials (Na-Bent, PFS).

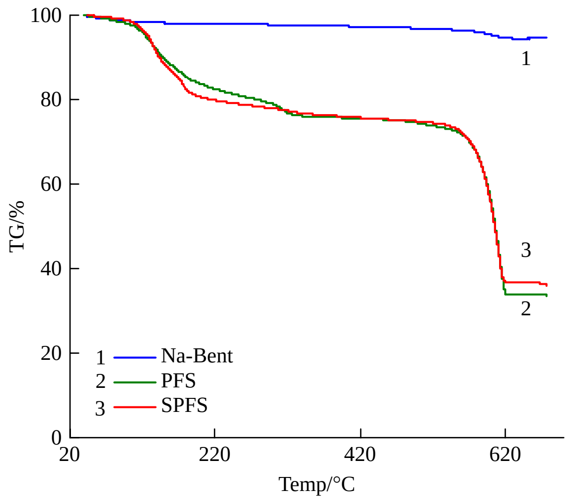


Figure 2 | TGA curves of Na-Bent, PFS and SPFS.

Flocculation procedures

All flocculation experiments were carried out in a 50 mL of batch reactor containing various amounts of flocculants and 50 mL of high concentration organic potato starch wastewater. Then, the batch reactors were shaken at 150 rpm for 3 min and 30 rpm for 1 min. After standing for about 10 min, the clear solution was taken out for analysis.

RESULTS AND DISCUSSION

Characterization of SPFS

IR spectra

The IR spectra of Na-Bent, PFS and SPFS were showed in Figure 1. The OH stretching vibration absorption peaks of interlayer water in the lattice structure of montmorillonite appears at 3,622 cm^{-1} (Feng & Wang 2005). The characteristic peak of adsorption water in interlayer appears at 1,643 cm^{-1}. The peaks near 999 cm^{-1} and 1,039 cm^{-1} were ascribed to the Fe-OH bending vibration (Russell 1979) and the stretching vibration of Si-O-Si in montmorillonite, respectively. The peaks near 600 cm^{-1} were

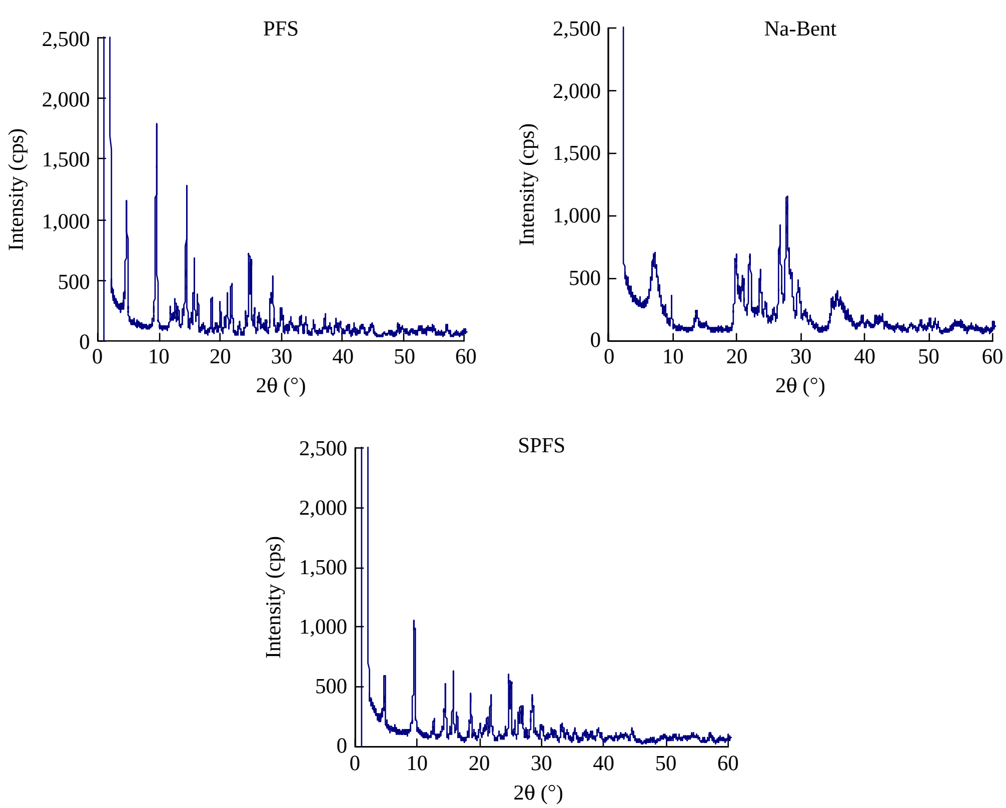


Figure 3 | The XRD charts of Na-Bent, PFS and SPFS.

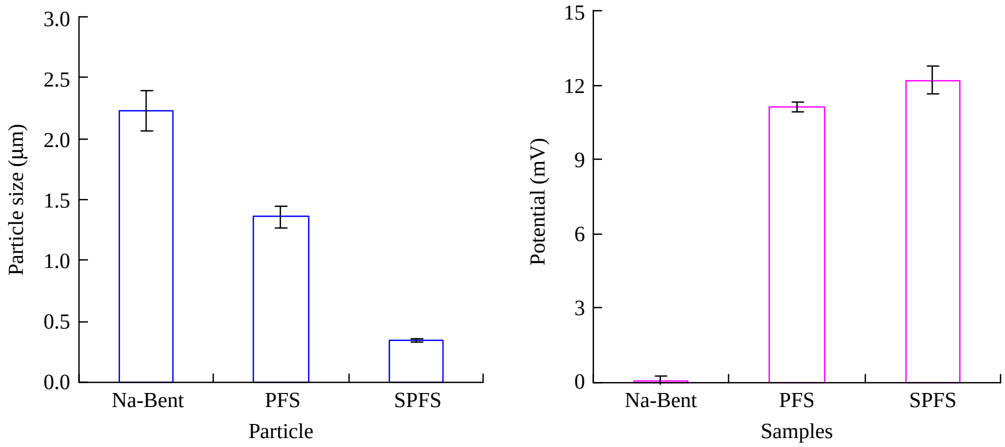


Figure 4 | The mean particle size and zeta potential of Na-Bent, PFS and SPFS.

the characteristic absorptions of sulfate in SPFS (Bellamy 1975), which was weaker than that of PFS. It was suggested that the SPFS was typical inorganic polymer composite.

TGA measurement

Based on the thermogravimetry analysis (TGA) of Na-Bent, PFS and SPFS (Figure 2), the total weight loss rates of Na-Bent, PFS, SPFS were 5.5%, 66.2%, 63.7%, respectively. For Na-Bent, the adsorbed water was lost in the range of R.T. – 100°C. The main interlayer water was lost in 130–210°C. The structural water was lost in 600–700°C (Ye & Liu 2004). For PFS and SPFS, there was more weight loss in this range than that of Na-Bent. It was suggested that the SPFS was decomposed when temperature was more than 600°C. The SPFS contained a certain amount of Na-Bent. Therefore, SPFS had less weight loss rate than PFS at 600–700°C.

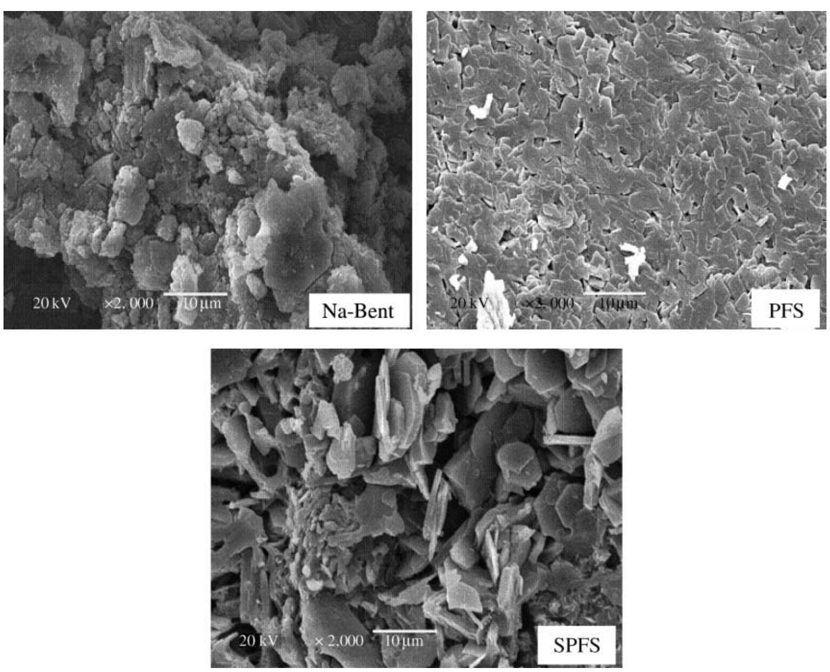
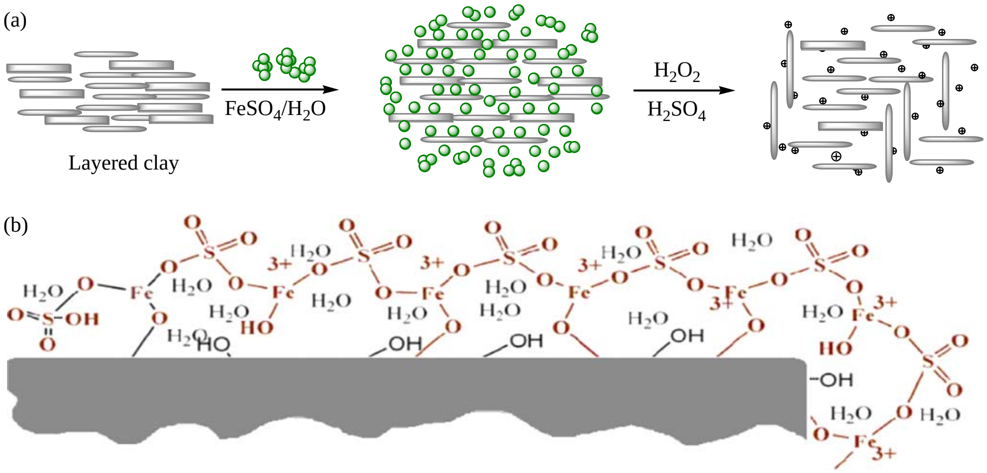


Figure 5 | The SEM images of Na-Bent, PFS and SPFS.



Scheme 1 | The reaction procedure for preparing SPFS (a) and the surface structure of SPFS.

X-ray diffraction of solid samples

The XRD spectra of the Na-Bent, PFS and SPFS were showed in Figure 3. Generally, a series of characteristic diffractive peaks of crystal materials can be observed at certain 2θ, instead of amorphous, in Na-Bent, PFS and SPFS. There was a distinct difference between PFS and SPFS in the XRD spectra. The diffractive crystals spectra such as Fe-OH ($2\theta = 21.3°$) can be observed in SPFS, which indicates that such as Fe^{3+} and SO_4^{2-} have been combined with the Na-Bent to form a new chemical bond.

The particle size and zeta potential of Na-Bent, PFS and SPFS

The information on the dispersion and charge neutralization ability of solid flocculants was obtained from the measurements of the particle size and zeta potential (Figure 4). The average diameters of particles of Na-Bent, PFS and SPFS in the suspension are 2.23 μm, 1.36 μm, 0.34 μm with a relatively narrow size distribution, respectively. It indicated that the particle size of SPFS is smaller than that of Na-Bent or PFS. The zeta potential of SPFS is higher than that of Na-Bent and PFS. It was suggested that the particles of Na-Bent are easier to agglomerate together in water than that of PFS.

Scanning electron microscope (SEM) analysis

The surface morphology of solid samples was observed by SEM (Figure 5). Na-Bent was layered amorphous aggregates and lamellar ambiguous edge. The dried PFS was piled up sheet, compact shape. SPFS looked like a kind of lamellar particle, which were loosely aggregated together.

Based on the above results, we suggested that the composite polyferric sulfate in Na-Bent (SPFS) was formed as following: After being dissolved in the Na-Bent suspension solution, the molecule of $FeSO_4$ should easily spread into the interlayer spacing of Na-Bent and polymerize in the interlayer spacing and surface. It caused the layer of Na-Bent to separate with each other, which reduced the diameter of particles. Therefore, the diameter of SPFS was smaller than the aggregate of PFS. The suggested reaction procedure and surface of SPFS were showed in Scheme 1.

Table 1 | The flocculation performance of Na-Bent, PFS and SPFS

Samples	Na-Bent	PFS	SPFS
COD of raw water (mg/L)	7,301	7,348	8,772
pH	6	6.5	6.5
Dose of flocculant (g/L)	4	5	1.8
Fe^{3+} (g/L)	–	0.87	0.302
COD removal value (mg/L)	462	1,659	4,070
COD removal rate (%)	8	22.6	46.6

Conditions: Volume of raw water: 1 L, in room temperature.

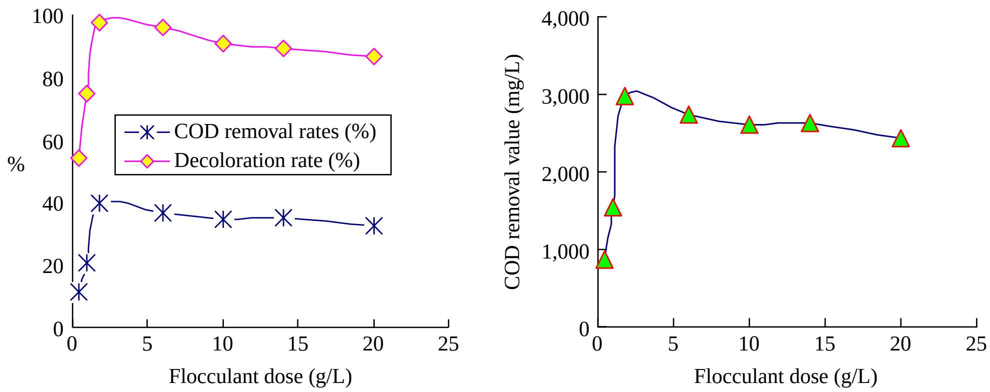


Figure 6 | The influence of flocculent dosage on COD removal rates, COD removal value and decoloration rate (Cond: $COD_{wastewater} = 7{,}514\,mg/L$, pH = 6.5, 25°C).

The flocculation behavior of SPFS for the potato starch wastewater

The flocculation behavior of the solid composite polyferric sulfate (SPFS) and its materials (Na-Bent, PFS) were measured (Table 1). The flocculation performance of SPFS was highly improved compared with Na-Bent and PFS. The dosage of SPFS was close to one third of that of PFS, but its COD removal rate was above two times than that of PFS. The dosage of SPFS was about half of that of Na-Bent. But its COD removal rate was near six times than that of Na-Bent.

As the flocculent properties of the potato wastewater on SPFS was not only due to its structure, but also conditions. Here, the influence of some factors, such as flocculant dosage, pH and coagulant aid, was investigated.

Effect of flocculent dosage

The effect of flocculent dosage on the flocculating capacity of SPFS was measured at room temperature (Figure 6). It was found that the optimum dosage of flocculent was 1.8 g/L. and the COD removal rate was 39.6% with COD removal value being 2,978 mg/L. Meanwhile, the decoloration rate of wastewater was 97.4% if the dosage of flocculent was 1.8 g/L.

Effect of pH

The effect of pH on the flocculation of SPFS was measured at different pH value (adjusted by diluted solution of HCl or NaOH). The results were presented in Figure 7. All the analysis showed that the optimum condition of pH value was 6.5. The COD removal rates was 38.7% and the COD

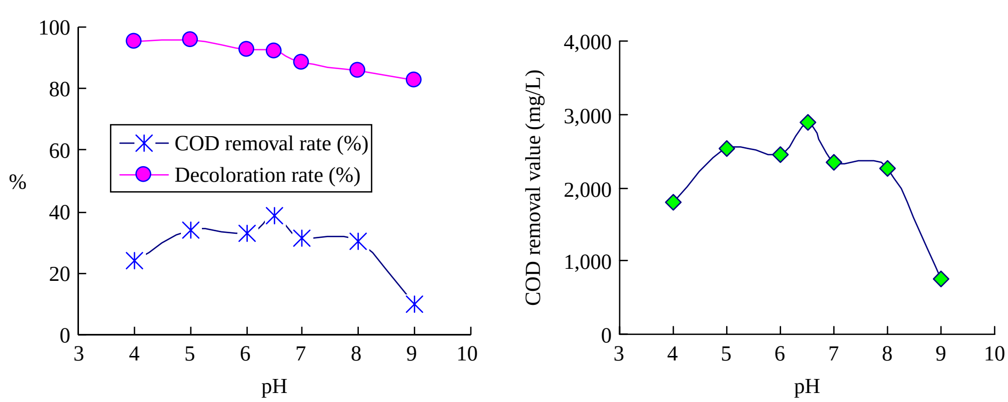


Figure 7 | The influence of pH on COD removal rates, COD removal value and decoloration rate (Cond: $COD_{wastewater} = 7{,}479\,mg/L$, SPFS: 1.8 g/L, 25°C).

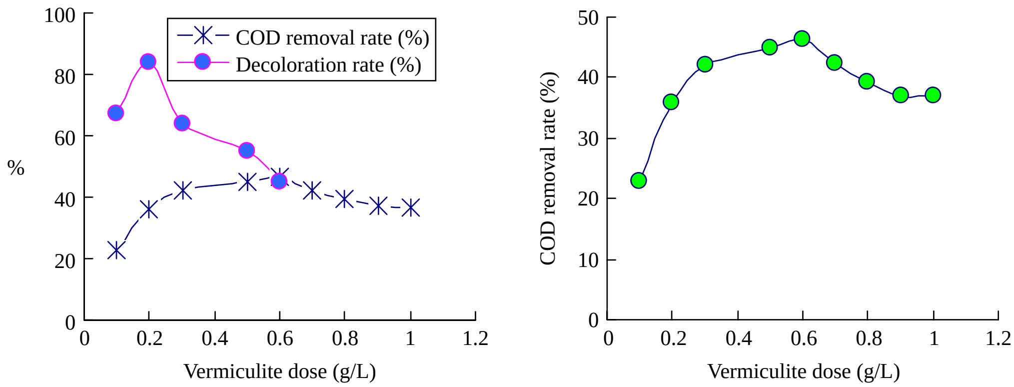


Figure 8 | The influence of vermiculite dosage as coagulant on COD removal rates, COD removal value and decoloration rate (Cond: $COD_{wastewater} = 8{,}772\,mg/L$, SPFS = 1.8 g/L, pH = 6.5, 25°C).

removal value was 2,898 mg/L if the flocculent dosage was 1.8 g/L, The decoloration rate of waste water was above 80% at the pH range of 3–7.

Effect of vermiculite dosage as coagulant

In order to increase the flocculating ability of SPFS for removal of COD, the vermiculite was added as coagulant. The effect of vermiculite dosage on COD removal value, COD removal rates and decoloration rate were investigated. The results were presented in Figure 8. It indicated that the optimum of vermiculite dosage was 0.6 g/L. The COD removal rates got to 46.6% with COD removal value being 4,070 mg/L. And the decoloration rate of wastewater was 84%.

CONCLUSIONS

A new kind of solid composite polyferric sulfate (SPFS) was prepared using a simple method. Its microstructure, surface morphology and functional groups were characterized by FT-IR, TG/DTA, particle size analysis, XRD and SEM. It was concluded that the polyferric sulfate was formed in the interlayer spacing and surface of bentonite by means of complexation. Comparing to Na-Bent and PFS, SPFS had significantly higher positive charge. The smaller particle size of SPFS, the distributed of particles in water was more evenly. Furthermore, the SPFS was applied to pretreatment the potato starch wastewater which contained high concentration organic matter. It indicated that the flocculation performance of Na-Bent was highly improved by complexed with PFS. The new kind of solid composite polyferric sulfate (SPFS) was also stable and convenient to be transported. That means this environment-friendly flocculating agent was a candidate used as highly efficient pretreating agent for the potato starch wastewater.

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