Application of Polysilicate Ferric Flocculant in Treatment of Tanning Wastewater

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Abstract: A new type of inorganic polymer flocculant polysilicate ferric(PSF) was prepared by using pyrite slag as raw materials and used as flocculant in the treatment of tanning wastewater. The infrared spectrometry and X-ray diffraction had been adopted to characterize the product structure. The infrared spectrometry research indicates that Fe-O, Si-O-Fe and other groups exist in the PSF, which implies that chemical bonding reaction takes place between Fe and silicon in the PSF. X-ray diffraction analysis indicates that PSF is the amorphous polymer created upon mutual reaction between Fe^{3+} and PSi. The application experiment results show that the removal rate of S^{2-}, SS, COD_{Cr}, Cr^{3+}, and chromaticity is 92.7%, 90.5%, 82.5 %, 80.2% and 90.1% respectively in the condition where temperature is normal, pH value is 7.5 and dosage of the coagulant is 80mg/L. The flocculation effects of PSF in the treatment of tanning wastewater are much better than those of PAC and PFS.

Key words: pyrite slag; polysilicate ferric flocculant; tanning wastewater; wastewater treatment

1 Introduction

As a new kind of inorganic polymer coagulant advantageous in good coagulation effects, a rich raw material source, and less post-treatment residue, Polysilicate ferric（PSF）is a hot topic[1-7] in research of inorganic polymer coagulants and has a wide application prospect in sewage treatment in nowadays. Pyrite slag is a kind of dump slag for production of sulphuric acid, producing 1t of sulphuric acid you will get 0.8~0.9t sulfate slag[8], and mainly adopting pyrite burning method to produce sulphuric acid, China discharges burned slag in tens of millions of tons yearly[9]. Generally, the iron content in pyrite slag is 30%~60%[10], and for iron resource tension is getting more and more serious and environmental protection requirements are getting more and more critical, people start to pay more attention to the complex utilization research of pyrite slag.

2 Experimental

2.1 Preparation of PSF

2.1.1 Raw Materials and Their Chemical Composition

Pyrite slag, whose main component is Fe_2O_3, secondary component is SiO_2, minor components are Al_2O_3, CaO, MgO ect., is the main raw material used to produce PSF flocculant. Tab. 1 gives their chemical composition. In the following experiment, the pyrite slag is extracted from boiler slag of some chemical plant in Heilongjiang province.

Tab. 1 Chemical composition of the raw materials %

Composition	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	Others
Content	67.42	17.94	5.23	2.32	1.15	3.78

2.1.2 Preparation Method

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PSF is a type of flocculant prepared through some processes of physical and chemical treatment. The technological flow is shown in Fig. 1, which is very simple.

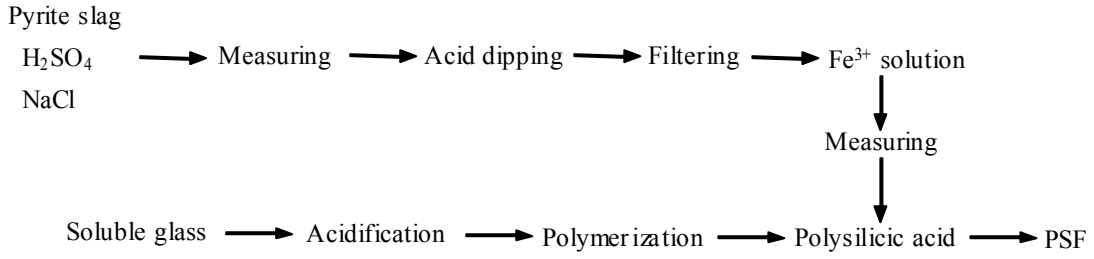

Fig. 1 Technological flow of PSF preparation

2.2 Main Reagent and Apparatus

PSF: self-prepared; PAC(polyaluminium chloride): industrial product; PFS(polyferric sulfate): industrial product; Ferron reagent: analytical reagent; iron powder: analytical reagent; anhydrous sodium acetate: analytical reagent; hydrochloric acid : analytical reagent; potassium bromide: analytical reagent.

Spectrum-one infrared spectrometer made by PerkinElmer Corporation(America), D/MAX 2200VPC X-ray diffractometer made by Rigaku Corporation(Japan), D-8401 multi-functional mixer made by Jiangsu Jintan Medical Instrument Factory, 722 spectrophotometer made by Shanghai Analytical Instrument Factory, and DBJ-621 timing variable speed agitator made by Suzhou Dalong Instrument Co. Ltd.

2.3 Wastewater Quality

The wastewater samples used in the experiment were taken from the comprehensive wastewater discharged from some tannery. At its wastewater outlet, the parameters are as follows: pH8.9, SS1633mg/L, S^{2-} 42.1mg/L, Cr^{3+} 59.5mg/L, COD_{Cr} 2781mg/L, BOD_5 584mg/L and colority 800 multiples.

2.4 Test Method

2.4.1 Infrared Spectroscopy Method

Dry a PSF sample at 105℃ in a drying oven, grind it into powder, then make the powder into analysis sample using KBr disc method, finally analyze sample' structure on the infrared spectrometer(scan range: $400cm^{-1}$～$4000cm^{-1}$).

2.4.2 X-ray Diffraction Method

Dry a PSF sample at 105℃ in a drying oven, then make it into solid sample, finally analyze the solid sample's structure on the infrared spectrometer.

2.4.3 Flocculation Test

DBJ-621 timing variable speed agitator was applied in the 500mL beaker. Four hundred of milliliters of tanning wastewater as well as an amount of flocculant PSF was put into the beaker; the agitator worked for 2min at the speed of 180r/min, so that the flocculant dispersed evenly; the running speed of the agitator was then reduced to 60r/min, at which the mixture was stirred for 10min; after the beaker was left still for 20min, the supernatant ranging from the liquor level to 25mm below the level was taken out for analysis. The iodometric method was used to determine S^{2-}, the national standard method was used to determine SS, the standard potassium dichromate method was used to determine COD_{Cr}, the diphenylcarbazide(DPC) spectrophotometry was used to determine Cr^{3+} and the dilution multiples method was used to determine colority.

3 Results and discussion

3.1 Infrared Spectrum Analysis

Fig. 2 shows the infrared spectrum of PSF flocculant.

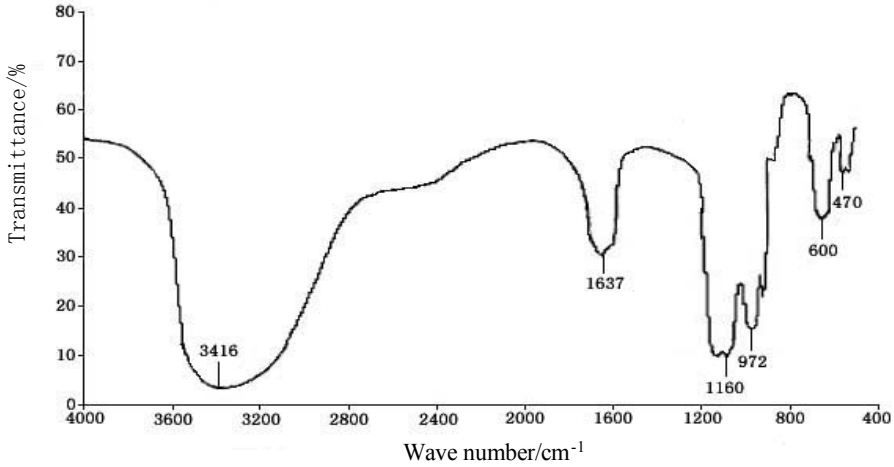

Fig. 2 Infrared spectrum of PSF flocculant

From Fig. 2, we can see there are obvious absorption peaks at 3416cm^{-1}, 1637cm^{-1}, 1160cm^{-1} and 600cm^{-1}: the strong and broad absorption peak around 3416cm^{-1} is caused by stretching vibration of —OH groups connected to iron ions in PSF, water molecules adsorbed in PSF, and —OH groups in coordinated water molecules in silicate; the medium strong peak at 1637cm^{-1} is caused by bending vibration of —OH groups in water molecules, namely H—O—H angle distortion frequency; the strong absorption peak at 1160cm^{-1} is caused by stretching vibration of Si—O groups; the absorption peak aground 972cm^{-1} is caused by bending vibration of Si—O—Fe; and absorption peaks around 600cm^{-1} and 470cm^{-1} can be regarded as peaks caused by stretching vibration of Fe—O.

According to the absorption peak caused by bending vibration of Si—O—Fe, namely an oxygen-cross-linked substance of silicon-oxygen tetrahedron and oxy-ferrite tetrahedron, we can determine that a nonionic bond reaction occurred between poly-Fe ions and poly-Si ions and produce Fe-Si polymer, i.e. PSF. According to absorption peaks at 3416cm^{-1}, 1637cm^{-1} etc., we can infer that PSF whose structure changes are directly affected by water molecules is still a kind of ferric polyhydroxylated polymer.

3.2 X-ray Diffraction Analysis

Fig. 3 shows the X-ray diffraction analysis of PSF flocculant.

From Fig. 3, we can see there is no diffraction peaks of $Fe_2(SO_4)_3$, Fe_2O_3, $Fe(OH)_3$, Fe_3O_4 nor SiO_2 in PSF samples, that is to say, Fe^{3+}, PSi and SO_4^{2-} have all participated in a polymerization reaction and produced a copolymer rather than having respective polymerization. The participation of Fe^{3+} makes PSF present crystal-phase-like relatively sharp diffraction peaks in the range of $2\theta=15 \sim 40°$. The polymerization of silicic acid is caused by glycidyl reaction of hydroxyls on adjacent silicic acid molecules, and this polycondensation reaction can produce chain molecules, cyclic molecules, even triatomic molecules and cause gelation. Fe^{3+} introduced will chelate and adsorb with hydroxyls on end groups of large PSi chain and cyclic molecules, and the more Fe^{3+} a PSF sample contains, the more hydroxyls will be chelated and adsorbed, and a special X-ray diffraction pattern of PSF is formed. The pattern shows, in polysilicates diffuse amorphous cells are gradually weakening and multiple small diffraction peaks which represent coexistence of multiple crystal phases are growing. That is to say, PSF is neither a substance of crystal structure nor a substance like amorphous PSi, but a amorphous polymer

produced in interaction between Fe^{3+}, SO_4^{2-} and PSi.

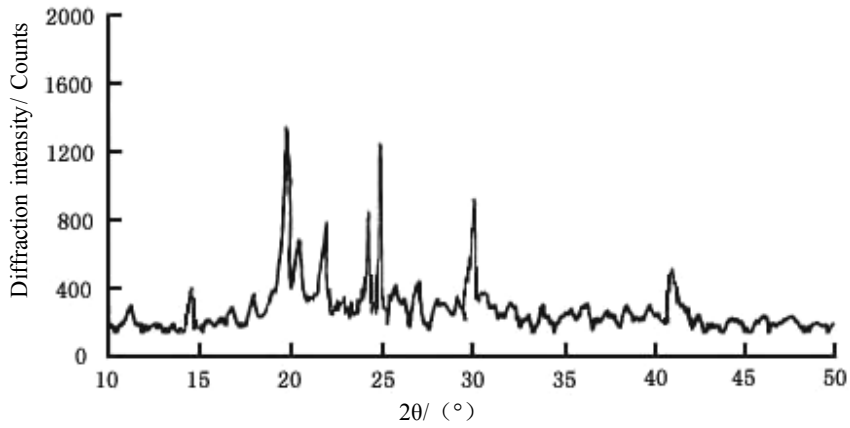

Fig. 3 X-ray diffraction analysis of PSF flocculant

Above X-ray diffraction analysis shows PSF is neither a substance of crystal structure nor a substance like amorphous PSi, but a amorphous polymer produced in interaction between Fe^{3+}, SO_4^{2-} and PSi.

3.3 Application of PSF Flocculant in the Treatment of Tanning Wastewater

According to the test method, under the conditions of normal temperature, pH value of 7.5 and flocculant dosage of 80mg/L, three different flocculants, namely, PSF, PAC and PFS, were used to treat wastewater sample respectively. After treatment, S^{2-}, SS, COD_{Cr}, Cr^{3+} and colority of the wastewater sample were measured, and the results are shown in Tab. 2.

Tab. 2 The results of treating tanning wastewater with different flocculants %

	Removal rate of S^{2-}	Removal rate of SS	Removal rate of COD_{cr}	Removal rate of Cr^{3+}	Removal rate of colority
PSF	92.7	90.5	82.5	80.2	90.1
PAC	59.7	72.8	65.4	66.2	62.8
PFS	79.3	69.4	61.6	63.4	55.2

Tab. 2 shows that the three flocculants are all effective to some extent in the treatment of tanning wastewater. However, the effect of flocculation of PSF is far better than that of such traditional flocculants as PAC and PFS. It can be comfirmed from the experimental phenomena. The floc in wastewater with PSF is biggest and settles fastest. This is because flocculant PSF contains a large quantity of Fe^{3+} ions, maintains a strong electrical neutralization capability. Moreover, PSF contains macromolecules of polysilicic acid, which provide strong adsorption bridging and network-capturing capacity, with which the hardly soluble compounds and fine particles can be separated from the wastewater. This further enhances the process of adsorption, flocculation and sedimentation.

4 Conclusions

(1) The infrared spectrometry research indicates that Fe—O, Si—O—Fe and other groups exist in the PSF. This implies that chemical bonding reaction takes place between Fe and Si in the PSF. This is chemical reaction, not simple mixing. —OH absorption peaks clarify that PSF whose structure changes are directly affected by water molecules is still a kind of ferric polyhydroxylated polymer.

(2) X-ray diffraction analysis shows PSF is neither a substance of crystal structure nor a substance like amorphous PSi, but a amorphous polymer produced in interaction between Fe^{3+}, SO_4^{2-} and PSi.

(3) PSF flocculant can effectively reduce S^{2-}, SS, COD_{Cr}, Cr^{3+} and colority in tanning wastewater. At room temperature, when sewage pH is 7.5, and with a dosage of 80mg/L, PSF flocculant can reduce S^{2-}, SS, COD_{Cr}, Cr^{3+} and colority in sewage by 92.7%, 90.5%, 82.5%, 80.2% and 90.1% respectively, its flocculation settlement performances are much better than those of PAC and PFS.

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