Application of Flyash-based Coagulant in Tanning Wastewater Treatment**

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Abstract: PBS (flyash-based coagulant) made by fly ash in coal-fired thermal power plants and blast furnace iron sludge extracted with a dilute H_2SO_4 was used as coagulant in the treatment of tanning wastewater. The influence of pH value, coagulant dosage and temperature on coagulation effect was investigated. The results showed that this coagulant had satisfactory results to treat tanning wastewater under the pH value ranging from 6 to 9, combined with polysilicate aluminium(PSA) flocculant. The removal rate of SS, S^{2-}, Cr^{3+}, COD_{Cr} and colority in tanning wastewater was 93.1 %, 92.8 %, 87.6 %, 83.3 % and 90.8 % respectively in the condition where temperature was normal, pH value was 7.0 and coagulant dosage was 70mg/L. The temperature had little impact on the removal rate of COD_{cr}. In comparison with the conventional coagulants, such as PAC (polyaluminium chloride) and PFS (polyferric sulfate), the coagulation performance of PBS coagulant was obviously superior to conventional coagulants. The coagulation mechanism of PBS coagulant in the treatment of tanning wastewater was also discussed.

Key words: coagulant; fly ash; tanning wastewater; coagulation mechanism

1 Introduction

Physical and chemical treatment with coagulants features small land occupation, simple equipment, easy operation and management, etc, and it is the most practicable measure for wastewater treatment. At present, coagulants and flocculants are used in large-scale industrial effluent treatment. Blast furnace iron sludge is a kind of solid waste generated in blast furnace gas cleaning during the iron smelting process. The granularity of blast furnace iron sludge, which contains a lot of ferric oxide and coke granule, is usually below 0.1mm. For chemical utilization, charcoal and iron ore concentrates are extracted from the iron sludge. Fly ash is a kind of waste discharged out of coal-fired thermal power plants. Coal is the major raw material for China's power industry and approximate 100,000,000t fly ash is discharged each year. The fly ash utilization rate is just 40%, and the fields of fly ash utilization mainly include brick manufacturing, road construction, cement and concrete production, sorting of floating beads, soil amelioration and so forth. The remaining fly ash is basically piled up and discarded, and as a result, numerous pieces of land are covered and the environment is seriously polluted. How to comprehensively utilize fly ash is an important subject of research for the environmental science today. The environmental protection researchers have done a lot of jobs in this regard and many remarkable achievements have been made[1-6]. Coal gangue is the major solid wastes in China's industrial production. Over years, great attention has been paid to treatment and comprehensive utilization of coal gangue home and abroad, unfortunately, the utilization rate is still very low, to be more exact, one-fourth of the total emission. There is a tremendous quantity of coal gangue in China, which is widely distributed, and it is a hard job to carry out treatment and comprehensive utilization of coal gangue. Therefore, it is of great significance to develop a new way to accelerate treatment and comprehensive utilization of the waste.

This paper is to prepare flyash-based coagulant(PBS coagulant) by adding blast furnace iron sludge into fly ash; to prepare inorganic high-molecular polysilicate aluminium(PSA flocculant) mainly using

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coal gangue; and to treat tanning wastewater using PBS and PSA and discuss their coagulation mechanisms.

2 Experimental

2.1 Raw Materials and Their Compositions

Fly ash from some power plant and blast furnace iron sludge from some iron and steel company in Qiqihar were used as the raw materials. Table 1 gives the major chemical compositions of the raw materials.

Tab. 1 Compositions of the raw materials %

Sorts	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	C
Fly ash	56.65	18.65	11.05	3.16	1.35	3.02
Iron sludge	7.46	3.32	47.65	3.35	1.28	30.58

PBS coagulant (self made); PSA flocculant (self made, see [7] of references); PAC and PFS were purchased from some chemical shop of the Municipal Light Chemicals Company.

2.2 Preparation of Coagulant PBS

60g fly ash, 30g iron sludge and the solubilizer were put into a 500mL beaker equipped with an agitator, then 150mL of 3.5mol/L H_2SO_4 were added into the beaker, which was slowly heated on an electric hot plate for 2.5h. Fly ash coagulant (PBS) was thus obtained. It was a kind of thick gray liquor, whose specific gravity was 1.5～1.6g/m^3, pH value was 1～2, aluminum sulphate content was 25～30g/L, and ferric sulphate was 35～40g/L.

2.3 Wastewater Quality

The wastewater samples used in the experiment were obtained from the comprehensive wastewater discharged from some tannery of Heilongjiang Province. At its wastewater outlet, the parameters were as follows: pH 8.9, S^{2-} 43.2mg/L, SS 1840mg/L, COD_{Cr} 2350mg/L, BOD_5 438mg/L, Cr^{3+} 46.4mg/L, and colourity 920 times.

2.4 Test Method

DBJ-621 variable speed agitator was applied in the 1L beaker. 500mL wastewater as well as an amount of fly ash-based coagulant (PBS) was put into the beaker; the agitator worked for 2min at the speed of 280r/min, so that the coagulant dispersed evenly; the running speed of the agitator was then reduced to 120r/min, at which the mixture was stirred for 8min; certain amount of flocculant PSA(30mg/L) was then added into the beaker, stirring was conducted at 160r/min for 1min; the running speed was adjusted to 60r/min for stirring for 8min; after the beaker was left still for 20min, the clear liquor ranging from the liquor level to 25mm below the level was taken out for analysis. The national standard method was used to determine SS, the iodometric method was used to determine S^{2-}, the diphenylcarbazide (DPC) spectrophotometry was used to determine Cr^{3+}, the standard potassium dichromate method was used to determine COD_{Cr} and the dilution multiples method was used to determine colourity.

3 Results and discussion

Associated with certain amount of flocculant PSA, coagulant PBS, which was obtained through acid treatment, was used for treatment of tanning wastewater, and the results are as follows.

3.1 Effect of pH on Coagulation

Under the conditions that temperature was normal and coagulant dosage was 70mg/L, dilute solutions

of sulfuric acid and sodium hydroxide were used to adjust the pH value of wastewater, thus observing the impact of pH value on the effect of coagulation. The results of this experiment are shown in Figure 1.

Figure 1 indicates that pH value has a strong impact on the coagulation effect of coagulant. In the range of pH 6～9, the coagulant PBS has remarkable effect of coagulation and pollutant removal. The colloid substances in the tanning wastewater usually carry negative electrical charges, while the coagulant contains a lot of Al^{3+} and Fe^{3+} ions. In the optimal range of pH value, Al(III) and Fe(III) are hydrolyzed into mononuclear and multinuclear hydroxy complex ions, which have the capability of electrical neutralization and are able to adsorb particles and compress electric double layer for destabilization of the particles. Further, the polysilicate maintains a macromolecular structure, and a powerful function of adsorption bridging. Therefore, PBS, associated with PSA, produces remarkable coagulation effect. The best coagulation effect could be achieved when pH value was 7.0, and in this condition, the removal rate was 93.1% for SS, 83.3% for COD_{Cr} and 90.8% for colourity.

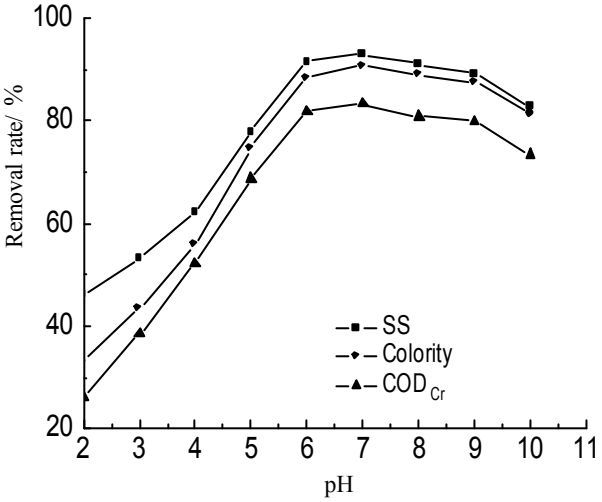

Fig. 1 Effect of pH on coagulation

3.2 Effect of Coagulant Dosage on Coagulation

In the conditions of normal temperature and pH value of 7.0, such coagulants as PBS, PAC and PFS were used to treat the wastewater sample respectively, and Figure 2 shows the relation between the dosage of coagulants and the removal rate of COD_{Cr}. From Figure 2, it can be seen that the effect of PBS in treating wastewater is much better than that of PAC and PFS. As the dosage of the coagulant increases, the removal rate of COD_{Cr} rises apparently; when the dosage of the coagulant reaches 60mg/L, the change of the removal rate of COD_{Cr} starts to slow down; when the dosage of the coagulant reaches 70mg/L, the removal rate of COD_{Cr} reaches the peak; after that, the removal rate of COD_{Cr} drops as the dosage of the coagulant increases. When the dosage of the coagulant is too small, the coagulation is insufficient, resulting in poor effect of coagulation; when the dosage of the coagulant is too big, the particles in the wastewater are enclosed by too much coagulant, and as a result, their surfaces are saturated, so that the particles lose the chance to combine with each other and reach another state of stability, in which it is hard for the particles to coagulate. Therefore, the effect of coagulation is poor too.

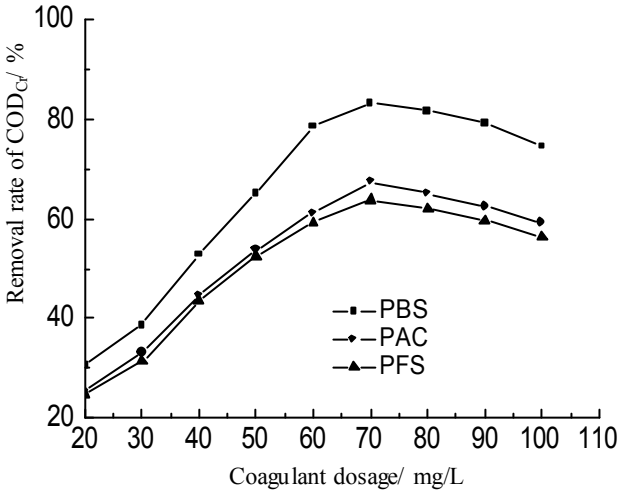

Fig. 2 Effect of coagulant dosage on coagulation

3.3 Effect of Temperature on Coagulation

The relationship between temperature and the removal rate of COD_{Cr} is shown in Figure 3.

As the temperature rises, the viscosity of wastewater decreases, Brown movement becomes fierce, and the inorganic coagulant hydrolyzes quickly, and as a result, coagulation is accelerated. Under the experimental conditions, sufficient time is provided for reaction and sedimentation, so the impact of temperature on removal rate of COD_{Cr} is very little.

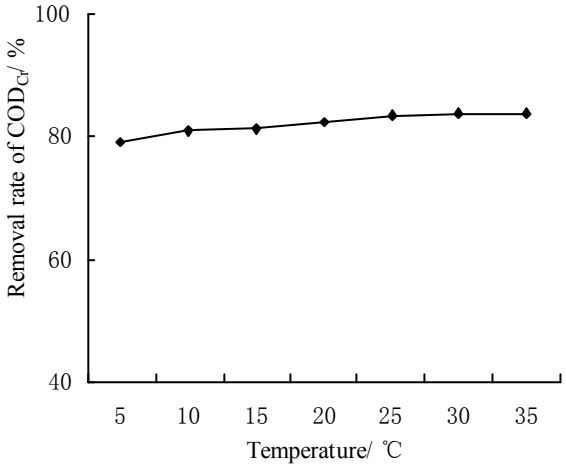

Fig. 3 Relationship between temperature and removal rate of COD_{Cr}

3.4 Comparison of the Removal Rate of Various Pollutants among Different Coagulants

Under the optimal conditions of treatment, three different coagulants, namely, PBS, PAC and PFS, were used to treat wastewater sample respectively. After treatment, SS, S^{2-}, Cr^{3+}, COD_{Cr} and colourity of the wastewater sample were measured, and the results are given in Table 2.

Tab. 2 Results of treating tanning wastewater with different coagulants %

Types of coagulant	Removal rate of SS	Removal rate of S^{2-}	Removal rate of COD_{cr}	Removal rate of Cr^{3+}	Removal rate of colourity
PBS	93.1	92.8	87.6	83.3	90.8
PAC	87.2	50.1	71.3	65.8	70.2
PFS	85.5	85.9	73.8	59.2	68.4

From Table 2, it can be seen that, together with flocculant PSA, the three coagulants are all effective to some extent in treatment of tanning wastewater. For removal of SS, the three coagulants are all remarkably effective, this is because the fly ash-based coagulant, PAC and PFS play the same role of coagulation, and produce basically the same effect of coagulation under the action of PSA. However, for removal of COD_{Cr} and colourity that depend on adsorption, coagulant PBS is the most effective, and its effect of coagulation is far better than that of such traditional coagulants as PAC and PFS. This indicates that PBS maintains remarkable performance of adsorption. The reason can be described with the results shown in Table 1. In the raw materials, particularly, in the iron sludge, there is a lot of C; coal will change into a kind of substance similar to active carbon structure with a great number of holes after incomplete burning at high temperature; the holes maintain extremely strong performance of adsorption, which is necessary for treatment of adsorbable matters in wastewater. PAC and PFS are common coagulants mainly for the purpose of coagulation only, so their performance in removal of COD_{Cr} and colourity is not as good as that of the fly ash-based coagulant.

4 The coagulation mechanism of coagulant PBS

(1) Compression of electric double layer and electrostatic neutralization. The fly ash-based coagulant contains a large quantity of Fe^{3+} and Al^{3+} ions, which are multiply charged, and can effectively reduce or eliminate the Zeta electric potential of the colloidal particles suspended in the wastewater, so that the repulsive force between the colloidal particles decreases and that it becomes easier for the colloidal particles to destabilize and coagulate. Further, the hydrolysis of these irons will result in many complicated polynulcear complexes. As the reaction of fasculation constantly goes on, the colloidal impurities

suspended in the wastewater coagulate easily.

(2) Adsorption. This action depends on the multi-hole feature and the specific surface area of fly ash. Fly ash maintains multiple holes, which adsorb the organic substances and colors in the wastewater. The surface of fly ash varies a lot after acid treatment.

The surface of fly ash particles is smooth and compact before acid treatment, and that after acid treatment, the surface of fly ash particles and the holes become rough with apparently increased specific surface area. Therefore, the surface of fly ash is activated after acid dipping at some high temperature. According to the theory of adsorption in wastewater treatment, the bigger the specific surface area of sorbent is, the better the adsorptive effect is. Therefore, activated fly ash adsorbs organic substances better.

(3) Adsorption-bridging and network-capturing. Since PSA contains macromolecules of polysilicic acid, as well as Fe^{3+} and Al^{3+} ions, which provide strong adsorption-bridging and network-capturing capacity, with which the hardly soluble compounds and fine particles can be separated from the water. This further enhances the process of adsorption, coagulation and sedimentation.

5 Conclusions

(1) PBS was found to be a very effective coagulant, together with flocculant PSA, capable of removing 93.1% of SS, 92.8% of S^{2-}, 87.6% of Cr^{3+}, 83.3% of COD_{Cr} and 90.8% of colourity from the wastewater sample under the optimum conditions of treatment.

(2) The efficacy of PBS in coagulating tanning wastewaer is mainly dependent on the stirring speed and time, pH value and dosage of coagulant. In the range of pH 6～9, coagulant PBS was quite effective in wastewater treatment. The optimum dosage of PBS for pollutants removal was 70mg/L.

(3) In comparison with the conventional coagulants, such as PAC and PFS, the coagulation performance of PBS coagulant was the best.

(4) There are abundant sources of raw materials for preparation of coagulant PBS, the PBS preparation process is very simple, and the PBS production cost is quite low, thus resulting in very low cost of wastewater treatment.

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