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Study on coagulation treatment of desulfurization wastewater of coal-fired power plants

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ABSTRACT

Taking water system of limestone-gypsum Wet Flue Gas Desulfurization (WFGD) device as object of study. First, this paper carries on the analysis to the quality of desulfurization wastewater, then in view of the water quality characteristic of desulfurization wastewater the paper proposes the materialized treatment method, and conducts the experimental study. In the materialized method selecting polymeric aluminum ferric silicate sulfate (PAFSS) as the coagulant, then using the orthogonal experiments determine PAFS best text condition under remove of the sulfide, the fluoride and the COD by PAFSS: the pH value 8~9,PAFSS throwing content 20ml/l, PAM throwing content 10ml/l, coagulation mixing time 25min, settling time 20min. Under the best test condition the treatment effect: after coagulation processing, sulfide elimination rate 99.3%; fluoride elimination rate 96.5%;COD elimination rate 78.5%. And the results achieve requests of GB 8978-1998" integrated wastewater discharge standard ".

Keywords: COD, wastewater of coal-fired power plants, coagulant, treatment processing, coagulation efficiency

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INTRODUCTION

With the development of China economy, people emphases on the environmental quality, moreover controlling the sulfur dioxide pollution has become a top priority of air pollution control[1,2].Among them, the flue gas desulfurization is more effective, the actual operable one of the measures. Yiyang Power Plant 2# 3# unit coal-fired boiler with electrostatic precipitator to clean the boiler flue gas SO_2 failed to meet the requirements of the national energy saving and emission standards, to meet energy saving requirements, and took limestone-gypsum wet FGD system purification of its flue gas[3,4].The main impurities of desulfurization wastewater is from flue gas, desulfurizing agent and processing water, it is acid, the content of suspended matter is high, its main ingredient is dust , desulphurization and Hg, Pb, Ni, As, Cd, Se, Cr heavy metal ions[5-9],heavy metal ions have strong pollution to environment, so this kind of wastewater must be purified.

Fly ash is a kind of solid waste discharged by coal-fired power plants and coal-fired boilers, very year one hundred million tons of fly ash piled up in China caused great impact on the environment[10]. The waste utilization use of fly ash, turning waste into treasure, has far-reaching significance in land conservation and environmental protection. In recent years, more and more fly ash in wastewater treatment and research, and has made certain achievements, forming a virtuous cycle of waste by waste[11].

In this paper, we will chose a kind of coagulant to remove the suspended matter, chromium ions ,COD, copper ions, sulfide in desulfurization wastewater, and reduce the environment pollution.

1. 1 *Research contents*

(1)Water quality analysis: determine the temperature, pH value, uspended substance, chromium ions, COD, copper ions, sulfide of desulfurization wastewater from a power plant.

(2) Remove the suspended solids in the wastewater using coagulation method, and determine the optimal conditions: choose the best coagulant from $FeCl_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $AlCl_3$, polymeric aluminum ferric sulfate (PAFS), polymeric aluminum ferric silicate sulfate (PAFSS), determine the dosage of coagulant, settling time, pH value of waste water.

(3) The orthogonal test of COD of coagulation treatment of desulfurization waste water and analysis of the results.

EXPERIMENTAL SECTION

2.1 *Materials and reagents*

Experimental reagents:$KMnO_4$, $FeCl_3$, $HOOCC_6H_4COOK$(Potassium biphthalate), KH_2PO_4, PAM(acrylamide), $Fe_2(SO_4)_3$, K_2Cr2O_7 (Potassiumdi chromate), Na_2HPO_4, $AlCl_3$, $C_{13}H_{14}N_4O$(DPCI).

Experimental apparatus:visible spectrophotometer,PH meter, electronic balance, six combined agitator, Photoelectric turbidity meter.

Desulfurization wastewater: it is taken from a power plant of yiyang city ,Hunan Province China, in this power plant the wet limestone flue gas desulfurization process is used.

2.2 *Method of water quality analysis on desulfurization wastewater*

(1) Pretreatment of wastewater: first we filtered out larger suspension in the water sample, added concentration of 5% NaOH, adjusted its pH value to the range of 9-10, the most of metal ions in water have generated hydroxyl, the solution was filtered after precipitation.

(2) Determination of suspended substance:using gravimetric method to determine the suspended substance [10].

(3)Determination of total chromium in waste water:using the method of diphenylcarbazide spectrometry to determine the chromium ions.

(4) Determination of the chemical oxygen demand (COD) in desulfurization wastewater: using the potassium dichromate method.

(5) Determination of turbidity: using a turbidity meter to determine the turbidity of waste water.

(6) Determination of the content of sulphur: using the Iodine quantity method.

(7)Determination of total copper ions in waste water: using the Atomic Absorption Spectrometry (AAS).

2.3 *preparation of coagulants*

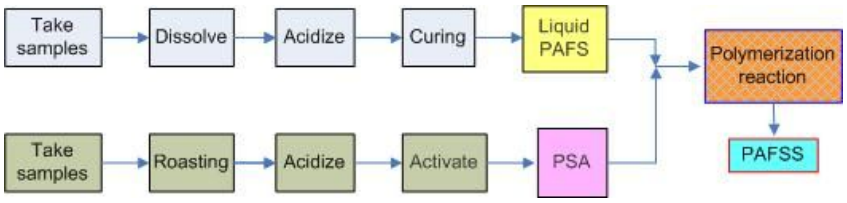

Figure 1. The preparation methods of polymeric aluminum ferric sulfate (PAFS), Polymeric aluminum ferric silicate sulfate (PAFSS)

The preparation methods of polymeric aluminum ferric sulfate(PAFS): weighed 12g of $FeCl_3$ and 6.5g of $Al2(SO_4)_3$ accurately, dissolved them in 100mL of water, then adjusted its pH value to 2 using the concentration of 5% NaOH, and stirred it at 60~70℃, it happened polymerization in the solution, the curing time was 6 hours, and the polymeric aluminum ferric sulfate(PAFS) was prepared. The total concentration of Fe(Ⅲ) and Al(Ⅲ) is 0.5mol/l, the molar ratio of Fe(Ⅲ) and Al(Ⅲ) is 3:2.

The preparation methods of polymeric aluminum ferric silicate sulfate (PAFSS): added 10g of fly ash and 2g of Na_2CO_3 in a evaporation pan, put it in a muffle furnace, roasted for 2h, made it cool to room temperature, then added concentration of 30% H_2SO_4, adjusted its pH value to 2.0, after 90 min of the activation reaction, the polysilicic acid(PSA) was prepared. In the condition of high-speed stirring, in the proportion of Si/(Fe + Al)=0.08,added the polysilicic acid(PSA) into the PAFS solution slowly, made the polymerization reaction happen

for 30min at room temperature, the polymeric aluminum ferric silicate sulfate (PAFSS) was prepared.

2.4 *Coagulation experiment*

Took 100ml of desulfurization wastewater after pretreatment, adjusted its pH value, added a certain amount of coagulant, started the mixer, stirred it in high-speed(about 300r/min) for 0.5min, stirred it in medium-speed(about 150r/min) for 5min, stirred it in low-speed(about 70r/min) for 10min, after 10min,added 1mL of PAM solution. Let the solution sit for a certain time, drained the supernatant with a 50mL injection tube, determined the water quality parameters of treated wastewater using single factor experiment method and orthogonal experiment method, the water quality parameters includes chemical oxygen demand (COD), turbidity, and studied on its flocculation performance.

RESULTS AND DISCUSSION

3.1 *Results of water quality analysis of desulfurization wastewater*

The water quality analysis of waste water is strongly acid is shown in Table 1:the waste water is acid,the suspended matter in the waste water pollution is serious, metal pollutants exceed the standard, the contents of COD and S^{2-} are very high, they exceed the standard severely.

Table 1. The results of water quality analysis of desulfurization wastewater

Factor	Experimental result
Temperature (℃)	15
suspended matter (mg/L)	12298
copper ion (mg/L)	1.42
Chromium ion(mg/L)	0.139
pH value	2.66
Turbidity (NTU)	268.8
Sulfide (mg/L)	28.5
COD (mg/L)	429.6

3.2 *Experiment of removing the turbidity of wastewater by Coagulation method*

3.2.1 Determination of the best coagulant

Took 100mL waste water with 5 250 ml beakers respectively, added $FeCl_3$ solution, $Fe_2(SO_4)_3$ solution, $Al_2(SO_4)_3$ solution, polysilicic acid(PSA) solution, polymeric aluminum ferric silicate sulfate (PAFSS) solution in these 5 beakers, each dosing quantity is 0.5 mL, added the same dosing quantity of coagulant, after coagulation mixing let the solution sit for 10min.

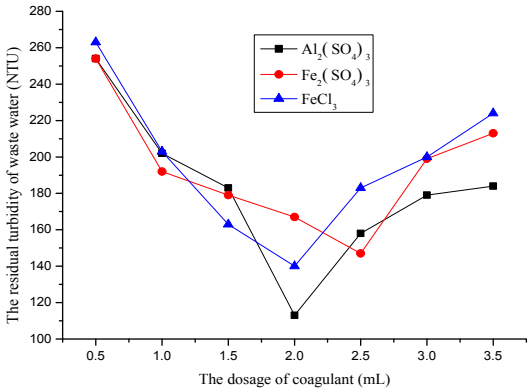

Figure 1. The impact of three kinds of inorganic coagulant dosage influence on the effect of coagulation

Observed the experimental phenomena, it can be found that, the first sample of appearing alumen ustum is polymeric aluminum ferric silicate sulfate (PAFSS) solution. It can be clearly seen from Figure 1 and Figure 2, polymeric aluminum ferric silicate sulfate (PAFSS) solution is the best coagulant, compared with polysilicic acid(PSA), the effect of removaling of suspended solids increases greatly, and in the process of storage and utilization, polymeric aluminum ferric silicate sulfate (PAFSS) is not corrosive to equipments. Compared with other coagulant, the flocculation speed of polymeric aluminum ferric silicate sulfate (PAFSS) is faster, the alumen ustum is bigger, the sedimentation velocity is faster, in addition, it has the function of decolorizing, removing heavy metal ions, reducing the concentration of COD or BOD. It not only integrates multiple advantages of poly aluminum

chloride, poly ferric and poly silicic acid, but also overcomes these shortcomings of poor stability of polysilicic acid, large residual colority of poly ferric and high concentrations of residual in poly aluminum processing. In the process of wastewater treatment, electrical neutralization reaction, adsorption bridging reaction and netting function happen at the same time, it produces a better coagulation effect.

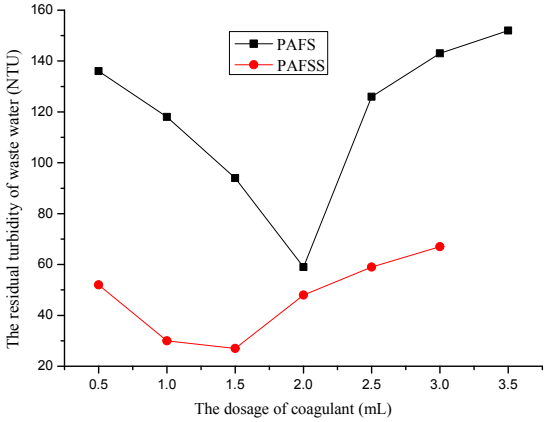

Figure 2. The impact of two kinds of high polymer dosage influence on the effect of coagulation

In order to improve the effect of coagulation further, polyacrylamide(PAM) was choosed as a coagulant aid, added polyacrylamide(PAM) and the 5 coagulant above in desulfurization waste water, the dosage of these 5 kinds of coagulant is the optimal dose, the mass concentration of PAM is 1‰, the dose is 1ml, the experimental results are shown in table 2.

Table 2. Effect of removal of turbidity of wastewater by 5 kinds of coagulant

Project	Turbidity of waste water :268.8 Temperature of waste water:15℃			Waste water,pH=8.66	
Coagulant	$FeCl_3$	$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$	PAFS	PAFSS
Optimal dosage (mL)	2.0	2.5	2.0	2.0	1.5
Residual turbidity without adding PAM	140	147	112	59	27
Residual turbidity after adding PAM	19	22	16	11	9

It can be seen from the experimental results in table 2 that, the addition of coagulant aid polyacrylamide causes the coagulation effect improves obviously. After comprehensive consideration, polymeric aluminum ferric silicate sulfate (PAFSS) is choosed as the best coagulant.

3.2.2 Determination of the best pH value

Took 100mL waste water with 8 250ml beakers respectively, put these beakers on a coagulation instrument, adjusted their pH value to 4.0,5.0,6.0,7.0,8.0,9.0,10.0,11.0 with concentration of 10% HCl and concentration of 10% NaOH, added 1.5mL of PAFSS coagulant and 1mL of PAM solution in these 8 beakers with a transfer pipette respectively, after coagulation mixing let the solution sit for 10min.

Under the condition of different pH value, the effect of PAFSS removal of suspended matters is shown in table 3.

Table 3. pH value of removal of turbidity of wastewater by PAFS

pH value	4	5	6	7	8	9	10	11
Residual turbidity(NTU)	116	74.7	44	34.68	22.07	13.35	11.33	11.8

Table 3 shows that, with the increasing of pH value, the turbidity of water reduced rapidly in first, then it reduced slowly to the lowest point, it raised slowly again. It can be seen clearly that, when the pH value is 10,the turbidity is at the lowest point, it is the optimal pH value. This is because the rising pH value of waste water to 9-10, increased the hydrolysing of Fe^{3+} and Al^{3+}, and increased the negative charge of polysilicic acid, so the flocculation effect was more obvious. And in the conditions of alkaline, of the chromium, lead, copper and other heavy metal ions formed hydroxide precipitation in waste water, these large sediment will sink with suspended matter because of trap effect, it improved the purification effect of wastewater.

3.2.3 Determination of the optimal dose of PAFSS

Took 100mL waste water with 6 250ml beakers respectively,adjusted their pH value to10,added 0.5mL,1mL, 1.5mL,2mL, 2.5mL,3mL of PAFSS coagulant in these 6 beakers respectively, after coagulation mixing added 1.0mL of PAFSS coagulant and 1mL of PAM solution in these 6 beakers with a transfer pipette respectively, let the solution sit for 10min.In the course of the experiment, recorded the following data: the formation process ,the size and the degree of dense of alumen ustum, the experimental results are shown in table 4.

Table 4. The experimental phenomena and results of different dosage

Serial number	Dosage (mL)	Experimental phenomena	Residual turbidity (NTU)
1	0.5	The alumen ustum is small and a bit more, the supernatant is turbid, the settling velocity of interface is slow.	21.65
2	1	The alumen ustum is big, the turbidity of supernatant is small, the settling velocity of interface is fast.	12.84
3	1.5	The alumen ustum is big and more, the supernatant is clear, the settling velocity of interface is fast.	8.44
4	2	The alumen ustum is big and more, the supernatant is clearer than the result of No3 experimental ,the settling velocity of interface is fast.	9.84
5	2.5	The alumen ustum is small, the supernatant is turbid, the settling velocity of interface is not fast.	9.86
6	3	The alumen ustum is small ,the supernatant is turbid, the settling velocity of interface is slow.	10.37

Table 3 shows that, with the increasing of dosage of PAFSS, the turbidity of water reduced rapidly in first, then it reduced slowly to the lowest point, it raised slowly again. It can be seen clearly that, when the dosage of PAFSS is 1.5ml,the adsorption capacity reached the maximum, the turbidity is at the lowest point, it is the optimal dosage. To solution containing a certain amount of suspended matter, the flocculation effect will enhance with the increasing of dosage, but when the flocculant dosing quantity is too much, the colloidal particles will occur charge repulsion, this leads to the flocculation effect reduce greatly.

3.2.4 Effect of temperature on coagulation effect

Took 100mL waste water with 6 250ml beakers respectively, adjusted their pH value to 10.0, added 1.5mL of PAFSS coagulant and 1mL of PAM solution in these 6 beakers with a transfer pipette respectively,it had coagulation reaction under the condition of different temperatures,then let the solution sit for 10min. The experimental results are shown in table 5.

Table 5. The optimum temperature of using PAFSS to remove suspended matter

Temperature(℃)	15	20	25	30	35	40
Residual turbidity(NTU)	24.5	13.2	9.17	8.04	8.1	8.21

It can be seen from the experimental results, when the water temperature rises above 30℃, the coagulation effect increases, this is because with the increase of temperature, the thermal motion of molecules increases, the floc formation becomes large, sedimentation velocity rises. So with the increase of temperature, the effect of wastewater treatment becomes better.

3.2.5. Determination of the optimal Settling time

Took 100mL waste water with 6 250ml beakers respectively, adjusted their pH value to 10.0, added 1.5mL of PAFSS coagulant and 1mL of PAM solution in these 6 beakers with a transfer pipette respectively, had coagulation experiments under the condition of 30℃, the experimental results are shown in table 6.

Table 6. Settling time of using PAFSS to remove suspended matter

Settling time (min)	5	10	15	20	25	30
Residual turbidity(NTU)	13.42	12.5	10.17	9.04	8.1	8.21

Table 6 shows that, with the increase of settling time, the turbidity of water reduced, when the settling time reaches 25min, it reduced to the lowest point, and it raised slowly again, so the optimal settling time is 25min.This is because ,there contains a lot of Al^{3+}, Fe^{3+} in PAFSS flocculant, these ions have high positive charge, it can compress the diffusion layer thickness, it can reduce the ζ potential of suspended particles in waste water too, and this reduces the overall potential energy, when the overall potential energy reduces to a certain value, the colloid flocculates. But with the increase of precipitation time, the water gradually becomes stable, the flocculation process is over.

3.3 Orthogonal experiment of COD

Among these factors, the pH value of waste water, the dosage of coagulant, the mixing time, the precipitation time

have great effect on the coagulation, so we selected these 4 factors as the orthogonal experimental factors. In order to cover the experiment, the level of each factor is four.

Table 7. The factors and their level of orthogonal experiment of COD

Factor / Level	pH value (A)	Dosage of coagulant (mL) (B)	Mixing time (min) (C)	Settling time (min) (D)
1	5	1.5	5	10
2	6	2.0	10	15
3	7	2.5	15	20
4	8	3.0	20	25

Took 100mL waste water with 16 250ml beakers respectively, adjusted their pH value according to table 7, added coagulant in these 16 beakers with a transfer pipette respectively, then had coagulation experiments.

The experimental results are shown in table 8. The parameter T is the COD value after processing, it is measured in mg/L; The parameter Q is the removal rate, it is measured in %.It can be known from the data in table 8, the factors have different effects on the water quality index. In table 8, the range value of the first column is the greatest, and the range value of 4th column is the smallest. This means that the changing of factor A has the highest impact on the water quality, and factor D has the lowest one, the sequence of the 4 factors is A > C > B > D. Therefore, pH value(factor A) is the most important factor. The higher the level of the factors is, the higher the removal rate is, so we selected the highest level of each factor, it is $A_2B_1C_4D_4$.

Table 8. The result of the orthogonal experiment(using PAFS to remove COD)

serial number	Factor				Experimental result	
	A	B	C	D	T	Q
1	1	1	1	1	137.82	67.92
2	1	2	2	2	196.58	54.24
3	1	3	3	3	161.15	62.48
4	1	4	4	4	120.18	72.02
5	2	1	2	3	152.71	64.45
6	2	2	1	4	82.15	80.89
7	2	3	4	1	124.03	71.13
8	2	4	3	2	95.32	77.81
9	3	1	3	4	160.55	62.63
10	3	2	4	3	146.27	65.95
11	3	3	1	2	187.85	56.27
12	3	4	2	1	201.89	53.00
13	4	1	4	2	111.58	74.02
14	4	2	3	1	158.58	63.08
15	4	3	2	4	196.74	54.21
16	4	4	1	3	146.17	65.98
T_1	256.66	269.02	271.06	255.13		
T_2	294.28	264.16	225.9	262.34		
T_3	237.85	244.09	266	258.86		
T_4	257.29	268.81	283.12	269.75		
t_1	64.16	67.25	67.76	63.78		
t_2	73.57	66.04	63.97	65.58		
t_3	59.46	61.02	66.5	64.72		
t_4	64.32	67.20	70.78	67.44		
R	14.11	6.23	6.81	3.66		
The best conditions	$A_2B_1C_4D_4$					

3.4 Coagulation experiment under the best experimental conditions

According to the experimental results above,the optimal experimental condition was selected as: the pH value of waste water is in the range of 8-9, the dose of PAFSS is 20ml/l, the dose of PAM is 10ml/l, the settling time after mixing coagulation is 25min. The coagulation experiment results under the best experimental conditions is shown in table 9.

Table 9. The coagulation experiment results under the best experimental conditions

Water quality index	Content (mg/l)	Removal rate (%)	The first-grade discharge standard (mg/l)	The second-grade discharge standard (mg/l)
Turbidity	8.1	96.9	—	—
COD	92.36	78.5	100	150
Sulfide	0.98	96.5	1.0	1.0
Total chromium content	0.03	78.4	1.5	—
Total copper content	0.25	82.4	0.5	1.0
suspended matter	82.35	99.3	70	150

CONCLUSION

(1) The desulfurization waste water is acid, it contains a large number of anions (such as F^-,S^{2-}), suspended matter and copper, lead, chromium, zinc and other heavy metal ions. The result of water quality analysis is:the temperature is 15℃,the total content of suspended matter is 12298mg/L, the total content of chromium is 0.139mg/L, the total content of copper is 1.42mg/l, the sulphide content is 32.5mg/l, pH value is 2.66,the concentration of COD is 429.6mg/L.

(2)The best coagulant was choosed from $FeCl_3$,$Al_2(SO_4)_3$,$Fe_2(SO_4)_3$,AlCl3, polymeric aluminum ferric sulfate (PAFS), polymeric aluminum ferric silicate sulfate (PAFSS),and the optimal coagulant is PAFSS, when the dosage of PAFSS is 15mL/L, the pH value is 10.0, the temperature is 30℃,and the settling time is 25min, the effect of coagulation is the best, the turbidity of waste water reaches 8.1.

(3)It shows that the maximum removal rate is 80.89% through orthogonal experiment of COD, and pH value and precipitation time are the main factors, when the pH value is 6.0, the dosage of PAFSS is 15mL/L, the dosage of PAM is 10mL/L, the mixing time is 20min, and the settling time is 25min,the removal rate of COD reached the highest value.

(4) The optimum conditions of desulfurization waste water treatment is: the pH value of waste water is in the range of 8-9, the dosage of PAFSS is 20mL/L,the dosage of PAM is 10mL/L,the settling time is 25min.The content of suspended matter, COD and sulfide of the treated wastewater reduce greatly, and the treated wastewater reaches national secondary standard.

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