

The issues in chromium-containing wastewater treatment by sodium pyrosulfite

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Abstract. It was found that appropriately increase weight ratio as well as attention to control pH in sedimentation and reduction phases can enhance the treatment effect of chromium-containing wastewater and prevent hexavalent chromium content rebounding after processing.

Introduction

Chromium-containing wastewater has great harm to environment, biology and human body, while chromium pollution is one of the important factors of environment pollution^[1,2]. Our organization which always attach importance to chromium-containing wastewater, collocate with professional processing flow, operating personnel and analyst responsible for monitoring treated wastewater^[4].

Several common methods for chromium-containing wastewater at present including : electrolytic reduction, chemical precipitation, ion exchange, photocatalysis method etc^[5,6]. Our organization has used successively ion exchange, ferrous sulfate reduction method in chromium-containing wastewater treatment. The advantage of ion exchange method contains better water quality after processing and the water and chromic acid can be reused , while the shortage are high investment and maintenance costs, complicated operation administration and resin oxidation problem. The main disadvantages of ferrous sulfate reduction method are large quantity of sludge and secondary pollution^[7].

Currently our organization take use of sodium pyrosulfite in chromium-containing wastewater treatment which has an easy operation procedure and get a stable and desirable effect, discharge water 100% up to the standard. The water after treatment has a better quality and less sludge and cost. The next tests show that considering these following points can get better effect.

Materials and methods

Experimental procedures. General procedure of chromium-containing wastewater treatment by sodium pyrosulfite: adjust pH to acidic → put in sodium pyrosulfite to degrade Cr⁶⁺ to Cr³⁺ → adjust pH to 6-9 to deposit Cr³⁺ → discharge supernatant and process sedimentation intensively.

Analyses. The preparation of chromium-containing solution (1.00g/l Cr⁶⁺) : accurately weigh 2.8329g potassium dichromate (AR) dissolved in 1000 ml volumetric flask, then dilute to calibration and shake well.

The basic analytical principles : Cr⁶⁺ can react with diphenyl carbazide to form a purplish red complex in acid, which can be measured by 721E spectrophotometer.

Results and discussion

Effect of pH and weight ratio. Treatment by sodium pyrosulfite in reduction phase.

The reaction process is as Eq. 1 :



Cr⁶⁺ has a great oxidability in the acidic condition, therefore adjust the solution to be acidic before reduction.

As shown in table 1, even there is a better effect in lower pH, but excessively low pH make sodium pyrosulfite is easy to decompose and generate SO₂, in addition, it will consume more alkali to adjust pH before discharge as a result increase the cost. Therefore the optimum pH is 3.0 for this study.

Table 1 Variations of degradation of Cr⁶⁺ concentrate with pH in reduction phase by sodium pyrosulfite

Cr ⁶⁺ concentrate before processing [g/L]	pH	Cr ⁶⁺ concentrate after processing [mg/L]			Reaction time [min]	The pH of solution after processing
		Na ₂ S ₂ O ₅ dosage 2.8g/L	Na ₂ S ₂ O ₅ dosage 3.2 g/L	Na ₂ S ₂ O ₅ dosage 4g/L		
1.0	1.2	200	0.02	--	<10	2.1
1.0	2.8	200	0.02	--	<30	3.3
1.0	3.7	200	0.34	0.02	>30	4.2
1.0	4.8	800	1.36	0.8	>30	4.8

Table 2 Variations of sedimentation efficiency and degradation of total chromium concentrate with pH in sedimentation phase

pH	Phenomenon	Total chromium concentrate in supernate [mg/L]
6.9	Precipitation is obvious and solution is wathet	12.1
7.6	Large precipitation and solution is wathet	2.6
8.1	Large precipitation and solution is colorless and transparent	1.4
8.8	Large precipitation and solution is colorless and transparent	0.06
9.3	Large precipitation and solution is colorless and transparent	0.45
10.3	Large precipitation and solution is colorless and transparent	1.97

In sedimentation phase , after oxidation-reduction reaction adjust pH to 7-9 with NaOH. The reaction process is as Eq. 2 :



When the pH is over 9, Cr(OH)₃ is apt to redissolve. When pH is under 6, it can't precipitate.

According to table 2 effluent total chromium concentrate is comparatively high as pH under 7. When the pH is between 7.6~9.3, total chromium concentrate is between 0.45~2.6mg/L. effluent total chromium concentrate is over 1.5mg/L as the pH over 10. Considering the chromium concentrate of actual wastewater is about 30mg/L commonly which is much less than the 1.0g/L experimental concentrate, so pH should be adjusted to 7-9 to meet the discharge standard.

Weight ratio. Table 1 also reveals that with the increase of sodium pyrosulfite the Cr^{6+} concentrate after processing decreases obviously. Calculated as the reaction between sodium pyrosulfite and Cr^{6+} , the theoretical weight ratio $\text{Cr}^{6+} : \text{Na}_2\text{S}_2\text{O}_5=1:2.74$. But in actual operation, the weight ratio $\text{Cr}^{6+} : \text{Na}_2\text{S}_2\text{O}_5$ ranges from 1:3.5-1:4, one the one hand the content of industrial sodium pyrosulfite is very low, on the other hand ensure processing Cr^{6+} can once finished to avoid the rework cost.

The rebound of Cr^{6+} after processing. When the Cr^{6+} concentrate in supernate is under 0.5 mg/L, discharge the solution. Nevertheless the content of Cr^{6+} will rebound and exceed the standard from analysis. That is because there is a small amount of $\text{Cr}(\text{OH})_3$ and Cr^{3+} in supernate which can turn to Cr^{6+} under certain conditions. The transform reaction process is as Eq. 3:



In order to get reliable consequence, Cr^{6+} concentrate after processing should be under 0.1 mg/L, and solution pH after processing should adjust to be between 7-9.

Conclusions

The statistics show that workshop has consumed about 4000Kg $\text{Na}_2\text{S}_2\text{O}_5$ 3 times of the theoretical calculation value to process chromium-containing wastewater in 2006. The primary cause is improper solution pH control which is the critical factor to influence Cr^{6+} transform to Cr^{3+} .

In order to get the desirable effect, the following 3 factors should be considered:

- (1) Adjust the pH=3 in reduction phase for adequate reaction.
- (2) Keep pH=7-9 in sedimentation phase to precipitate Cr^{3+} sufficiently and meet the discharge standard of total chromium.
- (3) To avoid the rebound of Cr^{6+} after processing, it should increase weight ratio of Cr^{6+} to $\text{Na}_2\text{S}_2\text{O}_5$ as 1:3.5-1:4 in reduction phase.

In the light of the research, under the certain conditions, pH=3 and actual operational weight ratio $\text{Cr}^{6+} : \text{Na}_2\text{S}_2\text{O}_5=1 : 3.5-1:4$, Cr^{6+} can be degraded to Cr^{3+} completely and come up with the discharge standard. It can save about 3000Kg $\text{Na}_2\text{S}_2\text{O}_5$ as this method and has already processed 1000L high concentration chromic acid wastewater with great economic and environment benefits.

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