Journal of applied science and engineering innovation Vol.1 No.2 2014
ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

Oxidation-Neutralization precipitation method in treatment of electroplating copper wastewater

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Abstract.A cable plant currently plates copper by electroplating, but the process will lead to a large number of highly acidic wastewater which contain high content of Cu^{2+} and Fe^{2+}。The factory currently uses neutralization and precipitation as the method to treat wastewater in stages, but color reversion phenomenon appeared. Study put forward the Fenton oxidation and $Ca(OH)_2$ precipitation as the process for treatment of wastewater.As the H_2O_2 dosage is 0.9L/m^3, the COD dropped to 8.9mg/L, the concentration of Cu^{2+} and Fe^{2+} were below the detection limit while the SO_4^{2-}has a better removal efficiency. This method not only can reach the standard of wastewater treatment, but also has higher cost advantage.

Keywords:copper wastewater, treatment, Fenton, neutralization and precipitation

1. Introduction

Electroplating is a craft process, which uses electrochemical method to decorate and protect surfaces of products as well as obtain new performance [1]. A certain cable factory utilizes acid pickling- electroplating-washing craft to carry out copper plating on the surface of cables, but the washing operation generates a great deal of waste water with high-concentration metal. At present, the factory adopts fractional neutralization precipitation method to deal with waste water. However, color reversion phenomenon appears in the process in which waste water is discharged outside, which makes water quality fail to satisfy related standards. Therefore, it is essential to find an economical and reasonable method which can make discharged waste water satisfy standards. The factory is anxious to find an economical and technically reasonable way to deal with waste water to ensure waste water satisfies standards when it is discharged outside.

Aiming at quality characteristic and matter specialty of waste water, the research puts forward Fenton oxidation-$Ca(OH)_2$ neutralization precipitation method to deal with copper plating waste water. Experiments verify that the waste water that has been dealt with by this method does not have the color reversion phenomenon so that it can be ensured that waste water satisfies standards when it is discharged outside. Thus, it provides some reference value for treatment related to copper plating waste water and the wastewater highly containing metal ions.

2. Material and Methods

2.1. Analysis of water quality

Samples of electroplating wastewater at the cable factory are taken to analyze water quality and compare it with related national standards. Results are shown in Table 1.

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Table 1 water quality analysis

	COD/mg/L	pH	$C_{Cu^{2+}}/mg/L$	$C_{Fe^{2+}}/mg/L$	$C_{Fe^{3+}}$/mg/L	$C_{SO_4^{2-}}/mg/L$
Water	79.1	2~3	63.2	297.3	3	5793
discharge standard	80	6~9	0.5	3		Not Mentioned

Waste water is featured by low pH as well as high Cu^{2+}, Fe^{2+} and concentration. Especially, we should note that waste water COD approaches emission standards and slight fluctuation of water quality will make effluent COD fail to reach the standards.

2.2. Detection methods

CODcr: potassium dichromate method (GB 11914-1989); pH: PHS-3C pH meter; Cu^{2+} concentration; Sodium diethydlthiocabamate spectrophotometric method (HJ/T 345-2007); barium sulfate gravimetric method that is used to measure content of sulfate radical (YS/T 581.8-2006) and chroma: Platinum Diamond colorimetric method (ISO 7887-1985).

2.3. Selection of technological process

It is known that hydroxide precipitation corresponding to Fe^{2+}, Fe^{3+} and Cu^{2+} is indissolvable matters, so the research plans to realize removal of metal ions by adjusting pH of waste water. By looking up related materials, Fe^{2+} and Cu^{2+} concentration in neutral solution can reach a trace level, while Fe^{3+} can only be eliminate completely in the environment with strong basicity. To sum up, the research plans to oxidize Fe^{2+}into Fe^{3+} and reduce its solubility product to realize the purpose that Fe^{2+} can be removed at a relative lower pH value. Because of rapid reaction and friendly environment, Fenton has been widely applied[2]. An acidic condition contributes to Fentonreaction[3]. A great many of free radicals generated when Fe^{2+} is oxidized into Fe^{3+} can reduce waste water COD and ensure waste water satisfies standards when it is discharged outside. Meanwhile, salt content of waste water can be reduced partially by adding moderate Ca^{2+}. Based on the foregoing aspects and the wastewater quality characteristic, the research uses Fenton oxidation-$Ca(OH)_2$ neutralization precipitation method to deal with copper plating waste water. The technological process is shown in Fig. 1.

Table2 TheKsp of common material

Material	$Cu(OH)_2$	$Fe(OH)_2$	$Fe(OH)_3$	$CaSO_4$
Ksp	2.2×10^{-20}	1.64×10^{-14}	1.1×10^{-36}	6.9×10^{-5}

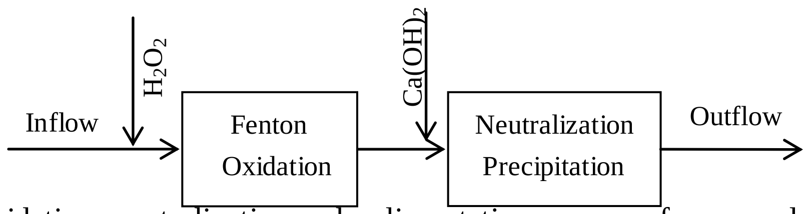

Fig. 1 Oxidation- neutralization and sedimentation process of copper plating waste water

Add some H_2O_2 to waste water to have Fenton reaction with Fe^{2+} in the waste water. By Fenton reaction, oxidize Fe^{2+} to a high-valence state and oxidize substances with reducibility in the waste water to reduce waste water COD. After complete reaction, add $Ca(OH)_2$ to adjust pH of the waste water and generate $CaSO_4$ precipitation. Then, place effluent quietly.

3. Results and discussion

3.1. Reaction mechanism

Processing methods are divided into two stages, the mechanism of the two stage are shown as follows.

Fenton oxidation and alkali neutralization and sedimentation. Reaction mechanisms of each stage are shown as follows[4-6].

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$, k=63$M^{-1}s^{-1}$ raction1

$\cdot OH + H_2O_2 \rightarrow HO_2 \cdot + H_2O$, k=2.7×$10^7M^{-1}s^{-1}$ raction2

$Fe^{3+} + HO_2 \cdot \rightarrow Fe^{2+} + H^+ + O_2$, k=2.0×$10^3M^{-1}s^{-1}$ raction3

$Fe^{2+} + HO_2 \cdot \rightarrow Fe^{3+} + HO_2^-$,k=1.2×$10^6M^{-1}s^{-1}$ raction4

$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$, k=3.2×$10^8M^{-1}s^{-1}$ raction5

Reaction 1 is a main reaction of Fenton reaction, which also leads to Fenton chain reaction. After Reaction 1, Reaction 4 and Reaction 5, Fe^{2+} is oxidized into Fe^{3+}. Reaction 1 generates strong oxidant OH and generation of OH^- is accompanied. In the acid environment, H^+ and OH^- react with each other. This not only drives chemical reaction equilibrium in Reaction 1 to move towards thee direction in which free radicals are generated but also restrains reduction process of Fe^{3+} in Reaction 3. Oxidation of OH for organic matters is a reaction process controlled by diffusion rate of matters, so it has good removal effect on low COD [7-8].

$Cu(OH)_2$, $Fe(OH)_3$ and $CaSO_4$ are indissolvable electrolytes. In combination with Table 2, it can be known that $Cu(OH)_2$ and $Fe(OH)_3$ generate precipitation at low pH to remove Cu^{2+} and Fe^{3+}. Use $Ca(OH)_2$ to adjust pH. Ca^{2+} and the waste water generate $CaSO_4$ precipitation. This can reduces the salt content of the waste water and attach to floc to accelerate precipitation rate.

3.2. Technological conditions

(1)Fenton reaction

In Fenton reaction, Fe^{2+} is oxidized into Fe^{3+} when it catalyzes H_2O_2 decomposition and leads to chain reaction. By looking up related materials and combining with Fenton reaction reaction principles, we can know the process is mainly controlled by H_2O_2/Fe^{2+}molar ratio and pH. To oxidize Fe^{2+} efficiently, it is essential to choose the foregoing three factors.

David L.S. et al.[9-11] carried out experiments and researches, and found that the higher $n(H_2O_2)/n(Fe^{2+})$ was, the less Fe^{2+} residual would be but the more H_2O_2 residual would be; otherwise, the more Fe^{2+} residual would be and the removal effect could not be achieved. When H_2O_2/Fe^{2+} molar ratio is 1:1, quantity of Fe^{2+} residual and H_2O_2 residual is the lowest. Thus, it has strong economicalefficiency. According to the following formula, it can be calculated that dosage of hydrogen peroxide is 0.6ml/L.

$$V_{H_2O_2} = \frac{C_{Fe^{2+}}}{56} \times 1 \times 32 \times \frac{100}{30} mL/L \quad (1)$$

According to Fenton reaction principles, it is known that the acidic condition contributes to Fenton reaction. By combining with some literatures and reports, we know the situation that pH is between 2 and 3 is beneficial implementation of Fenton reaction. Thus, Fenton reaction should be directly carried out in raw water pH.

According to literatures related to HRT, Fenton reaction and Fe^{2+} oxidation are usually finished within 1 hour at low concentration of COD. Thus, one hour is selected as the oxidation time for the reaction.

(2)$Ca(OH)_2$ dosage

According to standards, we know Cu^{2+} concentration of waste water emission must be lower than 0.5mg/L and total iron should be lower than 3mg/L. In combination with Fenton reaction principles, it is found that most of Fe^{2+} is oxidized into Fe^{3+}. Consequently, it will be ok if we consider precipitating Fe^{3+} completely.

ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

By combining with waste water discharge and cupric ion standard, the following formula can be obtained.

$$(C_{Cu^{2+}} \times 10^{-3}/64) \times (10^{pH-14})^2 = 2 \times 10^{-20} \tag{2}$$

$$C_{Cu^{2+}} \leq 5mg/L \tag{3}$$

According to the foregoing formula, we can obtain that Cu^{2+} concentration should be0.128mg/L when pH equals 7, if we want concentration of cupric ion to reach the lowest standard, i.e., pH=6.2.

By similar methods, it can be calculated that Fe^{3+} concentration is 6.2×10^{-11}mg/L when pH equals 7 in order that Fe^{3+} concentration reaches the lowest standard, pH=3.4. Considering national emission standards and the error range existing in actual operational process, the pH that equals 7 is selected as the most appropriate pH for neutralization and sedimentation.

Via the foregoing analyses, we decide that dosage of H_2O_2 is 0.9L/m_3 and use $Ca(OH)_2$ to adjust pH of the effluent to be 7.

Dosage of $Ca(OH)_2$ is decided and calculated according to field operation.

3.3. Results of wastewater treatment

Based on results of theoretical researches, bulk sample experiments are carried out at a laboratory. In accordance with analytical results in Section 3.2, add agent to the technological process. Results of effluent quality are shown in Table 4.

Tab 3 the quality of outflow

	COD/mg/L	pH	$C_{Cu^{2+}}/mg/L$	$C_{Fe^{2+}}/mg/L$	$C_{SO_4^{2-}}/mg/L$
Measured value	8.9	7	Below limit of detection	Below limit of detection	1512

Note: Actual dosage of H_2O_2 is 0.6L/m_3, HRT equals 1h and Actual dosage of $Ca(OH)_2$ is 0.96kg/m^3.

Results of actual treatment show that the color reversion phenomenon does not appear and all indicators satisfy requirements for waste water emission by using Fenton- neutralization precipitation method to deal with waste water.

4. Conclusion

(1) By calculation of chemical reactions, it is known that the technology that uses Fenton-neutralization precipitation method to deal with electroplating effluent is theoretically and completely feasible. Via verifying bulk samples, the color reversion phenomenon does not appear in waste water, concentration of Fe^{3+} and Cu^{2+} is lower than limit of detection, COD obviously reduces to about 10mg/L, the salt content is decreased and indicators of waste water satisfy requirements for waste water emission.

(2) When Fenton-neutralization precipitation method is used to deal with waste water, price of H_2O_2 and $Ca(OH)_2$finished industrial products is low. In addition, their dosage in operation is not high. Thus, the processing method is of high economicalpracticability.

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