The application of PAC and PAM in dynamic treatment of beryllium copper wastewater

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Abstract. The dynamic removal of beryllium and copper element was achieved by slanting plate clarifier after the wastewater of beryllium copper production line was settled by PAC and PAM. When the pH of wastewater was 9.0, PAC with a mass concentration of 50 mg/L at a flow rate of 200-250 L/h and PAM with a mass concentration of 2 mg/L at a flow rate of 150-200 L/h were injected in the wastewater sequence, respectively. The treated wastewater flowed through the slanting plate clarifier at a flow rate of 30 m³/h and then filtered continuously through the filtration device. The results show that Be²⁺ and Cu²⁺ concentrations are lower than 5 μg/L and 2 mg/L, respectively, which complies with the Standards of GB 8978—1996. Therefore, the Be²⁺ and Cu²⁺ elements in the wastewater can be removed at the same time.

1. Introduction
Beryllium copper is widely used in automotive, electrical and electronic, mold and other industrial sectors as an excellent fatigue-resistant and highly elastic conductive material. With the development of the industry, its application demand is also increasing [1]. Bronze copper production wastewater accounts for a large proportion of industrial pollution. Because sputum and its compounds can cause acute and chronic rickets [2], and may have carcinogenicity and genotoxicity [3], the treatment of strontium-containing sewage has also been studied and valued by scholars [4]. In the process of copper slag wastewater treatment, the concentration of Cu² in raw water is about 50-100 times that of Be². It is difficult to achieve the desired effect by using the traditional strontium-containing wastewater treatment process to remove bismuth copper at the same time.

The studied a method for simultaneously removing Be²⁺ and Cu²⁺ from the wastewater of the beryllium copper production line, that is, under certain pH control, the Be²⁺ and Cu²⁺ in the sewage are in an ideal sedimentation state, and a certain amount of polyaluminum chloride (PAC) is added. The flocculated sediment and copper hydroxide were flocculated, and then an appropriate amount of polyacrylamide (PAM) was added to enhance the flocculation effect, and the sediment was effectively separated from the sewage by a swash plate clarifier device.

2. Materials and methods
2.1. Instruments and equipment
iCAP6300 full spectrum direct reading plasma emission spectrometer, Thermo Fisher, USA; UV-2800 UV-visible spectrophotometer, Unico Shanghai Instruments Co., Ltd.; HUB-ZK double-resistant centrifugal sewage pump, Shanghai Ocean Water Pump Factory; Neutralization sewage tank; high level
overflow tank; intermediate water tank; quartz sand filter (30 m3/h); fiber ball filter (30 m3/h); OE-P200 automatic acid adding device, Shanghai Huaren; sloping plate Clarifier (slanting plate size 1000 × 2000 mm, two sets of 50 mm × 2 pieces, stainless steel 316L, plate spacing 60 mm, plate inclination 60°, capacity 30 m3).

2.2. Materials and reagents
The water sample is the daily sewage produced by a copper company in Ningxia, with pH of 4.0~7.0, Be2+ of 500~800 μg/L, Cu2+ of 40~60 mg/L, and no emulsified cutting liquid in the sewage.

Experimental materials: quartz sand (0.5~16 mm), polyester fiber ball (D50 mm).
Experimental reagent: 15% sodium hydroxide solution, Inner Mongolia Junzheng Chemical Energy Co., Ltd.; 5% PAC solution, Gongyi Hongyuan Water Purification Material Co., Ltd.; 0.2% PAM solution, Japan MT Aoke Polymer Co., Ltd. The mixing motor needs to be turned on during the preparation process, and the solid reagent is slowly added and stirred until completely dissolved.

2.3. Experimental methods
The sewage generated by the beryllium copper production process is lifted to the neutralization sewage tank by a double-resistant centrifugal sewage pump, the control flow rate is 30 m3/h, sodium hydroxide solution is added to the pipeline to adjust the pH to 9.0; The sewage pump raises the sewage in the neutralization tank to the high overflow tank, inputs the PAC into the pipeline at a certain flow rate, and inputs the PAM at a certain flow rate at the inlet of the high overflow tank. The high overflow overflow water flows into the swash plate clarifier and the control flow rate is 30 m3/h. The clear water above the swash plate clarifier flows to the middle tank, and the lower layer sludge reaches a certain mud level and is pumped into the mud tank by the mud pump, and is dried by a centrifuge and transported to a prescribed slag pool. The sewage in the middle tank is initially filtered by a quartz sand filter and then filtered again through a fiber ball filter to completely remove the sediment residue. The fiber ball filter can be discharged into the clear water pool for inspection. If the pH of the clear water solution is > 9.0, adjust it to pH ≤ 9.0 with an automatic acid addition device.

The mass concentration of Cu2 in the clear water pool was measured by a full-spectrum direct reading plasma emission spectrometer, and the mass concentration of Be2 in the clear water pool was detected by an ultraviolet-visible spectrophotometer. When Cu2 and Be2 can meet the GB 8978-1996 Integrated Wastewater Discharge Standard (Be2 < 5 μg/L, Cu2 < 2 mg/L), if they fail to meet the discharge standards, they will be returned to the original lagoon for reprocessing.

3. Results and Discussion
3.1. Effect of pH on the flocculation effect of Be2+ and Cu2+
The raw water pH was 6.5, the Be2+ was 770 μg/L, and the Cu2+ was 49 mg/L. PAC and PAM were sequentially added according to the amount of raw water, so that the dosages of PAC and PAM were 500 and 20 mg/L, respectively. The pH was adjusted to detect the Be2+ and Cu2+ of the supernatant after the original water was settled for 1 h. The results are shown in Fig.1.
It can be seen from Fig. 2 that at pH 9.0, both Be\(^{2+}\) and Cu\(^{2+}\) can achieve a satisfactory flocculation effect.

3.2. **Determination of PAC and PAM dosage**

The raw water pH was 6.1, Be\(^{2+}\) was 720 μg/L, and Cu\(^{2+}\) was 41 mg/L. The pH of the raw water was adjusted to 9.0, and the effect of different PAC dosages on the flocculation effect was examined. The results are shown in Fig. 2.

It can be seen from Fig. 3 that the removal rate of Be\(^{2+}\) is the best when the dosage of PAC is 500 mg/L, and the removal rate of Cu\(^{2+}\) is best when the dosage of PAC is 750 mg/L, but the dosage of PAC is The change trend was not obvious at 500–750mg/L. Considering the economic factors, the dosage of PAC was 500mg/L.

PAM has strong adsorption capacity for metal cations [5], PAM and PAC combination are more efficient in wastewater treatment, and have been widely concerned and applied [6]. The experimental raw water pH was 6.1, Be\(^{2+}\) was 720 μg/L, and Cu\(^{2+}\) was 41 mg/L. The pH of the raw water was adjusted to 9.0, and the dosage of PAC was 500 mg/L. The effect of PAM dosage on the flocculation effect of PAC and PAM was investigated. The results are shown in Fig. 3.
It can be seen from Fig. 4 that in the combination of PAC and PAM, the dosage of PAM is 20 mg/L, and the removal rate of Be$^{2+}$ is optimal. The Cu$^{2+}$ removal rate is optimal when the dosage of PAM is 30 mg/L, but PAM The dosage of 20~30 mg/L was not obvious. From the economical point of view, the dosage of PAM was 20 mg/L.

3.3. Determination of PAC and PAM joining traffic
In the raw water with a daily flow rate of 25 m$^3$/h, the pH is 6.5, the Be$^{2+}$ is 740 μg/L, and the Cu$^{2+}$ is 43 mg/L. The pH of the raw water was adjusted to 9.0. The effect of different PAC flow rate on the flocculation effect of PAC was investigated. The results showed that the removal efficiency of Be$^{2+}$ and Cu$^{2+}$ was the best when the PAC flow rate was 200 L/h. When the PAC flow rate was 200~250 L/h, Be$^{2+}$, The change trend of Cu$^{2+}$ removal rate is not obvious. Combined with working efficiency, the flow rate of PAC is 200~250 L/h.

In the raw water with a daily flow rate of 25 m$^3$/h, the pH is 6.5, the Be$^{2+}$ is 740 μg/L, and the Cu$^{2+}$ is 43 mg/L. Adjusting the pH of the raw water to 9.0, firstly input the PAC at 200 L/h, and then add PAM to the sedimentation test at different flow rates to investigate the effect of different flow rates of PAM on the flocculation effect of PAC and PAM combination. The results show that in the combination of PAC and PAM, When the PAM flow rate is 150 L/h, the Cu$^{2+}$ removal rate is the highest. When the PAM flow rate is 200 L/h, the Be$^{2+}$ removal rate is the highest, and when the PAM flow rate is 150~200 L/h, the Be$^{2+}$ and Cu$^{2+}$ removal rates change more gently. Considering the removal effect and working efficiency of Be$^{2+}$ and Cu$^{2+}$, the PAM flow rate is 150~200 L/h.

3.4. Swash plate clarifier flow test
The sewage in the high overflow trough flows through the sloping plate clarifier, which allows the sediment to be separated from the sewage more efficiently and achieves dynamic treatment. The effect of the flow rate of the swash plate clarifier on the sewage treatment effect was investigated. The results show that the sloping plate clarifier sewage flow rate is 10~30 m$^3$/h, which can achieve satisfactory purification and separation results. Considering the actual working efficiency, the sloping plate clarifier sewage flow rate is selected to be 30 m$^3$/h.

3.5. Process sewage direct discharge rate
The sewage detection data of a certain month's copper-copper wastewater production line after PAC and PAM combined process were randomly collected. The results are shown in Table 1.
Table 1. Sewage inspection data of the beryllium copper production line

| date | Be²⁺ (μg·L⁻¹) | Cu²⁺ (mg·L⁻¹) | direct discharge | date | Be²⁺ (μg·L⁻¹) | Cu²⁺ (mg·L⁻¹) | direct discharge |
|------|----------------|----------------|------------------|------|----------------|----------------|------------------|
| 1    | 3.2            | 0.75           | yes              | 13   | 4.2            | 0.77           | yes              |
| 2    | 3.4            | 0.62           | yes              | 16   | 1.8            | 0.15           | yes              |
| 5    | 0.8            | 0.01           | yes              | 19   | 7.0            | 0.96           | no               |
| 7    | 1.2            | 0.01           | yes              | 20   | 2.0            | 0.58           | yes              |
| 8    | 0.2            | 0.01           | yes              | 22   | 3.2            | 0.42           | yes              |
| 12   | 0.2            | 0.01           | yes              | 23   | 3.0            | 0.75           | yes              |

From the data in Table 1, the monthly direct discharge rate (the number of monthly qualified discharges per month/the total number of monthly sewage treatments × 100%) was calculated to be 91.67%.

4. Conclusion

Use PAC and PAM to enhance flocculation while removing Be²⁺ and Cu²⁺ from wastewater. At a pH of 9.0, a 500 mg/L PAC was added at a flow rate of 200-250 L/h, and a 20 mg/L PAM was added at a flow rate of 150-200 L/h, and the clarification was enhanced by a swash plate clarifier. Efficiency, Be²⁺ and Cu²⁺ removal rate can reach more than 99%, and the monthly direct discharge rate of sewage can reach more than 91%. The process method is stable, reliable, economical and practical, and provides a solution for sewage treatment of the beryllium copper production line.

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