Investigation of plating wastewater treatment technology for chromium, nickel and copper

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Abstract. Electroplating during chrome, nickel and copper production generates a large amount of wastewater, with plating wash water, plant wash water and equipment cooling and wash water comprising the main sources of wastewater. These wastewaters contain a variety of metal components, which causes the concentrations different. Metal ions can cause serious harm to humans, animals, plants and the environment; therefore, it is necessary to treat electroplating wastewater to remove these materials. Electroplating wastewater also contains a large number of complexes that are difficult to remove by simple precipitation. In this study, the iron reduction co-precipitation method was found to remove hexavalent chromium, decompose nickel and copper complexes and reduce chemical oxygen demand (COD) well. The average chromium-nickel-copper ion concentration was stable at 0.1 ppm, while the COD was stable between 20 and 30 ppm, enabling rapid processing by one-time treatment to meet the emission standards of China.

1. Introduction
Heavy metals have atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [1]. The rapid development of the metal plating, mining, fertilizer, tannery, battery production, paper and pesticides industries has led to increased amounts of heavy metal wastewaters being directly or indirectly discharged into the environment, especially in developing countries [2]. The composition of electroplating wastewater is complex, and pollutants can be classified into inorganic and organic pollutants. The pH of water changes greatly, COD\textsubscript{Cr} has a large coefficient of variation and there is high level of heavy metal during wastewater discharge. If the discharged electroplating wastewater does not meet the emission standard, it will cause serious pollution to the surrounding water bodies. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Heavy metals can be removed from inorganic effluent by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. However, these processes have significant disadvantages, such as incomplete removal, high-energy requirements, and production of toxic sludge [3]. Electroplating wastewater generally contains various ions of Cr, Ni, Cu, and Zn.
Hexavalent chromium is 100 times more toxic than trivalent chromium, and is easily absorbed by the human body. Cr(VI) accumulates in the food chain and causes severe health problems in humans including skin irritation, respiratory damage, intestinal corrosion, ulcers and even lung cancer [4]. However, Cr(III) is a trace element required by the human body.

Although nickel at levels above its critical level can cause serious lung and kidney problems, as well as gastrointestinal distress, pulmonary fibrosis and skin dermatitis [5], it is used in the electroplating industry. Electroplating wastewater containing excessive levels of nickel will lead to its enrichment in soil, resulting in human exposure and subsequent illness.

Although copper is a trace element required by humans, plants and other animals, intake of high levels of copper can have adverse effects. For example, the excessive intake of copper by humans leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous system problems, depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [6].

In this study, an iron reduction-coprecipitation method for wastewater treatment is proposed. This method reduces the levels of chromium, nickel and copper ions and forms high-concentration suspended large-particle compounds between heavy metal ions that can be subjected to adsorption-co-settlement. As the method is able to convert non-precipitable Cr(VI) to precipitable Cr(III), it can be used to remove heavy metal chromium. The changes in the removal rates of nickel and copper with time during the iron reduction-coprecipitation reaction are also discussed. Application of the developed method led to combination of the oxidation-reduction reaction and metal particle adsorption co-settlement, resulting in rapid reduction of the heavy metal ions to the target levels of Cr<0.5 ppm, r(VI)<0.1 ppm, Ni<0.1 ppm, Cu<0.1 ppm, and CODCr<50 ppm.

2. Experimental procedure
In this experiment, wastewater from an electroplating park in Ningbo containing chromium, nickel and copper at the specific concentrations shown in table 1 was used. Demonstration experiments were conducted to remove the heavy metals from the water.

| Table 1. Heavy metal ion concentrations in wastewater from an electroplating park in Ningbo. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Raw water concentration         | pH              | CODCr           | Cr<sup>VI</sup> | Cr<sup>III</sup> |
| Nickel                          | 200.93 ppm      | 9.8             | 890 ppm         |                 |
| Chromium                        | 257.76 ppm      | 2.9             | 254 ppm         | 111.6 ppm       |
| Copper                          | 152.46 ppm      | 1.2             | 537 ppm         |                 |

2.1. Chromium reduction, precipitation and coprecipitation
Experiment one measured the effects of direct precipitation separation, experiment two investigated reduced agent reduction-precipitation separation, experiment three evaluated reduced agent reduction-trivalent iron co-separation and experiment four investigated iron reduction-coprecipitation separation. Chromium content was measured using ICP Emission Spectroscopy. Briefly, a standard curve was generated using five groups of standard solutions, after which the total chromium concentration of the test solution was measured. An HZ-7000 electromeasurement system was used to measure the hexavalent chromium content of the raw liquid and the sample was tested according to CV cyclic voltammetry (pH=1). The reference electrode was made of Ag/AgCl, the positive and negative electrodes were graphite, the scanning speed was 20 mV/s, and the sampling interval was 0.5 s. Overall, 10 groups were measured, the first set potential was -1.5 V, and the second set potential was +1.5 V. At the end of the measurement, a CV cycle diagram of the raw water and reacted solution was obtained.

2.2. Nickel reduction, precipitation and coprecipitation
Experiments one through three investigated sedimentation separation, separation of ferric iron by
coprecipitation and iron reduction-coprecipitation separation, respectively. The nickel content of the samples was measured according to ICPS-7000.

2.3. Copper reduction, precipitation and coprecipitation
Experiments one through three investigated sedimentation separation, separation of ferric iron by coprecipitation and iron reduction-coprecipitation separation. The copper content of the samples was determined using ICPS-7000.

3. Results and discussion
After the iron reduction-coprecipitation reaction, the concentrations of heavy metals in liquids were analyzed and changes in the valence of elements were detected by ICP and an electrochemical measurement system to determine the residual concentrations of chromium, nickel, copper and the reduction ratio of Cr(VI). Comparing the change in concentrations of heavy metal components in liquid before and after the reaction revealed the removal efficiency of heavy metal components in a certain period. Testing and analysis of the experimental and the control group revealed the feasibility of the iron reduction-co-settlement.

3.1. Chromium reaction principle and results analysis
The experiment was conducted at room temperature (25°C), and the reaction principle was divided into two parts, reduction and co-sink. The reaction formulas [7] in the experiment are speculated to be:

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Cr}_2\text{O}_7^{2-} + \text{Fe} + 14\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (2)
\]

\[
\text{CrO}_4^{2-} + \text{Fe} + 8\text{H}^+ \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad (3)
\]

\[
-\text{Fe(OH)}_2^+ + \text{CrO}_4^{2-} \rightarrow -\text{FeCrO}_4^- + 2\text{OH}^- \quad (4)
\]

\[
-\text{Fe(OH)}_2^+ + \text{Cr}^{3+} \rightarrow -\text{FeOCrOH}^- + \text{H}^+ \quad (5)
\]

\[
\text{Cr}^{3+} + 3\text{OH}^- \leftrightarrow \text{Cr(OH)}_3 \quad (6)
\]

Under ideal reduction conditions, insoluble electrolyte chromium hydroxide precipitates partially decomposed in solution as an ion (equation (6)). When the precipitation rate of decomposition was equal to the rate of formation, the rate of dissolution of the precipitate reached equilibrium. According to the Ksp of chromium hydroxide at normal temperature, the theoretical elution amount of trivalent chromium in solution could be calculated as follows:

\[
\text{Ksp} = [\text{Cr}^{3+}] [\text{OH}^-]^3 = 6.3 \times 10^{-31}
\]

When the pH of the solution is 12, the dissolution concentration of Cr$^{3+}$ is as follows:

\[
[\text{Cr}^{3+}] [10^{-2}]^3 = 6.3 \times 10^{-31}, [\text{Cr}^{3+}] = 6.3 \times 10^{-25} \text{ (mol/L)}
\]

\[
\text{Cr}^{3+} = 51.996 \times 6.3 \times 10^{-25} = 0.328 \times 10^{-19} \text{ (mg/L)}
\]

According to the calculation results, the dissolution concentration of trivalent chromium is negligibly small, and the residual chromium ions were essentially hexavalent.

The results of cyclic voltammetry (CV) analysis of the raw water and treated liquids are shown in figures 1 and 2. In the fourth quadrant of the redox coordinate axis, the vertical distance from the highest point of the cycle curve to the X-axis is the content of Cr$^{6+}$ in the solution. After that, the curve gradually moves to the third quadrant from the highest point of the fourth quadrant. This change is expressed as the transition from Cr$^{6+}$ to Cr$^{3+}$. In above two figures, the vertical distances from the
highest point of the fourth quadrant to the X axis before and after the reaction are marked by vertical lines with a length ratio of 206: 0.48. The valence changes in hexavalent chromium in the liquid before and after the reaction could be visually seen through the length ratio.

![Graph showing electric current and voltage](image)

**Figure 1.** Chromium content before treatment.  **Figure 2.** Chromium content after treatment.

| Table 2. Measured chromium concentrations in treated water. |
|-----------------------------------------------------------|
| Experiment | Cr ppm | Cr$^{6+}$ ppm | COD ppm |
|-------------|--------|----------------|---------|
| One         | 134    | 82             | 176     |
| Two         | 2.01   | 0.24           | 153     |
| Three       | 1.02   | 0.08           | 89      |
| Four        | 0.092  | 0.06           | 35      |

When combined with the results of table 2, the treatment efficiency of $\eta_{Cr}$ and the reduction efficiency of $\eta_{Cr}^{6+}$ could be calculated in the iron reduction-coprecipitation method. The method of direct precipitation cannot be applied to the treatment of chromium wastewater because the hexavalent chromium ions must be reduced before precipitation. The iron reduction method (equations (2) and (3)) not only had a favorable effect, but also showed reduction rates of 99.95% for hexavalent chromium. When using the same reducing conditions for chromium wastewater, the effects of co-precipitation with ferric iron and chromium were better than those of the separate precipitation. Under certain conditions, the generated iron and chromium ions reached the effect of co-precipitation after the reaction.

$$\eta_{Cr}^{6+} = \frac{stockC_{Cr}^{6+} - C_{Cr}^{6+} \text{ filtrate}}{stockC_{Cr}^{6+}} \times 100\% = 99.95\%$$  \hfill (7)  

$$\eta_{Cr} = \frac{stockC_{Cr} - C_{Cr} \text{ filtrate}}{stockC_{Cr}} \times 100\% = 99.96\%$$  \hfill (8)

3.2. **Nickel reaction principle and results**

The experiment was conducted at room temperature, and the reaction principle was divided into two parts, reduction and co-sinking. The reaction formulas [7] in the experiment are speculated to be:

$$Ni^{2+} + Fe \rightarrow Fe^{2+} + Ni$$  \hfill (9)  

$$Ni(OH)_{2} \leftrightarrow Ni^{2+} + 2OH^{-}$$  \hfill (10)  

$$-Fe(OH)_{2}^{+} + Ni^{2+} \rightarrow FeO_{2}^{+}OH^{-} + H^{+}$$  \hfill (11)

According to the standard electrodes potential of Fe and Ni, which are $E_{0}^{0}Fe = -0.409V$ and $E_{0}^{0}Ni = -$
0.233 V, the oxidation of nickel ions is greater than that of iron ions so that iron can reduce nickel ions (equation (9)). However, as reaction time increased, the reduced nickel adhered to the surface of the iron, which caused the reaction rate to decrease; therefore, it was speculated that the reaction had an optimal time point. As the pH of the solution increased, nickel ions precipitated as hydroxides. Hence, according to the Ksp of nickel hydroxide, the theoretical elution concentration of nickel ion in solution could be calculated using equation (10).

\[
K_{sp} = [\text{Ni}^{2+}] [\text{OH}^-]^2 = 5.48 \times 10^{-16}
\]

When the pH of the solution is 12, the dissolution concentration of Ni\(^{2+}\) is as follows:

\[
[Ni^{2+}] [10^{-2}]^2 = 5.48 \times 10^{-16}, [Ni^{2+}] = 5.48 \times 10^{-12} \text{ (mol/L)}
\]

\[
Ni^{2+} = 58.69 \times 5.48 \times 10^{-12} = 0.322 \times 10^{-6} \text{ (mg/L)}
\]

According to the calculated results, if wastewater contained nickel that was in the presence of free ions, the concentration of nickel ions in the solution could be reduced by less than 0.1 ppm by direct precipitation.

### Table 3. Measured nickel concentrations in treated water.

|          | Ni  | COD\(_{Cr}\) |
|----------|-----|--------------|
| Experiment One | 11.63 ppm | 194 ppm |
| Experiment Two  | 2.367 ppm | 86 ppm |
| Experiment Three | 0.081 ppm | 25 ppm |

As shown in figure 3, during iron reduction and co-settlement (equation (11)), the reaction time had a significant effect on changes in nickel concentration. The maximum reaction rate was observed at 30–40 min. When the reaction time was 40 min, the concentration of nickel in the filtrate was less than 0.1 ppm, and the nickel concentration in the filtrate began to rise. Therefore, the optimum reaction time was 40 min. The treatment efficiency of the iron reduction-co-settlement method \(\eta_{Ni}\) was calculated using the results presented in table 3. Generally, there was a large amount of complexing agent added during nickel plating that led to the formation of complexed nickel molecules that were difficult to precipitate. Although the nickel wastewater was precipitated by a direct pH-elevation.
method, the concentration of nickel in the filtrate was still very high, and it was considered a complexed nickel molecule. However, the removal rate of heavy metal nickel reached 99.95% in the iron reduction-co-sinking experimental group, indicating that the iron reduction-coprecipitation method had a certain effect on decomposition of the complex.

\[
\eta_{\text{Ni}} = \frac{\text{stock}C_{\text{Ni}} - \text{filtrate}C_{\text{Ni}}}{\text{stock}C_{\text{Ni}}} \times 100\% = 99.95\%
\]

(12)

3.3. Copper reaction principle and result analysis

During the experiment, there was an obvious red deposit on the surface that was considered to be reduced copper. The experiment was conducted at room temperature, and the reaction principle was divided into two parts, reduction and co-sink. The reaction formulas [?] in the experiment are speculated to be:

\[
\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Fe}^{2+} + \text{Cu} \quad (13)
\]

\[
\text{Cu(OH)}_2 \rightleftharpoons \text{Cu}^{2+} + 2\text{OH}^- \quad (14)
\]

\[
-\text{Fe(OH)}_2^+ + \text{Cu}^{2+} \rightarrow \text{FeOCuOH}^+ + \text{H}^+ \quad (15)
\]

According to the reaction formula, the reduction and co-precipitation of copper ions was the main reason for the decrease in copper content. As the reaction time increased, the copper metal reduced by iron wrapped around the surface of the iron (equation (13)), which prevented further reaction. As a result, the maximum reduction efficiency was attained in the optimal reaction time. When the pH of the reaction was gradually increased, copper and iron ions precipitated as hydroxides and the theoretical concentration of copper ion in solution could be calculated according to the Ksp of copper hydroxide according to (equation (14)).

\[
\text{Ksp} = [\text{Cu}^{2+}] [\text{OH}^-]^2 = 4.8 \times 10^{-20}
\]

When the pH of the solution is 12, the dissolution concentration of Cu\textsuperscript{2+} is:

\[
[\text{Cu}^{2+}] [10^{-2}]^2 = 4.8 \times 10^{-20}, [\text{Cu}^{2+}] = 4.8 \times 10^{-16} \text{ (mol/L)}
\]

\[
\text{Cu}^{2+} = 63.54 \times 4.8 \times 10^{-16} = 0.305 \times 10^{-10} \text{ (mg/L)}.
\]

According to these equations, the dissolution of copper ions in solution is negligible.

As shown in figure 4, the reaction of iron reduction and co-precipitation (equation (15)) stabilized over 20 minutes as the reduced copper metal wrapped the surface of the iron carrier, decreasing the effective reaction area and thereby gradually lowering the reaction rate. The efficiency of the iron reduction-coprecipitation method \(\eta_{\text{Cu}}\) treatment and \(\eta_{\text{Cu}^{2+}}\) reduction were then calculated using the results shown in table 4. According to the calculation from the concentration of raw water, the reduction process played a crucial role as it accounted for about 88.06% of the entire processing efficiency. In the experimental group using the iron reduction-coprecipitation method, the removal rate of the heavy metal copper reached 99.94%, indicating good treatment efficiency.

| Table 4. Measured copper concentrations in treated water. |
|-----------------|-----------------|
|                | Cu | COD\textsubscript{Ct}  |
| Experiment One | 9.8 ppm | 249 ppm |
| Experiment Two | 5.15 ppm | 64 ppm |
| Experiment Three (After Reduction) | 18.2 ppm | 346 ppm |
| Experiment Three (After Precipitation) | 0.0922 ppm | 23 ppm |
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\[ Cu_{2+}^{\text{before reduction}} - Cu_{2+}^{\text{after reduction}} \]
\[ Cu_{2+}^{\text{before reduction}} \]

\[ \eta_{Cu^{2+}} = \frac{C_{\text{Cu}^{2+} \text{before reduction}} - C_{\text{Cu}^{2+} \text{after reduction}}}{C_{\text{Cu}^{2+} \text{before reduction}}} \times 100\% = 88.06\% \quad (16) \]

\[ \eta_{Cu} = \frac{\text{stock} \cdot C_{Cu} - C_{Cu \text{filtrate}}}{\text{stock} \cdot C_{Cu}} \times 100\% = 99.94\% \quad (17) \]

4. Conclusion

In this study, electroplating wastewater that contained chromium, nickel and copper was harmlessly treated based on the principle of iron reduction-precipitation. The reduction rate of hexavalent chromium was essential to treatment of the chromium wastewater. A reduction rate of 99.95\% of hexavalent chromium was achieved in a short time using the iron reduction method, while combination of this method with coprecipitation increased the removal rate to 99.96\%. In addition, for the treatment of nickel and copper wastewater, when the reaction time was 40 min and 30 min, the best removal rates of 99.95\% and 99.94\%, respectively, were attained. Under certain conditions, there was a great treatment effect on chromium-nickel-copper electroplating wastewater when the iron reduction-coprecipitation method was utilized.

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