Co-removal of hexavalent chromium during copper precipitation

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Abstract In our recent study using the nucleated precipitation technology to treat plating wastewater, it was found that about one half of hexavalent chromium was co-removed with copper, nickel and zinc. Since hexavalent chromium could not react with either hydroxide or carbonate to form precipitates, this study was undertaken to evaluate the mechanism(s) involved in the chromium co-removal.

Batch tests were conducted with synthetic solutions containing either only copper or both copper and hexavalent chromium. Metal precipitation was induced by adding Na₂CO₃ to different pH, and the quantitative removal of copper and chromium was determined. Besides, the [Cr]/[Cu] molar ratio of produced precipitates were also assessed in conjunction with the EDAX analysis to determine their compositions. Experimental results indicate that for pure copper solution, precipitation begins at pH 6.0, and completes at pH 7.0. The chemical forms of the precipitates are copper carbonates [CuCO₃.Cu(OH)₂ and CuCO₃.2Cu(OH)₂]. On the other hand, in a bi-metal solution of copper plus chromium, precipitation of copper begins at about pH 5.0, and copper precipitation is always accompanied by some chromium removal. From the removal stoichiometry of the two metals, it is found that at low pH, the co-removal is a result of “co-precipitation” which results in the formation of CuCrO₄ crystallites. Once such crystallites are formed, they provide a heterogeneous environment which enhances an early formation of copper carbonate at a lower pH (below 5.5). It is further found that once copper carbonate precipitates are produced, the remaining soluble will precipitate in such form, and at this stage further removal of copper is no longer accompanied by additional chromium removal. The test data also reflect that the produced copper carbonates are positively charged, as verified by zeta potential measurement, at pH below 7.5. Thus they are able to adsorb some anionic chromium (existing as chromate) through electrostatic attraction and/or inorganic ligand exchange. At pH of 6 to 10, the extent of adsorption decreases with increasing pH, and the adsorption capacity seems to coincide with the progressive reduction of positive zeta potentials of the precipitated particles.

Keywords Adsorption; chromium; copper; co-precipitation; co-removal; heavy metal removal; mechanism; precipitation

Introduction
Removal of heavy metals in aqueous solution typically involves the use of hydroxides, carbonates, or sulfides to induce metal precipitation. It has been well known that Cu²⁺, Ni²⁺, Zn²⁺ can form metal hydroxide, carbonate and sulfide precipitates. However, for continuous-flow operation, this kind of precipitation method requires the installation of separate chemical reaction tank and particle settling tanks. Besides, the settled precipitates still require further dewatering and/or solidification before the ultimate disposal. In the past five years, we have developed a single-step and space saving method for removing heavy metals from industrial wastewater using a fluidized sand bed. The new method is to allow soluble metals to become coated (or plated) on the sand surface through “nucleated precipitation”, which is also known as “pellet crystallization” (Huang and Li, 1997). This is a heterogeneous (surface) precipitation process, through which metals become deposited on sand particles (media) inside the reactor. It has been demonstrated that the presence of solid particles in solution can enhance the precipitation process. For example, metal precipitation can start when the concentration product of metals and inorganic ligands...
(precipitation barrier) is slightly higher than the $K_{sp}$ value in the presence of solids, while in homogeneous precipitation the concentration product must be approximately 40 to 50 times higher than the $K_{sp}$ value (Snoeyink and Jenkins, 1980). In our study using a synthetic soluble metal solution containing Cu, Ni, and Zn (each 60 mg/L), we were able to achieve 96–98% metal removal efficiency at pH 9.1 using the nucleated precipitation technology (Figure 1). For other initial metal concentrations, the removal efficiencies were mostly above 90% (Huang and Li, 1997; Huang, 1998; Huang, et al., 1999; Zhou, et al., 1999).

When we applied this technology to treat real plating wastewater containing fluctuating and higher metal concentrations (total metals exceeding 700 mg/L), besides the removal of copper and nickel, we also found that 50 to 60% of hexavalent chromium were co-removed, as shown in Figure 2. This was beyond our expectation since Cr(VI) does not react with either carbonate or hydroxide to form precipitates. Thus, this study was undertaken to examine the co-removal mechanisms.

**Experimental methods**

Experiments were carried out in a well-mixed batch reactor containing metal solutions to examine the co-removal of Cr(VI) with both copper and nickel. In this paper, only the co-removal with copper is addressed while the co-removal with nickel and zinc will be dealt with in a separate paper. During each batch test, a synthetic metal solution containing either only copper (150-mg/L Cu$^{2+}$) or copper plus chromium (150-mg/L Cu$^{2+}$ and 60-mg/L Cr$^{6+}$) was prepared. Then, 0.5-mN sodium carbonate solution was progressively dosed to the test solution through a burette to increase its pH and induce metal precipitation. At each intended pH, an equilibrium time of 20–30 minutes was allowed. Then 10-mL of the test solution was withdrawn and passed through a 0.45-µm membrane filter. The filtrate was acidified by concentrated HNO$_3$ for later AAS analysis to determine the remaining metal contents. In all cases, the test solutions were prepared from reagent grade chemicals (CuCl$_2$.2H$_2$O and K$_2$Cr$_2$O$_7$). Some of the produced precipitates were collected for EDAX and inorganic carbon analysis, and some were re-dissolved with nitric acid to determine...

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**Figure 1** High levels of heavy metal removal by nucleated precipitation

**Figure 2** Co-removal of hexavalent chromium during nucleated precipitation of Cu and Ni
their relative metal contents. Further, some copper carbonate precipitates were used to study their adsorption capacity for hexavalent chromium at different pH. The zeta potentials of copper carbonate surface charge were determined by a Zeta meter (Brookhaven Zeta Plus).

Measurements of pH were made using a pH meter (ORION 420-A, U.S.A). Daily calibrations with proper buffer solutions (pH 4.01, 7.00 and 10.01) were performed to ensure its accuracy. Soluble metal concentrations were determined by the *Standard Methods* 3500 (APHA, 1998) using an atomic absorption spectrophotometer (HITACHI Z-8200, Japan). The concentrations of soluble copper and chromium in each sample were determined by comparison with the calibration curves developed from a series of standard solutions prior to each analysis.

The carbonate content in copper carbonate precipitates was determined by a total carbon analyzer (Shimadzu TOC, Model-5000A, Japan) following the procedures set forth in *Standard Methods* 5310 (APHA, 1998). The measured carbon content was then used to determine the chemical composition of the metal precipitates.

**Results and discussion**

At the onset of this study, it was speculated that co-removal of chromium could be due to a couple of mechanisms: co-precipitation and adsorption. The term “co-precipitation” refers to the condition wherein aqueous copper and chromium interact with each other to form a precipitate that contain both copper and chromium with a defined stoichiometric relationship. On the other hand, adsorption refers to the situation in which Cr(VI) are adsorbed onto the surface of copper-bearing compound which is produced during the course of precipitation. There is no definite stoichiometric relationship between the adsorbent and the adsorbate (chromium).

To evaluate the mechanism of co-removal, we prepared two separate metal solutions: one containing only 150-mg/L copper and the other containing 150-mg/L copper plus 60-mg/L chromium. The initial pH was slightly above 2.0. Then for each solution, the pH was progressively increased by adding Na₂CO₃ to induce metal precipitation, which was evidenced by a reduction of soluble metal concentration. The test results are shown in Figure 3. For pure copper solution, precipitation of metal started at a pH of about 6.0, and all copper was precipitated out at pH of 7.0. From repeated determinations of the inorganic carbon contents in the precipitates (solids) obtained in the pH of 6.0 to 7.0, it was found that inorganic carbon accounted for 3.8 to 5.4% of the total dry weight of the solids. This seems to suggest that the precipitates contain a mixture of two compounds: CuCO₃.Cu(OH)₂ (containing 5.43% inorganic C) and CuCO₃.2Cu(OH)₂ (containing 3.77% inorganic C).

For the solution containing both copper and chromium, metal precipitation occurred at a much lower pH, around 5.0, and 98% of all copper was precipitated out at pH of 6.2. The relative percentages of copper and chromium remaining in solution at different pH are

![Figure 3](https://iwaponline.com/wst/article-pdf/46/4-5/413/426327/413.pdf)
shown in Figure 4. There are two important facts represented by the data shown in Figures 3 and 4. First, presence of chromium in the test solution was able to induce copper precipitation at one pH unit lower than that required for a pure copper solution. Second, precipitation of copper was always accompanied by some chromium removal, particularly at the very beginning of copper precipitation. The causes for these two phenomena may be reasonably explained as follows.

1. When pH approaches 5.0, copper and chromium (existing as chromate) interact with each other to form CuCrO$_4$ precipitate ($K_{sp} = 3.6 \times 10^{-6}$), and this is a “co-precipitation” phenomenon which contributes to the initial co-removal of chromium. Once CuCrO$_4$ is produced, the test solution becomes a heterogeneous phase which enhances the early formation of copper carbonate precipitates at a pH slightly higher than 5.0. As mentioned earlier from the inorganic carbon determination, the newly produced precipitates contain a mixture of CuCO$_3$, Cu(OH)$_2$ and CuCO$_3$.2Cu(OH)$_2$. Once the formation of copper carbonates starts, there is little, if any, further production of CuCrO$_4$ since its $K_{sp}$ value is much higher than that of copper carbonate ($K_{sp} = 1.4 \times 10^{-10}$) and copper hydroxide ($K_{sp} = 2.2 \times 10^{-20}$).

2. The copper carbonate precipitates produced at the lower pH (below 6.5) contain a high level of positive surface charges (as to be shown in the next section by zeta potential measurement), and thus, they are able to adsorb a certain amount of negatively charged chromate ions.

In order to verify the formation of CuCrO$_4$ during the co-precipitation stage, the precipitates produced at different pH were collected and rinsed with distilled water. Thereafter, the precipitates were dissolved in acid (5% HNO$_3$) solutions, and the resultant soluble copper and chromium concentrations were determined. The data were then used to calculate the [Cr]/[Cu] molar ratio of each precipitate. The results are shown in Figure 5. At pH of 5.0, the molar ratio was as high as 0.75, but the value quickly decreased to around 0.33 when pH was raised to 5.2. Evidently, at the low pH of 5.0, besides the formation of CuCrO$_4$, there was also some production of copper carbonate precipitates which resulted in a reduction of the [Cr]/[Cu] molar ratio. Although no data are shown here, in a separate test we intentionally increased the concentrations of both metals (i.e., 2,000 mg/L Cu and 10,000 mg/L Cr) to allow the co-precipitation to take place at a much lower pH, around 4.0. The molar [Cr]/[Cu] ratio for the produced precipitates was found to be 0.92. Thus, this seems to confirm that at low pH (less than 5.0), the main mechanism for chromium co-removal is by “co-precipitation”, through which CuCrO$_4$ is produced.

Upon confirming the “co-precipitation” process as the main mechanism for chromium co-removal at a low pH condition, our experimental tests were then extended to examine the other possible mechanism of the co-removal, i.e., “adsorption”. For this, we again prepared a 150 mg/L pure copper solution, to which Na$_2$CO$_3$ was added to induce copper precipitation.
precipitation at pH 7.0. Then the metal precipitates were settled, and rinsed 4 times with redistilled water before they were used to adsorb Cr(VI). The adsorption test was conducted in two different manners. The first was to allow adsorption to take place in a 60 mg/L Cr(VI) solution with an initial pH of 6.0. Upon equilibrical adsorption, the remaining soluble chromium was determined to calculate the extent of adsorption. Thereafter, the test solution pH was increased stepwise until it reached 10.0. At different target pH, the remaining concentrations of soluble chromium were measured, and the extents of chromium adsorption were determined. The results are shown by the solid line in Figure 6. The second test was conducted by preparing a series of chromium solutions, each having the same chromium concentration (60 mg/L), but adjusted to a different pH. Then to each solution was added a fixed amount of copper carbonate precipitates which were obtained from precipitating 150 mg/L copper with sodium carbonate. The extents of chromium adsorption at different pH were determined, as shown by the dashed line in Figure 6. It was found that in the first case, upon the initial chromium adsorption at pH 6.0, very little desorption took place by the subsequent increase of pH 10.0 (Figure 6). However, in the second case, the maximum adsorption took place at pH 5.5 to 6.5, but it quickly decreased at a higher pH. These data seem to suggest that the adsorption mechanism mainly involves electrostatic attraction and/or inorganic ligand exchange. At pH 5.5 to 6.5, the copper carbonate precipitates contain considerable amounts of positive surface charges, as evidenced by a high level of particles’ zeta potential as shown in Figure 7. These positive surface charges were able to attract the negatively charged monovalent HCrO$_4^-$ ions, which was the prevailing chromium species at this pH range. When the pH was progressively raised, the positive surface charges were quickly reduced (as shown by the reduction of zeta potential) and eventually shifted to the negative charge when the pH was higher than 7.5. At the same time, the chromium speciation was also shifted to the divalent CrO$_4^{2-}$. Both the reduction of
positive surface charge and the shifting of monovalent to divalent chromate form would cause a reduction of chromium adsorption. The data shown in Figure 6 also suggest that upon the initial chromium adsorption at pH 6.0, the adsorbed monovalent chromate (HCrO$_4^-$) are not converted to the divalent species (CrO$_4^{2-}$) by the subsequent increase of solution pH since there is very little desorption taking place at the higher pH. Upon adsorption of the negatively charged chromium, the zeta potential of copper carbonate precipitate was substantially. This further verifies that the adsorption mechanism is caused by electrostatic attraction, which reduces the intensity of positive surface charge on the adsorbent particles.

In order to gain a better insight into the quantitative incorporation of chromium into the copper precipitates, an EDAX analysis was made on some copper precipitates obtained from both co-precipitation and adsorption reactions, and the results are shown in Figure 8. It is clear that for a given amount of copper precipitates, the co-precipitation sample contains a much higher level of Cr than the adsorption sample.

Conclusions

The co-removal of Cr(VI) observed in the nucleated precipitation of copper is caused by two mechanisms: co-precipitation and adsorption. The former involves the formation of CuCrO$_4$ crystallites while the latter involves the attraction of negatively charged chromate ions to the positively charged copper carbonate precipitate. The exact pH for co-precipitation to occur depends on the concentration product of the two metals, but generally lies between 4.0 and 5.0. In this pH range, the co-precipitation mechanism accounts for the majority of chromium co-removal. After the formation of CuCrO$_4$ crystallites, the solution becomes a heterogeneous environment which can enhance an early production of copper carbonate particles at a pH lower than that required for the initiation of homogeneous precipitation (around pH 6.0). Once copper carbonate particles are produced, they are able to adsorb a certain amount of chromate ions. The extent of adsorption decreases with increasing solution pH since the quantity of positive surface charge on copper carbonate precipitates also decreases with increasing pH. The adsorption mechanism does not play a role in the chromium co-removal until there is some formation of the copper carbonate precipitates.

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