Study on Sludge Recirculation in a Metal Removal System

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This study was conducted with undergraduate students to evaluate the impact of chemical sludge recirculation on the overall removal efficiency and reduction of virgin chemicals. This project was also performed to demonstrate to students and faculty of the Civil Engineering Technology (CET) program at Southern Polytechnic State University (SPSU) the capabilities of the environmental laboratory, while encouraging the students to participate in applied research.

Studies conducted by Kolthoff and Overholser (1-2), and subsequent work by Davies, Leckie, Benjamin and others (3-7) have demonstrated the effectiveness of co-precipitation and the adsorptive capacity of hydrous oxides. Our intent was to increase the precipitate in contact with synthetic rinse water, and determine its impact on the overall efficiency of the precipitation process in two different scenarios. The first scenario evaluated consisted of a synthetic rinse water containing copper only. The second scenario consisted of rinse water containing different copper to iron ratios.

Materials

The precipitation experiments were conducted on synthetic rinse water containing approximately 50 mg/L Cu. Copper sulfate ($CuSO_4 . 5H_2O$, Fisher Scientific, Co.) was used as the copper source. The ionic background for the synthetic wastewater was maintained at approximately 10^{-2} M with sodium chloride. The pH of the rinse water was adjusted to 2.0 using HNO_3 (Fisher Scientific Co.). A Fe (III) stock solution prepared from $FeCl_3$ crystals (Fisher Scientific Co.) was used as a source of iron for the second set of experiments. Sodium hydroxide and calcium hydroxide solutions were used to adjust the pH, and to compare their effectiveness in the precipitation process.

Residual concentrations of copper were determined colorimetrically by reaction with bicinchoninic acid (Hach Methods)(8). This colorimetric method has an optimum operational range of 0.01 – 5.0 mg/L. All pH values were determined using an Accumet Basic pH meter Model AB15 (Fisher Scientific Co.), calibrated with certified Fisher Scientific buffer solutions at pH 4.0 and 7.0. Total suspended solids analyses were conducted according to the *Standard Methods* (9) on the recycled sludge.

Experimental Plan

The experimental plan of this study was developed to establish a base line for copper precipitation (one-component system), and compare these results with copper precipitation in the presence of iron (III) at different molar concentrations, with and without sludge recirculation (two-component system). Four different copper-to-iron ratios (1:0.45, 1:1, 1:1.5 and 1:2.5) and three recirculation rates (15, 30 and 50 mL/L) were investigated.

All experiments were performed in a jar test apparatus with square beakers to reduce the vortex effect. The samples were mixed in a jar test apparatus at 250 rpm for 1 minute, flocculated at 40 rpm for 15 minutes and finally allowed to settle for 45 minutes. Sludge separation took place immediately after the 45-minute sedimentation period on those samples used to generate fresh sludge. The addition of recycled sludge occurred immediately after fast mixing to avoid dissolution of the precipitate when put in contact with rinse water.

Samples of the supernatant were collected and analyzed for pH and total copper. Samples of the recycled sludge were analyzed for total suspended solids.

Results

The results of this study are analyzed as one-component or two-component systems. The one-component system corresponds to copper hydroxide precipitation, while the two-component system identifies the copper-iron precipitation process.

One-component system

The base line generated by precipitating copper with sodium or calcium hydroxides show that the two precipitants produce identical results (Figure 1). Consequently, the rest of the precipitation tests were conducted with calcium hydroxide. Recirculation of copper hydroxide at 15 mL/L and 25 mL/L did not produce any significant effect on copper removal when compared with precipitation without recirculation, as shown in Figure 2.

Two-component system

Copper-iron molar ratios of 1:0.2, 1:0.45,1:1 and 1:1.5 did not improve copper removal when compared with the results of the one-component system studied. However, an iron concentration of 110 mg/L, which corresponds to a copper-iron molar ratio of 1:2.5 enhances copper removal. At this copper-iron molar ratio, the pH range at which copper concentrations below 1 mg/L can be achieved by simple precipitation and sedimentation varies from 8.4 to 10.8 (Figure 3). This range is widened by approximately 1.3 units of pH, when compared with the pH range obtained in the one component system (9.7 to 10.7). Sludge recirculation at 15 mL/L and 30 mL/L increased the pH for precipitation even more. The pH for both recirculation rates, for effluent copper concentrations below 1 mg/L, varies approximately between 7.5 and 11.0 (Figure 4).

Figure 1. Copper Solubility Curves

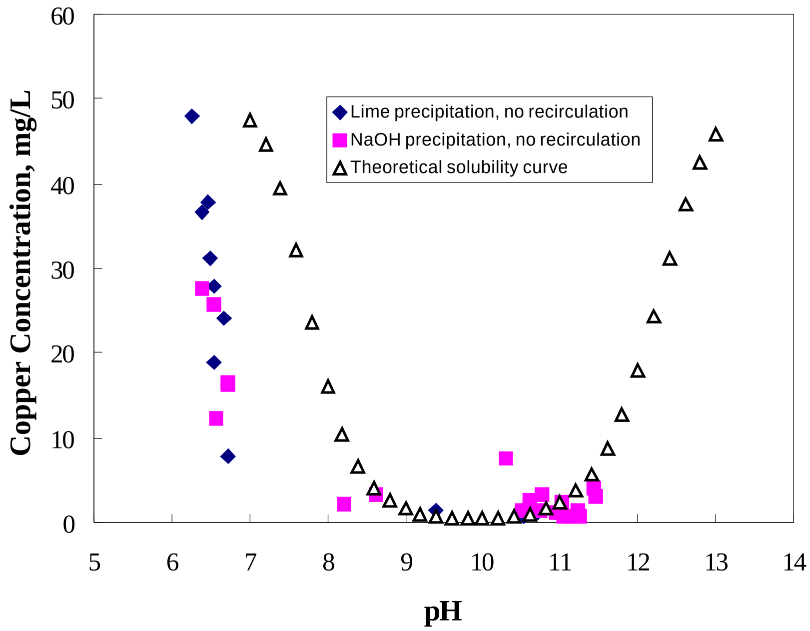


Figure 2. Copper Solubility with and without Sludge Recirculation

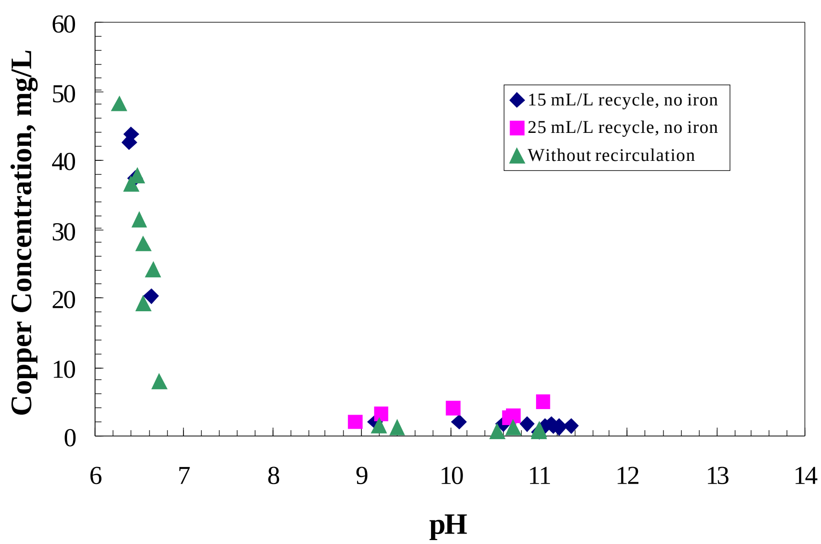


Figure 3. Copper Precipitation in Presence of Iron

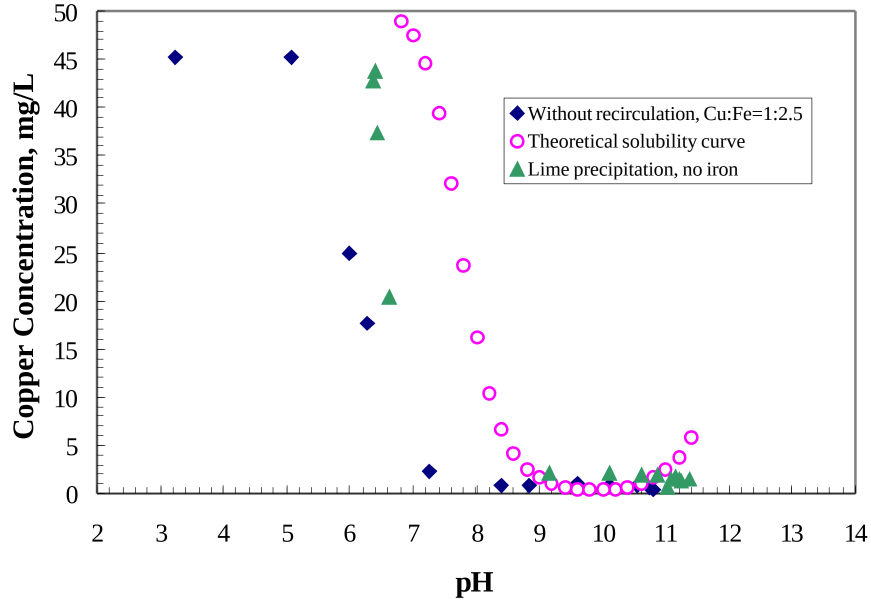
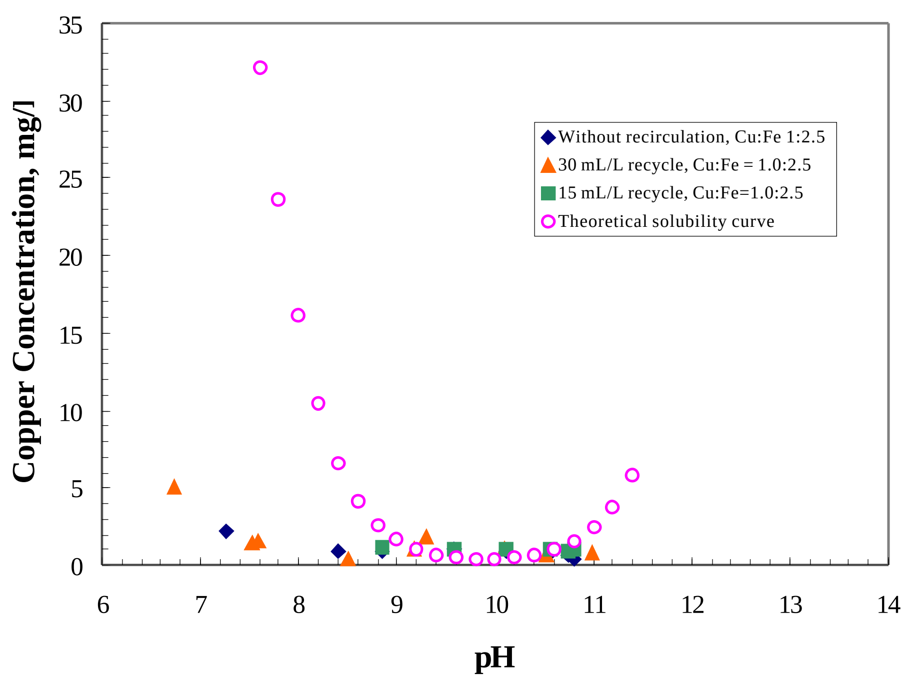


Figure 4. Copper Solubility in the Presence of 110 mg/L Fe



Based on experimental data, the amount of lime required to achieve a pH of 9.7 in a one-component system is approximately 2,750 mg/L. The amount of lime estimated to achieve a pH of 7.5 in a two-component system is approximately 900 mg/L. The reduction in the amount of lime would represent savings in the order of $ 8,614/year for a 40-liter per minute treatment system operating 24 hours per day, 365 days a year (Table 1).

Table 1. Reduction in Chemical Cost with Sludge Recirculation in a Copper:Iron Precipitation System

Precipitation System	Hydrated Lime Demand (lb/d)	Yearly Cost (@ $0.10/lb) [10]
Lime precipitation	350	$ 12,775
Lime:iron precipitation with sludge recirculation	114	$ 4,161

Lessons Learned

The experience gained during this study can be classified from the academic point of view and from the student perspective. From the academic point of view we learned three important lessons. The first lesson was that chemical sludge recirculation in the presence of iron may be a good alternative to improve operation strategies of metal precipitation systems. The second lesson refers to the balance between teaching and research. Since this was the first attempt to conduct an environmental study independent from academic laboratory experiments, this project exposed the demands of research vs. teaching in an institution dedicated almost exclusively to teaching and without graduate programs in engineering technology. It is extremely demanding for faculty to teach three different courses and conduct scholarly activities requiring laboratory work. Finally, despite the limitation of resources, it is possible to conduct studies that can motivate students to search for solutions to engineering problems.

From the student perspective, an appreciation was gained concerning the importance of valuable research in an academic environment. Perhaps for the first time, students were faced with real world applications and situations employing problem-solving skills along the subject lines for which they are studying. This type of research improves the skills and adds to the knowledge base of the student in a way that cannot be realized in the classroom environment. For example, the students witnessed firsthand the complexities of chemical addition in wastewater treatment, such as how small variations of chemicals produced a wide variety of results, most notably in sludge volumes. From a practical standpoint, students were faced with budget constraints and equipment limitations, and were challenged to complete the research in a method as accurate, yet cost effective, as possible.

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