Recovery of Cu(II) by chemical reduction using sodium dithionite: effect of pH and ligands
Yi-Hsuan Chou, Jui-Hsuan Yu, Yang-Min Liang, Pin-Jan Wang, Chi-Wang Li and Shiao-Shing Chen

ABSTRACT
Wastewaters containing Cu(II) and ligands are ubiquitous in various industrial sectors, and efficacy of copper removal processes, especially precipitation, is greatly compromised by ligands. Chemical reduction, being commonly employed for production of metal nanoparticles, is also effective for metal removal. Adjustment of pH and addition of ligands are important to control the particle size in metallic nanoparticle production. Exploiting the fact that ligands and metals coexist in many wastewaters, chemical reduction was employed to treat ligand-containing wastewater in this study. The experimental result shows that depending on pH, type of ligands, and copper:ligand molar ratio, copper could be removed by either the reduction or precipitation mechanism. Almost complete copper removal could be achieved by the reduction mechanism under optimal condition for solutions containing either EDTA (ethylenediaminetetraacetic acid) or citrate ligands. For solutions containing ammonia, depending on pH and Cu:ammonia molar ratio, copper was removed by both precipitation and reduction mechanisms. At pH of 9.0, formation of nano-sized particles, which readily pass through a 0.45 μm filter used for sample pretreatment before residual copper analysis, results in the lowest copper removal efficiency. Both cuprous oxide and metallic copper are identified in the solids produced, and the possible explanations are provided.

Key words | ammonium, citric acid, dithionite, EDTA, metallic copper, reduction

INTRODUCTION
Various industry sectors, such as semiconductor, printed circuit board (PCB), surface finishing, and electroplating, generate copper-containing wastewaters along with various organic or inorganic chelating agents such as cyanide, ammonia, EDTA (ethylenediaminetetraacetic acid), nitrilotriacetic acid, and citrate. Efficacy of treatment processes such as adsorption, coagulation or electrocoagulation for copper removal are greatly compromised by ligands (Jiang et al. 2008, 2010; Khelifa et al. 2015). Destruction of metal/chelate complexes is the key to obtain efficient metal removal (Jiang et al. 2008).

Chemical reduction has been employed for removing heavy metals using reductants such as borohydride (Gomez-Lahoz et al. 1992a, b), hydrazine (Chen & Lim 2002), and dithionite (Geoffroy & Demopoulos 2009; Wu et al. 2011a, b). Redox half-reaction equations of these three reductants are shown in reactions (1)–(3) with standard reduction potential (E°) ranging from −1.12 to −1.24 V (Chen & Lim 2002; Szecsody et al. 2004). Among these reductants, borohydride is the strongest reductant.

\[
\frac{1}{8} \text{BO}_2^- + \frac{3}{4} \text{H}_2\text{O} + \text{e}^- \leftrightarrow \frac{1}{8} \text{BH}_4^+ + \text{OH}^- \quad \text{E}^0 = -1.24 \text{ V} \quad (1)
\]

\[
\frac{1}{4} \text{N}_2 + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \frac{1}{4} \text{N}_2\text{H}_4 + \text{OH}^- \quad \text{E}^0 = -1.17 \text{ V} \quad (2)
\]

\[
\text{SO}_3^{2-} + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \frac{1}{2} \text{S}_2\text{O}_4^{2-} + 2\text{OH}^- \quad \text{E}^0 = -1.12 \text{ V} \quad (3)
\]

However, economical determination and metal reduction efficiency do not depend on the standard reduction potential alone. Other factors, such as chemical cost, pH and possibility of other side-reactions, also play crucial roles for selection of a suitable reductant. Table 1
shows the chemical cost of these reductants, found by searching for the price of the chemicals in bulk volume on the internet (www.alibaba.com/). Although the price of sodium borohydride per kilogram is the highest, the highest electron equivalent per mole of this chemical makes the cost of borohydride to reduce a kilogram of copper (assuming no other side-reaction except reduction of copper occurred) very comparable to the cost of sodium dithionite for a kilogram of copper reduced. Although the cost of hydrazine to reduce a kilogram of copper is the cheapest, dithionite is chosen in this study due to the extremely toxic and unstable nature of hydrazine.

The value of pH profoundly affects metal reduction efficiency. For example, the generation of hydrogen gas is a major side-reaction during copper reduction, and pH value has a great impact on copper reduction efficiency (Gomez-Lahoz et al. 1992a). A value of pH greater than 11 was suggested for reduction of metal using hydrazine (Chen & Lim 2002). It is known that dithionite decomposes rapidly via disproportional reaction under acidic conditions (Rinker et al. 1960; Geoffroy & Demopoulos 2009). Thus, Wu et al. (2011a) studied the reduction of copper under alkaline pH values, stating that the addition of ammonia to increase copper solubility is essential for improving copper reduction efficiency. The mechanism of copper reduction by dithionite in the presence of ammonia ligand was proposed by these authors as follows:

\[
\begin{align*}
\text{Cu}^{2+} + 4\text{NH}_3 & \rightarrow [\text{Cu(NH}_3)_4]^{2+} \\
[Cu(NH}_3)_4]^{2+} + S_2O_4^{2-} + 2\text{H}_2\text{O} & \rightarrow \text{Cu(s)} + 2\text{SO}_4^{2-} + \text{NH}_4^+ 
\end{align*}
\]

Other than alkaline pH values, Geoffroy & Demopoulos (2009) studied the reduction of selenite ions using sodium dithionite, reporting that the reduction reaction only occurs in acidic regions.

Based on this information, it is reasonable to assume that any ligands that could form complexes with copper, resulting in high copper solubility at alkaline pH values, will play the role of ammonia, as indicated by Wu et al. (2011a, b). To the best of our knowledge, no research has been conducted to investigate the effect of ligands on copper reduction by dithionite. Therefore, the objectives of this study are to investigate the effects of the type and concentration of ligands on reduction and removal of copper in consideration of the ubiquitous ligands such as ammonium, EDTA, and citric acids in metal-containing wastewater, and to study the effect of pH values on copper reduction and removal efficiency in consideration of both alkaline and acidic pH regions that have been reported for metal reduction using dithionite, and alkaline pH values explored by Wu et al. (2011a).

### EXPERIMENTAL

#### Chemical and materials

All chemicals are of reagent grade. Due to the instability of dithionite in solution, dithionite solution of 20.25 mM was prepared fresh before each experiment with sodium dithionite (Na$_2$S$_2$O$_4$, Alfa Aesar) dissolved in deionized water (DI). Copper solution (6.75 mM) was prepared by dissolving copper sulfate pentahydrate (Yakuri) in DI. EDTA (6.75 mM), citric acid (40.5 mM) and ammonia (54 or 27 mM) solutions were prepared, respectively, using EDTA disodium salt dehydrate (EDTA-Na$_2$), citric acid and ammonium hydroxide (NH$_4$OH) from J.T. Baker. NaOH and HNO$_3$ (both 1 N) were used for pH adjustment. Hydrogen peroxide solution (30%, Sigma) was used for termination of the reduction reaction.

#### Experimental methods

Solutions of copper and ligand of equal volume (50 mL) were mixed first with a magnetic stirrer or by aerating with N$_2$ gas. During mixing, pH of the mixture was adjusted to the desired value using NaOH or HNO$_3$. The chemical reduction reaction was then started with the addition of dithionite solution (50 mL). The resulting mixture has an initial copper

### Table 1 | Estimation of chemical cost for copper reduction using sodium dithionite, sodium borohydride and hydrazine

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Equivalent/mole</th>
<th>US$/kg</th>
<th>US$/Eq. mole</th>
<th>US$/kg Cu reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dithionite</td>
<td>2</td>
<td>0.6-2</td>
<td>52.23-174.11</td>
<td>1.64-5.48</td>
</tr>
<tr>
<td>Sodium borohydride</td>
<td>8</td>
<td>15-40</td>
<td>70.88-189</td>
<td>2.23-5.95</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>4</td>
<td>1-3</td>
<td>9.45-28.35</td>
<td>0.30-0.89</td>
</tr>
</tbody>
</table>

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concentration of 2.25 mM, and Cu:ligand:dithionite molar ratio is 1:1:3 and 1:6:3, respectively, for the EDTA system and citric acid system. Both 1:8:3 and 1:4:3 molar ratios are tested for the ammonia system. After 30 min, the reaction was terminated by adding a drop of H$_2$O$_2$. Samples were filtered with a 0.45 μm membrane filter and acidified with a drop of concentrated nitric acid before analysis for residual copper.

Analytical methods

Residual copper concentration was analyzed using a flame atomic absorption spectrophotometer (GBC 932 plus, Australia). The crystal phase of particles produced was identified using X-ray diffraction (XRD) analysis (Bruker AXS8 ADVANCEX ray diffraction system) by comparing the diffraction pattern with the database of the Joint Committee of Powder Diffraction Standards. A scanning electron microscope (SEM, Hitachi S-3000N) was used for analysis of particles collected.

RESULTS AND DISCUSSION

Effect of pH on reduction of Cu(II)

Copper removal efficiency as a function of pH ranging from 3 to 11 is shown in Figure 1, with Cu:ligand:N$_2$S$_2$O$_4$ molar ratio of 1:1:3 for the EDTA system, and both 1:8:3 and 1:4:3 for the ammonia system. Average copper removal efficiencies ranged from 72 to 100%, depending on pH, type of ligands, and Cu:ligand molar ratio. For solution containing EDTA ligand, the copper reduction/removal efficiency ranges from 96.6 to 99.6% with pH values ranging from 5 to 11, and it is only 85% at pH of 3.0. The lowest removal efficiency observed at a pH of 3.0 might be due to the rapid disproportional reaction of dithionite in the acidic condition (Rinker et al. 1960).

The rapid disproportional reaction of dithionite in the acidic condition, however, could not explain the pH effect on copper removal efficiency for the ammonia system. As indicated in Figure 1, the lowest removal efficiencies are observed at pH of 9.0. According to the copper species distribution modeled by commercial chemical equilibrium software (Mineql+), as shown in Figure 2, the dominant copper species at pH of 9.0 is Cu(OH)$_2$(S) and Cu(NH$_3$)$_4^{2+}$, respectively, for Cu:ammonia molar ratio of 1:4 and 1:8. For the solution with Cu:ammonia molar ratio of 1:4, the domination of Cu(OH)$_2$(S) indicated that copper hydroxide will precipitate upon pH adjustment. Indeed, the speculation is consistent with the appearance of solutions at the end of the reaction (see Figure 3) where the solution with

![Figure 1](https://iwaponline.com/wst/article-pdf/72/11/2089/465408/wst072112089.pdf)  
Effect of pH on reduction/removal of copper in the solution with Cu:ligand: Na$_2$S$_2$O$_4$ molar ratio of 1:8:3 and 1:4:3 for ammonia system and of 1:1:3 for EDTA system, respectively. Initial Cu concentration of 2.25 mM with magnetic stirring. Reaction time of 30 min. Error bars represent one standard deviation from the average of triplicate experiments with the exception of those for pH 7–11, for which five replicate experiments were conducted.

![Figure 2](https://iwaponline.com/wst/article-pdf/72/11/2089/465408/wst072112089.pdf)  
Distribution of Cu(II) species in ammonia system modeled by Mineql+ with assumption of close system. Cu:ammonia molar ratios of 1:4 and 1:8, respectively. Total copper concentration of 2.25 mM.
Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is green in color and murky, showing possible precipitation of copper hydroxide. As a result, copper removal observed at pH of 9.0 with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is possibly due to both precipitation of copper hydroxide and reduction of copper ions to metallic copper.

Conversely, the appearance of solution with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:8:3 at pH of 9.0 is red in color with very fine particles. Visual observation of filtrate of the solution through a 0.45 μm membrane shows a tea color, indicating the presence of copper nanoparticles. As a result, the low removal efficiency observed at this pH might be related to the production of nano-sized particles which readily pass through a 0.45 μm filter used for sample pretreatment before residual copper concentration analysis. In fact, in the production of nano-sized metallic particles several researchers (Wu & Chen 2004; Song et al. 2009; Chang et al. 2013; Tan & Cheong 2013; Sierra-Ávila et al. 2014) have stated the importance of pH adjustment and a capping agent or the addition of stabilizers in the control of the size of particles produced. Specifically, Wu & Chen (2004) reported the importance of ammonia addition for producing finer copper nanoparticles where ammonia ions not only can adjust solution pH but also act as a capping agent.

Other than EDTA, citrate is also a very common organic ligand, being found in typical copper-containing wastewater in the PCB production process (Industrial Process Cleaner Production and Green Technology Network n.d.). In this study, copper reduction in the presence of citrate was investigated with Cu:citrate molar ratio of 1:6 at pH of 6.0 where the dominant copper species are CuCit⁻ and Cu₂Cit⁺. As indicated in Figure 4, almost 100% of copper could be removed by reduction at a reaction time of 2 min. The result is very similar to those with a presence of EDTA, indicating that copper reduction by dithionite is quite effective at natural pH as long as copper ions are not precipitated.

**Solid analysis**

As indicated above, both precipitation of copper hydroxide and reduction of copper ions to metallic copper are the possible mechanisms for copper removal with Cu:ammonium: dithionite molar ratio of 1:4:5 at pH of 9.0. Thus, particle samples collected from experiments were subjected to XRD analysis, to identify the crystal phase of particles, and SEM analysis. Since these solids contain possibly both...
amorphous copper hydroxide solids as well as reduced metallic copper particles, a fraction of the samples was washed with DI several times to remove these fluffy copper hydroxide solids. Samples with or without DI washing were air dried and subjected to XRD and SEM analysis. As indicated in Figure 5(a) and 5(b), both cuprous oxide and metallic copper were identified in these samples. After washing with DI to remove amorphous copper hydroxide solid, the intensity of XRD signals is much higher than that of the sample without the DI washing. Wu et al. (2014) indicated that oxidation of metallic copper particles by atmospheric oxygen at the surface during sample handling is the possible reason that cuprous oxides are identified. It is possible that incomplete reduction of copper(II) ions during the reduction process might also result in the formation of cuprous oxides (Chang et al. 2015). Figure 5(c) and 5(d) are SEM pictures of particles before and after DI washing. The former shows some fluffy and amorphous solids. After washing with DI, particles with octahedral geometry, which is the possible geometric structure of cuprous oxides (Wu et al. 2014), appeared in the SEM picture.

CONCLUSIONS

In this study, solutions containing copper and ligands were treated with chemical reduction. Copper ions could be removed by either reduction or precipitation mechanisms depending on pH, type of ligands, and copper to ligand molar ratio. With the presence of EDTA or citrate ligands to prevent copper ions from precipitation, addition of dithionite to reduce copper is quite effective and extremely fast at natural pH. Under optimal conditions, a removal efficiency of more than 99% could be achieved. With ammonia ligand, the low removal efficiency at pH 9.0 might be related to the size of particles produced, as nano-sized particles readily pass through a 0.45 μm filter employed for sample pretreatment before residual copper concentration analysis. Both cuprous oxide and metallic copper are identified in the reduced solids. Re-oxidation of metallic copper particles by atmospheric oxygen during sample handling or incomplete reduction of Cu(II) ions during the reduction process might be the cause.

ACKNOWLEDGEMENT

The study was supported by the Ministry of Science and Technology of Taiwan under Grant Numbers 103-2221-E-052-001.

REFERENCES

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First received 27 February 2015; accepted in revised form 23 July 2015. Available online 17 August 2015