



Recovery of Cu(II) by chemical reduction using sodium dithionite



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HIGHLIGHTS

- Chemical reduction was employed to treat ligand-containing wastewater.
- Ligand type, pH, and mixing condition affect removal efficiency and mechanism.
- Cuprous and copper oxides are identified in the treated samples.

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ABSTRACT

Wastewaters containing Cu(II) along with ligands are ubiquitous in various industrial sectors. Efficacy of treatment processes for copper removal, especially precipitation, is greatly debilitated by ligands. Chemical reduction being commonly employed for production of metal nanoparticles has also been used for removing copper. Addition of ammonia was reported to be essential for improving copper reduction efficiency by increasing copper solubility at alkaline pH values. In this study, chemical reduction was employed to treat ligand-containing wastewater, exploiting the fact that ligands and metals are coexisted in many wastewaters. Result shows that copper ions were removed by either reduction or precipitation mechanisms depending on pH, type of ligands, and mixing condition. Complete copper reduction/removal was achieved under optimal condition. The lowest removal efficiency observed at pH 9.0 for ammonia system is due to formation of nano-sized particles, which are readily to pass through 0.45 μm filter used for sample pretreatment before copper analysis. Instead of producing metallic copper, cuprous and copper oxide are identified in the samples collected from ammonia system and EDTA system, respectively. Re-oxidation of metallic copper particles by atmospheric oxygen during sample handling or incomplete reduction of Cu(II) ions during reduction process might be the cause. Finally, reduction process was applied to treat real wastewater, achieving complete removal of copper but only 10% of nickel.

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1. Introduction

Copper-containing wastewaters are generated in various industry sectors, such as semiconductor, printed circuit board (PCB), surface finishing, and electroplating. Other than heavy metals, these wastewaters come with various organic or inorganic chelating agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), cyanide, and ammonia, which make removal of heavy metals from these wastewaters much more challenging (Jiang et al., 2008, 2010; Khelifa et al., 2013). It has been shown that metal removal efficiency by adsorption, coagulation or electrocoagulation is greatly impaired by presence of EDTA (Izquierdo et al., 2013; Khelifa et al., 2013). Destruction of

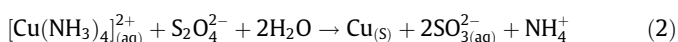
metal/chelate complexes is the key to obtain efficient metal removal (Jiang et al., 2008).

Electrochemical reduction of metals was proved to be an effective method for treating ligand/metal-containing wastewater (Huang et al., 2000; Voglar and Lestan, 2012). While metal is reduced and removed by cathode-deposition in electrochemical process, ligands are degraded simultaneously in anode, making reuse of these ligands impossible. To prevent anodic oxidation of chelating agents, separation of anodic and cathodic chambers with a cationic membrane was proposed (Juang and Lin, 2000). However, current efficiency is quite low (~30%) with ionic exchange membrane installed, and very low operation pH of 2.2 has to be maintained for efficient copper recovery. Meanwhile, anolyte has to contain enough concentration of sodium salts to prevent pH rising in the cathodic chamber and to reduce EDTA or NTA precipitation on to the membrane surface (Juang and Lin, 2000).

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Several researchers (Gomez-Lahoz et al., 1992a, 1992b; Chen and Lim, 2002; Geoffroy and Demopoulos, 2009; Wu et al., 2011a, 2011b) had explored chemical reduction for removal of heavy metals. The most of these studies suggested that alkaline pH values should be maintained to optimize the metal removal efficiency. For example, using sodium borohydride as the reductant for copper removal, Gomez-Lahoz et al. (1992a) recommended that the alkaline pH condition should be maintained in order to minimize the formation of hydrogen gas through the reaction of H⁺ with borohydride. The pH value as high as 11 was suggested by Chen and Lim (2002) who studied chemical reduction of precious metals by hydrazine. Wu et al. (2011a, 2011b) investigated recovery of copper ions as metallic copper by chemical reduction using dithionite. Without elaborating the reason why reduction reaction has to be conducted at alkaline condition, the authors stated that addition of ammonia to increase copper solubility at alkaline pH values was essential for improving copper reduction efficiency (Wu et al., 2011a). In their studies, pH values of high than 9.2 were maintained for the dominance of ammonia over ammonium, and the mechanism of copper reduction by dithionite in the presence of ammonia ligand was presented as follows:



It is known that dithionite decomposes rapidly via disproportionation reaction under the acidic condition (Geoffroy and Demopoulos, 2009), and this might be the underlying reason that alkaline pH values were investigated in the above-mentioned studies. Based on these information, it is reasonable to assume that any ligands that could form complexes with copper, resulting in high solubility of copper at alkaline pH values, will act the same role as did ammonia in the studies by Wu et al. (2011a, 2011b). Therefore, in this study we take the advantage of ligands, such as EDTA, that are ubiquitous in metal-containing wastewater and use sodium dithionite as reductant to reduce and recover copper.

Other than alkaline pH values, researchers have shown reductive precipitation of elemental selenium from selenious acidic solutions using sodium dithionite, reporting that the reduction reaction only occurs in acidic region (Geoffroy and Demopoulos, 2009). **Meanwhile, optimum pH of 2.5 has been reported for reduction of Cr(VI) to Cr(III) by bisulfite (Barrera-Díaz et al., 2012).** Therefore, reduction of copper under acidic pH region is warranted to be studied further.

Meanwhile, in the above mentioned studies the authors reported that the copper particles produced by chemical reduction were very small, and subsequent solid/liquid separation processes were needed. For example, Wu et al. (2011a, 2011b) integrated a high gradient magnetic separation system to remove metallic copper particles formed by chemical reduction. The size of copper particles ranges from less than 0.2 μm to around 0.5–1 μm depending on dithionite concentration (Wu et al., 2011a). Flocculation-sedimentation and sand filtration were employed by Gomez-Lahoz et al. (1992b) due to the very fine metal sludge produced. Actually, chemical reduction has long been employed for the production of metal nanoparticles (Chen et al., 2006; Hashemipour et al., 2011; Umer et al., 2012; Chang et al., 2013; Tan and Cheong, 2013) with the size of particles depending on the type of reductants, pH adjustment, and capping agent or stabilizers addition (Chen et al., 2006; Song et al., 2009; Chang et al., 2013; Tan and Cheong, 2013; Sierra-Ávila et al., 2014). In the current study, chemical reduction is employed as a wastewater treatment process, and the formation of nanoparticles should be avoided. Therefore, effects of pH and ligands on the size of particle produced and metal removal efficiency will be investigated.

It was shown that oxidation of dithionite is first order with respect to molecular oxygen and is one-half order with respect to the concentration of dithionite (Rinker et al., 1960). Therefore, dissolved oxygen will be a crucial factor affecting copper reduction efficiency. In this study, three mixing conditions, namely mechanical mixing by magnetic stir bar (oxygen-limited condition), mixing with air (oxygen-rich condition), and mixing with nitrogen gas (oxygen-depleted condition), are also conducted to explore the effect of mixing condition on copper reduction.

2. Experimental section

2.1. Chemical and materials

All chemicals are of reagent grade. Due to instability of dithionite in solution, dithionite solution of 20.25 mM was prepared fresh before each experiment by dissolving sodium dithionite (Na₂S₂O₄, Alfa Aesar) in deionized water (DI). Copper solution (6.75 mM) was prepared by dissolving copper sulfate pentahydrate (YAKURI) in DI. EDTA (6.75 mM) and ammonia (54 mM) solutions were prepared, respectively, using ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA-Na₂) and ammonium hydroxide (NH₄OH) from J.T. Baker. NaOH and HNO₃ (both 1 N) were used for pH adjustment. Hydrogen peroxide solution (30%, SIGMA) was used for termination of reduction reaction.

Chemical reduction was applied to treat liquid waste collected from the plated through holes (PTH) process in a PCB production line from a company in Taiwan specializing in production of flexible printed circuit (FPC) boards. The wasted liquid is denoted as copper sulfate liquid waste by the company. The sample was collected and tested within 2 d.

2.2. Experimental methods

Solutions of copper and ligand (EDTA or ammonia) of equal volume (50 mL) were mixed first with magnetic stirrer or by aerating with air or N₂ gas. During mixing, pH of mixture was adjusted to the desired value using NaOH or HNO₃. Chemical reduction reaction was then started with addition of dithionite solution (50 mL). The resulting mixture has initial copper concentration of 2.25 mM, and Cu:ligand:dithionite molar ratio of 1:1:3 and 1:8:3, respectively, for EDTA and ammonia systems. After 30 min, reaction was terminated by adding a drop of H₂O₂. Samples were filtered with 0.45 μm membrane filter and acidified with a drop of concentrated nitric acid before analysis for residual copper.

Chemical reduction was also used to treat sample collected from PCB production process with copper:dithionite molar ratio of 1:3 and without pH adjustment. Samples for residual copper analysis were taken at different reaction time, filtered with 0.45 μm membrane filter and acidified with a drop of concentrated nitric acid.

2.3. Analytical methods

A flame atomic absorption (AA) spectrophotometer (GBC 932 plus, Australia) was used for analysis of copper concentration. X-ray diffraction (XRD) analysis (Bruker AXSD8 ADVANCEX-ray diffraction system) was employed to identify the crystal phase of particles by comparing the diffraction pattern with the database of the Joint Committee of Powder Diffraction Standards (JCPDS). A field emission electron microscope (JEM-2100F, JEOL) operated at 200 kV was used to obtain transmission electron microscope (TEM) images. Sample for TEM analysis was prepared by placing a drop of filtrate through 0.45 μm membrane filter on a silicon wafer covered by carbon-coated copper grid, followed by drying

under vacuum at ambient temperature. A UV–Vis spectrophotometer (ThermoSpectronic, Helios Beta) was used to scan the surface plasmon resonance of nanoparticles (Soomro et al., 2014). Oxidation reduction potential (ORP) was measured using an ORP meter (HO-480, Horiba Advanced Techno, Japan). Total organic carbon (TOC) was analyzed using a TOC analyzer (TOC-V, Simadzu, Japan).

3. Results and discussion

3.1. Effect of pH on reduction of Cu(II)

Fig. 1 shows copper removal efficiency as function of pH ranging from 3 to 11 with Cu:ligand:Na₂S₂O₄ molar ratio of 1:1:3 and 1:8:3, respectively, for EDTA and ammonia solutions. Solution was mixed for 30 min with magnetic stir bar. For solution containing EDTA ligand, copper reduction/removal efficiency of 96.6–99.6% could be achieved with pH values ranging from 5 to 11, and it is 85% at pH of 3.0. The lowest removal efficiency observed at pH of 3.0 does comply with rapid disproportional reaction of dithionite in the acidic condition (Rinker et al., 1960). The lowest removal efficiency could be also related to the speciation of copper in different pH values. Geoffroy and Demopoulos (2009) reported that reduction of selenious acid to selenium using sodium dithionite only occurred in acids region, envisioning that hydrogen selenite ions, which is dominated species at pH > 2.5, might be nonreactive toward dithionite. In the current study, the lowest copper removal efficiency observed at pH 3.0 could also be explained by the domination of CuHEDTA⁻¹ over CuEDTA⁻² species (dominated species in the pH region of 4–11) at pH of 3.0 (see Fig. S1) with the former not being as reactive as the latter toward dithionite.

The rapid disproportional reaction of dithionite in the acidic condition, however, could not explain pH effect on copper reduction efficiency for ammonia system. As indicated in Fig. 1, almost 100% removal efficiency could be achieved at all pH values tested except pH 9.0. The effectiveness of copper reduction at acidic pH region is contradicted to those reported by Wu et al. (2011a) who believed that copper reduction was more effective at the alkaline pH region and addition of ammonia was essential for improving reduction efficiency by increasing copper solubility at alkaline pH. In Wu et al. (2011a) study, around 99% of copper removal

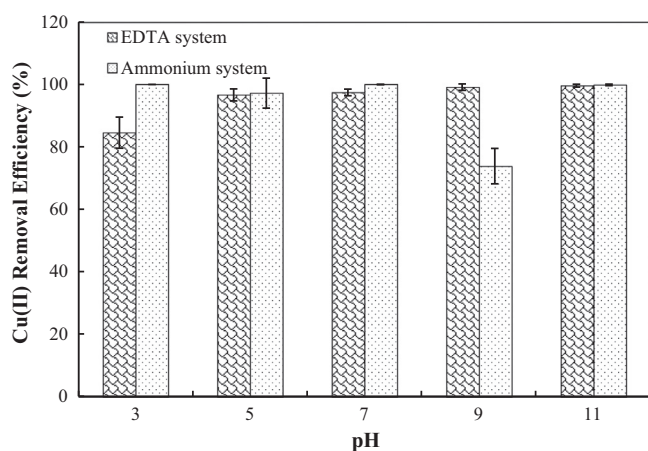


Fig. 1. Effect of pH on reduction/removal of copper in the solution with Cu:ligand:Na₂S₂O₄ molar ratio of 1:8:3 and 1:1:3 for ammonia and EDTA systems, respectively. Initial Cu concentration of 2.25 mM with magnetic stirring. Reaction time of 30 min. Error bars represent one standard deviation from the average of triplicate experiments with exception of those for pH 7–11 in which five replicate experiments were conducted.

efficiency was achieved with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 and pH of 9.5. To test if Cu:ammonia ratio might cause this discrepancy on pH effect observed in this study and study by Wu et al. (2011a), reduction experiment with solution having Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 was conducted at pH of 9.0, achieving ~95% of copper removal efficiency (data not shown). However, appearance of solution at the end of reaction (see Fig. S2) is quite different from that with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:8:3 (see Fig. 2). The solution with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is green in color and murky, showing possible precipitation of copper hydroxide. As indicated in Fig. S3, at pH of 9.0 about 40% of copper is in the form of Cu(OH)₂, which has already precipitated before addition of dithionite. As the result, effective copper removal observed in pH of 9.0 with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is due to precipitation of copper hydroxide instead of reduction reaction.

On the other hand, copper/ammonia complexes are the dominant copper species at pH values ranging 7–10 with Cu:ammonia ratio of 1:8 (see Fig. S4), and precipitation of Cu(OH)₂ is no longer possible except at the pH value of 11.0. As indicated in Fig. 2, with pH values of 3–7, very big aggregated particles were produced and easily settled to the bottom of beakers. The samples for residual copper analysis, i.e., filtrate of 0.45 μm filter, are clear. However, the solution at pH 9.0 is red in color with very fine particles presented, and the filtrate of this has tea color. The color of solution at pH of 11.0 is also different, showing greenish in color with fluffy flocs. As indicated in Fig. S4, formation of Cu(OH)₂ is possible at this pH, and the completed copper removal (as indicated in the clear filtrate) is due to both precipitation and reduction mechanisms.

The low removal efficiency at pH of 9.0 might be related to the size of reduced particles. In production of metallic nanoparticles, several authors (Song et al., 2009; Chang et al., 2013; Tan and Cheong, 2013; Sierra-Ávila et al., 2014) have stated the important of pH adjustment and capping agent or stabilizers addition in control of the size of particles produced. For example, Chang et al. (2013) showed that adding ammonium salt of poly(acrylic acid) (PAA-NH₄) during reduction formation of metallic copper particles could reduce particle size from 150 to 200 nm without addition of PAA-NH₄ to less than 50 nm with addition of PAA-NH₄. Wu and Chen (2004) reported the importance of ammonia addition for producing finer copper nanoparticles where ammonia ions not only can adjust solution pH and but also act as complex agent. To elucidate the possible cause of low removal efficiency at pH of 9.0, TEM analysis of the filtered sample were conducted. As indicated in Fig. 3(A), particles in the filtrate are in the nano-size region with size of around 5–10 nm (see inset figure). A UV–Vis spectrum of the filtrate (shown in Fig. S5) does not show distinguishable surface plasmon resonance peaks at 560–590 nm region (Soomro et al., 2014) rather show a shoulder at wavelength of greater than 560. It might be due to the very small nanoparticles present (Brumbaugh et al., 2014). Clear lattice spacings of copper could be seen by zooming in the particles as indicated in Fig. 3(B). The spacing of 0.24 nm, corresponding to (1 1 1) lattice planes of Cu₂O (Chen et al., 2005; Zhu et al., 2013). On the other hand, some aggregated particles with size of around 300–500 nm could be seen in the unfiltered sample (see Fig. 3(C)).

3.2. Effect of mixing condition on copper reduction efficiency

It was shown that oxidation of dithionite is first order with respect to molecular oxygen and is one-half order with respect to the concentration of dithionite (Rinker et al., 1960). Meanwhile, Cu nanopowders are chemically unstable and are readily re-oxidized by dissolved oxygen (DO) (Chang et al., 2013; Tan and Cheong, 2013). Thus, dissolved oxygen concentration will be

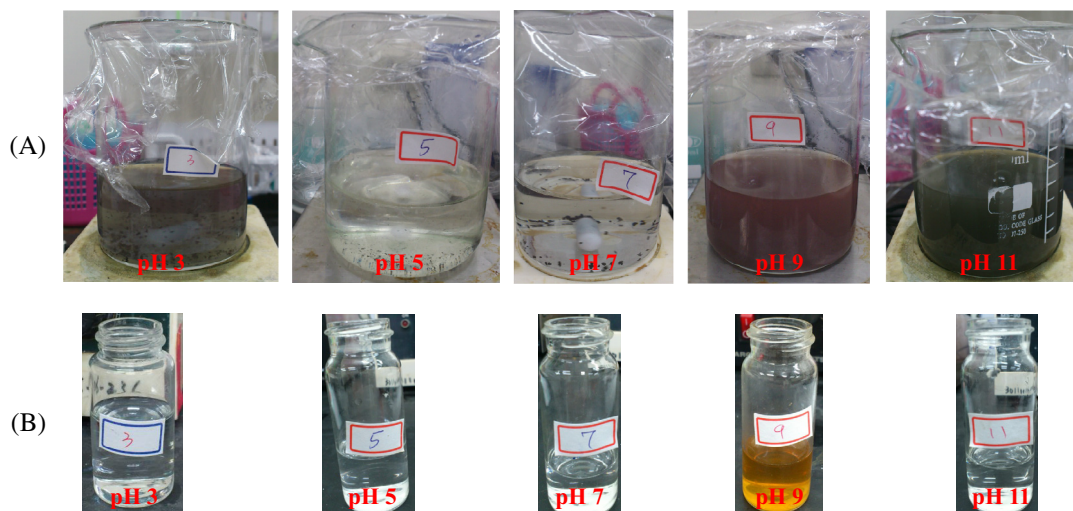


Fig. 2. Photos of (A) solution and (B) filtrate with various reaction pH values. Cu:ammonium:Na₂S₂O₄ molar ratio of 1:8:3. Initial Cu concentration of 2.25 mM with magnetic stirring. Reaction time of 30 min.

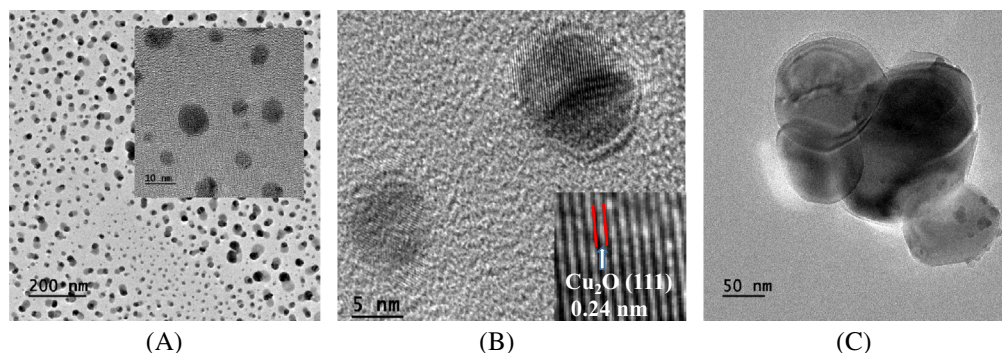


Fig. 3. (A) TEM of particles in the sample filtered through 0.45 μm filter, (B) close-up view of TEM picture to show lattice spacing of copper, and (C) TEM of particles before filtration. Experimental conditions: Cu:ammonia:Na₂S₂O₄ molar ratio of 1:8:3. Reaction pH of 9.0. Initial Cu concentration of 2.25 mM. Reaction time of 30 min.

a crucial factor affecting copper reduction efficiency. In this section, effect of mixing condition on copper reduction efficiency was conducted. Other than magnetic stirring, mixing with nitrogen gas or air purging were also studied. Both copper removal

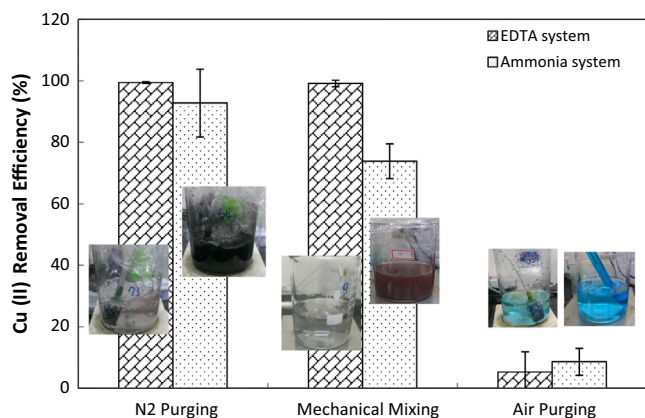


Fig. 4. Effect of gas purging or mixing with magnetic stirring on copper removal efficiency at pH 9. Experimental conditions: Cu:ligand:Na₂S₂O₄ molar ratio of 1:8:3 and 1:1:3 for ammonia and EDTA systems, respectively. Initial Cu concentration of 2.25 mM. Reaction time of 30 min. Error bars represent one standard deviation from the average of triplicate experiments.

efficiency and photos of solution taken at the end of reaction are shown in Fig. 4. The removal efficiency are in the order of N₂ purging > Mixing > air purging for both EDTA and ammonia systems. With N₂ purging, re-oxidation of chemically unstable Cu nanopowders is minimized (Chang et al., 2013; Tan and Cheong, 2013), and reduction efficiency is the highest. On the contrary, solution with air purging shows typical copper(II) blue color, indicating that dithionite is oxidized and/or Cu nanopowders is re-oxidized by DO.

3.3. Solid analysis

Particle samples collected from experiments with N₂-purging at pH of 9.0 were subjected to XRD analysis to identify the crystal phase of particles. As indicated in Fig. 5, cuprous oxide is the only crystal phase identified for sample collected from ammonia system, and cupric oxide is identified in the sample collected from EDTA system. The same finding was reported by Wu et al. (2011a), and these authors indicated that oxidation of metallic copper particles by atmospheric oxygen at the surface is the main reason that only cuprous and cupric oxides are identified. Other than re-oxidation of metallic copper nanoparticles by atmospheric oxygen during sample handling, incomplete reduction of copper(II) ions during reduction process might also result in the formation of cupric or cuprous oxides (Chang et al., 2013). Based on the

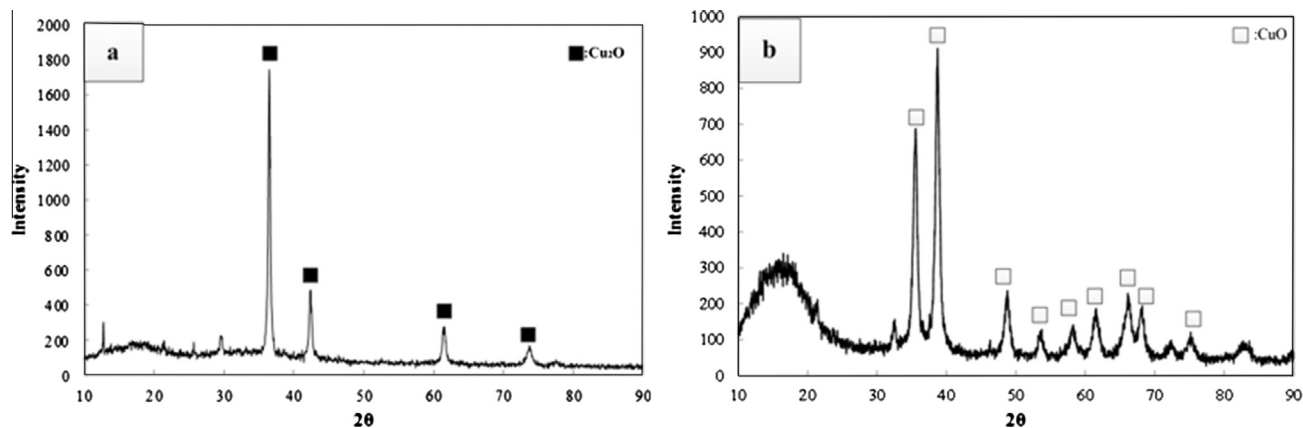


Fig. 5. XRD analysis of dried copper particles collected from experiments with only magnetic stirring at pH 9.0. (a) Particles from ammonia system. (b) Particles from EDTA system.

Table 1

Water quality parameters for wastewater collected from PCB production process before and after chemical reduction.

Parameters	Copper (mg L ⁻¹)	Nickel (mg L ⁻¹)	ORP (mV)	pH	TOC (mg L ⁻¹)
Raw water	4450.9	115.4	805	1.0	910
Treated water	2.9	101.0	35	1.0	691

observation of color of particles in the solution (see Fig. 4), i.e., black color (characteristic color of cupric oxide) in EDTA system, incomplete reduction of copper(II) ions during reduction reaction might be the main reason that metallic copper is not found in this study.

3.4. Copper sulfate liquid waste treated by chemical reduction

Copper sulfate liquid waste collected from PCB production process was treated with chemical reduction. As indicated in Table 1, the wastewater contains mainly copper ions with concentration of 4450.9 mg L⁻¹, and nickel ions with concentration of 115.4 mg L⁻¹. Other than heavy metals, there are organic materials, presumably organic ligands according to the information provided by PCB manufacturer, in the sample with TOC of 910.3 mg L⁻¹. Meanwhile, oxidation reduction potential of the sample is quite high (805 mV) which might be due to the very acidic pH of 1.0. Due to proprietary reasons, the company did not disclose the information about the organic materials contributing to TOC in the sample, and no attempt was made to identify them in this study as well.

Without adjustment of pH, dithionite was added to the liquid waste with copper:Na₂S₂O₄ molar ratio of 1:3. Right after reductant added, ORP dropped below 0 mV, and then rose gradually to 35 mV. The value of pH remained unchanged throughout the experiment. As indicated in Fig. 6, almost 100% of copper removal efficiency is achieved by chemical reduction at the reaction time of 5 min, while it is merely 10% for nickel removal efficiency. Photo of solution taken right after dithionite added is shown in Fig. S6(A), showing characteristic black color of cupric oxide. Meanwhile, the particles formed are quite big and settle easily when solution is not mixing (see Fig. S6(B)). Finally, as indicated in Fig. S6(C) the filtrate (through 0.45 μm filter) is very clear. The residual copper and nickel concentrations are 2.9 mg L⁻¹ and 101 mg L⁻¹, respectively, as indicated in Table 1. Chemical reduction could achieve discharge limit set by Taiwan EPA for copper (3 mg L⁻¹) but not nickel (1 mg L⁻¹). Further treatment is needed for nickel and TOC removal.

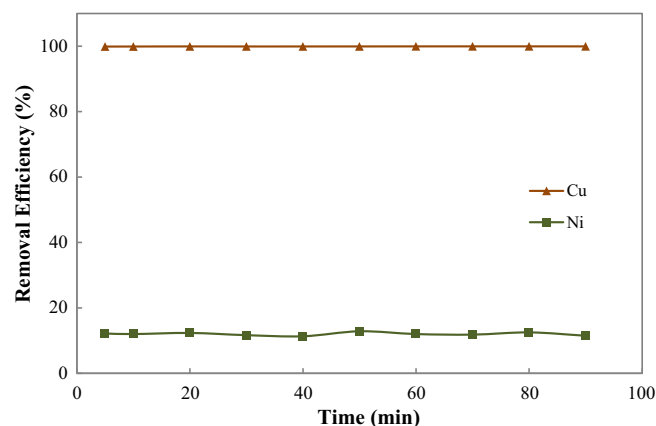


Fig. 6. Metal removal efficiency as a function of time for copper sulfate liquid waste collected from PCB production process. Copper:Na₂S₂O₄ molar ratio of 1:3.

4. Conclusions

In this study, chemical reduction with sodium dithionite was employed to recover copper from solution containing ligands. Result shows that copper ions could be removed by either reduction or simply precipitation mechanisms. Efficiency and mechanism of copper removal depend on pH, type of ligands, and mixing condition. Under optimal condition, removal efficiency of more than 99% could be achieved. For solution containing EDTA ligand, 96.6–99.6% of copper reduction/removal efficiency could be achieved with pH values ranging from 5 to 11, and it is only 85% at pH of 3.0. The lowest removal efficiency observed at pH of 3.0 does comply with rapid disproportional reaction of dithionite in the acidic condition.

Almost 100% removal efficiency could be achieved in ammonia system at all pH values tested except pH 9.0. The low removal efficiency at pH 9.0 might be related to the size of particles produced in which nano-sized particles are readily to pass through 0.45 μm filter used for sample pretreatment before residual copper concentration analysis.

Instead of producing metallic copper, cuprous and copper oxide are identified for samples collected from ammonia system and EDTA system, respectively. Re-oxidation of metallic copper particles by atmospheric oxygen during sample handling or incomplete reduction of Cu(II) ions during reduction process might be the cause.

Copper sulfate liquid waste collected from PCB production process was treated with chemical reduction. Chemical reduction

could achieve almost 100% of copper removal efficiency, complying the discharge limit set by Taiwan EPA for copper. However, it is not effective for removing nickel, achieving merely 10% of removal efficiency. Further treatment is needed for nickel and TOC removal.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2015.07.016>.

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