

25 removal efficiency observed at pH 9.0 for ammonia system is due to the formation of
26 nano-sized particles, which are readily to pass through 0.45 μm filter used for sample
27 pretreatment before residual copper analysis. Instead of producing metallic copper,
28 cuprous and copper oxide are identified in the samples collected from ammonia
29 system and EDTA system, respectively. Re-oxidation of metallic copper particles by
30 atmospheric oxygen during sample handling or incomplete reduction of Cu(II) ions
31 during reduction process might be the cause.

32 *Keywords: reduction; ligands; dithionite; metallic copper*

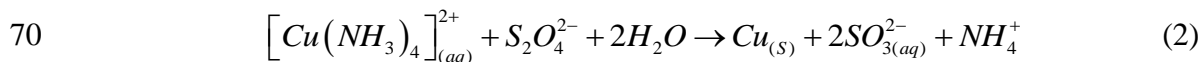
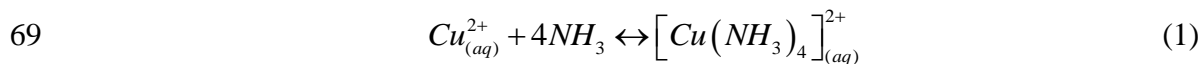
33 **1. Introduction**

34 Copper-containing wastewaters are generated in various industry sectors, such as
35 semiconductor, printed circuit board, surface finishing, and electroplating. Other than
36 heavy metals, these wastewaters come with various organic or inorganic chelating
37 agents such as EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid),
38 cyanide, and ammonia, which make removal of heavy metals from these wastewaters
39 much more challenging (Jiang et al. 2008, Jiang et al. 2010, Khelifa et al. 2013). It has
40 been shown that metal removal efficiency by adsorption, coagulation or
41 electrocoagulation is greatly impaired by presence of EDTA (Izquierdo et al. 2013,
42 Khelifa et al. 2013). Destruction of metal/chelate complexes is the key to obtain
43 efficient metal removal (Jiang et al. 2008).

44 Electrochemical reduction of metals was proved to be an effective method for
45 treating ligand/metal-containing wastewater (Huang et al. 2000, Voglar and Lestan
46 2012). While metal is reduced and removed by cathode-deposition in electrochemical
47 process, ligands are degraded simultaneously in anode, making reuse of these ligands
48 impossible. To prevent anodic oxidation of chelating agents, separation of anodic and
49 cathodic chambers with a cationic membrane was proposed (Juang and Lin 2000).
50 However, current efficiency is quite low (~30%) after membrane installed, and very
51 low operation pH of 2.2 has to be maintained for efficient copper recovery.
52 Meanwhile, anolyte has to contain enough concentration of sodium salts to prevent
53 pH rising in the cathodic chamber and to reduce EDTA or NTA precipitation on to the
54 membrane surface (Juang and Lin 2000).

55 Chemical reduction has been employed for production of metal nanoparticles
56 (Chang et al. 2013, Chen et al. 2006, Hashemipour et al. 2011, Park et al. 2007, Tan
57 and Cheong 2013, Umer et al. 2012), removal of heavy metals (Chen and Lim 2002,
58 Geoffroy and Demopoulos 2009, Gomez-Lahoz et al. 1992a, b, Wu et al. 2011a, Wu
59 et al. 2011b), and degradation of dyes (Gemeay 2002, Srividya et al. 1994). Wu et al.
60 (Wu et al. 2011a, Wu et al. 2011b) investigated recovery of copper ions as metallic
61 copper by chemical reduction using dithionite followed by separation of copper
62 particles with a high gradient magnetic separation system. Without elaborating the

63 reason why reduction reaction has to be conducted at alkaline condition, the authors
64 stated that addition of ammonia to increase copper solubility at alkaline pH values
65 was essential for improving copper reduction efficiency (Wu et al. 2011a). In their
66 studies, pH values of high than 9.2 were maintained for the dominance of ammonia
67 over ammonium, and the mechanism of copper reduction by dithionite in the presence
68 of ammonia ligand was presented as follows:



71 It is known that dithionite decomposes rapidly via disproportionation reaction under
72 the acidic condition (Geoffroy and Demopoulos 2009, Rinker et al. 1960), and this
73 might be the underlying reason that alkaline pH values were investigated in the
74 above-mentioned studies. Based on these information, it is reasonable to assume that
75 any ligands that could form complexes with copper, resulting in high solubility of
76 copper at alkaline pH values, will act the same role as did ammonia in the studies by
77 Wu et al. (Wu et al. 2011a, Wu et al. 2011b). Therefore, in this study we take the
78 advantage of ligands, such as EDTA, that are ubiquitous in metal-containing
79 wastewater and use sodium dithionite as reductant to reduce and recover copper.

80 Other than alkaline pH values, researchers have shown reductive precipitation of
81 elemental selenium from selenious acidic solutions using sodium dithionite, reporting

82 that the reduction reaction only occurs in acidic region (Geoffroy and Demopoulos
83 2009). Meanwhile, optimum pH of 2.5 has been reported for reduction of Cr(VI) to
84 Cr(III) by bisulfite (Barrera-Díaz et al. 2012). Therefore, reduction of copper under
85 acidic pH region will also be investigated in this study.

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

93 **2. Experimental section**

94 *2.1 Chemical and Materials*

95 All chemicals are of reagent grade. Due to instability of dithionite in solution,
96 dithionite solution of 20.25 mM was prepared fresh before each experiment by
97 dissolving sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$, Alfa Aesar) in deionized water (DI). Copper
98 solution (6.75 mM) was prepared by dissolving copper sulfate pentahydrate (YAKURI)
99 in DI. EDTA (6.75 mM) and ammonia (54 mM) solutions were prepared, respectively,
100 using ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA-Na_2) and
101 ammonium hydroxide (NH_4OH) from J.T. Baker. NaOH and HNO_3 (both 1 N) were

102 used for pH adjustment. Hydrogen peroxide solution (30%, SIGMA) was used for
103 termination of reduction reaction.

104 *2.2 Experimental methods*

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

114 *2.3 Analytical methods*

115 A flame atomic absorption (AA) spectrophotometer (GBC 932 plus, Australia)
116 was used for analysis of copper concentration. X-ray diffraction (XRD) analysis
117 (Bruker AXSD8 ADVANCEX-ray diffraction system) was employed to identify the
118 crystal phase of particles by comparing the diffraction pattern with the database of the
119 Joint Committee of Powder Diffraction Standards (JCPDS). A field emission electron
120 microscope (JEM-2100F, JEOL) operated at 200 kV was used to obtain transmission
121 electron microscope (TEM) images. Sample for TEM analysis was prepared by

122 placing a drop of filtrate through 0.45 μm membrane filter on a silicon wafer covered
123 by carbon-coated copper grid, followed by drying under vacuum at ambient
124 temperature. A UV–vis spectrophotometer (ThermoSpectronic, Helios Beta) was used
125 to scan the surface plasmon resonance of nanoparticles (Soomro et al. 2014).

126 **3. Results and Discussion**

127 *3.1 Effect of pH on reduction of Cu(II)*

128 Figure 1 shows copper removal efficiency as function of pH ranging from 3 to 11
129 with Cu:ligand: $\text{Na}_2\text{S}_2\text{O}_4$ molar ratio of 1:1:3 and 1:8:3, respectively, for EDTA and
130 ammonia solutions. Solution was mixed for 30 min with magnetic stir bar. For
131 solution containing EDTA ligand, copper reduction/removal efficiency of 96.6 to
132 99.6% could be achieved with pH values ranging from 5 to 11, and it is 85% at pH of
133 3.0. The lowest removal efficiency observed at pH of 3.0 does comply with rapid
134 disproportional reaction of dithionite in the acidic condition (Rinker et al. 1960). The
135 lowest removal efficiency could be also related to the speciation of copper in different
136 pH values. Geoffroy and Demopoulos (2009) reported that reduction of selenious acid
137 to selenium using sodium dithionite only occurred in acids region, envisioning that
138 hydrogen selenite ions, which is dominated species at $\text{pH} > 2.5$, might be nonreactive
139 toward dithionite. In the current study, the lowest copper removal efficiency observed
140 at pH 3.0 could also be explained by the domination of CuHEDTA^{-1} over CuEDTA^{-2}
141 species (dominated species in the pH region of 4 to 11) at pH of 3.0 (see Figure S1)

142 with the former not being as reactive as the latter toward dithionite.

143

144 [Insert Figure 1 here]

145

146 The rapid disproportional reaction of dithionite in the acidic condition, however,

147 could not explain pH effect on copper reduction efficiency for ammonia system. As

148 indicated in Figure 1, almost 100% removal efficiency could be achieved at all pH

149 values tested except pH 9.0. The effectiveness of copper reduction at acidic pH region

150 is contradicted to those reported by Wu et al. (2011a) who believed that copper

151 reduction was more effective at the alkaline pH region and addition of ammonia was

152 essential for improving reduction efficiency by increasing copper solubility at alkaline

153 pH. In Wu et al. (2011a) study, around 99% of copper removal efficiency was

154 achieved with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 and pH of 9.5. To test if

155 Cu:ammonia ratio might cause this discrepancy on pH effect observed in this study

156 and study by Wu et al. (2011a), reduction experiment with solution having

157 Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 was conducted at pH of 9.0, achieving

158 ~95% of copper removal efficiency (data not shown). However, appearance of

159 solution at the end of reaction (see Figure S2) is quite different from that with

160 Cu:ammonia:Na₂S₂O₄ molar ratio of 1:8:3 (See Figure 2). The solution with

161 Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is green in color and murky, showing
162 possible precipitation of copper hydroxide. As indicated in Figure S3, at pH of 9.0
163 about 40% of copper is in the form of Cu(OH)₂, which has already precipitated before
164 addition of dithionite. As the result, effective copper removal observed in pH of 9.0
165 with Cu:ammonia:Na₂S₂O₄ molar ratio of 1:4:3 is due to precipitation of copper
166 hydroxide instead of reduction reaction.

167

168 [Insert Figure 2 here]

169

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

180 precipitation and reduction mechanisms.

181 The low removal efficiency at pH of 9.0 might be related to the size of reduced
182 particles. In production of metallic nanoparticles, several authors (Chang et al. 2013,
183 Sierra-Ávila et al. 2014, Song et al. 2009, Tan and Cheong 2013) have stated the
184 importance of pH adjustment and capping agent or stabilizers addition in control of the
185 size of particles produced. For example, Chang et al. (2013) showed that adding
186 ammonium salt of poly(acrylic acid) (PAA-NH₄) during reduction formation of
187 metallic copper particles could reduce particle size from 150-200 nm without addition
188 of PAA-NH₄ to less than 50 nm with addition of PAA-NH₄. Wu and Chen (2004)
189 reported the importance of ammonia addition for producing finer copper nanoparticles
190 where ammonia ions not only can adjust solution pH and but also act as complex
191 agent. To elucidate the possible cause of low removal efficiency at pH of 9.0, TEM
192 analysis of the filtered sample were conducted. As indicated in Figure 3 (A), in the
193 filtrate particles are in the nano-size region with size of around 5-10 nm (see inset
194 figure). A UV-Vis spectrum of the filtrate (shown in Figure S5) does not show
195 distinguishable surface plasmon resonance peaks at 560-590 nm region (Soomro et al.
196 2014), showing a shoulder at wavelength of greater than 560. It might be due to the
197 very small nanoparticles present (Brumbaugh et al. 2014). Clear lattice spacings of
198 copper could be seen by zooming in the particles as indicated in Figure 3 (B). On the

199 other hand, some aggregated particles with size of around 300-500 nm could be seen
200 in the unfiltered sample (see Figure 3(C)).

201

202 [Insert Figure 3 here]

203

204 3. 2 *Effect of mixing condition on copper reduction efficiency*

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

209 Thus, dissolved oxygen concentration will be a crucial factor affecting copper
210 reduction efficiency. In this section, effect of mixing condition on copper reduction
211 efficiency was conducted. Other than magnetic stirring, mixing with nitrogen gas or
212 air purging were also studied. Both copper removal efficiency and photos of solution
213 taken at the end of reaction are shown in Figure 4. The removal efficiency are in the
214 order of N₂ purging>Mixing>air purging for both EDTA and ammonia systems. With
215 N₂ purging, re-oxidation of chemically unstable Cu nanopowders is minimized
216 (Chang et al. 2013, Tan and Cheong 2013), and reduction efficiency is the highest. On
217 the contrary, solution with air purging shows typical copper(II) blue color, indicating

218 that dithionite is oxidized and/or Cu nanopowders is re-oxidized by DO.

219

220 [Insert Figure 4 here]

221

222 3.3 Solid analysis

223 Particle samples collected from experiments with N₂ purging at pH of 9.0 were
224 subjected to XRD analysis to identify the crystal phase of particles. As indicated in
225 Figure 5, cuprous oxide is the only crystal phase identified for sample collected from
226 ammonia system, and cupric oxide is identified in the sample collected from EDTA
227 system. The same finding was reported by Wu et al. (2011a), and these authors
228 indicated that oxidation of metallic copper particles by atmospheric oxygen at the
229 surface is the main reason that only cuprous and cupric oxides are identified. Other
230 than re-oxidation of metallic copper nanoparticles by atmospheric oxygen during
231 sample handling, incomplete reduction of copper(II) ions during reduction process
232 might also result in the formation of cupric or cuprous oxides (Chang et al. 2013).
233 Based on the observation of color of particles in the solution (see Figure 4), i.e., black
234 color (characteristic color of cupric oxide) in EDTA system, incomplete reduction of
235 copper(II) ions during reduction reaction might be the main reason that metallic
236 copper is not found in this study.

237

238

[Insert Figure 5 here]

239

240 **4. Conclusions**

241 In this study, chemical reduction with sodium dithionite was employed to recover

242 copper from solution containing ligands. Result shows that copper ions could be

243 removed by either reduction or simply precipitation mechanisms. Efficiency and

244 mechanism of copper removal depend on pH, type of ligands, and mixing condition.

245 Under optimal condition, removal efficiency of more than 99% could be achieved.

246 For solution containing EDTA ligand, 96.6 to 99.6% of copper reduction/removal

247 efficiency could be achieved with pH values ranging from 5 to 11, and it is only 85%

248 at pH of 3.0. The lowest removal efficiency observed at pH of 3.0 does comply with

249 rapid disproportional reaction of dithionite in the acidic condition.

250 Almost 100% removal efficiency could be achieved in ammonia system at all pH

251 values tested except pH 9.0. The low removal efficiency at pH 9.0 might be related to

252 the size of particles produced in which nano-sized particles are readily to pass through

253 0.45 μm filter used for sample pretreatment before residual copper concentration

254 analysis.

255 Instead of producing metallic copper, cuprous and copper oxide are identified for

256 samples collected from ammonia system and EDTA system, respectively.
257 Re-oxidation of metallic copper particles by atmospheric oxygen during sample
258 handling or incomplete reduction of Cu(II) ions during reduction process might be the
259 cause.

260 **Acknowledgement**

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List of Figure caption

Figure 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 to 11 in which five replicate experiments were conducted.

Figure 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.

Figure 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.

Figure 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.

Figure 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.