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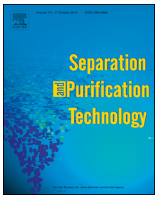

Effect of EDTA and CH_2O on copper recovery from simulated electroless copper plating spent rinse water by unseeded fluidized-bed granulation process

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ABSTRACT

Copper-contaminated industrial wastewaters are usually treated by large-footprint conventional technologies that generate high-moisture sludge. These disadvantages led to the development of the unseeded fluidized-bed granulation process (UFBGP), an innovative green technology with potential to simultaneously remove copper from electroless copper plating spent rinse waters and recover them as high-quality granules. Electroless copper plating rinse water is a complex aqueous matrix containing copper ions and organic additives such as ethylenediaminetetraacetic acid (EDTA) and formaldehyde (CH_2O) as complexing and reducing agents, respectively. Herein, we investigated copper removal and granulation from simulated electroless copper plating spent rinse waters containing EDTA and CH_2O via the unseeded fluidized-bed granulation process. Results showed that copper removal and granulation from simulated spent rinse waters containing 186 mg L^{-1} EDTA reached 93% and 78%, respectively. On the other hand, copper removal and granulation from simulated spent rinse waters with 0.019 mg L^{-1} CH_2O were 99% and 90%, respectively. However, simulated spent rinse waters containing both EDTA and CH_2O had copper removal and granulation of 94% and 84%, respectively. Scanning electron microscope images of the recovered granules showed clusters of irregularly-shaped spherical solids while the X-ray diffractograms of the solids revealed crystalline properties identical to those of the mineral azurite. Overall, the study demonstrated the effectiveness of the UFBGP in recovering high-quality copper granules from simulated industrial wastewaters.

1. Introduction

Copper (Cu) is a soft, reddish-gold, malleable metal usually found in minerals such as chalcocite (Cu_2S) and chalcopyrite ($CuFeS_2$) [1]. It is essential for living organisms but is not readily metabolized. While an average human adult needs a daily copper dosage of 1.2 mg, excessive copper intake is toxic and prolonged human exposure to copper even in low amounts may lead to irritation of the eyes, nose and mouth; kidney and liver damage, and even death [2]. Nevertheless, copper is continuously being mined for its excellent material properties such as high electrical and thermal conductivities. In the past decade, the rapid population growth and the development of urban lifestyle accelerated the global demands for copper. However, copper is non-renewable, non-biodegradable and can potentially bioaccumulate in organisms [3]. Hence, copper removal and recovery from various industrial waste streams is now becoming more relevant. High concentrations of copper can be found in wastewaters from metal finishing and electroplating processes [4]. Meanwhile, the United States Environmental Protection Agency or US EPA requires adequate treatment of copper contaminated industrial wastewaters and limits copper concentrations of effluents to 1.3 mg L^{-1} prior to their discharge to recipient waters [5,6].

Electroless or autocatalytic copper plating is a non-galvanic process of immobilizing copper on a substrate to enhance the aesthetic appearance of the material via the chemical reduction of copper ions in aqueous solution. It is different from immersion plating where the surface of the substrate is displaced by a more noble metal in solution such as when an iron substrate is immersed in a copper sulfate solution, iron dissolves and copper is plated on the surface of the substrate [7,8]. Both processes, however, do not require electric current to deposit a uniform copper thickness of about 127 μm on the target material [9].

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Copper-laden wastewaters arise from the alkali-free plating solutions which are repeatedly-used before disposal. These solutions contain 0.05–0.1 M copper, and some additives including 0.1 M ethylenediaminetetraacetic acid and 0.01 M formaldehyde which act as complexing and reducing agents, respectively [10]. After several turnovers, the bath is disposed and replaced by a fresh solution especially when the copper concentration in the bath is no longer adequate to provide good quality coating in successive plating operations [11]. Only 30–40% of the total copper in solution is effectively used in the plating process while the rest (up to 1000 mg L^{-1}) contaminates the spent rinse waters [12].

Several technologies are available for the treatment of electroless copper plating spent rinse waters such as chemical precipitation [13], ion exchange [14], membrane filtration [15], coagulation/flocculation [16], electrolytic recovery [11], reverse osmosis [17] and adsorption [18]. However, membrane filtration and reverse osmosis are limited by the high cost of membranes and problems associated with membrane fouling while electrolytic recovery is hampered by the high cost of electricity. On the other hand, ion-exchange and adsorption are inadequate in treating high-copper effluents and suffer from expensive disposal of spent adsorbents. Conventional chemical precipitation, though widely-used, requires a large footprint and generates high-moisture sludge that is difficult to handle.

These disadvantages of conventional chemical precipitation had been addressed by the fluidized-bed crystallization process [19–21], a technology superior to others because it also provides vigorous mixing and a large surface area (3,000–10,000 m^2/m^3) for reaction [22]. Its effectiveness in treating effluents containing phosphorus, fluoride and heavy metals such as Cu, Zn and Pb had been demonstrated [20,23,24]. The main drawback of the process, however, is its use of seed materials such as quartz or silica sand, which are of different composition as the desired product. The low quality of the recovered products impedes their usability.

The unseeded fluidized-bed granulation process (UFBGP) was developed to address product quality issues. Like its predecessor, (i) it offers a small footprint because of its vertical reactor configuration, (ii) it is efficient in metal removal and recovery, (iii) its operating cost is low, and (iv) its products have negligible moisture content (1–5%) [25–27]. The main difference is that UFBGP does not use seed materials which could compromise product purity and quality [28]. In addition, the technology has been applied to remove and recover heavy metals from synthetic wastewater such as Pb^{2+} [28], Ni^{2+} [25,29], Al^{3+} [30,31] Cu^{2+} [32], Zn^{2+} [33], and even organic salts in the form of phosphorus [34,35], oxalate [26], and calcium [21]. It has been demonstrated as a promising CO_2 capture technology specifically in the conversion of carbon dioxide trapped in water matrices into large, compact, high-purity, calcium carbonate granules [36]. Nevertheless, this technology has not been used to treat electroless copper plating spent rinse waters.

Herein, we investigated the applicability of the unseeded fluidized-bed granulation process in removing copper from simulated electroless-copper-plating spent rinse waters containing ethylenediaminetetraacetic acid and formaldehyde even without any preliminary treatment, and simultaneously recovering copper as a usable product. In this study, the influence of ethylenediaminetetraacetic acid and formaldehyde on copper removal and recovery was examined. In addition, the characteristics of the recovered products were analyzed by scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction spectroscopy.

2. Materials and methods

2.1. Chemicals

The simulated electroless copper plating spent rinse water was prepared using anhydrous copper sulfate ($CuSO_4·5H_2O$, > 99%, Shimakyu's Pure Chemicals), ethylenediaminetetraacetic acid or EDTA ($C_{10}H_{16}N_2O_8$, 99%, Scharlau) and formaldehyde (CH_2O, 37%, Katayama Chemical Co., Ltd.). Sodium carbonate (Na_2CO_3, > 99.5%, Panreac) was used as the precipitant solution. For the adjustment of solution pH, either nitric acid (HNO_3, 65%, Merck) or sodium hydroxide (NaOH, > 99%, Merck) was utilized. The standard solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ cm (Millipore System), while the simulated wastewater and precipitant solutions were prepared using reverse osmosis (RO) water.

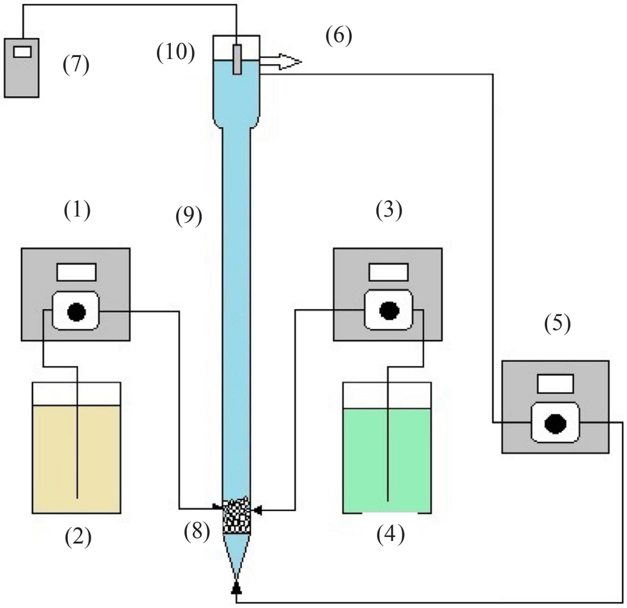

Fig. 1. Scheme of the fluidized bed system: (1) peristaltic pump for a precipitant solution, (2) precipitant solution tank, (3) peristaltic pump for a copper plating solution, (4) copper plating solution tank, (5) peristaltic pump for reflux flow, (6) effluent discharge, (7) pH/ORP meter, (8) glass beads, (9) reaction region, (10) effluent region.

2.2. Fluidized-bed set-up

The fluidized bed granulation set-up was composed of a 480-mL bench-scale cylindrical fluidized-bed reactor with three inlet ports at the reactor bottom, each connected to a peristaltic pump (Masterflex® L/S with Easy-Load 3 pump head, 77800-50, Cole-Parmer) to separately deliver (i) simulated electroless-copper-plating spent rinse water, (ii) precipitant solution and (iii) combined mixture reflux into the reactor (Fig. 1). The fluidized bed reactor can be subdivided into 2 distinct regions. The upper or effluent region had a diameter of 4.0 cm and 20.0 cm in height, while the lower or reaction region had a 2.0 cm diameter and a height of 80 cm. The larger diameter of the effluent region compared to the reaction region serves to reduce the fluid velocity from the reaction to the effluent region thereby preventing fine particles from going out with the effluent. The reflux flow, on the other hand, returns a portion of the combined mixture into the fluidized bed reactor so that fine particles continue to aggregate, increase in size and eventually form into granules. Glass beads, each with a diameter of 0.5 cm, were placed at the bottom of the reactor and packed at a height of 4.0 cm to ensure homogeneous fluid distribution into the reaction region and to provide a stable settling bed for the heavy granules. All experiments were conducted in triplicate runs at temperatures between 25–29 °C.

2.3. Granulation runs

The flow rates of the simulated spent rinse water and the precipitant

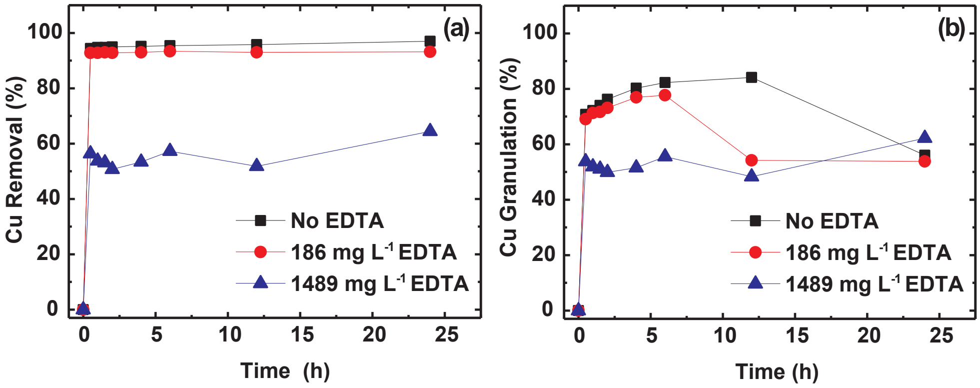

Fig. 2. Effect of varying EDTA concentration on (a) Cu removal and (b) Cu granulation.

solution were set to 25 mL min^{-1}. Reflux pump flow rate, however, was initially set at 5.5 mL min^{-1} and when the combined solution reached the reflux zone of the reactor, the flow rate was gradually increased to 35 mL min^{-1} to maintain bed fluidization. Influent copper concentration was maintained at 191 mg L^{-1} while the precipitant-to-metal molar ratio, $[CO_3^{2-}/\ Cu^{2+}]$ was varied at 0.5 intervals from 2.0–3.0. Simulated spent rinse waters containing EDTA concentrations of 186 and 1489 mg L^{-1} were used to evaluate the effect of EDTA on copper removal and granulation. Moreover, simulated spent rinse waters containing CH_2O concentrations of 0.15 and 0.019 mg L^{-1} were used to evaluate the effect of CH_2O on copper removal and granulation. Simulated wastewater containing both EDTA and CH_2O were likewise evaluated. Effluent pH was monitored by a pH/ORP meter (Suntex) throughout each run and the values ranged from 9.0 to 11.0. At the effluent region, two 15-mL samples were drawn from the reflux zone at predetermined intervals. One sample was unfiltered while the other was filtered with a 0.2-μm filter (0.2 μm GHP membrane, Pall). Both samples were acidified to pH < 2 using HNO_3 for digestion and stored in the refrigerator at 4 °C. The granules were recovered at the end of the 24 h run, then rinsed, air-dried, and characterized.

2.4. Determination of copper concentration in the effluent

Initial and residual copper concentrations were analyzed by an atomic absorption spectrometer (AAS, PerkinElmer AAnalyst 200) with a Lumina™ hollow cathode lamp for copper. Copper concentration in the filtrate defined removal efficiency. Cu removal (%) evaluates the reactions between copper ion $[Cu^{2+}]$ and the precipitant $[CO_3^{2-}]$ that can produce solid granules as presented in Eq. (1):

$$\text{Cu removal (\%)} = \frac{C_0 - C_D}{C_0} \times 100 \tag{1}$$

where C_0 is the influent copper concentration and C_D is the concentration of dissolved copper in the filtrate. The copper concentration in the unfiltered sample determines the amount of recovered copper as granules. Cu recovery (%) refers to the percentage of fine particles clustered together forming bigger granules as shown in Eq. (2):

$$\text{Cu recovery (\%)} = \frac{C_0 - C_D - C_F}{C_0} \times 100 \tag{2}$$

where C_F is the amount of copper as fines in the unfiltered sample.

2.5. Characterization of the recovered granules

The surface morphology of the recovered granules was analyzed by scanning electron microscopy (SEM, JEOL JXA-840, HITACHI S4100, Japan) while the surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR, Jasco FT/IR – 400). The crystalline phases of the granules were evaluated by an X-ray diffraction spectrometer (XRD – DX-2000 SSC, Rigaku) using Cu $K\alpha_{1+2}$ radiation of $\lambda(\alpha_1) = 0.154060$ nm and $\lambda(\alpha_2) = 0.154443$ nm at 30 mA and 40 kV. The sizes of the granules for each run was analyzed using Tyler sieves of varying mesh diameters.

3. Results and discussion

3.1. Effect of EDTA on copper removal and granulation

Ethylenediaminetetraacetic acid or EDTA ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$) is a widely-used complexing agent in electroless copper plating solutions. EDTA controls the rate of plating, grain composition, and other significant aspects [37]. In this study, the EDTA concentrations used in the simulated spent rinse waters were 186 and 1489 mg L^{-1} and the effects of EDTA on the copper removal and granulation were evaluated. The values for the range of EDTA concentrations were based on the reported concentrations of the complexing agent in actual electroless copper plating solutions.

In Fig. 2, copper removal from simulated plating wastewater in the absence of EDTA ranged from 94–96% while copper granulation reached a maximum of 84%. In the presence of high EDTA concentration of 1489 mg L^{-1}, low copper removal of 64% was achieved while copper granulation ranged from 54–62%. Lowering EDTA concentration to 1/8 of the previous concentration improved copper removal to 93% while copper granulation ranged from 54–78%. In aqueous phase, EDTA exists in its protonated form and readily binds with heavy metals usually at a 1:1 molar ratio to produce a stable complex and this reaction proceeds according to Eq. (3) [38].

$$Cu^{2+}(aq) + EDTA^{2-}(aq) \rightarrow CuEDTA^{2-}(aq) + 2H^{+}(aq) \tag{3}$$

Because of this, the treatment of effluents containing metal complexes becomes more difficult. Conventional chemical precipitation is inhibited because EDTA attracts toxic metals and the metal complex species remain dissolved in the waste stream [39]. Thus, copper in its complex form is difficult to precipitate. However, equilibrium is shifted by adding increased amounts of the precipitant. Nevertheless, copper and EDTA complexation limits the availability of copper ions for granule formation. The presence of EDTA inhibits the growth of granules by decreasing the growth site that leads to lower granulation. It is also possible to relate the decrease in granulation to the dissolution of granules and the formation of more fines. [25,40].

3.2. Effect of CH_2O on copper removal and granulation

Formaldehyde or CH_2O is the most commonly-used reducing agent for electroless copper plating applications. When a surface catalyzed work piece metal is immersed in the electroless copper plating solution with 1–3 mg L^{-1} of CH_2O, the copper in the solution is plated out onto the surface of the metal [41]. The presence of CH_2O with

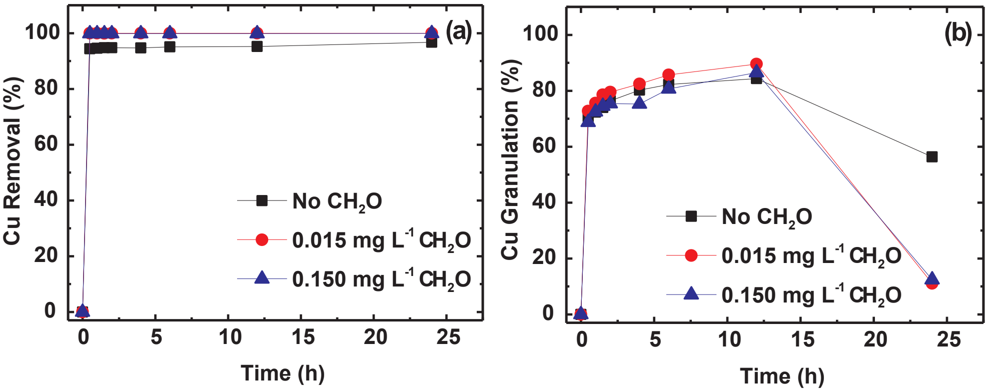

Fig. 3. Effect of varying CH_2O concentration on (a) Cu removal and (b) Cu granulation.

concentrations of 0.15 and 0.019 mg L^{-1} was chosen and varied to determine its effect on copper removal and granulation. The CH_2O concentration values were calculated based on the optimum concentration of copper present in the electroless copper plating solution. The other concentrations of CH_2O were used for comparison and testing for differences in the main results. A copper removal of around 99% did not show a significant difference in the variation of 0.150 and 0.019 mg L^{-1} CH_2O concentrations and solutions without CH_2O present in the electroless copper plating spent rinse water. Eq. (4) showed the reaction between CH_2O and copper ions resulting in the reduction of Cu(II) to Cu (I) and the formation of formic acid [42].

$$2Cu^{2+} + HCHO + H_2O \rightarrow 2Cu^{+} + HCOOH + 2H^{+} \tag{4}$$

The reduced copper has underwent disproportionation that produced a Cu(II) precipitate in the presence of other ions. Thus, higher copper removal was still achieved at solutions when there was no CH_2O in the solution (Fig. 3a).

As shown in Fig. 3b, copper granulation increased with time and attained maximum values in 12 h at 84% for solutions without CH_2O, 87% for solutions with 0.15 mg L^{-1} CH_2O, and 90% for solutions with 0.019 mg L^{-1} CH_2O. The base measure of CH_2O required for acceptable copper recovery was at 0.019 mg L^{-1} CH_2O [43]. Oxidation of CH_2O in solution triggers the formation of either hydrogen (H^{+}) or hydroxyl (OH^{-}) ions that increases the pH of the plating solution and further interrupt the quality and the rate of deposition [42].

3.3. Effect of EDTA and CH_2O on copper removal and granulation

The effects of the co-existence of EDTA and CH_2O in the simulated electroless copper plating spent rinse water on copper removal and granulation were examined in three different conditions: (i) 186 mg L^{-1} EDTA and 0.019 mg L^{-1} CH_2O, (ii) 186 mg L^{-1} EDTA and 0.15 mg L^{-1} CH_2O, and (iii) 1489 mg L^{-1} EDTA and 0.15 mg L^{-1} CH_2O. The results were compared against those which only used simulated electroless copper plating spent rinse water without the additives. Fig. 4a shows that copper removal was highest at 94% when the simulated wastewater contained 186 mg L^{-1} EDTA and 0.019 mg L^{-1} CH_2O. A decrease of 1% in copper removal was noted when the simulated wastewater contained 186 mg L^{-1} EDTA and 0.15 mg L^{-1} CH_2O. Meanwhile, copper removal further decreased to 58% when the concentrations of EDTA and CH_2O were 1489 mg L^{-1} and 0.15 mg L^{-1}, respectively. The overall granulation reaction in the simulated wastewater in the presence of both EDTA and CH_2O is shown in Eq. (5) [38] where L^{4-} is the EDTA anion.

$$CuL^{2-} + 2HCHO + 4OH^{-} \rightarrow Cu + 2HCOO^{-} + H_2 + 2H_2O + L^{4-} \tag{5}$$

As shown, copper is reduced from Cu(II) to Cu. The disproportionation of copper has resulted in further precipitation. The presence of EDTA inhibits the precipitation which decreases the copper removal. Hence, to achieve an effective removal of copper, the complexing agents (EDTA) present in the solution should be broken down first. In past studies, it has been reported that complexants such as EDTA, ammonia and malic acid in electroless plating baths can be effectively treated through chemical oxidation with ozone, potassium or sodium permanganate, sodium hypochlorite, chlorine, or ozone and ultraviolet-catalyzed hydrogen peroxide before metal removal [44].

There was also a significant change in the effect of the presence of EDTA and CH_2O on the copper granulation (Fig. 4b). The highest granulation of 84% was achieved when the combination of 186 mg L^{-1} of EDTA and 0.019 mg L^{-1} of CH_2O were present in the electroless copper plating spent rinse water. There was an 8% decrease in the granulation when the combination of 186 mg L^{-1} of EDTA and 0.15 mg L^{-1} of CH_2O were present in the solution. It further decreased to 59% granulation when the combination of 1489 mg L^{-1} of EDTA and 0.15 mg L^{-1} of CH_2O were also present. These results were relatively lower when compared to the 97% copper recovery when there was no EDTA and no CH_2O in the solution. EDTA inhibited the formation of granules due to the complexation of the metal while the oxidation of CH_2O initiates the development of either hydrogen or hydroxyl particles that increases the pH of the electroless copper plating solution [40].

3.4. Effect of EDTA and CH_2O and varying CO_3^{-2} pH on copper granulation

The presence of 186 mg L^{-1} EDTA and 0.019 mg L^{-1} CH_2O in the simulated wastewater had a notable effect on copper granulation. These concentrations of EDTA and CH_2O were selected based on the highest copper granulation attained. The flow rate of the simulated electroless copper plating spent rinse water was kept at 190 mg L^{-1}, the carbonate-to-copper molar ratio $[CO_3^{2-}/Cu^{2+}]$ at 2.5, and the value of the CO_3^{2-} pH was varied as follows: 9.0, 9.5, 10.0, 10.5, and 11.0.

Supersaturation is the driving force for granulation [29] and it is an essential condition for copper recovery from the simulated electroless copper plating spent rinse water. Copper precipitation is dependent on copper concentration, solution temperature, presence of anions and cations, duration and thermostatic stability of the solution [45–46]. Maintaining a high molar ratio increases the CO_3^{2-} pH. The pH of the precipitant affects the formation of copper hydroxo complex ions. At low and high pH levels, soluble copper hydroxo complex ions are formed in pure water. The copper hydroxo complex ions become less soluble in the system as the solution becomes basic. The rise in pH increases the concentrations of the hydroxide and carbonate ions as expressed in Eq. (6) [23].

$$CO_3^{-2} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-} \tag{6}$$

When the CO_3^{2-} pH was raised from 9.0 to 11.0, the degree of supersaturation of the solution increased resulting in a lower granulation. However, at CO_3^{-2} pH of 9.0–9.5 the total copper concentration in the effluent decreased, resulting in a slightly increased in the recovery from

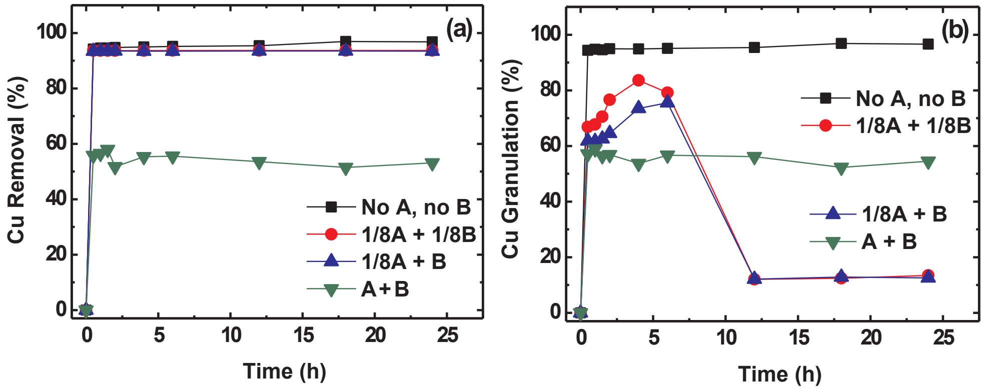

Fig. 4. Effect of varying concentrations of EDTA (A) and CH_2O (B) on (a) Cu removal and (b) Cu granulation.

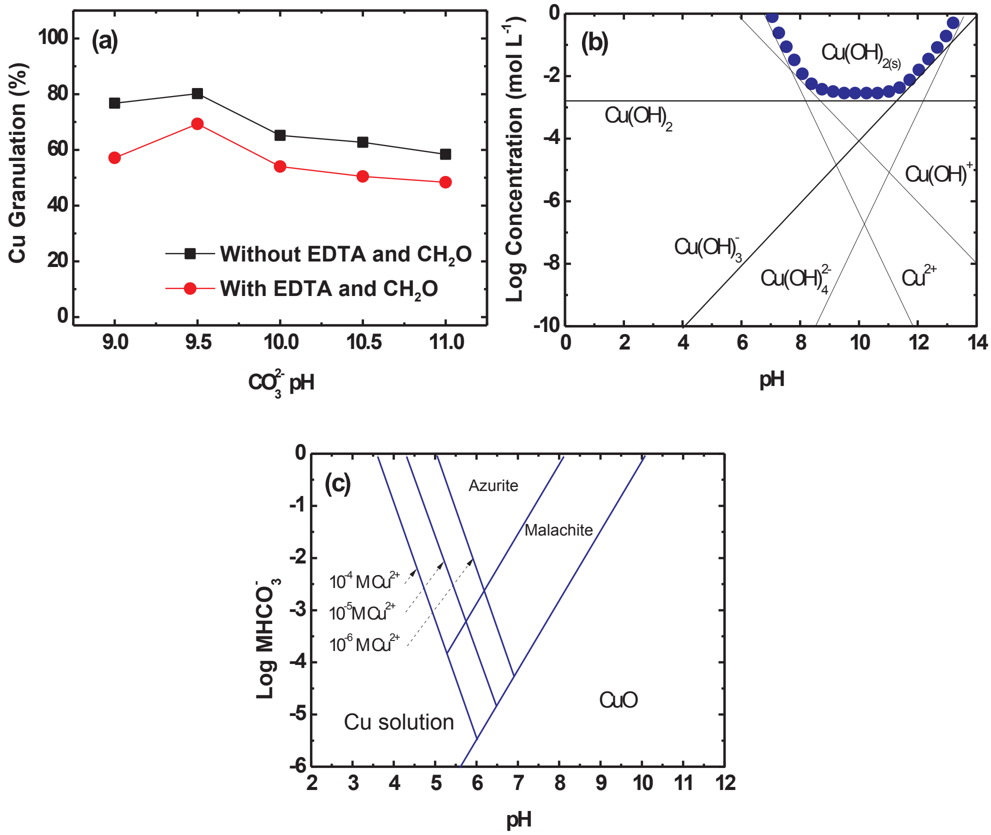

Fig. 5. Plots of (a) Cu granulation as a funtion of CO_3^{-2} pH, (b) the pC–pH diagram [(-log concentration) – (-log[H^+])] (Cuppett, 2006), (c) the equilibrium diagram of $CuO–H_2O–CO_3$ system (Sikka et al.,1991; Zhang, 1994; Franke and Mircea, 2005)

77 – 80% for solutions without EDTA and CH_2O, while when EDTA and CH_2O were present, a lower granulation of 69% was observed. It continuously dropped to 59% when CO_3^{2-} pH reached 11.0 for solutions without EDTA and CH_2O and 49% when EDTA and CH_2O were present. In these conditions, the solution was highly supersaturated in which homogeneous nucleation of both copper carbonate and copper hydroxide exist. The presence of carbonates and hydroxides of copper was evidently shown by the increase in the total copper concentration that made the effluent became turbid. The occurrence of homogeneous nucleation inhibits the copper to adhere on the formed solids leading to a lower solid recovery (Fig. 5a). The surface charge of a molecule is commonly reliant on the interface between the surface assemblies and the surface pH. From this time forward, the granulation of copper that can be accomplished at a predefined pH with respect to the surface charge of the granule is administered by the attraction to one another [31,47].

Four different copper species can be formed from pH of 8.5 to 12.0, namely: (i) copper hydroxides (Eq. (7)), (ii) copper carbonates (Eq. (8)), (iii) copper carbonate hydroxides in the form of malachite (Eq. (9)) and (iv) azurite (Eq. (10)) [48–50].

$$Cu^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2 \quad (7)$$

$$Cu^{2+} + CO_3{}^{2-} \rightleftharpoons CuCO_3 \quad (8)$$

$$2Cu^{2+} + 2OH^- + CO_3^{2-} \rightleftharpoons Cu_2CO_3(OH)_2 \quad (9)$$

$$3Cu^{2+} + 2OH^- + 2CO_3^{2-} \rightleftharpoons Cu_3(CO_3)_2(OH)_2 \quad (10)$$

Fig. 5b shows the distribution of copper species at different pH. The CO_3^{-2} pH determines the type of copper granules that can be recovered. At CO_3^{-2} pH of 9.5 showing the highest recovery, the granules

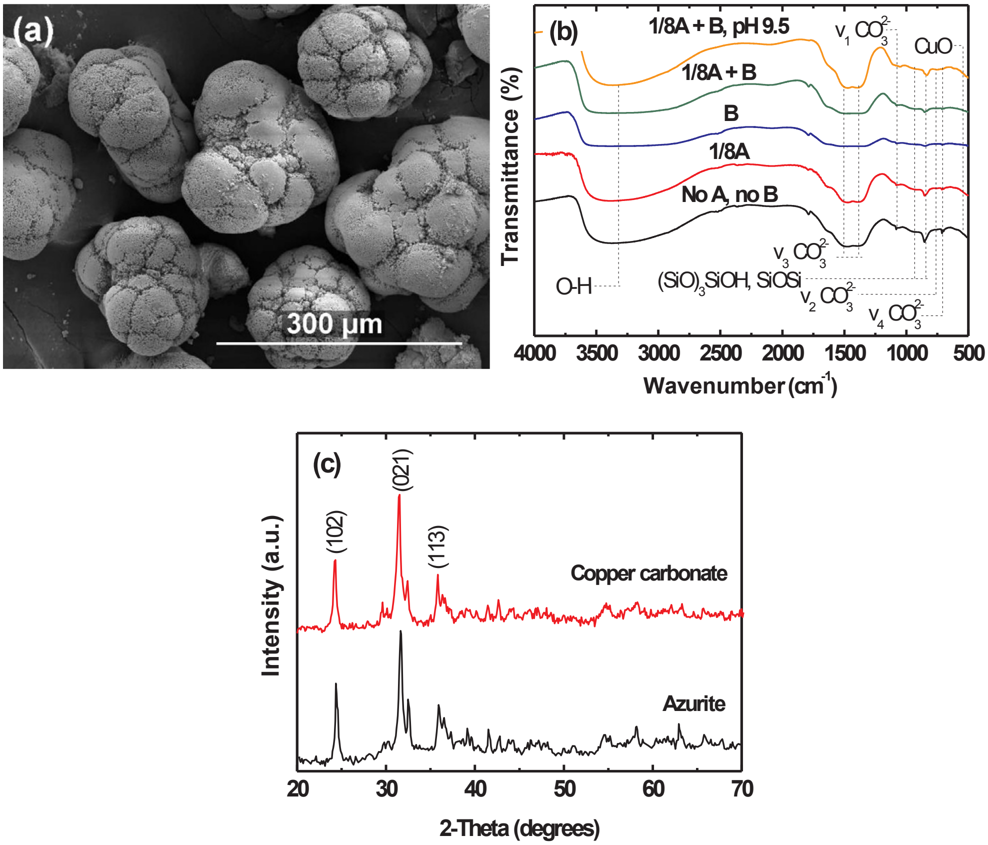

Fig. 6. (a) SEM image, (b) FTIR spectra, and (c) XRD patterns of the recovered granules.

recovered were azurite that is possible at effluent pH of 6.98 (Fig. 5c).

3.5. Characteristics of the recovered granules

Solid granules were collected at the end of the 24-h run duration. The sizes of the recovered granules ranged from 0.149 to 0.5 mm. The SEM micrograph of the recovered granules presented in Fig. 6a reveal the compact agglomerated granules with smooth and rounded surfaces. Between the two additives, EDTA had a more inhibiting effect on granulation than CH_2O that resulted in lower copper recovery.

The surface functional groups of the recovered granules can be analyzed from the FTIR spectra presented in Fig. 6b. The band between 3393–3506 cm^{-1} is attributed to OH stretching. As shown, the hydroxyl band of the solids recovered from the EDTA-containing simulated wastewater with lower pH is more defined and closely resemble those obtained using the control solution (without either EDTA or CH_2O). The bands between 1330–1513 cm^{-1} can be ascribed to anti-symmetric CO_3^{2-} stretching vibrations which are extremely weak while the band between 1064 and 1090 cm^{-1} indicate asymmetric CO_3^{2-} stretching vibrations. The band between 831–853 cm^{-1} is attributed to the out-of-plane CO_3^{2-} bending while that between 711–773 cm^{-1} signify a doubly degenerate in-plane CO_3^{2-} bending. When the CO_3^{2-} ion becomes twisted out of shape from the even planar symmetry, it splits into two fragments [51]. The band between 548–598 cm^{-1} is assigned to the weak Cu-O stretching [52]. The bands pertaining to Cu (II) are linked to carbonate and hydroxide anions. Meanwhile, the XRD diffractogram of the recovered granules as shown in Fig. 6c is identical to that of the monoclinic azurite ($Cu_3(CO_3)_2(OH)_2$).

4. Conclusions

The application of the unseeded fluidized bed granulation process or UFBGP in the treatment of simulated electroless copper plating spent rinse waters containing EDTA and/or CH_2O was successfully demonstrated. In the presence of 186 mg L^{-1} EDTA, copper removal and granulation reached 93% and 54–78%, respectively. Higher EDTA concentrations reduced copper removal and granulation due to the increased copper and EDTA complexation which effectively lowered the availability of copper for granule formation. Varying CH_2O concentration between 0.019 and 0.150 mg L^{-1} maintained copper removal at 99% throughout the 24-h run duration. Meanwhile, copper granulation reached 90% in the presence of 0.019 mg L^{-1} of CH_2O. When EDTA and CH_2O co-existed in the simulated wastewater at 186 mg L^{-1} and 0.019 mg L^{-1}, respectively, 94% copper removal and 84% granulation were obtained. Between the two additives, EDTA is more limiting than CH_2O and the presence of EDTA resulted in lower copper recovery. The sizes of the recovered granules ranged from 0.149 to 0.5 mm and their characteristics were examined by SEM, FTIR and XRD analyses. The SEM images showed that the recovered granules were smooth and compact aggregates. Meanwhile, the FTIR spectra of the granules showed absorption peaks for copper linked to carbonates and hydroxides. In addition, the XRD patterns revealed characteristic peaks identical to the mineral azurite or copper carbonate hydroxide ($Cu_3(CO_3)_2(OH)_2$).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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