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Research

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**Reclamation of cobalt and copper from single- and co-contaminated wastewater via
carbonate and hydroxide precipitation**

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Abstract

Wastewater containing cobalt and copper comprised of plating wash water, plant wash water, and equipment cooling and wash water is generated in the electroplating industry. These metals can be detrimental to humans, animals, plants, and the environment. Thus, it is necessary to treat electroplating wastewater to remove these toxic metals. Carbonate and hydroxide precipitation were utilized for the removal of Co(II) and Cu(II) from synthetic electroplating wastewater by jar tests in this work. The effects of solution pH, precipitant-to-metal ratio, and type of precipitant on the precipitation efficiency of cobalt and copper from the single- and co-contaminated systems were investigated. Carbonate precipitation achieved higher removal efficiency for both target metals in the single- and co-contaminated wastewater streams. Furthermore, it can operate at relatively low pH range of about 7.0-8.0. Cobalt in both pollutant systems was almost completely removed at pH 10.0 using both precipitant systems. Copper was found to be easily removed which was possibly brought about by precipitation-adsorption mechanism. The extent of the co-removal of cobalt with copper is significantly pH dependent. The effect of precipitant-to-metal ratio for cobalt and copper treatment varied in single- and co-contaminated streams. Carbonate precipitation led to lower sludge density than that of hydroxide precipitation.

Keywords: chemical precipitation; cobalt removal; copper system; hydroxide precipitation; wastewater stream

1. Introduction

With the progressing economy, and rapid growth and development of industries including mining and smelting operations, leather tanning, metal plating facilities, metal cleaning and fabrication, metal finishing, battery manufacturing, electrochemical, paint and pigment industries, heavy metals are being discharged into the aquatic streams to an increasing degree [1]. These recalcitrant and persistent pollutants are considered toxic, carcinogenic, and non-biodegradable which pose detrimental effects on biological environment and human health [2]. Thus, remediation of these contaminants in water and wastewater have been of particular concern.

Cobalt is a significant cofactor in Vitamin B12 responsible for the proper functioning of the brain and nervous system, and for blood formation. It is one of the most essential transition metals beneficial to human beings. However, excessive intake may be hazardous to both humans and animals. Moreover, exposure to high levels of cobalt may induce toxic effects and may cause goiter, thyroid damage, diarrhea, nausea, reproductive problems, hypertension, heart disease, bleeding, pulmonary diseases, hyperglycemia, hair loss, bone defects, and mutations in living cells [3,4]. With this, cobalt concentration in livestock wastewater and irrigation water should not exceed 1.0 and 0.05 mg L⁻¹, respectively [4]. On the other hand, copper is another beneficial metal ion present as trace amounts in our body and water resources. It regulates hemoglobin level, neuron action, mitochondrial respiration, and metabolism by cells. At higher concentrations, liver and kidneys can be affected to a great extent. Its accumulation can cause diseases such as anemia, Alzheimer's disease, and Parkinson's disease [5–8]. The permissible limits of copper in drinking water and effluent discharge are set to 2.0 and 1.3 mg L⁻¹, respectively [6]. At present, chemical precipitation, coagulation/flocculation, electrochemical method, ion exchange, membrane filtration and adsorption are the existing treatment technologies to remove heavy metals in water and wastewater

streams [9,10]. Among these current methods, chemical precipitation is the most widely utilized method in the industry particularly due to the simplicity of process control, effectivity over a wide range of temperature and relatively low operating cost [9,11]. Traditionally, chemical precipitation processes produce insoluble precipitates of heavy metals in the form of hydroxides, sulfides, carbonates, and phosphates. Chemical precipitation mechanism involves the reaction of dissolved metals in the solution with the precipitating agent producing insoluble metal precipitates. Consequently, very fine particles are generated, and their particle size can increase by using chemical precipitants, coagulants, and flocculation leading to removal as sludge. Once the metals precipitate leading to the formation of solids, they can easily be removed, and low metal concentrations can consequently be released. Removal efficiency of metal ions in the solution can reach optimum by changing the significant parameters including pH, temperature, initial metal concentration and charge of the ions [12]. Chemical precipitation process usually involves addition of reagents, pH adjustment inducing precipitation, flocculation, sedimentation and solid-liquid separation [11]. Oftentimes, alkaline reagents are utilized to raise the pH of the solution lowering the solubility of the metallic constituent, consequently leading to precipitation. It includes sulfide, hydroxide and carbonate precipitation [13]. Operating costs for hydroxide and carbonate precipitation processes are almost similar. They are of lower cost than sulfide precipitation [14].

Hydroxide precipitation removes heavy metals by the addition of alkalis (caustic or lime) to adjust the pH of the wastewater until the pollutant metal exhibits its minimum solubility. It is easy to operate, operates at ambient conditions, and appropriate for automatic control. The most significant advantage of this process is its low cost [15]. On the other hand, carbonate precipitation using sodium carbonate (Na_2CO_3) is a low-cost chemical precipitation process with added

advantages such as its simplicity, optimum treatment occurring at less pH levels and sludges with good filtration characteristics [11].

Few investigations have utilized chemical precipitation method in treating co-contaminated heavy metal wastewater streams, particularly containing cobalt and copper. Thus, the aim of the study is to investigate the influence of pH, precipitant-to-metal ratio, and type of precipitant on the co-removal of cobalt with copper from synthetic electroplating wastewater using carbonate and hydroxide precipitating agents since these pollutants co-exist in the said wastewater stream. Single-contaminated synthetic wastewater was also treated for comparison in terms of removal efficiency, and sludge volume generation.

2. Materials and methods

2.1. Chemicals

All reagents were of analytical grade and used without further purification. Cobalt sulfate heptahydrate (99%) was purchased from Sigma-Aldrich (China). Copper sulfate pentahydrate ($\geq 98.5\%$) and sodium carbonate ($\geq 99.5\%$) were provided by Fluka (Switzerland). Sodium hydroxide (NaOH, $\geq 97\%$) was obtained from Fisher Chemical (UK). Nitric acid (HNO_3) was purchased from Shimadzu's Pure Chemicals (Japan). A laboratory-grade RO-ultrapure water system (resistance $> 18.1 \Omega$) supplied deionized water for the experiments.

2.2. Batch experiments

Single-contaminated aqueous solutions of cobalt and copper with 12.6 mM concentration were prepared as well as co-contaminated aqueous stream where initial concentration of each metal was 12.6 mM where the molar ratio of Co to Cu is 1:1. Batch experiments of chemical precipitation

were conducted by jar tests as shown in Fig. 1 at different pH levels of 7.0, 8.0, 9.0, 10.0, 11.0, and 12.0, and precipitant-to-metal ratios ($[P]/[M]$) of 0.5, 1.0, 1.5, 2.0, and 2.5. All the experimental runs were carried out at room temperature. Na_2CO_3 and NaOH were used for carbonate and hydroxide precipitant precursors, respectively, to determine the effect of precipitants on the treatment of single- and co-contaminated streams. The mixture was stirred at 100 rpm for 10 min then 30 rpm for 50 min, and finally kept for settling to draw liquid sample for residual cobalt and copper analysis. For the cobalt and copper residue, the supernatant liquid was filtered with 0.22 μm syringe filter and digested with 1 mL HNO_3 (70%) to stop precipitation.

2.3. Analytical methods

Volumetric method was used to determine the estimated volume of the decanted sludge. The sludge volume at 30 min (SV_{30}) was determined using an Imhoff cone (Kartell Labware, Italy). The sludge settling rate (SSR , $\text{cm}^3 \text{min}^{-1}$) was determined in the reaction system given by Eq. (1). Cobalt and copper residues were measured by using inductively coupled plasma mass spectrometry (ICP-OES, JY 2000-2, HORIDA).

$$\text{Sludge settling rate, SSR } \left(\frac{\text{cm}^3}{\text{min}} \right) = \frac{V_{\text{sol'n}} - \text{SV}_{30}}{t_s} \quad (1)$$

Where $V_{\text{sol'n}}$ is total volume of the solution (cm^3), SV_{30} is the sludge volume at 30 min (cm^3) and t_s is the settling time (30 min).

3. Results and discussion

3.1. Theoretical computations

The treatability of Co and Cu via chemical precipitation in waste abatement applications is directly related to their solubilities in the solvent matrix. Their solubility profiles can be altered by one or

more of the following process modifications: (1) controlling the temperature of an aqueous solution, (2) adjusting the pH and reduction potential of the solution, or (3) setting supersaturation in a fixed-volume solution [16,17].

3.1.1. Cobalt speciation

Fig. 2a displays the distribution of soluble species of individual hydroxo Co^{2+} complexes. These hydro complexes always exist in water while different anions can form complexes with cobaltous ion based on stability constants. Common anions include SO_4^{2-} , OH^- , PO_4^{3-} , HCO_3^- , NO_3^- and CO_3^{2-} . These complexes form precipitates when the solubility product is surpassed [18]. Cobaltous ions, Co^{2+} , exist in acid and weak alkaline solutions depending on the extent of cobalt concentration. Increasing the pH will allow Co^{2+} to react with OH^- ions forming cobaltous hydroxide, $\text{Co}(\text{OH})_2$. Nevertheless, the $\text{Co}(\text{OH})_2$ precipitate may undergo re-dissolution into dicobaltite ions, HCoO_2^- , when the pH reaches greater than 13.4. Hydrolysis products of Co^{2+} are summarized varying from CoOH^+ to $\text{Co}(\text{OH})_4^{2-}$ [19] as indicated in Eqs. (2) to (5) together with their respective solubility products.

(4)

163 The total cobalt in water can be presented as

$$164 \quad [\text{Co}]_{\text{T}} = [\text{Co}^{2+}] + [\text{CoOH}^+] + [\text{Co}(\text{OH})_2^0] + [\text{Co}(\text{OH})_3^-] + [\text{Co}(\text{OH})_4^{2-}] \quad (6)$$

165 Factoring out $[\text{Co}^{2+}]$ and substituting Eqs. (2) to (5), Eq. (6) will be depicted as Eq. (7) and then
 166 simplified into Eq. (8). Eq. (8) is consequently rearranged as Eq. (9) to determine the value of
 167 $[\text{Co}^{2+}]$.

$$168 \quad [\text{Co}]_{\text{T}} = [\text{Co}^{2+}] \left(1 + \frac{\beta_1}{[\text{H}^+]} + \frac{\beta_2}{[\text{H}^+]^2} + \frac{\beta_3}{[\text{H}^+]^3} + \frac{\beta_4}{[\text{H}^+]^4} \right) \quad (7)$$

$$169 \quad [\text{Co}]_{\text{T}} = [\text{Co}^{2+}] \cdot \alpha_{\text{Co}} \quad (8)$$

$$170 \quad [\text{Co}^{2+}] = \frac{[\text{Co}]_{\text{T}}}{\alpha_{\text{Co}}} \quad (9)$$

171 Carbonate and hydroxyl anions react with cobalt cation to form CoCO_3 , $\text{Co}(\text{OH})_2$, or cobalt
 172 hydroxide carbonate as shown in Eqs. (10) and (11) [20]. In this case, cobalt hydroxide shows
 173 lesser solubility indicated in its smaller solubility product constant which pertains to higher
 174 probability of precipitation in the system compared to that of cobalt carbonate.

177 Applying the viewpoint of K_{sp} and the equilibrium of water ionization, we can calculate the
 178 necessary concentration of precipitant anions required for the formation of $\text{Co}(\text{OH})_2$ and CoCO_3
 179 precipitates presented in Eqs. (12) and (13), respectively:

$$180 \quad [\text{OH}^-] = \sqrt{\frac{K_{\text{sp}}(\text{Co}(\text{OH})_2)}{[\text{Co}^{2+}]}} \quad (12)$$

$$181 \quad [\text{CO}_3^{2-}] = \frac{K_{\text{sp}}(\text{CoCO}_3)}{[\text{Co}^{2+}]} \quad (13)$$

We apply 12.6×10^{-3} M as the concentration of Co^{2+} used in this study to determine the precipitant anion concentration. Thus, 7.08×10^{-7} M of OH^- is needed to obtain $\text{Co}(\text{OH})_2$ precipitate. Whereas 1.11×10^{-11} M of CO_3^{2-} is sufficed to produce CoCO_3 in the system.

3.1.2. Copper speciation

Like cobalt and other metals, copper interacting with water, forms free metal cations, different soluble complexes and insoluble particles or precipitates. Free copper, which is cupric ion (Cu^{2+}), is generally soluble and the preferential form at relatively low degree of pH (usually below pH 6) as shown in Fig. 2b and in the absence of anionic ligands [18]. As presented, Cu^{2+} is the most dominant species (greater than 80%) when the pH is 6.0 but its relative dominance decreased quickly as pH increased [18]. Soluble copper hydro complexes are formed at low and high pH range in pure water and given by the reactions below depicted as Eqs. (14) to (17). In the presence of anionic ligands, these complexes form precipitates such as $\text{Cu}(\text{OH})_2$, CuCO_3 , etc.

In pure water, the total copper can be depicted as follows:

$$[\text{Cu}]_T = [\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu}(\text{OH})_2^0] + [\text{Cu}(\text{OH})_3^-] + [\text{Cu}(\text{OH})_4^{2-}] \quad (18)$$

Substituting Eqs. (14) to (17), the total copper is presented as

$$[Cu]_T = [Cu^{2+}] \left(1 + \frac{\beta_5}{[H^+]} + \frac{\beta_6}{[H^+]^2} + \frac{\beta_7}{[H^+]^3} + \frac{\beta_8}{[H^+]^4} \right) \quad (19)$$

$$[Cu]_T = [Cu^{2+}] \cdot \alpha_{Cu} \quad (20)$$

Thus, the value of $[Cu^{2+}]$ is

$$[Cu^{2+}] = \frac{[Cu]_T}{\alpha_{Cu}} \quad (21)$$

3.2. Effect of pH

The effect of pH on the removal of cobalt and copper in the single- and co-contaminated systems was studied from pH levels of 7.0-12.0 treating 12.6 mM initial metal concentration and precipitant-to-metal ratio of 1.2 in 1 h of reaction time in a batch system. pH indicates the concentration of hydrogen ions (H^+) in the solution and controls the molecular net electric charge to alter the mobility of a known substance in the water matrix. A heavy metal with relatively low mobility, being insoluble, has a negative net charge (H^+ depletion) leading to precipitation out of the liquid phase. Generally, this phenomenon takes place in high pH zones and is usually termed as alkaline precipitation. Contrarily, a metal exhibiting high mobility (soluble) has a net positive charge caused by H^+ supplementation in the solution, consequently resulting to aqueous dissolution of metals in acidic environments [21]. Furthermore, the pH value of the reaction directly influences the concentration of carbonate ions in the reaction system, and then influences nucleation and growth of the crystalline precipitation during the treatment process [20]. Thus, pH is a relatively significant variable with regards to this process under investigation. The influence of pH on the behavior of cobalt in the single synthetic solution is presented in Fig. 3a. At stronger alkaline conditions (pH > 8.0), it was found that the cobalt removal efficiency approached complete removal. At pH 7.0, 72% removal was reached by carbonate precipitation while hydroxide precipitation brought about 59% removal leading to residual cobalt of 3.6 mM and 5.2

mM, respectively. At pH 9.0, the removal efficiency significantly increased using the carbonate and hydroxide precipitants achieving almost complete removal. At pH 11.0, the highest removal of cobalt (100%) was attained for both studied precipitants conforming to the standard set for cobalt. 100% cobalt removal was also achieved at pH values of 8.0 to 10.0 owing to Co(OH)_2 precipitation [22]. CoCO_3 and Co(OH)_3 can be produced in an acidic and moderate intensity alkaline solution in a carbonate or bicarbonate system. According to Lin et al. [23], Co(OH)_2 is usually formed in strong alkaline solution. In this present study, it was concluded that cobalt removal increased with increasing solution pH. Qasem et al. [24] affirmed that chemical precipitation process efficiency is improved at higher pH range from 9.0 to 11.0.

The generated sludge volume at 30 min by the single cobalt system was observed to determine the settleability of the sludge at different pH values under identical operating conditions depicted in Fig. 4a. For carbonate precipitation, the remaining sludge volume was found to increase when pH increased from 7.0 to 11.0 and decreased significantly at pH 12.0. This probably shows that the sludge particles are denser and more compact when the pH approaches neutral condition causing higher settleability and faster settling rate as presented in Fig. 4b. Likely cobalt carbonate exists at pH 7.0 showing significant decrease in the settleability from pH 8.0. CoCO_3 occurs at pH range of 6.9 to 7.5 as reported by Guo et al. [25]. Another study of Guo et al. [26] confirmed its existence at pH 7.10-7.25. The cobalt precipitate formed at pH 11.0 was observed to be black in color which is probably due to Co_3O_4 precipitation as described by Uddin and Baig [27]. Whilst at pH 12.0, brown precipitate was recovered which can be attributed to CoOOH precipitation [28,29]. The change in cobalt species at different pH levels is possibly caused by oxidation [23]. For hydroxide precipitation, there was a great increase in the remaining sludge from pH 8.0 to pH 9.0. A decreasing sludge volume was then observed from pH 9.0 to 12.0. These differences in the

sludge volume produced may be attributed to the type of precipitates formed, particle size, and particle density as divulged by Lacson et al. [30]. On the other hand, copper was easily removed using both carbonate and hydroxide precipitants as described in Figure 3b. Precipitation reactions of copper are shown below:

The $[\text{CO}_3^{2-}]/[\text{Cu}^{2+}]$ ratio used in this study is 1.2 which is in excess with the required carbonate based on the stoichiometric reaction presented as Eq. (22). The excess carbonate used possibly caused the high removal efficiency of the copper in the single system. This was possibly brought about by greater amount of carbonate ions interacting with the target copper ions. In addition, precipitation starts at pH 6.0 and all copper was precipitated out at pH 7.0 for pure copper solution with 150 mg L^{-1} of concentration [31]. A cationic metal is generally mostly dissolved at relatively low pH and becomes mostly sorbed at higher pH values as pH increases through a critical range 1-2 pH units wide. The high removal obtained in this system might also be due to precipitation and adsorption mechanisms most especially at higher pH levels. Copper possibly formed copper-bearing precipitates initially and the remaining copper in the solution was adsorbed on the surface of the precipitates formed in the system causing no residual copper left in the solution [32]. This occurrence could be due to electrostatic attraction and ligand exchange [33,34]. Furthermore, copper carbonate precipitates are known to have appreciable amount of positive surface charges ascribed to high level of particles' zeta potential. When the solution pH is gradually elevated, these positive surface charges are suddenly reduced and finally shifted to negative surface charge when the pH reaches higher than 7.5 [31]. This explains the possible phenomenon occurring in the single copper system using carbonate precipitation. At pH 12.0, there was an observed decrease in the

removal of copper using hydroxide which is probably caused by the re-dissolution of the precipitate in the solution and/or desorption of copper from the copper-bearing precipitate. With respect to the stoichiometry of the reaction shown in Eq. (23), the required $[\text{OH}^-]/[\text{Cu}^{2+}]$ molar ratio represents a hydroxide concentration 60% below the stoichiometric requirement which is affected by pH inducing copper precipitation. Similar results were obtained when hydroxide precipitation was used to treat single copper system reaching greater than 97% removal.

For carbonate precipitation, SV_{30} ranges from about 140 to 220 mL per liter of mixed copper and precipitant solution while about 70 to 180 mL per liter was observed for hydroxide precipitation as depicted in Fig. 4c. Malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$, dominates in the copper solution at pH between 7.0 and 8.0. It was also observed by Pérez Sánchez et al. [35] that malachite exists at pH up to 10.3. This could explain the similar sludge volume generated from pH values of 7.0 to 10.0 in the single copper system. At pH 11.0, the SV_{30} significantly decreased possibly due to azurite formation. At pH values between 6.0 to 7.0 and 10.3 to 14.0, azurite, $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$, could be the dominating species making it amphoteric. Black precipitate was observed at pH 12.0 which can be associated with CuO precipitation occurring at $\text{pH} > 10.3$. At pH 7.0 and 8.0 using hydroxide precipitation, $\text{Cu}(\text{OH})_2$ is the predicted precipitate which exists at pH values ranging from 5.5 to 10.3 [35]. This precipitate is also said to exist at intermediate pH levels typically in the pH range of 6.5-12.0 [18]. Minimal solubility of metal hydroxides leading to higher probability of precipitation is achieved at an approximate pH of 9.5-10.0 [36,37]. $\text{Cu}(\text{OH})_2$ is possibly formed at pH 9.0 and 10.0 exhibiting larger particle size affecting the sludge volume after 30 min. Grayish precipitate was formed at pH 11.0 while black precipitate was generated at pH 12.0 which could probably be caused by CuO precipitation [38].

To further validate the results drawn, the solubility products of 2.20×10^{-20} for $\text{Cu}(\text{OH})_2$ and 1.40×10^{-10} for CuCO_3 were used to calculate the pH and carbonate concentration for precipitating 12.6 mM Cu^{2+} (800 mg L^{-1}) unto $\text{Cu}(\text{OH})_2$ and/or CuCO_3 in an open atmospheric condition.

Precipitation $\text{Cu}(\text{OH})_2$ and CuCO_3 occurs when the solubility products are exceeded as shown below.

$$[\text{Cu}^{2+}][\text{OH}^-]^2 = \left(\frac{800}{63.55} \times 10^{-3}\right) (10^{-14+\text{pH}})^2 \geq 10 \times 2.20 \times 10^{-20} \quad (24)$$

$$[\text{Cu}^{2+}][\text{CO}_3^{2-}] = \left(\frac{800}{63.55} \times 10^{-3}\right) (\text{CO}_3^{2-}) \geq 10 \times 1.40 \times 10^{-10} \quad (25)$$

Where 63.55 is the molecular weight of copper (g mol^{-1}), 10 is the assumed saturation index for homogeneous precipitation, 2.20×10^{-20} is the solubility product of $\text{Cu}(\text{OH})_2$, and 1.40×10^{-10} is the solubility product of CuCO_3 .

Thus, $\text{pH} \geq 5.62$ is the starting pH for $\text{Cu}(\text{OH})_2$ precipitation whereas $[\text{CO}_3^{2-}] \geq 1.11 \times 10^{-7} \text{ M}$ is the carbonate concentration needed for CuCO_3 precipitation. In an open atmospheric carbonate system, carbonate concentration is given by the equation:

$$[\text{CO}_3^{2-}] = \frac{[\text{H}_2\text{CO}_3^*] \cdot K_{a,1} \cdot K_{a,2}}{[\text{H}^+]^2} \quad (26)$$

Where $[\text{H}_2\text{CO}_3^*] = [\text{CO}_{2(\text{aq})}] = 10^{-5} \text{ M}$, $K_{a,1} = 10^{-6.3}$, and $K_{a,2} = 10^{-10.3}$

Substituting all the values and rearranging, we get $[\text{H}^+] \leq 4.76 \times 10^{-8}$, and $\text{pH} \geq 7.32$. Thus, the calculations done and analyses suggest that homogeneous copper precipitation of $\text{Cu}(\text{OH})_2$ cannot take place until pH is greater than 5.62 for 12.6 mM Cu^{2+} in an open atmospheric condition which is roughly 1.7 pH unit lower than the CuCO_3 precipitation ($\text{pH} \geq 7.32$). The results affirm that precipitation occurred at these pH values. However, the actual carbonate concentration used in the treatment of copper in the system is greater than the calculated value. With this, copper could be precipitated at lower pH level compared to cobalt precipitation.

The behavior of Co(II) in the co-contaminated system was also studied in terms of the effect of pH on its removal in the presence of Cu(II) as presented in Fig. 5a. For both precipitants, increasing the pH increased the cobalt co-removal and co-precipitation with copper. Using sodium carbonate as precipitant, cobalt was removed to over 99% at pH 9.0. The same result was achieved by Safitri et al. [39] in treating cobalt in a multi-component heavy metal system reaching over 99% removal at pH 9.0. Cobalt removal efficiency reached greater than 99% at pH levels above 9.0. The optimum pH for maximum cobalt co-removal in the system is about pH 10.0 for both precipitants utilized similar with the results in the single cobalt system. The co-removal and co-precipitation of cobalt with copper was found to be greatly dependent on pH similar as the result presented by Sun et al. [34]. The co-removal of chromium through copper precipitation also depended highly on the solution pH of the reaction system which confirms the dependency of metal co-removal on solution pH [34]. As shown in Fig. 5b, copper was found to be removed easily at all the pH range studied in the co-contaminated system. Copper removal showed a similar trend with that of single copper system. In the co-contaminated system, copper removal also decreased at pH 12.0 possibly due to re-dissolution in the reaction system [40]. It was significantly observed that the co-existence of cobalt did not affect the removal efficiency of copper in the two-component system.

For sodium carbonate precipitant, the SV_{30} increased from pH 7.0 to pH 10.0 then slightly decreased at pH 11.0. At pH 12.0, a great decrease was observed in Fig. 5c. For hydroxide precipitation, around 200-500 mL L⁻¹ of SV_{30} was observed. The sludge volume generated in the co-contaminated system was observed to be greater than the single systems of cobalt and copper pollutants at all pH values. This could be associated with the greater total metal concentration, and higher amount of precipitant dosage used to treat two metals in the system. The total metal concentration ($[M]=[Co]+[Cu]$) is about 25.2 mM (12.6 mM Co and 12.6 mM Cu). Thus, the

necessary carbonate and hydroxide concentrations also increased probably causing greater sludge volume and slower settleability of precipitates (lower SSR) in the reaction system due to possible trapping of water molecules in the formed precipitates (Fig. 5d) [30]. Higher precipitant dosage as well as higher pH values lead to increase in nucleation number of particles and decrease in particle size, accordingly, causing slower sedimentation time in the precipitation system [9]. The behavior of the precipitates formed is seen to vary at different pH levels for both precipitants used.

3.3. Effect of precipitant-to-metal ratio

Based on the crystallization theory, particle nucleation and growth are dependent on the supersaturation level of the solution [41]. Higher saturation number yields greater particle nucleation rate. Precipitant concentration is also significant in the chemical precipitation process. Low precipitant concentration leads to growth of particles on pre-existing solids in the system. On the other hand, high precipitant concentration tends to promote rapid formation of new solid particles leading to increase in the particle number and reduction of the particle size [9]. As the precipitant concentration increases, the precipitant-to-metal ratio also increases. To establish the precipitant-to-metal molar ratio necessary to remove cobalt and copper in the single- and co-contaminated system, several experiments were conducted using 0.5-2.5 molar ratios under similar conditions. The highest cobalt removal (98%) was achieved with $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ ratio of 1.5 with reaction pH of about 8.5 in the single system as depicted in Fig. 6a. Based on the stoichiometric reaction (Eq. (10)), the carbonate-to-cobalt ratio needed to reach almost complete removal was 50% above the stoichiometric requirement. There was no further increase observed when the $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ ratio was further increased up to 2.5. On the other hand, $[\text{OH}^-]/[\text{Co}^{2+}]$ ratio of 2.0 showed the highest cobalt removal efficiency (84%) at the same reaction pH. This is affirmed from

the stoichiometry of the given reaction as Eq. (11). However, $[\text{OH}^-]/[\text{Co}^{2+}]$ ratio of 1.5 to 2.5 displayed no significant increase in the reduction of cobalt. Thus, $[\text{OH}^-]/[\text{Co}^{2+}]$ ratio of 1.5 was considered as the optimum value to treat cobalt in the single system.

Since the cobalt concentration was set at a specific value, the increase in $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ molar ratio will lead to a higher CO_3^{2-} ion concentration. Therefore, this leads to higher supersaturation according to Eq. (27). Moreover, lower radius of critical nucleation is caused by an increase in supersaturation which leads to easier nucleation based on the Gibbs-Thompson equation depicted as Eq. (28) [42]. Accordingly, precipitates with lower particle size will be formed under similar metal content as also mentioned above [26].

$$S = \sqrt{\frac{C_m \cdot C_s}{K_{sp} (ms)}} \quad (27)$$

Where S is supersaturation; C_m is the concentration of metal ions; C_s is the precipitant ion concentration; $K_{sp} (ms)$ is the precipitation solubility product constant.

$$\ln \frac{C}{C_s} = \frac{2\sigma \cdot M}{RT\rho \cdot r_{crit}} \quad (28)$$

Where C is the concentration of the solution, C_s is the supersaturation, σ is the surface tension, M is the molar mass, R is the thermodynamic constant, T is the thermodynamic temperature, ρ is the density, and r_{crit} is the critical radius.

At $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ of 1.5 to 2.5, the sludge volume did not significantly change as well as the reaction pH (about pH 8.5) as shown in Figs. 7a and 6a. It can be deduced that at this range the precipitate formed is of the same species which could possibly be $\text{Co}(\text{OH})_2$ instead of CoCO_3 despite using carbonate system. CoCO_3 might be oxidized to Co_3O_4 followed by reduction to form $\text{Co}(\text{OH})_2$ precipitate [23]. CoCO_3 is possibly precipitated at $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ of 0.5 ($[\text{CO}_3^{2-}] = 6.3 \times 10^{-3} \text{ M}$) brought about by the moderately alkaline pH (below pH 8.0). 0.5 as $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ ratio is more than enough to form CoCO_3 in the system based on the calculated necessary CO_3^{2-}

concentration in Section 3.1.1. However, the pH of the solution is still a governing factor in the type of precipitate forming in the reaction system. On the other hand, $[\text{OH}^-]/[\text{Co}^{2+}]$ molar ratio of 0.5 produced low sludge volume which may be associated with the low removal efficiency of cobalt in the reaction system.

We can see in Fig. 6b that there was no significant effect observed in the removal of copper under all the $[\text{P}]/[\text{M}]$ ratios studied for both precipitants in the study. This might be possibly caused by the pH used in the reaction system (around pH 8.0). The reaction pH for all the studied ratio is in the range of 7.5 to 8.5. This can be affirmed based from the calculated starting pH wherein $\text{Cu}(\text{OH})_2$ and CuCO_3 undergo precipitation. The sludge volume at 30 min was also determined as well as the settling rate of the sludge formed at different $[\text{P}]/[\text{M}]$ ratios presented in Figs. 7c and 7d. The discrepancies in the sludge volume generated together with the sludge settling rate is possibly affected by the differences in the reaction pH in the single copper system.

For the co-contaminated system, cobalt reached maximum removal at $[\text{CO}_3^{2-}]/[\text{M}]$ and $[\text{OH}^-]/[\text{M}]$ of 2.0 presented in Fig. 8a. There is no further increase observed when both molar ratios are increased to 2.5. For the single cobalt system, $[\text{CO}_3^{2-}]/[\text{Co}^{2+}]$ and $[\text{OH}^-]/[\text{Co}^{2+}]$ of 1.5 were found to be the optimal $[\text{P}]/[\text{M}]$ conditions which are lower than that of the co-contaminated system. Greater $[\text{P}]/[\text{M}]$ ratio is needed to treat cobalt in the co-contaminated system due to the fact this system contains two metals leading to higher supersaturation which makes it harder to precipitate. Moreover, there could be a competition between the cobalt and copper ions to interact with carbonate and hydroxide ions affecting the precipitation efficiency. Similar trend with the single copper system was found for the treatment of copper in the co-contaminated system seen in Fig. 8b. For the carbonate precipitation system, $[\text{CO}_3^{2-}]/[\text{M}]$ of 1.0 showed the greatest amount of sludge volume generated. On the other hand, $[\text{OH}^-]/[\text{M}]$ of 1.5 generated the largest SV_{30} . SV_{30}

recorded as observed in Fig. 8c are 450 to 620 and 120 to 500 mL L⁻¹ for carbonate and hydroxide precipitants, respectively, greater than that of the single cobalt and copper systems. In both single copper and co-contaminated systems, increasing the [P]/[M] ratio did not show any significant trend with the settleability of the precipitates in the reaction system depicted in Figs. 7d and 8d. Precipitant-to-metal ratio was found to be at optimum value of 1.2 in the study conducted by Mahasti et al. [43]. In contrary, [P]/[M] ratio necessary for treatment of cobalt and copper varied for the single- and co-contaminated wastewater stream in this study.

3.4. Effect of precipitant type

Cobalt removal by carbonate precipitation is significantly higher than that of hydroxide precipitation at weaker alkaline to neutral conditions in both single- and co-contaminated systems as shown in Fig. 9a. The precipitating agents used for removing cobalt from the simulated wastewater exhibited significant influence on the removal efficiency and resulting sludge in the system. Fig. 10 shows the supernatant volume for all the systems studied after 30 min of sludge settling. It was also found that the sludge formed by carbonate precipitation exhibits slower settling rate (lower supernatant volume) than that of hydroxide precipitation for all the pH values and [P]/[M] ratio studied for both systems. This may have been caused by less dense sludge particles and smaller particle size [30]. No general trend was found for the sludge volume formed from single cobalt and single copper systems. The results also show that even at increasing [P]/[M] ratios carbonate precipitation displayed better removal efficiency (lower residual Co) than hydroxide precipitation presented in Fig. 9b. Carbonate precipitation treatment can occur at pH values lower than that of hydroxide precipitation [44] which was evident in this study. Hydroxide system was found to be more effective in reducing the soluble zinc concentration than that of the

carbonate system in the study conducted by Patterson et al. [44]. Contrarily, carbonate system was found to be more effective and efficient in this study for the treatment of cobalt and copper in single- and co-contaminated streams. In the literature, hydroxide precipitation produces larger volumes of low-density sludge [37]. However, this study observed that the carbonate precipitation led to lower sludge density than the sludge generated by hydroxide precipitation. When particle recovery and reuse are added advantage, sodium carbonate is also better than sodium hydroxide as precipitant.

4. Conclusions

The behavior of cobalt in the single- and co-contaminated system showed similar removal at pH value of 10.0. Copper in the single system was easily removed in the system at pH values of 7.0-12.0 which may be due to precipitation-adsorption mechanism at pH values higher than 7.5. Copper probably forms initial copper-bearing precipitates and the remaining copper in the simulated wastewater stream is adsorbed on the surface of the precipitate formed in the system resulting to its complete removal. Precipitant-to-metal ratio necessary to treat cobalt varied for the single- and co-contaminated systems for both precipitants used. There was no significant effect on the copper system possibly due to excess precipitant dosage. The co-existence of cobalt did not affect the removal of copper in the co-contaminated wastewater stream. Carbonate and hydroxide precipitation systems are effective treatment methods in dealing with the metal pollutants contained in electroplating wastewater leading to high removal efficiency. In addition, carbonate precipitation was found to be a more effective and efficient treatment alternative to hydroxide precipitation, and soluble cobalt and copper can be removed from the wastewater streams using soda ash. One of the advantages of carbonate system with the hydroxide system was the operation

at lower pH values typically around 7.0-8.0. In terms of sludge volume, carbonate system had added advantage when the additional target is particle recovery and reuse.

Declarations

Availability of data and materials

All data generated or analyzed in this work are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no known competing financial interests.

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Authors' contributions

Khyle Glainmer N. Quizon conceptualized the study and carried out the experimental studies. Ming-Chun Lu provided conceptual and technical guidance for all the aspects of the work. Yao-Hui Huang commented, reviewed, and approved its completion. All authors read and approved the final manuscript.

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Fig. 1. Experimental set-up for single and co-contaminated systems.

Fig. 2. Speciation of (a) cobalt and (b) copper for soluble hydro complexes in pure water.

Fig. 3. Removal efficiency of (a) cobalt and (b) copper at different pH values using different precipitants (Conditions: $[\text{Co}]_0 = [\text{Cu}]_0 = 12.6 \text{ mM}$; $\text{pH} = \text{variable}$; $[\text{P}]/[\text{M}] = 1.2$).

Fig. 4. Sludge volume at 30 min and sludge settling rate at different pH values for cobalt (a-b) and copper (c-d) using different precipitants.

Fig. 5. Removal efficiency of (a) cobalt and (b) copper, (c) sludge volume at 30 min and (d) sludge settling rate in the co-contaminated system at different pH values using different precipitants.

Fig. 6. Removal efficiency (a) cobalt and (b) copper at different [P]/[M] values using different precipitants (Conditions: [Co]₀=[Cu]₀=12.6 mM; pH=8.0; [P]/[M]= variable).

Fig. 7. Sludge volume at 30 min and sludge settling rate at different [P]/[M] ratio for cobalt (a-b) and copper (c-d) using different precipitants.

Fig. 8. Removal efficiency of (a) cobalt and (b) copper, (c) sludge volume at 30 min and (d) sludge settling rate in the co-contaminated system at different [P]/[M] ratio using different precipitants.

Fig. 9. Residual cobalt concentrations at different heavy metals systems at different (a) pH values and (b) precipitant-to-metal ratio via carbonate and hydroxide precipitation.

Fig. 10. Supernatant volume after 30 min under different heavy metals systems at different (a) pH values and (b) precipitant-to-metal ratio via carbonate and hydroxide precipitation.