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The Removal of Cu (II) from Aqueous Solution using Sodium Borohydride as a Reducing Agent

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Abstract. The removal and recovery of metals from wastewater has been a subject of significant importance due the negative impact these toxic metals have on human health and the environment as a result of water and soil pollution. Increased use of the metals and chemicals in the process industries has resulted in generation of large quantity of effluents that contains high level of toxic metals and other pollutants. The objective of this work was to recover of Cu in its elemental form as metallic powder from aqueous solution using $NaBH_4$ as a reducing agent. Reductive precipitation was achieved in a batch reactor at 65°C using Cu powder as a seeding material. This study also investigated the effect of concentration of sodium borohydride ($NaBH_4$) as a reducing agent. The amount of $NaBH_4$ was varied based on mole ratios which are 1:1, 1:0.25 and 1:0.1 to recover Cu from synthetic wastewater. The results obtained showed that sodium borohydride is an effective reducing agent to recover Cu from wastewater. The optimum concentration of $NaBH_4$ that gives the best results the 1:1 molar ratio with over 99% Cu removal.

1. Introduction

The removal and recovery of metals from wastewater has been a subject of significant importance due to the adverse impact these toxic metals have on human health and the environment as a result of water and soil pollution [1]. Increased use of the metals and chemicals in the process industries has resulted in generation of large quantities of wastewater that contains high levels of toxic metals and other pollutants [1]. The presence Cu in the environment poses environmental disposal problems due to its non-biodegradability in the environment [2]. Unlike organic pollutants, the majority of which are susceptible to biological degradation, Cu ions do not degrade into harmless end products. Cu exists in most wastewater sources including, printed circuit board manufacturing, plating, wire drawing, copper polishing and paint manufacturing, wood preservatives and printing operations [3]. Copper is a toxic metal which may be accumulated in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. Drinking water with high Cu levels (≥1,300 ppb) may cause vomiting, diarrhea and stomach cramp [4]. The problem of recovering base metals like Cu as a pollutant from waste water is an important process and is becoming more important with the increase of industrial activities [5].

Several treatment methods such as precipitation, adsorption, ion-exchange and membrane technologies have been developed for metal remediation. Of these methods precipitation is the mostly widely used because it is the most economical method and easier to implement and operate on a large scale [6]. However, traditional precipitation methods using lime, sulfides or hydroxides recover metals in the form of a sludge which is not reusable and has to be disposed in landfills creating a potential environmental hazard and resulting in loss of valuable minerals. Due to the fast depletion of mineral reserves globally the current focus in effluent treatment is now on the recovery and re-use of these heavy metals rather than removal and disposal. So far none of this methods is capable of recovering metals in a form that is suitable for re-use hence there is a need to develop alternative technologies to meet technology based treatment. In this study, reductive precipitation was investigated as a possible method for remove and recover Cu in its elemental form.

2. Materials and methods

2.1. Equipment

A batch reactor with an overhead stirrer was used to ensure adequate suspension of the seeding material in solution. A thermometer was used to measure temperature. The atomic absorption spectroscopy (AAS;Tescan Vega 3 XMU l) was used to measure the concentrations of Cu in solution after reduction. X-Ray fluorescence (XRF;Rigaku ZSX Primus II) was used to determine the elemental composition of the powder product. Malvern Particle Analyser Mastersizer (2000) was used to measure the particle size distribution (PSD) of the powder using the laser diffraction technique. The powder morphology was captured using a Scanning Electron Microscopy (SEM; Thermo scientific ICE 3000 series) to determine the effect of sodium borohydride.

2.2. Materials

$CuSO_4.5H_2O$ salts supplied by Sigma Aldrich was used to prepare synthetic 0.5g/l Cu^{2+}solution. Cu powder supplied by Sigma Aldrich were used as seeding materials. Reverse osmosis water was used to prepare all the samples. NaOH supplied by Rochelle chemicals was used to adjust the pH. HNO_3 and H_2SO_4 supplied by Sigma Aldrich was used to prepare the residual solution for AAS analysis.acid respectively.

2.3. Methods

2.95 g of $CuSO_4.5H_2O$ was measured and dissolved in RO water to make a 0.5 g/L solution of Cu^{2+}. 500 ml of the solution was mixed with 0.161 g of $NaBH_4$ and 30 g of Cu powder making a 1:1 stoichiometric solution. The resulting solution was then heated to 65°C and then the pH was adjusted to 12 by adding 70 ml of 1 M NaOH. At the end of 3 min agitation and heating was stopped and the solution was allowed to cool. After settling the clear supernatant was decanted carefully leaving the seeding material and reduced metal in the beaker. The above procedure was repeated twice with fresh Cu solution and the same seeding material. After the third experiment the seeding material was discharged from the beaker. The seeding material was filtered using a Buchner vacuum filtration unit and dried for particle size distribution, elemental and morphology analysis. The reduced solution was then filtered and 100 ml of the sample was analysed for the residual metal concentration using Atomic Absorption Spectroscopy. To establish the effect of concentration of reducing agent the amount of $NaBH_4$ was varied based on mole ratios which are 1:1, 1:0.25 and 1:0.1.

3. Results and discussions

3.1. Effect of $NaBH_4$ concentration

Figure 1 shows the variation in % removal of Cu^{2+} in different molar ratios with the number of batch reduction.

Figure 1 shows that the % removal decreases from the 1st batch to the 3rd batch for all the molar ratios. This can be attributed to the plating of Cu which did not catalyze the reduction reaction meaning Cu was not autocatalytic. The highest percentage removal obtained was 99.7 % at 1:1 molar ratio as compared to the 1:0.25 and 1:0.1 molar ratios. This is due to the decrease in the NaBH4 concentration.

3.2. Reduction rate of Cu^{2+}

Figure 2 shows the variation of Fe^{3+} reduction rate from solution with successive number of densifications.

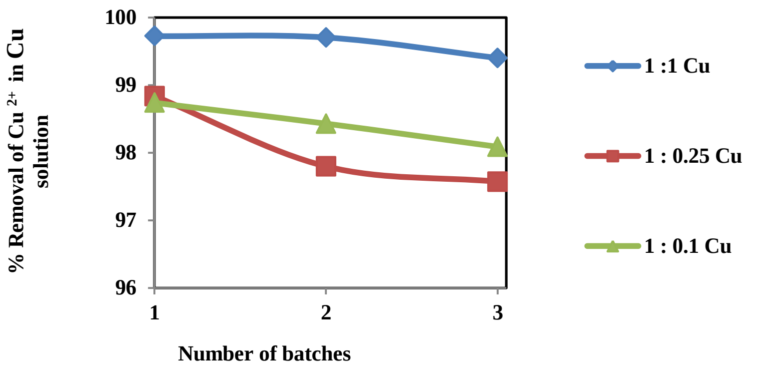

Figure 1. % Removal of Cu^{2+}using Cu powder as a seed material.

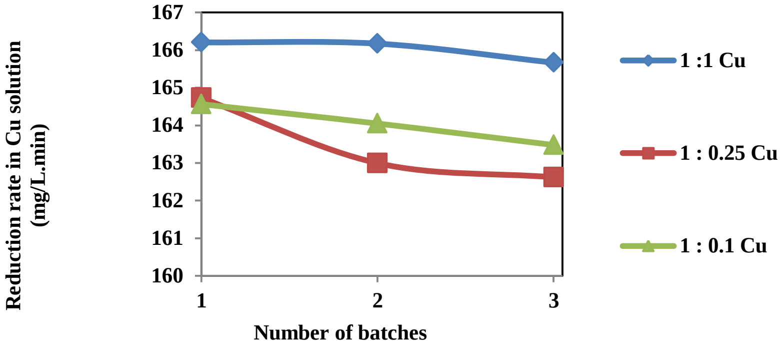

Figure 2. Reduction rate of Cu^{2+}

The reduction rate of copper in the Cu solution generally decreased from the 1st to the 3rd batch in Fig. 2. This is due to the fact that Cu plating decreases the effective surface activity of the seed decelerating the rate of reduction.

3.3. Effect of reduction on Cu powder purity

The composition of the powder produced was analysed using the X –ray Flourescence.Table 1shows the XRF analysis of Cu seed before and after reduction crystallization.

The % Cu content before reduction was 99.2% and after reduction there was rapid decrease in Cu content the lowest being at 1:1 molar ratio followed by the 1:0.25 and then the 1:0.1 molar ratios. It can be seen that as the concentration NaBH4 is reduced the purity of the powder increases. There was a dramatic decrease at 1:1 as compared to 1:0.25 and 1:0.1.This is attributed by the incorporation of decomposition products like sodium and borane being incorporated into the powder.

3.4. Effect of reductive precipitation on PSD

Figure 3 and Figure 4 shows the PSD analysis of BOFS before and after electroless plating.

Figure 3 shows that there was a shift in modal size from that of the seed indicating a generation of smaller sized particles which is evidence of breakage or nucleation. µm. The number distribution was uni-modal as depicted in Figure 4. Furthermore the trend was the same before and after reduction. The only difference is that smaller particles dominated at 1:1 molar ratio followed by 1:0.25 then 1:0.1.This trend resembles that as the smaller particles dominate, the higher the reducibility in the residual concentration hence 1:1 molar ratio was preferentially favored over 1:0.25 and 1:0.1.

Table 1. Copper powder purity in copper solution

	Before reduction	**After reduction**		
Elements	Cu seed	1:1	1:0.25	1:0.1
Na_2O	0.000	1.680	0.695	0.462
MgO	0.051	0.053	0.000	0.000
Al_2O_3	0.090	2.940	0.238	0.175
SiO_2	0.112	0.186	0.075	0.055
P_2O_5	0.042	0.044	0.059	0.053
SO_3	0.015	1.110	0.164	0.114
Cl	0.017	0.018	0.027	0.025
K_2O	0.000	0.005	0.000	0.000
Fe_2O_3	0.366	0.048	0.054	0.0368
NiO	0.106	0.000	0.053	0.0646
CuO	99.20	79.10	98.50	99.00
ZnO	0.000	0.057	0.000	0.000
Ag_2O	0.000	0.035	0.043	0.035
Cr_2O_3	0.013	0.000	0.000	0.000
CaO	0.012	0.026	0.000	0.019
MnO	0.000	0.012	0.000	0.000
PdO	0.000	0.000	0.029	0.000

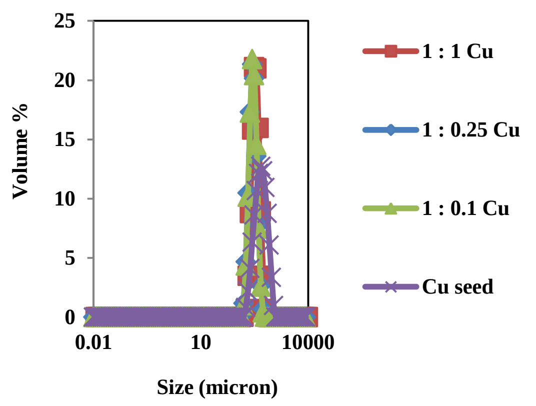

Figure 3. Evolution of PSD by volume distribution using Cu powder

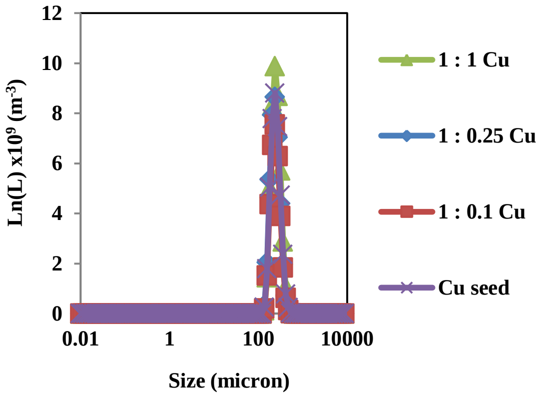

Figure 4. Evolution of PSD by number distribution using copper powder

3.5. Effect of electroless plating on particle morphology

Figure 5 shows the scanning electron micrographs of the Cu powder before and after reductive precipitation.

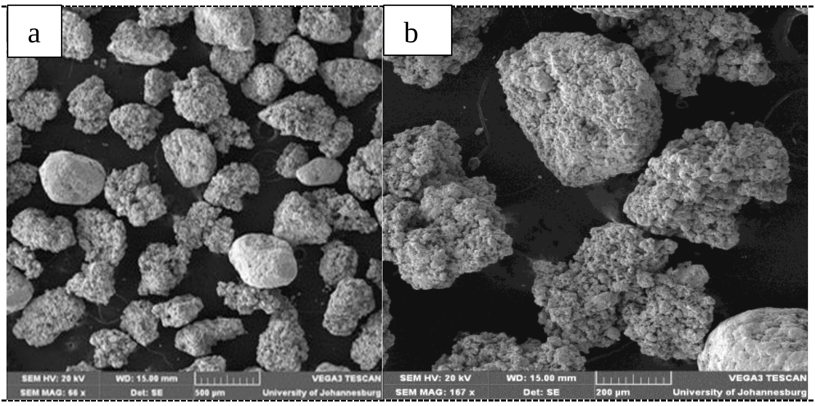

Figure 5. SEM of the Cu powder (a) before plating, (b)Cu powder after reductive precipitation.

The particles exhibited a nearly spherical structure and wide particle size range before and after reduction. However, it was seen that the particle size increased significantly after reduction. This is typical of particle aggregation.

4. Conclusion

Sodium borohydride was found to be an effective reducing agent as results in an increase in the rate of reduction. The optimum concentration of $NaBH_4$ that gave the best results was the 1:1 molar ratio which achieved over 99% removal of Cu. The treated effluents (wastewater) after reduction process is environmentally friendly as it meets a general limit for effluent discharge which is stipulated in the Johannesburg acceptance standards for effluents as 20mg/L for copper. Reductive precipitation using sodium borohydride recovers Cu in elemental form as metallic powder which can be re-used which is more economical than other methods such as precipitation agents which produces by-products such as sludge which are toxic and cannot be re-used resulting in loss of valuable minerals.

5. References

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