IOP Conference Series: Materials Science and Engineering

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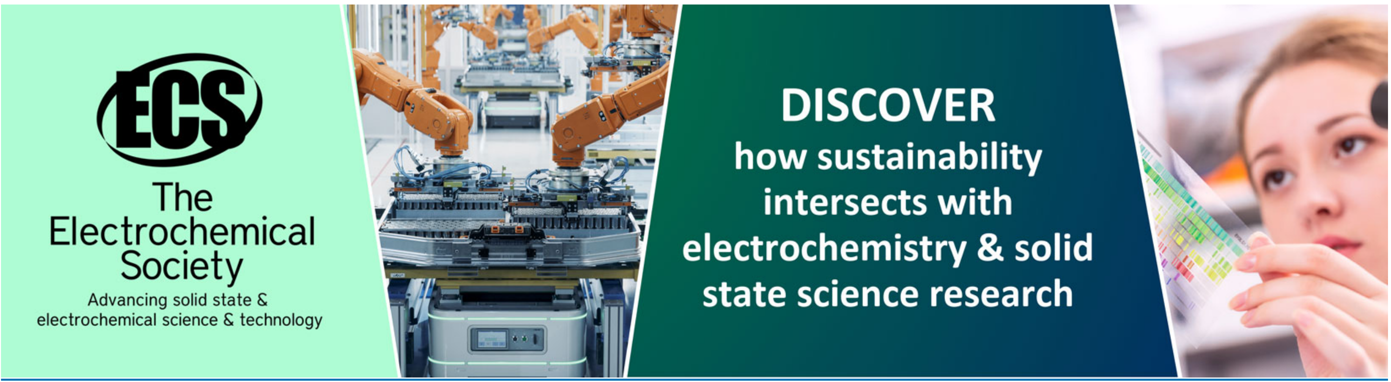
To cite this article: Nur Ain Zainuddin *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **551** 012122



IOP Conf. Series: Materials Science and Engineering **551** (2019) 012122 doi:10.1088/1757-899X/551/1/012122

Removal of Nickel, Zinc and Copper from Plating Process Industrial Raw Effluent Via Hydroxide Precipitation Versus Sulphide Precipitation

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Abstract. Electroless plating wastewater contains mixed metals element. Although precipitation is the most common method applied to remove metals from the wastewater, it fails to completely precipitate all the metals at a single pH. The present work evaluates the effectiveness of the sulphide and the hydroxide precipitation for removal of nickel, zinc and copper from industrial wastewater, namely acid rinse and nickel rinse samples. The optimum pH and coagulant dosage were determined via Jar Test for both types of samples. Sulphide precipitation removed heavy metals more efficient than hydroxide precipitation. For the acid rinse sample, 95.32% of nickel was removed using sulphide precipitation while 76.66% removal using hydroxide precipitation. For nickel rinse sample, 93.75% of zinc was removed using sulphide while 68.8% removal using hydroxide. 65.75% of nickel was removed using both sulphide and hydroxide. Total removal of copper was achieved for both hydroxide and sulphide precipitation, either from acid rinse or nickel rinse samples.

1. Introduction

Hydroxide treatment is the most common and widely used precipitation method for removal of heavy metal from industrial wastewater [1]. However, this method has its limitation in treating mixed metal effluents since all metal hydroxides do not completely precipitate at a single pH. Each type of metal hydroxide is favourable to precipitate at a certain pH range. According to the solubility-pH relationship, as shown by Fig. 1, the best-compromised pH for hydroxide precipitation process is pH 10-10.5 for nickel, pH 9.0-9.5 for zinc and pH 8.5-9.5 for copper. It shows that these heavy metals cannot be completely removed at single pH range. Hydroxide precipitates tend to resolubilize if the solution pH is not in the compromised range [2]. Besides, hydroxide precipitation produces a large amount of sludge which required further treatment before disposal. For sulphide precipitation, the optimum pH for copper is pH 8 while both nickel and zinc are at a range of pH 10-10.5. Therefore, nickel and zinc can be removed at a single pH using sulphide precipitation.

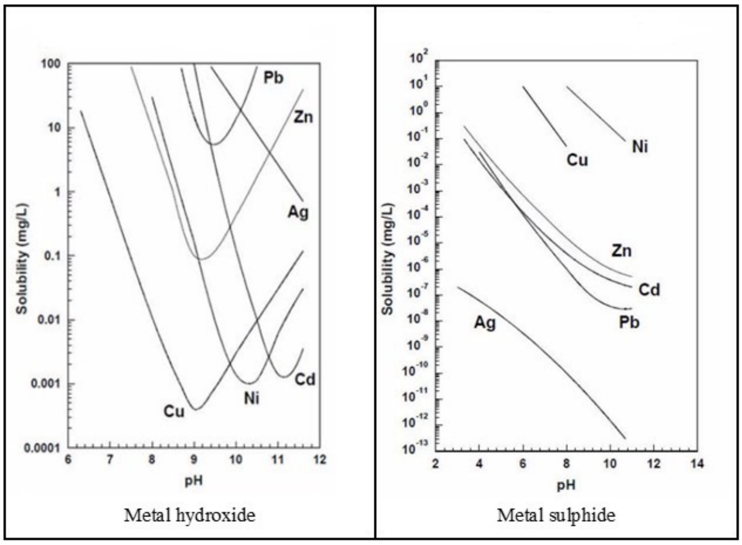

Figure 1. The solubility of metal hydroxide and metal sulphide on different pH [3].

Sulphide precipitation has advantages over hydroxide precipitation [4]. Sulphide can remove a high degree of metals compare to hydroxide due to the lower solubility of metal sulphide over a broad pH range [5]. Its reaction rate is faster than hydroxide precipitation due to the high reactivity between sulphide and heavy metal ions. The sludge generated is less compare to hydroxide precipitation. However, sulphide precipitation gains little attention because of the sulphide dosing and process control difficulty due to the sensitivity of the process [6]. It is found in limited application because of the potential of releasing toxic gaseous, hydrogen sulfide (H2S) emissions and operational difficulties [7].

The concentration of heavy metal in the electroless plating industry wastewater commonly not complies with the acceptable discharge concentration. For instance, aging wastewater at a nickel plating plant contained 2900 ppm of nickel ions [8]. According to the Environmental Quality (Industrial Effluent) Regulations 2009 by the Department of Environment (DOE), Malaysia [9], the acceptable discharged concentration for nickel and copper is 1.0 mg/L, while zinc is 2.0 mg/L. The purpose of this research is to evaluate the performance of hydroxide precipitation and sulphide precipitation for removal of heavy metals, namely nickel, zinc and copper from electroless plating wastewater. The optimum pH and coagulant dosage were also determined.

2. Methodology

2.1. Wastewater Description and Analysis

The wastewater was obtained from electroless copper plating Company A and Company B. Two different samples were obtained which were acid rinse from Company A and nickel rinse from Company B. Approximately 10 litres of each sample was collected. The heavy metal concentration in the wastewater was determined using multimeter portable colorimeter (HACH DR900), and HACH Method 8009, 8506 and 8105 was employed for zinc, copper and nickel, respectively.

2.2. Jar Test

Jar Test was carried out to evaluate the optimal pH and coagulant dosage of the precipitation process. The optimum pH and coagulant dosage for precipitation are required to enhance the coagulation process and to avoid overdose of the chemicals. The coagulant used in these experiments was ferric chloride (FeCl3). Firstly, the wastewater sample (300 mL) was poured into a series of ten beakers. The pH of the sample in each beaker was adjusted to ten different values (3, 4, 5, 6, 7, 8, 9, 10, 11 and 12) by adding H2SO4 or NaOH. Then, 0.5 mL of FeCl3 was added to each beaker/jar. A rapid mix was applied (150 rpm) for 3 minutes, and then it was reduced to 60 rpm for 15 minutes to promote larger floc formation. The mixer was turned off between 30 to 45 minutes to allow the flocs to settle down. Then, the turbidity of the sample was measured. The pH value that gave the lowest turbidity value was chosen as the optimum pH of the precipitation process. The Jar Test was repeated to determine the optimum coagulant dosage at the obtained optimum pH. Five beakers of the sample were prepared and different coagulant dosage was added in the respective beaker (0.2, 0.4, 0.6, 0.8 and 1.0 mL). At the end of the experiments, the mass of the suspended solid produced by each test was measured by the gravimetric method and the result was identified as the weight of sludge.

2.3. Hydroxide and Sulphide Precipitation
The removal of heavy metal by precipitation was carried out at the optimum pH and optimum dosage of coagulant. It was carried out by a stirring process at 150 rpm for 3 minutes. Then, the precipitant (either hydroxide or sulphide) was added into the sample and the mixing process was continued at similar speed for 5 minutes. NaOH and N2S were employed as the hydroxide and sulphide precipitant, respectively. Next, the anionic polymer (flocculant) was added and the speed of the mixing was reduced to 30 rpm and maintained for 15 minutes. For sulphide precipitation, the process was conducted in alkaline condition (pH 8 to 12) to prevent H2S gas formation [1, 7]. Therefore, the pH of the sample was adjusted to pH 8 to 12 using NaOH prior to adding the Na2S in the sample. The removal efficiency of heavy metals by hydroxide and sulphide precipitation was calculated.*Research Procedure*

3. Results and Discussion

3.1. Acid Rinse Sample
Figure 2 shows the turbidity and the weight of sludge at various pH using hydroxide and sulphide precipitation and (b) for acid rinse sample. Using hydroxide precipitation, the turbidity value at pH 3 was very high and was excluded in Figure 2(a). It is also found that pH 8 and pH 4 have the lowest turbidity which is about 0.10 mg/L. However, a higher weight of sludge was produced at pH 4 compared to pH 8. Furthermore, pH 4 is not complied with Standard B discharge requirement by the local authority. The pH of discharged wastewater needs to be controlled between pH 5.5 to pH 9 [5]. Therefore, the optimum pH for acid rinse sample using hydroxide precipitation is at pH 8 and was similar reported by Kurniawan, et al. [10].

Sodium sulphide (Na2S) was employed as the precipitant in sulphide precipitation process. However, directly mixing the Na2S into the sample will produce harmful hydrogen sulphide gas [7, 11]. The sample will turn black with a high turbidity value. This is associated with the acidic nature of the sample. To prevent this from happen, the sample was neutralized using NaOH prior to adding the Na2S in the sample. Figure 2(b) shows that the lowest turbidity value was achieved at pH 8, which was similar to the result obtained using hydroxide precipitation. However, sulphide precipitation produced 50% less sludge compares to hydroxide precipitation. At pH 8, hydroxide and sulphide precipitation produce 0.02 and 0.01 g of sludge, respectively. Blais, et al. [7] also reported less amount of sludge was produced by sulphide than hydroxide treatment.

Figure 3 shows the turbidity and weight of sludge obtained at various coagulant dosage. It was observed in Figure 3(a) that the lowest turbidity value was achieved using 0.4 mL coagulant by hydroxide precipitation while the lowest sludge production was obtained using 0.2 mL coagulant. The dosage of 0.4 mL was chosen as the optimum condition as 0.2 mL coagulant gave a slightly higher value of turbidity compared to 0.4 mL. Besides, choosing less than 0.4 mL dosage may reduce the efficiency of heavy metal removal. Underdosing of coagulant contributes to colloidal particle cannot be destabilized so it will disrupt the flocculation process, hence more amount of sludge will be produced. The amount of sludge produced at the optimum coagulant dosage was found to be 0.02 g. Increasing the coagulant dosage more than 0.4 mL increase the turbidity value. This is caused by attributed to charge reversal and destabilization of colloidal particles due to overdosing [12].

On the other hands, Figure 3(b) shows that the optimum coagulant dosage for sulphide precipitation was using 0.6 mL of coagulant. It gave the lowest turbidity value and sludge produced. The amount of optimum coagulant needed in sulphide precipitation is higher compared to hydroxide precipitation. More amount of coagulant is required due to low solubilities of most metal sulphide salt [13]. However, the volume of sludge production remains low compared to hydroxide precipitation.

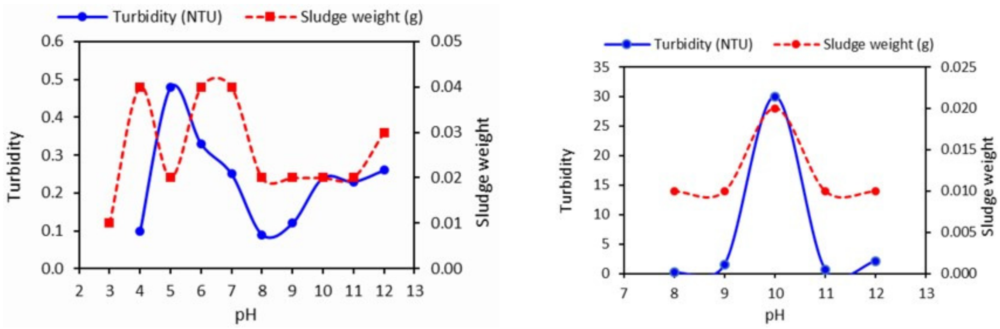

Figure 2. Turbidity and weight of sludge at various pH using (a) hydroxide precipitation and (b) sulphide precipitation for acid rinse sample.

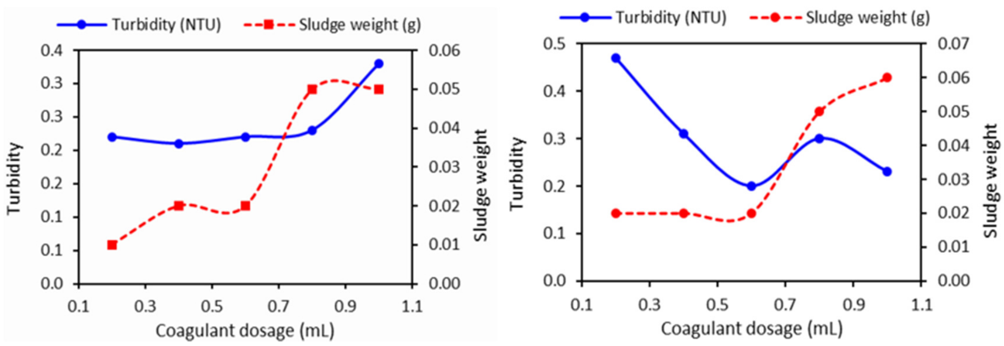

Figure 3. Turbidity and weight of sludge at various coagulant dosage using (a) hydroxide precipitation and (b) sulphide precipitation for acid rinse sample.

3.2. Nickel Rinse Sample

Figure 4 shows the obtained turbidity and sludge produced by the hydroxide and sulphide precipitation of nickel rinse sample. The turbidity values at more acidic conditions are excluded in the plot as their values are too high and exceeding the upper limit detection of the turbidity meter. For both types of precipitations, it is observed that the lowest turbidity was obtained at pH 10. However, hydroxide precipitation produced more sludge than sulphide precipitation at this pH.

For the effect coagulant dosage, the optimum amount of coagulant for nickel rinse sample by hydroxide precipitation was 0.6 mL, as shown in Figure. 5. Using this amount of coagulant, the obtained turbidity value and the sludge produce was the lowest (0.01 g). On the other hands, the

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amount of sludge gradually increases with the increase of coagulant dosage in sulphide precipitation process, as illustrated by Fig. 5(b). However, higher coagulant dosage (more than 0.8 mL) promotes a high value of turbidity. Although 0.2 mL produced the lowest amount of sludge, the turbidity was too high (127 NTU) and was excluded from the plot. Therefore, the optimum coagulant dosage was 0.4 mL for which it gave the lowest turbidity value with a reasonable amount of sludge produced.

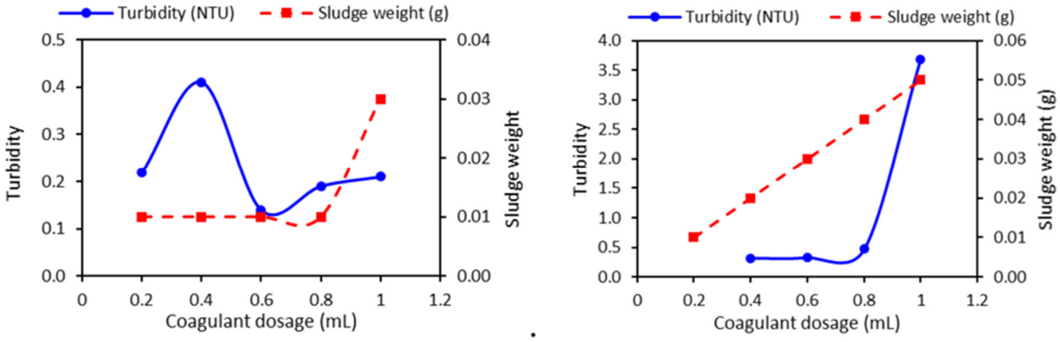

Figure 4. Turbidity and weight of sludge at various pH using (a) hydroxide precipitation and (b) sulphide precipitation for nickel rinse sample

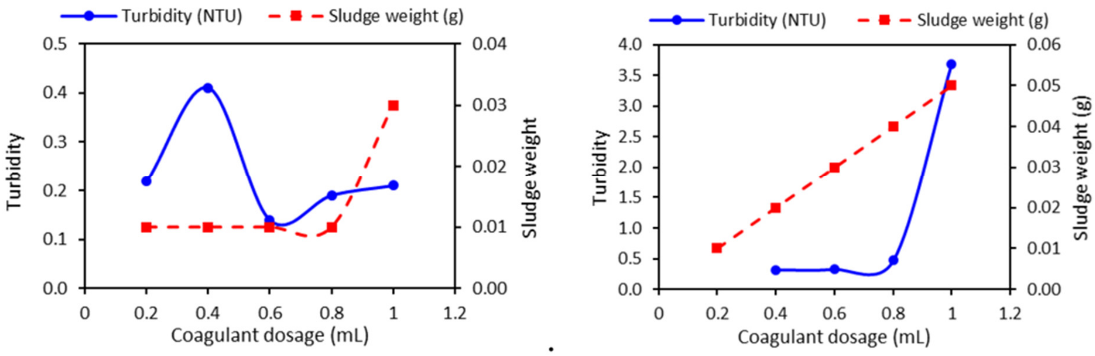

Figure 5. Turbidity and weight of sludge at various coagulant dosage using (a) hydroxide precipitation and (b) sulphide precipitation for nickel rinse sample.

3.3. Heavy Metal Removal

Table 1 tabulates the data for the initial concentration and percentage removal of metals by hydroxide and sulphide precipitation at their respective optimum pH and coagulant dosage. Acid rinse sample does not contain zinc, but it contains a high concentration of nickel and copper which is 12.32 and 15.52 mg/L, respectively. Both nickel and copper concentration do not comply with local authority standard limit which is 1.0 mg/L. The removal efficiency of nickel was 76.66% after the hydroxide precipitation process. Higher removal was obtained using sulphide precipitation (95.32%). A similar observation was found for removal efficiency of Zn in nickel rinse sample. According to Chen, et al. [5] and Fu and Wang [6], sulfide precipitation can achieve a high degree of metal removal over a broad pH. Additionally, total removal of copper was obtained for both type of samples using either hydroxide or sulphide precipitation. Removal of copper removal is very efficient in both method because at pH 8 copper is least soluble compared to nickel. It can be concluded that pH 8-9 is the optimum pH for copper removal while nickel is at pH 10-10.5 (as illustrated by Figure 1).

Table 1. Heavy metals removal from acid and nickel rinse samples by hydroxide and sulphide precipitation.

	Acid Rinse			Nickel Rinse		
	Ni	Zn	Cu	Ni	Zn	Cu
Initial concentration (mg/L)	12.32	ND	15.52	1.06	6.40	0.20
Percentage removal by hydroxide precipitation (%)	76.66	-	100	65.79	68.75	100
Percentage removal by sulphide precipitation (%)	95.32	-	100	65.79	93.75	100

ND - Non-detectable

4. Conclusions

In this research work, the optimum pH and coagulant dosage for hydroxide and sulphide precipitation of heavy metals were determined. At these optimum conditions, the performance of hydroxide and sulphide precipitation was compared. Sulphide precipitation was found to remove heavy metals (zinc, nickel and copper) more efficient than hydroxide precipitation. For acid rinse sample, 95.32% of nickel was removed using sulphide precipitation while 76.66% removal was obtained using hydroxide precipitation. For nickel rinse sample, 93.75% of zinc was removed using sulphide while 68.75% removal using hydroxide. A similar result was obtained for removal of nickel by both precipitation method. The removal efficiency of nickel was 65.79%. Additionally, total removal of copper was achieved for both sulphide and hydroxide precipitation in acid rinse and nickel rinse samples. As a conclusion, the performance of sulphide precipitation treatment was better than hydroxide precipitation as it removes a high amount of nickel, zinc and copper.

Acknowledgements

We acknowledge the facilities provided by the Universiti Teknologi MARA, Institute of Quality and Knowledge Advancement (InQKA) and Integrated Separation Technology Research Group (i-STRonG). The authors are grateful for financial support provided by the Faculty of Chemical Engineering, UiTM Shah Alam.

References

[1] Gunatilake S.K. 2015 J. Multidiscip. Eng. Sci. Stud. 1 12 .
[2] Brbooti M.M. et al. 2011 J Eng. Technol 29, 595
[3] Control and Treatment Technology for the Metal Finishing Industry. Industrial Environmental Research Laboratory. EPA 625/8-80-003, 1980.
[4] Lewis A et al. 2006 81, 197.
[5] Chen et al 2018 J. Water Process Eng. 26, 289
[6] Fu F et al. 2011 , J. Environ. Manage. 92, 407
[7] Blais J. F. et al. 2008 Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 12, 135
[8] Shih Y.J. et al. 2013 Sep. Purif. Technol. 104, 100
[9] Environmental Quality (Industrial Effluent) Regulations 2009, P.U.(A) 434/2009.
[10] Kurniawan T.A et al. 2006 Chem. Eng. J. 118, 83
[11] Veeken A.H.M et al. 2003 Water Res. 37, 3709
[12] Baghvand A.D et al. 2010 J. Environ. Sci 6, 442
[13] Mokone T.P. et al. 2012 Water Res. 46, 2088