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REMOVAL OF HEAVY METALS FROM ELECTROPLATING WASTEWATER BY FERRITISATION

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ABSTRACT

A laboratory scale reactor was designed for the purification of synthetic heavy metals containing wastewater and electroplating wastewater. The optimum conditions for ferritisation of heavy metal cations were studied with respect to the ratio of M^{2+} to Fe^{2+}, the O_2 flow rate, pH and temperature. The recommended ratio of Cu^{2+} to Fe^{2+}, Ni^{2+} to Fe^{2+}, and Zn^{2+} to Fe^{2+} were 1 to 2, 1 to 5 and 1 to 10, respectively. The optimum concentration of Fe^{2+} added to synthetic wastewater containing Cu-Ni, Cu-Zn, Ni-Zn and Cu-Ni-Zn were 800, 1,400, 1,600 and 1,400 mg l^{-1}, respectively. The Fe^{2+} concentration used to treat wastewater containing two and three heavy metal cations was 100-200 mg l^{-1} higher than the Fe^{2+} concentration used to treat wastewater containing a single heavy metal cation. The optimum O_2 flow rate, pH and temperature were 100 ml min^{-1}, 10 and 50 °C, respectively. Heavy metals in synthetic wastewater were removed > 99.5%. 99.80% of copper, 99.88% of nickel, 99.99% of zinc and 99.92% of iron were removed from electroplating wastewater.

KEYWORDS: ferrite sludge, wastewater purification, hazardous materials, precipitation, decontamination, recycling

1. INTRODUCTION

The metal finishing and plating industries produce the widest variety of metal cations in waste effluents. Technologies available for treating metal contaminated wastewater include chemical oxidation and reduction, precipitation as hydroxides, sulfides and xanthates, chemical displacement, evaporation, ion exchange, membrane separation and adsorption [1-6]. Precipitation, chemical oxidation and reduction, chemical displacement and adsorption processes generate other forms of hazardous wastes which also require highly regulated and costly disposal. Ion exchange, evaporation and membrane separation processes do not present a sludge disposal problem but do not appear to be economical. Several attempts have been made to precipitate the heavy metals as ferrites [7-12]. This process results in the formation of a ferrite sludge with magnetic properties. Its strong magnetic properties lead to a variety of applications, such as their use as toners for laser printing, pigments, magnetic bands and oil recovery from residues [13].

The aim of the study was to investigate the optimum conditions to treat synthetic wastewater containing copper, nickel and zinc. The experiments were conducted on single and a combination of double and triple metal cation containing solutions. The efficiency of the ferrite process for the purification of wastewater from the plating industry is also presented in this paper.

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2. MATERIALS AND METHODS

All glassware were washed with detergent in the ultrasonic bath for 1 hour and dried at 100°C for 30 minutes in the oven. All reagents were of analytical grade and were used without further purification. Stocks of Cu(II), Ni(II) and Zn(II) solution (1,000 mg l^{-1}) were prepared from $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$ and $ZnSO_2 \cdot H_2O$, respectively. Deionized water was used for preparation of all standards, synthetic wastewaters and reagent solutions.

The experimental setup is shown in Figure 1. The treatment was carried out in 1 liter of pyrex glass beakers. The required amount of $FeSO_4 \cdot 5H_2O$ was added to 500 ml of synthetic wastewater. The contents of the reactor were continuously and uniformly mixed by means of a mechanical stirrer. A water bath with a thermostat was used to regulate the temperature. A controlled flow of oxygen was introduced to the solution. The 99.97 % oxygen was purchased from Thai Industrial Gas Trading Company. The solution pH was measured continuously by a pH meter (Denver Instrument model 215). After treatment, the liquid was separated from the solid ferrite by filtration. The heavy metal concentration was quantified by atomic absorption spectroscope (Shimadzu model AA-680). The precipitated ferrite was analyzed by X-ray diffractometer (Bruker AG model D8 Advance), X-ray fluorescence spectroscope (Bruker AG model SRS3400) and Scanning electron microscope (Leo model 1455 VP). An industrial wastewater sample was obtained from an electroplating manufacturing plant located in Ladkrabang industrial estate. Three replications of all experiments were performed to test the repeatability and standard deviation.

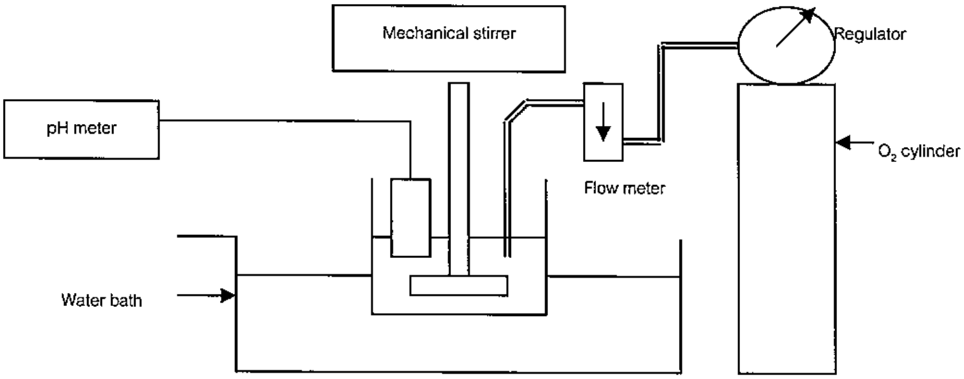

Figure 1 A laboratory scale reactor

3. RESULTS AND DISCUSSION

3.1 The optimum ratio of M^{2+} to Fe^{2+} for treatment of synthetic wastewater containing a single metal cation

The initial concentration of heavy metal used in this experiment was 200 mg l^{-1}. Conditions used in this experiment were a O_2 flow rate of 100 ml min^{-1}, a pH of 9, a temperature of 50°C and a contact time of 45 mins. From Figure 2 it could be seen that the earlier X-ray diffractometer signal was low because an insufficient amount of Fe^{2+} caused a low formation of ferrite sludge. When the ratio of M^{2+} to Fe^{2+} increased, ferrite sludge also increased steadily until ratios of Cu^{2+} to Fe^{2+}, Ni^{2+} to Fe^{2+} and Zn^{2+} to Fe^{2+} were 1 to 2, 1 to 5 and 1 to 10, respectively. The study, therefore, found what conditions would form the most ferrite sludge. Ratios of Cu^{2+} to $Fe^{2+}$and Ni^{2+} to Fe^{2+} obtained from this study are similar to the results of Demirel *et al.* [14] who conducted experiments with synthetic wastewater containing single Cu^{2+} (100 ppm) and single Ni^{2+} (90 ppm). However, the ratio of Zn^{2+} to Fe^{2+} obtained from this study is more than Demirel *et al.* [14] for synthetic wastewater containing only 77 ppm Zn^{2+}. When the amount of Fe^{2+} exceeded, the optimum, the X-ray diffractometer signal was likely to decrease. That could be described by the formation of metal ferrite, generally, caused by M^{2+} replacing Fe^{2+} in the octahedral position in the ferrite structure or magnetite ($Fe^{2+}O.Fe^{3+}{}_2O_3$) [15]. When the reaction is completed, it would form metal ferrite ($M^{2+}O.Fe^{3+}{}_2O_3$). But if there is an exceedance of Fe^{2+}, it would cause some sludge to be in the form of $M^{2+}{}_xFe^{2+}{}_{1-x}.Fe^{3+}{}_2O_4$ that causes the X-ray diffractometer signal of metal ferrite to decreases. The reaction is shown in equation 1 [16]

$$(3\text{-}x)\ Fe^{2+} + x\ M^{2+} + \tfrac{1}{2}\ O_2 + 6\ OH^{-} \longrightarrow M^{2+}{}_xFe^{2+}{}_{1-x}.Fe^{3+}{}_2O_4 + 3\ H_2O \qquad (1)$$

When considering the physical characteristics of sludge produced, sludge from Ni and Zn was pitch-black which is a good characteristic for ferrite sludge, whereas, sludge from Cu was black brown. This was caused by sludge being a mixed sludge of CuO and $Fe(OH)_2$. That red brown color was due to $Fe(OH)_2$. If the mixed sludge was brought to a heat of ≥ 800 °C for 2 days with O_2 as a catalyst, the quality of ferrite sludge would be better. And when considering the percentage removal of metals from Table 1, it was found that the three types of metals could be removed > 99 %. All the experiments were conducted in base conditions so, the heavy metals could precipitate as $M(OH)_2$.

Table 1 The percentage of metal removal and sludge color when varying ratio of metal ions to iron ions

Wastewater containing	$M^{2+} : Fe^{2+}$	Sludge color	Percentage of metal removal	
			M^{2+}	Fe^{2+}
Cu	1 : 1	Brown	99.06 ± 0.16	100.00 ± 0.00
	1 : 2	Black brown	99.70 ± 0.08	100.00 ± 0.00
	1 : 3	Black brown	99.65 ± 0.12	99.98 ± 0.02
	1 : 4	Black brown	99.54 ± 0.06	100.00 ± 0.00
	1 : 5	Black brown	99.55 ± 0.20	99.99 ± 0.01
	1 : 6	Black brown	99.50 ± 0.09	99.99 ± 0.01
	1 : 7	Black brown	99.54 ± 0.25	100.00 ± 0.00
	1 : 8	Black brown	99.55 ± 0.15	99.99 ± 0.02
Ni	1 : 2	Red brown	99.13 ± 0.06	99.98 ± 0.03
	1 : 3	Red brown	99.21 ± 0.08	99.99 ± 0.03
	1 : 4	Black brown	99.58 ± 0.04	100.00 ± 0.00
	1 : 5	Black	99.68 ± 0.12	99.99 ± 0.01
	1 : 6	Black	99.59 ± 0.10	99.99 ± 0.01
	1 : 7	Black	99.53 ± 0.11	100.00 ± 0.00
	1 : 8	Black	99.63 ± 0.02	99.99 ± 0.01
	1 : 9	Black	99.51 ± 0.15	99.99 ± 0.02
Zn	1 : 5	Black brown	99.07 ± 0.07	99.98 ± 0.03
	1 : 6	Black brown	99.05 ± 0.16	99.99 ± 0.04
	1 : 7	Black brown	99.13 ± 0.11	100.00 ± 0.00
	1 : 8	Black	99.22 ± 0.09	99.99 ± 0.00
	1 : 9	Black	99.23 ± 0.10	99.99 ± 0.03
	1 : 10	Black	99.51 ± 0.05	100.00 ± 0.00
	1 : 11	Black	99.48 ± 0.06	99.99 ± 0.01
	1 : 12	Black	99.44 ± 0.06	100.00 ± 0.00

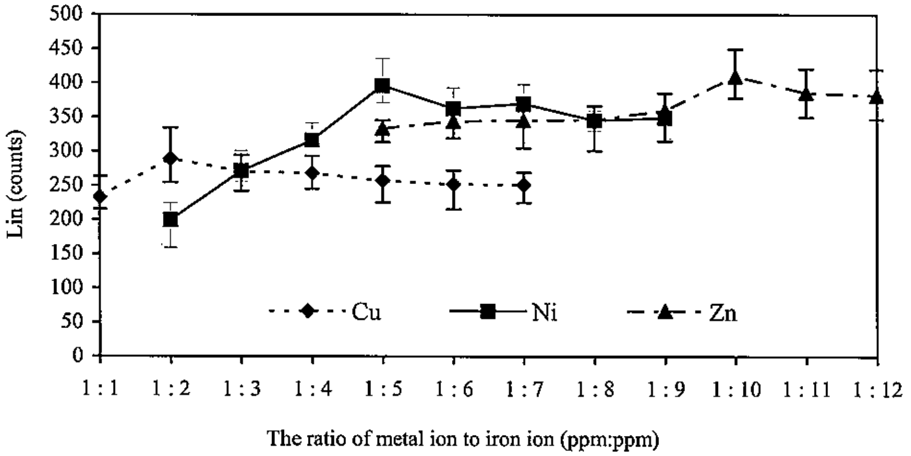

Figure 2 Relationship between the X-ray diffractometer signal (counts) and the ratio of metal ions to iron ions (ppm : ppm) in treatment of synthetic wastewater containing a single metal cation

3.2 The optimum concentration of Fe^{2+} for treatment of synthetic wastewater containing two and three metal cations

The initial mixed heavy metal concentration used was 200 mg l^{-1}. Concentrations of metals mixtures prepared were the same. In this experiment, the O_2 flow rate was 100 ml min^{-1}, the pH was 9, the temperature was 50 °C and the contact time was 45 mins. When considering the X-ray diffractometer signal in Figure 3, it was found that the optimum concentrations of Fe^{2+} that should be added to synthetic wastewater containing mixed Cu-Ni, Cu-Zn, Ni-Zn and Cu-Ni-Zn were 800, 1,400, 1,600 ,and 1,400 mg l^{-1}, respectively. Concentration of Fe^{2+} used for the treatment of synthetic wastewater containing multiple heavy metals were more than the concentration of Fe^{2+} used for the treatment of a single heavy metal by about 100-200 mg l^{-1}. Sludge obtained from all the experiments were black in color.

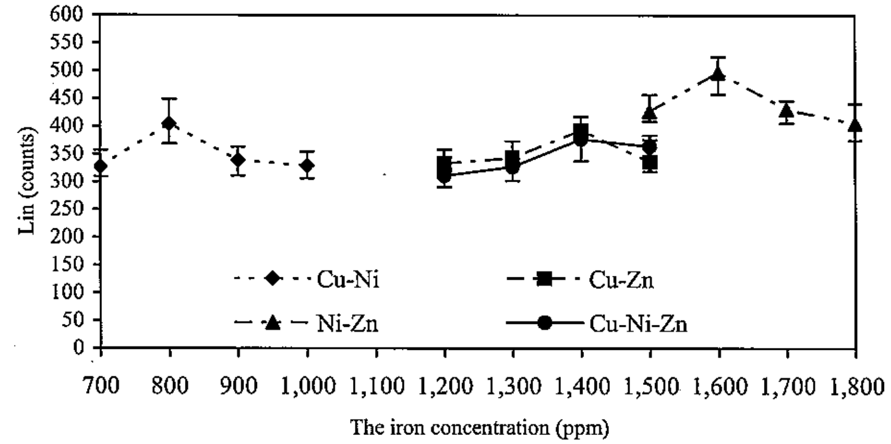

Figure 3 Relationship between the X-ray diffractometer signal (counts) and iron concentrations (ppm) in treatment of synthetic wastewater containing two and three metal cations

From table 2 it could be seen that percentages of Cu, Ni, and Zn removed were similar at >99%. When considering the percentage of Fe^{2+} removed in treatment of each type of wastewater, it was found that there were slight differences but most provided a high percentage of removal at >99.99% since Fe^{2+} could form iron hydroxide ($Fe(OH)_2$), goethite (α-FeO(OH)) and magnetite (Fe_3O_4). The magnetite forming equation is shown in equation 2 [17]

$$3\,FeSO_4 + 6\,NaOH + \tfrac{1}{2}\,O_2 \longrightarrow Fe_3O_4 + 3\,Na_2SO_4 + 3\,H_2O \tag{2}$$

Table 2 The percentage of metal removal when varying Fe^{2+} concentration in treatment of synthetic wastewater containing two and three metal cations

Wastewater containing	Fe^{2+} conc. (ppm)	Percentage of metal removal			
		Cu^{2+}	Ni^{2+}	Zn^{2+}	Fe^{2+}
Cu-Ni	700	99.63 ± 0.11	99.51 ± 0.06	-	100.00 ± 0.00
	800	99.83 ± 0.05	99.54 ± 0.04	-	99.99 ± 0.01
	900	99.82 ± 0.02	99.56 ± 0.10	-	99.99 ± 0.04
	1,000	99.83 ± 0.04	99.54 ± 0.03	-	99.99 ± 0.01
Cu-Zn	1,200	99.48 ± 0.17	-	99.03 ± 0.10	99.99 ± 0.01
	1,300	99.50 ± 0.04	-	98.95 ± 0.13	100.00 ± 0.00
	1,400	99.77 ± 0.11	-	99.51 ± 0.10	100.00 ± 0.00
	1,500	99.60 ± 0.05	-	99.44 ± 0.11	99.99 ± 0.01
Ni-Zn	1,500	-	99.19 ± 0.13	99.17 ± 0.04	99.99 ± 0.01
	1,600	-	99.35 ± 0.03	99.33 ± 0.05	100.00 ± 0.00
	1,700	-	99.29 ± 0.10	99.30 ± 0.15	99.99 ± 0.03
	1,800	-	99.28 ± 0.02	99.33 ± 0.03	99.99 ± 0.01
Cu-Ni-Zn	1,200	99.10 ± 0.03	99.57 ± 0.11	98.83 ± 0.03	99.99 ± 0.01
	1,300	99.12 ± 0.12	99.56 ± 0.03	99.02 ± 0.02	100.00 ± 0.00
	1,400	99.35 ± 0.04	99.86 ± 0.03	99.24 ± 0.04	100.00 ± 0.00
	1,500	99.30 ± 0.10	99.80 ± 0.02	99.12 ± 0.12	99.99 ± 0.02

Ferrite sludge obtained from the use of the optimum amount of Fe^{2+} for the treatment of synthetic wastewater was analyzed by X-ray fluorescence spectroscopy. The results are shown in Table 3: the percentage of Fe_2O_3 produced would be much more than other metal oxides. The sludge from wastewater containing mixed metal would have percentage of Fe_2O_3 more than that from wastewater containing a single metal.

Table 3 The percentage of metal oxide in ferrite sludge

Synthetic wastewater containing	The amount of Fe^{2+} used for the treatment	Metal oxide (%)			
		Fe_2O_3	CuO	NiO	ZnO
Cu	$M^{2+} : Fe^{2+} = 1 : 2$	71.90± 3.55	27.10± 3.28	-	-
Ni	$M^{2+} : Fe^{2+} = 1 : 5$	81.20± 4.26	-	18.70± 0.87	-
Zn	$M^{2+} : Fe^{2+} = 1 : 10$	88.80± 5.13	-	-	11.00± 1.36
Cu-Ni	800 ppm Fe^{2+}	86.90± 2.11	6.38± 2.88	6.53± 1.12	-
Cu-Zn	1,400 ppm Fe^{2+}	91.80± 5.03	3.98± 1.02	-	4.09± 0.24
Ni-Zn	1,600 ppm Fe^{2+}	92.80± 4.23	3.43± 1.15	3.57± 0.80	-
Cu-Ni-Zn	1,400 ppm Fe^{2+}	91.00± 3.00	2.88± 0.16	2.93± 0.96	2.96± 0.33

3.3 The optimum oxygen flow rate

The initial heavy metal concentration used was 200 mg l^{-1}. In this experiment, the pH was 9, the temperature was 50 °C and the contact time was 45 mins. An optimum amount of Fe^{2+} was used. It was found that when using an oxygen flow rate of 60 ml min^{-1}, the lowest percentage of Cu was removed at 99.31 % showing that the amount of oxygen is insufficient for the complete formation of Cu-ferrite (Table 4). The color of sludge obtained was red brown because this sludge would be a mixed sludge of CuO and $Fe(OH)_2$. When using oxygen flow rate of 100, 200, and 300 ml min^{-1}, the percentage of Cu removed was similar at about 99.7 % showing that exceeding the amount of oxygen caused no effect to the formation of Cu-ferrite and the color of sludge obtained would be black brown. Demirel *et al.* [14] conducted studies on Cu by using the same condition as this study. They found that the aeration rate variations showed no significant effect on Cu removal, and almost complete removal was attained in each case. From statistical analysis (ANOVA), it was found that the percentage of Ni removed was not significantly different at P = 95 % when using all oxygen flow rate showing that oxygen amount dissolves in water causing no effect on Ni removal. Sludge obtained from the treatment of Ni by using different oxygen flow rates from 60-300 ml min^{-1} was black. Oxygen flow rates that were either too low (60 ml min^{-1}) or too high (300 ml min^{-1}), caused low percentage removal of Zn of 98.40% and 99.03% respectively. The percentage of Zn removed when using oxygen flow rates of 100 and 200 ml min^{-1} was about 99.5%. This is due to the formation of metal ferrite shown by the equation 3 [18]

$$\begin{aligned} M^{2+} + Fe^{2+} + OH^- \longrightarrow\ & [Fe(OH)_2 + M^{2+}(OH)_2 + MO] + O_2 \\ & \qquad\qquad \downarrow \\ & [\text{Trivalent} + \text{Divalent hydroxo} - \text{complex}] \\ & \qquad\qquad \downarrow \\ & M^{2+}O.Fe_2O_3 \quad (\text{Metal ferrite}) \end{aligned} \tag{3}$$

If the amount of oxygen was insufficient, some trivalent and divalent hydroxo – complex compound would not change to metal ferrite and cause low percentage removal of in particular $Zn(OH)_2$ that could dissolve well when compared to other heavy metals. So, metal ferrite was hardly formed and exceeding the amount of oxygen could also interfere as well as shown in equation 4 [17]

$$2\,Fe^{2+} + \tfrac{1}{2}\,O_2 + 4\,OH^- \longrightarrow 2\,[\alpha\text{-}FeO(OH)] + H_2O \quad \underset{}{\text{Goethite}} \tag{4}$$

It caused Fe^{2+} in insufficient amounts for the formation of metal ferrite; and the sludge obtained was of low quality and its magnetic property decreased since goethite (α-FeO(OH)) has no magnetic properties [19]. All sludges obtained from treatment of Zn by using different oxygen flow rates from 60-300 ml min^{-1} was black.

Table 4 The percentage of metal removal when varying oxygen flow rate

Wastewater containing	O_2 flow rate (ml mim^{-1})	Sludge color	Percentage of metal removal	
			M^{2+}	Fe^{2+}
Cu	60	Red brown	99.31 ± 0.11	99.99 ± 0.02
	100	Black brown	99.70 ± 0.08	99.99 ± 0.01
	200	Black brown	99.70 ± 0.13	99.99 ± 0.01
	300	Black	99.71 ± 0.03	99.99 ± 0.03
Ni	60	Black	99.82 ± 0.14	99.99 ± 0.04
	100	Black	99.68 ± 0.12	99.99 ± 0.01
	200	Black	99.62 ± 0.04	99.99 ± 0.00
	300	Black	99.58 ± 0.15	99.99 ± 0.02
Zn	60	Black	98.40 ± 0.07	99.99 ± 0.00
	100	Black	99.51 ± 0.05	99.99 ± 0.00
	200	Black	99.50 ± 0.13	99.99 ± 0.01
	300	Black	99.03 ± 0.09	99.99 ± 0.01

3.4 The optimum pH

The initial heavy metal concentration used was 200 mg l^{-1}. In this experiment, the O_2 flow rate was 100 ml min^{-1}, the temperature was 50 °C and the contact time was 45 mins. The optimum amount of Fe^{2+} was used. At pH 9 to12 when the studies were on wastewater containing only copper cations, the percentage removal of Cu was about 99.7 % (Table 5). These results are not consistent with the hypothesis of Mandaokar *et al.* [20], that higher concentrations of metal ions require a higher pH. Studies on synthetic wastewater containing 50 ppm of copper found that the best pH was 10 (99.8 % removal). When increasing the pH from 9 to 12, percentage of Ni removed was not different at about 99.8 % and close to the results of Demirel *et al.* [14]. For Zn when doing the experiment at pH 9 to 11, it provided similar results as of to be able to remove Zn at about 99.5 %. However, at pH 12, the percentage removal decreased to 98.33 %. The experiment results were such that they may be caused by the ability of each heavy metal to dissolve varies when the pH changes. A heavy metal is an amphoteric substance, i.e., having a variation in dissolution in water at a range of pHs, e.g. Zn has the lowest dissolution in water at a pH of about 8 to 11 and has a higher dissolution at a pH > 11 or < 8, etc. In contrast, Demirel *et al.* [14] found that the pH change almost had no effect on zinc removal. In wastewater containing multiple metal cations the highest percentage removal of metal was obtained when conducting the experiment at pH 10.

Table 5 The percentage of metal removal when varying pH

Wastewater containing	pH	Percentage of metal removal		
		Cu^{2+}	Ni^{2+}	Zn^{2+}
Cu	9	99.70 ± 0.08	-	-
	10	99.70 ± 0.06	-	-
	11	99.63 ± 0.12	-	-
	12	99.66 ± 0.11	-	-
Ni	9	-	99.68 ± 0.12	-
	10	-	99.85 ± 0.12	-
	11	-	99.82 ± 0.10	-
	12	-	99.76 ± 0.06	-
Zn	9	-	-	99.51 ± 0.05
	10	-	-	99.50 ± 0.16
	11	-	-	99.49 ± 0.15
	12	-	-	98.33 ± 0.18
Cu-Ni	9	99.83 ± 0.05	99.54 ± 0.04	-
	10	99.88 ± 0.13	99.76 ± 0.17	-
	11	99.81 ± 0.03	99.45 ± 0.11	-
	12	99.80 ± 0.18	99.55 ± 0.12	-
Cu-Zn	9	99.77 ± 0.11	-	99.51 ± 0.10
	10	99.80 ± 0.09	-	99.63 ± 0.15
	11	99.32 ± 0.14	-	99.50 ± 0.04
	12	99.59 ± 0.05	-	99.00 ± 0.05
Ni-Zn	9	-	99.35 ± 0.03	99.33 ± 0.05
	10	-	99.69 ± 0.14	99.67 ± 0.06
	11	-	99.41 ± 0.12	99.35 ± 0.10
	12	-	99.28 ± 0.10	98.60 ± 0.17
Cu-Ni-Zn	9	99.35 ± 0.04	99.86 ± 0.03	99.24 ± 0.04
	10	99.85 ± 0.20	99.87 ± 0.17	99.72 ± 0.03
	11	99.67 ± 0.16	99.89 ± 0.08	99.55 ± 0.07
	12	99.81 ± 0.08	99.53 ± 0.16	98.00 ± 0.14

3.5 The optimum temperature

The initial heavy metal concentration used was 200 mg l^{-1}. An optimum amount of Fe^{2+} was used. In this experiment, the O_2 flow rate was 100 ml min^{-1}, the pH was 10 and the contact time was 45 mins. From the experiment it was found that the sludge obtained by conducting the experiment at a temperature of 30°C would be black brown. When this sludge was tested for its magnetic properties by dipping a magnetic bar into wastewater containing the sludge, it appeared that the sludge hardly stuck to the magnetic bar. That would be different from sludge obtained by conducting the experiment at a temperature of 50 °C and 70 °C. This sludge would be highly magnetic. Miyadai *et al.* [21] found that when conducting the experiment at a temperature of less than 40 °C, the majority of sludge obtained was goethite (α-FeO(OH)) and magnetite (Fe_3O_4). Goethite was brown or red brown in color. Theredore, increasing the temperature would help ferrite sludge to be stable and have greater magnetic properties. From Table 6 it was found that the percentage removal of most metals were >99%. However, selecting the optimum temperature will depend on the main objective of treatment e.g. if the need is to remove heavy metal only, a temperature of 30 °C should be selected to save electrical energy. However, if the need is to remove both heavy metals and obtain ferrite sludge with good magnetic properties for benefit of good precipitation by a magnet and to obtained sludge that is precipitated quickly, a temperature of 50 °C should be selected; and if the need is to obtained ferrite sludge that is of a very good quality and is highly stable, a temperature of 70 °C should be selected.

In this experiment a selected temperature of 50 °C provided removal of all metals on average of 99.7 ± 0.3%. It was assumed that this temperature was efficient at removal of metals; the remaining metal in wastewater did not exceed the specified industrial standards; accompanied with a sludge with magnetic properties that were sufficient to be precipitated by a magnet; the stability of the sludge was sufficient to as not to create any contamination in the environment easily; and also save energy [15]. From analysis of ferrite sludge caused by using optimum condition for treatment of synthetic wastewater containing a mixture of three heavy metals with scanning electron microscopy, it was affirmed that the effect was the mixing of three metal cations in the metal ferrite structure.

Table 6 The percentage of metal removal when varying temperature

Wastewater containing	Temperature (°C)	Percentage of metal removal		
		Cu^{2+}	Ni^{2+}	Zn^{2+}
	30	99.50 ± 0.09	-	-
	50	99.70 ± 0.06	-	-
	70	99.75 ± 0.06	-	
Ni	30	-	99.50 ± 0.09	-
	50	-	99.85 ± 0.12	-
	70	-	99.75 ± 0.12	-
Zn	30	-	-	98.51 ± 0.09
	50	-	-	99.50 ± 0.16
	70	-	-	99.73 ± 0.16
Cu-Ni	30	99.50 ± 0.09	99.55 ± 0.09	-
	50	99.88 ± 0.13	99.76 ± 0.17	-
	70	99.83 ± 0.13	99.60 ± 0.17	-
Cu-Zn	30	99.48 ± 0.09	-	99.27 ± 0.09
	50	99.80 ± 0.09	-	99.63 ± 0.15
	70	99.73 ± 0.09	-	99.86 ± 0.15
Ni-Zn	30	-	99.50 ± 0.09	99.53 ± 0.09
	50	-	99.69 ± 0.14	99.67 ± 0.06
	70	-	100.00 ± 0.01	100.00 ± 0.01
Cu-Ni-Zn	30	99.41 ± 0.09	99.65 ± 0.09	99.26 ± 0.09
	50	99.85 ± 0.20	99.87 ± 0.17	99.72 ± 0.03
	70	99.86 ± 0.20	99.87 ± 0.17	99.82 ± 0.03

3.6 Experiments performed on electroplating industry wastewater

Physical and chemical characteristics of electroplating industry wastewater are shown in Table 7. Given conditions used in this experiment were a Fe^{2+} concentration of 1,300 mg l^{-1}, an O_2 flow rate of 100 ml min^{-1}, a pH of 10, a temperature of 50°C and contact time of 45 mins. The percentage of removal of Cu, Ni, Zn and Fe were 99.80 ± 0.05 %, 99.88 ± 0.08 %, 99.69 ± 0.09 % and 99.99 ± 0.03 %, respectively. The sludge obtained from this experiment was black, easily precipitated and had magnetic properties. The percentage removal of Cu, Ni, Zn and Fe when treating synthetic wastewater were similar to when treating electroplating industry wastewater.

Table 7 Characteristic of wastewater from electroplating industry

Parameter	Value
Color	Pale green
pH	1.7
Temperature	25 °C
Cu	21.60 ppm
Ni	216.33 ppm
Zn	2 ppm
CN	< 0.4 ppm

4. CONCLUSIONS

The ferrite process can be a good alternative to treat wastewater containing both single and multiple heavy metals like electroplating wastewater. The ratio of M^{2+} to Fe^{2+} is very critical for ferrite formation. The Fe^{2+} concentration required for the formation of copper ferrite was much less than that required for the formation of nickel and zinc ferrite. The Fe^{2+} concentration used to treat wastewater containing two and three metal cations was higher than the Fe^{2+} concentration used to treat wastewater containing a single metal cation. The metal ferrites can be formed in the pH range of 9-12. When increasing the pH from 9 to 12, the percentage removal of Ni and Cu were not different. At pH 9-11, Zn could be removed about 99.5 %. At pH 12, the percentage removal of Zn decreased. The oxygen flow rate providing the highest percentage removal of heavy metal was 100 and 200 ml min^{-1}. Thus, in order to save energy, an oxygen flow rate of 100 ml min^{-1} should be used in the treatment. Ferrite could be formed at ≥ 50°C. The higher the temperature used the better the magnetic quality of sludge.

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