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The removal of heavy metals from refinery effluents by sulfide precipitation

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Abstract

This study investigated the selective precipitation of copper (Cu^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}) ions from industrial wastewater by using sodium sulfide (Na_2S). The effects of pH, time and free sulfide concentration on the selective precipitation were systematically investigated using synthetically prepared solutions and gold refinery wastewater. First, the optimum precipitation pH values of metals, the amount of Na_2S and time were determined by using synthetic solutions containing Cu, Ni and Zn single metal ions. The highest precipitation efficiencies were obtained at a pH of 4, 5.3 and 5.3 for Cu, Ni and Zn, respectively. Based on these results, the effects of Na_2S stoichiometry and time of precipitation were investigated with synthetically prepared solutions containing mixed metal ions (100 mg/L Cu^{2+}, 90 mg/L Ni^{2+} and 100 mg/L Zn^{2+}). Metal sulfide precipitation efficiencies increased with increasing amounts of Na_2S and reached a maximum at a ratio of 1:1.75 (Metal ion: Na_2S molar ratio). Lastly, the results obtained from the experiments performed with synthetic solutions were used for the metal sulfide precipitation from industrial wastewater. The precipitation from refining wastewater containing 10 g/L Cu^{2+}, 0.3 g/L Ni^{2+} and 3 g/L Zn^{2+} ions was achieved at pH values from 2.3 to 5.3. At a pH of 2.3, Cu^{2+} precipitated as CuS (Cu_2S) at 100% efficiency. While the Ni^{2+} concentration in the solution decreased by only 44% at a pH of 2.3, the Zn^{2+} concentration decreased by 52%. At a pH of 5.3, Cu^{2+} and Zn^{2+} precipitated together at 100%.

Keywords
Copper sulfide, Nickel sulfide, Precipitation, Sulfide precipitation, Metal sulfide

Introduction

Only 3% of the water in the world is fresh, and day by day, it is becoming more difficult to access clean water due to a rapidly increasing population. The main causes of pollution in clean water and soil resources are leachate, mine wastewater, municipal wastewater, urban surface flows and industrial wastewater discharged without sufficient cleaning (Prokkola, Nurmesniemi, & Lassi, 2020)(Buccheri et al., 2018). Industrial wastewater contains significant amounts of Chromium (Cr), Lead (Pb), Zinc (Zn), Arsenic (As), Copper (Cu), Nickel (Ni), Cobalt (Co), Cadmium (Cd) and Mercury (Hg), and most of these wastes are generated as a result of refinery and electroplating processes (Asokbunyarat, Lens, & Annachhatre, 2017)(Sampaio et al., 2010)(Menzel, Barros, García, Ruby-Figueroa, & Estay, 2021). Metal removal from water is important for environmental sustainability and assessing metallic resources. Many methods have been developed for metal ion removal from water. Chemical precipitation, electro-recovery, solvent extraction, ion exchange, and reverse osmosis methods, in particular, are used to remove metals from industrial wastewater (Asokbunyarat et al., 2017)(Veeken & Rulkens, 2003)(Fu & Wang, 2011). The chemical precipitation technique (MeS or Me(OH)n) is widely used in the removal of metal from wastewater, especially in developing countries (Stec, Jagustyn, Słowik, Ściążko, & Iluk, 2020). Hydroxide precipitation is essentially a neutralization method. This neutralization reaction takes place by adding calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), sodium carbonate (Na_2CO_3)(Trisnawati et al., 2021) or sodium hydroxide (NaOH) to the solution. Metal hydroxides have low solubility values and provide automatic pH adjustment; their application is easy and economical, all of which makes neutralization the most preferred chemical precipitation method, especially for small to medium-sized enterprises with low amounts of waste. However, this process produces excessive amounts of hydroxide sludge, and its disposal has long-term negative effects on the environment, as well as the additional costs caused by having to apply lime. Because of these factors, industrialized nations have not adopted this approach, especially by large enterprises, since the 1980s (Fu & Wang, 2011)(Van Hille, A. Peterson, & Lewis, 2005).

Another prominent application of chemical precipitation is metal sulfide precipitation. Metal sulfide sludge has better thickening and washing properties and reacts faster in comparison to metal hydroxide sludge. It also has low solubility at different pH ranges and enables more selective precipitation. All these characteristics of metal sulfide sludge have encouraged researchers to study this method (Prokkola et al., 2020)(A. Lewis & Swartbooi, 2006)(Jerroumi, Amarine, Nour, Lekhlif, & Jamal, 2020)(Ain Zainuddin, Azwan Raja Mamat, Imam Maarof, Wahidah Puasa, & Rohana Mohd Yatim, 2019)(A. Lewis & Van Hille, 2006). Extraction of most of the nonferrous metals carried out from sulfide ores, and sulfide agents are used in the production of some of them (Morcali et al., 2019) (Kartal & Timur, 2019) (Morcali et al., 2020). Therefore, the production of sulfide-precipitated metals can be carried out by feeding into the conventional system without the need for a new process. In addition to conventional production methods, metal production is also possible with processes such as molten salt electrolysis that allow the production of solid sulfur and metal at the same time (Ahmadi & Suzuki, 2021) (Kartal & Timur, 2019)(Kartal & Timur, 2018).

The most crucial factors influencing metal sulfide precipitation are pH, sulfaragent agent, and amount of sulfide reagent. Other factors affecting a particle's surface properties include local supersaturations that may vary according to the characteristic dissolution behavior of metals and control of the free sulfide ion concentration in solution. Water-soluble Na_2S, NaHS, $(NH_4)_2S$, solid FeS and CaS, as well as H_2S gas, produced biologically or via sulfate reduction, are usually utilized as sulfide reagents (Prokkola et al., 2020)(Veeken & Rulkens, 2003)(A. E. Lewis, 2010)(Gharabaghi, Irannajad, & Azadmehr, 2012a)(Kaksonen, Riekkola-Vanhanen, & Puhakka, 2003)(Kumar, Nandi, & Pakshirajan, 2021)(Zeng et al., 2021). Na_2S is an easy-to-use chemical that has been used in many studies with successful results. Bhattacharya et al. removed Cd, Zn, Cu, Pb, As and Selenium (Se) from complex wastewater using Na_2S as a sulfide reagent and optimum conditions were achieved at 60% of theoretical sulfide demand for a pH value greater than 8. Optimum conditions were applied in industrial copper smelter wastewater, and Cd, Zn and Cu 99% separation was achieved, while As and Se could be selectively precipitated by %98 and >%92, respectively (Bhattacharyya, Jumawan, & Grieves, 1979). Fukuta et al. investigated the effect of three different sulfide sources (Na_2S, Na_2S_2 and Na_2S_4) on the separation of Cu, Ni and Zn over different pH ranges. Na_2S was shown to be the most effective precipitation reagent compared to other sulfide reagents. They stated that at low pH, copper primarily precipitated as CuS, but Ni and Zn precipitated together only at increasing pH values. First, Cu^{2+} was separated at a pH of 1.4 to 1.5, then Zn^{2+} at a pH of 2.4 to 2.5, followed by Ni^{2+} at a pH of 5.5 to 6.0 (Fukuta, Matsuda, Seto, & Yagishita, 2018). Sampaio et al. investigated the selective separation of Cu and Zn in a continuously stirred reactor at 293 K using Na_2S sulfide reagent and a solution containing Cu and Zn, and they determined that Cu^{2+} precipitated as CuS, while Zn^{2+} precipitated as ZnS (Sampaio, Timmers, Xu, Keesman, & Lens, 2009). Sampaio et al., in another study, investigated the selective separation of Ni and Zn by using Na_2S as the sulfide reagent. They determined that selectivity was achieved by preventing supersaturation at the dosing points and by reducing the influent concentration (Sampaio et al., 2010).

Determining the optimal selective sulphurization conditions for metal recovery from wastewater is crucial since it will reduce the need for labor, energy, chemicals, and time in the subsequent stages of metal manufacturing. In this study, the selective conditions to precipitate Cu^{2+}, Ni^{2+} and Zn^{2+} from industrial wastewater at different pH levels were investigated by using a Na_2S sulfide reagent. First, the precipitation behavior of each metal was investigated by using synthetically prepared solutions containing a single metal ion. The required sulfide source and duration of the experiment were determined using a synthetically prepared solution containing Cu^{2+} ions. In the second step, the effects of Na_2S stoichiometry and reaction time on selective precipitation were investigated in the synthetically prepared solution containing mixed metal ions. Lastly, metals were removed from refinery wastewater using the optimum conditions indicated by the synthetic solutions.

Material and Methods

Synthetic solutions used in precipitation experiments were prepared using $CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}6H_2O$ and $ZnSO_4{\cdot}7H_2O$ chemicals (Merck). De-ionized water was used to prepare the synthetic solutions. The compositions of the synthetically prepared solution and refinery wastewater are shown in Table 1. Before each experiment, the pH electrode was calibrated using pH buffer solutions from Merck. Industrial wastewater with a pH of 2 was obtained from the gold refinery.

Table 1. Solutions used in experiments

Solution Type	Solution No	Metal ion	Ion concentration (mg/L)
Simulated wastewater (single)	1.1	Cu^{2+}	100
	1.2	Ni^{2+}	1200
	1.3	Zn^{2+}	12500
Simulated wastewater (mixed)	2	Cu^{2+}	100
		Ni^{2+}	90
		Zn^{2+}	100
Gold refinery wastewater	3	Cu^{2+}	10000
		Ni^{2+}	300
		Zn^{2+}	3000

Figure 1 depicts the basic operations performed in the experimental studies, including solution preparation, pH adjustment, precipitation, filtration, washing and drying of precipitates, and an analysis of metal ions remaining in the solution. The selective separation of Cu, Ni and Zn was systematically examined by carrying out the experiments in three steps. Firstly, the effects of pH, precipitation time, and Na_2S content on the sulfide precipitation in synthetically prepared solutions containing one metal ion (Cu^{2+}, Ni^{2+} and Zn^{2+}) were investigated. Secondly, the optimum pH, amount of Na_2S, and duration of experiment results used in the metal sulfide precipitation experiments with synthetically prepared solutions containing multiple metal ions were determined. Finally, the metal sulfide precipitation was performed using industrial wastewater based on the results obtained from the synthetic solutions containing multiple metal ions.

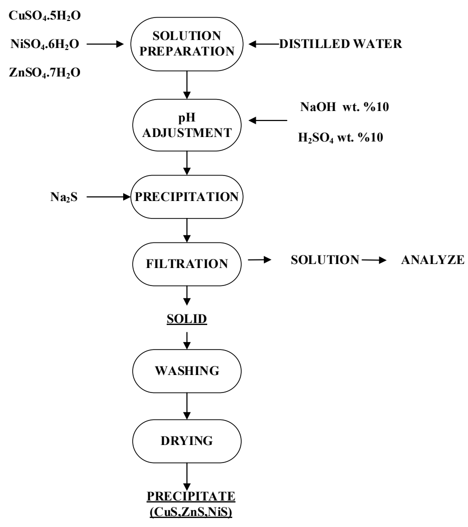

Fig. 1. Flow chart of the proposed procedure for the sulfide precipitation

The experiments were carried out in an open atmosphere at 293 K (20 °C), as in the case of industrial applications. A 10 wt. % H_2SO_4 solution and a 10 wt. % NaOH solution were used to adjust the pH in solutions.

The concentrations of the aqueous solution of the sulfurating agents were adjusted using deionized water according to the metal ion concentration in the solution. Sulfurating agents were added by hand. Synthetic solutions containing metal ions were prepared as 250 ml for each experiment. A 10 wt. % H_2SO_4 solution and a 10 wt. % NaOH solution were employed to control the pH level precisely after sulfurating chemicals were applied. After adding a prescribed amount of sulfurating agent to the sample solution, the solution was agitated for 30 minutes using a magnetic stirrer, and the metal sulfide created was filtered using a paper filter with a mean pore size of 1 µm.

A pH meter and pH electrode (WTW) was used for pH measurements in the solutions, an Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 800) was used for chemical analyses, and an X-Ray Diffractometer (Siemens D5000) was used for X-ray analyses. As for the analysis of heavy metals, the standard working conditions for AAS are listed in Table 2.

Table 2. Standard operating conditions of AAS for the analysis of metals.

Element	Flame	Wavelength (nm)	Slit size (nm)
Cu	Air/Acetylene	324.8	1.3
Ni	Air/Acetylene	232.0	0.2
Zn	Air/Acetylene	213.9	1.3

Results and Discussion

Metal sulfide precipitation from synthetic solutions containing a single metal ion

For the experiments performed with synthetic solutions containing a single metal ion, first, the pH range at which each metal had the lowest dissolution was determined by using Eh–pH diagrams for copper, nickel and zinc, respectively. At increasing concentrations in this range, the effects that reaction time, Na_2S stoichiometry, and pH changes in the solution had on precipitation were investigated by analyzing the metal ion concentration (mg/L) remaining in the solution.

The pH is the most significant factor in studies aiming at the selective precipitation of metal ions using Na_2S. The effect of pH on precipitation was investigated between pH 2 and 6. Figure 2 shows the effect of pH on the metal sulfide precipitation from a solution containing only Cu^{2+} ions. The curve shown in Figure 2 reveals that a pH of 4 resulted in the maximum precipitation efficiency. Fukuta et al., who conducted similar studies, obtained the highest precipitation efficiency at a pH of 1.4 to 1.5 (Fukuta et al., 2018). Although it is known that Cu^{2+} ions have a very high sulfide forming tendency, the highest precipitation efficiency that could be achieved was 97% in the experimental results, which was since the Cu^{2+} (mol)/Na_2S ratio was used at the theoretical ratio of 1:1.

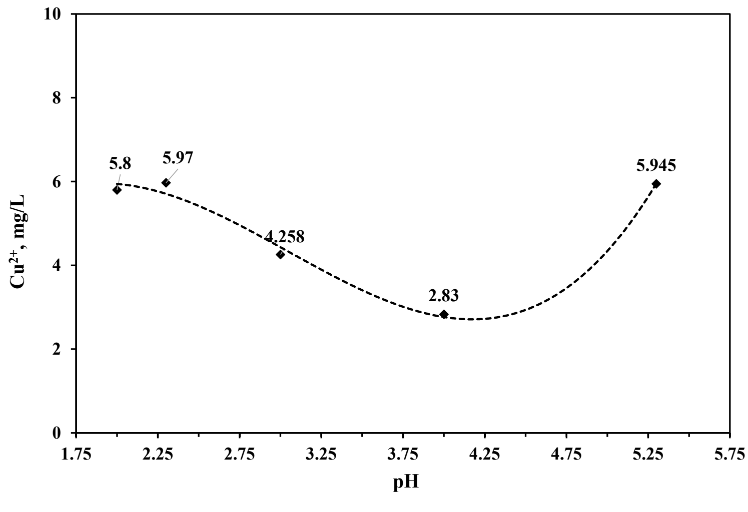

Fig. 2 Change in Cu^{2+} ion concentration in solution against pH at a Cu^{2+}:Na_2S 1:1(mol) ratio for 3600 s.

The amount of sulfide injected into the system is among the most vital factors in sulfide precipitation, along with pH. Sulfide reagents block the process by affecting the structure of precipitates depending on the amount of reagent and the application method. According to published literature, increasing the metal ion (mol) to Na_2S ratio from 1:1 to 1:1.75 improves precipitation efficiency. Based on the literature, the amount of Na_2S was investigated by using a synthetic solution containing Cu^{2+} ions at the metal ion (mol)/Na_2S ratio of 1:1 to 1:2. It was shown that the precipitation efficiency increased up to the Cu^{2+} (mol) × Na_2S stoichiometry ratio of 1:1.75 with increasing amounts of Na_2S (Figure 3). The level of precipitated metal ions did not change when the Na_2S stoichiometry was increased more than 1.75, which indicated that Cu^{2+} ions reached the maximum free sulfide ion level that could be used in the solution.

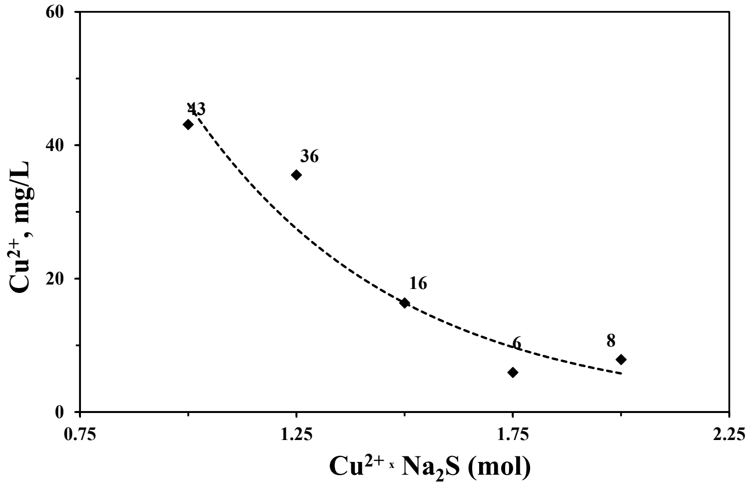

Fig. 3 The effect of Cu^{2+} (mol) × stoichiometric added Na_2S on the precipitation efficiency at a pH of 2.3 for 3600 s.

The optimum precipitation time was optimized in the solution containing only Cu^{2+} ions. The relationship between reaction time and sulfide precipitation was investigated by performing experiments at a pH of 2.3. Cu^{2+} ions started to precipitate as CuS (Cu_2S) from the start of the experiment, and the precipitation reaction was almost completed after 2700 seconds (Figure 4).

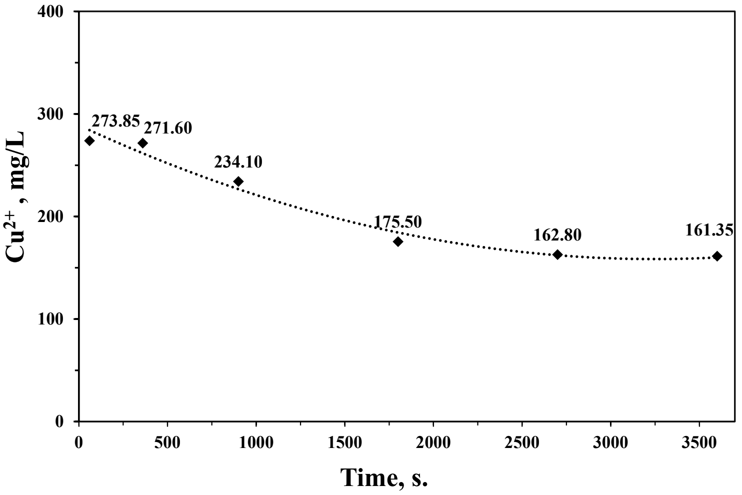

Fig. 4 Change in metal ion concentration with time at Cu^{2+}:Na_2S 1:1(mol) ratio at a pH of 2.3.

In contrast to Cu^{2+} ions, Ni^{2+} and Zn^{2+} precipitated at higher pH levels, according to the Eh-pH diagrams. Metal sulfide precipitation at higher pH values was investigated by precipitation of nickel sulfide from solutions containing Ni^{2+} ions at a pH from 2 to 6. The highest precipitation efficiency was achieved between pH 4 and 5 (Figure 5). The nickel sulfide precipitation efficiency was nearly 63% in this pH range, and this ratio was lower than those found in published literature. It was determined that this was due to the low Na_2S /Ni^{2+} (mol) ratio of 1:1 in the experiments compared to the literature. Jerroumi et al. studied the removal of Ni^{2+} from industrial wastewater using a Na_2S reagent under atmospheric conditions and achieved the highest metal nickel removal at a pH of 5 at an S^{2-}/Ni^{2+} ratio of 1.5:1. When examining Figure 5; it is seen that the results of the present study are compatible with those of Jerroumi et al. (Jerroumi et al., 2020).

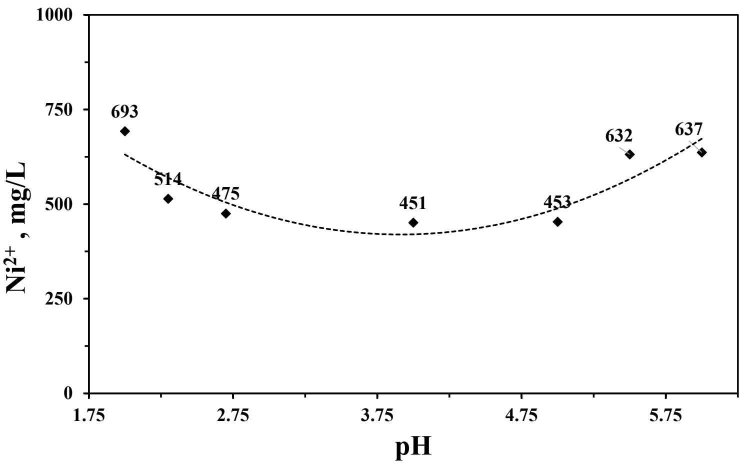

Fig. 5 Change in Ni^{2+} ion concentration in solution against pH at a Ni^{2+}:Na_2S 1:1(mol) ratio for 3600 s.

Zinc is the most commonly used metal in corrosion-resistant coating applications, and so it is also commonly found in industrial wastewater. The behaviour of metal sulfide precipitation from solutions containing only Zn^{2+} ions was investigated between a pH of 4 to 6. When examining the analysis curve showing metal ions remaining in the solution with respect to pH in Figure 6, it was determined that the Zn^{2+} concentration in the solution decreased from 12.5 g/L to 2.7 g/L over the pH range from 5 to 5.5, and the precipitation efficiency reached 78%, which revealed that pH 5.5 was a breaking point. Although the Zn^{2+} concentration in the solution was about to decrease, as shown in Figure 6, it was understood that beyond pH 5.5, this decrease was caused by hydroxide formation due to the difficult filtration of precipitated particles and thickened sludge formation.

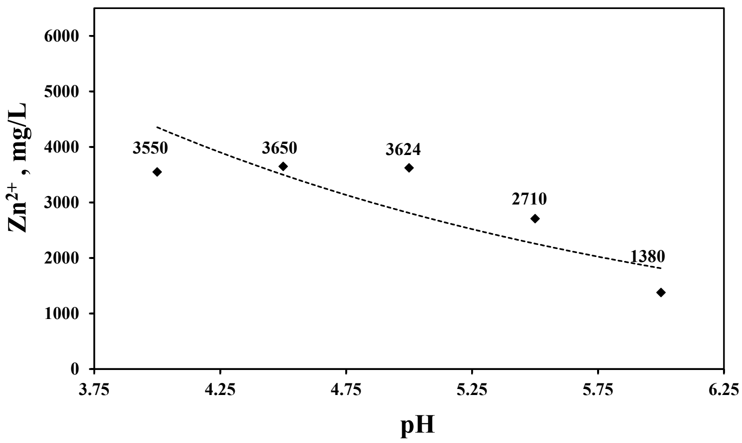

Fig. 6 Change in Zn^{2+} ion concentration in solution against pH at Zn^{2+}:Na_2S 1:1(mol) ratio for 3600 s.

Selective metal sulfide precipitation from synthetic solutions containing mixed metal ions

The effect of Na_2S stoichiometry on precipitation

Parameter control is an important factor in metal removal using selective sulfide precipitation from industrial wastes containing multi-metal ions. In the experiments performed with synthetic solutions containing single metal ions, the highest precipitation efficiency was obtained at pH 3 to 4 for Cu^{2+} ions, pH 4 to 5.3 for Ni^{2+} ions, and pH 5.3 for Zn^{2+} ions. The concentration of metal ions in the solution was found to drop and precipitation to rise with increasing Na_2S stoichiometry. The highest precipitation efficiency was achieved in a range from 1.5 to 1.75 times the concentration of each metal ion. Based on these results, the aim was to achieve selective separation in the synthetic solution experiments containing mixed metal ions. To increase the selective precipitation of Cu^{2+}, Ni^{2+} and Zn^{2+} ions, a pH value was selected in which all three ions did not precipitate simultaneously, rather than the optimum values obtained in solutions containing single metal ions. To achieve this, in the sulfide precipitation from solutions containing mixed metal ions, pH 2 to 2.5 was selected for Cu^{2+} ions and pH 5 to 5.3 was selected for both Ni^{2+} and Zn^{2+} ions.

The effect of the amount of Na_2S on metal sulfide precipitation from solutions containing multiple metal ions was investigated by performing experiments at 1.5 to 1.75 times the metal ion concentration. In the experiments performed in Me^{2+} (mol) × 1.5 Na_2S (mol) stoichiometry, it is seen in the graph shown in Figure 7 that at pH 2.3, 75% of Cu^{2+} precipitated, almost all the Ni^{2+} remained in solution without precipitation, and Zn^{2+} precipitated at a rate of 10%. When the pH of the solution was increased to 5.3, 100% of Cu^{2+} ions, 60% of Zn^{2+} ions and 33% of Ni^{2+} precipitated from the solution (Figure 8).

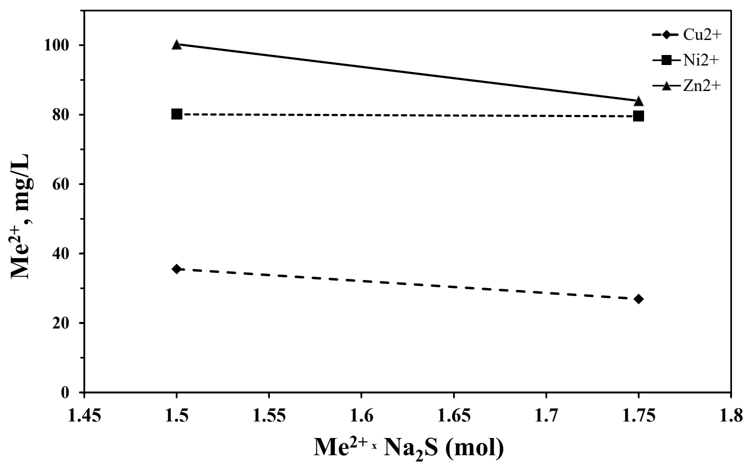

Fig. 7 The effect of Na_2S stoichiometry on precipitation at 2.3 pH for 3600 s.

In the experiments performed by increasing the Na_2S (mol) stoichiometry to 1.75, it was seen in the graph shown in Figure 7 that at pH 2.3, 86% of Cu^{2+} precipitated, Ni^{2+} remained in the solution without precipitation, and 5% of Zn^{2+} precipitated from the solution. When the pH of the solution was adjusted to 5.3, 99% of Cu^{2+} ions, 90% of Ni^{2+} ions and 99% of Zn^{2+} precipitated from the solution (figure 8). With increasing Na_2S stoichiometry, it was seen that the free sulfide ion that can be used by metal ions in the solution increased, and the precipitation efficiency also increased accordingly.

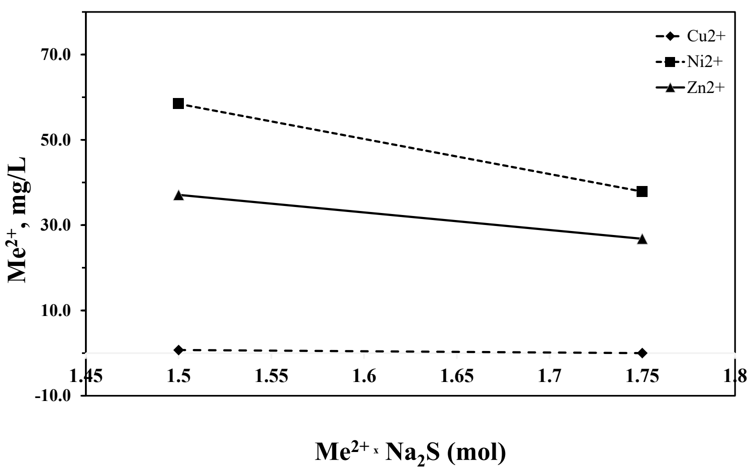

Fig. 8 The effect of Na_2S stoichiometry on precipitation at 5.3 pH for 3600 s.

The effect of reaction time on precipitation

The optimum reaction time was investigated by performing experiments between 3600 and 7200 s at pH 2.3 and 5.3. In these experiments, at a pH of 2.3, mainly Cu^{2+} ions precipitated, while Ni^{2+} ions partially precipitated and Zn^{2+} ions remained in the solution without precipitation (Figure 9). According to the literature, although the dissolution behavior of Ni^{2+} ions varies considerably, it was determined that the Ni^{2+} concentration did not change in these experiments carried out in an open environment. When examining the curves given in Figures 9 and 10, there was no change in the precipitation behavior of metal ions. Ions precipitated up to 3600s. After the 3600s, no significant change was observed in the number of ions. This shows that the reaction was completed in about 3600 seconds, as shown in the results for a single metal ion solution. Deng et al., who conducted Cu and Au precipitation using NaHS in glycine-cyanide solutions, determined that the reaction rate of the precipitation was fast, as 69.1% copper removal was achieved in 5 min, followed by a minor increase up to 72.8% at 30 min (Deng et al., 2019).

This shows that precipitation is quite slow compared to glycine-cyanide solutions. Estay et al. studied the sulfidation of Cu and Au in glycine-cyanide solution in SART (Sulfidization, Acidification, Recycling and Thickening) process. The results of the copper precipitation with regard to time showed a quick increase in copper precipitation in the first minute. They reported that the highest value was obtained in one minute, and then this conversion remained a stable value for up to 10 minutes (Estay et al. 2020).

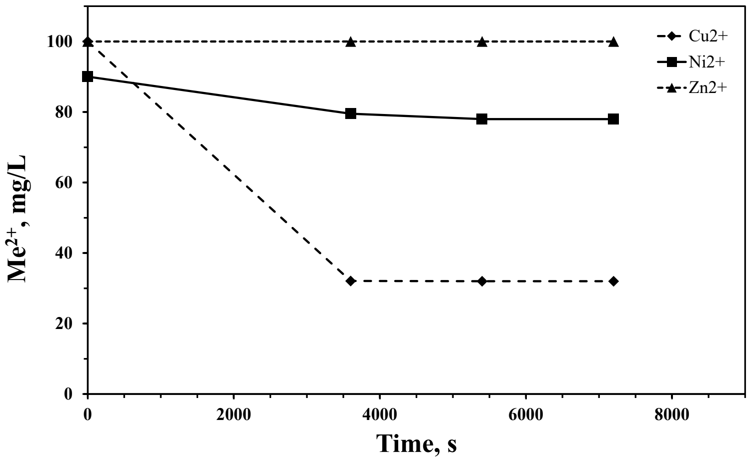

Fig. 9 The effect of reaction time on precipitation at 2.3 pH, Me^{2+}:Na_2S 1:1.5(mol) ratio.

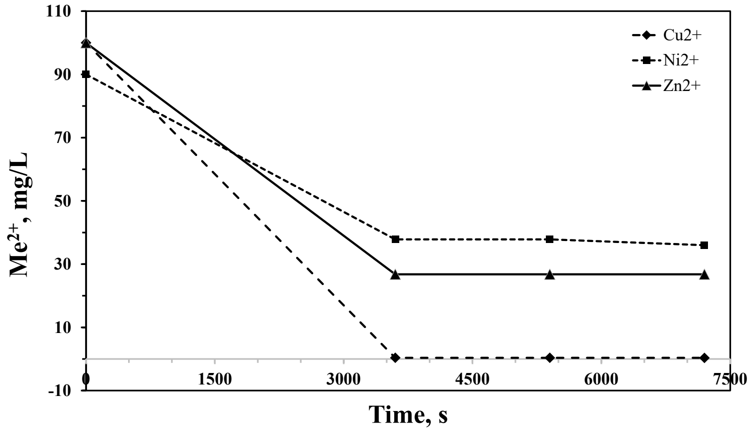

Fig. 10 The effect of reaction time on precipitation at 5.3 pH, Me^{2+}:Na_2S 1:1.5(mol) ratio.

Metal sulfide precipitation from industrial wastewater

In the experiments performed using industrial waste solutions, the optimum pH, Na_2S stoichiometry and duration of experiment parameters determined in the synthetic solution experiments were used. The effect of pH on metal ions in industrial wastewater was investigated, and metal ion concentration versus pH change is given in Figure 11. At a pH of 2.3, Cu^{2+} ions decreased from 100 mg/L to approximately 0.4 mg/L, and when the pH was increased to 5.3, all Cu^{2+} ions were observed to precipitate. While the Ni^{2+} concentration in the solution showed a 44% decrease at a pH of 2.3, the Zn^{2+} concentration decreased by 52%. It was observed that when the pH was increased to 5.3, all Cu^{2+}, Zn^{2+} and Ni^{2+} precipitated together.

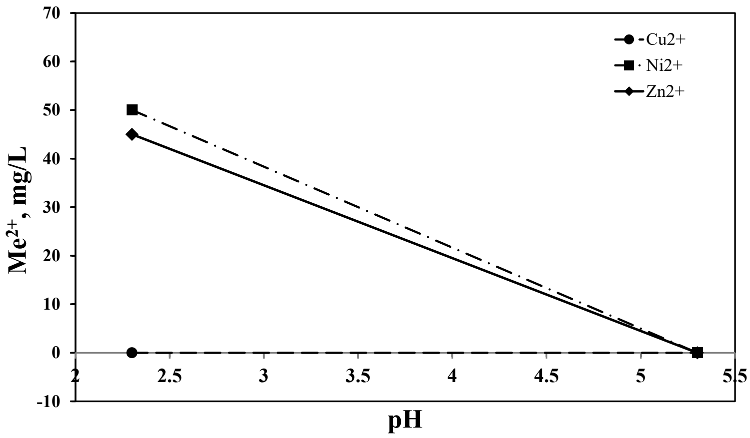

Fig. 11 The effect of pH change in the waste solution on the precipitation efficiency at a Me^{2+}:Na_2S 1:1.75 (mol) ratio for 3600 s.

It was seen that the metal concentration in the solution decreased with increasing pH, but all metal ions precipitated simultaneously at the pH values optimized for selective separation. It was seen, based on these results, that compared to the simulated solution results containing mixed metal ions, the precipitation efficiency of metal ions in the waste solution increased, but the selective separation rate decreased. Fukuta et al., in their experiments performed on electroplating wastes, achieved 94% Cu^{2+} separation from pH 1.4 to 1.5 (Fukuta et al., 2018). Gharabaghi et al., using thioacetamide as a sulfide source, achieved 90% Cu^{2+} separation at a pH of 2.5 (Gharabaghi, Irannajad, & Azadmehr, 2012b). When compared with the results obtained at a pH value of 2.3, almost 100% of Cu^{2+} ions precipitated, and the precipitation of other metal ions in addition to Cu^{2+} ions was an indication that the free sulfide ions in the solution are used by all metal ions, primarily by Cu^{2+} ions, under a certain stoichiometry.

The structure of the particles obtained as a result of waste solution precipitation was examined by X-ray diffraction analyses. The particles that precipitated at pH 2.3 were found to be in the form of CuS and Cu_2S. (Figure 12).

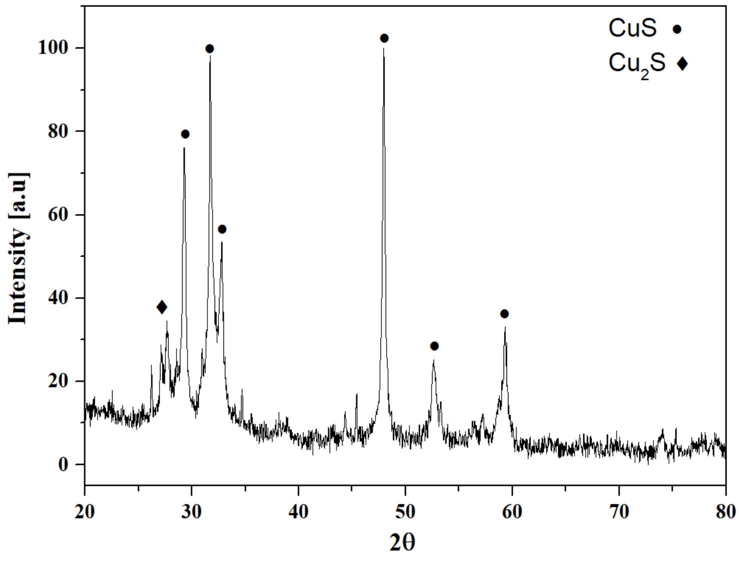

Fig. 12 XRD diffractogram of particles precipitated at pH 2.3 for a Me^{2+}:Na_2S 1:1.75 (mol) ratio for 3600 s.

Previous experiments showed that Ni^{2+} and Zn^{2+} ions precipitated at pH 5.3 simultaneously. By X-ray analyses, it was determined that the Zn^{2+} precipitated at a pH value of 5.3 had a ZnS structure, and the Ni^{2+} had a NiS structure. Sampaio et al. found that Zn^{2+} precipitated as a ZnS structure, especially in experiments performed at low temperatures (Sampaio et al., 2010).

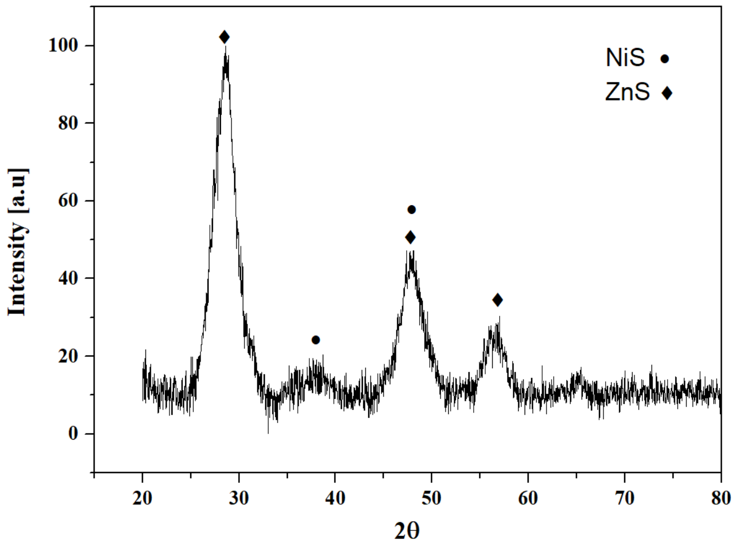

Fig. 13 XRD diffractogram of particles precipitated at pH 5.3 for a Me^{2+}:Na_2S 1:1.75 (mol) ratio for 3600 s.

Conclusions

In this study, metal removal from industrial wastewater containing multiple metal ions by selective metal sulfide precipitation was investigated under atmospheric pressure at 293 K (20°C). Na_2S was used as the sulfide source, which is cheap, easy to purchase and suitable for use in industrial applications in Turkey. The experimental results obtained can be summarized as follows:

- First, precipitation was made using synthetic solutions containing Cu^{2+}, Ni^{2+} and Zn^{2+} ions, respectively, and the highest precipitation efficiencies were obtained at pH 4, 5.3 and 5.3, respectively.
- The precipitation efficiency increased with an increasing amount of Na_2S up to the stoichiometric ratio of $Me^{2+} \times 1.75$, and there was no effect on the precipitation efficiency at higher Na_2S amounts.
- The rate of precipitation decreased by 2700 seconds after the sulfide reagent was added, and the reaction was completed after 3600 seconds.
- Due to high precipitation values at different pH values for Zn, Ni and Cu in synthetic and industrial waste solutions, a complete separation was achieved, but there was no separation between Zn and Ni.
- Cu^{2+} precipitated completely at a pH value of 2.3 in industrial wastewater, and when the pH was increased to 5.3, 100% of Ni^{2+} and Zn^{2+} precipitated, unlike the synthetic solutions.
- In the precipitation performed in wastewater, the particles that precipitated at pH 2.3 were in the structure of CuS and Cu_2S, while at pH 5.3, Zn^{2+} had a ZnS phase structure, and Ni^{2+} had a NiS structure.
- Selectivity was achieved in the separation of Cu^{2+} in wastewater, but not between Ni^{2+} and Zn^{2+}.

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