Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21584

95 (2017) 220–226
November

Selective precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} ions using $H_2S_{(g)}$ produced by hydrolysis of thioacetamide as the precipitating agent

Paula M.O. Silva[a,b], Giselle S.C. Raulino[c], Carla B. Vidal[b], Ronaldo F. do Nascimento[b,*]

[a]*Analytical Chemistry Department, Universidade Federal Fluminense (UFF), Outeiro de São João Batista, S/N, Bairro Centro, 24020-141, Niterói, RJ, Brazil, email: paulamarcelleufc@hotmail.com (P.M.O. Silva)*
[b]*Department of Analytical Chemistry and Physical Chemistry, Federal University of Ceará, Rua do Contorno, S/N Campus do Pici, Bl. 940 CEP: 60451-970, Fortaleza, CE, Brazil, Tel. +55 85 3366 9042; emails: ronaldo@ufc.br (R.F. do Nascimento), carlab.vidal@gmail.com (C.B. Vidal)*
[c]*Northeast College – Fanor Devry, Campus Dunas, Santos Dumont Avenue, 7800, 60191-156, Fortaleza, CE, Brazil, email: gisellescr@yahoo.com.br*

Received 8 April 2017; Accepted 25 October 2017

ABSTRACT

Precipitation using sulfide is an alternative method for the recovery and reuse of metal ions present in industrial effluents. This work explored the selective precipitation of Cu(II), Zn(II) and Ni(II) using $H_2S_{(g)}$ generated by the hydrolysis of thioacetamide. The studies were conducted on a laboratory scale in two stages. In the first stage, precipitation studies were performed for each individual ion (100 mg L^{-1}) at varying pH levels (0.5–6.0) and contact times (30–150 min). In the second stage, tests were performed in multielement solutions. Individual precipitation studies showed that Cu(II) precipitates in the first 30 min, and at all tested pH values, 99.9% of the copper ions were removed. The precipitation of Zn(II) required 60 min of contact time with the gas and a pH above 4.0 to reach greater than 95% removal of the ions. Ni(II) began to precipitate at pH 6.0 after 120 min and reached greater than 90% removal. In the second stage, the fractional precipitation studies of Cu^{2+}–Zn^{2+} and Cu^{2+}–Ni^{2+} systems, it was possible to separate and precipitate both metal ions above 90%. For the Zn^{2+}–Ni^{2+} system, rigid control of pH was required to separate the metal sulfides because of their very close pK_{ps} values, but a removal of 90% was achieved for both ions. The results of the fractional separation involving three metal ions, Cu(II), Zn(II) and Ni(II), were satisfactory and did not require the use of complexing agents.

Keywords: Selective precipitation; pH; Toxic metals; $H_2S_{(g)}$

1. Introduction

Currently, one of the most serious problems affecting the environment is chemical pollution with organic or inorganic contaminants from industrial waste [1,2]. Among these pollutants are toxic metals, which, in contrast to organic contaminants, are not biodegradable and tend to accumulate in living organisms [3].

The main sources of metallic waste are of industrial origin and are related to the metal finishing and metallurgical industries [4–6]. Due to the relative simplicity and low cost, the precipitation of metals using hydroxide is widely used in industry for removal of metal ions from waste [7]. However, this method has some serious limitations since it results in the production of an unstable mixture of metal hydroxides leading to another environmental problem. The use of sulfide as a precipitating agent has therefore been suggested. This offers some advantages over precipitation with hydroxides, such as the selective removal of individual metals, effluent treatment at concentrations of µg L^{-1} or mg L^{-1}, less interference from chelating agents, improved dewatering of sludge, and the possibility of recovering the metals [8,9].

---

* Corresponding author.

Although there are numerous studies about the precipitation of metallic sulfides, this field of research as a whole is not comprehensive [10]. As a result, some undefined points require careful study so that this methodology can be applied in wastewater treatment. The chemical equations and stoichiometry of the reactions involved need to be known so that the excessive metal or excessive sulfide are not generated in solution [11]. Furthermore, the concentration of the sulfide species is strongly related to the pH of the medium, and depending on the source of sulfide, other chemical equilibrium can be involved and may negatively influence the precipitation [9,10].

Several studies on sulfide precipitation using solid reagents (FeS and CaS), aqueous reagents (NaS, NaHS and NH_4S) or sources of hydrogen sulfide (H_2S) have been reported in the literature. It is also possible to use the decomposition of sodium sulfate ($Na_2S_2O_3$) as a source of sulfide for the precipitation of metals. In the preparation of nanocrystals, it is possible to use other sources of sulfide, including thiourea, thioacetamide, polyphenylene sulfide and carbon disulfide. However, since sulfides are often toxic gases, the most recent studies deal with the reuse of these gases in a sustainable way for industry, especially those who generate these gases as byproducts and are looking for ways to reuse the sulfides generated in their own chemical processes to treat their metallic effluents [12].

The most recent studies on the selective precipitation of metals use $H_2S_{(g)}$ produced by bioreactors. Janyasuthiwong et al. [13] studied the effect of pH on Cu, Ni and Zn removal by biogenic sulfide precipitation in an inversed fluidized bed bioreactor; the authors found that the initial metal concentration and pH played a major role in affecting the reactor performance in terms of sulfide production as well as sulfate and Ni removal efficiency. Ye et al. [14] investigated the removal of metals from lead–zinc mine tailings using bioleaching and followed by sulfide precipitation; according to the authors, a selective separation process can be used to recover Cu, Pb, Zn and Fe using sulfide precipitation in the bioleaching leachate. Oh et al. [15] studied the field application of selective precipitation for recovering Cu and Zn in drainage discharged from an operating mine. Lundström et al. [16] studied the copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions.

This paper presents a study on the influence of pH on the selective precipitation of single and mixed copper, nickel and zinc ions using hydrogen sulfide gas produced by the hydrolysis of thioacetamide.

2. Materials and methods

2.1. Chemical and reagents

Stock solutions of approximately 1,000 mg L^{-1} of metal ions were prepared from $Cu(NO_3)_2{\cdot}3H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$, which were of analytical grade and were purchased from Vetec (Rio de Janeiro, Brazil). The organic salt thioacetamide ($C_2H_3NH_2S$) was used to prepare the solution of the precipitating agent (analytical grade, Vetec, Rio de Janeiro, Brazil). Nitric acid (65% v/v, analytical grade, Vetec, Rio de Janeiro, Brazil) and sodium hydroxide (analytical grade, Vetec, Rio de Janeiro, Brazil) were used as auxiliary solutions of acid and base, respectively.

From the single-element stock solutions, which were 1,000 mg L^{-1}, mono and multielement solutions of approximately 100 mg L^{-1} were prepared by appropriate dilution for the studies on selective precipitation. A saturated solution of $C_2H_3NH_2S$ was prepared. Finally, HNO_3 at 1 and 0.5 mol L^{-1}, and NaOH at 1 and 0.5 mol L^{-1} were prepared as auxiliary solutions. Deionized water was used for all solutions.

2.2. Reaction system

For precipitation tests, a closed system of a side arm flask, hose, beaker, two metering pumps (acid/base) (Hanna, BL20) was coupled to a pH/ORP (oxidation reduction potential) controller (Hanna, pH 500 and mV 600 series) with a real-time microprocessor and a hot plate. The system is illustrated in Fig. 1.

The saturated solution of thioacetamide was heated to approximately 90°C in a closed system (sealed 50 mL side arm flask) to produce H_2S gas. The gas produced was fed through a hose to the reactor containing the metal ion solution. The pH of the solution was periodically adjusted by a pH/ORP controller at scheduled time intervals. The H_2S flow was kept between 1.0 and 2.0 mL min^{-1}.

2.3. Testing of individual precipitation of metal ions, Cu^{2+}, Zn^{2+} and Ni^{2+}

$H_2S_{(g)}$ was bubbled into 100 mL of the single-element solution of each metal at concentrations of approximately 100 mg L^{-1}. The profile of the precipitation of each metal at various pH values (2.0, 4.0 and 6.0) was tested. The pH of the metal solution in each test was adjusted and maintained at the values determined above. Each solution was exposed to the gas for up to 150 min with the pH being adjusted as necessary with 0.5 mol L^{-1} HNO_3 or 0.5 mol L^{-1} NaOH. The precipitate was filtered, and the remaining solution was analyzed every 30 min by flame atomic absorption spectrometry (FAAS).

The results of the single-element tests at various pH values were used to guide testing in the multielement systems.

2.4. Fractional precipitation of mixed metal ions Cu^{2+}, Zn^{2+} and Ni^{2+}

Studies on precipitation in metal mixtures were carried out using metal pairs first (Cu^{2+}/Zn^{2+}, Zn^{2+}/Ni^{2+} and Cu^{2+}/Ni^{2+}) and then all three ions in the same solution

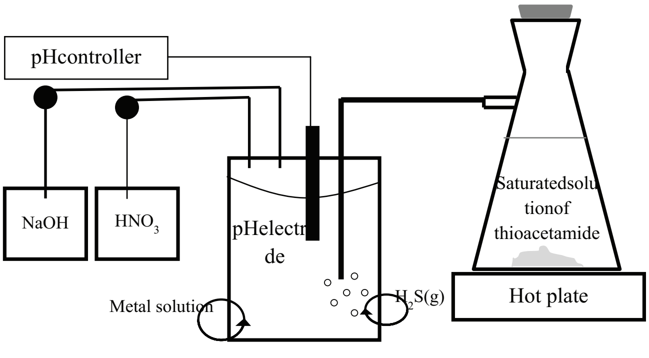

Fig. 1. System for $H_2S_{(g)}$ production and pH control.

($Cu^{2+}/Zn^{2+}/Ni^{2+}$). Using the same apparatus as before, $H_2S_{(g)}$ was bubbled through 100 mL of metallic solution (approximately 100 mg L^{-1}) at the optimized time and pH found in the single-element studies. The first precipitate formed was removed from solution by filtration. In the remaining solution, pH adjustments were made, and the residual concentrations of metal ions were determined by FAAS, after which precipitation was allowed to continue. The pH conditions were reset after the formation of each precipitate.

2.5. Determination of metal ions

Determination of the residual concentrations of metal ions was carried out using a flame atomic absorption spectrometer (FAAS) Varian model AA240FS. The standards used to prepare calibration curves and the detection wavelengths for each metal, as well as the typical linear range and the flame type used are shown in Table 1. The analytical curves were prepared from the standard 1,000 mg L^{-1} solutions (Carlo Erba, Italy) of each metal.

3. Results and discussion

3.1. Effect of pH on the precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} in single-element solutions

The pH has a substantial impact on the precipitation of metal ions with sulfide generated from the speciation of H_2S to HS^- (Eq. (1)). The main reaction to form the precipitate, MS and generate protons to reduce the pH is shown in Eq. (2). Eq. (3) relates the concentration of metal ion in solution, the K_{sp}, and the H^+ concentration:

$$H_2S \rightleftharpoons HS^- + H^+ \tag{1}$$

$$M^{2+} + HS^- \rightleftharpoons MS\downarrow + H^+ \tag{2}$$

$$\left[M^{2+}\right] = \left(\frac{1}{K_1 \cdot K_2}\right) \cdot \frac{K_{sp} \cdot \left[H^+\right]^2}{\left[H_2S\right]} \tag{3}$$

The results of tests of precipitation in single-element solutions are shown in Table 2. The tests indicated that pH has little influence on the precipitation of copper. In the first 30 min at pH 0.5, Cu^{2+} precipitates quantitatively. The same phenomenon was observed by Sampaio et al. [17] in the titration of copper ions with Na_2S at pH 2.0 and 3.0. This can partly be explained by the high value of pK_{ps} (35.1) of CuS precipitation, indicating that the copper ions react quickly with bisulfite.

Table 1
Operating conditions for flame atomic absorption spectrophotometer

Ion	Wavelength (nm)	Linear range (mg L^{-1})	Flame type
Cu^{2+}	324.7	0.5–5	air/acetylene
Zn^{2+}	213.9	0.5–2	air/acetylene
Ni^{2+}	232.0	0.5–5	air/acetylene

The percent removal of Cu^{2+} at each pH and time studied is shown in Fig. 2(a), and it can be seen that the conversion to copper sulfide was greater than 95% under all experimental conditions and over 99% in most cases.

Of the three metal ions studied, zinc was the most difficult to precipitate and quantify, in addition to complications in controlling the pH, since any decrease in pH slowed the precipitation process. The precipitate formed was very fine particles that gave a milky solution making it difficult to visualize and separate.

The percent removal of Zn^{2+} at each pH and time studied are shown in Fig. 2(b). The conversion to zinc sulfide was above 95% at pH 4.0 after either 60 or 90 min and up to 80% in most cases. Sampaio et al. [17] studied the influence of pH on precipitation of zinc at pH 3.0 and 4.0 and found that this ion easily precipitates at pH 4.0. At pH 6.0, the time of exposure to H_2S gas had little influence on the residual ion concentration.

The prevention of sudden changes in pH during zinc ion precipitation required greater attention. Lewis and Hille [18] observed that ZnS precipitate is soluble at pH 2.0 because of re-solubilization of the precipitate. The pH shows that saturation of the metal solution with H_2S shifts the equilibrium to the right, forming bisulfite ions that cause precipitation of ZnS. This precipitation generates H^+ ions which lower the pH and shift the equilibrium of precipitation to the left and causes the ZnS salt to redissolve.

In the nickel precipitation experiments, formation of a black precipitate was observed. During the NiS precipitation tests, H^+ ions are generated which increase the acidity of the solution and prevent spontaneous precipitation from occurring [19]. According to Hammack et al. [20], the theoretical limit of pH for Ni^{2+} precipitation by sulfide gas is 5.8. An increasingly acid environment limits H_2S dissolution and prevents its speciation. This suppresses the supply of HS^- ions which prevents precipitation.

The experiments to determinate if HS^- or S^{2-} were responsible for precipitation of NiS were inconclusive, but there was

Table 2
Test results of precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} ions

Total time (min)	pH	Theoretical concentration (mg L^{-1})	Residual concentration (mg L^{-1})		
			Cu^{2+}	Zn^{2+}	Ni^{2+}
30	0.5	100.0	ND	–	–
	2.0		ND	–	96.42
	4.0		1.36	12.76	–
	6.0		3.47	27.44	–
60	2.0	100.0	–	–	89.13
	4.0		ND	0.71	–
	6.0		ND	25.13	29.58
90	4.0	100.0	–	ND	–
	6.0		–	16.08	–
120	2.0	100.0	–	–	80.86
	6.0		–	11.58	13.47
150	6.0	100.0	–	–	1.48

ND, not detected.

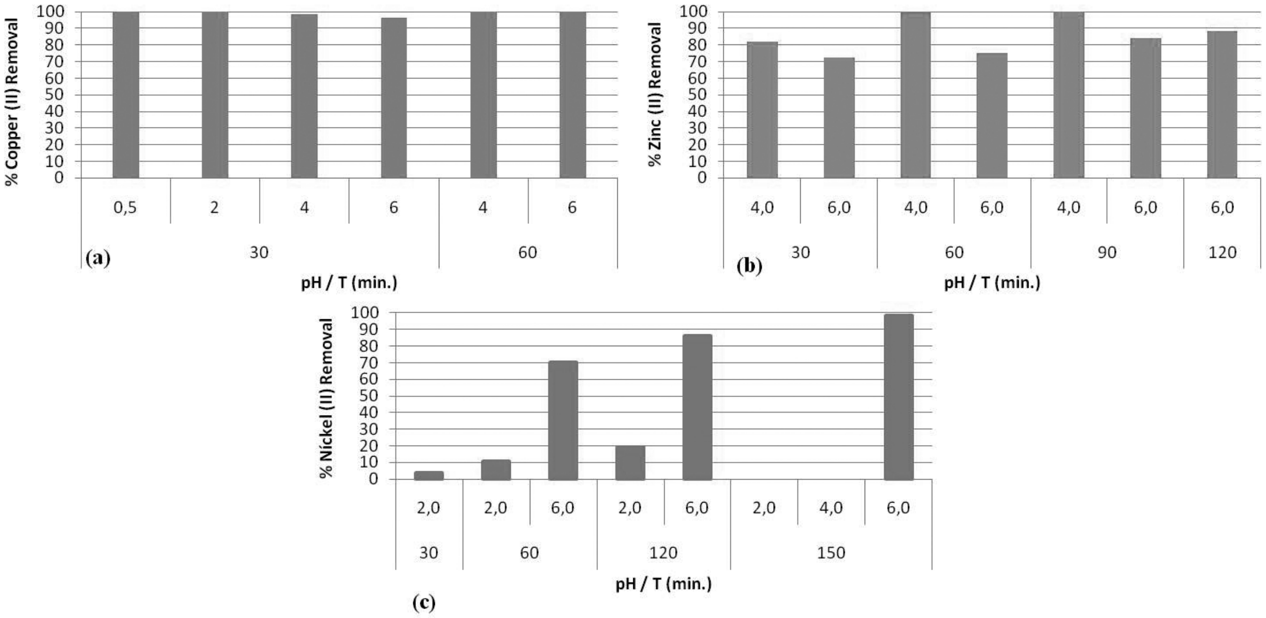

Fig. 2. Percent removal of metal ions: (a) Cu^{2+}, (b) Zn^{2+} and (c) Ni^{2+}.

enough evidence to confirm that $H_2S_{(aq)}$ cannot precipitate Ni^{2+} as the sulfide at ambient conditions. Some studies suggest that bisulfite ions (HS^-) are responsible for NiS precipitation because the sulfite ion (S^{2-}) was not present in significant concentrations regardless of pH. It has also been shown that the precipitation of Ni^{2+} sulfite using $H_2S_{(g)}$ cause the pH of the solution to decrease which limited the progress of the reaction due to the low supply of reactive HS^- ion [18,21,22].

In this study, of the three metals tested, Ni^{2+} was the most dependent on pH. When the metallic solution (100 mg L^{-1}) was exposed to H_2S gas, precipitation only began at pH 6.0. As seen in Fig. 2(c), removal percentages above 95% are achieved only after 150 min of exposure at pH 6.0.

At pH 2.0, the residual concentration of nickel in solution tends to decrease with increasing exposure time (Table 2). High concentrations of H^+ ions in solution limited H_2S speciation, thus preventing nickel precipitation as NiS. For tests at pH 6.0, the nickel solution was exposed to H_2S gas for longer and the pH was strictly controlled with NaOH, since any change in pH cause problems in precipitation.

Various studies have reported that the use of a combination of sulfite and base to control pH can lead to complete precipitation of a metal ion, and it can allow the selective precipitation of a single metal at different pH values [20,23,24]. Other researchers such as Bryson and Bijsterveld [24] used ammonium sulfide to precipitate manganese and cobalt and control the pH. Esposito et al. [25] added $NaHCO_3$ to raise the pH to precipitate ZnS with Na_2S and biogenic sulfite. Karbanee et al. [19] promoted speciation of H_2S into HS^- with NaOH to precipitate NiS.

3.2. Fractional precipitation of metal ions Cu^{2+}, Zn^{2+} and Ni^{2+} in two element solutions

The study of individual ion systems served as basis for understanding the behavior of precipitation in a multielement system. The order of precipitation predicted by the pK_{sp} values (Eqs. (4)–(6)) was followed; beginning with copper ion, then zinc and finally nickel:

$$Cu^{2+} + HS^- \rightleftharpoons CuS_{(s)} + H^+ \qquad pK_{sp} = 35.1 \tag{4}$$

$$Zn^{2+} + HS^- \rightleftharpoons ZnS_{(s)} + H^+ \qquad pK_{sp} = 23.8 \tag{5}$$

$$Ni^{2+} + HS^- \rightleftharpoons NiS_{(s)} + H^+ \qquad pK_{sp} = 20.7 \tag{6}$$

3.2.1. Copper/zinc

The Cu–Zn system is the most studied in the literature [10,26]. The results of residual ion concentration vs. time of exposure to H_2S gas for the fractional precipitation of Cu^{2+}/Zn^{2+} are described in Table 3. The CuS and ZnS precipitates are easily recognized during exposure to H_2S gas. The precipitation of copper ion occurs at first contact with gas, initially muddying the solution and then forming sharp brown flakes. There was no need to adjust pH during Cu precipitation since the initial acidic pH was maintained by the H^+ ions produced during H_2S speciation. The precipitate was separated by filtration and the residual concentrations of copper and zinc ions were determined. The pH of the solution was then adjusted to precipitate zinc.

ZnS is characterized by a milky precipitate; it is finely particles which are difficult to visualize and separate. Throughout the reaction it was necessary to adjust the pH. Zinc precipitation began shortly after the pH reached 4.0, and more than 99% precipitation was achieved (Fig. 3(a)). The time of exposure to the gas was higher due to sudden changes in pH that promoted the re-dissolution of ZnS precipitate that had already formed.

The results show that it is possible to obtain a quantitative separation between Cu and Zn ions through rigid control of pH, as predicted by single-metal solution experiments and literature values of pK_{sp}.

3.2.2. Copper/nickel

The results of the residual ion concentrations and exposure times to H_2S gas for the fractional precipitation of Cu^{2+}/Ni^{2+} ions are described in Table 4. The CuS and NiS precipitates are dark, making it difficult to differentiate them during the experiments. However, the nickel precipitation is extremely dependent on pH and therefore did not interfere with the copper precipitation. Copper precipitation occurred in much the same manner as it did in the Cu^{2+}/Zn^{2+} system. There was no need to adjust the pH during Cu^{2+} precipitation due to the continuous supply of H^+ ions from H_2S speciation. The precipitate was separated by filtration and remaining solution was analyzed by FAAS. The pH of the solution was readjusted to precipitate nickel.

NiS is formed as small, black flakes that easily settle out of solution. Nickel remained in solution until the pH reached 6.0 where total precipitation of the metal ions in solution occurred. As shown in Fig. 3(b), a removal up to 99.0% of the ions was achieved. During the experiments, the phenomenon of co-precipitation was not observed and the pH was adjusted to counteract any variations.

The results show that it is possible to obtain a quantitative separation between Cu^{2+} and Ni^{2+} ions by careful control of pH, as predicted by the single-metal solution experiments.

3.2.3. Zinc/nickel

Based on the values of pK_{sp} in Eqs. (5) and (6), the line between zinc and nickel is rather narrow which makes co-precipitation more likely in this case. The single-element

Table 3
Test results of the fractional precipitation of Cu^{2+}/Zn^{2+}

Total time (min)	pH	Residual concentration (mg L^{-1})	
		Cu^{2+}	Zn^{2+}
40	1.50	2.40	88.06
90	4.00	ND	ND

ND, not detected.

Table 4
Test results of fractional precipitation of Cu^{2+}/Ni^{2+}

Total time (min)	pH	Residual concentration (mg L^{-1})	
		Cu^{2+}	Ni^{2+}
40	1.50	1.30	89.74
120	6.00	ND	ND

ND, not detected.

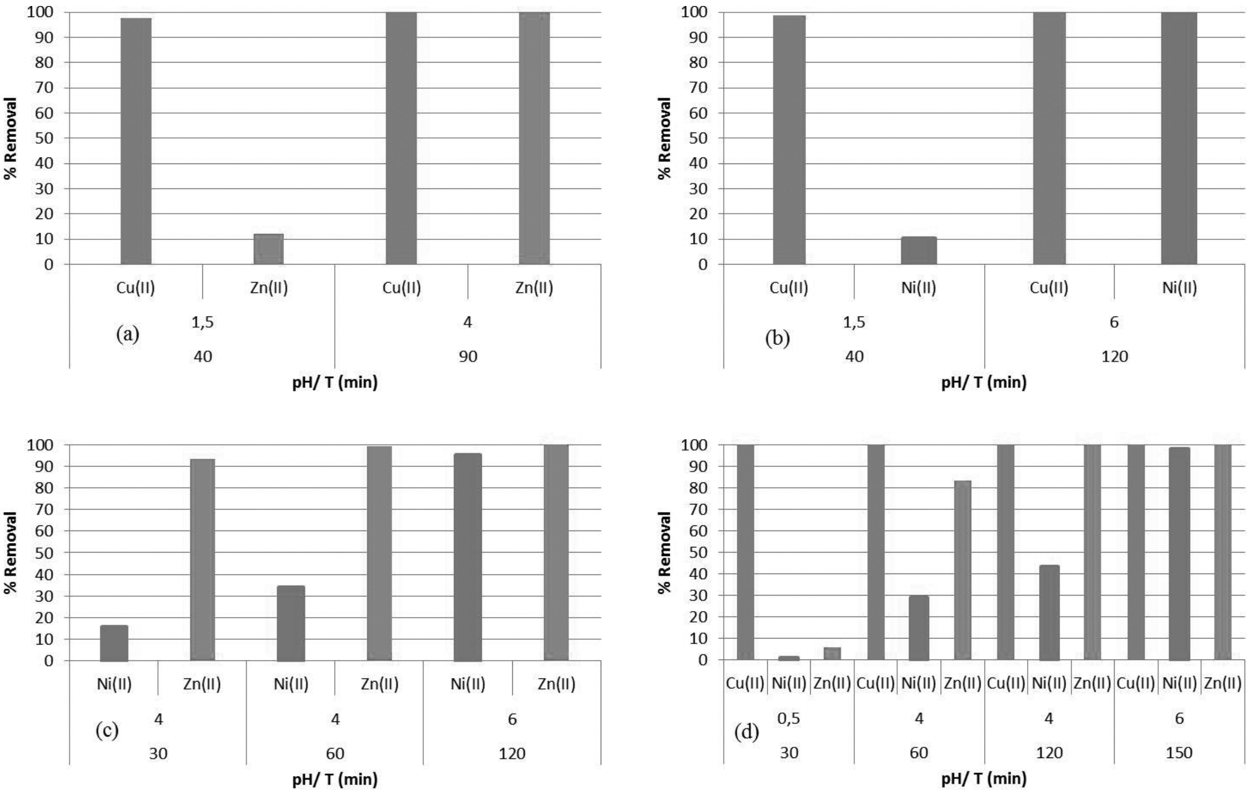

Fig. 3. Percent of fractional precipitation of metal ions in two-element and multielement systems: (a) Cu^{2+}/Zn^{2+}, (b) Cu^{2+}/Ni^{2+}, (c) Ni^{2+}/Zn^{2+} and (d) $Cu^{2+}/Zn^{2+}/Ni^{2+}$.

Table 5
Test results of fractional precipitation of Zn^{2+}/Ni^{2+}

Total time (min)	pH	Residual concentration (mg L^{-1})	
		Zn^{2+}	Ni^{2+}
30	4.0	6.73	84.13
60	4.0	0.88	65.74
120	6.0	ND	4.76

ND, not detected.

Table 6
Test results of fractional precipitation of $Cu^{2+}/Zn^{2+}/Ni^{2+}$

Total time (min)	pH	Residual concentration (mg L^{-1})		
		Cu^{2+}	Zn^{2+}	Ni^{2+}
30	0.5	ND	94.08	98.75
60	4.0	ND	16.70	71.70
120	4.0	ND	ND	56.50
150	6.0	ND	ND	2.10

ND, not detected.

studies showed that in precipitation with $H_2S_{(g)}$ generated from thioacetamide hydrolysis, the optimal pH for zinc is 4.0, and for nickel it is 6.0. The precipitation data are described in Table 5.

The results were consistent with what was predicted from the single-element experiments. As shown in Fig. 3(c), there is a small reduction in the residual concentration of nickel, likely due to the transfer of water vapor during thioacetamide hydrolysis to the metal solution. Nickel precipitation began shortly after the pH was adjusted to 6.0, and more than 95.0% of the metal was isolated.

The pH control study revealed that it is possible to quantitatively separate ions with close pK_{sp} values without adding a complexing agent. During zinc precipitation (white color), the black flakes indicative of NiS precipitation were not observed.

3.3. Fractional precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} in multielement solutions

The selective precipitation of Cu^{2+}, Zn^{2+} and Ni^{2+} with $H_2S_{(g)}$ in multielement systems was studied, and the results are shown in Table 6.

Similar to previous experiments, the pH was controlled and precipitates were separated by filtration and the remaining solution was analyzed by AAS. The pH of the solutions was then readjusted according to previous experiments. The results of fractional precipitation of the three metals studied are shown in Table 6 and Fig. 3(d). With 150 min of exposure to the gas, the metal ions are precipitated selectively and percentages of precipitation are 100% for copper, 80% for zinc and 97% for nickel.

4. Conclusion

The present study showed the influence of pH on precipitation of copper, nickel and zinc ions using H_2S gas as the precipitating agent.

In tests with single-element solutions, favorable pH values were found to precipitate each metal ion: 2.0–6.0 for copper, 4.0 for zinc and greater than 6.0 for nickel. Precipitation rates were above 90% for the three metal ions in this system.

According to the literature and confirmed by the experimental work, the selective precipitation of metal ions occurs by reaction with HS^- ions in solution and is pH dependent.

The results of fractional separations in two-element systems were satisfactory. In Zn^{2+}/Ni^{2+} separation, rigid control of pH is critical to separate the metallic sulfides because of their very close pK_{sp} values.

The results of fractional separation involving three metal ions were satisfactory and do not require complexing agents.

Acknowledgments

The authors are grateful for the funding and support provided by the following project: "Precipitação e recuperação de metais pesados de águas residuais oriundas das indústrias do segmento mineral de jóias por biogás gerado de reator biológico" (Proc. No. 059.01.00/10) – Cearense Foundation for Scientific and Technological Development Support – FUNCAP.

References

[1] D.Q. Melo, C.B. Vidal, T.C. Medeiros, G.S.C. Raulino, A.D. Luz, M.C. Pinheiro, R.F. Nascimento, Biosorption of metal ions using a low cost modified adsorbent (*Mauritia flexuosa*): experimental design and mathematical modeling, Environ. Technol., 37 (2016) 2157–2171.

[2] C.B. Vidal, D.Q. Melo, G.S.C. Raulino, A.D. Luz, C. Luz, R.F. Nascimento, Multielement adsorption of metal ions using Tururi fibers (*Manicaria saccifera*): experiments, mathematical modeling and numerical simulation, Desal. Wat. Treat., 57 (2016) 9001–9008.

[3] D.Q. Melo, V.O. Sousa Neto, F.C.F. Barros G.S.C. Raulino, C.B. Vidal, R.F. Nascimento, Chemical modifications of lignocellulosic materials and their application for removal of cations and anions from aqueous solutions, J. Appl. Polym. Sci., 133 (2016) 43286 (1–22).

[4] G.S.C. Raulino, C.B. Vidal, A.C.A. Lima, D.Q. Melo, J.T. Oliveira, R.F. Nascimento, Treatment influence on green coconut shells for removal of metal ions: pilot-scale fixed-bed column, Environ. Technol., 35 (2014) 1711–1720.

[5] K. Upadhyay, Solution for wastewater problem related to electroplating industry: an overview, J. Ind. Pollut. Control, 22 (2006) 59–66.

[6] F. Glombitza, Treatment of acid lignite mine flooding water by means of microbial sulfate reduction, Waste Manage., 21 (2001) 197–203.

[7] J.L. Huisman, G. Schouten, C. Schultz, Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry, Hydrometallurgy, 83 (2006) 106–113.

[8] D.Q. Melo, C.B. Vidal, A.L. da Silva, T.C. Medeiros, G.S.C. Raulino, R.N. Teixeira, P.B.A. Fechine, R.F. Nascimento, S.E. Mazzeto, D. Keukeleire, Removal of Cd^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+} ions from aqueous solutions using tururi fibers as an adsorbent. J. Appl. Polym. Sci., 131 (2014) 40883 (1–12).

[9] V.F. Albuquerque, A.L. Barros, A.C. Lopes, R.F. Nascimento, A.B. Santos, Removal of the metal ions Zn^{2+}, Ni^{2+}, and Cu^{2+} by biogenic sulfide in UASB reactor and speciation studies, Desal. Wat. Treat., 51 (2013) 2093–2101.

[10] A.E. Lewis, Review of metal sulphide precipitation, Hydrometallurgy, 104 (2010) 222–234.

[11] M. Gharabaghi, M. Irannajad, A.R. Azadmehr, Selective sulphide precipitation of heavy metals from acidic polymetallic aqueous solution by thioacetamide, Ind. Eng. Chem. Res., 51 (2012) 954–963.

[12] O. Jorquera, A. Kiperstok, E.A. Sales, M. Embiruçu, M.L. Ghirardi, S-systems sensitivity analysis of the factors that may influence hydrogen production by sulfur-deprived *Chlamydomonas reinhardtii*, Int. J. Hydrogen Energy, 33 (2008) 2167–2177.

[13] S. Janyasuthiwong, E.R. Rene, G. Esposito, P.N.L. Lens, Effect of pH on Cu, Ni and Zn removal by biogenic sulfide precipitation in an inversed fluidized bed bioreactor, Hydrometallurgy, 158 (2015) 94–100.

[14] M. Ye, G. Li, P. Yan, J. Ren, L. Zheng, D. Han, S. Sun, S. Huang, Y. Zhong, Removal of metals from lead-zinc mine tailings using bioleaching and followed by sulfide precipitation, Chemosphere, 185 (2017) 1189–1196.

[15] C. Oh, Y.-S. Han, J.H. Park, S. Bok, Y. Cheong, G. Yim, S. Ji, Field application of selective precipitation for recovering Cu and Zn in drainage discharged from an operating mine, Sci. Total Environ., 557–558 (2016) 212–220.

[16] M. Lundström, J. Liipo, P. Taskinen, J. Aromaa, Copper precipitation during leaching of various copper sulfide concentrates with cupric chloride in acidic solutions, Hydrometallurgy, 166 (2016) 136–142.

[17] R.M.M. Sampaio, R.A. Timmers, Y. Xu, K.J. Keesman, P.N.L. Lens, Selective precipitation of Cu from Zn in a pS controlled continuously stirred tank reactor, J. Hazard. Mater., 165 (2009) 256–265.

[18] A. Lewis, R.V. Hille, An exploration into the sulphide precipitation method and its effect on metal sulphide removal, Hydrometallurgy, 81 (2006) 197–204.

[19] N. Karbanee, R.P. van Hille, A.E. Lewis, Controlled nickel sulfide precipitation using gaseous hydrogen sulfide, Ind. Eng. Chem. Res., 47 (2008) 1596–1602.

[20] R.W. Hammack, D.H. Dvorak, H.M. Edenborn, The Use of Biogenic Sulfide to Selectively Recover Cooper and Zinc from Severely Contaminated Mine Drainage, A.E. Torma, J.E. Wey, V.L. Lakshmanan, Eds., Biohydrometallugical Technologies, The Minerals, Metals and Materials Society, Warrendale, PA, 1993, pp. 631–639.

[21] A.A. Migdisov, A.E. Williams-Jones, L.Z. Lakshtanov, Y.V. Alekhin, Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur, Geochim. Cosmochim. Acta, 10 (2002) 1713–1725.

[22] J. Qian, X. Zhu, Y. Tao, Y. Zhou, X. He, D. Li, Promotion of Ni^{2+} removal by masking toxicity to sulfate-reducing bacteria: addition of citrate, Int. J. Mol. Sci., 16 (2015) 7932–7943.

[23] E. Skavås, A. Adriaens, T. Hemmingsen, A Comparative study of sulphite oxidation under alkaline conditions by use of wall-jet flow cell and rotating disc electrode, Int. J. Electrochem. Sci., 1 (2006) 414–424.

[24] W. Bryson, C.H. Bijsterveld, Kinetics of the precipitation of manganese and cobalt sulphides in the purification of a manganese sulphate electrolyte, Hydrometallurgy, 27 (1991) 75–84.

[25] G. Esposito, A. Veeken, J. Weijma, P.N.L. Lens, Use of biogenic sulfide for ZnS precipitation, Sep. Purif. Technol., 51 (2006) 31–39.

[26] M.T. Alvarez, C. Crespo, B. Mattiasson, Precipitation of Zn(II), Cu(II) and Pb(II) at bench-scale using biogenic hydrogen sulfide from the utilization of volatile fatty acids, Chemosphere, 66 (2007) 1677–1683.