Influence of selected conditions on the efficiency of carbonate precipitation of Cu(II), Ni(II), Pb(II) and Zn(II) ions

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ABSTRACT

The aim of this work was to find optimal process conditions for carbonate precipitation of heavy metal ions from monocomponent and binary multicomponent solutions using Na_2CO_3 as an alternative precipitant. The research work was done in the Laboratory for Instrumental methods at the Faculty of Technology, University of Tuzla.

Na_2CO_3 precipitant was added to the prepared synthetic monocomponent and binary multicomponent heavy metal solutions with initial concentrations of 500 mg/L in doses to achieve pH 8 at the selected mixing speeds (0, 100, 300 and 800 rpm) and mixing time (0, 15 and 30 minutes).

The results of the influence of solution mixing showed that the removal percentages of Cu(II), Ni(II) and Zn(II) were equal in monocomponent and binary multicomponent solutions, in contrast to Pb(II). Testing the influence of time showed that the efficiency of heavy metal ion removal was in most cases the best immediately after the addition of the precipitant to the heavy metal solution, which suggests that with a longer mixing time, the formed solid carbonate particles dissolve, reducing the removal efficiency.

Carbonate precipitation is a simple method that does not require many technological operations in the wastewater industry, and testing these selected process conditions in laboratory will help to better understand the kinetics and mechanisms of particle formation, as well as the fact that most metal ions are well removed with a shorter mixing time as well as at lower mixing speeds.

Keywords: carbonate precipitation, heavy metals, Na_2CO_3, removal efficiency, mixing speed, time

1. INTRODUCTION

The definition of heavy metals most often refers to metals whose specific density is greater than 5 g/cm^3 [1]. Heavy metals are found in nature in very low concentrations, however, in larger quantities they are very dangerous [2]. Heavy metals are major environmental pollutants and are mainly of anthropogenic origin, most often commercial and industrial, but they are also naturally found in the biosphere. The growth of the world's population and industrialization are creating large amounts of wastewater that contain large amounts of heavy metals and are therefore a threat to the environment [3]. The reason why researchers around the world are assessing the concentrations of heavy metals in the air, water and soil is that millions of people are affected by this problem [4]. A global problem today is the pollution of natural waters with heavy metals such as Cu(II), Ni(II), Pb(II) and Zn(II) which are persistent in the environment, bioaccumulate and biomagnificate in the food chain and are toxic [5]. Exposure to heavy metals can cause consequences such as ingestion, inhalation, and dermal absorption [6].Therefore, there is great importance for the removal of heavy metals from the environment, and according to a review of the literature, there are various methods for removing these toxic substances. Methods for removing heavy metals from natural waters include adsorption, flotation, ion exchange, chemical precipitation, membrane-based filtration, coagulation, flocculation, phytoremediation, and electrochemical methods [7], [8]. In this paper, chemical precipitation was investigated as a simple and easy-to-operate method for the removal of heavy metals. By chemical precipitation we mean a method in which heavy metal ions are converted into solid particles under the influence of an appropriate agent by adjusting the pH [9]. The most commonly used precipitant for the removal of heavy metals is lime, however, a good alternative that also respects the principles of green chemistry and provides good removal efficiency is actually carbonate precipitation using $CaCO_3$ and Na_2CO_3 [10]. Therefore, based on the previous experience of the authors of this paper on the topic of carbonate precipitation of metal ions using Na_2CO_3, this paper investigates the influence of very important process conditions on the precipitation of metal ions in monocomponent and binary multicomponent solutions, namely the mixing speed (rpm) and the mixing time of the solution (min.). The importance of researching mixing speed and mixing time on the effectiveness of carbonate precipitation of metal ions is very important in terms of reducing precipitation time, electricity consumption and reducing the consumption of Na_2CO_3 precipitant dose. Also, the importance of this research is reflected in the lack of scientific works available on this topic.

2. MATERIAL AND METHODS

2.1. Instrumentation

Instruments used for the experimental part of this work were: Atomic absorption spectrometer, Perkin Elmer Aanalyst 200, pH meter GLP Crison, analytical balance Kern ADDB, (0,001 g)

2.2. Chemicals and reagents

During the experimental work, the following chemicals were used: standard solutions of Cu, Ni, Pb and Zn, Merck, Germany. Other chemicals were of p.a. grade: Na_2CO_3, Sisecam Soda Lukavac, $Cu(NO_3)_2 \cdot 3H_2O$, Pliva Zagreb, $Ni(NO_3)_2 \cdot 6H_2O$, Semikem, Sarajevo, $Pb(NO_3)_2$, Alkaloid, Skopje, $Zn(NO_3)_2 \cdot 6H_2O$, Kemika, Zagreb, blue and black ribbon circle, Fioroni, France.

2.3. Dose of added precipitant (Na_2CO_3)

In this research, the precipitant Na_2CO_3 was added with a concentration of 2 g/L as an alternative to a more toxic and expensive precipitant such as NaOH. Table 1. shows the doses of precipitant used in this work in order to achieve the appropriate pH 8 at which the carbonate precipitation of the mentioned ions from monocomponent and binary multicomponent systems was performed.

Table 1. Dose of precipitant Na_2CO_3

Metals	dose of Na_2CO_3, mL/100 mL
Cu(II)	75
Ni(II)	2

Pb(II)	7
Zn(II)	40
Cu-Ni(II)	3
Pb(II)-Zn(II)	10

2.4. General procedure

Carbonate precipitation was carried out in such a way that in 100 mL solutions of monocomponent metals Cu(II), Ni(II), Pb(II) and Zn(II) initial concentrations of 500 mg/L and binary multicomponent solutions of metals Cu(II)-Ni(II) and Pb(II)-Zn(II) initial concentrations of 500 mg/L added a certain dose of precipitant Na_2CO_3. Precipitant was also added to adjust pH 8 for all metals in monocomponent and binary multicomponent solutions. The chosen pH 8 is because some metal ions dissolve again at higher pH values, which the authors of this paper confirmed in earlier research. After the specified time of mixing the solutions, the solutions were filtered first through the black and then through the blue ribbon circle. On the same day, metal samples were measured on FAAS, and then the efficiency of removal of metal ions from the solution was calculated (E, %):

$$E = Ci – Cf /Ci \cdot 100$$

where: E, % removal efficiency, Ci – initial metal concentration (mg/L), Cf – final metal concentration (mg/L). Data are given as the mean of three replicates.

3. RESULTS AND DISCUSSION

3.1. Influenence of solution mixing speed on the efficiency of precipitation of Cu(II), Ni(II), Pb(II), Zn(II), Cu(II)-Ni(II) and Pb(II)-Zn(II) systems

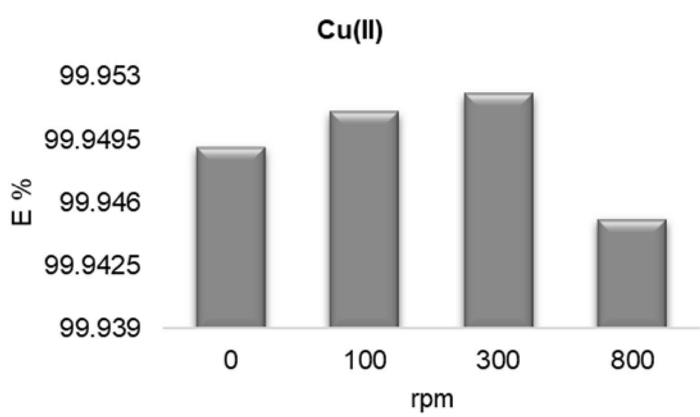

Fig. 1. Influence of solution mixing speed (rpm) on the efficiency of precipitation of Cu(II) ions using sodium carbonate

Conditions: Cu(II) 500 mg/L, pH 8, t = 5 minutes

The highest Cu(II) ion removal efficiency using sodium carbonate as a precipitant was achieved at 300 rpm, while this value decreased with further increase of the mixing speed. In fact, the lowest Cu(II) ion removal efficiency (E<99.945%) was recorded at 800 rpm. Begić et al. 2020 investigated the efficiency of Cu(II)-Ni(II) removal from industrial wastewater using Na_2CO_3 at optimal pH values and found that the highest efficiency of Cu(II) ion removal (E=66.125%) was at a mixing speed of 300 rpm, which was confirmed in this work that a speed of 300 rpm is the best for Cu(II) ion removal [11].

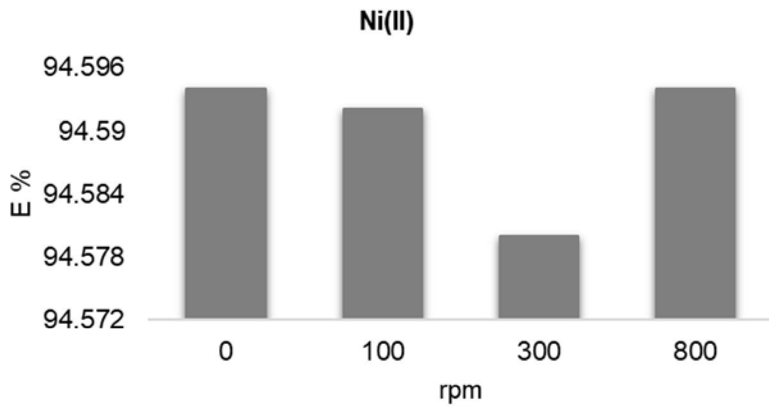

Fig. 2. Influence of solution mixing speed (rpm) on the efficiency of precipitation of Ni(II) ions using sodium carbonate
Conditions: Ni(II) 500 mg/L, pH 8, t = 5 minutes

The same removal efficiency values were achieved without mixing and when the mixing speed of the solution was 800 rpm, and these values were 94.594%. The lowest value was at a mixing speed of 300 rpm (94.58%). Junuzović et al. 2019 investigated the effect of pH (pH≈7.80) on the precipitation of Ni(II) and Cu(II) ions from monocomponent solutions using sodium carbonate at a solution stirring speed of 300 rpm and found that Ni(II) had a lower removal percentage compared to Cu(II), which is consistent with the results obtained in this work [12].

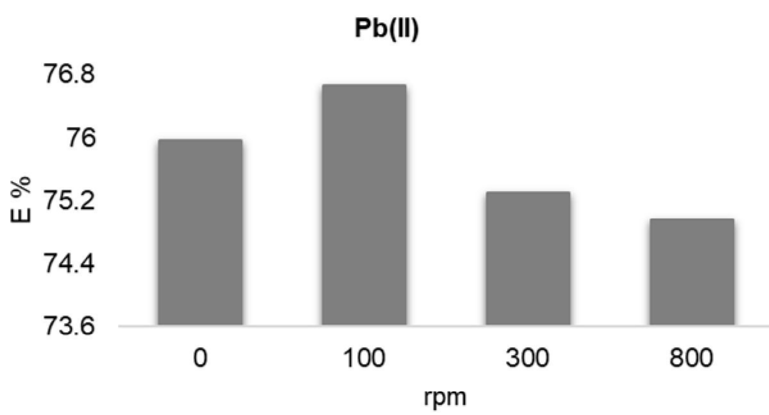

Fig. 3. Influence of solution mixing speed (rpm) on the efficiency of precipitation of Pb(II) ions using sodium carbonate
Conditions: Pb(II) 500 mg/L, pH 8, t = 5 minutes

When it comes to Pb(II) ions, the best carbonate precipitation efficiency was at 100 rpm, while with further increase of mixing solutions, the carbonate precipitation efficiency decreased. Thus, the lowest value was 74.952% at a speed of 800 rpm.

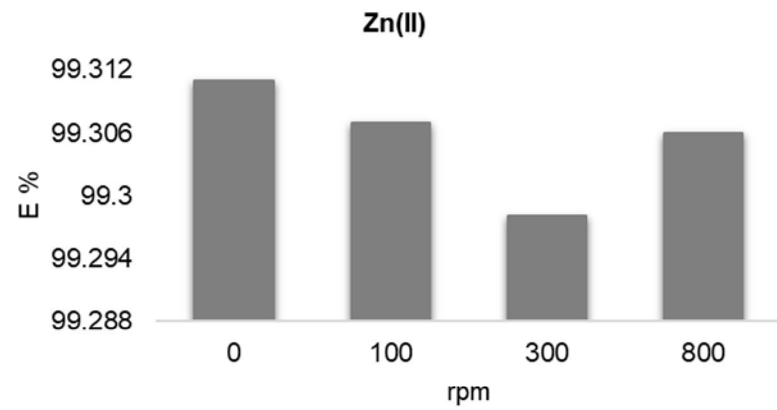

Fig. 4. Influence of solution mixing speed (rpm) on the efficiency of precipitation of Zn(II) ions using sodium carbonate

Conditions: Zn(II) 500 mg/L, pH 8, t = 5 minutes

Compared to the previous three tested metals, the highest carbonate precipitation efficiency was recorded for Zn(II) ions at 0 rpm, while it further decreased at mixing speeds of the solution on 100 and 300 rpm.

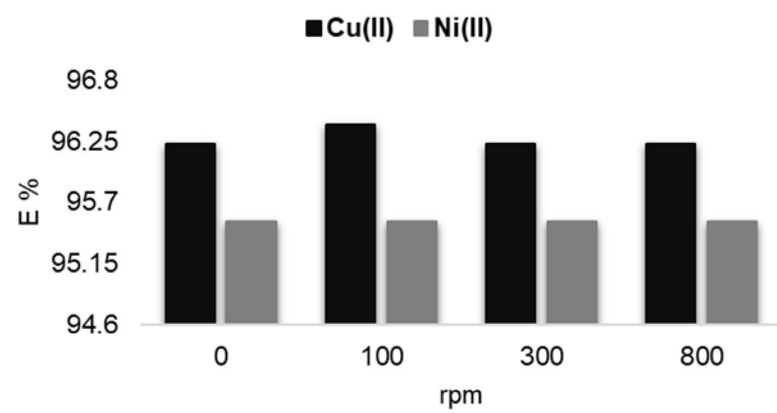

Fig. 5. Influence of solution mixing speed (rpm) on the efficiency of precipitation of Cu(II) and Ni(II) ions in a binary multicomponent system using sodium carbonate

Conditions: Cu(II) and Ni(II) 500 mg/L, pH 8, t = 5 minutes

In a binary multicomponent system consisting of Cu(II) and Ni(II) at the same initial concentrations, mixing time of 5 minutes, and pH values, significant differences in the efficiency of carbonate precipitation were observed. Namely, the highest efficiency of carbonate precipitation of Cu(II) ions was at a mixing speed of 100 rpm (E=96.394%), while with further increasing the mixing speed, the efficiency of carbonate precipitation decreased linearly. The same behavior of Cu(II) ions (highest precipitation efficiency) was observed in a monocomponent solution (Fig 1.) when the optimal mixing speed of the solution was 100 rpm. Similar behavior was shown by the Ni(II) ion in the binary multicomponent system when the efficiency of carbonate precipitation was 95.528% at 800 rpm, while a slightly lower value of 95.523% was achieved at 0 rpm compared to the monocomponent metal system when the same values of the efficiency of carbonate precipitation were obtained at the same speeds (Fig.2).

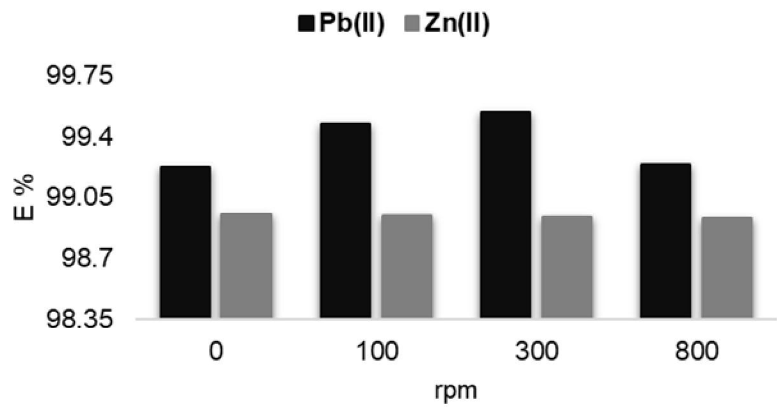

Fig. 6. Influence of binary solution mixing speed (rpm) on the efficiency of precipitation of Pb(II) and Zn(II) ions in a binary multicomponent system using sodium carbonate

Conditions: Pb(II) and Zn(II) 500 mg/L, pH 8, t = 5 minutes

When it comes to the binary multicomponent system of Pb(II) and Zn(II) ions under the same laboratory conditions as the previous mixture of Cu(II) and Ni(II), the optimal mixing speeds differed. Thus, Pb(II) ions were best removed from the solution at a mixing speed of 300 rpm, while Zn(II) ions were best removed without mixing the solution (0 rpm). Compared to the results from the monocomponent solutions (Fig. 3 and Fig.4), it can be noted that Pb(II) ions had the highest precipitation efficiency at 100 rpm, while Zn(II) ions in the binary multicomponent system behaved the same as in the monocomponent system with the best precipitation efficiency at 0 rpm.

3.2. Influenence of time on the efficiency of precipitation of Cu(II), Ni(II), Pb(II), Zn(II), Cu(II)-Ni(II) and Pb(II)-Zn(II) systems

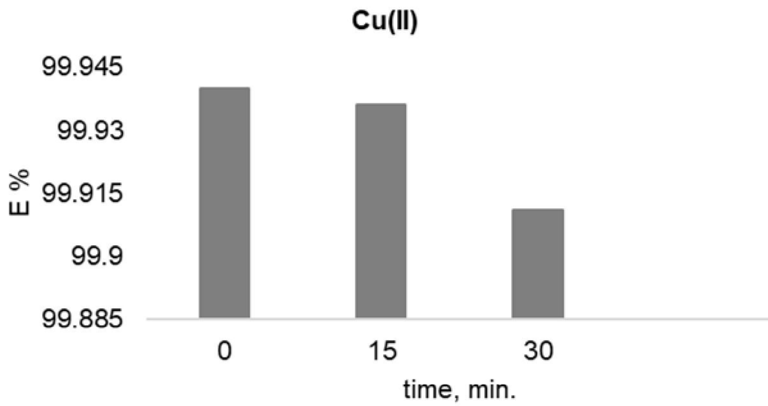

Fig. 7. Influence of time (minutes) on the efficiency of precipitation of Cu(II) ions using sodium carbonate

Conditions: Cu(II) 500 mg/L, pH 8, 300 rpm

By increasing the mixing time of the solution, the efficiency of carbonate precipitation of Cu(II) ions decreased after 15 and 30 minutes. The efficiency of carbonate precipitation had the best result without mixing solution, that is, immediately after dosing the precipitant with the metal solution (E>99.940%).

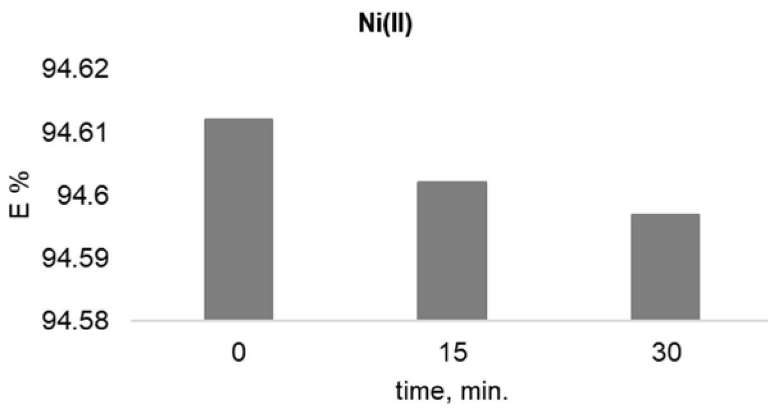

Fig. 8. Influence of time (minutes) on the efficiency of precipitation of Ni(II) ions using sodium carbonate

Conditions: Ni(II) 500 mg/L, pH 8, 300 rpm

By increasing mixing of the solution, the efficiency of carbonate precipitation of Ni(II) decreased, as with Cu(II) under the same laboratory conditions. The highest carbonate precipitation efficiency for Ni(II) ion was 94.612%.

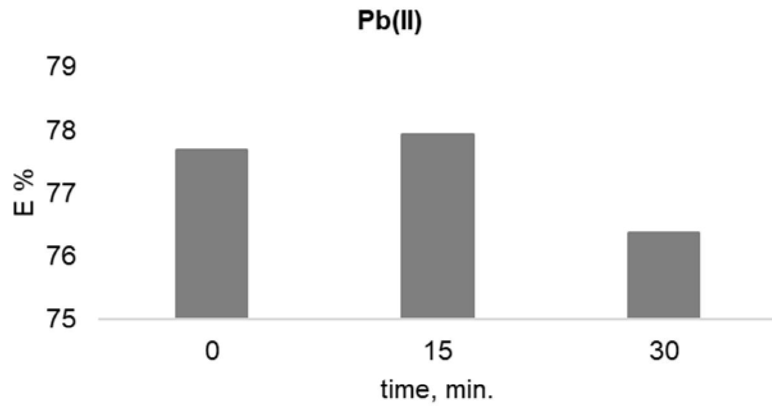

Fig. 9. Influence of time (minutes) on the efficiency of precipitation of Pb(II) ions using sodium carbonate

Conditions: Pb(II) 500 mg/L, pH 8, 300 rpm

The highest efficiency of carbonate precipitation was recorded when the duration of mixing the solution was 15 minutes, while increasing time of mixing the solution, the efficiency of precipitation was reduced, as with the previous two tested metals. Selimović et al. 2020 investigated the influence of pH on the efficiency of removing Pb(II) ions from monocomponent solutions using Na_2CO_3 under process conditions: time 5 minutes, solution mixing speed 300 rpm, pH 8.38, and obtained a removal efficiency of 99.814%, which indicates that a shorter precipitation time is required, and confirmed by the results of this work where a worse result was obtained with a longer time (t=30 min, E=76.366%) [13].

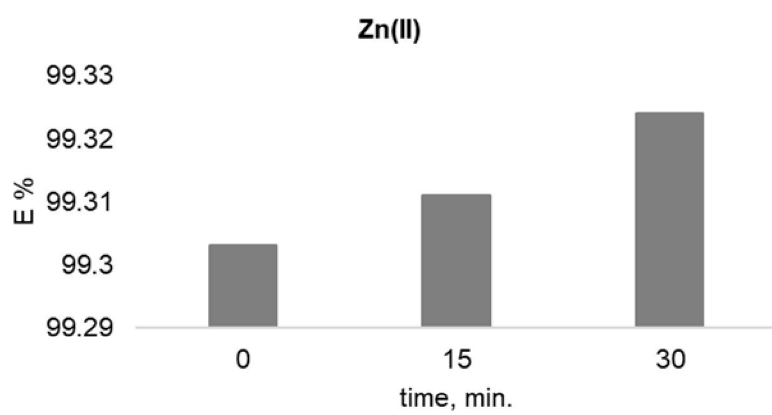

Fig. 10. Influence of time (minutes) on the efficiency of precipitation of Zn(II) ions using sodium carbonate

Conditions: Zn(II) 500 mg/L, pH 8, 300 rpm

Unlike Cu(II), Ni(II) and Pb(II) ions, Zn(II) ions required a longer duratation solution mixing time to achieve higher carbonate precipitation efficiency. The best efficiency of precipitation Zn(II) ions was achieved with time of mixing solution 30 minutes (E=99.324%). Wierzba et al. 2022 examined the influence of time from 0.5 to 5 h on the precipitation of Cu(II) and

Zn(II) using $CaCO_3$, where equilibrium is reached after about 3 h for the mentioned metals [14]. Therefore, it is evident that a longer time is required for Zn(II) ions to precipitate in the form of solid particles.

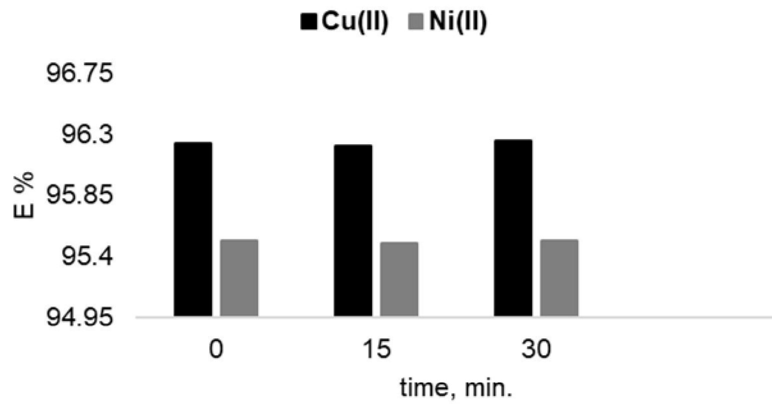

Fig. 11. Influence of time (minutes) on the efficiency of precipitation of Cu(II) and Ni(II) ions in a binary multicomponent system using sodium carbonate
Conditions: Cu(II) and Ni(II) 500 mg/L, pH 8, t = 5 minutes

The effect of mixing time of binary multicomponent solutions of Cu(II) and Ni(II) at an initial concentration of 500 mg/L on the efficiency of carbonate precipitation was highest for Ni(II) ions without mixing (0 min.) and this value was 95.521%, while for Cu(II) ions it was achieved at the longest mixing time (30 min.) and this value was 96.247%. Compared to monocomponent solutions when the best achieved Cu(II) precipitation efficiency required a time of 0 minutes, Ni(II) ions behaved similarly in monocomponent and binary multicomponent solutions when they achieved the best precipitation efficiency (0 min.) at the same mixing times of the solutions. Zhang and Duan, 2020 examined the precipitation of three selected metal ions using synthetic magnesium hydroxy carbonate and found that good removal efficiency was achieved already at a time of 0 to 3 min, but that no significant changes in removal efficiency occurred with further increase in reaction time, which is consistent with the results obtained in this work [15].

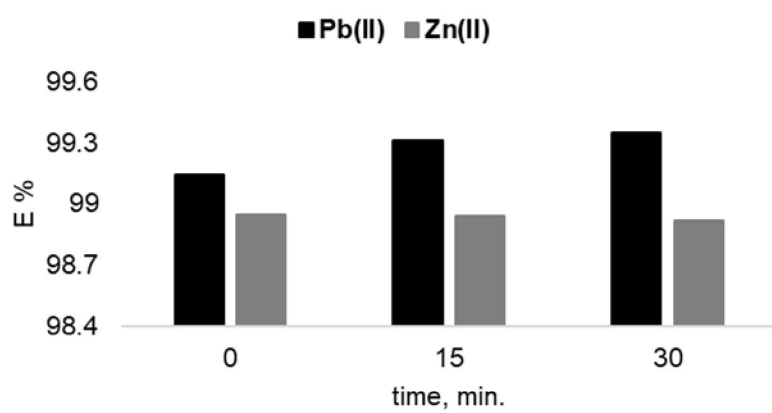

Fig. 12. Influence of time (minutes) on the efficiency of precipitation of Pb(II) and Zn(II) ions ions in a binary multicomponent system using sodium carbonate
Conditions: Pb(II) and Zn(II) 500 mg/L, pH 8, t = 5 minutes

The influence of time had a positive effect on the efficiency of removing Pb(II) ions, so that at the longest mixing time of the solution, a carbonate precipitation efficiency of 99.350% was achieved, while for Zn(II) ions, mixing of the solution was again not necessary, because the best carbonate precipitation efficiency was achieved at a time of 0 minutes and was 98.944%. The overall nucleation rate strongly depends on the mixing conditions, as it depends in a very nonlinear way on the level of supersaturation [16]. In comparison with the monocomponent solutions of Pb(II) and Zn(II), when a time of 15 and 30 minutes was required for the best results of the carbonate precipitation efficiency of the mentioned metals. In relation to the binary multicomponent system of Cu(II) and Ni(II) (Fig. 11), Ni(II) ions behaved like Zn(II) ions, while a longer time was required for the removal of Cu(II), as is the case with Pb(II) ions.

3.3. Statistical analyses

Since in each statistical factor the agreement between the measured values is good, it is less than the critical factor.

Table 2. ANOVA single factor for monocomponent metal solutions (mixing speed)

Groups	Count	Sum	Average	Variance
rpm	4	1200	300	126666,7
Cu(II)	4	399,797	99,94925	9,58E-06
Ni(II)	4	378,36	94,59	4,53E-05
Pb(II)	4	302,885	75,72125	0,578149
Zn(II)	4	397,222	99,3055	2,97E-05

Table 3. ANOVA single factor for binary multicomponent metal solutions (mixing speed)

Groups	Count	Sum	Average	Variance
rpm	4	1200	300	126666,7
Cu(II)	4	385,066	96,2665	0,007228
Ni(II)	4	382,087	95,52175	2,36E-05
Pb(II)	4	397,464	99,366	0,026266
Zn(II)	4	395,765	98,94125	8,09E-05

Table 4. ANOVA single factor for monocomponent metal solutions (time)

Groups	Count	Sum	Average	Variance
min	3	45	15	225
Cu(II)	3	299,787	99,929	0,000247
Ni(II)	3	283,811	94,60367	5,83E-05
Pb(II)	3	231,984	77,328	0,707539
Zn(II)	3	297,938	99,31267	0,000112

Table 5. ANOVA single factor for binary multicomponent solutions (time)

Groups	Count	Sum	Average	Variance
min	3	45	15	225
Cu(II)	3	288,697	96,23233	0,000261
Ni(II)	3	286,538	95,51267	0,000162
Pb(II)	3	297,8	99,26667	0,012097
Zn(II)	3	296,799	98,933	0,000301

4. CONCLUSION

The selected heavy metal ions precipitated differently in the form of insoluble carbonates both individually and in binary mixtures. Thus, Ni(II) and Zn(II) ions in monocomponent solutions had the highest removal efficiency at 0 rpm, while Cu(II) and Pb(II) had it at speeds of 300 rpm and 100 rpm, respectively. In mixtures, Cu(II) and Pb(II) ions again required higher mixing speeds to be better removed from the solution, compared to Zn(II) which again showed that no mixing was required at all to achieve the best removal efficiency. The effect of time on the removal efficiency showed that Cu(II) and Ni(II) ions precipitated very quickly in the form of solid particles (0 min), while the remaining two heavy metal ions required a longer time to achieve a better result. Ni(II) and Zn(II) ions showed better removal efficiency at the shortest time of the precipitation process (0 min), while Cu(II) and Pb(II) ions needed a longer time to achieve better removal efficiency.

REFERENCES

[1] Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N. (2014). Toxicity, mechanism and health effects of some heavy metals. PMC. 7(2), 60-72. doi: 10.2478/intox-2014-0009

[2] Das, S.K., Grewal, S.A., Banerje, M. (2011). A brief review: Heavy metal and their analysis. Inter. Jour. of Pharmaceutical Sciences Review and Research. 11(1), 13-18.

[3] Mitra, S., Chakraborty, A.J., Tareq, A.M., Emran, T.B., Nainu, F., Khusro, A., Idris, A.M., Khandaker, M.U., Osman, H., Alhumaydhi F.A., Simal-Gandara, J. (2022). Impact of heavy metals on the environment and human health: Novel therapeutic insights to counter the toxicity. Journal of King Saud University-Science 34(3). doi:https://doi.org/10.1016/j.jksus.2022.101865

[4] Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, MR. Sadeghi, M. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium, and Arsenic. Front. Pharmacol. PMC. 12:643972. doi: https://doi.org/10.3389/fphar.2021.643972
[5] MathuMitha, C., Mohan Raj, V., Sangeetha, R., George S., Ragumaran M. (2021). A review on the effect of heavy metal contamination and its impact on the environment. Intern. J. Zool. Invest. 7(2), 762-771. doi: https://doi.org/10.33745/ijzi.2021.v07i02.061
[6] Abd Elnabi, M. K., Elkaliny, N. E., Elyazied, M. M., Azab, S. H., Elkhalifa, S. A., Elmasry, S., Mouhamed, M. S., Shalamesh, E. M., Alhorieny, N. A., Abd Elaty, A. E., Elgendy, I. M., Etman, A. E., Saad, K. E., Tsigkou, K., Ali, S. S., Kornaros, M., & Mahmoud, Y. A. -G. (2023). Toxicity of Heavy Metals and Recent Advances in Their Removal: A Review. Toxics, 11(7), 580. https://doi.org/10.3390/toxics11070580
[7] Gahrouei, A.E., Rezapour, A., Pirooz, M., Pourebrahimi, S. (2024). From classic to cutting-edge solutions: A comprehensive review of materials and methods for heavy metal removal from water environments. Desalination and Water Treatment. 319. 100446. doi: https://doi.org/10.1016/j.dwt.2024.100446
[8] Türkmen, D., Bakhshpour, M., Akgönüllü, S., Aşır, S., Denizli, A. (2022) Heavy Metal Ions Removal From Wastewater Using Cryogels: A Review. Front. Sustain. 3:765592. doi: 10.3389/frsus.2022.765592
[9] Mazur, L.P., Cechinel, M.A.P., U. de Souza, S.M.A.G., Boaventura, R.A.R., Vilar, V.J.P. (2018). Brown marine macroalgae as natural cation exchangers for toxic metal removal from industrial wastewaters: A review. Jour, of Environmental Management. 223. 215-253. doi: https://doi.org/10.1016/j.jenvman.2018.05.086
[10] Li, X., Zhang, Q., Yang, B. (2020). Co-precipitation with $CaCO_3$ to remove heavy metals and significantly reduce the moisture content of filter residue. Chemosphere. 239. 124660. doi: https://doi.org/10.1016/j.chemosphere.2019.124660
[11] Begić S., Junuzović, H., Selimović, A., Salkić, M., Cvrk, R., Ahmetović, M. (2020). Influence of pH and precipitating agent on the removal of heavy metal cations from industrial samples. Int. jour. of engineering sciences & research technology. 9(10). doi: https://doi.org/10.29121/ijesrt.v9.i10.2020.6
[12] Junuzović, H., Begić, S., Selimović, A., Đozić, A., Cvrk, R., Melisa Ahmetović, M. (2019). Efficiency of Carbonate Precipitation and Removal of Copper and Nickel Ions from their Monocomponent and Two-component Aqueous Solutions. Int. JouR. for Research in Applied Sciences and Biotechnology. 6(6). 11-15. doi: https://doi.org/10.31033/ijrasb.6.6.3
[13] Selimović, A., Junuzović, H., Begić, S., Cvrk, R. (2020). Efficiency of Precipitation and Removal of Pb(II) and Zn(II) Ions from Their Monocomponent and Two-Component Aqueous Solutions Using Na_2CO_3. Springer Nature Switzerland AG. I. Karabegović (Ed.): NT 2019, 569–575. doi: https://doi.org/10.1007/978-3-030-18072-0_65
[14] Wierzba, S., Makuchowska-Fryc, J., Kłos, A., Ziembik, Z., & Ochędzan-Siodłak, W. (2022). Role of calcium carbonate in the process of heavy metal biosorption from solutions: synergy of metal removal mechanisms. Scientific Reports. 12. 17668. doi: https://doi.org/10.1038/s41598-022-22603-4
[15] Zhang, Y. and Duan X. (2020). Chemical precipitation of heavy metals from wastewater by using the synthetical magnesium hydroxy carbonate. Water Sci. Technol. 81(6). 1130–1136. doi: https://doi.org/10.2166/wst.2020.208
[16] Zauner, R. and Jones G.A. (2002). On the influence of mixing on crystal precipitation processes—application of the segregated feed model. Chemical Engineering Science. 57(5). 821-831. doi: https://doi.org/10.1016/S0009-2509(01)00417-1