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TECHNOLOGYINFLUENCE OF pH AND PRECIPITATING AGENT ON THE REMOVAL OF
HEAVY METAL CATIONS FROM INDUSTRIAL SAMPLESSabina Begić^{*1}, Halid Junuzović², Amra Selimović², Mirsad Salkić², Ramzija Cvrk³ & Melisa Ahmetović⁴^{*1}Department of Chemical technology, Faculty of Technology, University of Tuzla, Bosnia and Herzegovina²Department of Analytical chemistry, Faculty of Technology, University of Tuzla, Bosnia and Herzegovina³Department of Food technology, Faculty of Technology, University of Tuzla, Bosnia and Herzegovina⁴Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, Bosnia and HerzegovinaDOI: <https://doi.org/10.29121/ijesrt.v9.i10.2020.6>

ABSTRACT

The purpose of this research was to examine the influence of pH and type of precipitating agent on the removal of heavy metal cations from industrial wastewater samples by method of chemical precipitation. Three precipitating agents were used: Na₂CO₃, NaOH and waste sludge from the Solvay process. Samples of industrial wastewater, in which the presence of Cu (II) and Ni (II) was determined, have been taken from the electroplating process, and samples in which the presence of Zn (II) was determined, have been taken from the galvanizing process. The experimental results showed that the highest percentage of removal of these cations was at pH > 7 for each precipitant used, with NaOH proving to be the best precipitating agent, followed by Solway waste sludge and Na₂CO₃.

KEYWORDS: chemical precipitation, pH, precipitation agent, cations, real samples.

1. INTRODUCTION

The pressure on industries for reduction of heavy metals in wastewater is on the rise [1], as heavy metal pollution has become one of the most serious environmental problems today [2]. Any toxic metal may be called heavy metal, irrespective of their atomic mass or density [3]. Their toxicity depends on several factors including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals [4]. Few heavy metals, such as Fe, Zn, Cu, Co, Cr, Mn and Ni, are required in trace amounts for the proper biological metabolism; however, their higher concentrations may have toxic effects on living organisms. Others, such as Pb, Hg, Cd and As, are not suitable for biological functions and are positively toxic [5]. They are usually present in waste waters in dilute quantities (1-100 mg/L) and at neutral or acidic pH values (pH < 7) [6]. In order to reduce the risk of their negative impact on living organisms, it is necessary to remove them from industrial wastewater as much as possible before its disposal. Methods for removing heavy metals include: chemical precipitation, adsorption, ion exchange, membrane filtration, coagulation-flocculation and flotation [7]. Chemical precipitation is one of the commonly employed and conventional processes for heavy metals removal from wastewater [8], and it is used primarily for the removal of metal cations [9]. Precipitation of metals ions is carried out converting them to their insoluble hydroxide, carbonate or sulfide forms, usually by the addition of various precipitating agents like alum, lime, iron salts etc. [10]. The efficiency of the process depends mostly on the initial heavy metal concentration and pH value of water during the treatment, but also on the speed and time of mixing the precipitant-water system. The most common and widely used precipitation method for removal of heavy metal from industrial waste water is through the addition of hydroxide compounds which convert soluble heavy metal ions into insoluble metal hydroxides [11]. The solubility of individual metal hydroxides as a function of pH is shown in Figure 1. For copper, nickel and zinc cations, the formation of insoluble precipitates is in pH ranges: 8.5-9 for Cu (II), 10-10.5 for Ni (II) and 9-9.5

for Zn (II). Theoretical hydroxide precipitation curves normally found in plating baths indicate that there is no ideal pH for a multiple-metal system

[12]. The disadvantage of hydroxide precipitation of metal ions is the large amount of non-dense precipitate as a secondary pollutant which is more difficult to filter. Sodium carbonate, which belongs to the important group of alkaline materials produced by the chemical industry [13], can be used as metal cations precipitant. Carbonate precipitation using Na_2CO_3 takes place at lower pH compared to the hydroxide precipitation, and metal carbonate precipitates are denser than hydroxide precipitates, so they are easier to separate [14]. One of the disadvantages of chemical precipitation methods is the demand for precipitating agents i.e. chemicals, which in the case of high concentrations of heavy metals to be removed, or large amounts of water to be treated, can be significant and cause high process costs. It is therefore important to research the possibilities of using alternative precipitating agents.

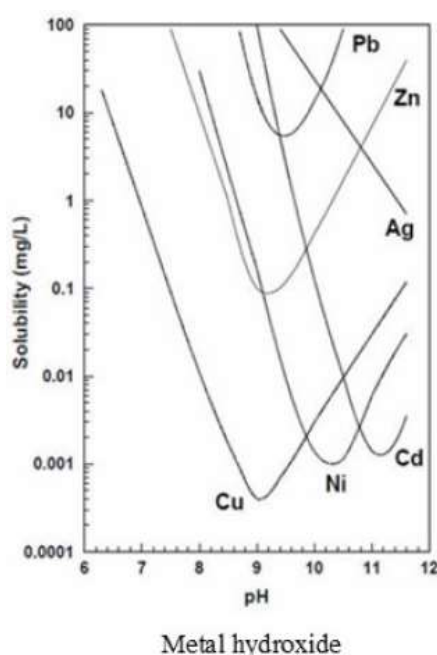


Figure 1. Solubility diagram for metal hydroxides [15]

Although Solvay process for Na_2CO_3 production is economical, yielding a product of high quality [16], these industrial plants produce waste and byproducts that may result in environmental problems [17]. However, the waste sludge from the Solvay process (lime sludge) has high pH value and CaO content, and as such has the potential for precipitation of metal cations in water. In this paper, we compared the effects of different precipitating agents on removal of heavy metal cations, where sodium hydroxide, sodium carbonate and waste sludge of the Solvay process were used as precipitants.

2. MATERIALS AND METHODS

Reagents

The following chemicals were used in this research: standard solution of Cu (II), 1000 mg/L, Merck; standard solution of Ni (II), 1000 mg/L; standard solution of Zn (II) 1000 mg/L, NaOH, min 98%, Neratovice, Czech Republic, Na_2CO_3 , min. 99.30%, Sisekam Soda, Lukavac, waste sludge from Solvay process, Sisekam Soda, Lukavac, HNO_3 , 65%, Neratovice, Czech Republic; demineralized water ($< 1 \mu\text{Scm}^{-1}$).

Industrial samples

In the experimental part, wastewater samples from two industrial plants were used. In the first plant, wastewater was taken from the electroplating process (A- sample), and in the second plant it was taken from the galvanizing

process (B-sample). The initial pH and heavy metal concentration of samples A and B were measured (Table 1) to determine the required concentrations of precipitants. A pH meter GLP 21 CRISON with resolutions of 0.1,

0.01, 0.001 was used to measure the initial pH values, and initial concentrations of heavy metals were determined by method of *atomic absorption spectrometry (AAS)*, using Perkin Elmer Analyst 200 instrument.

Table 1. Initial pH and concentration of heavy metal ions industrial wastewater samples

	A-sample	B-sample
Initial pH (dimensionless)	0.6	6.7
Concentrations of heavy metal cations (mg/L)	Cu(II) = 28.000 Ni(II) = 32.953	Zn(II) = 5.145

Precipitating agents

Table 2. presents the types of precipitating agents and their quantities which were used for the removal of heavy metal ions from industrial waste water samples.

Table 2. Types and dosed quantities of precipitating agents

A-sample	2.5 mol/L NaOH (ml/100 ml sample)	6.50	7.20	7.60	7.80	8.00	9.00
	Na ₂ CO ₃ (g/100 ml sample)	5.00	7.00	10.00	15.00	17.00	30.00
	Waste sludge (g/100 ml sample)	10.00	30.00	40.00	50.00	55.00	60.00
B-sample	0.1 mol/L NaOH (ml/100 ml sample)	1.00	3.00	5.00	7.00	9.00	15.00
	2g/l Na ₂ CO ₃ (ml/100 ml sample)	5.00	10.00	25.00	30.00	50.00	80.00
	Waste sludge (g/100 ml sample)	0.05	0.50	1.00	3.00	6.00	10.00

Sodium hydroxide solutions of concentrations 2.5 mol/L and 0.1 mol/L were prepared for hydroxide precipitation. 2.5 mol/L NaOH solution was used for precipitation of copper- and nickel ions in A-sample, due to very low pH value of the sample, and 0.1 mol/L NaOH was used for precipitation of zinc ions in B-sample. Carbonate precipitation of metal ions in A-sample was performed by adding sodium carbonate in solid form to wastewater samples, while Na₂CO₃ solution of 2 g/L concentration was used for precipitation of zinc ions in B-sample. In earlier experiments, waste sludge from the Solvay process have been prepared and used in solid form as precipitant [18], and that same agent of chemical composition shown in Table 3. was used in this research as precipitating agent.

Table 3. Chemical composition of the lime sludge by XRF method [18]

Chemical species	Content (%)
CaO	58.131
Cl	12.572
Na ₂ O	3.905
SiO ₂	2.558
MgO	2.274
Fe ₂ O ₃	1.433
SO ₃	1.201
Al ₂ O ₃	1.008
P ₂ O ₅	0.082
K ₂ O	0.068

SrO	0.033
MnO	0.025

Precipitation Experiment

Heavy metal precipitation was performed under laboratory conditions by pipetting 100 mL of each wastewater sample into a separate 250 mL glass container, then adding the certain amount of one precipitant to each container followed by solution stirring at rate of 300 rpm. After the mixing time of 5 minutes, separation of the precipitate which were formed by the reaction between heavy metal cations and precipitant was performed by filtration through Whatman® quantitative filter paper, 125 mm in diameter, first through a black ribbon circle and then through a blue ribbon circle. The percentage of removal of cations from wastewater sample was calculated for each heavy metal according to the following formula:

$$Er = \frac{C_0 - C_1}{C_0} \cdot 100 \quad (i)$$

where Er (%) is the removal efficiency, C_0 (mg/L) the initial concentration of heavy metal in nontreated sample and C_1 (mg/L) the final concentration of heavy metal after precipitation and filtration of the sample.

3. RESULTS AND DISCUSSION

In all experiments conducted in this research, increasing the doses of precipitants in the samples led to an increase in the pH of the media, which resulted in the formation of metal precipitates and their more efficient removal from the treated samples. The effects of pH changes on the heavy metal removal efficiency for all precipitants used are presented in Figures 2-4 for Cu (II) and Ni (II) and Figures 5-7 for Zn (II). The removal efficiency of metal ions from the A-sample using 2.5 mol/L NaOH as a precipitating agent is shown in Figure 2. A significant increase in the removal efficiency of Cu (II) was obtained at $pH > 6$, while Ni (II) required higher pH values, i.e. $pH > 8$, which may be explained by the differences in solubility of their hydroxides, shown in Figure 1. The removal efficiency of Ni (II) was relatively low at $pH < 7$, while a significant increase was observed at $pH > 7$. This is similar to the results of hydroxide precipitation of nickel, obtained by Escudero *et al.* [19] by increasing the pH of the medium, where significantly smaller amounts of precipitated Ni were in the pH range of 3-7, compared to those in the pH range of 9-13.

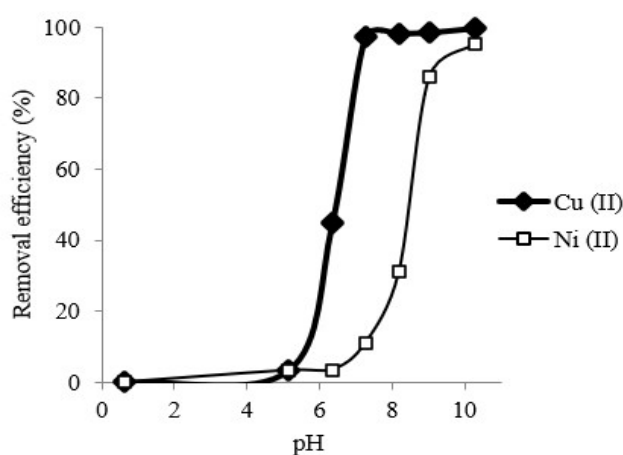


Figure 2. Influence of pH on the removal efficiency of Cu (II) and Ni (II) using 2.5 mol/L NaOH as a precipitating agent

By increasing the pH of the sample above 9, the differences in Er values between copper and nickel were less; at pH 10.3, Er was 99.821% for Cu (II) and 95.256% for Ni (II). This may also be related to the differences between their solubilities in Figure 1, which are less in the pH range of 9-10.

Overall, the efficiency of metal ion removal by chemical precipitation from the A-sample was higher for copper than for nickel. In the research of heavy metal removal from plating process industrial raw effluent, conducted

by Zainnudin *et al.* [20], hydroxide precipitation also provided a higher percentage of copper removal than nickel, although the initial concentration of Cu (II) in the treated sample was higher.

Influence of pH on the removal efficiency of Cu (II) and Ni (II) from A-sample using solid Na₂CO₃ as a precipitating agent is shown in Figure 3.

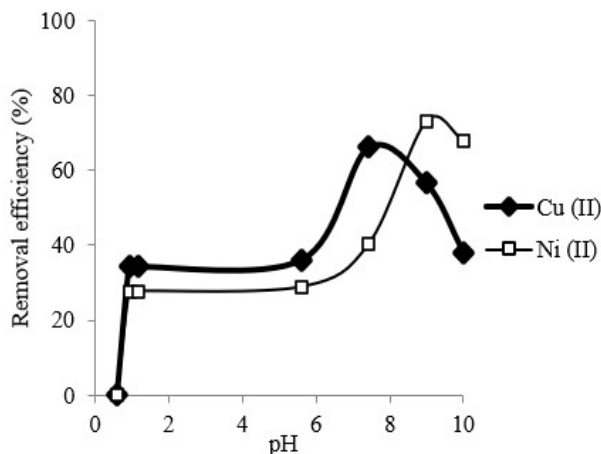


Figure 3. Influence of pH on the removal efficiency of Cu (II) and Ni (II) using solid Na₂CO₃ as a precipitating agent

The use of sodium carbonate resulted in a higher percentage of removal of copper and nickel from the A-sample at lower pH values (pH <6) than when NaOH was used. This advantage of Na₂CO₃ over NaOH, as well as other advantages including better characteristics of obtained precipitates and sludges, have been reported [21; 22]. The maximum Er value for Cu (II) was achieved at pH 7.43 (66.125%), and for Ni (II) at pH 9 (73.061%). By further increasing the pH value of treated sample, the efficiency of removal continuously decreased for both copper and nickel. Junuzović *et al.* found that the highest percentage of Cu (II) removal from a solution which contained Cu (II) and Ni (II) of initial concentrations of 500 mg/L, obtained at approximate pH 7 [23]. Negrea *et al.* found that the optimum pH value for the removal of Cu (II) from the waste waters using Na₂CO₃ is pH 7 [24].

Figure 4. shows the results obtained by using waste sludge from the Solvay process, as a precipitating agent for the removal of Cu (II) and Ni (II) from A-sample. The sludge used has a unique chemical composition dominated by the calcium fraction presented in Table 3 in the form of CaO. This gives the sludge alkaline properties, similar to those of lime sludges, and therefore the possibility of acting as a precipitating agent.

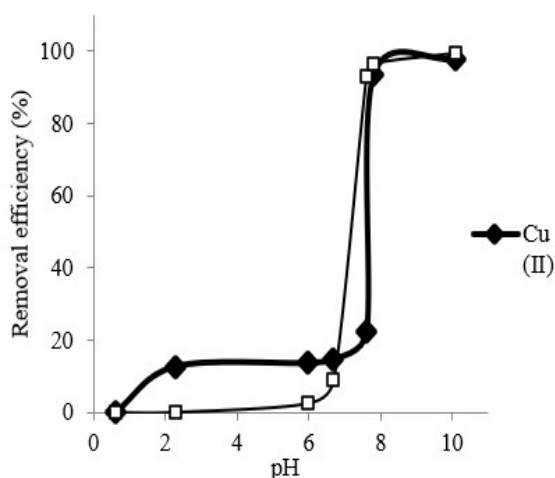


Figure 4. Influence of pH on the removal efficiency of Cu (II) and Ni (II) using waste sludge as a precipitating agent

At $\text{pH} < 7$, the removal efficiency for both copper and nickel was similar to that of carbonate. Although the sludge used has a unique chemical composition dominated by the calcium fraction presented in Table 3 in the form of CaO . This gives the sludge alkaline properties and the ability to act as a neutralizing and precipitating agent. Other

researches have confirmed the possibility of using waste sludge with a high CaCO_3 content, either to neutralize wastewater, or to remove heavy metals [25; 26; 27]. The experimental results showed lower percentage of removal for both copper and nickel at $\text{pH} < 7$, compared to the results obtained using NaOH and Na_2CO_3 . The largest increase in the removal of Cu (II) and Ni (II) was observed in the pH range 6.69-7.8, and maximum Er values for copper (97.796%) and Ni (99.342%) were obtained at pH 10.08. Compared to the results of maximum removal efficiency using the other two precipitants, the effects of waste sludge on precipitation in A-sample were similar to those of NaOH , although the Er values were comparatively lower.

The removal efficiency of Zn(II) from the B-sample using 0.1 mol/L NaOH as a precipitating agent is shown in Figure 5. Increasing the dose of precipitant in the treated sample had a positive effect on the efficiency of zinc removal. At pH of 9.35, the highest removal of zinc was achieved (100%). This is in agreement with findings of Pang *et al.*, who have used hydroxide precipitation method with NaOH to treat synthetic wastewater samples of various Zn (II) concentrations, ranging from 5 to 90 mg/L and determined minimum solubility of Zn (II) that falls in the pH range of 8.7 to 9.6 for each Zn (II) concentration [28]. Junuzović *et al.* have performed hydroxide precipitation using 0,1 mol/L NaOH to remove zinc from its synthetic aqueous solution of initial concentration 50 mg/L Zn (II) , and obtained maximum removal efficiency at higher pH (10.83) [29].

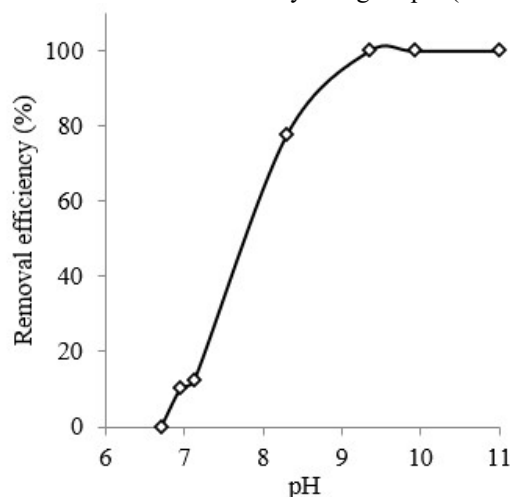


Figure 5. Influence of pH and NaOH on the removal efficiency of Zn (II)

The efficiency of carbonate precipitation using Na_2CO_3 (g/L) as a precipitation agent for the removal of Zn (II) from B-sample is shown in (Figure 6.).

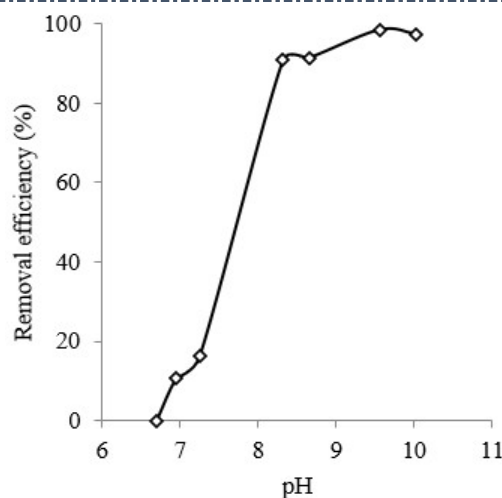


Figure 6. Influence of pH and Na_2CO_3 on the removal efficiency of Zn (II)

The addition of Na_2CO_3 gradually increased the pH of the solution as well as the percentages of Zn (II) removal. The highest percentage of Zn (II) removal (98.483%) was achieved at pH 9.55. Although the use of sodium carbonate as a precipitation agent, the highest efficiency of Zn (II) removal was obtained at a similar pH value as with the use of NaOH precipitant, the percentage of removal was slightly lower. Selimović *et al.* have performed carbonate precipitation with Na_2CO_3 as a precipitant to remove zinc from its synthetic aqueous solution of initial concentration 50 mg/L Zn (II), and obtained maximum removal efficiency of 100% at pH of 9.16 [30]. Lupa *et al.* have used NaOH 30% and Na_2CO_3 10% for zinc removal and observed that while increasing the amount of Na_2CO_3 in solution increases pH and degree of precipitates forming and removal, in the case of NaOH increase take place the redissolving of these [31].

Figure 7. shows the results obtained by using waste sludge from the Solvay process, as a precipitation agent to remove Zn (II) from B-sample. The largest increase in the removal of zinc was observed in the pH range 7.1-7.92, and maximum Er value (93.586 %) was obtained at pH 9.66. However, compared to the results of maximum removal efficiency using the other two precipitants, the efficiency of Zn (II) precipitation and removal using waste sludge was lower.

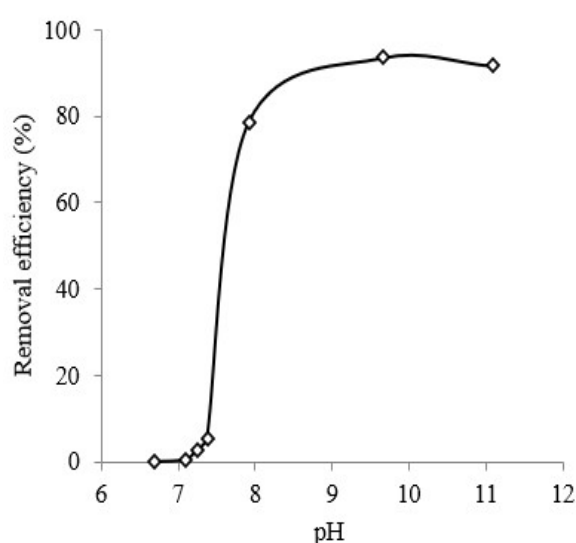


Figure 7. Influence of pH and waste sludge from Solvay process on the removal efficiency of Zn (II)

4. CONCLUSION

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[59]



The results of the present research confirmed the possibility of using sodium hydroxide, sodium carbonate, as well as waste industrial sludge of high calcium fraction, as precipitation agents in industrial wastewater treatment processes for the removal of heavy metal ions. At pH>7, the most efficient precipitant for removing copper and nickel from waste water was NaOH, followed by waste sludge, while at pH <5.5 sodium carbonate was more efficient than other precipitants. Overall efficiency of precipitants was higher at Cu(II) removal; however, in alkaline solutions, sodium carbonate and waste sludge showed higher efficiency for removing Ni(II) than of Cu (II). Sodium hydroxide has also been shown to be more effective in removing Zn (II) from wastewater. Significant efficiency of copper and nickel removal from their binary systems, as well as removal of zinc from monocomponent aqueous solutions, can be achieved only at pH> 8.

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