

Efficiency of Carbonate Precipitation and Removal of Copper and Nickel Ions from their Monocomponent and Two-component Aqueous Solutions

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ABSTRACT

The effect of pH and initial concentration on the removal of Cu(II) and Ni(II) ions from their monocomponent and two-component aqueous solutions using Na₂CO₃ as a chemical precipitation agent was investigated in this paper. Monocomponent aqueous solutions of Cu(II) and Ni(II) ions with their initial concentrations of 50 and 500 mg/L and two-component aqueous solution with initial concentration of 500 mg/L were prepared. The precipitation was carried out by batch method at room temperature by stirring the solution at 300 rpm for 5 minutes, resulting in the formation of precipitates. The resulting precipitate was separated by filtration from the solution. The experiment proved that Na₂CO₃ is a good agent for removing Cu(II) and Ni(II) ions from their monocomponent water solutions of 50 and 500 mg/L concentration and two-component water solution with initial concentration of each metal 500 mg/L. The percentage of Cu(II) removal was higher at lower pH values compared to Ni(II) removal.

Keywords-- carbonate precipitation, water treatment, Na₂CO₃, copper, nickel

I. INTRODUCTION

Water is an essential nutrient required for life [1]. However, increasing human development, industrialization and population growth have exerted alarming and diverse pressures on the quality, quantity and access to water resources [2]. Traditionally, microbiological quality of drinking water has been the main concern, but over the last decades the attention of the general public and health officials on the importance of chemical quality and the threat of chemical pollutants

have increased with the increase of our knowledge on the hazards of chemical substances [3].

The chemical contaminants represent the most dangerous types of contaminants found in the water for many reasons, they are non-biodegradable environmentally and their high toxicity at very low concentrations in addition to the cumulative impact in the bodies of living organisms [4]. Whereas, heavy metals in wastewater cause special concern in recent times due to their recalcitrance and persistence in the environment [5].

The term of heavy metals is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity [6]. The most common heavy metals found in wastewaters are lead, copper, nickel, cadmium, zinc, mercury, arsenic, and chromium [7].

Wastewater containing copper and nickel can be produced by several industries [8], agriculture, mining and metallurgical processes, and runoffs also lead to the release of pollutants to different environmental compartments [9].

The only way to find the new water resource is the reuse of treated wastewater [10]. Nowadays different methods have been developed for removing heavy metals such as copper and nickel from water and wastewater. These technologies include membrane filtration, ion-exchange, adsorption, chemical precipitation, nanotechnology treatments, electrochemical and advanced oxidation processes [11]. Chemical precipitation is most applicable among these technologies and considered to be the most economical [12]. This method implies the change in form of materials dissolved in water into solid particles [13]. The particles

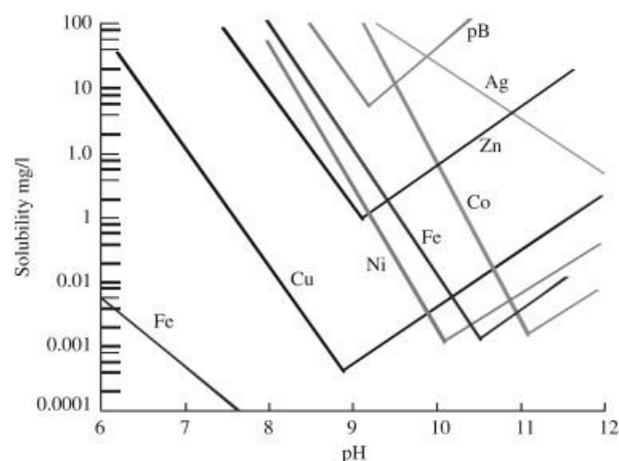
can then be aggregated by chemical coagulation and removed by filtration or sedimentation [14]. It is used primarily for the removal of metal cations with positive and negative charge but also for removal of anions such as fluoride, cyanide, and phosphate, as well as organic molecules [15]. A typical chemical precipitation method involves four stages: addition of reagents, adjustment of pH to form the precipitate, flocculation, sedimentation and solid-liquid separation [16]. Chemical precipitation includes hydroxide precipitation, sulfide precipitation and carbonate precipitation.

Hydroxide precipitation which provides removing heavy metals by adding an alkali, such as caustic or lime, to adjust the wastewater pH to the point where the metal exhibit its minimum solubility [17]. The process operates at ambient conditions and its operation is easy and suited to automatic control. The most important advantage of the process is its low cost [18].

Sulphide precipitation is a fast, easy and environmentally friendly method which provides to work in wide pH ranges and to reuse/recycle them in metal smelting processes [19].

Carbonate precipitation using Na_2CO_3 is low-cost technique that could remove heavy metals in a simple manner. The great variability with respect to geological setting, climatic environment, water chemistry, and biological activity limits generalizations about mechanisms of carbonate sedimentation [20]. This method was investigated because optimum treatment occurs at less pH values and sludges are reported to have good filtration characteristics [21]. As every technology, these processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge [22].

The optimum pH for metal removal correspondes to pH values predicted by the theoretical metal hydroxide solubility diagram. The solubility of metal hydroxides, depending on the pH, is shown in Figure 1.



Experimentally determined solubilities of metal hydroxides
Figure 1: Solubility of metal hydroxides [23]

II. EXPERIMENTAL PART

The aim of this study was to investigate the influence of the initial concentration of Cu(II) and Ni(II) ions and pH of water medium on removal of these heavy metals from their monocomponent and two-component aqueous solutions using a carbonate precipitation agent, Na_2CO_3 .

2.1. Materials

In experiment were used chemicals of analytical grade: copper(II) nitrate trihydrate (Pliva, Zagreb, Croatia); nickel nitrate hexahydrate (Semikem, Sarajevo, Bosnia and Herzegovina); copper standard solution, 1000 mg/L Cu(II) in 0.5 M nitric acid (from $\text{Cu}(\text{NO}_3)_2$) and nickel standard solution 1000 mg/L, Ni(II) in 0.5 M nitric acid (from $\text{Zn}(\text{NO}_3)_2$) from Merck; nitric acid, min. 65% (Lach-Ner, Czech Republic); sodium carbonate (Sisecam Soda Lukavac, min. 99,30%).

The laboratory glassware (laboratory glasses, pipettes, funnels) were first washed with detergent, then washed with water and immersed in nitric acid solution. Finally, they were washed with demineralised water and allowed to dry naturally at room temperature.

2.2. Preparation of precipitant and metal ion aqueous solutions

Na_2CO_3 of concentration 2 g/L was used as the precipitation agent (precipitant). The solution of precipitant was prepared with demineralised water and then homogenized. Monocomponent solutions of copper (Cu(II)) and nickel (Ni(II)) of two different initial concentrations (50 mg/L and 500 mg/L) were also prepared, as well as the two-component aqueous solution where initial concentration of of each metal (Cu(II) and Ni(II)) was 500 mg/L. All aqueous solutions of metals were prepared with demineralized water and homogenized thereafter. After that, the initial pH value of each prepared solution was measured.

2.2. Precipitation experiment

Carbonate precipitation was used as a method to remove heavy metal ions of Cu(II) and Ni(II) from water. An appropriate volume of precipitation agent was added to each mono-component and two-component water solution of metals and a change in pH was monitored. Volumes of Na_2CO_3 used in the experiment are given in Table 1.

Table (1): Volumes of Na_2CO_3 added to monocomponent and two-component aqueous solutions of Cu(II) i Ni(II)

Monocomponent solutions of heavy metals	Volumes of 2 g/L Na_2CO_3 (mL)				
	1,00	7,00	8,50	10,00	20,00
50 mgCu(II)/L	1,00	7,00	8,50	10,00	20,00
500 mgCu(II)/L	10,00	65,00	70,00	80,00	100,00
50 mgNi(II)/L	0,15	1,00	5,00	10,00	20,00

500 mgNi(II)/L	0,20 0	1,00	10,0 0	70,0 0	100,0 0
Two- component solutions of heavy metals					
500 mgCu(II)/L 500 mgNi(II)/L	1,00	10,0 0	20,0 0	50,0 0	100,0 0

The carbonate precipitation process was carried out by pipetting 100 mL of heavy metal water solution into a 250 mL laboratory beaker. An appropriate amount of precipitant was added to the solution, and the solution was stirred at 300 rpm for 5 minutes. After stirring, the pH of the solution was measured by direct potentiometry. Separation of the precipitate was performed by filtering through Whatman® quantitative filter papers 125 mm in diameter, first through a black ribbon circle and then through a blue ribbon circle. All samples were stored in polyethylene bottles until measured on flame atomic absorption spectrometry.

Efficiency of carbonate precipitation and removal of Cu(II) and Ni(II) ions from their monocomponent and two-component aqueous solutions was determined by chemical analysis of heavy metal content in samples before and after the treatment with Na₂CO₃ and filtration of samples.

Atomic absorption spectrometry is an analytical technique that measures the concentrations of elements. Flame atomic absorption spectrometry (FAAS) still keeps its importance despite the relatively low sensitivity; because it is a simple and economical technique for determination of metals [24]. A series of standard solutions was prepared for each metal. Obtained equations of calibration curves were $y = 0,1963x - 0,012$, $R^2 = 0,9986$ for copper and $y = 0,043x + 0,0482$, $R^2 = 0,9951$ for nickel.

The following equation was used for calculation of removal efficiency:

$$Er = \frac{C_0 - C_1}{C_0} \cdot 100$$

Where Er (%) is the removal efficiency, C₀ (mg/L) is the initial concentration of heavy metal in untreated sample and C₁ (mg/L) is the final concentration of heavy metal, after precipitation and filtration of the sample. The removal efficiency for both monocomponent (concentrations 50 mg/L and 500 mg/L) and two-component (concentration 500 mg/L) solutions was calculated.

III. RESULTS AND DISCUSSION

In this work, Na₂CO₃ of concentration 2 g/L, was used as a precipitating agent for removal of copper

and nickel from their monocomponent and two-component aqueous solutions.

The efficiency results of removal of Cu(II) and Ni(II) ions from their monocomponent aqueous solutions of initial concentrations 500 mg/L are presented in Figure 2. At initial pH of water solution of copper (4.0) only the soluble form of Cu(II) was present. Addition of the carbonate precipitant resulted in the formation of precipitates in the form of sludge and a high removal rate (96.381%) at a pH of 5.66. Increasing the amount of added precipitant further increased the pH of the solution as well as the removal rates. The highest percentage of Cu(II) removal was 99.939% and was obtained at pH 9.36. A higher pH value than the above achieved a slightly lower percentage of removal (99.899%), which can be explained by the re-dissolution of the precipitates, in accordance with the theoretical diagram of the solubility of copper hydroxide.

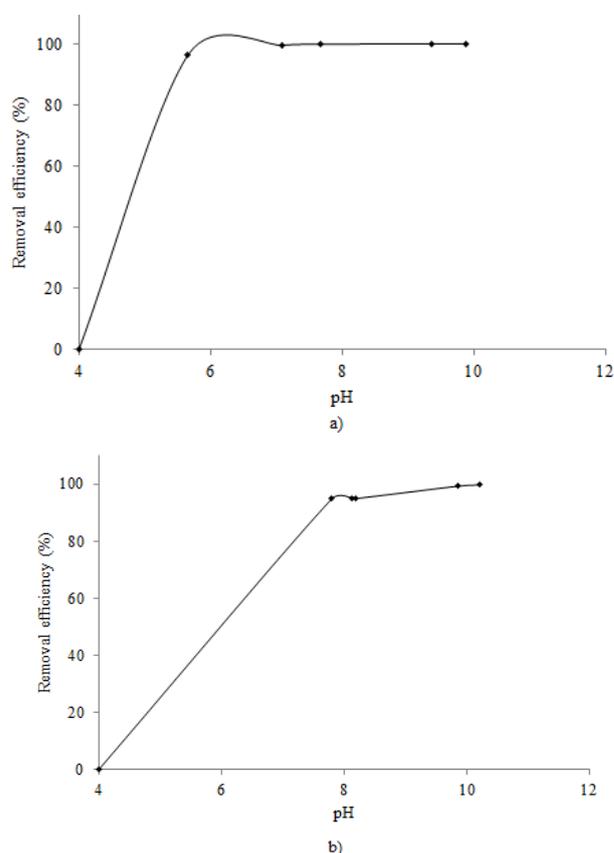


Figure 2: Effect of pH on the efficiency of removing a) Cu(II) and b) Ni(II) from their monocomponent aqueous solutions of initial concentrations 500 mg/L

By the process of precipitation of Ni(II) from its aqueous solution of an initial concentration of 500 mg/L using Na₂CO₃, already at a pH of 7.80 a percentage of 94.843% removed Ni(II) was achieved. Compared to Cu(II), a lower percentage of removal was observed for Ni(II) at the same initial concentration. Although a further increase in the pH of the aqueous solution

gradually increased the percentage of Ni(II) removal, the maximum removal percentage (99.741%) was lower than the percentage of Cu(II) removal and was achieved at higher pH of the solution (10.22) compared to the pH of the aqueous Cu(II) solution.

The efficiency of removing the Cu(II) and Ni(II) ions from their monocomponent aqueous solutions of initial concentrations 50 mg/L is shown in Figure 3. The complete removal of Cu(II) using Na₂CO₃ was achieved at a pH of the solution from 7.32 to 9.50. A further increase in the added precipitant and the pH of the solution resulted in an increase in the residual concentration. This can be due to the fact that the precipitate re-dissolves [25a]. In the case of removal of Ni(II) from its aqueous solution of 50 mg/L initial concentration, a lower removal rate (68.558%) was achieved at a solution pH of 8.22 compared to that which was achieved at same pH values in the case of Ni(II) initial concentration of 500 mg/L.

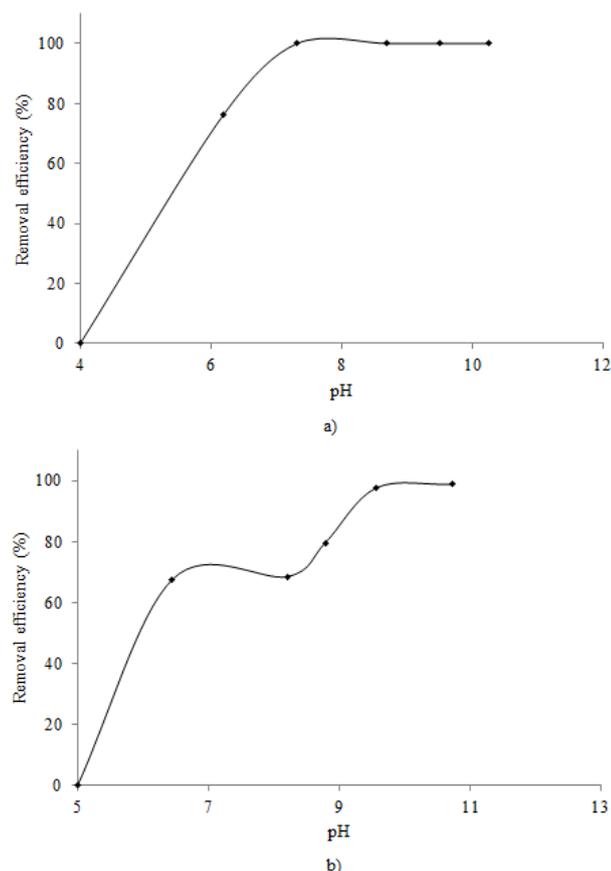


Figure 3: Effect of pH on the efficiency of removing a) Cu(II) and b) Ni(II) from their monocomponent aqueous solutions of initial concentrations 50 mg/L

A further increase in the pH of the solution continued a slight increase in the percentage of removal, which at pH 10.73 was 99.830%. Compared with the Cu(II) removal process of the same initial concentration, the removal of Ni(II) using Na₂CO₃ gave poorer results.

In the process of removing Cu(II) and Ni(II) from their two-component aqueous solutions in which the initial concentrations of both metals were 500 mg/L (Figure 4), both metals showed the same precipitation kinetics, with the efficiency of Cu(II) removed being slightly higher than Ni(II).

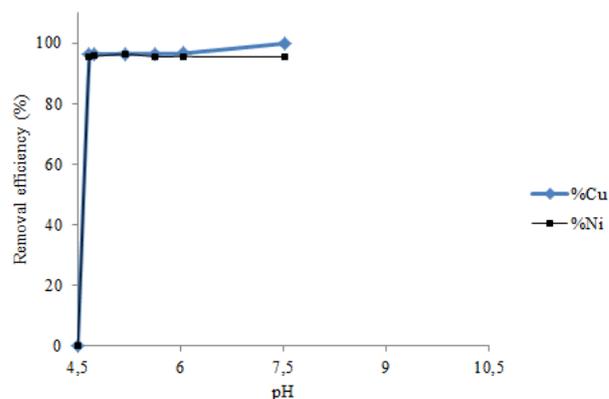


Figure 4: Effect of pH on the efficiency of removing Cu(II) and Ni(II) from their two-component aqueous solutions of initial concentrations 500 mg/L

The highest percentage of Cu(II) removal was 99.918% and was at an approximate pH of 7, which confirms the fact that the residual Cu(II) ion concentration decreases by increasing the pH to 7 [25b]. The highest percentage of Ni(II) removed from the two-component aqueous solution was 96,229%, which was lower than that of Cu(II) and was achieved at a lower pH. Most process wastewaters contain mixed metals and so precipitating these different metals as hydroxides can be a tricky process [26].

V. CONCLUSION

In this work, carbonate precipitation was used to remove Cu(II) and Ni(II) ions from their monocomponent and two-component different initial solution concentrations, which implies the use of Na₂CO₃ as the precipitation agent. Carbonate precipitation involves the addition of a precipitate in different volumes to a solution containing heavy metal ions at a pH value at which insoluble products are formed and which can be easily separated by filtration. Na₂CO₃ has proven to be a good precipitating agent for the removal of Cu(II) and Ni(II) ions from their monocomponent solutions of concentrations 50 and 500 mg/L and two-component solutions of concentration 500 mg/L. Complete removal of Cu(II) ions was achieved at its initial concentration of 50 mg/L in the pH range from 7.32 to 9.50. An even better percentage of Cu(II) ion removal was achieved at its initial concentration of 500 mg/L over the same Ni(II) ion concentration. Removal of Cu(II) ions from a two-component solution containing Cu(II) and Ni(II) ions gave better results and was achieved at a lower pH than Ni(II) ions.

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