Chemical Precipitation of Cations from Aqueous Solutions using Waste Sludge from the Solway Process as a Potential Agent

Halid Junuzović1, Amra Selimović2, Sabina Begić3, Abdel Đozić4, Ramzija Cvrk5, Melisa Ahmetović6 and Hurija Alibašić7

1Sen. Asst., Department of Analytical Chemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
2Asst. Prof. Dr., Department of Analytical Chemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
3Assoc. Prof. Dr., Department of Analytical Chemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
4Assoc. Prof. Dr., Department of Environmental Engineering, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
5Assoc. Prof. Dr., Department of Food Technology, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
6Sen. Asst., Department of Physical chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA
7Asst., Department of Food Technology, Faculty of Technology, University of Tuzla, BOSNIA & HERZEGOVINA

ABSTRACT

Chemical precipitation is a useful conventional process to remove heavy metals from aqueous solutions. In this work, a waste sludge from the Solway process was used as a precipitation agent for the precipitation of Cu (II), Ni (II), Pb (II) and Zn (II) ions with an initial concentration of 50 mg/L. The results of the research showed that the waste sludge from the Solway process completely removed Pb (II) ions from the solution in the pH range of 8.39 -11.74, also good efficiency was shown in other cations. The maximum precipitation efficiency for Cu (II) is 99.890% at pH 10.98, Ni (II) 99.940% at pH 11.81, Zn (II) 99.616% at 10.1. Waste sludge is proved to be a good precipitate for cation separation.

Keywords: chemical precipitation, heavy metals, waste sludge

I. INTRODUCTION

Water occupies about 71% of the earth’s surface and yet it is one of the scarcest commodities especially in the developing countries of the world [1]. Water pollution occurs when pollutants are discharged directly or indirectly into the water bodies without adequate treatment to remove the harmful compounds [2]. The serious challenges of today are water shortage and pollution for many countries [3]. Due to the development of urbanization and industrialization, the problem of heavy metal pollution has become a serious environmental problem [4]. Since heavy metals are nonbiodegradable, they accumulate in the environment and subsequently contaminate the food chain of humany cause various diseseases [5] [6]. Some of the main negative effects of water pollution according to Wang & Yang remain a major source of morbidity and mortality in China [7]. Some other researchers have proven that exposure to heavy metals during critical periods of development can influence changes in embryo and germline of the offspring; and later on affect the disease susceptibility in adults [8]. The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel and zinc, all of which cause risks for human health and the environment [9]. The chemical industry is a major source of various pollution accidents [10]. Examples of sources of environmental pollution by heavy metals include mining operations, refining ores, sludge disposal, fly ash from incinerators, the processing of radioactive materials, metal plating, or the manufacture of electrical equipment, paints, alloys, batteries, pesticides or preservatives, automobiles [11].

With the development of researches, the treatments of waste water have reached a certain level [12]. Removal of heavy metals from industrial waste waters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations [13].

One of the most simplest process for removing heavy metals from waste water is chemical precipitation. Chemical precipitation is used to remove ionic constituents from water by the addition of counter-ions to reduce the solubility. It is used primarily for the removal of metallic cations, but also for removal of anions such as fluoride, cyanide, and phosphate, as well as organic molecules such as the precipitation of phenols and aromatic amines by enzymes and detergents and oily...
emulsions by barium chloride [14]. Generally speaking, precipitation is a method of causing contaminants that are either dissolved or suspended in solution to settle out of solution as a solid precipitate, which can then be filtered, centrifuged, or otherwise separated from the liquid portion [15]. Adjustment of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation [16]. Chemical precipitation processes can also process very toxic waste waters [17]. However, these methods have several disadvantages such as unpredictable metal ion removal, high reagent requirement, generation of toxic sludge, etc [18]. There are three types of chemical precipitation which include hydroxide, carbonate and sulfide. Of all the treatment techniques, heavy metal hydroxide precipitation is the most commonly employed because of its low-cost and simplicity [19]. The optimum pH for removal of most of heavy metals from CMDW by the chemical precipitation using sodium hydroxide was 8 except for Ca, Sr and B (pH 10 or higher) [20].

Figure 1 shows theoretical solubility of metal hydroxides vs. pH. It can be seen from the figure that the optimal pH is to achieve the minimum solubility for Cu (II) in the range of 8, 5-9, pH 10-10.5 for Ni (II), pH 9.5-10 for Pb (II) and pH 9-9.5 for Zn (II).

In this paper, the aim was to examine the influence of the added precipitate and the pH value of the solution on the efficiency of metal ion precipitation from aqueous solutions with an initial concentration of 50 mg/L. Waste sludge from the soda factory in Bosnia and Herzegovina was used as a precipitation agent. Previous research has been done using this precipitating agent, and in this paper they have continued.

The Table 1 shows the results of the analysis of the elemental chemical composition of the precipitate using the method of X-ray fluorescence spectrometry.

![Figure 1: Theoretical solubility of metal hydroxides vs. pH [21].](image)

| Chemical species | Content (%) |
|------------------|-------------|
| CaO              | 58,131      |
| Cl               | 12,572      |
| Na₂O             | 3,905       |
| SiO₂             | 2,558       |
| MgO              | 2,274       |

Table 1: Results of the chemical composition analysis of the precipitant by XRF method [22]
II. EXPERIMENTAL PART

2.1. Materials

In this study were used the following chemicals: nitrite salts for the preparation of metal solutions with a concentration of 50 mg/L of Cu(NO$_3$)$_2$ · 3H$_2$O, Ni(NO$_3$)$_2$ · 6H$_2$O, Pb(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ · 6H$_2$O; standard solution of copper, 1000 mg/L Cu in 0.5 mol/L nitric acid (from Cu(NO$_3$)$_2$); standard solution of nickel, 1000 mg/L Ni in 0.5 mol/L nitric acid (from Ni(NO$_3$)$_2$); standard solution of lead, 1000 mg/L Pb in 0.5 mol/L nitric acid (from Pb(NO$_3$)$_2$); standard solution of zinc, 1000 mg/L Zn in 0.5 mol/L nitric acid (from Zn(NO$_3$)$_2$); HNO$_3$ 65%; demineralized water (< 1 µS cm$^{-1}$).

The chemical composition of the precipitate is presented in Table 1. The precipitate was first dried at room temperature for several days in a thin film, then ground to a granulation of 0.01-0.25 mm and dried at 105 °C.

2.2. Precipitation experiment

Metal solutions with an initial concentration of 50 mg/L were prepared by dissolving nitrate salts for each individual metal with demineralized water in 1 liter volumetric flasks. Then, 100 ml of the metal solution was pipetted into a 250 ml beaker, an appropriate dose of precipitate was added, and the solution was stirred for 5 minutes at 300 rpm. After mixing the solution with the magnetic core, the pH was measured. pH meter model GLP 21 CRISON was used for measured. The solution was then filtered through filter paper. Filtrate samples were stored until measurement on FAAS in polyethylene volumetric flasks. The measurement was performed on the FAAS model Perkin Elmer Analyst 200 instrument.

The precipitation efficiency using sludge from the soda plant was calculated as follows:

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

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

III. RESULTS AND DISCUSSION

The efficiency of metal ion precipitation from aqueous solutions using waste sludge as a precipitation agent is shown in Figures 2-9.
Figure 2: Precipitation efficiency of Cu (II) initial concentration 50 mg/L depending on the mass of the precipitate

For the precipitation of Cu (II) ions from an aqueous solution with an initial concentration of 50 mg/L and a pH of 5.03, it was necessary to add 0.05 g/L of precipitating agent to achieve a removal rate of 67.394% (Figure 2). By adding a precipitate dose of 0.4 g/L, the removal percentage achieved was 89.582% and the pH was 7.01. The highest efficiency of Cu (II) ion precipitation from the aqueous solution was achieved before the pH value of 10.98 and was 99.890% (Figure 3). A further increase in the pH and dose of the added precipitate leads to a decrease in the precipitation efficiency. Thus, at a pH value of 12.34, the percentage of removal of Cu (II) ions was 99.589%, which is in accordance with the solubility diagram of metal hydroxides.

Figure 3: Precipitation efficiency of Cu (II) initial concentration 50 mg/L depending on the pH
The percentage of removal of Ni (II) ions from the aqueous solution at an initial concentration of 50 mg/L was 72.914% at a pH of 8.31 (Figure 4). Increasing the pH to 8.48 leads to a significant increase in the percentage of removal of Ni (II) ions. By further increasing the dose of the precipitate, the efficiency of removal of Ni (II) ions was increased and the pH value of the solution was increased. The highest removal percentage was 99.940% at a pH of 11.81 and a dose of added precipitate of 10 g/L (Figure 5).
The efficiency of precipitation of Pb (II) ions with an initial concentration of 50 mg/L from an aqueous solution by the addition of a precipitate achieved a removal percentage of 92.434% at the lowest dose of 0.08 g/L (Figure 6.), while the pH value of the solution was 6.32.

(Figure 7.). Further addition of the precipitate (0.2-10 g/L) achieved maximum removal of Pb (II) ions from the aqueous solution in the pH range of 8.39 to 11.74. In relation to the percentage of removal of Ni (II) ions which was 72.914% at the same dose of precipitate of 0.2 g/L in Pb (II) ions, the maximum percentage of removal was achieved and it was 100%. To further increase the pH of the solution to 11.93, it was necessary to add 20 g/L of precipitate, reducing the removal efficiency of Pb (II) ions (99.446%). Kavak has shown the maximum Pb (II) removal efficiency by chemical precipitation obtained at the optimum conditions was 99.42% [23].

Junuzović et al. investigated removal efficiency of Pb (II) in binary system Pb-Zn where highest achieved percentage of metal removal was 99.844% for Pb (II) and 99.849% for Zn (II), where the pH value of the treated solution was 10.64 [24].
The efficiency of precipitation of Zn (II) ions with an initial concentration of 50 mg/L from an aqueous solution by the addition of a precipitate achieved a removal percentage of 93.956% at the lowest dose of 0.1 g/L (Figure 8), while the pH value of the solution was 6.17 (Figure 9). By further increasing the dose of precipitate and the pH of the aqueous solution, maximum removal of Zn(II) was not achieved as was the case with Pb (II) ions. At a pH value of 10.1, the precipitation efficiency was the highest and amounted to 99.616% with the added amount of precipitate even 10 times higher than the initial added dose. Increasing the pH value and the dose of the precipitate shows a decrease in the efficiency of precipitation of Zn (II) ions, which is in accordance with the diagram for the solubility of metal hydroxides.

IV. CONCLUSION
Based on the obtained experimental results, the waste sludge from the Solway process can be used as an alternative means for cation precipitation from aqueous solutions, which was shown by this research as well as the research done so far.

The percentage of removal of Pb (II) ions was in the pH range from 8.39 to 11.74 and was 100%, while for the other four metals it was lower. The lowest removal percentage was for Zn (II) 99.616% at pH 10.1, while for Cu (II) it was 99.890% at pH 10.98, and slightly higher for Ni (II) 99.940% at pH 11.81.

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