Precipitation and Separation Cations from Binary Aqueous Systems using Waste Sludge from the Solway Process

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ABSTRACT
In addition to soda, the Solway production process yields large amounts of waste sludge that contains a high percentage of CaCO3 and Ca(OH)2. In this paper, solid waste sludge from a soda factory in Bosnia and Herzegovina of a certain granulation was used to remove metal ions from the binary system initial concentrations of 500 mg/L. The research results showed that the precipitation efficiency for the binary system Cu - Ni was 99.810% at a pH of 11.42 for Cu2+ and 99.889% for Ni2+ at a pH of 10.86, while for the binary system Pb - Zn it was 99.84% at the same pH value of 10.64. This research has shown that it is very difficult to separate and remove metal precipitation from binary systems because the optimal pH for one metal does not correspond to another metal.

Keywords: Heavy Metals, Precipitation, Waste Sludge, Solway Process

I. INTRODUCTION
Pollution is considered as one of the most serious problems that faces human societies in the whole world especially in the developing countries. Though produced by man himself and his activities, it has deleterious effects on human’s environments and resources [1]. Water pollution occurs when pollutants are discharged directly or indirectly into the water bodies without adequate treatment to remove the harmful compounds [2]. Pollution of surface water has increased due to the industrial effluents, waste municipal and agricultural drainage water that discharge directly into it [3]. There are numbers of water pollutant which has been categorized into inorganic pollutants, organic pollutants, pathogens, thermal pollution, and radioactive pollutants etc [4]. Inorganic pollutants are released into the environment due to activities of mining, industry, transportation and urban activities [5]. Thus inorganic pollutants include heavy metals and metalloids. As evidenced by catastrophic cadmium and mercury poisonings in Japan, heavy metals belong to the most toxic environmental pollutants [6]. Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and bioaccumulative nature [7]. Generally heavy metals refers to the elements such as Cd (cadmium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead), and Zn (zinc) and etc. Despite natural existence, various anthropomorphic sources have contributed to an unusually high concentration of heavy metals in the environment [8]. Heavy metals are also considered as trace elements because of their presence in trace concentrations (ppb range to less than 10 mg/L) in various environmental matrices [9]. Metal toxicity depends upon the absorbed dose, the route of exposure and duration of exposure, i.e. acute or chronic [10].

In the last few decades, several methods have been developed and extensively investigated for heavy metal removal [11]. These methods are including such unit operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations [12]. Chemical precipitation refers to reacting dissolved metals with precipitant of some sort so that the metals to be removed are rendered insoluble, so that they can then be separated from the water. Raising the pH to a neutral or an alkaline level will precipitate most heavy metals as metal hydroxides [13]. Most process wastewaters contain mixed metals and so precipitating these different metals as hydroxides can be a tricky process [14]. Each type of metal hydroxide is favourable to precipitate at a certain pH range [15a]. If the pH value is above the optimum for
the precipitation of hydroxide metals, their dissolution will occur. Figure 1. is shown the solubility of metal hydroxide on different pH. According to Figure 1. precipitation for investigated metals will be in the narrow range of pH. For Cu\(^{2+}\) pH 8.5-9, pH 10-10.5 for Ni\(^{2+}\), pH 9.5-10 for Pb\(^{2+}\) and pH 9-9.5 for Zn\(^{2+}\).

The Solvay Process aims at the production of soda ash [16]. Along with soda, however, this process gives a large quantity of production wastes so-called distiller fluid in the form of highly mineralized suspension, which is a serious disadvantage of the method [17]. The Solvay process involves the aqueous reaction of NaCl, CO\(_2\), and NH\(_3\) rendering, after five steps, sodium carbonate as well as solid and liquid wastes [18]. Selimović et al., investigated the application of sediments from the Solway process as a possible precipitate since it contains a certain amount of CaCO\(_3\) and Ca(OH)\(_2\). Their results showed that the precipitate from the Solway process was a very good precipitate where it removed up to 99.9% of heavy metal ions such as Cu\(^{2+}\), Ni\(^{2+}\), Pb\(^{2+}\) and Zn\(^{2+}\) from the monocomponent initial solution concentrations of 500 mg/L [19].

Therefore, binary aqueous systems Cu-Ni and Pb-Zn with total concentrations of 500 mg/L were prepared and waste sludge from the Solway process was used as a precipitation agent in this paper.

![Figure 1: The solubility of metal hydroxide on different pH [15b]](image)

II. EKSPERIMENTAL PART

2.1. Materials

In this research were used the following chemicals: Cu(NO\(_3\))\(_2\) · 3H\(_2\)O, min. 99.5 %, Pliva, Zagreb; Ni(NO\(_3\))\(_2\) · 6H\(_2\)O, min. 99 % Semikem, Sarajevo; Pb(NO\(_3\))\(_2\), min. 99.5% Alkaloid, Skopje; Zn(NO\(_3\))\(_2\) · 6H\(_2\)O, min. 99 %, Kemika, Zagreb; standard solution of Cu\(^{2+}\), 1000 mg/L, Merck; standard solution of Ni\(^{2+}\), 1000 mg/L; standard solution of Pb\(^{2+}\) 1000 mg/L Merck; standard solution of Zn\(^{2+}\) 1000 mg/L, HNO\(_3\), 65%; demineralized water (<1 µS cm\(^{-1}\)).

The precipitant used for this experiment is taken from the waste basin and from the soda production plant in Bosnia and Herzegovina. The preparation of the precipitate was performed in an appropriate manner. After proper sampling of the material, it is spread out in a thin film and dried for some time at room temperature. Since the material contained larger particles, it had to be ground to the appropriate granularity (0.01-0.25 mm) and dried at 105 °C. The precipitate thus prepared was used to remove metal ions from binary aqueous solutions with an initial concentration of 500 mg/L.

2.2. Precipitation experiment

The experimental part was carried out as follows. For binary Cu-Ni and Pb-Zn systems with a total concentration of 500 mg/L, solutions were prepared by dissolving the appropriate salt mass with demineralizing water. Chemical precipitation was performed by adding the appropriate mass of precipitate to the binary metal system with an initial concentration of 500 mg/L and stirring 300 rpm for 5 minutes, measuring the pH of the solution was performed using a combined glass electrode model GLP 21 CRISON, with a resolution of 0.1, 0.01, 0.001, filtering the samples through Whatman\® quantitative filter papers 125 mm in diameter, first through a black ribbon circle and then through a blue ribbon circle and storing the samples in polyethylene flasks until measuring and measuring the metal content in the filtrate by FAAS method. A Perkin Elmer Aanalyst 200 instrument was used to measure the metal content in the filtrate.

Before measuring the heavy metal content by the FAAS method, and after filtration into polyethylene flasks, 0.2 mL of concentrated nitric acid was added to each sample. Nitric acid is added to samples for two reasons. The first reason is to lower the pH below 2 immediately after sampling. The second reason is due to the digestion that is necessary before measuring on an atomic absorption spectrometer. The purpose is to destroy the matrix that would otherwise interfere with the atomization process. Also, by digestion, all oxidation states of metals pass into one.

A series of standard solutions of exactly known concentrations for all four metals was prepared by pipetting stock solutions with an initial concentration of 1000 mg/L into 50 mL volumetric flasks. After that, the flasks were refilled to the mark with 0.03 mol/L HNO\(_3\).
After reading the exactly known concentrations of the batch of standard solutions on FAAS, each individual sample was measured under identical conditions. The efficiency of chemical precipitation can be calculated from the following formula:

\[ Er = \frac{C_0 - C_1}{C_0} \times 100 \]

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

In the process of removing Cu\(^{2+}\) and Ni\(^{2+}\) of initial concentration of 500 mg/L from the binary system by precipitation, the removal efficiency of each of them changed by increasing the dose of the precipitate. Thus, at lower doses of the precipitate, the precipitation efficiency was higher with Ni\(^{2+}\) compared to Cu\(^{2+}\). However, with increasing dose of the precipitate, the efficiency of Cu\(^{2+}\) precipitation increased significantly (Figure 2).

![Figure 2: Influence of precipitate concentration on the efficiency of Cu\(^{2+}\) - Ni\(^{2+}\) ion precipitation from the binary system](image1)

The dominance of Cu\(^{2+}\) precipitation over Ni\(^{2+}\) began in the neutral pH range (Figure 3). The initial pH value of the binary Cu - Ni solution was 5.17. The addition of the precipitate increased the pH. At a pH of 7.5, the percentage difference in removal was 3% higher for Cu\(^{2+}\). Redissolution of Ni\(^{2+}\) metal ions into the solution began at a pH of 11.42%, while for Cu\(^{2+}\) it continued to increase. This means that the optimal pH value for one metal is not conducive to another metal. The optimal pH value for the removal of Ni\(^{2+}\) ions is less than 11.42.

![Figure 3: Influence of pH value on the efficiency of Cu\(^{2+}\) - Ni\(^{2+}\) ion precipitation from the binary system](image2)

In the process of removing Pb - Zn ions with an initial concentration of 500 mg/L from the binary system. Already with the addition of 0.1 g/L precipitate to the binary system, a significant removal efficiency was achieved (Figure 4). Higher affinity for removal was shown by Zn\(^{2+}\) ion where as much as 99.049% of this ion was removed, while slightly lower affinity was shown by Pb\(^{2+}\) ion where 83.471% was removed. With further addition of the precipitate, the removal efficiency increased linearly until an additional 8 g/L of precipitate was added. After this point, the removal efficiency for both metals decreased.

![Figure 4: Influence of precipitate concentration on Pb\(^{2+}\) - Zn\(^{2+}\) ion precipitation efficiency from binary system](image3)

The pH value of the binary system before the addition of the precipitate was 3.79, which is significantly lower than the pH value of the binary system Cu - Ni. After each addition of a portion of the precipitate, the pH value of the solution increased linearly. The differences in the precipitation efficiency of the mentioned two...
metals were more pronounced at pH values of the treated solution lower than 6.87 (Figure 5), while at higher pH they were smaller.

(Sdiri and Higashi, 2013) in experiments of simultaneous removal of heavy metals from aqueous systems using limestone, they found that the simultaneous presence of Zn and Pb favored the removal of Zn$^{2+}$, but not Pb$^{2+}$. Increased zinc removal in the presence of lead suggests a coprecipitation mechanism that increases zinc removal [20].

The obtained results show that the highest achieved percentage of metal removal was 99.844% for Pb$^{2+}$ and 99.849% for Zn$^{2+}$, where the pH value of the treated solution was 10.64. Above the optimal pH value for precipitation, there was a redissolution of metal ions in the solution. According to the diagram for the solubility of metal hydroxides at different pH, the optimal pH values for the removal of metal ions are at lower values than obtained experimentally.

![Figure 5: Influence of pH value on the efficiency of Pb$^{2+}$ - Zn$^{2+}$ ion precipitation from the binary system](image)

IV. CONCLUSION

Precipitation and separation of metal ions from binary systems based on different pH values using waste sludge from the Solway soda production process gave good experimental results. The removal efficiency for the binary system Cu - Ni was 99.810% at a pH of 11.42 for Cu$^{2+}$ and 99.896% for Ni$^{2+}$ at a pH of 10.86. These results showed once again that the separation of metal ions using a precipitate containing a high percentage of CaCO$_3$ and Ca(OH)$_2$ from selected systems is a tricky process. The maximum efficiency of metal ion removal in the second binary system (Pb - Zn) was 99.84% at pH 10.64.

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