

REMOVAL OF LEAD AND ZINC IONS FROM THEIR MONOCOMPONENT AND TWO-COMPONENT AQUEOUS SOLUTIONS USING SODIUM HYDROXIDE

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: The hydroxide precipitation method, using NaOH as a precipitant agent, was conducted to treat synthetic monocomponent and two-component water solutions of Pb^{2+} and Zn^{2+} with initial concentrations of 50 and 500 mg/l of each metal. The effect of pH and initial concentration of lead and zinc ions on their removal were investigated. The precipitation experiments were carried out by batch method that involves the mixing of NaOH with solutions containing metal ions to occur nucleation, solid growth and subsequent separation of precipitates from solution by filtration. The results showed that the removal efficiency was increased by increasing of pH and initial concentration of metal ions in their water solutions. Hydroxide precipitation method using NaOH is an efficient technique for the removal of lead and zinc ions from their monocomponent and two-component water solutions of different concentrations, with maximum removal efficiency in the pH range of 10.32 to 11.39.

KEYWORDS: heavy metal, chemical precipitation, wastewater, sodium hydroxide.

INTRODUCTION

Comprising over 70% of the Earth's surface, water is undeniably the most valuable natural resource existing on our planet [1]. However clean water supplies are under threat from urbanisation, industry and agricultural development [2]. Among various types of water pollutants, heavy metals are the largest class of contaminants and also the most difficult to treat [3].

Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow [4]. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries [5].

Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms [6]. The heavy metals linked most often to human poisoning are lead, mercury, arsenic and cadmium, while other heavy metals, including copper, zinc and chromium are actually required by the body in small amounts, but can also be toxic in larger doses [7]. The toxic metals and their ions are

not only potential human health hazards but also to another life forms [8]. Therefore, the application of appropriate treatment methods is necessary for their removal from contaminated water.

Water and wastewater treatment has been widely investigated with different available techniques including precipitation, sedimentation, reverse osmosis, ion-exchange, membrane process, electrochemical and adsorption [9]. Among them, precipitation process is one of the common treatment methods that used for removal of heavy metals and other pollutants [10]. Precipitation has been long used for heavy metal removal, based on the addition of chemical reagents to induce an increase of pH value, in order to manage a destabilization of the electrical charges responsible for the retention of such cations in leachates and metal containing effluents [11]. In the precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates that can be separated from the water by sedimentation or filtration and the treated water is then decanted and appropriately discharged or reused [12]. The precipitation can be carried out using hydroxide, carbonate or sulfide, depending on which type of precipitant is added to the waste water. Of all the treatment techniques, heavy metal hydroxide precipitation is the most commonly employed because of its low-cost and simplicity [13]. The solubility of the precipitation products and therefore the removal degree of heavy

metals from the waste water depends on the value of the pH, on the initial concentration of metallic ions in the solution, on the nature of precipitation agent and also on the nature and concentration of other chemical species which are present in the solution [14]. The solubility of metal hydroxides, depending on the water pH, is presented in Figure 1.

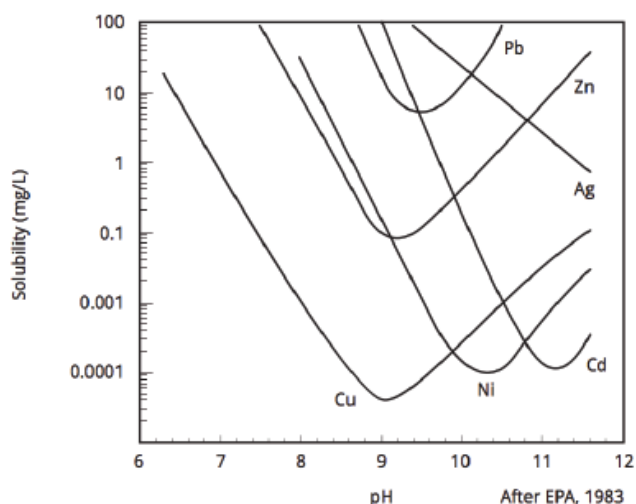


Figure 1. Solubility of metal hydroxides [15]

Given the above, the aim of this study was to determine the effects of pH and initial concentrations of Pb(II) and Zn(II) in water on the efficiency of lead and zinc removal from their monocomponent and two-component aqueous solutions using sodium hydroxide (NaOH).

MATERIAL AND METHODS

All chemicals used for the experimental part of the work were of analytical grade: Fluka sodium hydroxide, 1 mol/L, lead(II) nitrate (Alkaloid AD Skopje, Republic of Macedonia), zinc nitrate hexahydrate (Kemika, Zagreb, Croatia), lead standard solution 1,000 mg/L Pb in 0.5 M nitric acid (from $\text{Pb}(\text{NO}_3)_2$) and zinc standard solution 1,000 mg/L Zn

in 0.5 M nitric acid (from $\text{Zn}(\text{NO}_3)_2$) from Merck, Nitric acid, min. 65% (Lach-Ner, Czech Republic). All glassware was first washed with detergent and rinsed with tap water, then soaked in water solution of HNO_3 , and rinsed with deionized water.

Aqueous solution of sodium hydroxide with molar concentration of 0.1 mol/L was used as precipitant. The solution was prepared by dilution with deionized water. For each heavy metal, its monocomponent aqueous solutions of high and low initial concentrations (500 and 50 mg/L) were prepared. In addition, a two-component aqueous solution was prepared in which each metal had a concentration of 500 mg/L. Preparation of metal ion aqueous solutions was performed as follows. Metals, which are in the form of nitrate salts, were accurately weighed, then quantitatively transferred to volumetric flasks of 1L and diluted to the mark with deionized water. Each aqueous solution was homogenised, its initial pH value was measured and the chemical precipitation process was performed with these samples.

In order to evaluate the effect of pH on the removal efficiency, precipitation experiments were conducted with different pH conditions, by adding increasing quantities of the precipitation agent to monocomponent and two-component aqueous solutions of Pb^{2+} i Zn^{2+} . Sodium hydroxide volumes used in experiments are given in Table 1. The precipitation procedure was carried out by transferring 100 mL of metal ion solution of the appropriate concentration to a 250 mL glass. Then, a specific volume of precipitant was added to the glass and mixed with the solution by a magnetic stirrer at a rate of 300 rpm, and total mixing time was 5 min. After the required mixing time, the pH of the solution was measured and the filtration of aqueous solution of heavy metals was carried. The Whatman NO.42 filter paper was used to remove precipitates. Each filtrated sample was stored in polyethylene bottle till analysis.

Table 1. Volumes of NaOH added to monocomponent and two-component aqueous solutions of Pb^{2+} i Zn^{2+}

Initial concentrations of heavy metals in water	Volumes of 0,1 mol/L NaOH (ml) for precipitation of heavy metals					
500 mg/L Pb^{2+}	3.00	3.50	4.00	5.00	7.00	10.00
50 mg/L Pb^{2+}	0.06	0.10	0.20	0.60	3.00	6.00
500 mg/L Zn^{2+}	5.00	12.00	13.50	14.50	15.00	20.00
50 mg/L Zn^{2+}	1.00	1.30	1.50	2.00	5.00	10.00
500 mg/L Pb^{2+} 500 mg/L Zn^{2+}	1.00	5.00	10.00	20.00	50.00	100.00

Removal of lead and zinc from their aqueous solutions using sodium hydroxide was determined by analysis of initial Pb^{2+} and Zn^{2+} concentrations in samples before the treatment and their concentrations after the treatment with NaOH and filtration of samples.

Concentrations of metal ions were quantified by flame atomic absorption spectroscopy (FAAS), with air/acetylene type of flame. FAAS is of use in any analytical laboratory where elemental determinations are made [16] and generally, with air/acetylene flame lead and zinc can be determined [8]. The drawing of the calibration curve was performed using a 0.2, 1, 5, 7 and 10 mg/L standard solutions of Pb^{2+} and 0.2, 0.5, 1, 1.5 and 2 mg/L standard solutions of Zn^{2+} and measuring their absorbance by FAAS. Obtained equations of calibration curves were

$$y = 0,0196x + 0,0035 \text{ for lead and}$$

$$y = 0,4394x + 0,1256 \text{ for zinc.}$$

The following equation was used for calculation of removal efficiency:

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

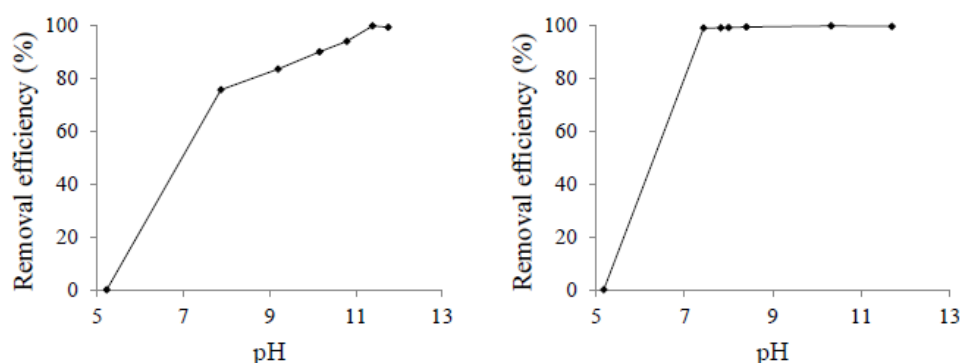


Figure 2. Effect of pH on the efficiency of removing a) Pb^{2+} and b) Zn^{2+} from their monocomponent aqueous solutions of initial concentrations 500 mg/L

Based on data from Tab. 1 and results from Fig 2. it can be seen that the increase in volume of precipitant added to samples of heavy metal aqueous solutions resulted in increased pH of the treated samples, which in turn resulted in increased efficiency of heavy metal removal. The higher removal efficiencies at high pH are related to high concentrations of OH^- ions in solution, which react with metal ions and convert them to insoluble precipitates that can be removed from the solution by filtration.

The removal efficiency for lead ions was above 90% at pH values beyond 10, while for zinc ions the efficiency was already 99.149% at pH of 7.43. This is

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.

The effect of initial concentration on the removal efficiency was assessed by determining the removal efficiency from monocomponent aqueous solutions of 50 and 500 mg/L for each heavy metal, and from two-component aqueous solutions in which each metal had a concentration of 500 mg/L.

RESULTS AND DISCUSSION

In this study, the lead and zinc ion removal experiments from their monocomponent and two-component aqueous solutions were carried out using NaOH as a precipitant. Sodium hydroxide is commercially available low cost chemical, so it can be easily utilized as precipitating agent [17]. The efficiency results of removal of lead and zinc ions from their monocomponent aqueous solutions of high initial concentrations (500 mg/L) are presented in Fig. 2.

in correlation with solubility of their hydroxides, presented at Fig.1. as zinc form insoluble precipitates at lower pH values compared to lead ions. The maximum removal efficiencies using NaOH were obtained for Pb^{2+} (99.866%) at pH of 11.39 and for Zn^{2+} (99.959%) at pH of 10.32. Chen et al. [12] conducted a hydroxide precipitation of heavy metals from their aqueous solutions of 500 mg/L concentrations. They found that the optimum pH values for chemical precipitation by sodium hydroxide were 10.5 for Pb^{2+} and 10 for Zn^{2+} . Adjustment of pH to the basic conditions (pH 9-11) is the major parameter that significantly improves heavy metal removal by chemical

precipitation [6]. In order to evaluate the effect of pH on the lead removal efficiency, Karimi [15] conducted hydroxide precipitation experiments with different pH conditions in a range from 3 to 11 and using $\text{Ca}(\text{OH})_2$. He concluded that the optimum removal efficiency for actual and synthetic wastewater was at pH 9 to 11.

However, as the pH changed beyond the optimal value, removal efficiency for Pb^{2+} and Zn^{2+} was somewhat lower (99.397% and 07.047%). That is due to amphoteric properties of metal hydroxides, as precipitates of amphoteric metals like zinc and lead, tend to redissolve as the pH changes beyond the optimal range.

Efficiency results of removal of lead and zinc ions from their monocomponent aqueous solutions of

low initial concentrations (50 mg/L) are presented in Fig. 3.

When hydroxide precipitation of heavy metals was carried out at lower initial concentrations of lead and zinc ions in their monovalent aqueous solutions (50 mg/L), maximum removal efficiencies were 98.256% for Pb^{2+} at pH of 10.63 and 99.694% for Zn^{2+} at pH of 10.83, which are lower values compared to those obtained at high initial concentrations of both metal ions (500 mg/L).

Similar observations are found in other works. Pang et al. [18] performed hydroxide precipitation on the selected heavy metal ions, using NaOH. The percent removals of Pb^{2+} were 96.9, 93.3, 69.0, and 98.3% for the initial concentrations of 14, 7, 3 and 1.5, mg/L, respectively.

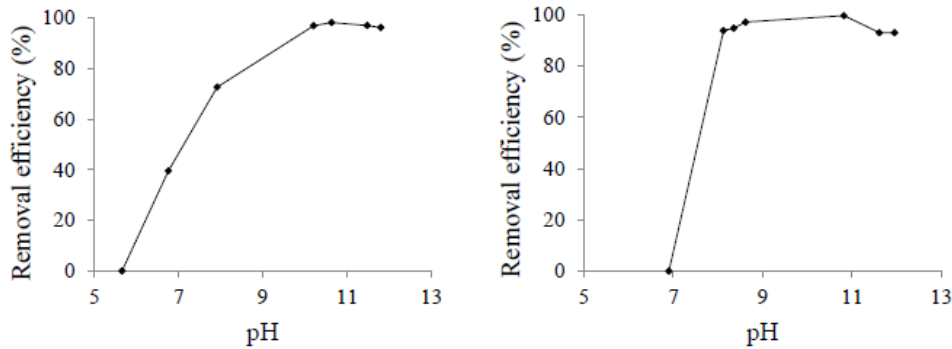


Figure 3. Effect of pH on the efficiency of removing a) Pb^{2+} and b) Zn^{2+} from their monocomponent aqueous solutions of initial concentrations 50 mg/L

Their results for percent removals of Zn^{2+} showed similar trend. Karimi [15] obtained the removal efficiencies of 88.8% and 75.5% at pH of 11, using $\text{Ca}(\text{OH})_2$ for 600 and 300 mg/L Pb^{2+} initial concentrations. He proposed that the higher removal efficiency at higher concentrations relate to the formation of more and larger precipitates and agglomeration of these solids together.

From the Fig. 3. it can be seen that, in the case of zinc, significant increase in the efficiency of removal was achieved in the narrow pH range. Pang et al. [18] observed that the percent removal of Zn^{2+} increased tremendously from pH 5 to 7, i.e. an average increment of 53.6% removal was observed in that pH range for 5, 8, and 10 mg/L of Zn^{2+} . In this study, due to high initial pH of metal solutions of Zn^{2+} , the removal efficiency increase of 93.836% was achieved in pH range 6.9 – 8.13 50 mg/L. For both metals, due to the amphoteric properties of their hydroxides, the increase in pH above the optimum values resulted in reduced removal efficiency.

Efficiency results of removal of lead and zinc ions from their two-component aqueous solutions with 500 mg/L initial concentrations of each metal are presented in Fig. 4.

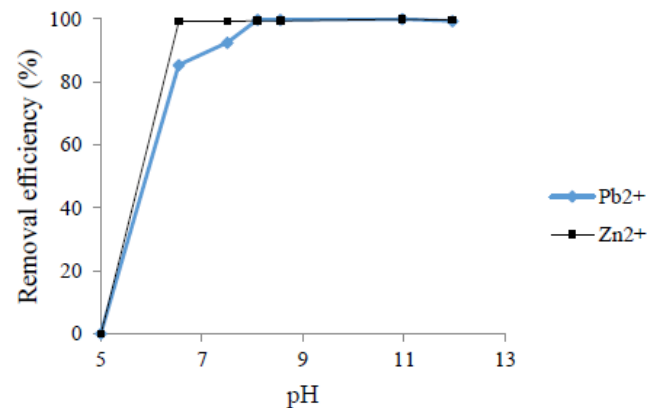


Figure 4. Effect of pH on the efficiency of removing Pb^{2+} and Zn^{2+} with initial concentrations of 500 mg/L from their two-component aqueous solutions

The results show a higher removal efficiency for Zn^{2+} at lower pH values, while with further pH increase, the percentage of Pb^{2+} removed is increased compared to the Zn^{2+} . These could be explained by amphoteric nature of lead and zinc. Mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution [19]. Maximum removal efficiencies for heavy metal ions from their two-component aqueous solutions were obtained at pH value of 10.96, and they were 99.983 % for Pb^{2+} and 99.930% for Zn^{2+} . Compared to the results obtained by precipitation of heavy metals in their low-concentration monocomponent aqueous solutions, the efficiency of removal was higher for both metals, which is consistent with the observations of higher removal efficiency for metals from their monocomponent aqueous solutions of high concentration.

CONCLUSION

Chemical precipitation of soluble metal ions as insoluble metal hydroxides is simple method for removing metal contaminants from water based on changing its pH value. Sodium hydroxide was found to be an effective and relatively low cost precipitant agent for the removal of Pb^{2+} and Zn^{2+} from their monocomponent and two-component synthetic water solutions of 50 and 500 mg/l initial concentrations of both metals. Maximum removal efficiencies for lead and zinc can be obtained in pH range of 10.32 to 11.39. Removal efficiency for both metals is higher when their initial concentrations in water are higher, and compared to lead, zinc can efficiently precipitate at lower pH values, i.e. with lower volume of added precipitant. However, amphoteric mixed metals such as lead and zinc, may each other influence on efficiency of their removal from water, since the ideal pH for precipitation of one metal, may re-dissolve another metal precipitate back into water solution.

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