Removal of lead heavy metal from wastewater by crystallization process and investigation of the effective parameters

Parvaneh Khalati, Maryam Tahmasebpoor[1], Seyed Jamaleddin Peighambardoust

Faculty of Chemical & Petroleum Engineering, University of Tabriz, Tabriz, Iran

ABSTRACT

Increase in population and industrialization of societies have caused the production of large amounts of inorganic, organic and biological pollutants. Lead is one of the heavy metals having high and long-term toxicity even at low concentrations which limits the reusability and recyclability of industrial wastewaters so it must be removed. In this study, the removal and recovery of Pb from synthetic wastewater by a new form of precipitation method named crystallization process in a batch system was investigated. This process has gained increasing attention in recent years because of being in access, low cost, high efficiency and no need to recover the used materials. The efficacy of removal was dependent on the factors such as *pH*, initial lead concentration, carbonate:lead molar ratio and amount of seed crystals. The results of the experiments performed in this study showed that when the *pH*=8, the initial concentration of lead is 100 mg /L, the molar ratio of carbonate to lead is 3:1 and the amount of seed particles is 0.25 g dissolved in 100 ml, the lead removal efficiency is obtained as 99 %. The present study demonstrates that Pb can be successfully removed and recovered as PbCO3 crystals in a batch reactor.

KEYWORDS

Water treatment, Heavy metals, Pb removal, Crystallization process, Parametric study

[1]**Corresponding Author Email: tahmasebpoor@tabrizu.ac.ir**

1. Introduction

Lead (Pb) is a heavy metal widely spread throughout the environment. Wastewaters containing lead are discharged by many anthropogenic activities, such as driving, the metallurgical industry, electroplating and metal finishing [1]. This contaminant can affect almost every organ in the body, accumulating over time [2]. A wide range of treatment processes for the removal and recovery of heavy metals from wastewaters have been developed during the years. Conventional methods, such as precipitation, electrolysis, ion exchange, and adsorption have been used in the past decades [3]. Among them, precipitation is the most commonly used process. However, cost for the subsequent treatment for the precipitates or sludge is normally high [4]. Thus, new concepts for minimizing of the discrete precipitates in the solution have to be developed and applied in the operation. This new method is crystallization. Production of relatively large crystals may be realized by means of seeded crystallization, where the seed not only induces and promotes crystallization but also the acts as a carried of the precipitate to be recovered [5]. This procedure can be done in a batch or continues system. There are a number of situations where batch operation is chosen instead of continuous system; mainly because of the advantages such as being in access, low cost, high efficiency and no need to recover the used materials. Important factors on the lead removal by the crystallization process are *pH*, lead concentration, carbonate to lead molar ratio and amount of seed [5]. This study explored the applicability of the crystallization process in a batch reactor on the removal and recovery of lead from synthetic wastewater using carbonate precipitation agent and sands as seed crystals.

2. Methodology

The synthetic lead wastewater was prepared by dissolving lead nitrate ($Pb(NO_3)_2$, Merck, Germany) as stock solution with a specific concentration (500 mg/L). Sodium carbonate (Na_2CO_3, Merck, Germany) used as the precipitant (0.008M) was also dissolved in another stock solution whose *pH* was conditioned by sodium hydroxide (NaOH, Merck, Germany) and nitric acid (HNO_3, 70%, Merck, Germany). Synthetic wastewater and precipitant solutions for the experimental runs were also prepared using deionized water. The *pH* levels were supplied by *pH* meter (*pH* /mV/Temperature Bench Meter, Romania). All the experiments were carried out in the batch beaker at laboratory temperature of 20-25 ºC. 100 mL of lead solution with a specific concentration containing a specific amount of sand were dosed into the beaker. While the mentioned mixture was being agitated by a mechanical stirrer at 250-300 rpm, 0.008 M Na_2CO_3 solution with different carbonate to lead molar ratio was added to the beaker. Each experiment lasted for 6 h, after which the solution was discarded from the filter (Ø 125mm) and tested for determination of Pb using atomic absorption spectrophotometer (AAS). The removal efficiency of the reactor (η) is expressed by Equation (1).

$$\eta = \frac{Cpb,0 - Cpb,t}{Cpb,0} \times 100 \qquad (1)$$

Where $C_{Pb,0}$ is initial lead concentration and $C_{Pb,t}$ is lead concentration that was determined by atomic absorption spectrophotometer (AAS).

3. Discussion and Results

3.1. Effect of *pH*

The setup was operated at varying *pH*s from 6 to 10 to observe its effect on the Pb removal efficiency from the synthetic wastewater and also to determine the optimum *pH* of the operation. As displayed in fig.1, the highest lead removal efficiency at *pH* 8 was obtained > 99%, while initial Pb_2^+ concentration of 100 mg/L, molar ratio of carbonate to lead 3:1 and 0.25 g sands. On the other hand, theoretical calculations performed by Patterson et al. showed that the minimum lead concentration in lead-carbonate precipitation reaches the lowest value at *pH* ranged from 7.5 to 9.0 [6]. Our findings here coincided with these values. It can be concluded that the *pH* value should be controlled around 8.

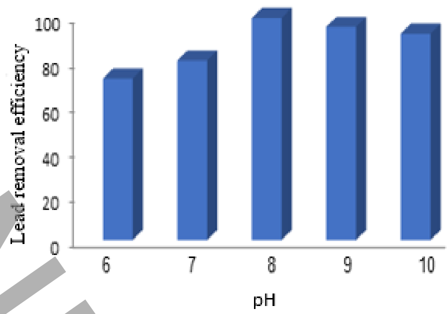

Figure 1. Effect of *pH* on lead removal efficiency at $[Pb^{2+}]$= 100 mg/L, $[CO_3^{2-}]$: $[Pb^{2+}]$=3:1 and 0.25 g sand

3.2. Effect of initial Pb_2^+ concentration

The setup was operated at varying initial Pb_2^+ concentration (100 mg/L to 400 mg/L) to observe its effect on the Pb removal efficiency while the other parameters were fixed (*pH* 8, molar ratio of carbonate to lead :3 to 1 and sand amount 0.25 g). As seen in fig 2, the highest lead removal efficiency occurred at 100 mg/L. Decreased with increasing the initial lead concentration.

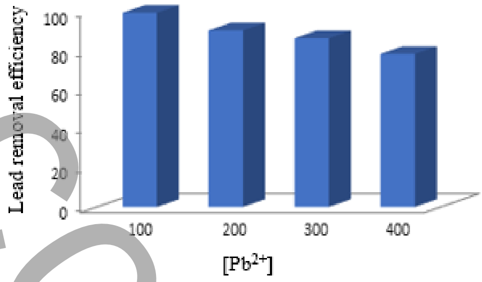

Figure2. Effect of [Pb^{2+}] on lead removal efficiency at *pH*=8, [CO_3^{2-}]: [Pb^{2+}] =3:1 and 0.25 g sand

3.3. Effect of sand amount

To illustrate the effect of the sand amount on the lead removal efficiency, the batch reactor was operated at four different amounts of sand: 0.1 g, 0.25 g, 0.5 g and 1 g. As seen in fig 3, by increasing the amount of sands from 0.1g to 0.25g, the effiency of lead removal also increased. This can be explained by larger surface areas available for crystallization of the lead precipitates provided by larger amounts of sands in the reactor. However, further increase in the amount of seed particles leads to a gradual decrease in the percentage of lead removal. This is mightily attributed to the lower growth of crystals in the presence of excessive substrates for the deposition of lead and carbonate ions., This leads to the creation of heterogeneous crystals with very small sizes which pass through the filter and are not considered in the calculation of lead removal efficiency.

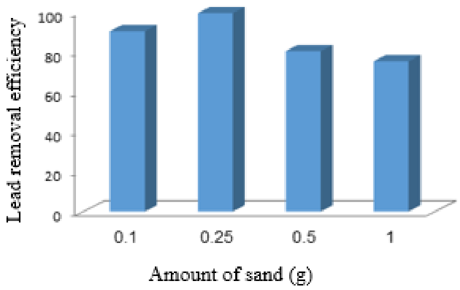

Figure 3. Effect of sand amount on lead removal efficiency at *pH*=8, [Pb^{2+}] = 100 mg/L and [CO_3^{2-}]: [Pb^{2+}]=3:1

3.4. Effect of [CO_3^{2-}]:[Pb^{2+}] molar ratio

The setup was operated at varying carbonate: lead molar ratios (1:1, 2:1, 3:1 and 4:1) to observe the effect on the Pb removal efficiency. Highest lead removal efficiency of >99% was reached at carbonate: lead molar ratio of 3:1. By reducing the molar ratio of carbonate to lead from the optimal ratio (3 to 1), the percentage of lead removal also decreased, so that when this ratio is 1 to 1, lead carbonate is less likely to precipitate; due to the low volume of carbonate and low ion collision, and heterogeneous crystals are formed, resulting in a significant removal percentage. On the other hand, by increasing the molar ratio of carbonate: lead to 4:1, the percentage of lead removal decreased. It seems that due to the high presence of carbonate ions in the solution, they react with lead ions before the deposition on the sand particles. Therefore, a large part of lead ions is converted into homogeneous crystals which pass through the filter and are not considered in the calculation of lead removal efficiency.

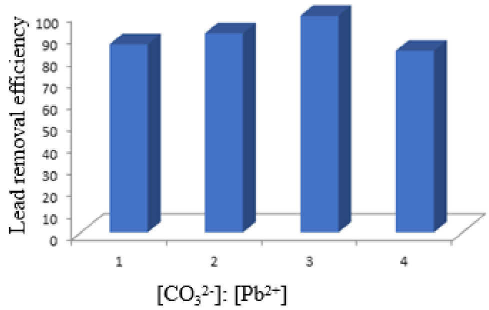

Figure4. Effect of [CO_3^{2-}]: [Pb^{2+}] on lead removal efficiency at *pH*=8, [Pb^{2+}] = 100 mg/L and 0.25g sand

4. **Conclusion**

Lead can be removed and recovered successfully as lead carbonate crystals using the seeded batch reactor. Based upon the results of this study, when the *pH* is in the range between 8 to 9, the initial concentration of lead is 100 mg/L, the molar ratio of carbonate to lead is 3:1 and the amount of seed particles is 0.25 g dissolved in 100 ml, the lead removal efficiency is obtained as 99%.

5. **References**

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