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Parametric Study on the Removal of Lead and Recovery as Lead Carbonate in Simulated Lead Acid Battery Industry Wastewater

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Lead (Pb) is notorious for its elevated and persistent toxicity, even at extremely low concentrations, posing limitations on the reusability and recyclability of industrial wastewater. This investigation focused on extracting Pb from simulated lead acid battery industry wastewater in the form of Lead Carbonate ($PbCO_3$) granules through the fluidized-bed homogeneous granulation process. Achieving a Pb granulation efficiency of 97.55 % and total removal efficiency of 99.67 % required maintaining the operating pH within the 9.4-9.6 range, coupled with a carbonate-to-lead molar ratio of 1:1 and an initial concentration of 2600 ppm for 72 h reaction time. Most of the recovered crystals are less than 0.42 mm in size. This study highlights the potential for Pb recovery as $PbCO_3$ from contaminated wastewater using fluidized-bed granulation technology.

1. Introduction

In recent times, increased awareness regarding environmental sustainability and the negative impacts of heavy metal pollution has compelled industries to review and reconsider their waste management procedures. Lead has emerged as a notable environmental concern among the various pollutants due to its toxicity and enduring presence in ecosystems (Raj and Das, 2023). The lead-acid battery industry, a pivotal player in the global energy storage sector, has significantly contributed to lead contamination in wastewater (Rand, 1997).

Lead, a crucial component in lead-acid batteries, poses substantial health and environmental risks when not managed appropriately. The wastewater produced by the lead-acid battery industry frequently contains heightened levels of lead, posing potential threats to aquatic ecosystems, soil quality, and human health (Chen et al., 2012). Recognizing the urgency of addressing this matter, there is a growing emphasis on devising and implementing effective strategies to eliminate lead from wastewater.

Various techniques have been developed to eliminate Pb from lead-acid battery industry wastewater (LABIW), encompassing coagulation (Varma et al., 2021), ion exchange, electrodialysis, membrane filtration, reverse osmosis, adsorption, and precipitation. Among these methods, the prevalent and favored approach, particularly for metal recovery, is chemical precipitation (Chalaris et al., 2023). In chemical precipitation, precipitants such as carbonates, oxides, and sulfides are generated to facilitate the removal of the target metals (Lupa and Cocheci, 2023). Nevertheless, chemical precipitation, irrespective of the precipitant employed, faces the issue of sludge generation, leading to elevated wastewater treatment costs due to the necessity for dewatering (Udomkitthaweewat et al., 2019). Additionally, the requirement for a larger treatment area in chemical precipitation becomes a drawback, potentially overshadowing the benefits of target metal recovery and rendering the method impractical. In contrast, fluidized bed homogeneous granulation (FBHG) represents a water treatment technology characterized by an intensified granulation process and is considered an enhanced iteration of chemical precipitation (Le et al., 2021). Several studies have been conducted and successfully removed and recovered essential substances in wastewater through FBHG like oxalate removal in bauxite wastewater (Mamuad et al., 2022), phosphate (Le et al., 2021), and zinc (Udomkitthaweewat et al., 2019) to name a few. Fluidized Bed Homogeneous Granulation (FBHG) is influenced by a variety of factors that affect

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the efficiency of lead removal and the quality of the resulting lead carbonate particles. These factors include pH, molar ratio and reactant concentration. An existing study conducted the removal and recovery of lead in wastewater but never consider the wastewater from LABIW (Chen et al., 2015). This technology addresses nearly all the drawbacks associated with traditional methods, providing a more efficient and sustainable approach.

This paper delves into the necessity of mitigating lead contamination in lead-acid battery industry wastewater, examining the existing challenges and potential remedies. By exploring innovative technologies, regulatory frameworks, and best practices, this study aims to contribute to a sustainable and responsible approach to treating and eliminating lead from industrial wastewater. As the world moves towards greener and more environmentally conscious practices, discovering efficient methods to diminish lead pollution becomes crucial for the continued progress of the lead-acid battery industry while minimizing its ecological impact.

2. Methods

The solutions employed in this study were formulated using laboratory-grade chemicals. Lead Nitrate ($Pb(NO_3)_2$) crystals with a purity of 99.0 %, Anhydrous Sodium Carbonate (Na_2CO_3) with 99.0 % purity, Sodium Hydroxide (NaOH) with 95 % purity, and Nitric Acid (HNO_3) with a purity of 69–71 % were obtained from Union Chemical Ltd. Zinc Nitrate ($ZnNO_3$) with a purity of 97 % was provided by Choneye Pure Chemicals. Buffer solutions at pH 4 and pH 7 were procured from Suntex Instruments Co., Ltd. Deionized (DI) water, with a resistivity of 18.2 ΩM (Millipore System), served as the solvent for preparing standard solutions. Synthetic wastewater and precipitant solutions for the actual experimental runs were created using reverse osmosis water.

The measurement of pH levels was carried out using a pH/ORP Transmitter/Controller (Suntex TS-1 Portable meter). Before each experiment, the pH meter/controller underwent calibration. To ensure precision and consistency in readings or data, the Atomic Absorption Spectrophotometer (Perkinelmer PinAAcle 500) was configured to undergo a minimum 30-minute stabilization period.

The experimental procedures utilized a fluidized-bed reactor (FBR) system shown in Figure 1. The bench-scale glass FBR, possessing a volume of 0.45 L, exhibits a diameter of 4.0 cm and a height of 133 cm. At the base of FBR, three inlets are linked to a peristaltic pump, regulating the flow of synthetic LABIW, precipitant, and recirculation or reflux. Glass beads, having a diameter of 0.35 cm, are positioned at the bottom of FBR, specifically at a height of 3 cm, to support the crystallization bed and regulate solution flow within the reaction region. Furthermore, a pH/ORP transmitter/controller (Suntex TS-1 Portable meter) with a sensitivity of ± 0.05 is installed on top of the FBR to monitor and regulate the pH of the effluent solution. Crystals collected post-experiment underwent oven drying at 105 °C for a minimum of 2 h before undergoing analysis.

Three parameters, pH, molar ratio, and concentration were considered to investigate its effect on the removal of Pb in simulated LABIW and recovered it at $PbCO_3$.

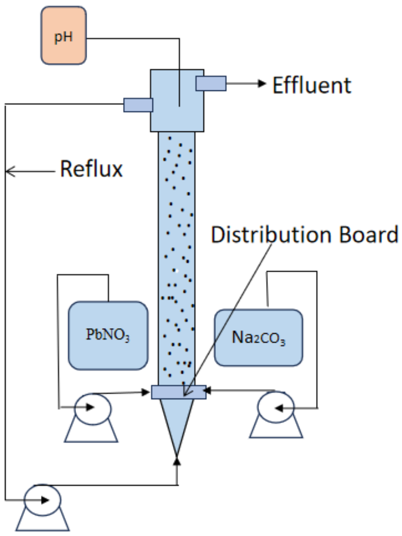

Figure 1: Schematic diagram of the fluidized bed reactor

3. Results and Discussion

3.1 Effects of pH

The pH level plays a crucial role in the removal of metals by the crystallization process, and its effect can vary depending on the specific metal ions involved. The pH of the solution can affect the crystal structure and growth during the crystallization process. Controlling the pH allows for the manipulation of crystal size, shape, and purity. The solubility of metal compounds can be highly dependent to pH. By manipulating the pH, it is possible to control the solubility of metal salts, aiding in their removal through granulation. Optimal pH control is essential to achieve efficient removal of metals from solutions in various industrial and environmental applications. In the case of Pb removal, at the end of 72 h reaction time, high removal efficiency is observed for both granulation and total removal efficiency as shown in Figure 2. Lead easily precipitates with carbonate ions due to the formation of insoluble $PbCO_3$ because of a chemical reaction. The reaction can be represented as follows:

$$Pb^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow PbCO_{3(s)} \quad (1)$$

The solubility product constant (K_{sp}) for $PbCO_3$ is relatively small, indicating that $PbCO_3$ has low solubility in water (Jurgens et al., 2019). This property is utilized in various water treatment processes and environmental remediation efforts where the goal is to remove lead from aqueous solutions. By adjusting the pH of the solution to a range where carbonate ions are present and $PbCO_3$ is less soluble, lead can be effectively removed through precipitation. In the study, all the pH ranges considered obtained favorable results at pH 8.5, 9.5, and 10.5 which all obtained more than 99 % efficiency both for granulation and total removal efficiency. Results showed that the granulation and total removal efficiency of lead with carbonate is slightly affected by pH. It can be observed that the highest removal efficiency is achieved at a pH equal to 9.5. The result is like the results obtained by De Luna et al. (2015), where the highest removal of lead was achieved at pH 8-9. Another study also claimed that at pH 10, the optimized condition for the removal of lead was obtained (Hoang et al., 2019).

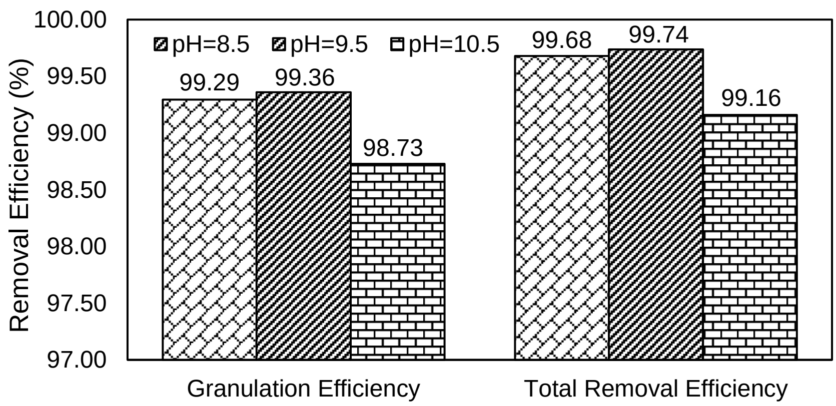

Figure 2: Effect of pH on the granulation and total removal efficiency of Pb removal in LABIW

3.2 Effects of concentration

The effect of concentration has been investigated and results showed that higher concentration favors the removal of lead in wastewater. All the concentrations considered observe high efficiency for both granulation and total removal efficiency with 97.36 % as the lowest and 99.71 % as the highest as shown in Figure 3. The highest efficiency was obtained from the lead concentration of 2600 ppm. The solubility of lead compounds, such as $PbCO_3$, is influenced by the concentration of lead ions in the solution. As the concentration of lead ions increases, the likelihood of reaching or exceeding the K_{sp} for $PbCO_3$ also increases (Blais et al., 2008). When the solution becomes saturated with lead ions, further increases in concentration can lead to precipitation of $PbCO_3$ granules. Like the results obtained from the study investigating the effects of lead initial concentration on its removal efficiency. Higher concentration favors higher removal of lead in wastewater (De Luna et al., 2015).

3.3 Effects of molar ratio

The molar ratio determines the stoichiometry of the precipitation reaction. It specifies the proportions in which the reactants combine to form the precipitate. An appropriate molar ratio ensures that all metal ions are consumed in the reaction, leaving no excess metal ions in the solution (Turhanen et al., 2015). An improper molar ratio can lead to the formation of undesired compounds or side reactions (Taylor et al., 2023). Excess precipitant might react with other ions in the solution, generating unwanted byproducts. In this study, although the molar ratio of 1.25 obtained the highest removal efficiency both for granular and total removal as observed in Figure 4. In terms of total removal and granulation efficiency, molar ratios of 1 and 1.25 are not far from each other. Showing even a minimal difference in removal efficiency of lead in wastewater can be valuable for several reasons, especially given the stringent regulatory standards and the significant health and environmental impacts of lead contamination. Minimal differences in removal efficiency may seem insignificant at first glance, but their implications are broad and impactful like ensuring regulatory compliance, protecting human health and the environment, optimizing operational processes, and providing economic and competitive advantages.

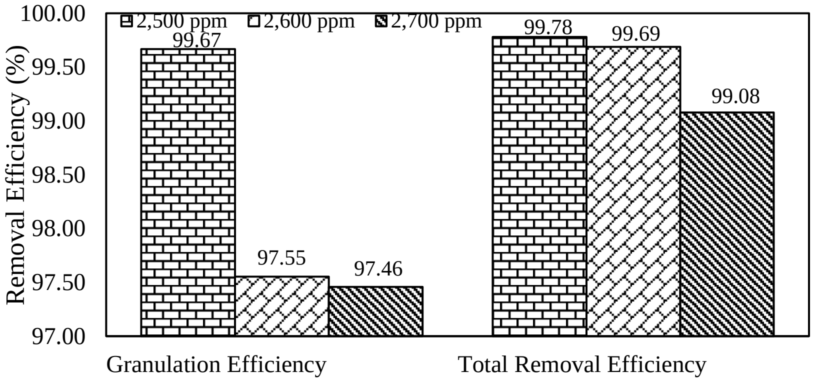

Figure 3: Effect of concentration on the granulation and total removal efficiency of Pb removal in LABIW

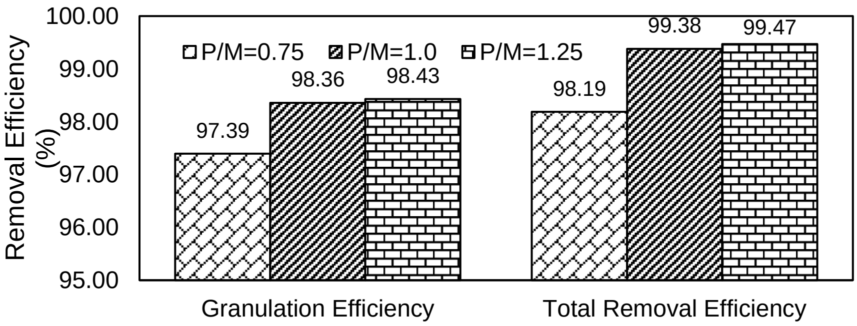

Figure 4: Effect of molar ratio on the granulation and total removal efficiency of Pb removal in LABIW

3.4 Characterization of solids recovered in terms of particle size distribution

Ensuring a tight particle size distribution is frequently sought to maintain uniform product quality. By managing the FBHG process, the rates of crystal growth and formation can be controlled which impacts the ultimate size distribution. The analysis of $PbCO_3$ crystals recovered from FBHG produced significant findings, offering valuable insights into the characteristics of the reclaimed particles. For the 72-h reaction time, most of the particles recovered were less than o.42 mm in all the parameters considered as shown in Figure 4. Minimal particles with more than 0.5 mm are also present in all the parameters considered. A greater number of particles recovered higher than 0.5 mm can be observed at a pH of 9.5, a concentration of 2700 ppm, and a molar ratio of 1.25. The results showed that the size of crystals in the FBHG process could be affected by reaction time or residence time. Extended residence time in the FBHG may result in larger crystals due to prolonged growth periods (Cruz et al., 2021). SEM analysis of the particles recovered exhibited the size and shape as well as the overall appearance like rhombohedra form as shown in Figure 7. The surface of the particle is rough and growth features can be observed which indicates that particles agglomerate or form clusters.

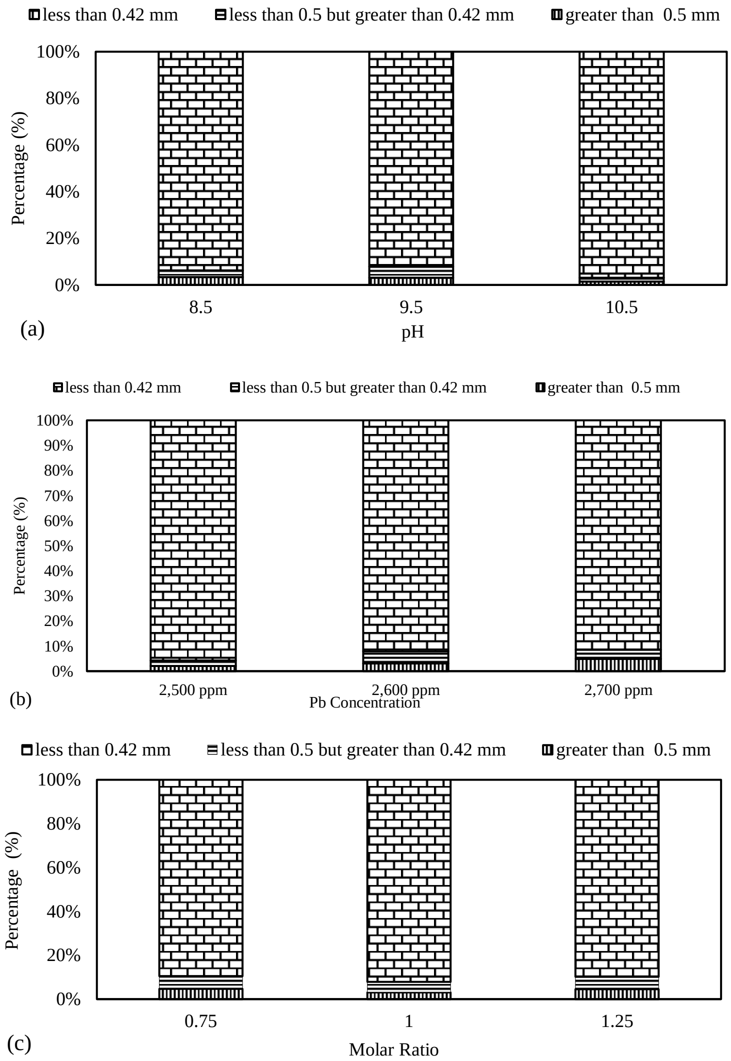

Figure 5: Particle size distribution of solids recovered in terms of (a) pH, (b) concentration, and (c) molar ratio

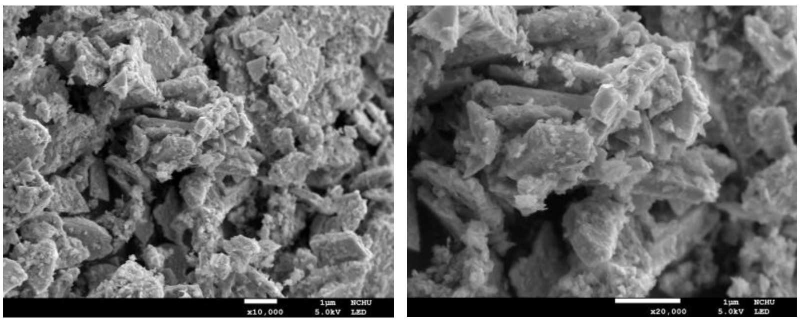

Figure 6: SEM images of the $PbCO_3$ recovered

4. Conclusions

Lead can be effectively eliminated and reclaimed as $PbCO_3$ granules through the utilization of a fluidized-bed reactor, with the removal and recovery processes taking place simultaneously. The research successfully showcased the viability of employing the crystallization process within a fluidized-bed reactor for the extraction and retrieval of lead from synthetic lead acid battery industry wastewater. FBHG advantages include higher efficiency and purity of crystals and optimized reactant usage compared to chemical precipitation. Furthermore, it revealed that homogeneous granulation in a fluidized bed reactor can yield exceptionally high lead conversion efficiencies, consistently reaching more than 99 % across various operating conditions. The removal efficiencies were found to be influenced by operational parameters such as pH concentration and molar ratio, with an optimal condition achieving a remarkable more than 99 % removal efficiency. Most of the particles recovered were less than 0.42 mm in size at 72 h reaction time. Particles recovered were rough and rhombohedral in shape and underwent agglomeration. It is recommended that the process be conducted longer to investigate the growth rate of particles recovered since particles could grow larger with extended reaction time. An optimization study could also be conducted to investigate the optimum parameters suitable for the process to obtain the optimum conditions for the granulation, total removal as well as particle size of the study.

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