Recovering Zinc from electroplating wastewater by crystallization in a pellet reactor

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Abstract. A pellet reactor (PR) was used to investigate the ability for zinc recovery from electroplating wastewater. The pellet reactor is a fluidized bed reactor, in which the nucleated precipitation of heavy metals occurred on the surface of seeding material. The zinc removal efficiency was 75% at molar ratio \([\text{CO}_3^{2-}] / [\text{Zn}^{2+}]\) of 2.5, the flowrate of 16 L/h, sand’s diameter of 0.25 – 0.5 mm, and sand’s mass of 50 g. The elemental analysis of zinc carbonate and zinc hydroxide crystallization was analyzed by X-ray energy dispersive spectrometer (EDS) and the surface was characterised by Scanning electron microscope (SEM) to get the morphological observation of the pellets after 38-day operation. This study demonstrated that the fluidized bed reactor can be considered a feasible method for zinc removal efficiency from electroplating wastewater to achieve sustainable development.

Keywords: zinc recovery; pellet reactor; crystallization; electroplating wastewater.

1. Introduction

Environmental protection has been concerned in Vietnam due to rapid industrialization development, in which environmental pollution caused by wastewater is one of the most important issues that needs to be considered. In particular, plating industry wastewater contains certain toxic substances such as chromium, nickel, copper, zinc, cyanide ... which adversely affect harmfully aquatic environment if not being well treated before discharging. This problem not only affects the quality of the water resource, but also damage to the human health such as cancer, cholera, diarrhea and typhoid [1]. So far, there have been many methods of heavy metals removal in wastewater such as: coagulation [2], ion exchange resin, precipitation, biological methods [3], adsorption [4]... In reality, these techniques are affected by the following factors: operation cost, toxic sludge production, removal efficiency, easy or complex operation [5]. Some previous studies mentioned that pellet reactor for metal recovery has these advantages like low sludge formation (dry pellets), a small footprint, less chemical usage, and no sludge handling [6]. The pellet reactor was used to remove hardness [7,8], fluoride [9,10], phosphate [11], heavy metals [12,13]. By using fluidized bed with quartz sand, the calcium hardness could be removed with 86% when the reactor was operated with the optimum conditions such as flowrate of 60 L/h, the seeding height of 0.5 m, pH of 9.5, seeding material size of 0.2 -0.4 mm, and recycle ratio of 60% [8]. Similarly, Tran et al., 2015 showed that by using pellet reactor as the pretreatment method, the removal
efficiency of calcium and nickel from the wastewater could be achieved with 74% and 94.4%, respectively to reduce ion exchange membrane scaling potential and enhance the longevity of electrodialysis bipolar membrane system [14]. In addition, Aldaco et al., 2007 optimized the operational parameters to get the highest calcium and heavy metal removal efficiency and used mathematic model to see the kinetic of seeding material size growth in the pellet reactor [10]. Moreover, the reactor network-oriented model was denoted for calcium phosphate precipitation to validate with experimental calcium phosphate precipitation efficiency [10]. In practice, this is a reactor with a height of 5 to 10 m and a diameter of 1.5 to 3 m, containing seeding material such as garnet sand from 0.2 to 0.6 mm. The seeding materials become fluidized when the inlet water a is pumped upward at a suitable superficial velocity. In the pellet reactor, crystallization occurs on the surface of common used silica sand. In this zone, the water is mixed with a caustic reagent (NaOH or Ca(OH)₂). After crystallization on the surface, the pellets become heavier (to a maximum pellet diameter of 1 mm), then sink to the bottom of the reactor, from where they are regularly discharged and replaced by fresh seeding material.

In this study, the heavy metals removal and recovery from electroplating wastewater using pellet reactor were investigated with precipitation/crystallization process using Na₂CO₃ chemicals. By adding Na₂CO₃ together with the inlet water from the bottom of the reactor, more ZnCO₃ and Zn(OH)₂ are covered on seeding material leading the bigger size, having a higher sedimentation velocity, and will be extracted at the reactor bottom.

\[
\begin{align*}
\text{Na}_2\text{CO}_3 & \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \\
\text{Zn}^{2+} + \text{CO}_3^{2-} & \rightarrow \text{ZnCO}_3 \downarrow \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 \downarrow \\
\text{ZnCO}_3 + \text{sand} & \rightarrow \text{nucleated precipitation} \\
\text{Zn(OH)}_2 + \text{sand} & \rightarrow \text{nucleated precipitation}
\end{align*}
\]

Optimizing parameters affecting treatment efficiency such as flow rate, influent pH of wastewater, (CO₃²⁻)/(Zn²⁺) molar ratio, seeding mass were studied. The surface of pellets was examined by SEM microphotography to get the morphological observation. Finally, the zinc removal and recovery efficiency with the real wastewater in long-time operation was investigated to see the technical feasibility in electroplating wastewater treatment.

2. Material and methods

2.1. Materials

Wastewater for experiment was taken from the electroplating company (Binh Duong province) with the influent concentration of Zn²⁺ of 30 - 120 mg/L, pH from 4-5 and COD of 307 – 399 mg/L. The synthetic water in this investigation was prepared by adding ZnCl₂.2H₂O (China) into the water to get the initial zinc concentration of 30 mg/L. Sodium carbonate (Na₂CO₃. H₂O) (China) was used as an agent of crystallization reaction to inject to the pellet reactor by peristaltic pumps TRIW 8800-2004 and Labor-Schlauchpumpe PLP 66. Sand was washed and sieved with size of 0.25 – 0.5 mm for a seeding material.

2.2. Pellet reactor

The lab-scale pellet reactor is columnar with conical reactors on the top, 150 mm height and a diameter of 16 mm (Figure 1). The wastewater was pumped upwards the fluidized bed through inlet water tube (d = 5 mm) without recirculation. At the same time, a mixture of Na₂CO₃ with a flow rate of 1 L/h was injected at a point 3 cm away from the bottom of the pellet reactor (D = 2 mm) to adjust the operational conditions as given in Table 1.

In this study, the synthetic water was used to run in the series of experiments to optimize the operational parameters (Table 1). The real electroplating wastewater was used in the long-term experiment to see the technical feasibility in zinc removal and recovery. Every run of experiment was operated 6 hours
continuously. Samples of the effluent were taken at 60 min intervals, and the value of efficiency was the average of 3 times taking sample. These three samples are at 4 h, 5 h, and 6 h running to make sure the stability of the reactor. Zinc concentration was analyzed by with 797 VA Computrace for Voltammetric Trace Analysis (Metrohm AG, Switzerland). The zinc concentration was analyzed with the filtered and non-filtered samples. The non-filtered sample included discrete precipitation of Zn$^{2+}$ and dissolved Zn$^{2+}$ ion which did not crystalize on sand while the filtered sample existed dissolved Zn$^{2+}$ ion.

The surface morphology of pellets was analyzed by scanning electron microscopy (SEM) (FESEM S4800) (Hitachi, Japan) and elemental analysis was performed using an X-ray energy dispersive spectrometer (EDS) (HORIBA H-7593 (ENGLAND)) with 10 kV accelerating voltage.

3. Results and discussion

3.1. Effect of superficial velocity on zinc removal efficiency

The effect of superficial velocity (SV) on zinc removal performances was studied by changing from 60 m/h to 80 m/h. Correspondingly, the flowrate increased from 12 to 16 L/h and the hydraulic retention time decreased from 1.8 to 1.13 min, respectively. These experiments were carried out by keeping pH at 8, the $[CO_3^{2-}]/[Zn^{2+}]$ molar ratio of 2 and sand mass of 40 g. The zinc removal efficiency increased
with the increase in superficial velocity from 60 to 80 m/h (Figure 2). Since the superficial velocity increased, the percentage of expanded bed raised from 70 cm to 130 cm, respectively. When the porosity of the expanded bed increased, there were more surface area for the precipitation attached on the sand. This led to an increase in the zinc removal efficiency from 17.2% to 46.7% with the non-filtered samples. However, it can be seen that the increase in filtered samples was not significant due to the occurrence of homogeneous crystallization.

When sodium carbonate was injected into the pellet reactor, the precipitation of heavy metals occurred with two types: nucleated precipitation and discrete precipitation. The nucleated precipitation was coated on the sand surface while discrete precipitation (fine particles) referred to occur in the bulk solution. Since the discrete precipitation as fine particle would be gone out of the reactor, the filtered removal efficiency was not considered significantly [15]. The optimized conditions was chosen based on the non-filtered removal efficiency. In this study, the precipitation of zinc carbonate or zinc hydroxide took place not only on the surface of the seeding material but also in the solution, which are both homogeneous and heterogeneous processes. Figure 2 showed that the zinc removal efficiencies of filtered and non-filtered samples were 17.2% and 56.1% (SV 60 m/h); 34.9% and 63.2% (SV 70 m/h); 46.7% and 60.2% (SV 80 m/h), respectively. These results indicated that when increasing the superficial velocity, the production of fine particles (discrete precipitation) in the effluent decreased, most of ZnCO$_3$ and Zn(OH)$_2$ precipitation occurred on the surface of the sand (nucleated precipitation) under conditions of the increasing superficial velocity. Although the higher superficial velocity, the better the non-filtered removal efficiency, in this study, if the flowrate increased over 16 L/h, the seeding material was washed out of the reactor, the effect of higher superficial velocity was not studied. Therefore, the optimum superficial velocity was chosen at 80 m/h corresponding with the flowrate of 16 L/h.

![Figure 2. Influence of the superficial velocity on Zinc removal efficiencies.](image)

### 3.2. Effect of pH of wastewater on Zinc removal efficiency

To investigate the effect of pH on zinc removal efficiency, the pH was adjusted from 7 to 10, other parameters such as flowrate, the molar ratio of carbonate and zinc, mass of sand were kept constant with the value of 16 L/h, 2 and 40 g, respectively.

During pellet reactor treatment, two reactions occurred:

\[
\text{Zn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{ZnCO}_3 \quad \text{with } K_{sp} = 3.10^{-17} \text{ at } 25^\circ\text{C} \quad [13] \quad (1)
\]

\[
\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad \text{with } K_{sp} = 1.46.10^{-10} \text{ at } 25^\circ\text{C} \quad [13] \quad (2)
\]

Zinc precipitates as ZnCO$_3$ and Zn(OH)$_2$ are formed when the saturation degree exceeds the solubility product constant $K_{sp}$. According to [13], the $K_{sp}$ of hydroxide was smaller than that of carbonate, therefore, Zn(OH)$_2$ is less soluble than ZnCO$_3$, and so precipitated before ZnCO$_3$. In this study, sodium carbonate was injected into the reactor, zinc was combined with carbonate, forming not only zinc carbonate but also zinc hydroxide. When pH increased from 7 to 10, the zinc removal performance increased from 19.1% to 48.6% for non-filtered samples. However, the efficiencies of filtered samples were decreased from 64.8% to 53.7% with the increase pH from 8 to 10 (Figure 3). This proved that
when pH increased, CO$_3^{2-}$ and OH$^-$ concentration increased, that led to higher supersaturation and more precipitation of ZnCO$_3$ and Zn(OH)$_2$ occurred as the nucleated precipitation. This meant that most of ZnCO$_3$ and Zn(OH)$_2$ precipitated on the sand surface as pH increased. Therefore, it can be concluded that pH 10 was the optimum condition to get the high zinc removal efficiency in both filtered and non-filtered samples.

3.3. Effect of [CO$_3^{2-}$]/[Zn$^{2+}$] molar ratio on Zinc removal efficiency

The effect of [CO$_3^{2-}$]/[Zn$^{2+}$] molar ratio was carried out to determine the suitable ratio required for optimal zinc removal efficiency by Na$_2$CO$_3$ solution Figure 4. The flowrate was 16 L/h, mass of sand was 40 g, and pH was kept at 10. In theory, the precipitation of ZnCO$_3$ was achieved theoretically as the molar ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] = 1. However, when running the pellet reactor with continuous mode, the hydraulic retention time HRT was short with 1.13 minutes (corresponding with flow rate of 16 L/h); therefore, it is difficult to get 100% precipitation at molar ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] =1. With this reason, in this study, the effect of this molar ratio was investigated.

Figure 4 showed that the increase in [CO$_3^{2-}$]/[Zn$^{2+}$] led to the increase in the zinc removal efficiency. As the molar ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] increased, more carbonate was added, the equation: CO$_3^{2-}$ + H$_2$O $\rightarrow$
HCO$_3^-$ + OH$^-$ shifted to the left; therefore, increased the amounts of carbonate and hydroxide in the solution. With higher CO$_3^{2-}$ and OH$^-$ concentration, higher supersaturation, which in turn achieved fast primary nucleation. Nevertheless, when the ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] was higher than 3, the zinc removal efficiency seemed to be lower (Figure 4). According to [9], nucleation took place only heterogeneously on the sand at low supersaturation, while, both homogeneous and heterogeneously nucleation occurred at higher supersaturation, which was proved by the obtained results of 8% of fines formation with a fluoride concentration of 100 mg/L, but 51% with a concentration of 300 mg/L. The optimum ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] was chosen at 2.5 to achieve the high zinc removal efficiency. In conclusion, the effects of initial pH and [CO$_3^{2-}$]/[Zn$^{2+}$] molar ratio on the precipitation of zinc compound were significant due to their effects on the supersaturation level which is the thermodynamic driving force behind precipitation and crystallization.

3.4. Effect of sand mass on Zinc removal efficiency

Figure 5 presents the effect of sand mass in pellet reactor on zinc removal efficiency at a flowrate of 16 L/h corresponding with HRT of 1.13 min. The mass of sand was changed from 40 g to 60 g, pH was kept at 10 and the molar ratio of [CO$_3^{2-}$]/[Zn$^{2+}$] was 2.5. It is observed that when seeding mass increased in the pellet reactor leading more places for nucleation, the efficiency of zinc removal also increased. When sand mass increased from 40 to 50 g, the efficiency increased from 78.9% to 83.6% with filtered samples and 62.3% to 79.6% with non-filtered samples; however, the sand mass increased more to 60 g, there was a decrease in zinc removal efficiency from 83.6% to 73.1%. This is due to with same superficial velocity but higher sand mass, the fluidized bed could not be expanded leading to less contacting surface area, decreasing the nucleation potential. From these above results, the sand mass of 50 g was the optimized value to obtain both non-filtered and filtered zinc removal efficiency.

![Figure 5. Effect of seeding material mass on zinc removal efficiency.](image)

3.5. Long-term operation for zinc recovery

In order to investigate whether the long-term operation feasible or not, recovery experiment was carried out for more than one month with 2 stages with the optimum parameters: the ratio of chemicals [CO$_3^{2-}$]/[Zn$^{2+}$] of 2.5, the flowrate of 16 L/h, pH of 10, the sand mass of 50 grams with the real electroplating wastewater. In the first stage within 30 days, the initial concentration was 30 mg/L, the removal efficiency was around 78%. In the second stage, the zinc concentration was increased to 120 mg/L to test the zinc removal and recovery feasibility of the pellet reactor with higer concentration. The efficiency decreased slightly to 60%. After 38-day operation, the change of sand weight before and after the treatment process (by dissolved in HNO$_3$ 1N solution) was showed in Table 2, in which the increase in mass of sand proved that the precipitation of zinc occurred on the sand.
As seen in Figure 7, the sand was larger and the mass increased significantly. Table 2 showed the heavy metal precipitation on the sand proved by the increase in sand’s mass. After washing with acid solution, the mass of the origin sand just reduced little from 2 g to 1.96 g, because some components in the sand were dissolved in acid, however, with the treated sand, the increase in mass was 0.61 g after stage 1 and 1.66 g after stage 2, which proves that after the recovery process, the zinc carbonate and zinc hydroxide were crystallized and adhered to the surface of sand grains. With 50g used in the pellet reactor, zinc could be recovered with mass of 26.25 g within 8 days when the initial concentration was 120 mg/L.

| Table 2. The change in mass of sand before and after running in the pellet reactor |
|---------------------------------|---------------------------------|-----------------|
| Mass before dissolved in acid, g | Mass after dissolved in acid, g | Difference, g   |
| Initial sand                    | 2                               | 1.96            | 0.04            |
| Sand after 1st stage            | 2                               | 1.39            | 0.61            |
| Sand after 2nd stage            | 2                               | 0.34            | 1.66            |

3.6. Microscopic analysis

The color and size of pellets after and before heavy metal removal were different, the color of used pellet was whiter (Fig. 7). Therefore, it is clear that ZnCO$_3$ and Zn(OH)$_2$ were precipitated and covered on the surface of the sand. Figure 8 showed SEM and EDS microphotographs of the pellets before and after the crystallization process. With SEM, there were changes in the morphology of the pellets during the experiments: some precipitates appeared on the sand. The difference in elemental percentage of sand
before and after recovery experiments confirmed Zn elements were present on the surface of the sand. The relative atomic percentage of Zn increased from 0 to 56.22 % (w/w), while the percentage of Si decreased from 31.15 to 2.7% (w/w). Moreover, it was demonstrated that the recovered zinc had a purity of about 56 wt %. The atomic percentages of zinc, carbon, and oxygen were 23.87%, 12.76%, and 60.45%, respectively, which can easily satisfy the molar ratios (1:1:3) in the zinc carbonate compound (ZnCO$_3$). Moreover, the rest percentage of zinc and oxygen could be counted in the contribution of zinc hydroxide (Zn(OH)$_2$). Therefore, it can be confirmed that the mixture of ZnCO$_3$ and Zn(OH)$_2$ probably attached and crystallized on the sand surface.

![Figure 8. SEM (x 500) and EDS of pellets before (a) and after treatment (b) with sand.](image)

### 3.7. The feasibility of pellet reactor in zinc removal from wastewater

In view of the natural resource scarcity, heavy metal recovery and wastewater treatment by a pellet reactor is very interesting concerning sustainability. The optimized operational conditions were obtained at: the ratio of chemicals [CO$_3^{2-}$] / [Zn$^{2+}$] = 2.5; the flowrate of 16 L/h; pH of 10; sand mass of 50 grams, the heavy metal removal efficiency was 75% when the initial concentration of 30 ppm. The high removal efficiency was up to 75% without sludge production shows that the obtained environmental benefits of the pellet reactor were resource recovery and wastewater treatment before being discharged. In this study, the synthetic wastewater was used for optimizing the operational conditions and the real electroplating wastewater was tested for long-term experiment. The results showed that the zinc removal efficiency from real wastewater was decreased slightly compared to that of synthetic wastewater. Therefore, it is believed that even though there were other interfering ions in the real wastewater and maybe with the scale up of the column for full-scale application, the effectiveness of the heterogeneous crystallization process still remains if the optimum conditions are controlled well. By recovering zinc from wastewater, the effluent concentration decreases, contaminant loading is reduced, and the quality of the surrounding aquatic environment is improved. Moreover, zinc is recovered on the sand so it is easy to collect and reuse for other production. Therefore, zinc recovery as zinc carbonate and zinc hydroxide by fluidized bed reactor can be considered a feasible method to achieve sustainable development.
4. Conclusions
A feasible method was proposed to remove and recover zinc from wastewater by a pellet reactor. A pellet reactor was used to precipitate and crystallize the zinc carbonate and zinc hydroxide on the sand. The optimized conditions were obtained at: the ratio of chemicals \([\text{CO}_3^{2-}] / [\text{Zn}^{2+}] = 2.5/1\); the flowrate of 16 L/h; pH of 10; sand grains' mass of 50 grams, the heavy metal removal efficiency was 75% ± 0.4% when the initial concentration was 30 ppm. After treatment, \(\text{Zn}^{2+}\) concentration in the effluent water nearly meets Vietnam discharge standard QCVN 40: 2011/ BTNMT for industrial wastewater. The heavy metal recovery mass was 26.25 after 8 days with the initial concentration of 120 mg/L. To summary, the pellet reactor is technically and economically feasible for removing and recovering the heavy metal from wastewater with optimum parameters. This method helps recovering heavy metal from the wastewater, reducing the amount of sludge discharged into the environment and exploiting the natural resource for raw materials supply.

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