

## HEAVY METAL REMOVAL FROM WASTEWATER BY PELLET REACTOR

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### ABSTRACT

Wastewater from plating industry with high concentration of heavy metal has been concerned as a serious problem for environment. Therefore, it is necessary to find an efficient method to treat this kind of wastewater before being discharged into the environment. In this paper, the aim was to evaluate the feasibility of a pellet reactor to treat the plating wastewater. The hydraulic retention time, the initial pH and molar ratio of carbonate to heavy metal was investigated to optimize the heavy metal removal efficiency in the pellet reactor. The results showed high removal efficiency in the pellet reactor could be achieved 65%, 71% and 67% of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  with ratio of  $CO_3^{2-}$ /metal of 2.5, flow meter of wastewater of 16 L/h, initial pH of 9.5, the mass of sand of 50 gram. After pellet reactor treatment, the seeding materials was analyzed with SEM microphotograph and elemental analysis to see the different morphology, element atomic percentage of the sand before and after pellet reactor.

**Keywords:** Heavy metal removal; precipitation; crystallization; pellet reactor; wastewater treatment; Fluidized bed reactor

### 1. INTRODUCTION

Water plays a very important role in the process of metabolism, but now water resource has been declining in quality and quantity. The industry development, the fast growth of population and the expanding of urban area have increased the pressure on this resource. In particular, heavy metal pollution is an extremely urgent problem not only in Vietnam but also in many parts of the world.

Heavy metal pollution in water is not only caused by industrial and domestic wastewater but also from other sources (transportation, coal burning, waste incineration, fertilizer, pesticide, etc.). Particularly in Vietnam, the water pipes are too old, so they are likely to be corroded, causing pollution of heavy metal (Zn, Pb, Cd...) into the water environment. Heavy metals, either in gaseous or solid waste, cause water pollution by settling into river, lake or ground surfaces and being absorbed by rainfall into the aquifer.

Various methods such as precipitation [1-2], adsorption [3-4], ion exchange [5] and

membrane separation [6] can be used to remove heavy metal from wastewater and prevent environmental pollution when discharged. Among them, precipitation was common used by using a mixing tank to add the chemical to have precipitation process, then remove the solid by sedimentation. However, this process has many drawbacks such as solid waste disposal with high water content, large footprint and operation skills [7].

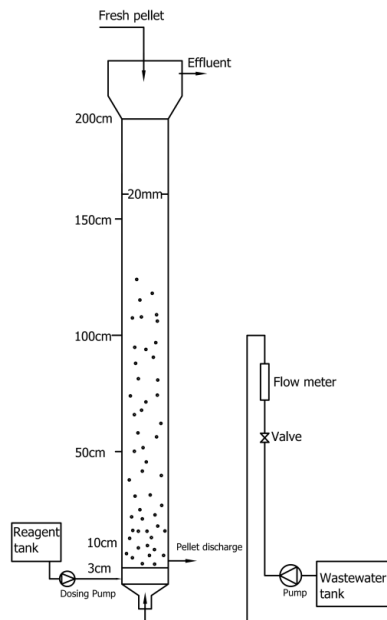
In recent years, many researchers studied the new technology to overcome the aforementioned disadvantages. Mahvi et al, 2005 [8] has proven the pellet reactor have the feasibility in removing hardness (calcium and magnesium) from water for drinking water. Similarly, phosphate recovery [9], fluoride and metal removal [7, 10] was also studied and high efficiency was achieved. Zhou et al. (1999) found that the metal removal efficiency by the pellet reactor could attain 92-95% depending on the initial concentration at the optimum pH [7]. Mahvi et al. (2005) noticed that using a pellet reactor to have crystallization would overcome many

disadvantages of convention precipitation process by mixing with chemical and sedimentation such as: smaller size, compact model, no solid waste production with large content of water, and crystal grains recovery in case of calcium removal [8]. In recent years, Procorp Enterprises LLC has used a pellet reactor to recover phosphate from wastewater to reduce the amount of natural resource for fertilizer production [9].

Due to the demand of wastewater treatment, the study was proposed to use a pellet reactor to remove the zinc, copper and cadmium by changing the initial pH, molar ratio of carbonate to heavy metal, mass of seeding material and hydraulic retention time was studied to optimize the heavy metal removal of pellet reactor.

## 2. MATERIALS AND METHODS

Synthetic wastewater was prepared by adding  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  into tap water, resulting in 30 ppm of initial concentration of heavy metal.



**Fig.1.** A pellet reactor for heavy metal removal

In this study, a pellet reactor with a height of 1.5 m and a, 16 mm diameter was used to study the effect of pH and superficial velocity on the precipitation efficiency. The fluidized bed was filled with garnet sand (30 - 50 g, 250 - 450  $\mu\text{m}$ ). Wastewater was pumped from the

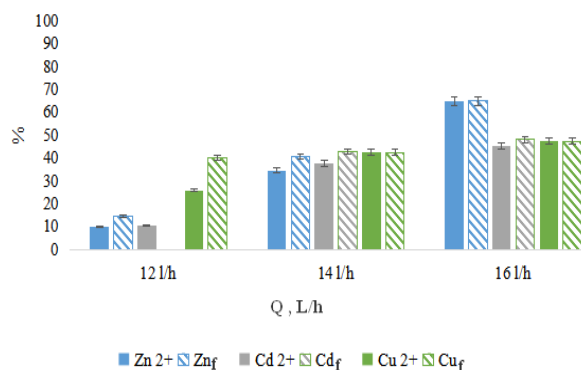
bottom to the top with a flow rate from 12 to 14, 16 L/h, a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  with a flow rate of 1 L/h was injected from the bottom of the pellet reactor to adjust the pH and ratio of  $[\text{CO}_3^{2-}]/[\text{Me}^{2+}]$  of 1.5 - 3. The alkalinity dose was varied to investigate the effect of pH from 8 to 9.5 to get the precipitation and the mass of seeding was studied from 30 to 50 g.

Samples of pellet reactor effluent were taken at every 1h intervals thereafter in 6h continuous. Heavy metal concentrations ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ) for samples collected from pellet reactor treatment using Spectrum Instrument (747 Professional VA). Surface morphology of sand before and after pellet reactor was analyzed by scanning electron microscopy (SEM) (FE SEM S4800 HITACHI, JAPAN) and elemental analysis was performed using an X-ray energy dispersive spectrometer (EDS) (EDX H-7593 HORIBA ENGLAND).

## 3. RESULTS AND DISCUSSIONS

### 3.1. Effect of flow rate on heavy metal removal

Three pellet reactor experiments were conducted continuously for 6 h by changing the flow rate from 12 L/h to 16 L/h, pH of 9.5 and the ratio of  $[\text{CO}_3^{2-}]:[\text{Me}^{2+}]$  of 2.5 and seeding mass of 30 g was kept constant. The flow rate was not adjusted lower than 12 L/h and higher 16 L/h since seeding bed was not expanded if the flow rate was small and seeding material was out of the reactor with the high flow rate.



**Fig.2.** Heavy metal removal efficiency in the pellet reactor under the effect of flow rate

In the wastewater, carbonate was not present in the water, therefore, sodium carbonate was added into the water to enable the reaction  $Me^{2+} + CO_3^{2-} = MeCO_3$  and  $Me^{2+} + 2 OH^- = Me(OH)_2$

In Fig.2, when the flow rate increased from 12 L/h to 16 L/h, the average precipitation efficiency of heavy metal increased from about 10% over 40% to 50%.

Normally, when the flow rate increased, the hydraulic retention time decreased, leading to the decrease in the removal efficiency. However, in this study, the results was opposite. This can be explained by the surface area of seeding bed. When the flow rate was not high with 12 L/h and 14 L/h, it was enough force to make the sand fluidized, so that surface area of seeding material was not high for the precipitate attached on the sand. When increase the flow rate to 16 L/h, the bed was expanded to have enough surface area, the precipitate attached on the sand and the removal efficiency increased.

Fig. 2 also showed the heavy metal removal performances of both filtered and unfiltered samples were not different when flow rate increased to 16 L/h. These results indicated that there was nearly no production of fine particles in the effluent. Most of metal precipitation occurred on the surface of the sand.

### 3.2. Effect of molar ratio of carbonate to heavy metal on heavy metal removal

An increase in the carbonate-to-heavy metal molar ratio from 1.5:1 to 3:1 led to the increase in the supersaturation level. This corresponds to an increase of the average removal efficiency; since supersaturation is the dynamic driving force for precipitation and crystallization.

According to Zhou et al. (1999), when the ratio was higher than 4/1, the quality of the effluent was low and when the ratio was higher than 2/1, the effluent concentration of metal increased [7].

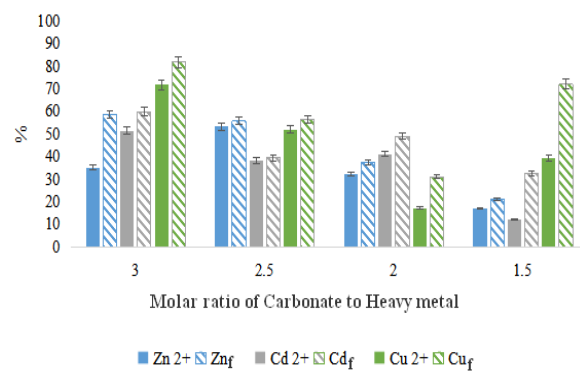


Fig.3. Heavy metal removal efficiency in the pellet reactor under the effect of molar ratio

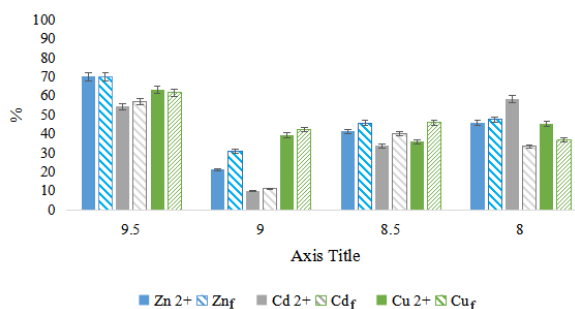
However, with this study, Fig. 3 showed that at the ratio of 1.5/1 and 2/1, the effluent concentration of heavy metal was high. The total effluent metal concentration was much greater than the soluble concentration, this phenomenon was caused by the formation of fine that did not adhere to the sand due to low supersaturation (insufficient amount of  $CO_3^{2-}$  and  $OH^-$ ). Similarly, when this ratio was high (3/1) leading to high concentration of  $OH^-$  and  $CO_3^{2-}$  in pellet reactor, the total metal concentration was still high but low in soluble concentration of heavy metals. This means the heavy metal was discretely precipitated before attaching to the grains of sand to form a nuclear precipitation. According to Aldaco et al. (2005), nucleation took place only heterogeneously on the sand at low supersaturation, while homogeneous nucleation tended to happen at higher supersaturation [10]. But with this study showed that homogeneous nucleation happened even at both low and high supersaturation.

At ratio of 2.5/1, the heavy metal efficiency was high, and the pellet reactor worked quite stably over time, the difference between the total metal concentration and the soluble metal concentration was not much. Nucleation took place only heterogeneously on the sand. Therefore, the ratio of 2.5/1 was chosen as the optimal condition for pellet reactor operation.

### 3.3. Effect of initial pH on heavy metal removal

The pH plays an important role in determining the removal efficiency because pH affects precipitation process in the fluidized bed reactor. In Fig 4, we see that when the pH increased, the metal removal efficiency increased more significantly. Alkalinity of water was produced by ions  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . pH of the wastewater was in the range of 8-9.5, the alkalinity of water exists 2 ions  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . When pH in water increased to 8.3, bicarbonate ions became carbonate ions and when pH was 10.2, almost all bicarbonate ions become carbonate. Therefore, the pH was studied in the range of 8, 8.5, 9, 9.5 in order to have  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  in the wastewater. When the pH increases,  $\text{HCO}_3^-$  converts to  $\text{CO}_3^{2-}$ , which enhanced the precipitation efficiency.

Fig 4 showed that the pellet reactor has quite high performance of Zn and Cd removal at pH = 9.5 than at pH = 8. At pH = 8, cadmium carbonate precipitated but precipitated did not attach to the seeding because the total concentration of cadmium (including dissolved cadmium) in the effluent was much higher than that of the filtered cadmium concentration. The total concentrations of Zn and Cu and the concentration after the filtration was not much different, but the efficiency of the whole process was not high.



**Fig.4.** Heavy metal removal efficiency in the pellet reactor under the effect of initial pH

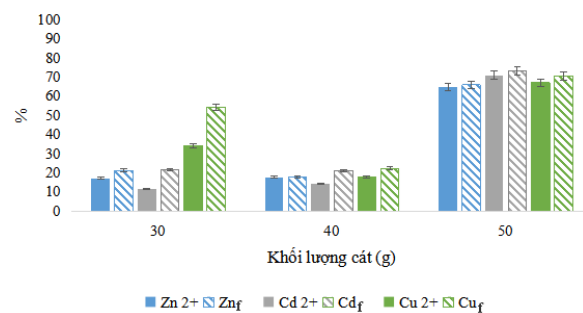
At pH = 8.5, and pH = 9, the precipitate occurred as fine particles that did not adhere to the material particles with a small amount

because the total metal concentrations and the metal concentrations after filtration were not much different but the efficiency is not high.

At pH = 9.5, the heavy metal efficiency was high because at this pH, most bicarbonate ions converted into carbonate ions and precipitated with metal ions as metal carbonate, the difference in metal concentration between filtered and unfiltered samples was not much, that means the precipitate adhered to the surface of seeding material and became the crystals on the sand. Therefore, the optimal pH was chosen at 9.5.

### 3.4. Effect of seeding mass on heavy metal removal

According to Fig. 5, with the sand weight of 30g and 40g, the efficiency of heavy metal removal was low. When the initial concentration of 30 ppm, with this amount of sand, surface area was not enough to precipitate completely on the surface, which resulted in increase in the effluent concentration. The difference between the concentration of total metal and the concentration of dissolved metals was quite large.



**Fig.5.** Heavy metal removal efficiency in the pellet reactor under the effect of seeding mass

With 50g of sand and 30 ppm initial concentration, the metal removal efficiency was quite high, especially Cd removal efficiency of 70%.

From the aforementioned results, optimal weight of sand of 50g was chosen. When running the pellet reactor with the flow rate of

16L/h, pH of 9.5, mass of 50 gram, the difference between total metal concentration and dissolved metal concentration was not large, the Zn, Cd, Cu removal efficiency was high with nearly 70%. This proved that pellet reactor had feasibility in removing heavy metal from wastewater with high performance, no sludge production, simple operation with one reactor.

### 3.5. SEM of seeding material

Garnet sands as seeding before and after the pellet reactor were washed with distilled water, dried and analyzed by SEM.

SEM images (Fig.6) showed that the heavy metal precipitation attached on the seeding and became crystals. Therefore, it could be concluded that with the influent concentration of heavy metal ( $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ), the nucleation happened only on the seeding.

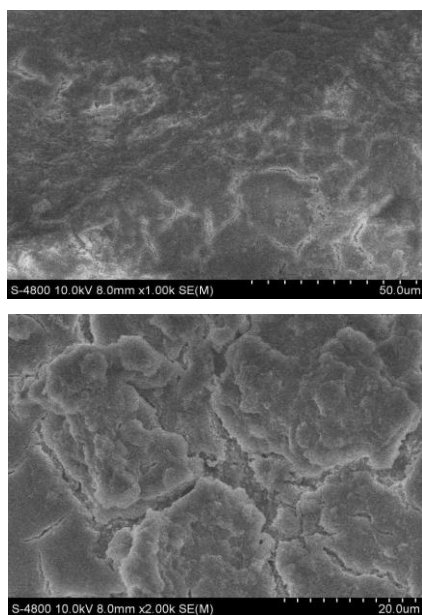


Fig.6. SEM of seeding before and after pellet reactor

Table 1. Elemental analysis results (atomic %) of sand before and after pellet reactor

Element	Atomic % (Before treatment)	Atomic% (After treatment)
C K	74.08	41.41
O K	6.50	45.67
Al K	19.09	1.71
Si K	0.34	4.79
Cu L	0.00	3.71
Zn L	0.00	1.42
Cd L	0.00	1.29
Total	100	100

This was confirmed by the elemental analysis listed in Table 1: the relative percentage of  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  increased from 0 to 3.71%, 1.42% and 1.29%, respectively. This means the heavy metal from wastewater precipitated and attached on the surface of seeding material.

### 4. CONCLUSION

These results proved that pellet precipitation in a fluidized bed was viable for removing the heavy metal ( $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ) potential from wastewater without formation of fine particles. The pellet reactor had the capacity to remove  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  with:  $66 \pm 18\%$ ;  $71 \pm 7.6\%$ ; and  $67 \pm 14\%$ , respectively from the wastewater at the optimal flow rate of 16 L/h, initial pH of 9.5, the molar ratio  $[CO_3^{2-}]/[metal]$  of 2.5 and the seeding mass of 50g.

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