RECOVERY OF NICKEL FROM INDUSTRIAL WASTEWATER BY HOMOGENEOUS FLUIDIZED-BED GRANULATION: EFFECTS OF INFLUENT NICKEL CONCENTRATION, CO_3:Ni RATIO AND PH OF THE PRECIPITANT

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ABSTRACT

Nickel removal and recovery from industrial wastewater are beneficial to minimize its toxicity in the environment. Due to nickel's increase in demand, these may be able to slowly contribute to the economical profit of the industry in the future. The study was carried out in order to determine the effects of varying influent nickel concentration, molar ratio of CO_3:Ni and pH of carbonate precipitant in removal and granulation of nickel ion in wastewater using homogeneous fluidized-bed granulation. Through the use of laboratory scale fluidized-bed, continuous process was conducted producing different effects driven by supersaturation. The removal of nickel ranges from 91-99% at different conditions. To attain low effluent concentration (2.3-4.8 ppm), an excess concentration of carbonate is needed. Molar ratio of 1.5-2.5 is suggested for influent nickel concentration of 100-300 ppm attaining 97.39 - 98.83% removal. The best operating parameters in forming nickel hydroxycarbonate granules are 200 ppm influent nickel concentration with 2.0 molar ratio at pH 10.7 producing 98.83% removal and 97.76% granulation with 8.59 effluent pH.

Keywords: nickel, nickel carbonate, nickel carbonate hydroxide, fluidized-bed, granulation, homogeneous process

1. Introduction

Nickel is usually applied in decorative, engineering and electroforming industries due to its high corrosion and temperature resistance. It is desirable in combining with other metals to form mixtures such as alloys and compounds in forming various usable products. However, its broad usage and industries' growing interest may later on lead to problems in health and environment due to its toxicity at higher concentrations.

Chemical precipitation is one most common way to remove heavy metals such as nickel, with hydroxide or sulfide as the precipitants. It is widely used because of its simple usage and low chemical cost. Though, the down side of this treatment method is the formation of sludge that may increase its cost due to dewatering.

The use of fluidized-bed is receiving wide attention in most of the heavy metal removal studies (Guillard & Lewis, 2002; Lee & Yang, 2005; Zhou et al., 1999). This became popular because of its low sludge formation in the treated effluent. This is usually performed using heterogeneous reaction wherein the metal is made to react with the precipitant in the surface of seeding materials such as quartz and silica sand. However, in this study, removal of nickel was conducted by homogeneous granulation fluidized-bed, by reaction of nickel ion with carbonate ion in supersaturation state to form granules without using any seeds.

The study aims to determine the effects of formation of granules by varying three operating parameters: influent nickel concentration (100ppm, 200ppm, 300ppm and 400ppm), CO_3:Ni molar ratio (2.0, 1.0 and 0.5) and pH value of precipitant (10.5, 10.8 and 11.0). The formation of these granules will help the removal of nickel from synthetic wastewater. Sizes and number of the granules formed will also be measured at different factors. Furthermore, the composition and characterization of the formed granules were analyzed using SEM, EDS and FTIR.

2. Methodology

2.1. Influent solutions

Nickel solution was prepared using $NiSO_4 \cdot 6H_2O$ (99%) that was acquired from Shimakyu's Pure Chemicals and the precipitant solution was prepared using Na_2CO_3 from Panreac. Both solutions were dissolved in RO (reverse osmosis) water. The operating parameters were varied at 100ppm, 200ppm, 300ppm and 400ppm influent nickel concentrtaion, 2.0, 1.0 and 0.5 molar ratio (CO_3:Ni) and 10.5, 10.8 and 11.0 pH value of precipitant.

2.2. Fluidized-bed reactor

The 1.35L glass column with inner diameter of 4 cm and height of 100 cm was used as fluidized-bed reactor (FBR) for homogeneous granulation reaction. The reactor was filled with 0.5 cm diameter glass beads, packed at a static height of 4 cm. The rector is composed of three bottom inlets: for the reactants (wastewater and precipitant) and the recycled solution; and two top outlets: for the treated effluent and recycled solution. The FBR column is equipped with pH meter to monitor pH of the effluent and peristaltic pumps to control flow rates of influent solutions as well as the recycled solution.

2.3. Fluidized-bed granulation

The experiment was conducted in a continuous granulation method at room temperature. Generally, the nickel-containing wastewater and precipitant solution was pumped at the same flow rate of 25 mL/min onto the opposite sides at the lower end of the reactor in an upward direction. In addition, an average reflux rate of 60 mL/min was introduced in order to increase the residence time of the metal in the reactor, to keep the granules at fluidized state, and to further dilute the concentrated solution in the inlet of the reactor. To study the effect of every parameter, each parameter has been changed progressively keeping the other two constant to form nickel carbonate granules inside the FBR. To adjust the pH of the precipitation reagent, 0.12M HNO_3 (69%) from Panreac and 4M NaOH (98%) from Shimakyu's Pure Chemicals were added until the desired pH of the solution was achieved.

The pH measurements of the solutions in the FBR effluent were constantly monitored. Samples were obtained at the reflux level at the top of the reactor at different operation times, where half of the sample was filtered using 0.45 µm filters (0.45 µm GHP membrane, Pall). These were used to determine the nickel removal efficiencies. Effluent samples were subjected to AAS to determine the retained nickel concentration.

2.4. Effluent and granules analysis

Liquid samples obtained from the reactor at different time intervals were used for effluent nickel concentration analysis. Dissolved and total nickel concentration in the effluent were both determined by Atomic Absorption Spectrometer (AA Analyst 200, Perkin Elmer).
Total removal of nickel was obtained after filtration of fluidized treated wastewater, using the formula:

$$\%Removal = \frac{C_0 - C_D}{C_0} \times 100$$

where *% Removal* calculates the efficiency of the total removal of nickel ion concentration for the wastewater solution after filtration, *Co* is the initial nickel concentration in the synthetic wastewater, while C_D is the concentration of dissolved nickel after fluidized-bed treatment. To attain its efficiency, the dissolved nickel residual was measured after filtering the treated wastewater with the use of a 0.45-micrometer membrane filters.

All the formed granules contain nickel ions that were removed after the treatment. These granules are essential for the removal and recovery of nickel during wastewater treatment. The formula below shows the granulation efficiency using fluidized bed.

$$\%Granulation = \frac{C_0 - C_T}{C_0} \times 100$$

where *% Granulation* is the percentage of nickel granules concentration formed during the fluidization process, C_T represents the total nickel concentration of the effluent in the reactor.

After 72 hours of continuous run, granules formed in the FBR were retrieved and air-dried. The granules collected were subjected to sieve analysis for size distribution and were further characterized using scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and Fourier transform infrared (FT/IR-410 Jasco).

3. Results and discussions

3.1. Effect of influent concentration and molar ratio variations on heavy metal removal and granulation efficiencies

Granulation and removal efficiencies were affected by the change in influent nickel concentration and molar ratio of carbonate to nickel ion CO_3:Ni at operating time of 72 hours. An excess concentration of the precipitant is needed in order to produce granules due to the effect of supersaturation. Figure 1 shows the effect of increasing molar ratio at different influent nickel concentration. Increasing the molar ratio resulted in higher removal and granulation efficiencies, but this depends on the combination of different factors.

An increase in influent nickel concentration resulted in the formation of fines at the reflux level of the FBR, as proven by the study conducted by Lee and Yang (2005). They suggest that increasing influent metal concentration favors supersaturation; thus, resulting in higher tendency of producing fines. Accordingly, at higher influent concentration, the increase in removal efficiency is not as steep as that of lower influent concentration, forming parabolic-like curve as the molar ratio increases.

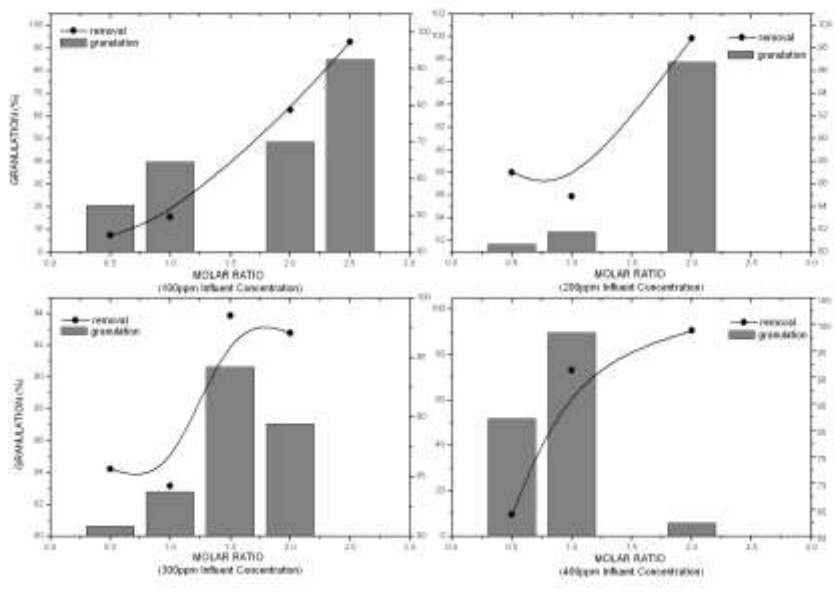

Figure 1: Effect of varying molar ratio and influent nickel concentration on nickel removal and granulation efficiencies

3.2. Effect of pH variation on heavy metal removal and granulation

Figure 2 shows nickel removal by varying molar ratio of the precipitant regardless of the influent concentration used. Increasing the molar ratio resulted in a pH value increase due to the high concentration of carbonate that made the solution more basic. Results show that higher removal efficiency was attained by increasing the pH value of the precipitant due to high granulation and precipitation rate. Although low removal efficiency (<50%) and greater number of fines were produced at pH >10.0, a continuous increase in removal percentage was attained as pH increases until it reached a value of 10.7 - attaining highest removal percentage at 98.83%. Thereafter, the removal efficiency decreased when the pH was increased further; this was the effect because at higher pH, $Ni(OH)_2$ predominates. In addition, due to the amphoteric character of $Ni(OH)_2$, it re-dissolves at increasing pH resulting in high supersaturation; thus, attracting nucleation and attrition.

Conversely, granulation efficiency was also affected by pH variation. As shown in Figure 2, granulation increased with pH change. Therefore, this indicates that at higher pH, more carbonate is being reacted with nickel forming more granules compared with lower pH, and supersaturation can be controlled up to pH 10.7. This means that the effluent from the wastewater treatment facility has to be neutralized after the precipitates were removed (Tai et al., 2006). In this experiment, the recommended pH value of the precipitant was kept at around 10.7 to 10.8 resulting in 97% to 99% removal efficiency with effluent pH 8.3 to 8.6.

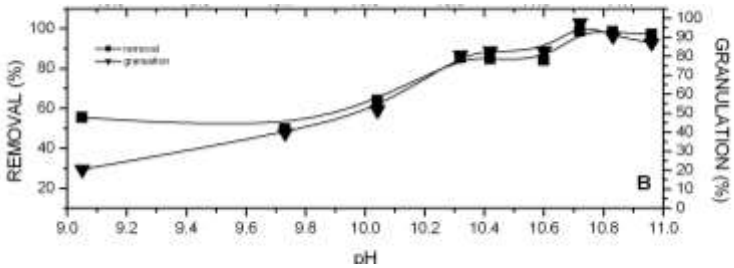

Figure 2: Effect of pH value on the removal of nickel

Shown in Table 1 are the recommended conditions for maximum results using pure nickel as wastewater. This indicates that among all the conditions used, 200 ppm influent nickel concentration with molar ratio of 2.0 and carbonate pH of 10.72 attained the highest removal efficiency at 98.83%.

Table 1: Highest efficiencies using pure nickel synthetic wastewater.

FACTORS			PERFORMANCES		
Synthetic wastewater concentration (ppm)	CO_3:Ni ratio	pH value	pH effluent	Granulation (%)	Removal (%)
200	2.0	10.72	8.59	97.76	98.83
300	1.5	10.8	8.31	90.65	98.51
100	2.5	10.8	8.6	84.8	97.39
300	2.0	10.96	8.53	87.07	97.08
400	1.0	10.32	8.02	89.75	91.38

3.3. FTIR, SEM and EDS analysis

The result of FTIR shows the presence of hydroxyl groups at the broad band 3447.13 cm-1 and carbonate group at ranges between 1596.77 cm-1 and 1555.31 cm-1. As expected, the formed granules were hydrated nickel carbonate. The sample formed smooth-surfaced and hollowed granules due to the fast reaction of carbonate and nickel in the system. Most of the formed granules were coarse having sizes between 0.2 mm and 2 mm.

The morphologies of the granules through SEM image were difficult to determine because the agglomeration of the precipitates was high. Also, the precipitates were hard to grow to become typical crystals. The agglomerates, which were composed of fines, might be due to the prolonging of the reaction time, collision of fines due to fluidization, and controlled supersaturation state in the reaction.

According to the EDS determination, the purity of the recovered nickel was around ~50 wt %. In addition, the atomic percentages of nickel, carbon and oxygen are, ~22%, ~21% and ~56%, respectively, producing $NiCO_3$ compound. The exact composition and the ratio of nickel to carbonate to hydroxide of the granules were not precisely established. Some parts of the surface of the precipitates were cracked when dried; this is probably due to friction and attrition between the granules.

4. Conclusions

Prolonging operation time produced more solid and stable form of nickel hydroxycarbonate granules. Increasing influent concentration, molar ratio and pH (up to 10.7) also increase removal, granule size and number, however this must be controlled to minimize effect of high supersaturation. For an influent nickel concentration of 100-300 ppm, molar ratios of 1.5-2.5 are suggested to attain 97.39 - 98.83% removal (2.3-4.8 ppm). The highest removal and granulation efficiencies were achieved using 200 ppm influent nickel concentration and 2.0 molar ratio at pH 10.7 producing 98.83% removal and 97.76% granulation with 8.59 effluent pH.

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