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Removal of nickel by homogeneous granulation in a fluidized-bed reactor

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HIGHLIGHTS

- Homogeneous fluidized-bed granulation process formed nickel carbonate hydroxide granules.
- Nickel removal of 98.8% and 97.8% granulation were reached at optimum conditions.
- 200 mg L^{-1} influent nickel, 2.0 [CO_3^{2-}:Ni^{2+}] MR and 10.7 precipitant pH as best condition.

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ABSTRACT

Heavy metal removal is a significant task that protects our water resources. Fluidized-bed homogeneous granulation process (FBHGP) was used to treat nickel containing wastewaters by recovering nickel in the form of nickel carbonate hydroxide granules with low moisture content rather than soft sludge. This study investigated nickel removal and recovery through HFBGP by determining the effects of varying influent nickel concentrations, [CO_3^{2-}: Ni^{2+}] molar ratios, and pH of the precipitant. This was conducted in a continuous process using a laboratory scale fluidized-bed reactor that determined the effects driven by supersaturation. The best operating conditions that resulted in a 98.8% nickel removal and 97.8% granulation efficiency were 200 mg L^{-1} influent nickel concentration, 2.0 M R of [CO_3^{-2}:Ni^{+2}], and 10.7 pH of precipitant. Based on SEM analysis, the granules formed have sizes between 0.50 mm and 0.15 mm. EDS results showed that the atomic percentages of nickel carbon, and hydrogen were ~50%, ~9–12%, and ~35% respectively, representing the nickel carbonate compound. The XRD results showed the low symmetry of the granules formed that confirmed the characteristics of nullaginite mineral of $Ni_2(CO_3)(OH)_2$.

1. Introduction

The degradation of fresh water resources and the extraordinary upsurge in wastewater discharge have been linked to fast world-wide population growth and industrial development. The effluents from domestic or manufacturing sources generally contain soluble forms of heavy metals that are harmful to the environment and humans (European Commission, 2002).

Nickel concentration in river waters and lakes is very low usually less than 0.01 mg L^{-1}. In areas where nickel is mined and refined, the highest nickel concentrations in drinking water have been found to be are around 0.072 mg L^{-1} (ATSDR, 1997). The maximum allowable nickel concentration in water is 0.02 mg L^{-1} (Kocjan et al., 2002). Nickel pollution in water can be attributed to dyeing operations, mining, galvanization, smelting, the manufacture of batteries, metal finishing, and alloying process results in health problems because nickel is toxic and environmentally unfriendly at high concentrations (Dean et al., 1972; Chiu et al., 1987; Gupta et al., 1998; Guillard and Lewis, 2001; Pandey et al., 2007; Blais et al., 2008; Peng et al., 2014). However, like other heavy

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metals such as cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, silver and zinc, nickel in wastewater is closely monitored owing to its toxicity (Dean et al., 1972; Chiu et al., 1987; Guillard and Lewis, 2001). The discharge and disposal of wastewater should be carefully controlled and the wastewater should be treated to minimize the impacts of nickel contamination on receiving bodies of water.

The recovery of nickel from wastewater using various approaches has been studied. Methods of nickel recovery include electrocoagulation (Pandey et al., 2007), ion-exchange (Piekema and Giesen, 2001), adsorption (Zhou et al., 1999; Costodes and Lewis, 2006; Aldaco et al., 2007; Chen et al., 2015), electrodeionization (Andrus, 2000), and electrodialysis (Zhou et al., 1999). The most commonly used method is chemical precipitation, in which the precipitants are hydroxides or sulfides (Blais et al., 2008; Varma et al., 2013; Peng et al., 2014). This method is simple and economical, but the accumulation of sludge increases its cost as dewatering is required (Horikawa and Hirasawa, 2000; Lee and Lee, 2005). Conventionally, the precipitation method of treatment requires a large space, and the fluidized-bed reactor (FBR) solves the problem of the space required to conduct the treatment method (de Luna et al., 2015).

Recent investigations have established the use of the FBR process to remove heavy metals (Zhou et al., 1999; Horikawa and Hirasawa, 2000; Guillard and Lewis, 2002; Lee and Lee, 2005; Lee and Yang, 2005). In 2006, Costodes and Lewis used an FBR (with silica sand and seeds) to crystallize nickel hydroxyl-carbonate. They observed active mechanism proceeded during the reactive crystallization of nickel hydroxyl-carbonate onto the surface of silica sand. They found that the amount of fines (nickel carbonate free radicals) was correlated with the degree of supersaturation. Metal precipitation onto the surface of sand in a series of FBRs has been used to remove zinc, nickel and copper from industrial wastewater. Dosing the precipitant drip-wise yielded better nucleated precipitation than slug dosing (Zhou et al., 1999). An FBR without reflux but with sand filtration at the discharge line was utilized to treat copper-containing wastewater by precipitating the copper onto the sand grain surface. A removal efficiency of 96% with a 10 mg L^{-1} influent copper concentration was achieved at an optimal [C_T:Cu^{2+}] MR of 2–2.5 and a pH range of 8.4–8.6 (Lee et al., 2004).

Fluidized-bed granulation (FBG) has advantages over chemical precipitation. It uses small amounts of chemicals and produces granules with a low moisture content. The fluidized-bed process forms little sludge, making it more convenient for use in a heterogeneous reaction of a metal with a precipitant on the surface of seeding components, such as silica sand and quartz (Gupta et al., 1998; Zhou et al., 1999; Andrus, 2000; Guillard and Lewis, 2001; Piekema and Giesen, 2001; Costodes and Lewis, 2006; Aldaco et al., 2007; Pandey et al., 2007; Chen et al., 2015). This process has been used extensively to treat different wastewaters that contain heavy metals or inorganic acids such as Ni, Cu, As, Zn, boric acid, fluoride, and phosphorous acid (Aldaco et al., 2007; Huang et al., 2007; Boonrattanakij et al., 2011; Coman et al., 2013; Su et al., 2013; Benvenuti et al., 2014). In an FBR, an adequate amount of fine nuclei of the metal salts has enough active surfaces, subsequently forming homogeneous granules. Nucleation and grain growth then occur, forming highly pure granules of increasing size. The FBR supports interactions that are comparable to those involved in conventional precipitation, but the nuclei formation and granulation mechanisms can be empirically identified with the hydraulic limits in the metastable region, to form solid granules rather than a soft slurry (Chen et al., 2015). Pollutants that are removed from wastewater are converted into hard granules (Su et al., 2013).

The goal of this work is to recover nickel from synthetic wastewater using an FBR granulation process. Supersaturated carbonate ions reacted with nickel ions to form nickel carbonate hydroxide granules. This experiment involved a homogeneous process, so no seed is present in the system. The operating parameters were optimized. The variable operating parameters were the influent nickel concentration [100 mg L^{-1}, 200 mg L^{-1}, 300 mg L^{-1}, and 400 mg L^{-1}], [CO_3^{2-}:Ni^{2+}] molar ratio (MR) [1.0, 1.5, 2.0, and 2.5], and pH value of the precipitant [10.5, 10.7, 10.8, and 11.0]. The effects of the parameters on metal recovery and granule formation were determined. The structure of the formed granules was determined by using a scanning electron microscope (SEM) to observe the surface morphology, an energy dispersive spectrometer (EDS) to reveal the elemental distribution, and an X-ray diffraction spectrometer (XRD) to reveal the elemental composition.

2. Materials and method

2.1. Process

The upper part and the effluent region of the 1.35 L glass laboratory-scale FBR that was used herein had an inner diameter of 4.0 cm and a height of 20 cm. The lower part and the reaction region of the reactor had an inner diameter of 2.0 cm and a height of 80 cm. In the reaction region, homogeneous nucleation, nuclei growth and particle growth occurred. The bottom part of the reactor was packed with glass beads with a diameter of 0.5 cm to a static height of 4.0 cm. The bottom part of the bed had three inlets - two through which the synthetic wastewater and precipitant enter on both sides of the reactor, and one for the recycled solution. The two outlets at the top of the reactor are for the treated effluent and the recycled solution.

All solutions were prepared from reagent-grade chemicals and used without further purification. $NiSO_4 \cdot 6H_2O$ (99%) was purchased from Shimakyu's Pure Chemicals. It was used for the preparation of the nickel solution. The precipitant solution was Na_2CO_3 (99.5%) from Panreac. To achieve the desired pH of the precipitant solution, 0.1 M HNO_3 (69%, Panreac) and 4.0 M NaOH (98%, Shimakyu's Pure Chemicals) were added. The water that was used for the preparation of standard solutions and synthetic wastewater was deionized using a laboratory-grade reverse osmosis (RO) ultrapure water system with a resistance of 18 MΩ. A pH/ORP Transmitter/Controller (Shin-Shang Tech Instruments Co., Ltd. PC-310) with an accuracy of ±0.05 was used to measure the pH of the effluent and the precipitant solution.

2.2. Nickel carbonate hydroxide granulation in the FBR

The homogeneous FBR granulation process was conducted continuously at room temperature. Nickel-containing synthetic wastewater and the precipitant solution were pumped upward at opposite sides at the bottom of the reactor at the same flow rate of 25 mL min^{-1}. Initially, at supersaturation state, small nuclei started to grow in the reactor. These eventually formed nickel carbonate granules, which were too heavy to overflow, but settled at the bottom of the reactor. Formed granules were visible in 4–5 days. Reflux at a rate of 60 mL min^{-1} was carried out to increase the residence time of the nickel in the reactor, to keep the granules in a fluidized state and thereby to dilute the concentrated solution in the inlet of the reactor, as displayed in Fig. 1. The operating parameters were varied to determine their effects in the formation of nickel carbonate granule.