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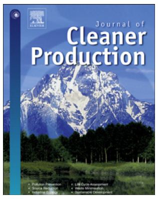

Simultaneous removal of ammonia and manganese from electrolytic metal manganese residue leachate using phosphate salt

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ABSTRACT

Ammonia and manganese were simultaneously removed from electrolytic metal manganese residue leachate using phosphate salt. The influence of different N:P ratios and pH were investigated. Phase transition and decomposing behavior of precipitates and the characterization of the precipitates pyrolysis were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential thermal analysis, and scanning electron microscope. In the laboratory experiment, under the condition of 1:1.15 N:P ratio and 9.5 pH value, removal efficiencies of ammonia and manganese from the residue leachate were achieved 95.0% and 99.9%, respectively, and remaining concentration of orthophosphate was as low as 12 mg L^{-1}. In the process, manganese was first removed as $Mn_3(PO_4)_2 \cdot 7H_2O$, and then ammonia was removed as $NH_4MgPO_4 \cdot 6H_2O$. In addition, $MgNaPO_4$, $MgHPO_4$, $Mg_2P_2O_7$, Na_3PO_4 and MnO_2 were generated during precipitate pyrolysis process, and the ammonia removal efficiency decreased from 84.0% in the first cycle to 66.0% in the fifth, and manganese removal efficiency was approximately 99.0%. Economic evaluation shows that recycling the precipitates for three times could save 68.4% cost on average, compared to the use of pure chemicals.

1. Introduction

Electrolytic metal manganese residue leachate (EMMRL) containing manganese and ammonia is generated from the long-term deposition of electrolytic metal manganese residue (EMMR) (Ning et al., 2010; Xu et al., 2014; Zhou et al., 2014). To produce 1 ton of metal manganese, 10–12 tons of EMMR would be produced, and the situation is getting worse as the grade of manganese ores decreases with the depletion of mineral resources (Duan et al., 2011; Peng et al., 2011); thus more EMMRL is generated. Water contaminated with manganese and ammonia is harmful to human health: intake of high concentrations of manganese causes manganese psychosis, an irreversible neurological disorder (Sharma et al., 2007). High levels of ammonia in the body can lead to blue baby syndrome, liver damage, and gastric cancer (Gupta et al., 2000). Hence, pollution caused by EMMRL has seriously blocked the development of the manganese industry, and developing harmless EMMRL treatment methods is extremely urgent, and removal of manganese and ammonia is the key to this treatment.

Several methods for removing manganese and ammonia have been investigated (Quan et al., 2010). The existing methods for treating ammonia include biological processes (Kalyuzhnyi et al., 2006), ion exchange (Wei et al., 2011), membrane separation (Kim et al., 2013), electrolysis (Huang et al., 2014b) and precipitation (Karak et al., 2015). For manganese purification, natural adsorbents (Emmanuel and Rao, 2009), oxidation and precipitation of manganese (Gantzer et al., 2009), and biological treatments (Burger et al., 2008) are commonly used. However, these methods are costly and complicated and cannot simultaneously remove manganese and ammonia; some of them can produce secondary pollution.

Phosphate can be used to remove manganese (Chubar et al., 2015); struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation is a feasible method to remove ammonia from all kinds of high-concentration wastewater due to its high reaction rate and low residual ammonia concentration (Wang et al., 2013). The reaction equation is as follows:

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$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\downarrow + H^+ \quad (1)$$

In this study, the mechanisms for simultaneously removing ammonia and manganese from EMMRL using phosphate salt only were investigated. The influence of different N:P ratios and pH on the precipitation process were evaluated. Phase transition and decomposing behavior of precipitates, and the pyrolyzed precipitates were characterized by a scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and X-ray diffraction (XRD); an economic evaluation of the cyclic process was performed.

2. Materials and methods

2.1. Raw materials

The EMMRL used in this study was collected from Jiayuan Mining Co. Ltd. (Chongqing, China), and immediately put in the refrigerators at 4 °C prior to any analysis. The compositions of EMMRL are presented in Table 1. To simultaneously remove ammonia and manganese from EMMRL, $NaH_2PO_4 \cdot 2H_2O$ was used as a phosphate source. All the chemical reagents (analytical grade) used in this study were purchased from Chongqing Boyi Chemical Reagent Co., Ltd., China and applied without further purification. Purified water was provided by the Water Purification System (HMC-WS10), and all experiments were carried out at room temperature.

2.2. Experimental procedure

To investigate the effect of different phosphate salt concentrations on the removal efficiency of manganese and ammonia, the N:P ratio was varied from 1:1.10 to 1:1.35. Briefly, 500 mL of EMMRL was poured into a 1 L breaker, and then $NaH_2PO_4 \cdot 2H_2O$. 2.0 N NaOH was added to EMMRL to adjust the pH to the ideal value. The active solution was stirred using a magnetic stirrer at the pH of 9.5 and settled for 30 min. Finally, the solution was purified using a 0.45 μm membrane filter for component analysis. To analyze the difference chemical characteristics between the precipitates and synthetic struvite, the latter was prepared by mixing equal molar quantities of magnesium sulfate and ammonium dihydrogen phosphate. Additional details regarding this method were described by M.I.H.Bhuiyan (Bhuiyan et al., 2008).

Ammonia removal efficiency (R_{NH_3-N}, %) and manganese removal efficiency (R_{Mn}, %) are separately defined by Eqs. (2) and (3) as follows:

$$R_{NH_3-N} = \frac{C_{NH_3-N,0} - C_{NH_3-N,t}}{C_{NH_3-N,0}} \cdot 100\% \quad (2)$$

$$R_{Mn} = \frac{C_{Mn,0} - C_{Mn,t}}{C_{Mn,0}} \cdot 100\% \quad (3)$$

Where C_{NH_3-N} (mg L^{-1}) is the ammonia concentration and C_{Mn} (mg L^{-1}) is the manganese concentration. Subscripts 0 and t indicate the initial and sampling times, respectively.

Table 1
pH and concentrations (mg L^{-1}) of different components in the electrolytic metal manganese leachate.

Parameter	Value
pH	4.50 ± 0.1
COD	125 ± 12.0
BOD	78 ± 6.0
NH_3-N	856 ± 6.0
TP	11 ± 1.0
K	24.3 ± 1.5
Ca	20.6 ± 3.2
Mg	1957 ± 15.0
Fe	2.1 ± 0.5
Al	4.6 ± 1.1
Mn	1805 ± 13.0
Na	85 ± 2.0

2.3. Experiments on recycling of precipitates

Recycling of precipitates was conducted as follows: (1) Initial precipitates: the precipitates were formed when the N:P ratio was 1:1.15 at pH 9.5; (2) Pyrolysis of precipitates: the precipitates formed in step 1 or step 3 (see below) were filtered and pyrolyzed at 110 °C for 3 h using a 2:5 of NaOH:precipitate mass ratio; (3) Recycling of precipitates: the precipitates obtained after pyrolysis were added to EMMRL (500 mL). The pH value of the mixed solution was adjusted to 9.5 with 2.0 N NaOH solutions and magnetically stirred for 30 min. After settling for 30 min, the precipitates were collected using a 0.45 μm membrane filter and washed three times with deionized water, and then dried in an oven at 40 °C for 48 h. The collected precipitates were then recycled, and step 2 and 3 were then repeated.

2.4. Analytic methods

The compositions of the EMMRL, ammonia, and orthophosphate (PO_4-P), as well as the chemical oxygen demand (COD) were analyzed via Standard Methods (APHA, 1998). Manganese was determined via atomic absorption spectrophotometry (AAS) (HITACHI 180/80, Japan) in flame. Ammonia and PO_4-P in the supernatant after the precipitation were measured via Nessler's Reagent spectrophotometry and vanadomolybdo-phosphoric acid colorimetric method, respectively. The pH value of the solution was measured using an ultra-trace sample volume-type pH electrode (PHS-3C, Shanghai, China). The dried precipitates were analyzed by X-ray diffraction (XRD; DMAX-RB; Rigaku, Japan) and Scanning Electron Microscopy (SEM; S4800; HITACHI, Japan). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed on the precipitates and synthetic struvite by using a Pyris 6 TGA Perkin Elmer thermogravimetric analyzer under nitrogen gas. FT-IR spectra were obtained by using a Magna 550II FT-IR spectrometer (Nicolet, USA) via the KBr pellet method.

3. Results and discussion

3.1. Effect of N:P ratio and pH

The pH of the EMMRL was adjusted at different N:P ratios, and the removal efficiencies for manganese and ammonia are shown in Fig. 1. Using struvite precipitation in the landfill leachate, the optimum pH values of 8.8–9.4 (Gunay et al., 2008), 9 (Di Iaconi et al., 2010) and 9.5 (Zhang et al., 2009) were reported. When the pH was less than 8.1, $Mn[(H_2O)_6]^{2+}$ was the main form in the solution, and $Mn(OH)_2$ was the predominant form when pH greater than 8.1 (Jung and Jun, 2016; Um and Hirato, 2014).

As shown in Fig. 1(a), at a given pH, the ammonia removal efficiency gradually increased as phosphate dose increased; at a given N:P ratio, the ammonia removal efficiency increased as pH value increased. In Fig. 1(b), the manganese removal efficiency increased