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Research article

Sulfate removal from wastewater using ettringite precipitation: Magnesium ion inhibition and process optimization

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ABSTRACT

One of the main challenges in industrial wastewater treatment and recovery is the removal of sulfate, which usually coexists with Ca^{2+} and Mg^{2+}. The effect of Mg^{2+} on sulfate removal by ettringite precipitation was investigated, and the process was optimized in the absence and presence of Mg^{2+}. In the absence of Mg^{2+}, the optimum conditions with sulfate removal of 99.7% were obtained at calcium-to-sulfate ratio of 3.20, aluminum-to-sulfate ratio of 1.25 and pH of 11.3 using response surface methodology. In the presence of Mg^{2+}, sulfate removal efficiency decreased with increasing Mg^{2+} concentration, and the inhibitory effect of Mg^{2+} matched the competitive inhibition Monod model with half maximum inhibition concentration of 57.4 mmol/L. X-ray diffraction and Fourier transform infrared spectroscopy analyses of precipitates revealed that ettringite was converted to hydrotalcite-type (HT) compound in the presence of Mg^{2+}. The morphology of precipitates was transformed from prismatic crystals to stacked layered crystals, which confirmed that Mg^{2+} competes with Ca^{2+} for Al^{3+} to form HT compound. A two-stage process was designed with Mg^{2+} removal before ettringite precipitation to eliminate the inhibitory effect, and is potential to realize sludge recovery at the same time of effective removal of sulfate and hardness.

1. Introduction

Sulfate (SO_4^{2-}) is a common and nontoxic constituent of natural waters and wastewaters, and is present in high concentrations in some industrial wastewaters, such as mining, metallurgical, textile, landfill, fertilizer and flue gas desulfurization (FGD) wastewater (Jiang et al., 2013; Kabdaşlı et al., 2016; Silva et al., 2010; Tait et al., 2009; Tolonen et al., 2016). High concentrations of SO_4^{2-} can cause the mineralization of water, corrosion of reinforced steel, scaling of equipments, damage to mammals and generation of toxic and corrosive hydrogen sulfide in the sewer system (Cao et al., 2011; Pikaar et al., 2014). Environmental agencies in many countries have limited the SO_4^{2-} concentrations for industrial effluents to control water pollution and protect water pipes (Runtti et al., 2016; Silva et al., 2012). Increasingly strict legislation for water conservation and reuse requirements in recent years, such as Water Pollution Control Action Plan in China (State Council-2015-17), makes new demands on sulfate removal. For instance, zero liquid discharge (ZLD) process for FGD wastewater, which usually consists of membrane concentration, evaporation and crystallization units to achieve the complete separation of salt from wastewater, required efficient sulfate removal because sulfate not only deposits on the surface of membrane and evaporator, but also has an adverse effect on the recovered salt purity. Therefore, efficient sulfate removal was essential for both effluent discharge and ZLD process.

Sulfate removal can be realized by biological treatment, membrane filtration, ion exchange/adsorption and chemical precipitation (Kijjanapanich et al., 2013; Qian et al., 2015; Silva et al., 2010, 2012). Biological treatment with sulfate-reducing bacteria is suitable to low or moderate sulfate loadings (Qian et al., 2015; Silva et al., 2012), but its application is usually hindered by the shortage of organics, the inhibition of high salinity and metal ions in the wastewater (Mothe et al., 2017), and the generation of hydrogen sulfide (Runtti et al., 2016). Reverse osmosis and electrodialysis are both effective for sulfate removal, but the high

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investment and operation costs obstacle their full-scale applications (Silva et al., 2010, 2012). Chemical precipitation through adding barium or calcium salts is rapid and effective for sulfate removal (Benatti et al., 2009). Compared to the cost and toxicity of barium salts, lime precipitation was more suitable but its efficiency was limited due to the high solubility of $CaSO_4$ ($pK_{sp} = 3.70$) (Runtti et al., 2016; Silva et al., 2012), especially in the industrial wastewater with high salinity. As a sulfate salt with lower solubility ($pK_{sp} = 43.13$) (Almasri et al., 2015) than that of $CaSO_4$, ettringite $[Ca_6Al_2(OH)_{12}(SO_4)_3{\cdot}26H_2O]$ is a modification of high pH lime precipitation, and is considered as a promising way for sulfate removal (Kabdaşlı et al., 2016; Tolonen et al., 2016). To date, numerous studies have focused on the influence of different parameters, including pH value, aluminum-to-sulfate molar (Al/S) ratio, calcium-to-sulfate molar (Ca/S) ratio and temperature, on sulfate removal (Almasri et al., 2015; Kabdaşlı et al., 2016), and achieved interesting findings. Nevertheless, detailed information on interaction influence of above parameters and process optimization for ettringite precipitation was hardly found in literature, which would further enhance sulfate removal efficiency and promote the practical application of ettringite precipitation.

Sulfate usually coexists with calcium (Ca^{2+}) and magnesium (Mg^{2+}) in industrial wastewaters, such as FGD wastewater (Lai et al., 2014), mine drainage (Tolonen et al., 2015), landfill leachate (Tait et al., 2009). The presence of Ca^{2+} in wastewater decreases the addition of lime and enhances the significance of ettringite precipitation. As for Mg^{2+}, the concentration was varied from 2.00 to 2.25 mmol/L (Silva et al., 2012) to 90.4 mmol/L in mine wastewater (Tolonen et al., 2015), 2.92 mmol/L in aluminium anodising wastewater (Álvarez-Ayuso and Nugteren, 2006), and 157.0 mmol/L in FGD wastewater (Lai et al., 2014). It is reported that Mg^{2+} has adverse effects on the formation of ettringite in cement paste (De Weerdt et al., 2014), and prevents sulfate removal as gypsum (Tolonen et al., 2015). However, the effects of Mg^{2+} on ettringite precipitation are scarcely reported, and it should be essential for process design and very useful for understanding the precipitation behavior in real wastewater rich in Mg^{2+} and sulfate.

The aims of this study are to optimize sulfate removal and investigate the effect of Mg^{2+} on the ettringite precipitation. The collected precipitates were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy to evaluate their composition and morphology in the absence and presence of Mg^{2+}. A four-stage treatment process for efficient removal of sulfate and hardness from FGD wastewater was proposed for ZLD system. The results obtained in this study are expected to provide an insight for ettringite precipitation and an effective process for sulfate removal in the presence of Mg^{2+}.

2. Materials and methods

2.1. Source of wastewater

Stock solutions were prepared to form artificial wastewater by dissolving an analytical reagent grade of $Na_2SO_4{\cdot}6H_2O$ and anhydrous $CaCl_2$ chemicals in deionized water to get initial SO_4^{2-} and Ca^{2+} concentrations of 24.0 and 57.6 mmol/L. FGD wastewater used in this study was taken from Nantong coal-fired power plant, Jiangsu, China. The main characteristics of FGD wastewater were as follows: pH of 5.52 ± 0.04, suspended solid (SS) of 12.92 ± 1.98 g/L, volatile SS (VSS) of 1.17 ± 0.07 g/L, chemical oxygen demand (COD) of 266.7 ± 23.1 mg/L, Ca^{2+} of 38.1 ± 1.5 mmol/L, Mg^{2+} of 175.2 ± 23.7 mmol/L, SO_4^{2-} of 24.9 ± 2.7 mmol/L, total dissolved solids of 30895 ± 612.35 mg/L and conductivity of 30.75 ± 0.07 mS/cm.

2.2. Sulfate removal optimization in the absence of Mg^{2+}

Response surface methodology (RSM) is usually applied as a reliable statistical technique for experiment design and data analysis (Zhou et al., 2014a). In this experiment, three variables with three levels were selected: Ca/S ratio (1, 3 and 5), Al/S ratio (0.5, 1.5 and 2.5) and pH (10, 11 and 12). The sulfate removal efficiency (SRE) was selected as the response variable. Design Expert Software (version 8.0.6) equipped with Box-Behnken design was employed to analyze the effects of three variables on SRE and to obtain optimal conditions. To achieve different Ca/S and Al/S ratios, the concentration of Ca^{2+} and Al^{3+} was adjusted by dissolving anhydrous $CaCl_2$ and $AlCl_3{\cdot}6H_2O$ in the artificial wastewater, respectively. The pH was adjusted by 6 mol/L NaOH solution and recorded by an HQ30d portable meter (Hach, USA). All the 17 runs were stirred at 250 rpm for 60 min and settled for 60 min. The supernatant was taken to determine the concentration of sulfate.

2.3. Effects of Mg^{2+} on sulfate removal

2.3.1. Batch experiment

Batch experiments were implemented in the RSM-optimized condition for sulfate removal using a flocculator (ZR4-6, China) at 25 ± 0.5 °C. Twelve initial Mg^{2+} concentrations (0, 5, 10, 20, 30, 40, 60, 80, 100, 120, 140 and 160 mmol/L) were used to evaluate the effect of Mg^{2+} on ettringite precipitation by adding analytical reagent grade of $MgCl_2{\cdot}6H_2O$ into the artificial wastewater. Then anhydrous $CaCl_2$ and $AlCl_3{\cdot}6H_2O$ were added to achieve the optimal ratios of Ca/S (3.20) and Al/S (1.25), respectively. The pH was adjusted to the optimized pH of 11.3 by 6 mol/L NaOH solutions. All runs were stirred at 250 rpm for 60 min and settled for 60 min. Then, the supernatant was taken to determine concentrations of SO_4^{2-}, Mg^{2+} and Ca^{2+}. The settled precipitates were washed thoroughly with deionized water to eliminate chlorine ions and dried in an oven at 50 °C that did not change the nature of precipitates for solid analysis (Zhou et al., 2015).

2.3.2. Inhibition model

The % inhibition ratio (IR) of Mg^{2+} on SRE is defined as

$$IR = (1 - SRE_i/SRE_0) \times 100\% \qquad (1)$$

where, SRE_0 and SRE_i are SREs in the absence and presence of Mg^{2+}, respectively.

The relationship between SRE and Mg^{2+} concentration can be described by a competitive inhibition Monod equation (Zhou et al., 2014b, 2015)

$$SRE_i = SRE_0 \frac{K_i}{K_i + c_{Mg}} \qquad (2)$$

where, c_{Mg} is the concentration of Mg^{2+}, mmol/L; K_i is the half maximum inhibition concentration of Mg^{2+}, mmol/L. The multiplicative inverse of SRE_i is linear with the concentration of Mg^{2+}.

$$\frac{1}{SRE_i} = \frac{1}{SRE_0} + \frac{c_{Mg}}{K_i SRE_0} \qquad (3)$$

2.4. Sulfate removal in the presence of Mg^{2+}

Batch experiments were designed to eliminate the inhibitory effects of Mg^{2+} on sulfate removal by using the artificial wastewater and real FGD wastewater. Two contrast experiments, two-stage process and one-stage process, were conducted for artificial