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Selection of cost-effective magnesium sources for fluidized struvite crystallization

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ABSTRACT

Struvite crystallization has been considered a promising approach to recover phosphorus from wastewater. However, its practical application is limited, probably because of the high cost of magnesium (Mg). In this study, a comprehensive economic analysis was conducted using five Mg sources ($MgCl_2$, $MgSO_4$, MgO, $Mg(OH)_2$, and bittern) during the operation of a pilot-scale fluidized bed reactor (FBR), using swine wastewater as the case matrix. First, the economic operating conditions were investigated, and subsequently, the performance and the costs of the five Mg sources were compared. The results indicated that the FBR could be operated most economically at pH of 8.5 and Mg to phosphorus (Mg/P) molar ratio of 1.5. Under these conditions, no significant differences in phosphorus removal and product quality could be found between the five Mg sources. Selecting the most economical Mg source was thus highly dependent on the prices of the reagents and Mg sources. Low-solubility Mg sources were preferable when NaOH was priced higher, while high-solubility Mg sources proved more economical when HNO_3 was expensive. The bittern was the most economical choice only when the distances for total inorganic orthophosphate removal and struvite recovery were shorter than 40 and 270 km, respectively. The current study provides an overview of the economic selection of an Mg source, which can help reduce the cost of struvite crystallization.

Introduction

Phosphorus is one of the essential elements for life, representing energy flow on a cellular level (Westheimer, 1987). As phosphorus has no natural circulation cycle, it can only be mined from phosphate rock and ends up in marine sediments. Unfortunately, phosphate rock is a non-renewable source and its global demand has increased exponentially since the 19th century due to the surge in population (Cordell et al., 2009). Based on the current rate of consumption, phosphate rock will be exhausted within 90 years (Pinnekamp et al., 2003). Thus, it is crucial to recover phosphorus. Struvite ($MgNH_4PO_4{\cdot}6H_2O$) crystallization has been gaining attention since it can simultaneously reduce eutrophication and address the scarcity of phosphorus rock resources (Ye et al., 2014). Harvested struvite has been confirmed to be an effective fertilizer for a range of crops, better than commercial fertilizers in some cases (Esemen et al., 2009; Mihelcic et al., 2011).

Although struvite crystallization technology has the dual advantages of protecting the environment and conserving resources, and has been conducted for several decades, its application is hampered, mainly due to high operating cost (Mihelcic et al., 2011; Rogalla, 2010; Ueno and Fujii, 2001). In general, the operating cost of struvite crystallization is mainly associated with the cost of reagents, power, and in some cases, additional transportation (Barbosa et al., 2016).

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Notably, the reagent accounts for the majority of the cost (Quintana et al., 2004), and to date, much research has been conducted with the aim of reducing the reagent cost (Huang et al., 2014b). It has been reported that using low-cost Mg can lower the overall operating cost by 18%–81%, without complex or additional operations (Dockhorn, 2009; Gunay et al., 2008; Huang et al., 2010, 2011; Lahav et al., 2013). Therefore, choosing cost-effective Mg sources seems to be the most direct approach to reducing the cost of struvite crystallization (Quintana et al., 2004).

To date, various Mg sources, which can be classified according to solubility, have been tested in struvite crystallization: high-solubility (*i.e.*, $MgCl_2$ and $MgSO_4$) and low-solubility (*i.e.*, MgO, $Mg(OH)_2$, and $MgCO_3$). Because of their high solubility and reactivity, $MgCl_2$ and $MgSO_4$ are extensively used in lab-scale and commercial-scale processes. Phosphate recovery efficiency over 90% can be achieved (Kataki et al., 2016; Moerman et al., 2009; Schick et al., 2009; Ye et al., 2014). The low-solubility sources MgO, $Mg(OH)_2$, and $MgCO_3$ also have an application in struvite crystallization because of their lower price and alkaline features (Gunay et al., 2008; Huang et al., 2010, 2014a; Ueno and Fujii, 2001; Yu et al., 2013). In terms of original source, some Mg-abundant industrial byproducts or liquids have shown potential to be Mg sources, such as wood ash (Sakthivel et al., 2012), seawater (Lahav et al., 2013; Crutchik and Garrido, 2011; Shin and Lee, 1998), and bittern (Lee et al., 2003; Ye et al., 2011). Wood ash is the powder left after wood combustion, and contains 59.7–89.1 g Mg/kg (Etiégni and Campbell, 1991). Studies show that it could precipitate 99% of phosphate; however, the product was far from pure struvite and frequently contained high concentrations of heavy metals (Sakthivel et al., 2012). Seawater is a natural potential Mg source and has been successfully used to recover up to 99% of the phosphate from hydrolyzed urine. However, coprecipitates (*i.e.*, magnesium calcite and calcite) were observed owing to the presence of calcium (Liu et al., 2013). Bittern is the solution remaining after the crystallization of sodium chloride from brine or seawater (Matsumiya et al., 2007; Quintana et al., 2004). As a byproduct of the sea salt industry, bittern contains extremely high concentrations of Mg^{2+} (2000–3000 mg/L) and is considered a promising source of cost-efficient Mg (Liu et al., 2013). The use of bittern can achieve an auspicious recovering phosphate efficiency (80%–90%) with reduced reagent cost (Etter et al., 2011). However, as with seawater, its application is limited to coastal areas because longer distances would increase both cost and inconvenience. Moreover, the usage of these Mg sources could lead to the formation of impurities and other precipitates, which would significantly influence the quality and safety of the product (Matsumiya et al., 2007). Recently, pure Mg has also been tested as a potential Mg source. It has been shown, using an electrochemical approach, that an Mg electrode can release Mg, the cost of which is competitive with $MgCl_2$ and $MgSO_4$ but exceeds dosing with MgO (Hug and Udert, 2013). Another novel method is the combined fluidization of Mg and graphite pellets using an air bubbling column, which can achieve a stable phosphate removal rate (approximately 95%) and high struvite purity (95.8%) (Huang et al., 2015). Although effective, the direct usage of pure Mg as the Mg source in larger-scale struvite crystallization is still questionable, because the costs of installation and operation (*i.e.*, air blowing) are unknown (Huang et al., 2015; Hug and Udert, 2013).

As mentioned above, various Mg sources can be used during struvite crystallization, but an approach for cost-effective selection of the Mg sources is still unclear, especially when struvite recovery is conducted using a fluidized bed reactor (FBR). For example, it is widely believed that the low-solubility Mg sources (*i.e.*, MgO or $Mg(OH)_2$) are more economically efficient than the high-solubility ones (*i.e.*, $MgCl_2$ or $MgSO_4$) (Huang et al., 2014a; Ueno and Fujii, 2001; Yu et al., 2013). However, this conclusion cannot be widely accepted because it applies to stirred reactors (Huang et al., 2014a; Yu et al., 2013). Mg source selection is likely to differ based on specific hydrodynamic conditions in the FBR (Birnhack et al., 2015), in which the low-solubility Mg sources might not have enough time to dissolve before being flushed out, subsequently influencing the phosphorus removal rate (Laridi et al., 2005). Therefore, pretreatment of low-solubility Mg sources is generally necessary, which introduces additional costs. Additionally, transportation costs, which would become the major limitation for using free Mg sources, are often ignored in existing economic analyses, and should be taken into consideration (Matsumiya et al., 2007; Quintana et al., 2004).

Although various Mg sources are available, $MgCl_2$, $MgSO_4$, MgO, $Mg(OH)_2$, and bittern were selected as the Mg sources to be studied due to the prospect of their practical application. The aim of this study was to identify the most cost-effective Mg source for fluidized struvite crystallization from swine wastewater. The most economical operating conditions (*i.e.*, pH and Mg/P) were first investigated; subsequently, the operating costs and struvite characteristics resulting from the use of the above-mentioned five common Mg sources were comprehensively compared. Finally, a rule for Mg source selection for struvite crystallization using FBR was derived.

1. Materials and methods

1.1. Swine wastewater and Mg resources

Swine wastewater was collected from an anaerobic digester of a pig farm (Xiamen, China). The composition of the swine wastewater is presented in Table 1. The initial molar ratio of Mg/N/P was 0.8/11.0/1.0, demonstrating that additional Mg sources are necessary for struvite precipitation.

Four commercial industrial grade (IG) chemicals ($MgCl_2$, $MgSO_4$, MgO, $Mg(OH)_2$) and one byproduct of the sea salt industry (bittern) were used as Mg sources. IG-$MgCl_2$ was purchased from Xilong Co. Ltd. (Beijing, China); IG-$MgSO_4$, IG-MgO, and IG-$Mg(OH)_2$ were supplied by the Laizhou Zhongguan Magnesium Co. Ltd. (Shandong, China); and the bittern was obtained from Zhangpu Saltern (Fujian, China). The components and prices of the five Mg sources are presented in Table 2.

1.2. Experimental design

1.2.1. Pretreatment of low-solubility Mg sources

The two low-solubility Mg sources (*i.e.*, IG-MgO, IG-$Mg(OH)_2$) were dissolved prior to use because of their low solubility. First, the amount of acid needed was calculated, with the aim of ascertaining the concentration of Mg^{2+} and pH in the solution at different acid dosages. The batch experiments were performed in a six-linked agitator (ZR4-6, ZRWATER,

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