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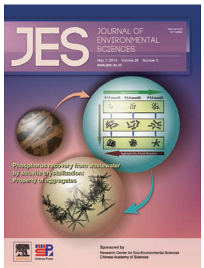

Phosphorus recovery from wastewater by struvite crystallization: Property of aggregates

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ABSTRACT

Struvite crystallization is a promising method to remove and recover phosphorus from wastewater to ease both the scarcity of phosphorus rock resources and water eutrophication worldwide. To date, although various kinds of reactor systems have been developed, supporting methods are required to control the struvite fines flushing out of the reactors. As an intrinsic property, aggregation is normally disregarded in the struvite crystallization process, although it is the key factor in final particle size and therefore guarantees phosphorus recovery efficiency. The present study developed a method to analyze the characteristics of struvite aggregates using fractal geometry, and the influence of operational parameters on struvite aggregation was evaluated. Due to its typical orthorhombic molecular structure, struvite particles are prone to crystallize into needle or rod shapes, and aggregate at the corners or edges of crystals. The determined fractal dimension (D_{pf}) of struvite aggregates was 1.52–1.31, with the corresponding range of equivalent diameter ($d_{0.5}$) at 295.9–85.4 μm. Aggregates formed in relatively low phosphorus concentrations (3.0–5.0 mmol/L) and mildly alkaline conditions (pH 9.0–9.5) displayed relatively compact structures, large aggregate sizes and high aggregation strength. Increasing pH values led to continuous decrease of aggregate sizes, while the variation of D_{pf} was insignificant. As to the aggregate evolution, fast growth in a short time followed by a long steady stage was observed.

Introduction

Excess nitrogen and phosphorus (P) discharged into the environment lead to eutrophication and are toxic to aquatic species in the receiving waters, and are therefore regarded as pollutants. Moreover, phosphorus rock is an important and non-renewable resource, making a major contribution to agricultural and industrial development. Due to the scarcity of phosphorus rock resources, recovering P as struvite ($MgNH_4PO_4 \cdot 6H_2O$) from wastewater, such as swine wastewater and sludge anaerobic supernatant, has gained importance as a means of capturing and recycling P (Gilbert, 2009). The recovered product is preferred as a good fertilizer in agriculture for its slow release rate and much lower impurity levels than other phosphate fertilizers (Rahman et al., 2011).

To date, various kinds of reactors have been developed at laboratory, pilot and full scales and have shown great potential in recovering struvite (Le Corre et al., 2009; Forrest et al., 2008). However, issues remain on the degree of crystal growth and the formation of crystal fines. Struvite fines produced are easily flushed out of the reactor and decrease the P recovery efficiency, so that supporting methods are normally required to control the fines. Harris et al. (2008) used quartz and periclase grains as seed materials so that the grain surfaces could serve as nucleation sites for struvite precipitation. Le Corre et al. (2007) applied ferric chloride, aluminum sulfate, and polyDADMAC as coagulants to agglomerate struvite fines into large particles.

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Other researchers used stainless steel meshes or improvements in hydraulic and saturation conditions to collect suitable crystal sizes (Forrest et al., 2008; Song et al., 2007; Perera et al., 2009). Actually, aggregation is unavoidable in the crystallization or precipitation of sparingly soluble salts (Kim et al., 2011), and is also observed in the struvite crystallization process (Le Corre et al., 2007; Huang et al., 2006). Aggregation is the key factor to determined the final particle size. However, since it is unpredictable and hard to measure, the aggregation process is often disregarded in comparison with other processes, such as nucleation and crystal growth (Kim et al., 2011; Moussaouiti et al., 1996). Disregarding aggregation may lead to inaccurate characterization of the physical properties of the powder product, including crystal size distribution and shape, and can involve errors in the estimation of nucleation and crystal growth rates (Kim et al., 2011; Moussaouiti et al., 1996). As for the struvite crystallization process, little information is available regarding the structure of struvite aggregates and their size distribution.

Fractal geometry, which was founded by Mandelbrot in 1975, has often been used to describe the irregular structures of geometric objects, such as sediments, flocs, latex, and conditioned water treatment residuals, as presented in **Table 1**. Aggregates generated in crystallization processes have been shown to be fractal, since they possess self-similar and scale-invariant properties (Liu et al., 2000; Helalizadeh et al., 2006). The aggregate structure can be described by the fractal dimension, a parameter expressing the degree of aggregate compactness by which primary particles fill the space within the nominal volume occupied by an aggregate. The present study therefore presented a method to analyze the characteristics of struvite aggregates using fractal geometry. The influence of process parameters, including P concentration, pH value and shear rate on struvite aggregation was investigated, and the evolution of struvite aggregates was also identified. The outcomes will be important in providing further information on the practical application of improving particle size and aggregate compactness in the struvite recovery process.

1 Materials and methods

1.1 Solution preparation

P concentration levels of the solutions (3–15 mmol/L) adopted in this study were representative of swine wastewater and sludge digestion supernatant produced in China, as described by MEPC (2002) and Wang et al. (2010). Stock solutions containing NH_4^+-N, PO_4^{3-}-P and Mg^{2+} were prepared by dissolving $NH_4H_2PO_4$ and $MgCl_2{\cdot}6H_2O$ into deionized water, respectively. These solutions were stored at 4°C for further experiments.

1.2 Determination of the states for struvite crystal formation

There are three states for crystal formation, undersaturated, metastable and over saturated (Le Corre et al., 2009). Crystallization is impossible in the under saturated state. In the metastable state, the solution is saturated and crystallization occurs heterogeneously, which means that crystal formation is induced by seed addition. As to the oversaturated state, spontaneous crystallization occurs rapidly and abundantly without the need for seeding. In industrial phosphate production, the spontaneous crystallization technique is widely practiced due to high productivity and smoother continuous operation in controlled supersaturation. To define the states of solution where struvite crystallization can occur spontaneously, preliminary experiments were conducted to identify the minimum limit of spontaneous precipitation, based on the method described by Ali and Schneider (2006). The experiments were carried out in a dark room using a light scattering device (red laser pointer) in which laser light passed through reactive solution. Synthetic solutions of different concentrations were prepared by mixing $MgCl_2$ and $NH_4H_2PO_4$ and setting the molar ratio of Mg:N:P at 1:1:1. Reactive solutions were slowly brought up to saturation level by adding 2 mol/L NaOH until the first appearance of a crystal cloud was detected. The corresponding pH value at crystallization occurrence was recorded as the minimum pH for spontaneous precipitation. Subsequent experiments were conducted in the over saturated region.

Saturation index (SI) was used to describe the saturation

Table 1 Boundary fractal dimension of different materials

Object	D_{pf}	Literature
Kaolin flocs	1.06–1.23	He et al., 2012
Lime softening flocs	1.22–1.38	Vahedi and Gorczyca, 2011
Cohesive sediment	1.25–1.36	Stone and Krishnappan, 2003
Conditioned water treatment residuals	1.50–1.80	Dong et al., 2011
Conditioned sludge	1.34–1.48	Chu et al., 2004
Struvite aggregates	1.31–1.52	Present study

D_{pf} is a two-dimensional boundary fractal dimension, calculated by regression analysis of the logarithm of the projected areas versus the logarithm of their corresponding perimeters.