Chemosphere 165 (2016) 211–220

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

An efficient approach for phosphorus recovery from wastewater using series-coupled air-agitated crystallization reactors

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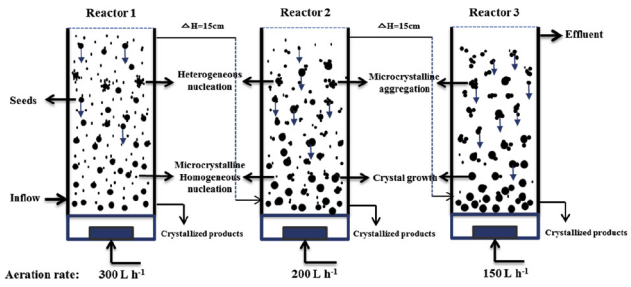
HIGHLIGHTS

- Multistage-induced crystallization process is used to enhance phosphorus recovery.
- The new process consists of three series-coupled air-agitated crystallization reactors.
- A high average phosphorus recovery efficiency of 95.82% is obtained.
- The main feature of the process is the aggregation and precipitation of microcrystalline.
- The developed process has a broad application in phosphorus recovery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 March 2016
Received in revised form
22 August 2016
Accepted 1 September 2016
Available online 18 September 2016

Handling Editor: Y Liu

Keywords:
Phosphorus recovery
Homogeneous nucleation
Hydroxyapatite
Multistage-induced crystallization
Series-coupled reactors

ABSTRACT

Homogeneous nucleation of hydroxyapatite (HAP) crystallization in high levels of supersaturation solution has a negative effect on phosphorus recovery efficiency because of the poor settleability of the generated HAP microcrystalline. In this study, a new high-performance approach for phosphorus recovery from anaerobic supernatant using three series-coupled air-agitated crystallization reactors was developed and characterized. During 30-day operation, the proposed process showed a high recovery efficiency (~95.82%) and low microcrystalline ratio (~3.11%). Particle size analysis showed that the microcrystalline size was successively increased (from 5.81 to 26.32 μm) with the sequence of series-coupled reactors, confirming the conjectural mechanism that a multistage-induced crystallization system provided an appropriate condition for the growth, aggregation, and precipitation of crystallized products. Furthermore, the new process showed a broad spectrum of handling ability for different concentrations of phosphorus-containing solution in the range of 5–350 mg L^{-1}, and the obtained results of phosphorus conversion ratio and recovery efficiency were more than 92% and 80%, respectively. Overall, these results showed that the new process exhibited an excellent ability of efficient phosphorus recovery as well as wide application scope, and might be used as an effective approach for phosphorus removal and recovery from wastewater.

1. Introduction

Phosphorus is not only a limited and nonrenewable mineral resource but also an essential nutrient for all living organisms, with utmost importance for the development of human society (Cordell

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.001
0045-6535/

et al., 2011; Withers et al., 2015). On the contrary, excessive levels of phosphorus discharged into the natural water bodies will result in serious eutrophication (Conley et al., 2009; Lewis et al., 2011). Therefore, phosphorus recovery from wastewater can prevent the loss of nutrient resources and minimize the environmental impact of excess phosphorus on receiving waters. Municipal wastewater is a hidden source of phosphorus, and 15–20% of the world's phosphorus demand can be theoretically satisfied by recovering and recycling phosphorus from wastewater (Yuan et al., 2012; Qiu et al., 2015). Enhanced biological phosphorus removal (EBPR) process, as a key technology in many sewage treatment plants, provide a phosphate-rich stream (anaerobic supernatant, AS) to make phosphorus recovery and reuse feasible (Yuan et al., 2012).

Various technologies have been developed for and applied to phosphorus removal and recovery from wastewater (Lewis et al., 2011; Wu et al., 2014; Li et al., 2014; Zhang et al., 2015; Tian et al., 2016). Crystallization approach using hydroxyapatite (HAP, $Ca_5(PO_4)_3OH$) (Kim et al., 2006; Tervahauta et al., 2014) and struvite (magnesium ammonium phosphate (MAP), $MgNH_4PO_4$) (Hao et al., 2013; Zhou et al., 2015) has apparent advantages in phosphorus recovery efficiency and quality of crystallization products. Compared with MAP for phosphorous recovery, HAP crystallization can be used to recover phosphorous from wastewater containing low concentration of phosphorus, especially the AS of the EBPR process (Moerman et al., 2009; Mañas et al., 2011). It is promising to recover phosphorus in the form of HAP than other forms from the industrial viewpoint, and HAP can be valorized in agriculture as a slightly soluble fertilizer (Hosni et al., 2008; Okano et al., 2013; Qiu et al., 2015).

Both the occurrence and development of HAP crystallization follow three chemical stages: formation of supersaturation, nucleation (crystal birth), and crystal growth (Karapinar et al., 2006). The supersaturation of solution is the precondition of crystallization reaction, and it is also the key to obtain high-quality crystal products (Stumm and Morgan, 2012). However, rapid nucleation and consequent creation of large amounts of microcrystalline with poor settleability occur at high levels of supersaturation of solution; this phenomenon is termed as homogeneous nucleation and has a negative effect on the phosphorus recovery and removal efficiency (Christoffersen et al., 1989; Karapinar et al., 2006). The presence of seeds (calcite, dolomite, quartz sand, etc.) can reduce the activation energy barrier of forming crystallized products, thereby making it easier to form crystals and precipitate microcrystalline on the surface of seeds (Song et al., 2006). Karapinar et al. (2006) reported that the increased levels of supersaturation of solution could decrease phosphorus recovery efficiency (precipitation on seeds), and although the total precipitation efficiency was increased, the seeded precipitation efficiency was decreased with the saturation index (SI) of solution. The levels of supersaturation during the crystallization process can be controlled using low reagent concentrations. However, high levels of supersaturation ($SI > 0$) are produced even at low reagent concentration in the HAP crystallization process because of the low solubility of the products (2.35×10^{-59}, 25 °C) (Kumar et al., 2004). To avoid the negative effects caused by the homogeneous nucleation on phosphorus recovery, innovative technologies are needed.

The seeded air-agitated reactor (Kim et al., 2006; Moerman et al., 2009) and fluidized bed reactor (FBR) (Seckler et al., 1996a, 1996b; Battistoni et al., 2005) have been demonstrated as viable alternatives for phosphorus recovery. The processes are mainly based on the formation of phosphorus-containing inorganic salts onto the seed materials, and the precipitates are induced by adding precipitator into the reactor (Seckler et al., 1996a, 1996b; Moerman et al., 2009). However, HAP crystallization is merely formed in alkaline conditions and needs a mixed state. Increasing the pH of wastewater by adding alkali (sodium hydroxide) requires complicated and expensive equipment to add chemical agents with a pH sensor (Suzuki et al., 2002). On the contrary, it is difficult to achieve perfect mixing in an FBR with an even distribution of supersaturation (Costodes and Lewis, 2006). The air-agitated reactor can provide an increasing pH and perfectly mixed reaction system by aerated stirring for HAP crystallization (Battistoni et al., 1997; Suzuki et al., 2002). Li et al. (2010) studied the feasibility of HAP crystallization in an air-agitated reactor, and the results showed that a large amount of orthophosphate was removed from solution, but most of the generated microcrystalline left the reactor in the effluent streams as fine particles, rather than depositing onto the seeds. The results agreed with those obtained by Seckler et al. (1996a, 1996b) for phosphorus removal in an FBR. Similar results were also reported in the study of the recovery of sparingly soluble compounds with the crystallization reaction (Costodes and Lewis, 2006; Aldaco et al., 2007; Mokone et al., 2012). The reactor can be operated with recirculation stream and/or multiple reagent feed points to overcome the drawback of homogeneous nucleation that results in low recovery efficiency; this helps to reduce the level of supersaturation by diluting the reagent concentration fed into the reactor (Seckler et al., 1996a, 1996b; Mokone et al., 2012). However, the results showed that changing the recirculation flow rate and/or increasing the number of reagent feed points had a limited effect on process efficiency for the recovery of sparingly soluble compounds.

In the present study, an efficient approach for phosphorus recovery using three series-coupled air-agitated crystallization reactors was developed and characterized. The performance of the new process was investigated by measuring the orthophosphate content and SI in the series-coupled reactors. The characteristics of crystallized products were also analyzed by scanning electron microscopy (SEM) with energy-dispersive spectrometer (EDS), X-ray diffraction (XRD), and particle size analysis. Finally, various concentrations of phosphorus-containing solution were investigated to broaden its applications for phosphorus recovery from wastewater.

2. Materials and methods

2.1. Experimental apparatus and procedures

The experimental program consisted of two parts. The first part was designed to assess the performance of single continuously air-agitated reactor for HAP crystallization (Fig. S1(a)). The air-agitated reactor was developed in our previous research and consisted of precipitation area, buffer area, and reaction area, with a maximum working volume of 2.5 L (Li et al., 2010; Shi et al., 2012). The experimental conditions were as follows: a seed dose of 30 mg L^{-1} (calcite, particle size of 0.15–0.21 mm), hydraulic retention time (HRT) of 0.5 h, aeration rate of 300 L/h, and room temperature (25 ± 2 °C). The second part was designed to assess the performance of series-coupled continuously air-agitated reactors for HAP crystallization (Fig. S1(b)). The experimental conditions were the same as the first part in every crystallization reactor, except that the aeration rate was gradually reduced from reactor 1 to reactor 3. The aeration intensity of reactors 2 and 3 were 200 and 150 L h^{-1}, respectively. The stock solutions for HAP formation were continuously pumped into reactor 1, and then successively flowed past the subsequent reactors. To prevent the loss of seeds, the outlets of every reactor were coated with a 120 ASTM mesh sieve (0.12 mm).

2.2. Solution preparation

The AS was collected from an EBPR process (anaerobic–anoxic/nitrifying two-sludge process) established by our group (Shi et al., 2012), and the concentrations of constituents are shown in