Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–9

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Phosphorous recovery by means of fluidized bed homogeneous crystallization of calcium phosphate. Influence of operational variables and electrolytes on brushite homogeneous crystallization

Patrick S. Caddarao [a], Sergi Garcia-Segura [b], Florencio C. Ballesteros Jr [a], Yao-Hui Huang [c], Ming-Chun Lu [b,*]

[a] Environmental Engineering Graduate Program, College of Engineering, University of the Philippines, Diliman, Quezon City, Philippines
[b] Department of Environmental Resources Management, Chia-Nan University of Pharmacy and Science, Tainan 71710, Taiwan
[c] Department of Chemical Engineering, Sustainable Environment Research Center, National Cheng Kung University, Tainan, Taiwan

ARTICLE INFO

Article history:
Received 26 September 2017
Revised 7 December 2017
Accepted 8 December 2017
Available online xxx

Keywords:
Fluidized-bed reactor
Phosphate homogeneous crystallization
Water treatment technologies
Granulation process
Phosphate removal

ABSTRACT

Phosphate recovery from wastewaters is one of the major engineering challenges to securing the worldwide food production. Fluidized-bed heterogeneous crystallization of struvite has been one of the most considered technologies. Nevertheless, the recovery of other phosphate products could be of the major interest at industrial level. Thus, in this work we present the recovery of calcium phosphate salts as brushite by a novel fluidized-bed homogeneous crystallization (FBHC) process. The no requirement of seeds in FBHC reactor allows obtaining high-purity crystals. The operational parameters of the FBHC process have been optimized in order to achieve the higher degree of granulation and to obtain the most homogeneous distribution of granules sizes. Thus, the treatment of 1500 mg/L of phosphate at pH 9.0 with a ratio of 1.2:1.0 of $[Ca^{2+}]$:$[PO_4^{3-}]_T$ leads to the obtaining of ca. 90% of granulation with crystals of 0.5 mm of diameter. The influence of electrolytes typically found in TFT-LCD industry has been further considered. The characterization of the spheroidal crystals obtained allowed identifying brushite (calcium hydrogenphosphate salt) as unique crystal phase.

1. Introduction

Phosphorous is an indispensable chemical in fertilizers composition along with nitrogen species. Unlike nitrogen, phosphorous is a non-renewable resource [1–3]. The mining extraction of phosphate rocks is depleting dramatically mineral reserves. Thus, ascertaining phosphorous sources will not become only an engineering challenge but also of high social relevance in order to securing worldwide food production [1].

Phosphorous in wastewaters contributes to the eutrophication of waters [4,5]. About 90% of incoming phosphorous in water treatment plants is lost in the form of sewage sludge [6–8]. The development of water treatment technologies able to recover phosphate for its reuse in industrial manufacturing processes could contribute in a double beneficial way: (i) removal of phosphorous as pollutant from water sources, and (ii) secondary alternative phosphorous source. Phosphorous removal has been considered by using different technologies such filtration [9,10], coagulation [11], electrocoagulation [12,13], electrodyalisis [14], capacitive deionization [15] or biological treatments with photosynthetic organisms [16,17]. The mentioned processes do not allow phosphorous recovery for reuse.

Precipitation is a low-cost and highly efficient methodology for phosphorous removal. Unfortunately, the recovery of phosphorous from the precipitation sludge with high moisture content is not possible. Fluidized-bed crystallization (FBC) emerges as a promising environmental-friendly technology of phosphorous recovery [2,6,20,22]. FBC presents several advantages in front of conventional precipitation such as the use of fewer chemicals and the obtaining of crystallized particles (granules). Fluidized-bed reactors have been applied to the treatment of wastewaters containing inorganic pollutants such as Ni^{2+}[27,28], Cu^{2+}[29], Pb^{2+} [30,31], fluoride [32,33] and phosphorous [34,35]. The main disadvantage of FBC is that crystals grow onto supports (seeds). The different composition of these seeds leads to unpurified products that would inevitably affect the recyclability of the recovered crystals by FBC [30,32,34]. This work presents phosphorous recovery by a novel process without seeds so-called fluidized-bed homogeneous crystallization (FBHC). Here, the final product is obtained solely

* Corresponding author.
E-mail addresses: mmclu@mail.cnu.edu.tw, mclu@ms17.hinet.net (M.-C. Lu).

https://doi.org/10.1016/j.jtice.2017.12.009

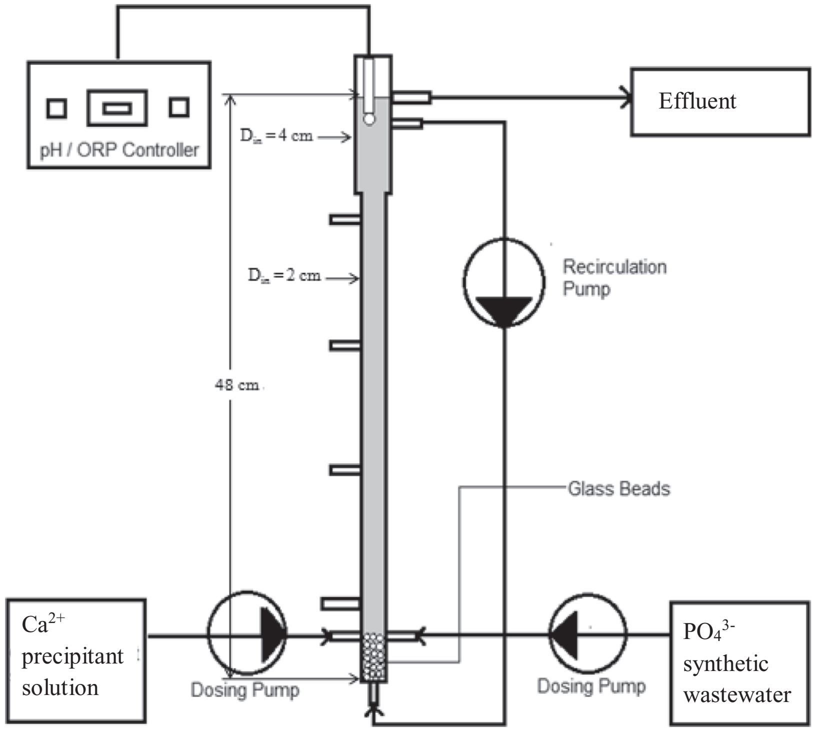

Fig. 1. Scheme of fluidized-bed reactor for homogeneous crystallization.

by homogeneous crystallization instead of conventional heterogeneous growing of the product onto the active surface of seed material [7,28,30]. FBHC is conducted under mild conditions of supersaturation where moderate amounts of fine nuclei agglomerate forming sufficient active sites to promote homogeneous crystal growth of high-purity granules. The main differences of FBHC to conventional technologies should be highlighted as (i) sludge is not produced, (ii) phosphorous is not only removed but recovered, and (iii) high pure granules are produced.

The formation of insoluble phosphate salts such struvite magnesium ammonium phosphate ($K_{ps} = 7.58 \times 10^{-14}$) is known because its natural precipitation in the sludge pipes at water-treatment plants [2,4,6,18–20]. However, other phosphate salts should be considered because of their interest from industrial/manufacturing points of view [8, 21–23]. Calcium phosphates (brushite) is used for several medical/biological applications as bioceramic in orthopedic and dental application, cancer therapies, food additive and biotechnological applications [24,25]. Furthermore, brushite is a phosphorous source for fertilizer or phosphoric acid manufacture [26].

In this work, obtaining of brushite crystals from synthetic effluents was studied by means of FBHC process. Variables of influence were studied in order to optimize removal with major granulation percentages. FBHC was conducted in presence of different electrolytes typically found in TFT-LCD industry effluents to evaluate the feasible application of this technology on the treatment of actual effluents. The characterization of the crystals allowed a better understanding of brushite crystallization mechanism and FBHC process.

2. Experimental

2.1. Chemicals

Phosphate solutions were prepared with KH_2PO_4 of high purity degree (>99.5%) purchased from Merck. Calcium chloride (96% purity) used as precipitant was supplied by Ferak Berlin GmbH. Reaction zone pH was maintained by the addition of little amounts of NaOH or HCl acquired from Merck. Ammonium molybdate tetrahydrated, potassium antimony (III) oxide tartrate trihydrate, and L(+)-Ascorbic acid of analytical grade used in the colorimetric quantification of phosphate were purchased from Panreac. The electrolytes used to simulate the industrial effluent were of analytical grade supplied by Sigma-Aldrich. All solutions were prepared using high-purity water from a Millipore Milli-Q system with resistivity > 18 MΩ cm.

2.2. Fluidized-bed homogeneous crystallization reactor

The fluidized-bed reactor (Fig. 1) consisted of a 550 mL cylindrical glass tube reactor divided in two sections: (i) Lower section of 80 cm height and 2 cm of inner diameter, (ii) upper section of 15 cm height and 4 cm of inner diameter. The treated solution was recirculated through the reactor with a peristaltic pump at variable flow rate to ensure fluidization of obtained granules. Achieving fluidization conditions is mandatory to ensure the formation of insoluble granules. Thus, up-flow solution recirculated should surpass the minimum fluid velocity (U_{mf}) where the flow compensate the gravitational force of the particles maintaining the particles in fluidized state [30,36,37]. For a low Reynolds (Re) number, as applied in FBHC process, the U_{mf} can be defined by expression (1).

$$U_{mf} = [0.0007(Re)_{mf}{}^{-0.063}]\frac{g{d_p}^2(\rho_p - \rho_f)}{\mu} \quad (1)$$

where g is the gravitational acceleration, d_p is the equivalent particle diameter, ρ_p is the particles density, ρ_f is the fluid density and μ is the fluid viscosity. Due to the nucleation, nuclei agglomeration and crystal growth mechanism, the particles change their d_p in function of time. Consequently, recirculation flow should be modified according to ($\delta d_p/\delta_t$) variation to maintain the granules in the fluidization state. Fluidization state was ascertained by