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Effect of sulphate(VI) ions on CSD of struvite – neural network model of continuous reaction crystallization process in a DT MSMPR crystallizer

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Abstract

Complex effect of sulphate(VI) ions on the continuous struvite ($MgNH_4PO_4 \cdot 6H_2O$, MAP) reaction crystallization process kinetics in DT MSMPR crystallizer and its final results was modeled numerically using artificial neural networks. Network was used as a multidimensional correlation between selected technological control process parameters (three inputs representing $[SO_4^{2-}]_{RM}$: 0.05 – 1.0 mass %, pH: 9–11 and mean residence time: 900 – 3600 s) and 43 size–channels of struvite product CSD (43 outputs corresponding to L within the $5.0 \cdot 10^{-7}$–$1.8 \cdot 10^{-4}$ m range). Network model reproduces experimental, nonlinear $\ln n(L)$ data correctly and accurately. Presenting CSD in a form of population density distribution $\ln n(L)$ made direct theoretical insight and identification of potential various kinetic mechanisms dominating for required $<[SO_4^{2-}]_{RM}$, pH, $\tau>$ vectors in various L ranges possible.

Keywords: Struvite; phosphprus recycling; sulphate(VI) ions; reaction crystallization; continuous DT MSMPR crystallizer; crystal size distribution; neural network model

1. Introduction

Cleaning technology of industrial, municipal and agricultural wastewater streams containing phosphate(V) ions integrated with effective phosphorus recovery is a subject of intensive research

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worldwide. One of promising technical variant to solve this problem is continuous reaction crystallization process in especially designed crystallizer construction. Controlled reaction between phosphate(V), magnesium and ammonium ions provides sparingly soluble product – struvite ($MgNH_4PO_4 \cdot 6H_2O$, MAP), which can be utilized directly in agriculture as a valuable mineral fertilizer [1–5]. Correct coupling, integration and control (within a possible range) of all process stages, including: supersaturation generation, its space distribution by multi–scale mixing effects and discharging through nucleation and crystals growth, accompanied by eventual aggregation/agglomeration or attrition/breakage creates attractive technological possibility of indirect affecting crystal size distribution (CSD) of crystalline struvite, thus product properties adjustment to meet the current market standards.

Wastewater, however, are the most often complex mixtures of various ingredients, regarded as impurities in respect to recyclable phosphate(V) ions. Since eventual large scale purification of wastewater from impurities is economically ineffective (frequent composition oscillations), research attention should be focused on reliable prediction of impurities co-presence effects, mainly resulting from their individual concentrations and proportions, on struvite continuous reaction crystallization process course and final results (mainly CSD).

One of inorganic impurities frequently present in industrial and municipal wastewater are sulphate(VI) ions (usually from SOITEX (silk and textile industry) wastewater, where chloride, sulphate(VI) and phosphate(V) ions are released from the postprocessed dyes decomposition [6]). Based on systematic measurements it was estimated, that in typical wastewater their average concentration is ca. 0.07 mass % [7]. Their presence in cleaned wastewater can potentially modify – in a complex and unpredictable manner – the struvite continuous reaction crystallization process course, resulting product CSD, struvite crystals shape, purity, characteristic sizes and other statistical parameters of CSD (L_m, L_{50}, L_d, CV), as well as even partly control the aggregation/agglomeration phenomena [8]. Because potential deviations from the results attributed to pure $NH_4^+ – Mg^{2+} – PO_4^{3-}$ model systems are essential for possibly precise estimation of struvite CSD, some efficient predictive tools are strongly required in design practice. Considering complexity of continuous struvite reaction crystallization process and not totally identified partial interrelations between all sub–processes in various scales, artificial neural network (ANN) technique was used for its numerical model elaboration [9–11].

2. Experimental

Laboratory experiments covering continuous phosphate(V) ions removal from its water solutions (1.0 mass % of PO_4^{3-}) in co-presence of sulphate(VI) ions (from 0.05 to 1.0 mass % of SO_4^{2-}) by struvite reaction crystallization process with the use of magnesium and ammonium ions in stoichiometric proportions, were carried out in DT MSMPR (*Draft Tube, Mixed Suspension Mixed Product Removal*) crystallizer unit with internal circulation of suspension resulting from propeller stirrer. Reaction crystallization of struvite ran in isothermal conditions 298 K, at pH 9 arranging mean residence time of suspension in a crystallizer working volume τ 900 s. For two selected concentrations of sulphate(VI) ions in a feed solution (0.1 and 0.5 mass % of SO_4^{2-}) complementary tests at pH 10 and 11 (τ 900 s), as well as for τ 1800 and 3600 s (pH 9) were also done [12, 13].

Crystallizer was continuously provided with a feed stream preprocessed in external mixer-reservoir using analytical grade components (magnesium chloride $MgCl_2 \cdot 6H_2O$, ammonium dihydrogenphosphate(V) $NH_4H_2PO_4$ and sodium sulphate(VI) Na_2SO_4 – POCh Gliwice, Poland) and deionized water (Barnstead – NANOpure DIamond). Such defined mixture was continuously dosed by pump into circulation profile – DT section (mixing rate: 6.6 ±0.1 s^{-1}; descending flow of circulated suspension). Between the crystallizer body and DT element (ascending suspension flow) water solution of