

Effect of Copper (II) Ions on Quality of Struvite Produced in Continuous Reaction Crystallization Process at the Magnesium Ions Excess

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ABSTRACT

The research results concerning continuous removal of phosphate (V) ions from solutions containing 1.0 or 0.20 mass % of phosphate (V) ions and 0.2 or 0.5 mg/kg of copper (II) ions using magnesium and ammonium ions addition are presented. Continuous reaction crystallization of struvite $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$ ran both under stoichiometric conditions and at 20% excess of magnesium ions (pH 9, τ 900 s). It was concluded, that presence of copper (II) ions in a process system influenced product quality moderately advantageously. Mean size of struvite crystals enlarged by ca. 6% only. Lower concentration of phosphate (V) ions and excess of magnesium ions caused, that products of ca. 9% - 13% larger crystal mean size (up to ca. 40 μm) were removed from the crystallizer. Presence of struvite crystals and copper (II) hydroxide were detected analytically in the products (Cu in a product varied from 6 to 90 mg/kg). Presence of copper (II) ions favored crystallization of struvite in the form of tubular crystals.

Keywords: Struvite; Phosphate(V) Ions; Copper Ions; Continuous Reaction Crystallization; DT MSMMPR Crystallizer; Crystal Size Distribution; Product Quality

1. Introduction

Recovery of phosphate(V) ions from wastewaters (called phosphorus recycling [1]) is based on precipitation followed by mass crystallization of sparingly soluble phosphate salts, the most often magnesium ammonium phosphate(V) hexahydrate, $\text{MgNH}_4\text{PO}_4 \times 6\text{H}_2\text{O}$, struvite (solubility product $\text{p}K_{\text{sp}}$ 9.0 - 13.26) [2]. The substrates used in this process are usually crystalline magnesium and ammonium salts or waste solutions containing magnesium or/and ammonium ions in sufficiently large concentrations. Yield and quality of manufactured product depend mainly on chemical composition of wastewater, pH and the assumed technological and equipment solutions [2-7]. Essential factor influencing course and results of struvite reaction crystallization process is composition of impurities present in wastewater [2,8]. Even small amount of impurity can inhibit or catalyze struvite precipitation reaction, influence nucleation rate and crystal growth rate, crystals shape and their eventual agglomeration [9-12]. Some metal ions in alkaline environment of struvite reaction crystallization process can

form sparingly soluble hydroxides or phosphates, what essentially modifies chemical composition of the product and often limits the possibilities of its further application in agriculture [13].

One of impurities present e.g. in liquid manure or in wastewaters from mineral fertilizer industry are copper(II) ions [14]. The research results concerning influence of three process parameters: molar ratio of substrates (stoichiometric conditions or 20% excess of magnesium ions in relation to concentrations of phosphate(V) and ammonium ions), concentration of phosphate(V) ions (1.0 or 0.20 mass %) and concentration of copper(II) ions (0.2 or 0.5 mg/kg) in solution feeding the continuous DT MSMMPR (*Draft Tube, Mixed Suspension Mixed Product Removal* [15]) type crystallizer on struvite product quality are presented in this work. The research tests ran at pH 9 for constant mean residence time of struvite crystal suspension in the crystallizer τ 900 s. Process yield defined as final concentration of PO_4^{3-} ions in a postprocessed mother solution was determined. Product crystal size distributions and their statistical parameters (L_m , L_{50} , L_d , CV) were calculated. Crystals shape (L_a/L_b) and their agglomeration effects were estimated. Copper content in a product was determined analytically.

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2. Material and Methods

Scheme of laboratory plant for the tests of struvite continuous reaction crystallization process in copper (II) ions presence is shown in **Figure 1**. Steering, control and acquisition of measurement data streams were carried out with the use of PC computer. For precise control of experimental plant operated in steady-state mode IKA labworldsoft program was used. Working volume of the crystallizer was 0.6 dm³. Crystallizer was a glass cylindrical tank (D 120 mm, H 123 mm), in a bottom part equipped with external heating/cooling coil (thermostated with water circulation system), providing isothermal process conditions. In central axis of the apparatus cylindrical circulation profile (*Draft Tube*, DT, d_{dt} 57 mm, h_{dt} 53 mm) was placed, inside which three-paddle propeller mixer (d_m 55 mm) operated. Inlet ports of reacting substances, alkalisng solution and removal port of product crystal suspension are indicated in **Figure 1**. Crystallizer was continuously provided with feed solution prepared earlier in a mixer device using chemically pure substances (magnesium chloride $MgCl_2 \times 6H_2O$, ammonium dihydrogenphosphate(V) $NH_4H_2PO_4$ and copper (II) chloride $CuCl_2 \times 2H_2O$ (p.a. POCh Gliwice, Poland) and deionised water (Barnstead – NANOpure Diamond). The solution was introduced into circulation profile (mixer speed: $6.6 \pm 0.11/s$; suspension movement – downward). Between crystallizer body and DT element (suspension movement – upward) aqueous solution of sodium hydroxide of concentration 20 mass % NaOH was dosed in proportions providing the assumed, con-

trolled value of pH. Temperature in a crystallizer was 298 ± 0.2 K. Research tests ran under stoichiometric conditions (molar proportions between the substrates $[PO_4^{3-}]_{RM} : [Mg^{2+}]_{RM} : [NH_4^+]_{RM} = 1 : 1 : 1$) and at 20% excess of magnesium ions ($[PO_4^{3-}]_{RM} : [Mg^{2+}]_{RM} : [NH_4^+]_{RM} = 1 : 1.2 : 1$). Concentration of phosphate (V) ions in a feed was 1.0 or 0.20 mass %. Corresponding concentration of magnesium ions was thus: 0.256 or 0.0512 mass % – in stoichiometric conditions, and 0.307 or 0.061 mass % – at their 20% excess. Concentration of ammonium ions was: 0.190 or 0.0380 mass %, appropriately, while concentration of copper ions was 0.2 or 0.5 mg/kg. Continuous reaction crystallization of struvite ran at pH 9 (± 0.1) for mean residence time of suspension in a crystallizer τ 900 s (± 20 s). After establishing in the crystallizer the required parameter values, process in steady state ran through the next 5τ . After this time whole crystallizer content was transferred to vacuum filter. Product crystals were not washed. Using adequate analytical methods for each test run there were determined: solid phase content in product crystal suspension (M_T), chemical composition of mother liquor and solid phase (plasma emission spectrometer ICP–AES CPU 7000, spectrometer IR PU9712, atomic absorption spectrometer iCE 3000, spectrophotometer UV–Vis Evolution 300), product crystal size distribution (solid particle laser analyser Coulter LS–230) and crystals shape (scanning electron microscope JEOL JSM 5800LV). Accuracy of process data determination in the continuous laboratory plant was estimated to be ca. 10%.

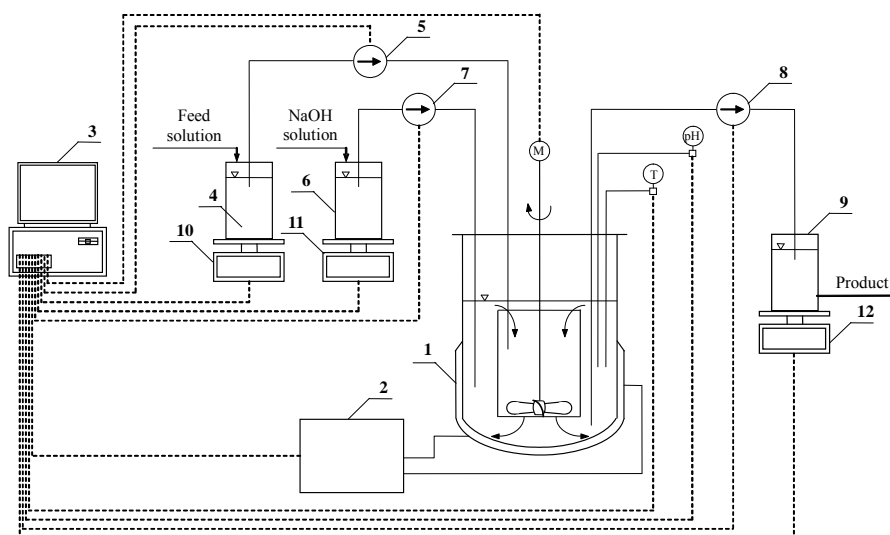


Figure 1. Laboratory test stand scheme of continuous crystallizer with a propeller stirrer for reaction crystallization of struvite, 1 – DT MSMPR type crystallizer with internal circulation of suspension, 2 – thermostat, 3 – computer, 4 – reservoir of feed mixture: aqueous solution of $NH_4H_2PO_4$, $MgCl_2$ and $CuCl_2$, 5 – feed proportioner (pump), 6 – alkalinity agent tank: aqueous solution of NaOH, 7 – proportioner of NaOH solution, 8 – receiver (pump) of a product crystal suspension from the crystallizer tank, 9 – storage tank of product crystal suspension, 10, 11, 12 – electronic balances, M – stirrer speed control/adjustment, pH – alkaline/acid reaction control/adjustment, T – temperature control/adjustment.

3. Results and Discussion

The research and analytical test results are presented in **Table 1**. From the table it results, that increase in concentration of copper(II) ions in a feed influenced product crystal size distribution moderately advantageously. For example, under stoichiometric conditions, for $[\text{PO}_4^{3-}]_{\text{RM}}$ 1.0 mass %, mean product crystal size L_m increased from 27.5 to 29.3 μm (by ca. 6%), while median crystal size L_{50} from 19.4 to 22.4 μm [14]. Growth L_m with the increase in copper(II) ions concentration in a process system is connected with general decrease of the smallest struvite crystals amount in a population of solid product. For $[\text{Cu}^{2+}]_{\text{RM}}$ 0.2 mg/kg crystal fraction of sizes below 5 μm in a product was 15.7%, whereas for $[\text{Cu}^{2+}]_{\text{RM}}$ 0.5 mg/kg this fraction decreased to 13.0%, thus shrank by ca. 17%. The largest struvite crystal size did not, however, varied (ca. 140 μm), whereas dominant crystal size (L_d , corresponding to maximum in differential distribution), even slightly decreased (L_d 25.5 \rightarrow 24.8 μm). In **Figure 2(a)** exemplary volumetric (mass) size distribution of struvite crystals produced in presence of 0.5 mg/kg of copper(II) ions in a feed ($[\text{PO}_4^{3-}]_{\text{RM}}$ 1.0 mass %, pH 9, τ 900 s) is presented. In **Figure 3(a)** there was presented scanning electron microscope image of product sample, which crystal size distribution was presented in **Figure 2(a)**. Detailed data concerning influence of copper(II) ions concentration ($(1-10)\times 10^{-5}$ mass %) and technological parameters (pH 9–11, τ 900–3600 s) of struvite continuous reaction crystallization process from solutions containing 1.0 mass % of PO_4^{3-} ions under stoichiometric conditions are presented in [14]. Influence of these pa-

rameters on mean size L_m (μm) of product struvite crystals was elaborated in a form of empirical correlation [14]:

$$L_m = 6.748 \times 10^2 [\text{Cu}^{2+}]_{\text{RM}}^{0.052} \text{pH}^{-1.956} \tau^{0.243} \quad (1)$$

Five time decrease of phosphate(V) ions concentration in a crystallizer feed (from 1.0 to 0.20 mass %) resulted in increase in mean struvite crystal size L_m by 9–13% (No. 3 and 4 in **Table 1**). Solution supersaturation at the crystallizer inlet decreased. Thus struvite nucleation rate, strongly dependent on supersaturation is decreased, as well. It resulted in decrease of nuclei amount, thus larger size of crystals removed from the crystallizer (compare **Figures 2(a)** and **(b)**, as well as **Figures 3(a)** and **(b)**).

From the comparison of **Figures 2(a)** and **(b)** it results, that feeding the crystallizer with solution of concentration 0.20 mass % phosphate(V) ions both number and size of the largest struvite crystals increased. The largest size of struvite particles produced at $[\text{PO}_4^{3-}]_{\text{RM}}$ 0.20 mass % was 210 μm (**Figure 2(b)**), whereas at $[\text{PO}_4^{3-}]_{\text{RM}}$ 1.0 mass % it was 140 μm only (**Figure 2(a)**). Fraction of the smallest size particles in a product did not, however, decrease. In results mean size of product crystals increased by 2.7 μm only: from 29.3 to 32.0 μm (tests No. 2 and 4 in **Table 1**).

It can be assumed, that it is a net effect of smaller struvite nucleation rate corresponding to lower working supersaturation level in a crystallizer and smaller content of solid phase in a mixed and circulated suspension (M_T 24.3 \rightarrow 5.0 kg struvite/ m^3 of suspension), limiting thus excessive crystal attrition effects. From the analysis of presented experimental data it results, that influence of

Table 1. Effect of copper(II) ions on the results of continuous struvite reaction crystallization process in DT MSMRP crystallizer. Process parameters: temperature 298 K, pH 9, mean residence time of suspension in the crystallizer τ 900 s.

No.	Feed		Suspension		Crystal product characteristics*					
	$[\text{PO}_4^{3-}]_{\text{RM}}$ mass %	$[\text{Cu}^{2+}]_{\text{RM}}$ mg/kg	M_T kg crystals/ m^3	$[\text{PO}_4^{3-}]_{\text{ML}}$ mg/kg	L_m μm	L_{50} μm	L_d μm	CV %	L_d/L_b –	$[\text{Cu}]_{\text{product}}$ mg/kg
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$										
1	1.0	0.2	24.4	170	27.5	19.4	25.5	92.9	6.6	6
2	1.0	0.5	24.3	168	29.3	22.4	24.8	84.5	6.5	16
3	0.20	0.2	4.9	154	31.1	22.4	28.2	93.9	6.7	28
4	0.20	0.5	5.0	152	32.0	21.8	28.7	96.8	6.6	76
Molar proportions of reagent ions in a feed: $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$										
5	1.0	0.2	24.6	26	28.8	23.0	25.9	92.8	6.6	7
6	1.0	0.5	24.8	22	33.9	24.6	26.9	94.9	6.4	20
7	0.20	0.2	5.0	24	33.0	24.6	30.5	90.2	6.6	31
8	0.20	0.5	5.1	20	39.7	27.3	41.6	92.4	6.4	90

*Without product crystal washing; tests No. 1 – 2 see [14]; Average concentration of Cu^{2+} ions in mother solution: 0.05 – 0.10 mg/kg. $L_m = \sum x_i L_i$, where: x_i – mass fraction of crystals of mean fraction size L_i ; L_{50} – median crystal size for 50 mass % undersize fraction; L_d – crystal mode size; $\text{CV} = 100(L_{84} - L_{16})/(2L_{50})$, where: L_{84} , L_{16} , L_{50} – crystal sizes corresponding to 84, 16 and 50 mass % undersize fractions.

these process parameters on the final crystal size distribution of struvite can be regarded only as a moderate.

Excess of magnesium ions in relation to phosphate(V) and ammonium ions concentrations in a crystallizer feed ($[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$) influenced the process results generally advantageously (tests No. 5-8 in **Table 1**). For example, mean struvite crystal size L_m enlarged from 32.0 to 39.7 μm (by ca. 24%) for $[\text{PO}_4^{3-}]_{\text{RM}}$ 0.20 mass % in presence of copper ions of concentration 0.5 mg/kg (**Figure 2(c)**). Higher supersaturation of magnesium ions in struvite precipitation environment influenced partial components of the continuous reaction crystallization process generally advantageously. Their net effect (higher nucleation rate, however also higher crystals growth rate) produced more favourable crystal size distribution of struvite. In **Figure 3(c)** there is presented scanning electron microscope image of exemplary product crystals. From the comparison of crystal size distributions presented in **Figures 2(b)** and **(c)** it results, that at magnesium ions excess both number and size of the largest struvite crystals increased ($L_{\text{max}} 210 \rightarrow 220 \mu\text{m}$). Simultaneously number of the smallest struvite particles decreased. Crystal fraction of sizes smaller than 5 μm represented 9.7% (**Figure 2(c)**). In result the dominant crystal size L_d increased from 28.7 up to 41.6 μm , and mean size L_m – from 32.0 to 39.7 μm (tests No. 4 and 8 in **Table 1**).

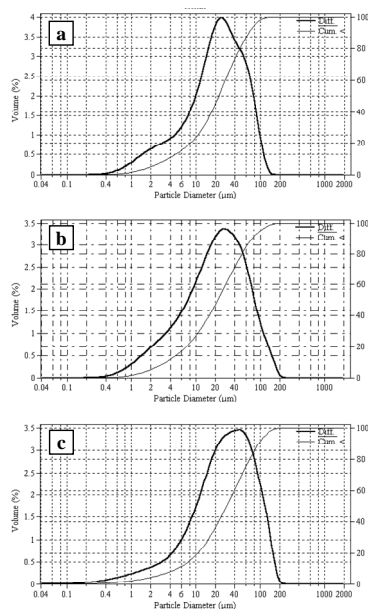


Figure 2. Exemplary differential (left scale) and cumulative (right scale) volumetric (mass) size distributions of struvite crystals produced in continuous reaction crystallization process in presence of 0.5 mg/kg of copper(II) ions in a feed: a) $[\text{PO}_4^{3-}]_{\text{RM}}$ 1.0 mass % and b) $[\text{PO}_4^{3-}]_{\text{RM}}$ 0.20 mass %, for $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1 : 1$, and c) $[\text{PO}_4^{3-}]_{\text{RM}}$ 0.20 mass % for $[\text{PO}_4^{3-}]_{\text{RM}} : [\text{Mg}^{2+}]_{\text{RM}} : [\text{NH}_4^+]_{\text{RM}} = 1 : 1.2 : 1$ – corresponding to tests No. 2, 4 and 8 in **Table 1.**

From the data presented in **Table 1** it also results, that homogeneity within product crystal population was practically constant. The CV coefficient value representing quantitatively inhomogeneity within crystal sizes varied within the 90.2%-96.8% range (excluding only one strongly deviated value: 84.5%) with the average value of 93.4%. It is relatively high CV value, suggesting large diversification within product crystal sizes (CV for ideal DT MSMPR crystallizer is 50% [15]).

From the analysis of scanning electron microscope images of exemplary products (**Figure 3**) it results, that struvite crystal habit was practically constant. Based on planimetric measurement results involving 50 crystals randomly selected from three microscope images (from each product population) it was concluded, that average ratio of their length L_a to their width L_b varied within relatively narrow range from 6.4 to 6.7, depending on process parameter values (**Table 1**). These values were close to geometrical proportions within struvite crystals produced in the same crystallizer unit from aqueous solutions of NH_4^+ , Mg^{2+} and PO_4^{3-} ions without impurities [12]. Less than moderate agglomeration within struvite crystals were reported in the products (**Figure 3**), especially within larger crystals. It can be thus regarded, that advantageous process conditions were established in the crystallizer, limiting excessive aggregation and agglomeration between crystals of the main product component. From the presented product microscope images (**Figure 3**) it also results, that in struvite population characteristic in shape tubular crystals are present. Most of them, especially larger crystals, demonstrated, however, distinct ruptures and crashes along longitudinal axis, numerous surface cracks and deformed edges, being the proof of significant tensions in their structure (see **Figure 4**). These crystals, shaped during unconstrained growth, are especially susceptible for the action of shear stresses generated by turbulent flow of mother solution, as well as on secondary contact nucleation [15].

In **Table 1** there are presented the analytically determined concentration values of phosphate (V) ions in a postprocessed mother solution. It can be practically assumed, that this concentration stabilised on relatively constant and low level $161 \pm 9 \text{ mg PO}_4^{3-}/\text{kg}$ under stoichiometric conditions and $23 \pm 3 \text{ mg PO}_4^{3-}/\text{kg}$ at magnesium ions excess. Average efficiency of phosphate (V) ions removal from the feed was thus 91%-99%. Magnesium ions excess in relation to phosphate (V) and ammonium ions concentrations influenced process yield advantageously. Concentration of phosphate (V) ions in a postprocessed mother solution was ca. 7 time smaller compared to stoichiometric conditions. In **Table 1** there are also presented the analytically determined values of copper(II) ions concentration in a postprocessed mother solution, as well as copper(II) content in a product. Con-

centration of copper (II) ions in a feed was modified from 0.2 to 0.5 mg Cu²⁺/kg). It was concluded, that average concentration of copper (II) ions in a postprocessed mother solution decreased to 0.05-0.10 mg Cu²⁺/kg. In a product copper (II) hydroxide appeared (pK_{sp} 19.32) in amount from 6 to 90 mg/kg (copper based calculations), depending on copper (II) ions concentration in a feed and process parameters. Raise of $[Cu^{2+}]_{RM}$ from 0.2 to 0.5 mg/kg caused, that copper content in a product increased from 6 to 16 mg/kg ($[PO_4^{3-}]_{RM}$ 1.0 mass %). Lower concentration of phosphate (V) ions in a feed (0.20 mass %), thus smaller amount of product struvite (M_T 4.95.0 kg crystals/m³ suspension) caused, that relative content of copper in a product increased ca. 5 time. Excess of magnesium ions in a process system caused, that copper content in a product increased by ca. 15% in average.

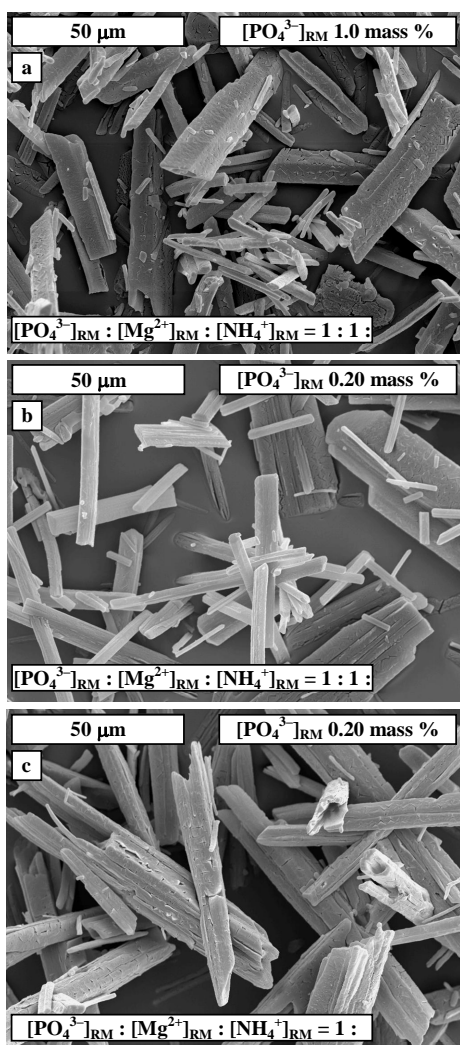


Figure 3. Scanning electron microscope images of struvite crystals produced in a continuous DT MSMR type crystallizer in presence of 0.5 mg/kg of copper(II) ions. Process parameters: a) test No. 2, b) test No. 4 and c) test No. 8 in Table 1 (corresponding to Figure 2).

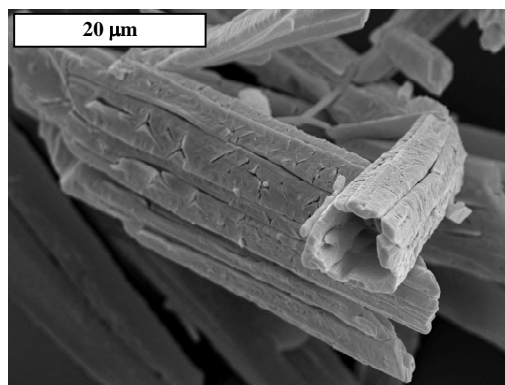


Figure 4. Habit and surface morphology of struvite crystals produced in presence of copper(II) ions (corresponding to Figure 3c).

4. Conclusions

In presence of copper (II) ions struvite crystal products of mean size from 27.5 to 39.7 µm and large size diversification (average CV 93.4%) were manufactured. It was observed, that with the increase in concentration of copper(II) ions from 0.2 to 0.5 mg/kg in a feed mean size of product crystals L_m increased insignificantly, only by ca. 6%. Decrease of phosphate (V) ions concentration in a feed from 1.0 to 0.20 mass % resulted in raise of mean size of struvite crystals by 9-13%. Similarly, excess of magnesium ions in relation to phosphate (V) and ammonium ions concentrations influenced process results advantageously. Mean size of product crystals increased by 13% in average. Excess of magnesium ions in a process system strongly, advantageously influenced the struvite continuous reaction crystallization process yield. Concentration of phosphate (V) ions in a postprocessed mother solution decreased to 23 ± 3 mg/kg, what can be regarded as a very good result of their removal from the feed. Precipitation of phosphate (V) ions in presence of copper(II) ions results in production of not only struvite crystals, but also copper(II) hydroxide particles (copper based – from 6 to 90 mg/kg).

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