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DANIEL STUMPF*, SAMUEL GROS*, BERND HEINZMANN**, MATTHIAS KRAUME*

PHOSPHORUS RECOVERY BY INDUCED MAP-PRECIPITATION

ODZYSKIWANIE FOSFORU POPRZEZ INDUKOWANE STRĄCANIE FOSFORANU AMONOWO-MAGNEZOWEGO

Abstract

Different air flow rates were tested in a 1-L batch and a 45-L pilot reactor to optimize the parameters for MAP precipitation for phosphorus recovery in a large-scale plant. The pilot reactor was designed as an airlift reactor and the required pH values for precipitating MAP were reached by stripping CO_2 of a model solution. The result was the same for all flow rates: about 85–90% of phosphorus was recovered as MAP at steady state. Hence it is promising, that the process for an optimized precipitation of MAP can been successful scaled up.

Keywords: phosphorus recovery, MAP precipitation, CO_2 stripping, airlift reactor

Streszczenie

W instalacjach 1-L (okresowej) i 45-L (pilotażowej) zastosowano różne wydatki gazu dla optymalizacji parametrów strącania fosforanu amonowo-magnezowego (struvit) dla odzysku fosforu w instalacji rzeczywistej. Instalacja pilotażowa stanowiła reaktor airlift. Wymagane, dla strącania struvitu, wartości pH uzyskiwano poprzez striping CO_2 z roztworu. Wyniki były podobne dla wszystkich wydatków: w stanie ustalonym około 85–90% odzyskiwanego fosforu. To wskazuje na możliwość optymalnego powiększenia skali procesu strącania fosforanu amonowo-magnezowego.

Słowa kluczowe: odzyskiwanie fosforu, strącanie fosforanu amonowo-magnezowego, striping CO_2, reaktor airlift

* Dipl.-Ing. Daniel Stumpf, Dipl.-Ing. Samuel Gros, Prof. Dr.-Ing. Matthias Kraume, Institut für Prozess- und Verfahrenstechnik, Technische Universität Berlin.
** Dr. Bernd Heinzmann, Berliner Wasserbetriebe (Berlin Water).

1. Motivation

The natural phosphorus deposits are likely to run out in the next 90 years [1]. However, phosphorus is a vital product for all organisms and an essential nutrient for plants. Unfertilized soils often do not have enough plant-available phosphorus and as a result must be fertilized. There are different areas of research to recover phosphorus [2, 7]. A possible phosphorus recovery process consists of the precipitation, crystallization and separation of magnesium ammonium phosphate (MAP or struvite) in different process waters [1].

The sludge of a wastewater treatment plant with enhanced biological phosphorus removal is an effective source for phosphorus. An attractive way of recovering phosphorus from digested sludge is the precipitation in the sludge directly, as part of the continuous treatment process. The sludge of a digester is under anaerobic conditions, so that the assimilated phosphorus of the microorganisms from the biological phosphorus removal process is released [3].

The Berliner Wasserbetriebe (Berlin Water) implemented an induced MAP precipitation by aerating digested sludge to avoid incrustations in the sludge chain, particularly in the treatment equipment [4]. As a result of the aeration, carbon dioxide is stripped, raising the pH-value [5]. Magnesium chloride is added and phosphorus is precipitated as MAP. This process, shown as a scheme in Fig. 1, needs to be optimized for a safe treatment process and a maximum amount of recovered phosphorus as MAP from digested sludge. After separating and cleaning, the obtained MAP could be reused as a fertilizer.

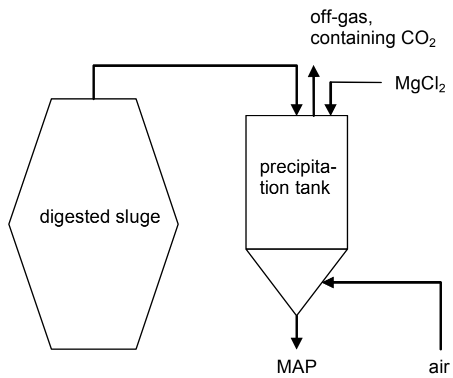

Fig. 1. Scheme of the MAP-precipitation at Berlin Water

Rys. 1. Schemat wytrącania MAP w Berliner Wasserbetriebe

At first, 1-Litre batch tests were performed using a model system to examine the MAP-crystallization kinetics. Different parameters like e.g. the aeration flow rate were investigated. The aim was to find setting parameter for a pilot reactor for the continuous production of MAP. This reactor is designed as an airlift reactor for an improved mixing and stripping of the dissolved CO_2 and enhanced separation of the MAP-crystals. A comparison of the results of the 1-L batch test and the first results of the pilot reactor will be presented in this work.

2. Experiments

2.1. 1-L-batch tests

To understand the precipitation of MAP, 1-L batch experiments were conducted. Fig. 2 shows a scheme of the 1-L batch reactor used. The reactor has a diameter of 108 mm. At first, a model solution was used ($n_{PO4\text{-}P}$:n_{Mg} = 1:1, $c_{PO4\text{-}P}$ = 330 mg/L, c_{Mg} = 258,95 mg/L, $c_{NH4\text{-}N}$ = 1250 mg/L, buffer), which contained the respective ion concentrations of the real digested sludge of a wastewater treatment plant of Berlin Water. The batch reactor volume was saturated with CO_2 to get the same pH-value as in the real system (pH 7). After adding $MgCl_2$, the CO_2 was stripped by supplying air ($\dot{V}$ = 100 – 500 L/h). To determine the amount of precipitated crystals, the residual dissolved concentrations of magnesium, ammonium and phosphate in the batch reactor were measured by an ion chromatographic analyser. Also the pH value was measured during the experiment.

After ending the batch test the whole volume of the 1-L reactor was filtered. The filtrate was dried at 30 °C until it reached a constant weight and the total mass of the precipitated crystals was measured (Sartorius BP221S). Furthermore samples of the precipitated MAP were identified under a microscope (light-optical microscope, Zeiss) to receive information about the shape of the crystals. Typical shapes of MAP crystals like the orthogonal and cross shape were identified, which were described by Pschyrembel et al. [6].

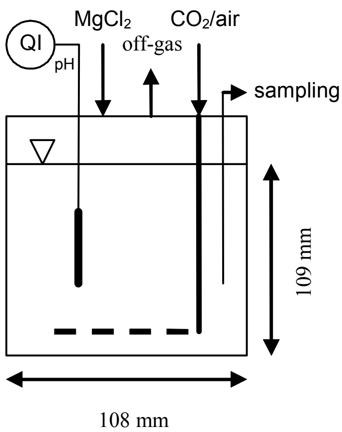

Fig. 2. Flow sheet of the 1-L batch

Rys. 2. Schemat reaktora o 1-L

2.2. Pilot reactor

For the scale up of the precipitation experiments a 50-L pilot airlift reactor was designed on basis of the results of the 1-L batch tests. The main aim was the optimization of the MAP precipitation to assign the results for a planned large-scale precipitation reactor at the waste water treatment plant of Berlin Water. The investigated pilot reactor configuration is shown in Fig. 3. First experiments were conducted as batch scale with a liquid volume of 45 L. Thus a transferability of the 1-L tests results and a verification of the precipitation in the new reactor configuration were possible. A model solution which was saturated with CO_2 like described in section 2.1. was used.

The pilot reactor consists of two concentrically cylinders, one with an outer diameter of 300 mm and an internal cylinder with an outer diameter of 200 mm. At the bottom of the internal cylinder the gas sparger is located. The bottom of the pilot reactor has a cone-shape with a valve for the outlet of the precipitated crystals. The aeration in the inner cylinder induces a loop circulation as it is known for airlift reactors with two sections: a riser and a downcomer.

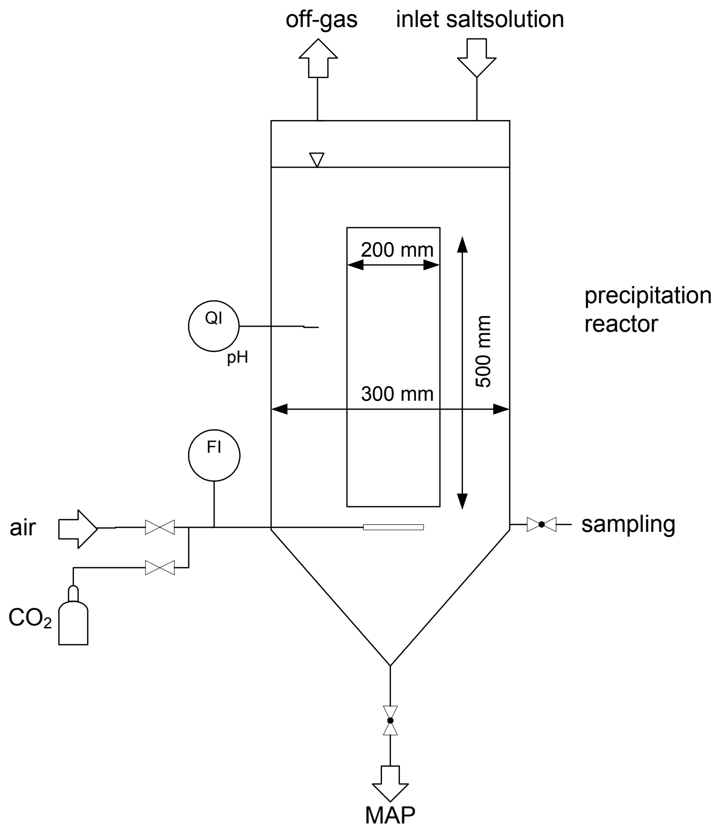

Fig. 3. Flow sheet of the pilot reactor

Rys. 3. Schemat reaktora pilotażowego

3. Results

In this configuration the aeration has two functions: to mix the solution and to strip the solved carbon dioxide. The pH is thereby increased and MAP precipitates as saturation is exceeded. The MAP crystals grow up and leave the circulation with a terminal size. Thus they settle down in the cone bottom. After ending the experiment the volume of the cone bottom was filtered. The filtrate was dried at 30 °C to a constant weight and the total mass of the precipitated crystals were measured like in the 1-L batch tests.

Samples of the precipitated MAP were investigated under the microscope to get information about the shape of the crystals of the pilot reactor as well. Furthermore the particle size distribution of the dried crystals was studied. For that sieves with different mesh sizes were used (300 µm, 200 µm, 150 µm, 90 µm, 60 µm, 33 µm). Various research works on particle sizes of MAP are described by Corre et al. [7].

The influence of different parameters was investigated in numerous batch tests. These were particularly the stoichiometrical dosing of $MgCl_2$ and gas flow rates. The detailed methods and results of the tests are described in Stumpf et al. [8a, 8b]. In this work the results of the 1-L batch tests were compared with the results of the pilot scale reactor.

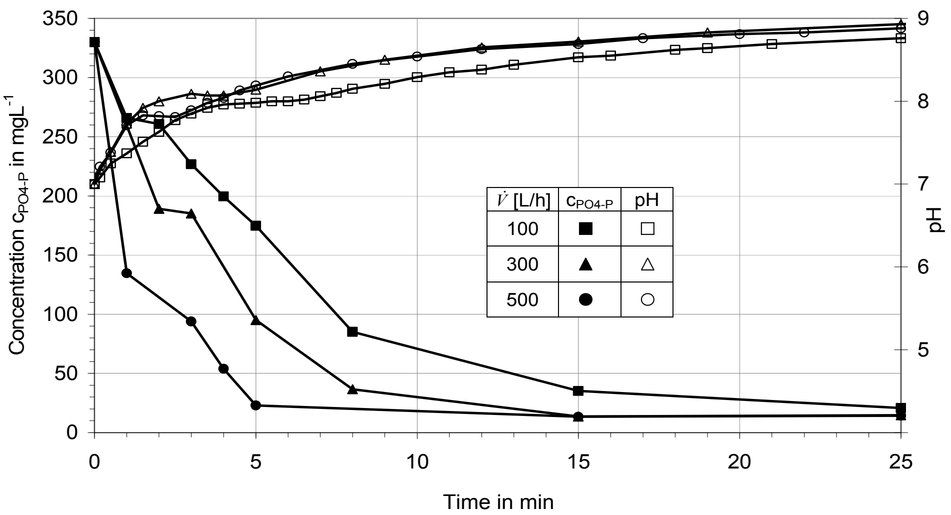

Fig. 4. MAP precipitation in a model solution at different air flow rates ($\dot{V}_{1-3}$) in a 1-L batch

Rys. 4. Wytrącanie MAP w reaktorze 1-L dla różnych przepływów ($\dot{V}_{1-3}$)

As can seen in Fig. 4, MAP crystals precipitated after several minutes by stripping CO_2 (indicated by decreasing residual dissolved phosphate concentration and rising pH). Different air flow rates were tested in both systems to optimize the parameters for the pilot plant. When a high air flow rate $\dot{V}$ was adjusted ($\dot{V}_3$ = 500 L/h), the precipitation took less time than at lower aeration rates ($\dot{V}_1$ = 100 L/h and $\dot{V}_2$ = 300 L/h). However, at all flow rates tested, the result was the same: about 85% of phosphorus was recovered as MAP at the end of the experimental time.

This result was also observed in the pilot reactor. Fig. 5 shows the phosphate concentration for the pilot reactor. Eliminations of about 90% were reached in 120 minutes at an air flow rate of 500 L/h. Hence, at all flow rates tested, always 85–90% of solved phosphate was precipitated as MAP at the end of the experiments. Therefore it can be said the final result was dependent on the amount of the stripped CO_2.

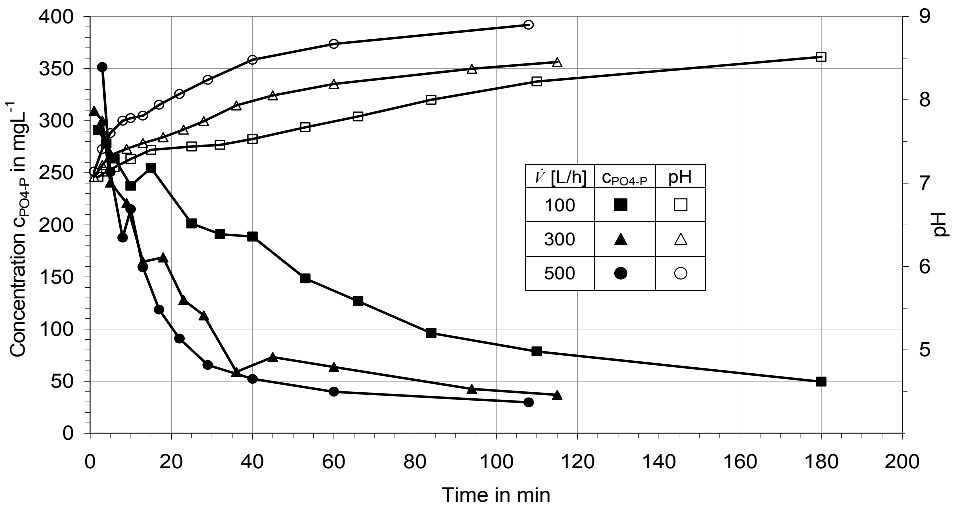

Fig. 5. MAP precipitation in a model solution at different air flow rates ($\dot{V}_{1-3}$) in the pilot reactor

Rys. 5. Wytrącanie MAP w reaktorze pilotażowym dla różnych przepływów ($\dot{V}_{1-3}$)

Figure 6 shows the results of the sieve-experiments. The identified average size as a result of the particle size distribution was shown to be 90–150 µm for all flow rates in the pilot reactor. At lower aeration rates ($\dot{V}$ = 100 L/h) particle sizes partially shift to 200 and 300 µm. So the particle sizes were larger than at higher air flow rates. At low supersaturations conditions larger crystals can build up than in high supersaturations [9]. The supersaturation is depending on a well mixed chemical system and the amount of stripped CO_2. It is assumed, that at lower circulation velocities the supersaturation is lower than at high circulation velocities with a faster stripping of CO_2.

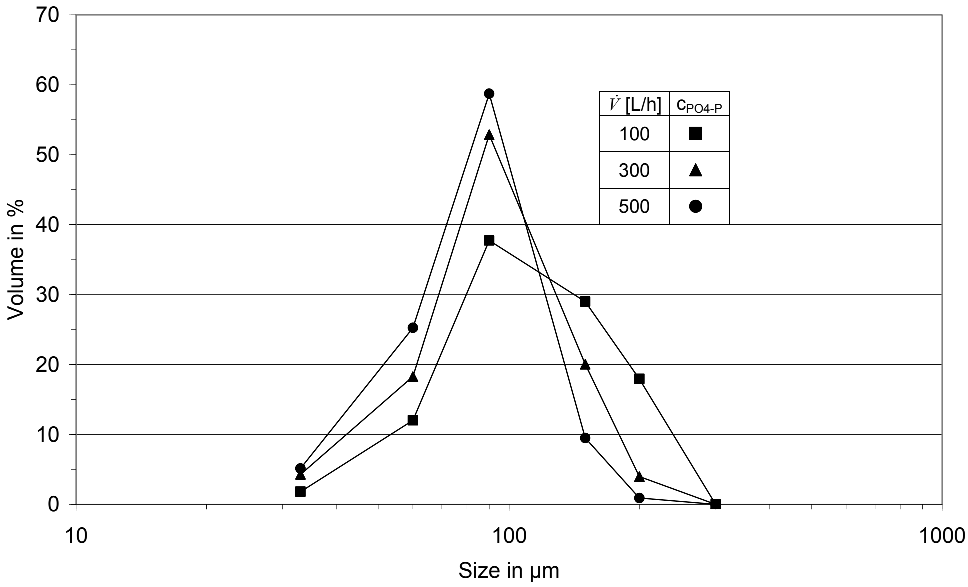

Fig. 6. Particle size distribution of MAP for different air flow rates in the pilot reactor

Rys. 6. Rozkład wielkości cząstek MAP dla różnych przepływów powietrza w reaktorze pilotażowym

The general goal for the precipitation process is to recover a maximum amount of phosphorus. As seen in Fig. 7 a yield of up to 90 % (yield y_{MAP}, Eq.(1)) is obtained in the pilot plant experiments

$$y_{\mathrm{MAP}} = m_{\mathrm{MAP,\,real}} / m_{\mathrm{MAP,\,possible}} \tag{1}$$

$$m_{\mathrm{MAP,\,possible}} = c_{\mathrm{PO4\text{-}P}} \cdot V_{\mathrm{PR}} \cdot M_{\mathrm{MAP}} / M_{\mathrm{PO4\text{-}P}} \tag{2}$$

For a high air flow rate ($\dot{V}_3$), this amount was reached after one hour. At the same time, 58% of yield$_{\mathrm{MAP}}$ at $\dot{V}_1$ was reached and 80% at $\dot{V}_2$. This means, recovering of MAP in a short time requires a high air flow rate and a fast stripping of CO_2.

However, for the phosphorus recovery it is also necessary to have a defined particle size for a successful separation of the crystals from the solution. Additionally to the particle size distribution, MAP crystals were identified under a microscope. Fig. 8 shows pictures of two samples. The samples are taken after 5 minutes and after 75 minutes during the precipitation in the pilot plant. As can be seen, the crystals grow from about 30 µm to near 300 µm in about 70 minutes at an aeration rate of 300 L/h. This was the maximum crystal size for the whole experimental time at $\dot{V}_2$.

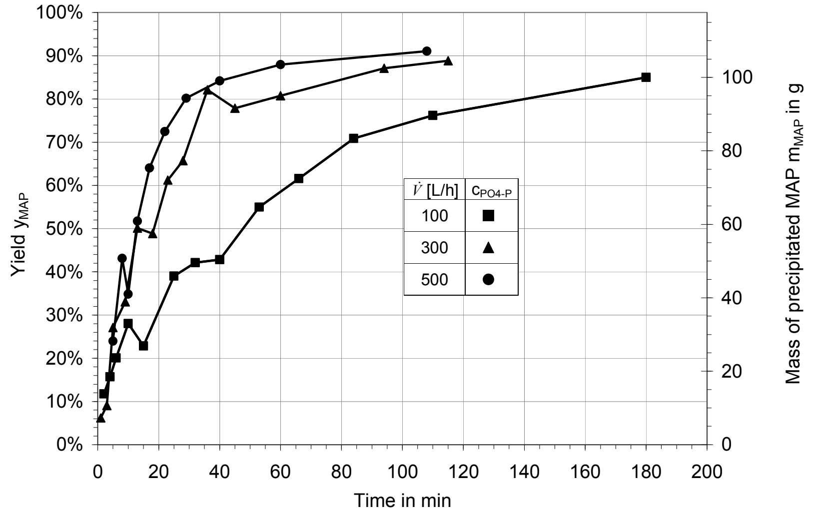

Fig. 7. $Yield_{MAP}$ in a model solution at different air flow rates ($\dot{V}_{1-3}$) in the pilot reactor

Rys. 7. Uzysk MAP w rozwiązaniu modelowym dla różnych przepływów powietrza ($\dot{V}_{1-3}$) w reaktorze pilotażowym

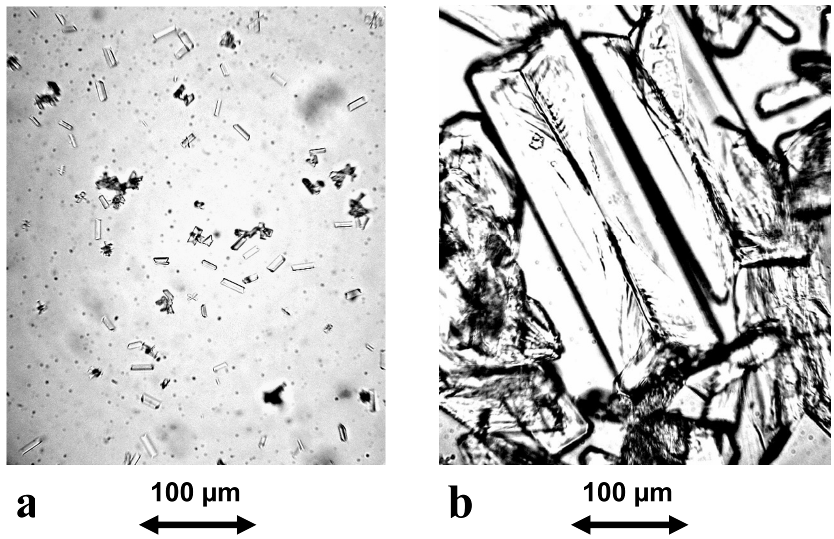

Fig. 8. Microscopical pictures of MAP crystals,
after 5 minutes a) and after 75 minutes b) of aeration (300 L/h) in the pilot plant

Rys. 8. Mikroskopowe obrazy kryształów MAP
po 5 a) i 75 minutach b) aeracji (300l/h) w instalacji pilotażowej

4. Conclusions

MAP crystals start precipitating after several minutes in a model solution by stripping CO_2 (indicated by decreasing phosphate concentration and rising pH). The compared results of a 1-L and a 45-L pilot reactor correspond at all flow rates: about 85–90 % of phosphorus was recovered as MAP at steady state. These results are similar to other research results [10, 11]. Hence it is promising, that the process for an optimized precipitation of MAP can be successfully upscaled. It can be noticed that the optimal precondition for the pilot reactor is given when the air flow rate for mixing the system and for stripping CO_2 for a maximum MAP precipitation are aligned with the particle size distribution. For further experiments it is important, that the supersaturation should be moderate and the circulation velocity is not too low, otherwise the crystals settle down before they can grow enough.

Symbols

c	– concentration	[mg/L]
CO_2	– carbon dioxide	
MAP	– magnesium ammonium phosphate (struvite)	
m	– mass	[g]
M	– molecular weight	[g/mol]
n	– amount of substance	[mol]
pH	– pH-value	
$\dot{V}_{1, 2, 3}$	– air flow rates	[L/h]
V_{PR}	– reactor volume	[L]
y_{MAP}	– yield of MAP (the possible amount of total mass of MAP)	[%]

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