Continuous Phosphorus Recovery by Heterogeneous Nucleation: Challenges in Solid-Liquid Separation

Dipl.-Ing. Eva Förster*,
Dipl.-Ing. Sarah Illies, Dr.-Ing. Harald Anlauf, Prof. Dr.-Ing. Hermann Nirschl
Institute of Mechanical Process Engineering and Mechanics (MVM),
Karlsruhe Institute of Technology (KIT)
E-Mail: eva.foerster@kit.edu

ABSTRACT

Phosphorous (P) is an essential natural resource of limited availability. Furthermore, many countries, including Germany, have no access to P sources and are entirely dependent on P imports to cover their demand. Therefore the recovery of P is a topic of distinct importance. In the past decades a manifold of processes for P recovery from wastewater have been developed. The P-RoC-process (Phosphorus Recovery by Crystallization) is a technique developed by Competence Center for Material Moisture (CMM), KIT, based on crystallization of P on a Calcium-Silicate-Hydrate (CSH) substrate [1]. The feasibility of the approach has been shown on the lab scale and also as a semi-batch process on the pilot scale in a side stream of a municipal sewage plant. For full implementation of the process, a transition from semi-batch to a continuous process is desirable. However a crucial question still to be solved is the removal of the P-loaded substrate from the process.

Challenges for the CSH separation are the particle size distribution that will result in a distribution in reaction kinetics and thus a difference in P coverage with particle size. Additionally comminution of the highly porous particles might also be an issue. The task at hand thus requires a separation unit that allows for classification as well as for separation of the particles. In this paper we present how the continuous classification and separation of P-loaded CSH is solved by using a hydrocyclone. For this cause an experimental setup was developed in order to realize the continuous P crystallization on CSH substrate and removal of CSH on the pilot scale.

KEYWORDS

Classification, Hydrocyclone, Phosphate, Scale-up, Solid-Liquid-Separation, Wastewater

1. Introduction

Phosphorus (P) is an essential element, since it serves as a storage of genetic information, and as a carrier of metabolism. Phosphorus is a not renewable and therefore limited resource. Different thermal and chemical processes for recycling P from wastewater have been developed over the past decade. A promising method is the PRoC-process (Phosphorus Recovery by Crystallization) which was developed by CMM, KIT. The process is based on the crystallization of P on porous Calcium-Silicate-Hydrate (CSH) substrate. This serves due to its high specific surface area as crystal nucleus. Furthermore, due to the discharge of hydroxide ions the setting of appropriate reaction conditions for the formation of phosphate-containing mineral phases is supported by this material. The core of the process is a crystallization reactor. Wastewater and CSH-particles are brought into the crystallization reactor and stirred for a certain time. The reaction time is dependent on the effluent to be treated with times up to two hours. Afterwards the complete suspension is brought into a sedimentation tank, where the P-depleted water is separated from the P-loaded material. The resulting product is hydroxyapatite or struvite, which can be directly used as secondary phosphate. The conventional PRoC-process operates semi-continuous, resulting in a deterioration of efficiency. In order to increase the efficiency of the PRoC-process, different CSH materials are investigated to meet the requirements of a continuous process. These requirements include substantially high and fast reactivity of the particles, a good mixing in the reactor in order to avoid an enrichment of coarse material. In the present work the sedimentation tank is replaced with a hydrocyclone which now allows the continuous operation mode.

2. Materials and Methods

Materials

For the classification as well as for the crystallization experiments, different Calcium-Silicate-Hydrate (CSH) particles, all with a density of 2560 kg/m³, were used. An overview about the particles is given in Table 1.

Table 1: Overview about the particles used

short name	product name	producer
CSH 1	Circolit®	Cirkel
CSH 2	0,1 Circosil®	Cirkel
CSH 3	0,5 Circosil®	Cirkel
CSH 4	Silyzit®	Silikalzit

The particle size distributions of the particle systems are very different as shown in Figure 1. The range of the mean particle sizes is between 9.5 µm and 700 µm (Table 2). For kinetic measurements, a 100 mg/l P (phosphorus) solution was used. The removal of P out of the solution was determined according to DIN EN ISO 6878:2004.

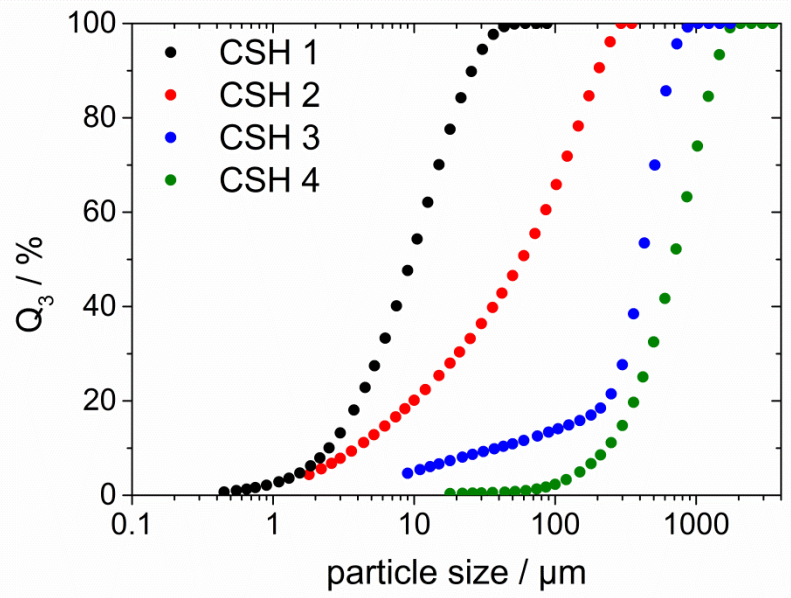

Figure 1: Particle size distribution of the calcium-silicate-hydrate (CSH) used

Table 2: Mean particle sizes of the CSH systems used

particle system	mean particle size [µm]
CSH 1	9.53
CSH 2	58.12
CSH 3	413.84
CSH 4	694.88

To determine the grade efficiency of the hydrocyclone, particle size distributions of the samples are determined by sieving.

Methods

The determination of the P-removal kinetic was realized on the lab-scale. Five mass percent CSH were given to 15 ml P-solution. After certain times, samples were taken for the photometric determination of the remaining P concentration in the solution.

Gas adsorption measurements were conducted to determine the specific surface area of the particles.

The classification of the CSH particles was realized in pilot scale. The scheme of the process is shown in Figure 2. Suspension, consisting of five mass percent CSH and water is continuously fed to the pressure vessel and pneumatically fed to the hydrocyclone. The pressure vessel allows the pulsation free transport of the suspension.

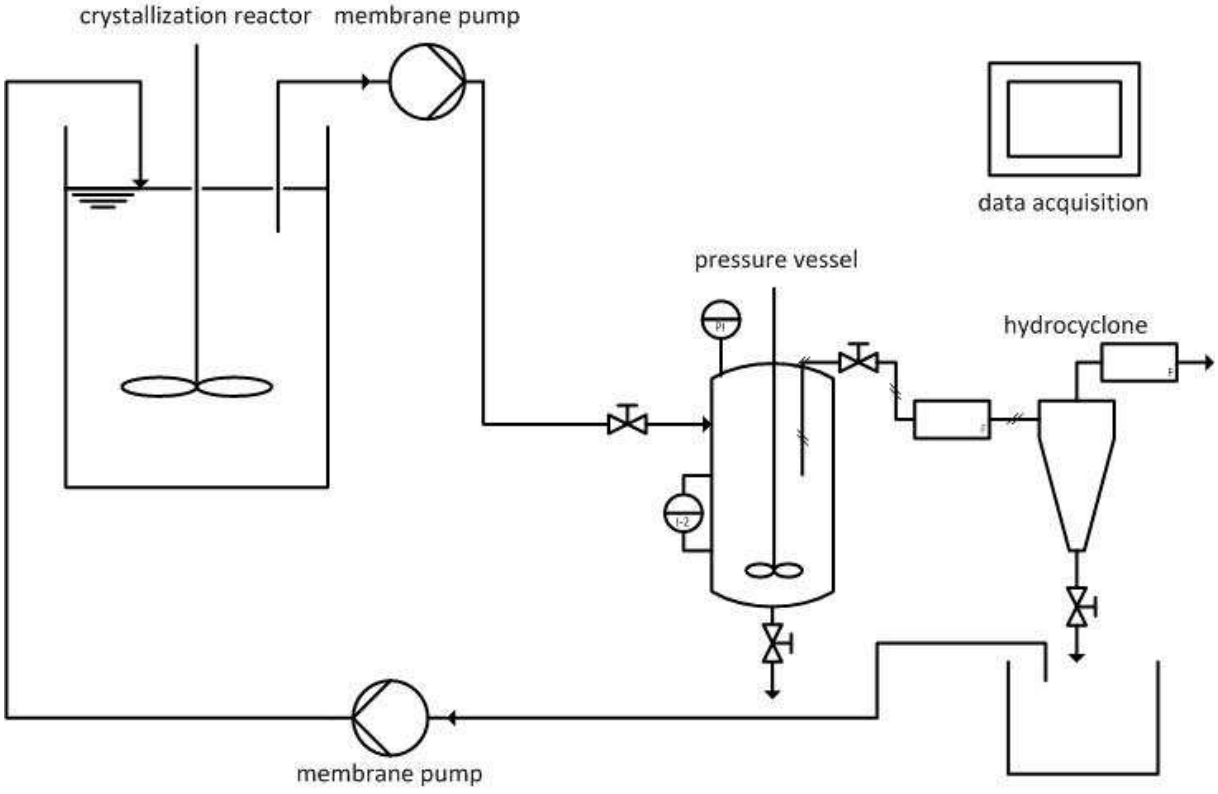

Figure 2: Flow sheet of the classification process

In order to find the most appropriate operation mode to separate the respective material from the water, different operation modes can be realized. As the large particles tend to grind during the process, the coarse particles on the underflow are returned into the crystallization reactor, where they are grinded again and new

surface area is created to bind new P. Small and already loaded particles can be directly clarified from the waste water.

3. Results and Discussion

P-Elimination

The P-elimination out of a model wastewater solution with 100 mg/l P over the time is shown in Figure 3. The four CSH samples investigated differ significantly in P-elimination kinetics as well as in maximum P-elimination. CSH 2 achieves nearly 100 % P-elimination after 5 minutes. For CSH 4, however, even after 120 minutes the P-elimination is 80 %.

The P-elimination data in Figure 3 can be explained by the difference in specific surface area shown in Table 3. It is evident that the P-elimination kinetics are directly dependent on surface area, as it is expected.

With regard to process efficiency, it is thus important to not only examine the particle size but also the specific surface. All in all, CSH 2 is the most suitable particle system to achieve rapid P-removal out of wastewater.

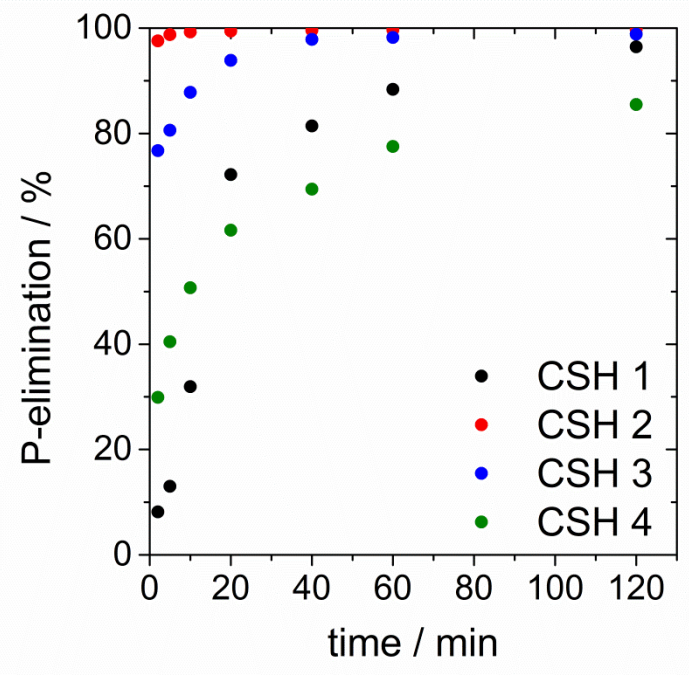

Figure 3: P-elimination in dependence of the material and the time

Table 3: Specific surfaces of the particle systems used

Particle system	Specific surface [m²/g]
CSH 1	36.4
CSH 2	63.5
CSH 3	58.8
CSH 4	25.6

Since the crystallized particles are the product of value in the form of secondary phosphate, they have to fulfill several conditions. For an easy handling and to prevent undesired dust formation, the product must not be too fine. Contrarily, the product must not be too coarse to prevent sedimentation in the reactor during the process. Furthermore, longer dwell times have to be realized to achieve good P-eliminations.

Particle classification

In a first step, the previously in the semi-batch process used material CSH 4 is investigated with regard to its classification by the hydrocyclone. As particles of CSH 4 tend to abrasion, an increase of fine particles over process time is observable. In order to increase the efficiency of the process, fine P-loaded particles leave the process by overflow of the hydrocyclone whereas coarse particles leave by underflow and are recycled to the crystallization tank, where they are abrased and loaded again. The grade efficiency of the hydrocyclone in dependence of the underflow diameter is shown in Figure 4. The volume flow at the inlet was kept constant at 1 m³/h.

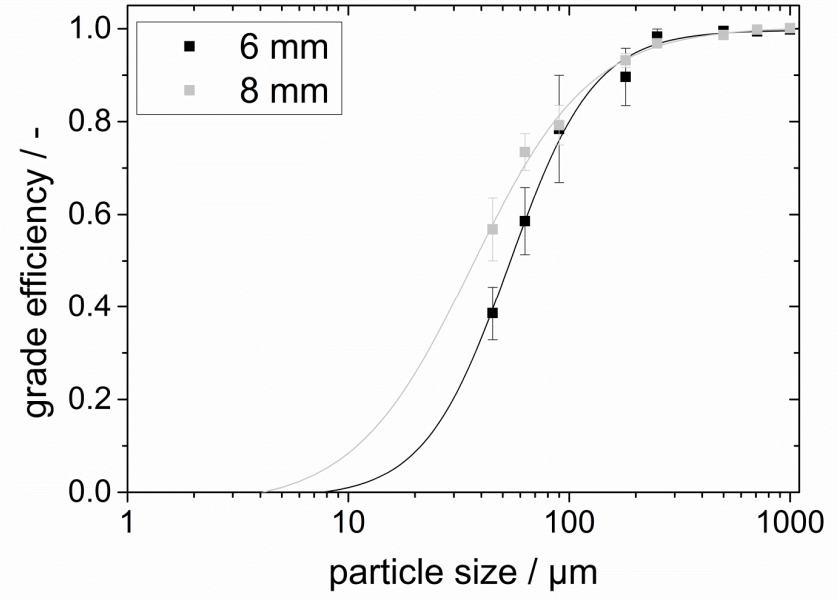

Figure 4: Grade efficiency in dependence of the underflow diameter.

The larger the underflow diameter, the more fine particles leave the underflow, which shifts the grade efficiency into direction of smaller particles. Additionally, the grade efficiency becomes sharper with decreasing underflow diameter by simultaneously less fine particles in the underflow. Table 4 shows the classification quality at different underflow diameters.

Table 4: Classification quality κ at different underflow diameters.

Underflow diameter (mm)	x_{50} (µm)	κ (-)
6	54.09	0.38
8	37.27	0.27

4. Conclusion

The efficiency of the P-elimination is highly dependent on the specific surface and therefore the porosity of the CSH particles. The hydrocyclone used is a good, flexible and cost efficient alternative for particle separation or classification in dependence of the operation mode. Both, classification and clarification can be realized in dependence of the particle system. For further investigation of the continuous process operation, it is recommended to select a particle system which on the one hand shows fast reaction kinetics and high maximum P loads and on the other hand can be easily separated in a hydrocyclone.

[1] Ehbrecht, A. / Fuderer, T. / Schönauer, S. / Schuhmann, R.: "Phosphorus Recovery by Crystallization - Implementation with municipal sewage water". In: Integrated Water Resources Management (IWRM), Karlsruhe, Germany. Hartwig Steusloff [Hrsg.]: 290-297. 21.-22. November 2012.