A novel cascade reactive crystallization process for phosphorus recovery

Ph.D. project by ***Liubov Vasenko***
Email: liva@kbm.sdu.dk

UNIVERSITY OF SOUTHERN DENMARK

Department of Chemical Engineering, Biotechnology and Environmental Technology
Faculty of Engineering, University of Southern Denmark

Project Period: January, 2016 – December, 2018

This Ph.D. study is a part of a larger project ReCoverP the overall goal of which is to increase the phosphorus recovery from wastewater and transform this into high quality P-products that can be used in agriculture and industry.

Introduction

Phosphorus is one of the major nutrients needed for all living organisms. Phosphorus compounds are widely used in industry, medicine, fertilizers production etc. The main source of phosphorus is used to be the phosphate rock but accordantly to different sources its reserves are dropping down and probably will be over within next 60 – 130 years. At the same time, wastewater contains a large amount of P which can be recycled and reused. Recovering P from wastewater streams seems to be the best way for achieving P sustainability.

Nowadays, the developed crystallization technologies of P recovery include only one stage of crystallization process, which doesn't allow obtaining the P-product of high quality at the same time with achieving the sufficient degree of phosphorus removal from wastewater. Thus, the development of two stage crystallization technology will allow to produce the high purity P-product at the first stage and to accomplish a high P removal in the second stage.

The aim of this project is to develop the cascade crystallization technology for calcium phosphate and struvite precipitation as well as the optimisation of the new technology in regards with the yield and purity of obtained P-products, degree of P recovery from wastewater stream and the improvement of the overall economy of the process.

Theoretical background

The idea of designing a novel cascade reactive crystallization process stems from the comprehensive consideration of the solution chemistry of the ions and the multicomponent solid-liquid equilibrium involved in the crystallization of calcium phosphate and struvite. As it is shown in Figure 1, the solubility of dicalcium phosphate dihydrate (DCPD, $CaHPO_4 \cdot 2H_2O$) and struvite (MAP, $MgNH_4PO_4 \cdot 6H_2O$) in terms of the conditional solubility product P_s are both pH dependent. The solubility of DCPD is lower than the solubility of struvite at lower pH, which implies that high purity DCPD might be crystallized at pH about 5 – 6 by proper dosing calcium ion to the system. It can also be seen that the solubility of struvite approaches a very low minimum at pH around 10, which suggested that a high P-removal can be obtained at pH 9 – 10.

Thermodynamics

Cascade reactive crystallization process can be described by reactions:

- ***DCPD:***

$$Ca^{2+} + HPO_4^{2-} + 2H_2O \leftrightarrow CaHPO_4 \cdot 2H_2O \qquad (1)$$

- ***MAP:***

$$NH^{4+} + Mg^{2+} + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O \qquad (2)$$

P_s has been computed from the solubility product K_{SP}:

- for ***DCPD:***
  $K_{SP} = 2.32 \times 10^{-7}$;
- for ***MAP:***
  $K_{SP} = 4.266 \times 10^{-14}$.

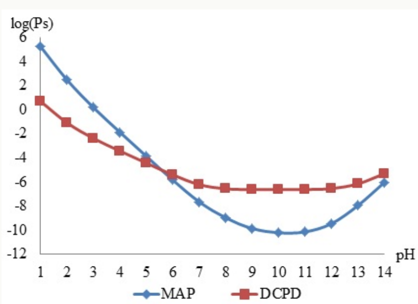
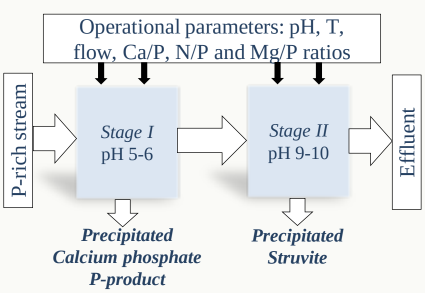


Figure 1. Conditional solubility of DCPD and MAP according to pH variation.

Process design development and optimization



Optimization of the process in regards with the yield and purity of P-products as well as with the overall economic effect will be done by trying different operational parameters of the process such as pH; T; Ca/P, N/P and Mg/P ratios in the WW stream at the each stage.

Stages of research

1. ***Feasibility study*** of two stage crystallization process with the use of artificial solutions for modulation of WW stream will determine the possibility of precipitation of DCPD and MAP under the specific conditions;
2. ***Laboratory experiments*** with real WW will allow implementing the results obtained at the previous stage to the real P-rich stream obtained from the project partners.
3. ***Process scale up.*** The aim of this stage is to scale up the process on the bigger pilot scale and to double check the optimal parameters of the process. It is planed late in the project and it will be done on the base of one of our project's partners - Lappeenranta University of Technology in Finland in terms of the change of the research environment.

References

Rosemarin. Peak phosphorus, the next inconvenient truth?. – 2nd International Lecture Series on Sustainable Sanitation. World Bank, Manila. October 15, 2010.

J. Doyle et. al. Fundamental chemistry and control of struvite precipitation. Second Int. Conf. on the Recovery of Phosphorus from Sewage and Animal Wastes, Noordwijkerhout, The Netherlands (2001).

W. Stumm. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters / W. Stumm., J.J. Morgan. – 3rd ed. – Environmental Science and Technology: A Wiley-Interscience Series of Texts and Monographs (Vol. 105). John Wiley&Sons, USA. 2013. 1040 p.