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Membrane crystallization for phosphorus recovery and ammonia stripping from reject water from sludge dewatering process

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ABSTRACT

Membrane crystallization (MCr) have been applied on real wastewater to study the potential of recovering phosphorus as struvite ($MgNH_4PO_4{\cdot}H_2O$). The performance of MCr shows a stable flux at recovery factor of 70%. To facilitate struvite precipitation, magnesium has been added in the molar ratio of 1:1.3 of P:Mg. A recovery of 60% phosphorus have been obtained at pH of 8.3 and at recovery factor of 70%. Furthermore, the MCr process allows to produce an ammonia-rich stream on the permeate side, due to the hydrophobic nature of the membrane and the transport of volatile compounds through the membrane. This liquid stream can be considered to be used directly as a fertilizer product.

1. Introduction

It is becoming common that industries and society want to exploit their resources due to environmental regulations, economic gain and sustainable standpoint. In this perspective, waste streams have to be turned into resources in the most environmental-friendly, economic and sustainable way. An example can be found at wastewater treatment plants (WWTPs) in the perspectives of producing energy in form of biogas and nutrients in form of mainly phosphorus and nitrogen [1]. Other factors such as emissions, pollutions, footprint and flexibility [2] are also important constrains to take into account when designing future WWTPs according to the guidelines of the process intensification strategy [3]. The process intensification strategy aims to develop novel equipment and techniques that, compared to those commonly used, dramatically improves manufacturing and processing, by decreasing equipment size, improving raw material to production ratio, decreasing energy consumption and waste production, and ultimately results in cheaper, sustainable technologies [3–5]. Several procedures in wastewater treatment can be reevaluated in order to meet process intensification. For instance, there is focus on phosphorus recovery and reuse from wastewater due to impending risk of depletion of the existing phosphorus reserves within the next 100 years [6]. Phosphorus in the inlet to the WWTP is much lower comparing with the content in the sludge or the content in the liquid removed from the sludge during the dewatering process (termed reject water). In the inlet, phosphorus is bound biologically or chemically and therefore, not accessible for recovery. During the digester treatment part of the biological bound phosphorus is released to the liquid, thus the reject water can be used for phosphorus recovery. It is more feasible to recover phosphorus from WWTPs, which apply biological treatment (e.g. enhanced biological phosphorus removal) as more phosphorus is release during digestion whereby high phosphorus concentrations are obtained in the reject water that can subsequently be recovered. Normally, the reject water is returned to earlier stages of the treatment process causing higher concentrations of phosphorus, which increases the need for chemical dosing and the risk of scaling of pipelines and other equipment. For this reason, there is also operational advantages of recovering phosphorus. Therefore, many WWTPs have implemented phosphorus reuse as fertilizers in form of applying sludge directly on agricultural fields, incinerating the sludge or by implementing fluidized bed reactors for phosphorus recovery from the reject water.

However, problems related to heavy metal accumulation in soil limit the direct use of sludge or the ash from incineration and therefore, the fluidized bed reactors have gained increasing attention. At industrial scale, phosphorus in the form of struvite precipitation ($MgNH_4PO_4{\cdot}6H_2O$) is carried out in e.g. Denmark, Japan (PHOSNIX), Canada (Ostara), Netherland (PHOSPAQ™, AirPrex), and Germany (Seaborne, AirPrex) [7]. Other compounds such as calcium phosphate can also be a potential way to fix phosphorus from wastewater [8,9], but is not today practiced in the same extend as struvite recovery. However, one of the main obstacles for phosphorus recovery is low recovery factors and high expenses for adding of chemicals such as

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magnesium. Moreover, it can be challenging to control the precipitation if the wastewater composition or other influencing factors change. Therefore, it is an objective to look toward alternative methodologies, such as membrane engineering, for improving the phosphorus recovery process. Some studies have focused on phosphorus recovery by means of membrane technology as for instance forward osmosis [10–14], selective electrodialysis [9], osmotic membrane bioreactor [15] and their integration [16]. Other novel membrane operations i.e. membrane distillation (MD) and membrane crystallization (MCr) have been previously suggested for a well-controlled recovery of minerals from complex solutions, but has never been used directly for phosphorus recovery. MD and MCr are based on a vapor pressure gradient across a hydrophobic microporous membrane, which enables only volatile compounds to go through the membrane. MD and MCr are found in several configurations, but the simplest type is the direct-contact membrane distillation configuration, which uses liquids on both sides of the membrane. The vapor pressure gradient is induced as a temperature gradient by heating the feed solution normally in the range of 40–65 °C. The volatile compounds evaporate near the membrane surface, pass the membrane as vapor and are then being condensed at the cold permeate side. Despite, being a thermal process, MD and MCr can be operated using waste heat or low-grade heat since the temperature requirements are relative low. Moreover, no high-pressure pumps are necessary and therefore, the electrical energy is significantly reduced with respect to conventional pressure-driven membrane operations. MD and MCr can be operated at much higher concentrations, which is out of the scope of pressure-driven membrane operations. Moreover, the hydrophobic nature of the membrane ensures that the permeate quality is very high. Previous studies on MD for wastewater treatment has mainly been used to concentrate the draw solution in FO [10,17] or to recover ammonia [18–21]. MD and MCr are practically the same process. The difference is that MCr is operated until saturation of the solution, which causes the minerals/biomolecules present in solution to nucleate and grow. The advantage of MCr is the well-controlled and easy tunable precipitation at low energy requirements, which are difficult to obtain from normal crystallization processes [22,23]. MCr has previously been applied on desalinated brine for recovery of NaCl and $MgSO_4 \cdot 7H_2O$ [24,25], NaCl from wastewater from oil and gas industry [26], Na_2SO_4 from industrial waste [27–29] and for crystallization of various biomolecules [23,30,31]. However, MCr has never been applied for phosphorus recovery. The objective of this study is, therefore, to make a proof-of-concept of utilizing membrane distillation and membrane crystallization for concentration of real reject water with simultaneously recovery of phosphorus. The aim is to recover phosphorus as struvite since this is the compound produced normally from WWTPs in full-scale.

2. Materials and methods

The wastewater utilized in this study is obtained from Aaby wastewater treatment plant in Aarhus, Denmark. The plant treats 84,000 PE using biological phosphorus removal. The wastewater stream used in this study is termed reject water, which for this particular plant is a mixture of the liquid phase from the dewatering process before and after the digester. The composition and the characteristics of the reject water are given in Table 1. The MD and MCr tests have been carried out on reject water coming directly from the WWTP.

Table 1
Composition of reject water obtained from Aaby wastewater treatment plant.

pH	7.98
Conductivity	7.65 mS/cm
o-P	228 mg/L
NH_4	1306 mg/L
Mg	2.71 mg/L

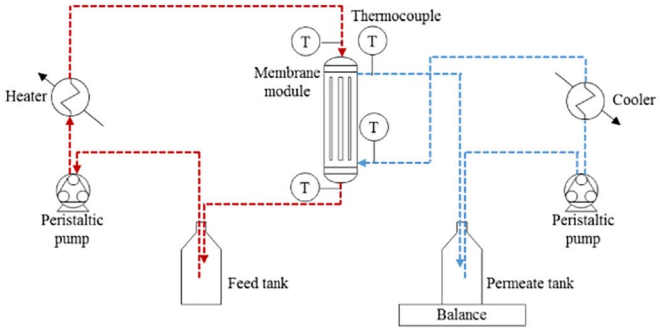

Fig. 1. Flow diagram of MD and MCr setup.

2.1. Composition analysis

Ortho-phosphate (o-P) and ammonium have been measured spectrophotometric according to the procedure given in Danish Standards [32–34]. Prior to o-P analysis, the samples have been filtered through a 0.45 µm filter and conserved with 4 M H_2SO_4 (10 µl/ml sample). Magnesium in the sludge has been determined by atomic absorption spectroscopy (AAS). For all Mg analyses, an air-acetylene flame has been utilized.

2.2. Membrane distillation and membrane crystallization

MD and MCr have been carried out on a lab-scale plant as illustrated in Fig. 1. The feed temperature has been adjusted to around 45, 55 and 65 °C with a flowrate of 20 L/h. The hollow fiber membrane modules used for all experiments have been made using Membrana Accurel® PP S6/2 hollow fiber membranes. The membrane hollow fibers have an outer diameter of 2.5 mm, an inner diameter of 1.6 mm and a wall thickness of 0.45 mm. The porosity of the membranes is 73% with a PMI pore size of 0.2 µm. The total membrane area of the 20 fibers is 0.043 m^2. In the MCr test, magnesium has been added to the reject water before starting the experiment. Aaby wastewater treatment plant is currently running a fluidized bed reactor for struvite precipitation with addition of $MgCl_2$. Normally, $MgCl_2$ is added in the ratio of 1.3 × Mg with respect to phosphate [35] and therefore, the same molar ratio has been used in current study. Samples for o-P analysis have been taken before adding magnesium and in every hour during the experiment. The pH has been adjusted to 8.3 by 1 M NaOH before the experiment in order to facilitate struvite precipitation.

2.3. Crystal characterization

The produced crystals have been analyzed by light microscope (Zeiss Axioskob) connected to a computer. The samples have been prepared by withdrawing 1 ml of solution containing the crystals. The solution has been spread on a glass plate and imaging through the microscope. The produced crystals have been analyzed by x-ray diffraction (XRD) and inductively coupled plasma optical emission spectrometry (ICP-OES). For XRD analysis the crystals have been dried and used directly, whereas for ICP-OES analysis the crystals have been dissolved in super pure nitric acid.

3. Results and discussion

3.1. Membrane distillation

The performance of the MD tests is shown in Fig. 2. As expected the flux increases with temperature and illustrates a constant flux at recovery factors above 70% (Fig. 2a). The stable flux for all the