Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode

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ABSTRACT

As mineral resources of phosphorus are limited, the use of alternative phosphorus sources such as wastewater becomes an increasingly important option. In this study, the recovery of phosphorus from pretreated sewage sludge is examined, using nanofiltration for the removal of heavy metals from the product stream. The membranes DL, NF270, AS and Duracid were tested in a bench scale filtration unit at pH values of 0.5 and 1.5. The dependence of flux and separation efficiency on transmembrane pressure (TMP) and on permeate recovery was studied. Thanks to the ion-selectivity of nanofiltration membranes, multivalent metal cations were rejected effectively, while neutral and negatively charged phosphorus compounds could be collected in the permeate. It was shown that heavy metals and metals had retention values higher than 0.94, while a retention lower than 0.3 was reached for phosphorus. The retention of phosphorus was found to increase at higher TMPs and with decreasing pH value. The phosphorus yield could be improved significantly if diafiltration was applied. By doing so, a maximum phosphorus yield of 83.7% could be reached at a permeate recovery of 90%.

1. Introduction

Phosphorus is an essential nutrient for plant growth and plays a major role in agriculture. In order to achieve a sustainable food production, all phosphorus that is removed from the fields with the harvested crop must be replaced by fertilizers with an equivalent phosphorus content. Today, the main raw material for fertilizer production is phosphorus rock that is mined from the earth's crust [1]. However, only few regions worldwide have phosphorus deposits while many others depend entirely on imports, for example Western European countries [2]. Not only are the remaining resources of decreasing quality, but it is also estimated that they will be depleted in less than 380 years [1–4]. As a consequence, the mineral phosphorus prices will increase and the need for alternative phosphorus sources will rise [5]. Phosphorus recovery from urban wastewater has been found to be a particularly promising option [1,6].

In most wastewater treatment plants, nutrients are removed from the water stream in order to prevent the eutrophication of water bodies. The sewage sludge acts as a sink for phosphorus and contains around 90% of the influent phosphorus load. It is thus a suitable

process stream for the recovery of phosphorus [7]. Some recovery processes include the dissolution of chemically and biologically bound phosphorus by sludge dissolution in order to produce a phosphorus-rich liquid phase. From this fluid, phosphates can be precipitated and used as a phosphorus source for fertilizer production [8]. Phosphorus recovery targets the production of a pure and plant available compound such as magnesium ammonium phosphate (MAP), while the co-precipitation of metals and especially heavy metals is unfavourable. Nanofiltration is a promising technique for the removal of contaminating metals from the phosphorus-rich liquid prior to the precipitation step.

Nanofiltration is a pressure driven separation process that is situated between ultrafiltration and reverse osmosis, reaching a molecular weight cut-off (MWCO) around 300 g/mol [9,10]. Nanofiltration membranes have a dense active layer that contains charged functional groups on its surface. As a consequence, nanofiltration membranes are not only size-selective, but also ion-selective and their performance depends heavily on the pH of operation [9,10]. If the dissolution of sewage sludge is done by acidic dissolution, the feed stream for the filtration step has a pH value around 1.5 [7,11]. Under these conditions, nanofiltration membranes exhibit a strong positive surface charge and phosphorus is mainly present in the form of undissociated or only mono-dissociated phosphoric acid. This leads to a high efficiency of the separation process, in which

multivalent metal cations are retained, while neutral and mono-valent species like phosphoric acid pass the membrane to a high degree.

It was shown by other authors that nanofiltration is a suitable technique for the purification of phosphoric acid [12] and that membranes with an increased chemical stability under acidic conditions are being developed [13]. Some research focused particularly on nanofiltration for the recovery of phosphorus from sewage sludge and sewage sludge ash [11,14,15]. Based on these studies, a nanofiltration process with a high phosphorus yield in the permeate was developed in this work. Compared to previous studies, relatively low transmembrane pressure (TMP) was applied and different nanofiltration membranes were tested. Experiments were performed at pH=0.5 and 1.5, so that the pH dependence of the separation efficiency could be studied. By semi-continuously redituting the feed fluid with pH adjusted water, diafiltration conditions were approached in order to increase the product yield of the process.

2. Materials and methods

2.1. Pretreatment of sewage sludge

For the preparation of a suitable nanofiltration feed fluid, digested sludge with a dry matter content of 45 g/L was used. The sludge was taken from the wastewater treatment plant ARA Birs (Birsfelden, Switzerland) that is treating mainly urban wastewater. After dilution with 33 mL deionized water per 100 mL sludge, 1.2 mL of sulphuric acid (96% purity, Carl Roth) was added per 100 mL sludge in order to adjust pH=1.5 and to dissolve the phosphorus contained in the sludge. The acidic dissolution was then carried out on a magnetic stirring panel with 270 rpm for a duration 3 h. The leached sludge was centrifuged (30 min, 30,000g, Avanti J-25I, Beckman Coulter) and

remaining solids were removed from the centrifugation supernatant by coarse filtration with a cellulose filter (MN 615, Macherey-Nagel) and subsequent ultrafiltration at TMP=10 bar (membrane PM UP150, Microdyn Nadir). The most abundant elements in the permeate were sulphur, iron and phosphorus, while most heavy metals were present in concentrations around 1.4 mg/L or below (Table 1). This fluid was used as a feed for subsequent nanofiltration experiments.

2.2. Preparation of nanofiltration experiments

The nanofiltration membranes under study were DL (DL NF Series, GE), NF270 (Filmtech NF270, Dow), Duracid (Duracid NF Series, GE) and AS (NanoPro AS-3012, AMS) (Table 2). Before they were used, DL, NF270 and Duracid were immersed in deionized water and AS was immersed in 0.7% benzalkonium chloride (95% purity, Sigma-Aldrich) solution for 24 h. Three circular flat sheet membranes with a total membrane area of 84 cm^2 were built into a crossflow filtration system (Triple System Model F1, MMS) and nanofiltration was operated at 20 °C and TMP= 10 bar in closed-loop mode for membrane compaction, membrane swelling and in order to reach stable filtration conditions. After 24 h, pressure tests were performed in order to determine the pure water flux dependence on TMP of each membrane. Then, the water was drained and 1.5–2 L of the ultrafiltration permeate was used as a feed fluid for nanofiltration. The pH in the fluid was adjusted by the addition of sulphuric acid prior to nanofiltration. Due to their limited chemical stability, DL and NF270 were tested at pH=1.5, while the experiments with AS were done at pH=0.5. In order to compare both pH values, Duracid was tested at pH=0.5 and pH=1.5.

2.3. Nanofiltration experiments

When stable conditions were reached in the filtration system, the transmembrane flux was measured and permeate samples were taken at TMP=5; 7; 10; 15 bar, cross-flow velocity of 1.6 m/s and 20 °C. After the pressure tests, the system was operated continuously at 20 °C, TMP=7 bar and a crossflow velocity of 1.6 m/s. The filtration conditions were controlled by means of an electric feed pump, a pressure control valve and a double jacketed reservoir for feed cooling. The retentate was lead back into the feed reservoir, while the permeate was lead into a beaker on a weighing scale for permeate flux measurement. In one reference experiment, nanofiltration was performed in this way until a minimum retentate hold-up of 120 mL was reached in the filtration unit. In other experiments, nanofiltration was run until a permeate recovery of 50% was reached. In these cases, the collected permeate was stored before the feed was filled up with purified water to its original volume. Before dilution, pH=0.5 or 1.5, respectively, was adjusted in the water by addition of sulphuric acid. The filtration and dilution procedure was repeated a second and a third time, thus approaching diafiltration conditions (Fig. 1). Additional pressure tests were done at the end of the second filtration run. The last filtration run was operated until the minimum retentate hold-up was reached. Samples were taken in the feed

Table 1
Composition of ultrafiltration permeate (averaged from 4 samples).

	Concentration	
S	4490 ± 210	mg/L
Fe	1280 ± 90	mg/L
P	820 ± 40	mg/L
Ca	590 ± 90	mg/L
K	149 ± 3	mg/L
Al	110 ± 12	mg/L
Na	108 ± 11	mg/L
Mg	98 ± 4	mg/L
Zn	23.3 ± 0.5	mg/L
Cr	1.4 ± 0.2	mg/L
Pb	0.52 ± 0.07	mg/L
Ni	0.42 ± 0.04	mg/L
Cu	0.3 ± 0.2	mg/L
As, U, Cd, Hg	Below detection limit	
Turbidity	12.4 ± 0.8	NTU
TOC	182 ± 2	mg/L

Table 2
Characteristics of the membranes used for nanofiltration.

	NF270	DL	AS	Duracid	
Material	Polyamide	Polyamide	Polymer	Polymer	
Maximum TMP	41	41	70	82	bar
Water permeability (TMP=7 bar)	60	29	8	8	L/m^2/h
Contact angle [16]	30	42	–	–	deg
MWCO	200–400	150–300	180	–	g/mol
Isoelectric point [16]	pH=4.5	pH=4	–	–	
pH range long term	2–11	3–9	0–12	0–9	
pH range short term	1–12	2–10.5	0–13	0–9	
pH tested	1.5	1.5	0.5	0.5; 1.5	