

Potentials of using nanofiltration to recover phosphorus from sewage sludge

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ABSTRACT

Due to the depletion of mineral phosphorus resources there is an increasing demand for efficient phosphorus recovery technologies. In this study the potential of nanofiltration to recover phosphorus from pre-treated sewage sludge is investigated. The efficiency of three commercial nanofiltration membranes (Desal 5DK, NP030; MPF34) was tested using model solutions. Desal 5DK showed the best selectivity for phosphorus. A pH of lower than 1.5 was found to be most suitable. Desal 5DK was used on four different sewage sludge ash eluates and on one sewage sludge. In these experiments it was shown that a separation of phosphorus from undesired components such as heavy metals was possible with significant variations in the efficiency for the different ash and sludge types. Additionally the achievable product recovery was investigated with model solutions. A product recovery of 57.1% was attained for pH 1 and 41.4% for pH 1.5.

Key words | ash, nanofiltration, phosphorus recovery, sewage sludge

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INTRODUCTION

Phosphorus is an essential element for all organisms playing a fundamental role in cell activity processes like energy transfer, protein synthesis and genetic storage (Smil 2000). Since phosphorus cannot be absorbed from the air by plants like nitrogen it is transferred to the soil by decay of organisms and taken up by plants from the soil according to the natural cycle of matters. Only in a very long process of 10^6 – 10^9 years (Emsley 1980) phosphorus is transferred from organic material into mineral phosphorus deposits called phosphate rock. Being comparatively scarce, phosphorus is mainly the limiting growth factor for plants and animals being highly dependent on the cycle of matters (Smil 2000). Intensive agriculture and disposal of organic waste by human activity disturb the natural balance. In order to gain sufficient yields to furnish a growing world population artificial fertilisers are used in agriculture leading to an increasing exploitation of the mineral phosphorus

resources. This further disturbance of the natural cycle of matters leads to an expected time limit of about 50–100 years until the phosphorus rock is exhausted (Driver *et al.* 1999). In this time interval costs for phosphorus products will increase due to a decreasing quality of the remaining resources (Steen 1998).

Due to an increasing demand for food and the need of further phosphorus products beside fertilisers there is recently much effort put into the investigation of alternative phosphorus sources. The recycling of phosphorus from wastes is a promising approach providing additionally a possibility to re-establish partly the natural balance. As 80% of phosphorus is used as fertilisers and phosphorus is naturally present in biomass biological waste offers the main potential for recovery (Steen 1998). Biological waste includes waste derived from organisms and can therefore be sewage sludge, animal manures and plant residues. Due to the phosphorus elimination in the

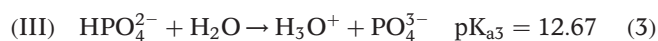
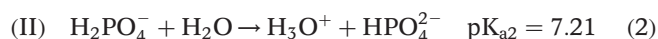
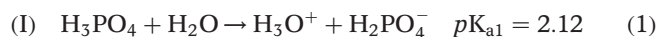
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waste water treatment plants, carried out to prevent the receiving water from eutrophication, sewage sludge makes up the phosphorus sink in waste water treatment, concentrating phosphorus deriving from biological waste as well as from detergents. About 89% of the phosphorus present in the waste water is transferred into the sludge (Pinnekamp *et al.* 2003).

This paper examines the potential of a special method for the phosphorus recycling from sewage sludge, possibly also applicable to other biological waste. There are already several techniques developed for the phosphorous recovery which apply to several points in the waste water treatment process (Pinnekamp *et al.* 2003), effluent, process water, sewage sludge and sewage sludge ash. The aim is to separate phosphorus from harmful substances in the sludge which are a main obstacle to agricultural sludge application (Schnurer 2002). Furthermore, the recycling process has to be ecological and economically beneficial, i.e. with low costs, energy and chemical demand, producing a well available product.

Nanofiltration is a versatile membrane filtration technology situated between ultrafiltration and reverse osmosis regarding to its molecular weight cut off of 150–1000 D (Melin & Rautenbach 2004). It combines the separation effects of sieving (dominating in ultrafiltration) and of mass transfer due to diffusion like in reverse osmosis membranes (Tanninen *et al.* 2004). Particles are unable to pass the nanofiltration membranes, which are applicable for the separation of dissolved substances. The mass transfer through the membrane is furthermore influenced by surface charges on the membrane. Since the membrane charges depend on the H^+ -concentration the separation efficiency is highly dependent on the pH. In acidic conditions nanofiltration membranes are usually positively charged and negatively charged for high pH values (Childress & Menachem 2000). Therefore in acidic conditions monovalent negatively charged ions or uncharged molecules can permeate to a relative high amount whereas positively charged ions are rejected increasingly according to size and valence. This principle for acidic conditions offers a possibility for the recovery of phosphorus from sewage sludge after a pre-treatment realising low pH, dissolution of phosphorus and elimination of particles. Dissolved phosphorus is mainly present as $H_2PO_4^-$ and H_3PO_4 for acidic

conditions and mainly as uncharged H_3PO_4 for a pH below 2 due to its dissociation constants:



Therefore phosphorus can permeate to a considerably higher amount than multivalent positive metal ions in acidic conditions. This principle has been successfully applied for the purification of phosphoric acid and the separation of sulphuric acid from metal ions (González *et al.* 2002; Manis *et al.* 2007).

MATERIAL AND METHODS

Experimental design

The experiments were performed with a tempered stirred membrane test cell containing a circular flat sheet membrane with an area of 73.9 cm² situated on a sintered metal plate (1.4404). The cell consists of stainless steel (1.4571) with magnetic stirring and is pressurised by an inert gas (N₂). The testing series were done according to a specific chain of procedures (Figure 1).

The conditioning of the membranes before starting the experiments consisted of immersion in deionised water for 24 hours to remove the glycerine layer. Standard salt tests were performed to prove the integrity of the active layer and for the characterisation of the membrane properties. In the standard salt test magnesium sulphate (2 g/l) or sodium sulphate (2.4 g/l) were used according to the manufacturer information for one hour. The results of the standard salt tests were gained by conductivity measurement (Konduktometer 703 from Knick, Germany) and subsequent retention calculation. The cleaning procedure contained cleaning of all parts of the stirring cell with deionised water especially the membrane, the sintered metal plate and the permeate line and was repeated after the standard salt test and after each experiment. In the course of the cleaning procedure deionised water was permeated for 1–2 hours at 15 bar. The cleanliness was proved

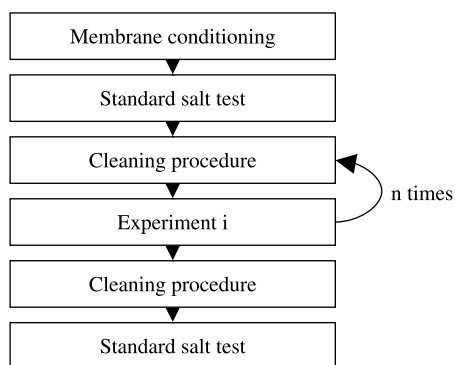


Figure 1 | Membrane filtration experiments procedure with the stirring cell.

by conductivity measurement of the feed and permeate. The cell was defined as clean when measuring a conductivity of less than $80 \mu\text{S}/\text{cm}$.

The model solutions were prepared using phosphoric acid (Honeywell Riedel-de Haen, Germany, 85%), sulphuric acid (Merck, Germany, 95–97%), caustic soda (Merck, Germany, 32%) and sulphate salts ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 99.5%, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 99–100.5% supplied by Merck, Germany). The salts for the standard salt tests were purchased from Applichem, Germany ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 95%) and Scharlau, Germany (NaSO_4 99%).

Analytics

Ion concentrations were measured with ICP-OES. The zeta potential was measured using a PAAR EKA-Electro Kinetic Analyzer RV 4.0 Prototype.

Sludge pretreatment

Two sewage sludge ashes as well as one sewage sludge (Sl) were tested for the potential of phosphorus recovery. The two types of ashes were precipitated with aluminium (A/Al) respectively iron salts (A/Fe). The sludge (Sl) and fractions of the ashes (A/Al/S, A/Fe/S) were pretreated by elution with sulphuric acid with a final pH of 1.5. Further fractions of the ashes (A/Al/N, A/Fe/N) were treated with nitric acid accordingly. For the ash elution an ash/acid ratio of 1/10 was chosen and performed in an upside down shaker for 12 hours with a temperature of 20°C (Schaum et al. 2004; Schaum & Cornel 2005). For all pre-treatments particle

removal by centrifugation and filtration (with Schleicher & Schuell 589/1 filters) was the final step.

Membranes

Three types of flat sheet membranes were tested. Desal 5DK (5DK) manufactured by GE Osmonics was obtained from Desalogics GmbH. NP030 was purchased from Microdyn-Nadir GmbH and MPF34 from Koch Membrane Systems.

Measured parameters:

The following parameters were measured in the experiments:

- retention for the component i :

$$R_i = 1 - \frac{c_{Pi}}{c_{Fi}} \quad [-] \quad (4)$$

- permeate recovery:

$$\xi = \frac{V_P}{V_F} \quad [\%] \quad (5)$$

- product recovery for the component i :

$$\eta = \frac{m_{iP\omega}}{m_{iF\alpha}} \quad [\%] \quad (6)$$

with: c_{Pi} = concentration of i in the permeate; c_{Fi} = concentration of i in the feed; V_P = permeated volume; V_F = feed volume; $m_{iP\omega}$ = mass of i permeated over the filtration time; $m_{iF\alpha}$ = mass of i in the feed before the filtration.

RESULTS AND DISCUSSION

Comparison of several commercial membranes

Three commercial membranes were examined with respect to their suitability to separate phosphorus from metal ions and hence their adequacy for an application for sludge treatment. For each membrane type a series of experiments with model solutions were performed to provide reproducible testing conditions. The model solutions contained a concen-

Table 1 | Composition of the model solutions

No.	pH [-]	P [g/l]	Fe [g/l]	Cu [g/l]	S [g/l]	Acetic acid [g/l]
M1	1.5	5	1	0.05	0.6	10
M2	1.5	3	1	0.05	0.6	10
M3	1.5	5	0.4	0.05	0.3	10
M4	2	5	1	0.05	0.6	10

tration of phosphorus, iron, sulphate and copper realistic for pretreated sewage sludges (see Table 1). Pretreated sludge is simulated using tap water as basis and the addition of acetic acid as an organic component.

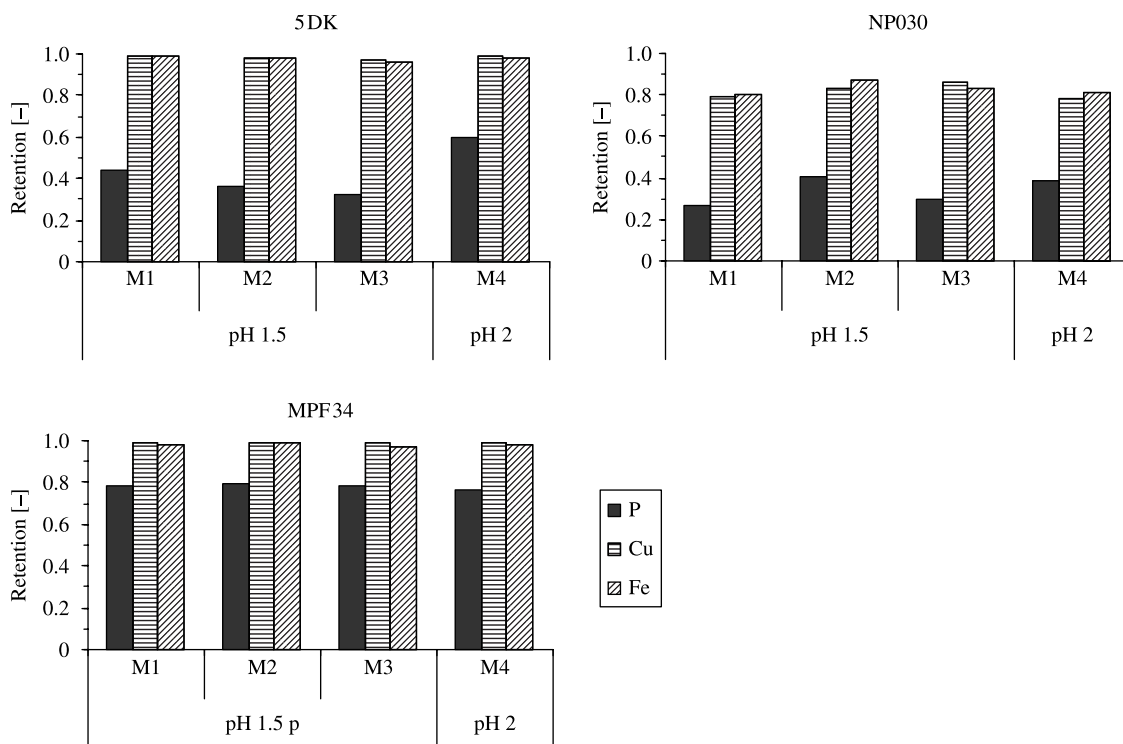
In former experiments the pH dependency known from the theory and from literature was confirmed for simple model solutions resembling the concentration range of real sludges. The experiments showed a high decrease in rejection of phosphorus by 5DK at a pH lower than 2 (Niewersch *et al.* 2007). The pH dependency was further evaluated in this study by using two pH values in the area of interest: pH 1.5 and pH 2. Figure 2 shows the retention for the different model solutions, the three membrane types

and the dependence on the pH. The operational parameters pressure, temperature and stirring rate remained constant at 25 bar, 25°C and 230 1/min.

The retention measured with 5DK was in all cases higher than 0.96 for the positively charged metals iron and copper, between 0.32 and 0.44 for phosphorus at pH 1.5 and 0.60 at pH 2. The phosphorus rejection for M2 was 0.1 and for M3 0.12 lower than for M1 indicating an influence of a lower iron and phosphorus concentration on the phosphorus retention.

The membrane NP030 revealed a higher permeability both for metal ions and for phosphorus. The phosphorus retention was between 0.27 and 0.3 for a phosphorus feed concentration of 5 g/l but considerably higher for pH 2 and for 3 g/l phosphorus. These results could indicate a dependency on the phosphorus concentration i.e. that a higher concentration enhances the permeability being the reverse tendency in comparison to the experiments with 5DK.

MPF34 rejected metal ions and sulphur to a high extent but offered also a low permeability for phosphorus so that the selectivity for a separation was relatively low. A clear

**Figure 2** | Retention for phosphorus (P), copper (Cu) and iron (Fe) for filtration experiments with 5DK, NP030 and MPF34. Parameters: 25 bar, 25°C, 230 1/min.

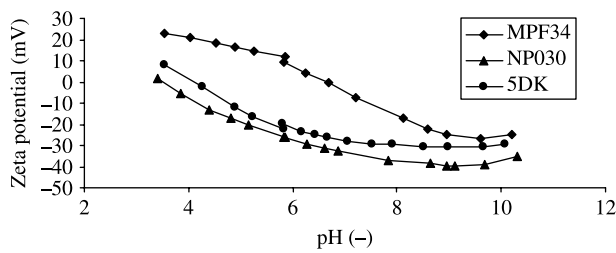


Figure 3 | Zeta potential measured for MPF34, NP030 and 5DK.

dependency on the concentration or the pH could not be observed.

The molecular weight cut off of 5DK (150–300D (Tanninen & Nyström 2002) and MPF34 (200D [manufacturer information]) is not significantly different. Differences between the phosphorus retention of these membranes are therefore possibly caused by surface charge characteristics. The zeta-potential, a measure for the surface charge, was higher for MPF34 than for 5DK possibly causing the higher phosphorus rejection. For NP030 no manufacturer information was available about the molecular weight cut off. The low retention for both, the positive ions and phosphorus, is probably caused by a combination of lower

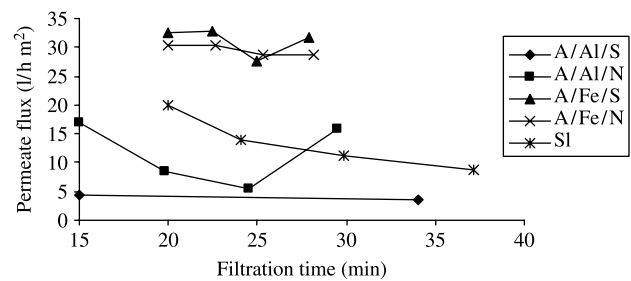


Figure 4 | Permeate flow measured for the filtration of sewage sludge ashes (A/Al/S, A/Al/N, A/Fe/S, A/Fe/N) and a sludge (SI). Parameters: 25°C, 230 l/min, 70 bar (ashes), 25 bar (sludge).

membrane charge, corresponding to the low zeta-potential measured for acidic conditions (Figure 3) and a higher molecular weight cut off.

According to the results 5DK offers the highest selectivity for the separation of phosphorus and positively charged ions of the three tested membrane types.

Experiments with real sludge

The experimental set up developed by the use of model solutions was applied on sludge and sludge ashes with 5DK as the most promising membrane from the pre-experiments.

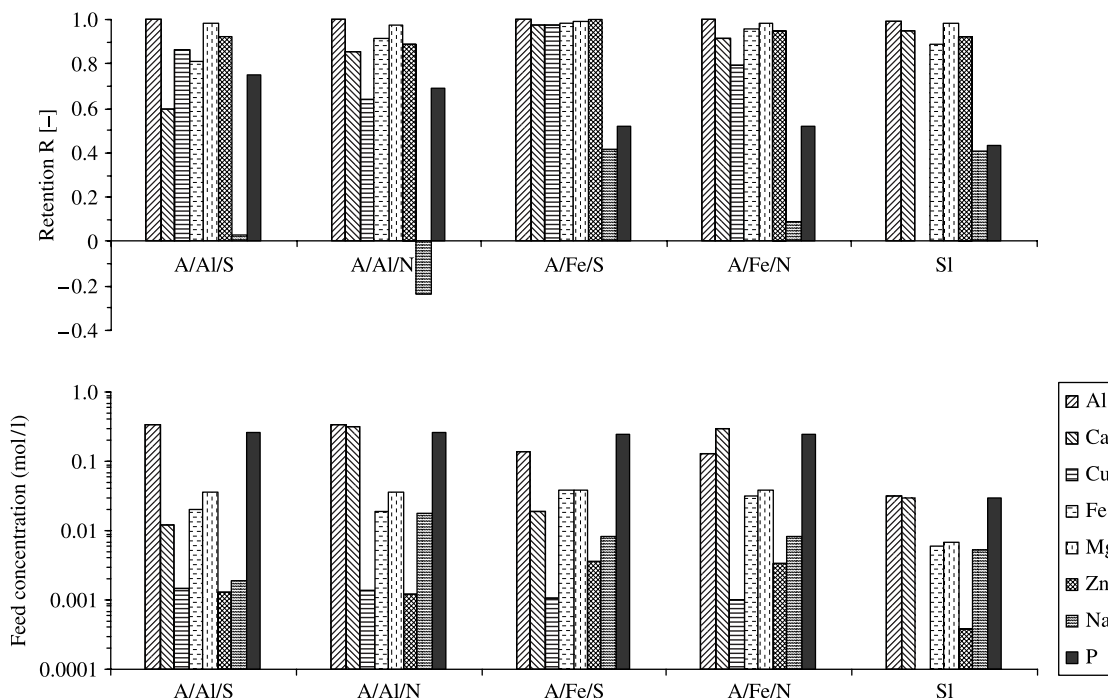


Figure 5 | Retention measured for the filtration of sewage sludge ashes (A/Al/S, A/Al/N, A/Fe/S, A/Fe/N) and a sludge (SI). Parameters: 25°C, 230 l/min, 70 bar (ashes), 25 bar (sludge).

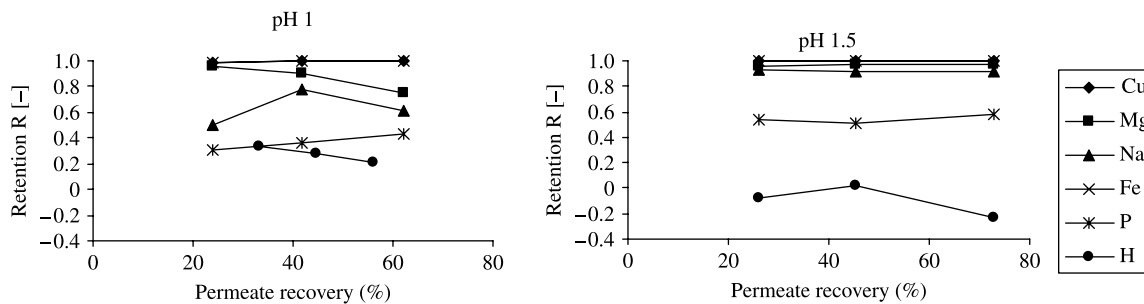


Figure 6 | Retention for phosphorus (P), copper (Cu), iron (Fe), magnesium (Mg), sodium (Na) and hydrogen ions (H^+) with MPF34. Parameters: 25 bar, 25°C, 230 l/min.

In the filtration experiments with eluates of the ashes a much higher pressure (70 bar) had to be applied since the permeate flux was very low at the pressure of 25 bar which was sufficient for the model solution experiments. The filtration of the eluate of SI was conducted at a pressure of 25 bar. As shown in Figure 4 the permeate flow in the ash experiments showed only a slightly decreasing tendency over the filtration time whereas the flow in the sludge experiments decreased from 20 l/(m²·h) to less than 10 l/(m²·h). This indicates that the sludge filtration was affected to a higher degree by fouling due to the incomplete particle elimination. The low permeate flow for the ash eluates seems to be mainly caused by the high osmotic pressure due to the high concentration of dissolved components.

In the first 20 minutes (permeate recovery below 20%) of the filtration the concentrations of the relevant components were measured in the feed and permeate and the retention of these components was calculated (Figure 5). For the eluates of sludge ashes coming from a waste water treatment with phosphorus elimination using aluminium salts (A/Al/S, A/Al/N) a significantly higher phosphorus retention was measured than for those from a waste water treatment with phosphorus precipitation using iron salts (A/Fe/S, A/Fe/N). For the latter eluates as well as for the sludge SI the phosphorus recovery was between 43% and 52% being similar to the results from the pre-experiments with model solutions.

According to the results the selectivity of 5DK for phosphorus is comparable to the model solution experiments for sludge ash type “iron precipitation” and the sludge. For this sludge ash type as well as for the sludge the separation is possible. The composition of the sludge ash type “aluminium precipitation” seems to be critical for the separation process.

There is still need for further experimental studies to investigate the relevant influencing factors.

Influence of the recovery on the retention of ions and on the permeate flux

The rejections for the several components measured in the first experiments reflects the concentration ratios between permeate and feed in one time point and simulates one point in a membrane module respectively. To evaluate the possible overall efficiency the rejection rates were measured for different permeate recoveries and the phosphorus product recovery was calculated. Since the first experiments showed high phosphorus permeability for a pH lower than 2, these further experiments were performed with the model solution M1 adjusted to pH 1 and pH 1.5. With increasing permeate recovery the phosphorus retention slightly increased but was below 0.6 for pH 1.5 and below 0.4 for pH 1. The retention of multivalent metal ions remained high, above 0.98 for copper

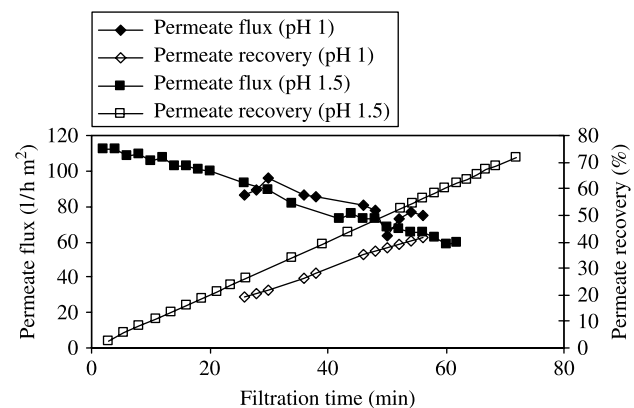


Figure 7 | Permeate flux and recovery for pH 1 and pH 1.5 depending on the filtration time. Parameters: 25 bar, 25°C, 230 l/min.

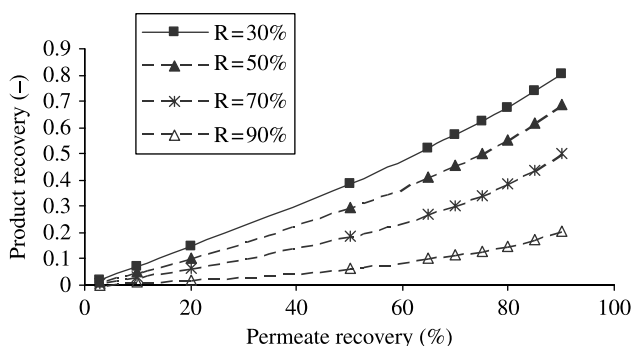


Figure 8 | Calculated product recovery versus total permeate recovery.

and iron and above 0.75 for magnesium. The strength of the separation ability of negatively and positively charged ions by the 5DK membrane was shown by the difference of the phosphorus retention and the retention of the only monovalent cation sodium (Figure 6).

As documented in (Niewersch *et al.* 2007) the permeate flux increases strongly with a decreasing pH. This observation is confirmed by the results presented in Figure 7 regarding the measured permeate flux and the permeate recovery over the filtration time. The permeate flux was about $8 \text{ l}/(\text{m}^2 \cdot \text{h})$ higher for pH 1 than for pH 1.5. The permeate flux decreased with filtration time and increasing permeate recovery but remains on a high level above $60 \text{ l}/(\text{m}^2 \cdot \text{h})$ over the whole filtration. The decreasing permeate flux is caused by the increasing concentration of solutes in the feed implicating a higher osmotic pressure (Tanninen *et al.* 2003).

Reaching a permeate recovery of 72% (pH 1.5) and 62% (pH 1) at the end of the experiments the product recovery for phosphorus was 41.4% and 57.1%. This relatively low process efficiency could be enhanced significantly by obtaining a higher permeate recovery by means of a longer filtration time. The longer filtration time for the stirred cell corresponds to a greater membrane area likely to be arranged in a multi-stage process for the technical realisation. A calculation of the product recovery depending on the permeate recovery and the retention (Figure 8) shows that an increase of the permeate recovery to 90% implicates a phosphorus product recovery of 68% for a retention of 0.5. Furthermore the realisation of lower retention rates for phosphorus offers the potential of higher product recovery. A phosphorus recovery of 0.4

(as realised for pH 1) leads to a product recovery of 73% of a permeate recovery of 90%.

CONCLUSION

After an acidic treatment of sewage sludge as well as sewage sludge ash, it was possible to separate the dissolved phosphorus from the dissolved metal ions. The comparison of two ash types showed a significant variation of the retention of phosphorus. Further experimental studies have therefore to investigate the relevant influencing factors for the retention of phosphorus.

As showed in experiments with varied permeate recovery the efficiency of the separation depended on the pH and the permeate recovery. The efficiency could be increased significantly from a measured value of 57.1% product recovery at 41.4% permeate recovery and 50% phosphorus retention to a value of 68% product recovery if applying a process with a permeate recovery of 90% (with 0.5 phosphorus retention) which is a promising value for a phosphorus recovery process.

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