

Closing the cycle: phosphorus removal and recovery from diluted effluents using acid resistive membranes

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Abstract

New regulations in many developed countries call for a significant reduction in phosphorus concentration for effluents released to the environment. At the same time, recovery of phosphorus - a non-renewable resource used mainly as fertilizer - from anthropogenic waste is extensively studied and bolstered as a crucial component in maintaining future food security. Thus far studies on phosphorus recovery mainly focused on concentrated streams, although diluted effluents such as treated wastewater often contain a significant portion of the phosphorus mass. Here we propose a new approach for the simultaneous removal and recovery of phosphorus from diluted effluents using a membrane characterized by high phosphate rejection and acid resistance. High P rejection allows for the concentration of phosphorus in the retentate until recoverable calcium-phosphate precipitants are formed, while acid resistance

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enables a simple and effective chemical cleaning of the membrane. Factors affecting the removal and recovery of phosphorus during filtration are studied here experimentally and through thermochemical modeling. Avoiding CaCO_3 precipitation in the retentate was found critical as it results in severe scaling. In contrast, calcium-phosphate precipitates mostly in the bulk, resulting in colloidal fouling which is manageable by maintaining sub-critical permeate flux. Using thermochemical modeling we show that selecting Ca-P precipitation over CaCO_3 is feasible by operating at neutral pH, requiring none or very little acid addition. Calcium-phosphate deposits were easily removed from the feed channel through acid-cleaning, and the membrane performance was completely restored. Furthermore, phosphorus removal by nanofiltration was shown to require less operating expenses compared to the conventional ferric chloride addition. Our results therefore demonstrate the potential of this new approach as a step forward towards closing the anthropogenic phosphorus cycle.

Keywords: Nutrients recovery; Phosphate; Nanofiltration; Secondary Effluent; Tertiary Treatment; Wastewater

1. Introduction

The element phosphorus (P) is at the center of two major global issues, i.e. food security and environmental conservation [1]. P is one of the primary macro-nutrients (together with nitrogen (N) and potassium (K)) required for plant growth and is therefore widely applied as fertilizer. Currently, P is supplied to the fertilizer industry predominantly via mining of calcium-phosphate (Ca-P) rocks, which are composed mainly of the thermodynamically

cally stable hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) minerals. Extraction of P from these ores is typically performed through their dissolution in sulfuric acid, producing concentrated phosphoric acid as the main product and solid gypsum (CaSO_4) as a byproduct [2]. Phosphoric acid could be then used for producing a range of soluble N-P-K fertilizers suitable for fertigation commonly applied in modern agriculture. Despite being relatively economic, P production from Ca-P rocks cannot be considered sustainable, since it is based on a non-renewable resource. Estimations of the timescale required for depletion of P ores range from few decades to several centuries [3], however rising prices and the limited spread of large Ca-P deposits to only a few countries may pose a threat to global food security even in the near future.

Following its application and consumption, the disposal of excess P into the environment impairs aqueous ecosystems. Since P is the limiting nutrient in many freshwater ecosystems its introduction results in increased growth of microorganisms (eutrophication), which deplete dissolved oxygen creating anoxic conditions. Water quality is significantly reduced in terms of turbidity, odor and toxicity, and services provided by P enriched water bodies in terms of both water-supply and recreation are severely hindered. Moreover, native aqueous organisms often cannot survive this transformation, thus the biodiversity significantly drops. Consequently, there is a strong incentive to further decrease P discharge limitations required for treated wastewater (effluent). In a recent life-cycle analysis study [4] found that enforcing the $\text{P} < 0.1 \text{ mg/l}$ limit instead of the widely used $\text{P} < 1 \text{ mg/l}$ would significantly

reduce eutrophication.

P concentration in domestic wastewater is in the range of 1-20 mg-P/l and varies considerably between different regions and seasons. Conventional biological treatment typically removes 15-25% of the P concentration [5], leaving most of the P mass in the secondary effluent. To further reduce P effluent concentration, chemical precipitation of P by Al and Fe salts is commonly applied. The disadvantages of this method are high chemical consumption and increased sludge volume. When properly designed, the enhanced biological P removal (EBPR) operational approach could achieve the $P < 1 \text{ mg/l}$ target with minimal increase in sludge volume. Even $P < 0.1 \text{ mg/l}$ is attainable under certain conditions [5] and with the addition of carbon source. However, like any biological process, EBPR suffers from large (relatively to physico-chemical processes) fluctuations in effluent quality. Therefore, further polishing step is usually required for meeting low P discharge requirements [6]. The chemical precipitation method is commonly applied for this purpose. Adsorption by metal hydroxides, most commonly Fe and Al, is another approach enabling very low P effluent concentration [7]. Though extensively studied, P adsorption is not widely used mainly due to costs associated with the adsorbing material and / or the regeneration process [7, 8].

Combining P removal with P recovery was widely adopted as a sustainable approach to simultaneously address the negative environmental impacts and the impending P global shortage [9]. Works on phosphate recovery from wastewater have thus far almost exclusively focused on concentrated streams, e.g. sewage sludge [10], 'black water' [11], or the supernatant originating from sludge dewatering following anaerobic biological treatment [12].

Direct P extraction from wastewater was also suggested [13]. However, recovery of P from the secondary effluent was scarcely studied, even though secondary effluent often consists a significant portion of the P mass entering the wastewater treatment plant. Studies on this topic thus far focused almost exclusively on sorption processes [8, 14], i.e. adsorption of P, its subsequent desorption and separation from the regeneration solution. Although feasibility was demonstrated in these studies, long term functionality of the adsorbing materials which may be hindered by irreversible adsorption or erosion is yet to be proven [7].

Here we suggest an alternative approach based on membrane filtration for the removal and recovery of P from effluents having low P concentration. The approach offers increased robustness compared to biological processes and significantly reduced chemicals demand compared to sorption and chemical precipitation. Unlike these methods which mainly aims to remove P, the approach suggested here simultaneously removes and recovers P from diluted solutions such as secondary effluents. A proof of concept is demonstrated through theoretical and experimental results.

2. Description and rationale of the suggested approach

The approach suggested here comprises of a membrane filtration step in which Ca^{2+} and phosphate ions are concentrated, thus inducing Ca-P crystals formation in the retentate stream. Ca-P crystals remaining on the membrane surface or in the feed flow channel are removed by applying acid-cleaning. To facilitate this scheme, a non-porous membrane characterized by high phosphate rejection and high stability in strongly acidic solutions is required.

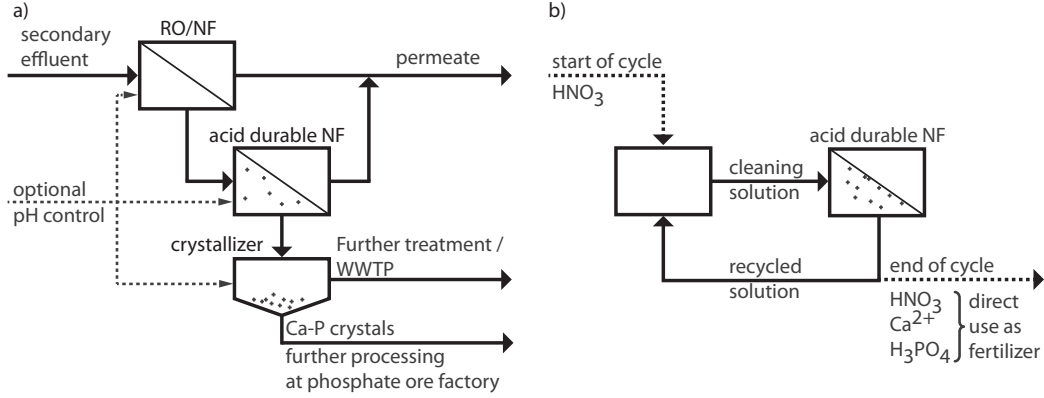


Figure 1: Schematic description of the new treatment concept. (a) Continuous, high-recovery membrane filtration coupled to a crystallizer for calcium-phosphate recovery. (b) Batch cleaning cycle utilizing nitric acid and generating N-P-Ca fertilizer solution, which can be used locally.

Currently, to the best of our knowledge, only nanofiltration (NF) non-porous acid-durable membranes are commercially available [15], although increased acid stability was demonstrated for surface modified reverse osmosis (RO) membranes [16]. RO is increasingly studied and already applied on a large scale for potable water reclamation from wastewater (in e.g. Singapore and California), while NF was suggested as an advanced tertiary treatment [17] for removing contaminants such as heavy metals [18] and emerging organics [19]. 'Tight' NF membranes also provide partial NaCl removal, thus preventing soil salinization when the effluent is reused for irrigation [20]. Therefore, although P removal and recovery is the focus of this work, the suggested operational approach should also be viewed as a potential solution for Ca-P scaling within RO/NF wastewater treatment at high permeate recovery.

As seen in Fig. 1a, tertiary wastewater is continuously filtered through a

two stage nanofiltration cascade with an acid-durable non-porous membrane in the second stage. The two stage approach enables local pH control to control inorganic salt precipitation. Further, the membrane for the first stage is not restricted to acid-resistant membranes providing a higher degree of freedom in the system design. Pretreatment is required for removing colloids from the feed, however it may be omitted in case membrane bioreactor is applied for the secondary treatment [19]. The process is aimed at achieving high recovery ratio (i.e. the ratio of permeate flow to feed flow) which is both economically and environmentally beneficial as it increases the output of reclaimed water, while at the same time minimizes the volume of concentrate, allowing for more efficient treatment and resource recovery. With the increase of recovery ratio, P_T and Ca^{2+} concentrations increase until supersaturation with respect to a certain Ca-P solid phase is sufficiently high for overcoming the kinetic barrier and inducing its chemical precipitation. According to [21], this phenomenon is currently the main limitation on permeate recovery in NF/RO of secondary effluents.

Chemical precipitation during filtration could occur either in the retentate solution (homogeneous or seeded heterogeneous precipitation), forming small suspended colloids and particles, or on the membrane surface / feed channel spacer (heterogeneous surface precipitation), forming a scaling layer. In both cases the water flux (productivity) and rejection (functionality) are hindered, however particulate fouling is more influenced by the hydrodynamic conditions and is thus easier to regulate. Evidence from previous studies suggests that particulate and colloidal deposition are the principal mechanisms for

the case of Ca-P fouling [22, 23, 24]. As a result, below a particular permeate flux, which may be termed the ‘threshold flux’ [25], most of the Ca-P particles will not accumulate rapidly on the surface, but rather conveyed out of the feed channel by the tangential flow. This enabled a 32 days of stable operation in a real wastewater RO plant study [26].

Typically, the retention time in the membrane is not sufficient for approaching solid-liquid equilibrium (saturation). Therefore, in order to recover phosphorus as Ca-P solids further precipitation and crystallization are carried out in a seeded crystallizer. This step could also be used for decreasing supersaturation between consecutive membrane stages [27]. Increased phosphorus recovery could be achieved by adjusting the pH in the crystallizer. The resulting Ca-P solid minerals are transferred to further processing at a phosphate ore beneficiation factory as illustrated in Fig. 1a. The feasibility of recovering Ca-P from supersaturated solutions using a pellet reactor was demonstrated by [28]. Further in this text we discuss the effects of NF retentate pH and recovery ratio on potential P recovery from a thermochemical point of view.

Even when operating below the threshold flux, long term decline in performance is still expected due to Ca-P microcrystals retained by the feed spacer or randomly deposited on the membrane surface. Moreover, heterogeneous precipitation on the membrane surface could not be ruled out completely. As previously shown, membrane performance could be completely restored by acid-cleaning [26]. Nevertheless, frequent acid cleaning of stan-

standard polyamide RO/NF membranes is generally undesirable since it shortens the effective lifespan of the membrane. Furthermore, the acid concentration in the cleaning solution is limited by the minimal pH value permitted by the manufacturer (typically $\text{pH} > 1-2$). Since both the kinetics of dissolution and the thermodynamic dissolution potential decrease with increasing pH, this limitation affects the cleaning duration, the volume of cleaning solution needed and the phosphorus concentration in the exhausted cleaning solution. However by placing acid-durable membrane elements in the stages susceptible to Ca-P fouling, frequent and efficient cleaning with concentrated acids is permitted.

Using membranes with high acid resistance allows for the application of nitric-acid (HNO_3) which was found to be more aggressive towards polyamide NF membranes compared to sulfuric acid [29]. As seen in Fig. 1b, when HNO_3 is used in the acid cleaning step for dissolving the Ca-P solid foulants, it generates a solution containing the macro-nutrients N&P, which could be applied locally as fertilizer by mixing it with irrigation water. The presence of Ca^{2+} ions in the solution will result in the additional benefit of reducing the SAR (sodium adsorption ratio) thus maintaining the aggregated structure of the soil. Using hydrochloric acid (HCl) for the purpose of cleaning is also possible, however this practice will enrich groundwater with unwanted Cl^- ions. Sulfuric acid is not suitable for this purpose since CaSO_4 will precipitate on the membrane upon Ca-P dissolution.

3. Materials and Methods

3.1. Experimental

A cross-flow nanofiltration setup, supporting a flow cell housing a 70 sqcm flat sheet membrane, was used in the filtration experiments. The setup includes a high pressure pump and a booster pump for controlling the pressure and flow independently (Schematics of the experimental system are given in the supporting information). The Membrane used was Duracid by GE Osmonics, the membrane was compacted prior to experiments by filtering distilled water at 40 bars for 5 hrs. The rejection of sodium-phosphate salts at different pH values was determined by electric conductivity. Measurements were repeated until steady-state conditions were observed. The pH was adjusted by the ratio of NaHPO_4 to NaH_2PO_4 added to the solutions while the total concentration of phosphate was 0.1M. These rejection experiments were performed at low recovery ratio, with the permeate stream constantly directed back to the feed tank.

For the scaling experiments, three different salt mixtures were used as specified in 1. In these experiments the recovery ratio was slowly increased by continuously extracting permeate out of the system. Ion concentrations in the feed and permeate were determined by ion chromatography (cations: Agilent 1100, Metrosep C4 column (Methrom), eluent: 1 mM oxalic acid, 1.2 mM nitric acid, flowrate = 1.4 ml/min, temperature = 35 C, conductivity detector ; anions: Agilent 100, PRP-X100 column (Chromatographie Service), eluent: 4-hydroxybenzoic acid pH 8.5, flowrate = 2 ml/min, temperature = 35 C, conductivity detector). The pH was measured using an Orion Star A211 pH

meter by ThermoFisher with ROSS Triode pH/ATC electrode. Standard 3-point calibration was performed at the beginning of each day. Acid-cleaning was performed at TMP of 8 bars for both scaling experiments.

3.2. *Theormochemical modeling*

All thermochemical calculations were performed with the computer program PHREEQC[30], using the minteq.v4 database, which is the thermochemical database maintained by the USEPA. Both speciation calculations (see Fig. 2b) and precipitation potentials (see Figs. 6-7) were performed using Python scripts running the IPhreeqc com module. Secondary effluent composition was obtained from [24]. For calculating the ion composition C at a certain recovery ratio S , the following mass-balance based equation was used,

$$C(S) = C_f(1 - S)^{-R} \quad (1)$$

Where C_f is the feed concentration and R is the rejection. Eq. 1 is valid when the local rejection over the relevant recovery ratio is constant and was previously validated for NF of groundwater [31]. In the current case, only Na^+ and Cl^- exhibited a significant change in rejection when concentrated synthetic effluents were used as feed (see Table 1). In that case, Eq. 1 was used separately in two different recovery ranges (0-80% and 80-90%) and the average rejection (rejections are shown in Table 1) of two ends of each range was used. The Python scripts, including the solution compositions used are included as supplementary material.

4. Results and discussion

4.1. Experimental results

High rejection of P by the acid durable membrane at all operation conditions relevant for the continuous filtration step (Fig. 1a) is a prerequisite for the approach suggested here. Since P rejection by the Duracid membrane used was previously tested only with highly acidic solutions [10], filtration experiments of sodium-phosphate salts at the applicable pH range (6-8) were performed. The high P rejections seen in Fig. 2a indicate that the Duracid membrane could be employed in the phosphate polishing step. At pH 7-8, rejections exceeded 97% even at low permeate flux, while at pH 6 P rejections in the range 92-95% were measured. The effect of pH on P rejection also seen in Fig. 2a is a direct result of the phosphate species distribution for the 0.1M solutions plotted in Fig. 2b. Increasing the pH from pH 6 to pH 7 resulted in a significant increase in rejection, while only an incremental increase was seen when the pH was further increased to 8. This is in accordance with the significant absolute decrease (from 0.1M to 0.03M) in the concentration of the more permeable monovalent ion H_2PO_4^- when the pH is increased from 6 to 7, compared to the relatively low absolute decrease (from 0.03M to 0.003M) when pH is further increased from 7 to 8.

High P rejection at neutral and mildly acidic pH is highly beneficial in the context of the suggested approach since formation of CaCO_3 crystals in the retentate could be avoided by means of pH adjustments. Preventing CaCO_3 crystallization is critical with respect to both P recovery and membrane performance. At basic pH, CaCO_3 solids hinder Ca-P crystallization through competition over Ca^{2+} ions. In case both Ca-P and CaCO_3 solids are formed

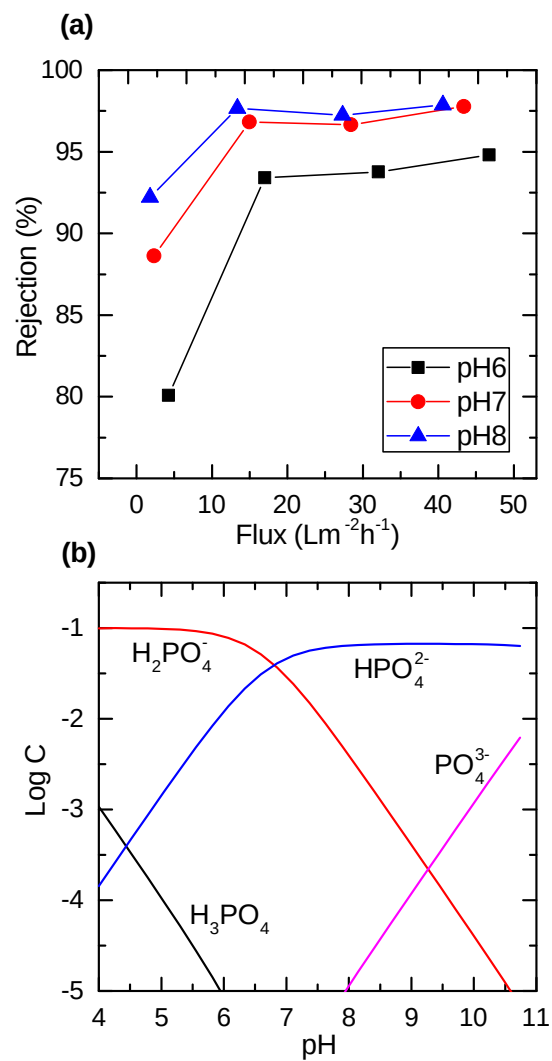


Figure 2: (a) Rejection of sodium phosphate salts by the acid durable NF membrane at varying permeate flux and pH values. (b) Distribution of the dominant phosphate species in a 0.1M Na-P solution as a function of pH.

or co-precipitate, the weight fraction of P in the resulting sediment decreases, making P recovery less economically attractive. In addition, the effect of CaCO_3 scaling on membrane performance at low flux is markedly more severe compared to Ca-P precipitation as demonstrated by the experimental results shown on Fig. 3 and Fig. 4 respectively and further discussed below. The desired rejections of other ions apart from calcium and phosphate depends on the purpose of the tertiary membrane-filtration treatment performed. In case the purpose is partial or complete desalination, high rejection rate for monovalent ions is required. As seen in table 1, at ionic concentrations representing secondary effluent, the commercial acid-durable membrane used here exhibit high rejections for both multi and monovalent ions. Increasing ionic concentrations to levels expected at higher recovery ratios resulted in higher selectivity as multivalent ions rejection was only slightly affected, while Na^+ and Cl^- rejections dropped. P rejection was almost unaffected by the increased ion concentrations. Since at the pH values used (6.8-7.1) $\sim 50\%$ of P is in the monovalent form, the significantly higher rejection for this ion over the smaller monovalent ions indicates the dominance of steric exclusion mechanism. These rejection properties along with low-pH compatibility makes this membrane suitable to be used within the approach depicted in Fig. 1 when partial desalination is desired. In case complete desalination is not the purpose, low rejection of Na^+ and Cl^- is preferred in order to minimize the trans-membrane osmotic pressure difference and decrease energy consumption. This latter is addressed in a study currently underway.

In order to examine the different effects on membrane performance result-

Table 1: Total P and ion rejections obtained with the Duracid NF membrane. Feed ionic composition were chosen to simulate a. secondary effluent (pH = 7.8-8.0; $C_T = 175$ mg/l as CaCO_3); and b. secondary effluent concentrated by nanofiltration at approx. 80% (P_T & $\text{Ca}^{2+} \times 5$; pH = 6.8-7.1; $C_T = 25$ mg/l as CaCO_3) and 90% (P_T & $\text{Ca}^{2+} \times 10$; pH = 6.8-7.1; $C_T = 25$ mg/l as CaCO_3) recovery ratios. Inorganic carbon content was reduced in the concentrated solutions to avoid rapid CaCO_3 scaling.

	P_T	Ca^{2+}	Na^+	Cl_-	SO_4^{2-}	Mg^{2+}
Sec. effluent						
Conc. (mg/l)	5 ± 2	38 ± 11	115 ± 28	122 ± 30	12 ± 3	2-3
Rejection (%)	99 ± 1	99 ± 0.5	91 ± 2	92 ± 3	5 ± 0.2	>95
80 % recovery						
Conc. (mg/l)	23	220	160	470	160	19
Rejection (%)	>99	96	72	82	>99	>94
90 % recovery						
Conc. (mg/l)	44	455	220	895	198	19
Rejection (%)	98	97	50	77	>99	>94

ing from CaCO_3 vs. Ca-P scaling, filtration and cleaning experiments were conducted at conditions highly favouring the precipitation of either CaCO_3 or Ca-P. The synthetic feed solutions simulated concentrated secondary effluents such as obtained in the retentate originating from a high recovery NF/RO step. As seen in Fig. 3 when operating at high supersaturation with respect to calcite, the flux rapidly decreased to third of its original value after an induction period of ~ 20 minutes. This rapid flux decline and the lack of visible precipitants in the feed/concentrate tank indicate that CaCO_3 precipitation occurred heterogeneously on the membrane surface, forming a scale layer which significantly increased the hydraulic resistance of the membrane. This result agrees with membrane autopsy performed by [32] which revealed CaCO_3 surface scale formation on RO and NF membranes

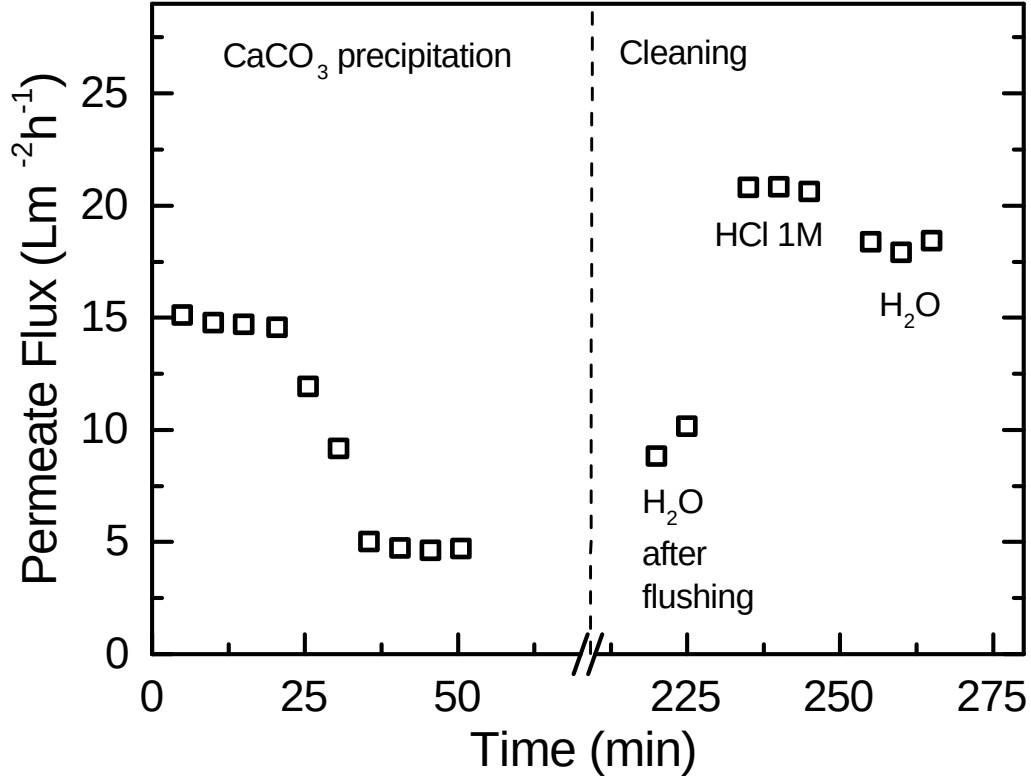


Figure 3: Permeate flux development during filtration of synthetic secondary effluent concentrate (Applied pressure: 8 bars. pH = 8), which is highly supersaturated with respect to calcite (feed solution compositions are given in table 1), followed by a distilled water permeation experiment, an acid cleaning step (1M HCl) and an additional distilled water permeation experiment.

Flushing the membrane with pure water only partly restored the flux, pointing at surface scaling which is hard to remove by hydrodynamic shear. At least 33% of the flux increase after flushing can be explained by a 2 bars reduction in osmotic pressure difference between the feed and permeate solutions (even without considering concentration-polarization), while the rest of the flux increase is due to removing colloidal or loose CaCO_3 crystals. Acid-

cleaning with 1 M HCl restored the pure water permeability to the value measured previously for the clean membrane ($21 \text{ lm}^{-2}\text{hr}^{-1}\text{bar}^{-1}$), indicating that the scaling layer was completely removed. Flux during acid cleaning was slightly higher. The right, probably due to changes in the membrane structure at this extreme pH.

The development of permeate flux during the filtration of a solution having high precipitation potential of Ca-P, shown in Fig. 4, was markedly different from the case of CaCO_3 . When operating at TMP of 8 bars the permeate flux only slightly decreased due to the increase of feed concentration and the osmotic pressure difference. After 140 minutes, in which no significant flux reduction occurred, the solution supersaturation was artificially increased by adding CaCl_2 and NaH_2PO_4 , resulting in the appearance of a white colloidal precipitant in the feed/concentrate tank. Notably, in spite of the high feed turbidity the permeate flux increased back to its original value, which is explained by the accelerated Ca-P crystallization resulted in lower ion concentration and decreased the osmotic pressure difference. Subsequently, the pressure was increased to 20 bars resulting in the initial increase of permeate flux, followed by a sharp 50% decrease after 50 minutes of filtration. This response to fouling and to applied pressure variation seen in Fig. 4 is typical to the case of colloidal suspensions filtration, where short term deviation from the pure water flux only occur above the threshold flux. Thus our results suggest that Ca-p fouling was mostly of colloidal nature, in accordance with [23].

Following the Ca-P deposition experiment, membrane cleaning was per-

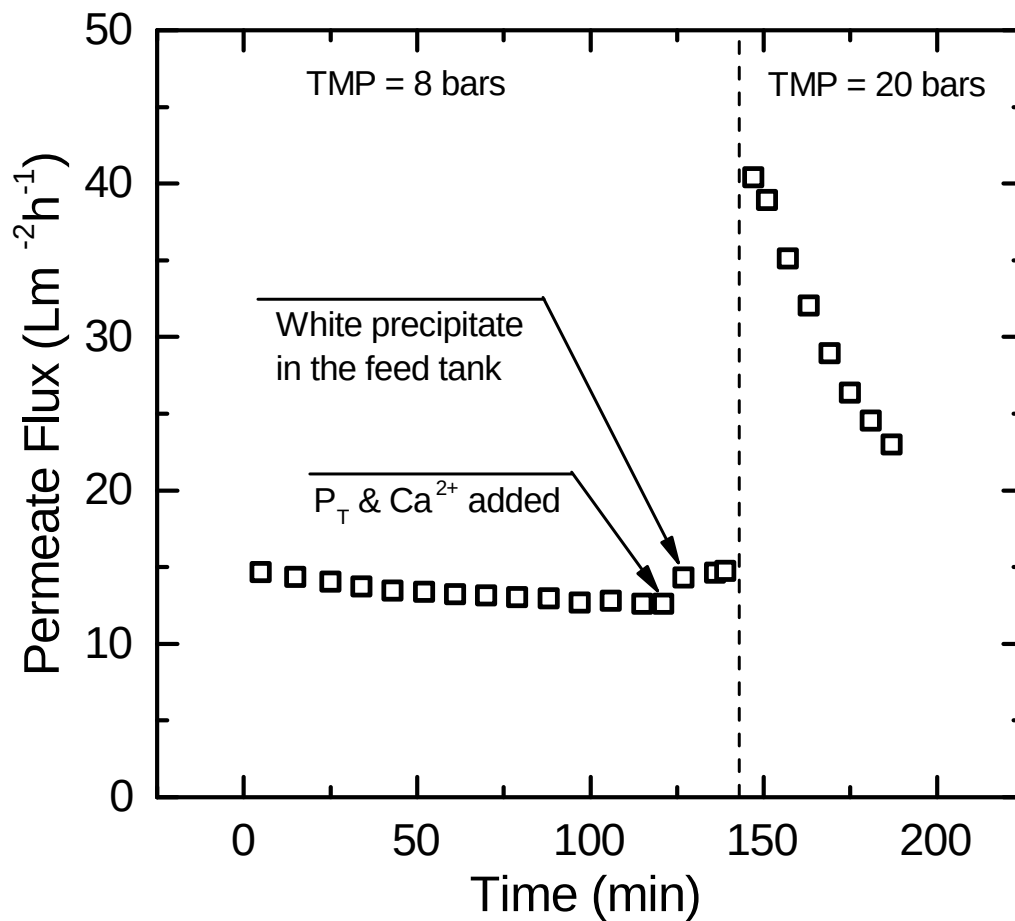


Figure 4: Permeate flux development during filtration of synthetic secondary effluent concentrate, which is highly supersaturated with respect to various Ca-P phases including ACP and HAP. Supersaturation was artificially increased after 2 hrs by adding calcium and phosphate salts. TMP was raised from 8 to 20 after 2.5 hrs. Feed solution compositions are given in table 1. pH was held constant at 7.

formed by first circulating pure water through the feed channel and subsequently applying acid cleaning with 0.1 M nitric acid. As seen in Fig. 5, prior to acid cleaning the flux at 8 bars ($15 \mu\text{m/s}$) was similar to the flux during Ca-P deposition (Fig. 4), although the osmotic pressure difference was lower, indicating that part of the Ca-P solids remained on the membrane surface. On the other hand, the non-linear response of permeate flux to the increase in TMP suggested the occurrence of Ca-P colloids in the feed-side solution. During acid cleaning, the permeate flux increased close to the level of pure water at low TMP's, while at the highest TMP the permeate flux increased sub-linearly due to ion concentration-polarization. After the acid cleaning, the pure water flux showed a linear response to TMP and the membrane permeability was restored to its original value. Ca^{2+} and P concentrations in the cleaning solution following acid cleaning were found to be 3.87 and 2.74 mM respectively. The Ca/P ratio was 1.41, which is between the value usually assigned to ACP (1.5) and the one assigned to octacalcium phosphate (1.33), indicating that full transformation to HAP ($\text{Ca/P} = 1.66$) has not occurred.

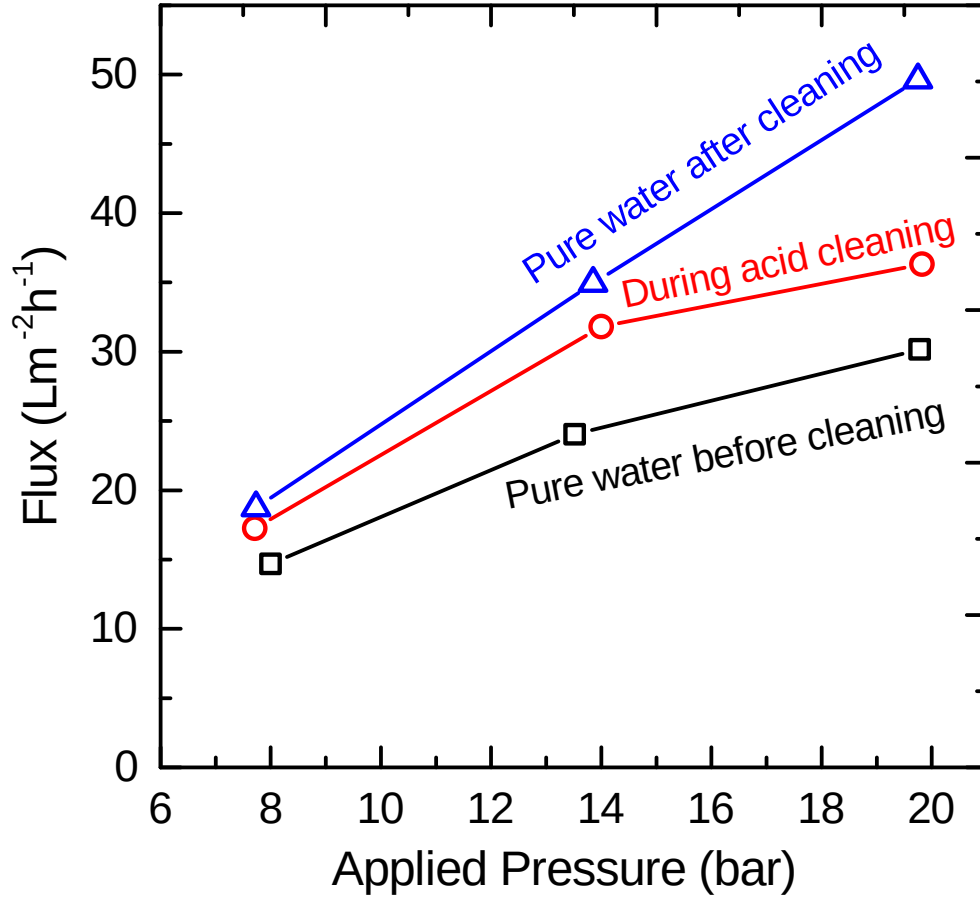


Figure 5: Permeate flux as a function of applied trans-membrane pressure following the filtration of supersaturated Ca-P solution. Acid-cleaning for several minutes with 0.1M HNO₃ fully restored the water permeability of the membrane

The results shown in Fig. 3 and Fig. 4 indicate that by avoiding CaCO₃ and operating at sufficiently low permeate flux, sustainable filtration is achievable. Fortunately, CaCO₃ precipitation could be efficiently avoided by re-

ducing the pH via strong acid dosing, a solution which is both simple and relatively cheap. The target pH depends on the thermodynamics and kinetics controlling the formation of Ca-P and CaCO_3 phases. These in turn are strongly influenced by the solution composition (e.g. pH, C_T , P_T , ionic strength, specific interactions with other ions [33, 34], organic matter[35] and temperature. Thermochemical analysis, such as presented in Fig. 6 and Fig. 7 provide useful guidelines regarding the pH required for selective precipitation of Ca-P crystals for known rejections and feed compositions.

4.2. Theoretical results

Theoretical phosphorous precipitation potential (PPP) for two Ca-P phases at different recovery ratios are shown in Fig. 6 along with CaCO_3 precipitation potential (CCPP) with respect to calcite. The first Ca-P phase considered is hydroxylapatite (HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which is the most thermodynamically stable Ca-P phase [33]. However, HAP usually does not precipitate directly from supersaturated solutions due to unfavorable kinetics. Instead, HAP occurs through a series of phase transformations, starting from the phase which precipitates directly from solution. Here we consider amorphous calcium phosphate (ACP) as the latter based on previous work [36, 13, 37], however we do note that other Ca-P phases e.g. di-calcium phosphate (CaHPO_4) and octa-calcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) may also precipitate first, depending on conditions and composition [33]. Precipitation potential is chosen here over the more common SI (saturation index), due to its clearer quantitative meaning, i.e. the theoretical amount of a solid phase which will precipitate from a supersaturated solution until solid-liquid

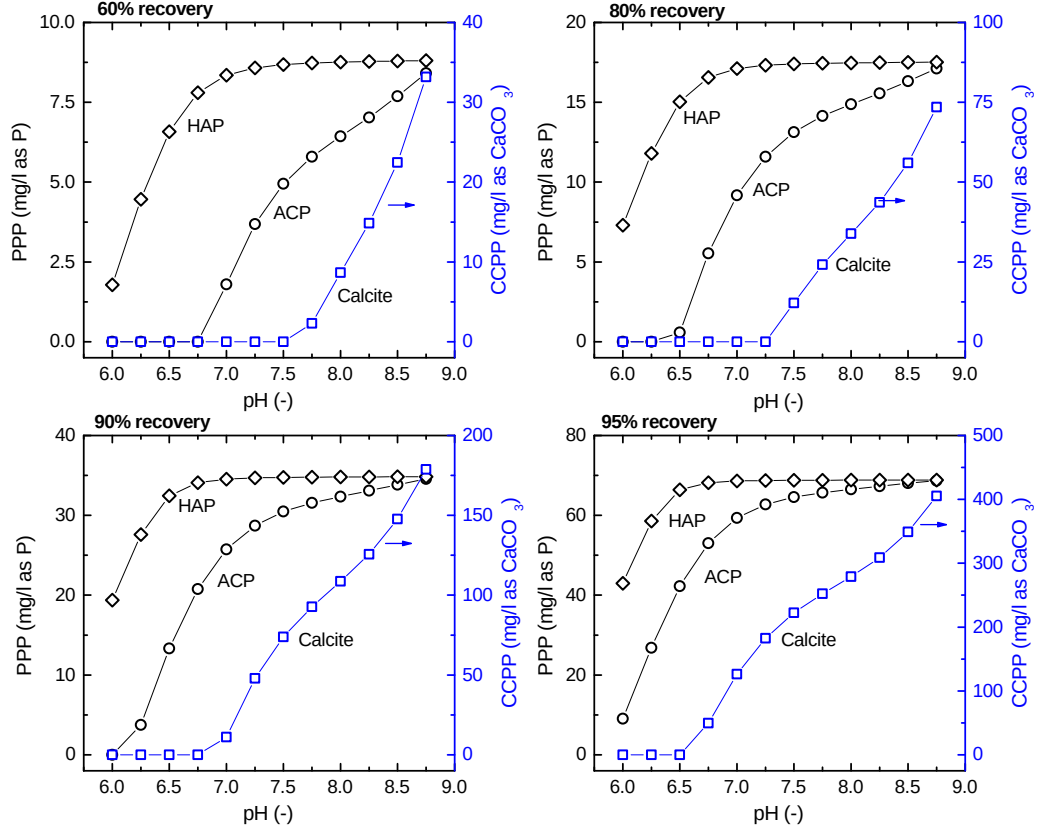


Figure 6: Precipitation potential (the theoretical amount of solid phase which would precipitate from 1L of solution until solid-liquid equilibrium is reached) of hydroxyapatite (HAP), amorphous calcium phosphate (ACP), and calcite as a function of pH, at different recovery ratios. Solution composition at each recovery ratio was calculated using feed composition from [24] and current experimental rejections (table 1). For the Ca-P phases the phosphate precipitation potential (PPP) is shown while for calcite the calcium carbonate precipitation potential (CCPP) is shown. Here precipitation potentials were calculated separately for each phase assuming only one solid phase is formed.

equilibrium (saturation) is reached.

Precipitation potential results shown in Fig. 6 provide useful information regarding two important aspects of the process, i.e. scaling propensity and the amount of P which could be recovered. In Fig. 6, precipitation potential of each phase is calculated independently, without considering competition over the common Ca^{2+} . In this manner, the conditions where precipitation is thermodynamically impossible, are obtained for the potentially scaling phases (ACP and calcite). As expected, the limiting pH decreases with recovery ratio, while precipitation potentials at higher pH values increase due to increased concentrations of scaling ions. The results demonstrates the challenge of mitigating Ca-P scale formation at high permeate recovery where the limiting pH < 6.5 and large amounts of acid is needed due to the carbonate buffer system. In contrast, controlling calcite scaling through pH modification is feasible even at high permeate recovery. This difference in limiting pH values between ACP and calcite throughout the permeate recovery range is critical to the suggested operational scheme, since it provides a simple handle for controlling the precipitating phase. It is noted that the pH of the retentate stream could change significantly during the filtration process [38], which may require inter-stage pH control as illustrated in Fig. 1. Inter-stage acid injection may be used to tackle the trade-off between P rejection and $CaCO_3$ scaling.

While low pH is required for preventing $CaCO_3$ scaling, operation at excessively low pH values hinders both P removal, due to lower P rejection

(see Fig. 2, and recovery. For the water composition analyzed here, at pH < 6.5 , full recovery of P, marked by the HAP PPP asymptote on Fig. 6, is not obtainable even for 95% permeate recovery. At pH > 7 , almost complete recovery of P through HAP precipitation is thermodynamically obtainable, however at high permeate recovery, the high CCPP is likely to induce calcite formation. On top of the thermodynamic considerations, precipitation and phase transition kinetics also plays a major role in determining the extent of scaling and the practical amount of recoverable P. As indicated by the gap between the ACP and HAP PPP curves depicted in Fig. 6, the transformation rate of ACP (or other Ca-P phase) to HAP (or to other meta-stable phase) could have a considerable effect on the mass of P which would precipitate from the concentrate after a given retention time. This has implications on the crystallization reactor at the concentrate outlet, which has to be designed according to the P recovery goal. In case NaCl removal is not required, the retentate could be recycled back to the wastewater treatment plant, which leaves only the permeate stream and precipitated Ca-P solids as P outflows and increases P recovery.

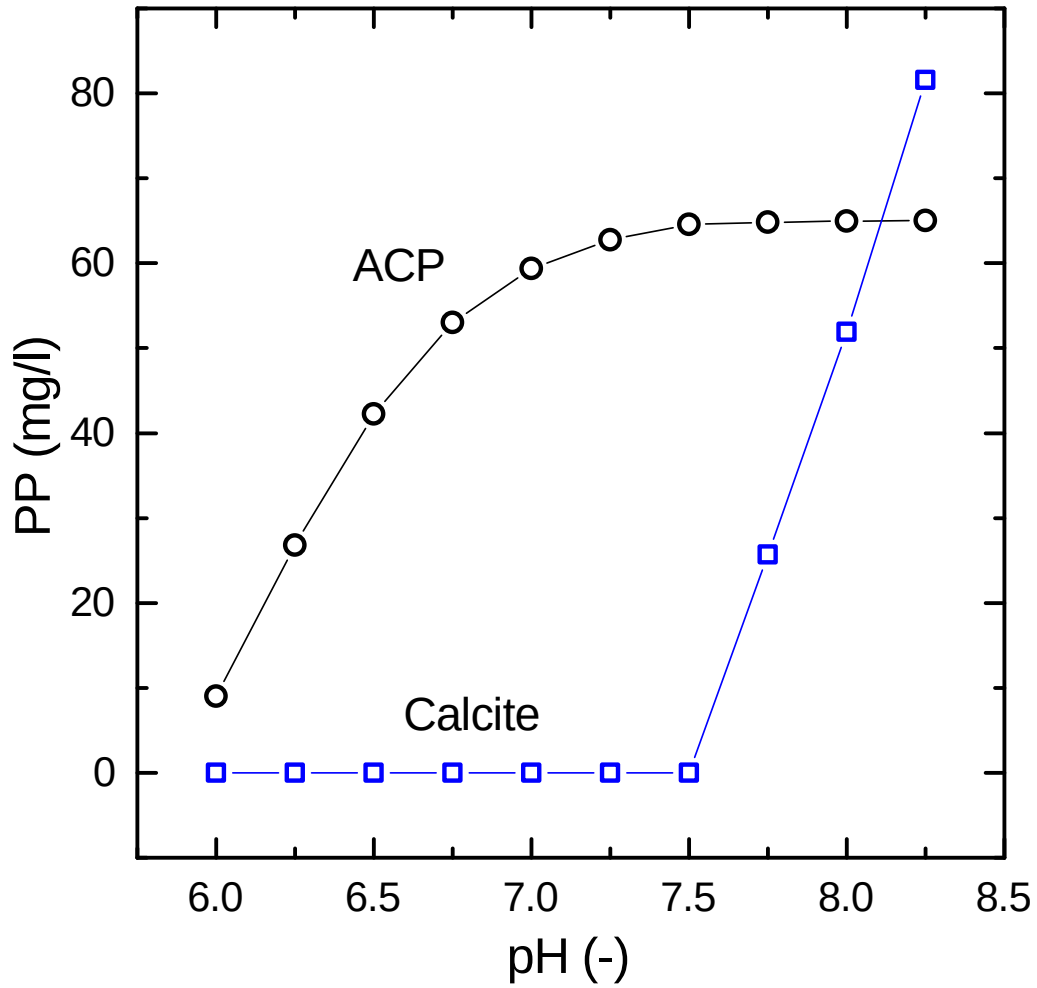


Figure 7: Precipitation potential of amorphous calcium phosphate (ACP) and calcite at 95% recovery ratio. Here precipitation potentials were calculated simultaneously for both phases which were allowed to compete over the common ion Ca^{2+} . Other details are as in Fig. 6.

While the analysis shown in Fig. 6 shows the limiting pH below which calcite precipitation is thermodynamically restricted, finite nucleation and crystallization kinetics allow operation at higher pH without calcite scaling.

Higher retentate pH results in increase in both P removal (higher rejection) and recovery (decrease Ca-P solubility). From that perspective, it is useful to examine the competitive solid-liquid equilibrium between calcite and ACP as presented in Fig. 7. At 95% recovery, when both phases compete on the common Ca^{2+} ions, calcite precipitation starts only at pH 7.5, whereas for the non-competitive equilibrium analysis calcite precipitation starts already at pH <6.5. This pH difference translates to additional ~ 20 mg/l of P which could be potentially recovered from the retentate i.e increase from $\sim 60\%$ to $>90\%$ of P recovery as ACP. In addition to being thermodynamically favorable at high recovery ratio, ACP crystallization should be also accelerated due to seeding effect. Since at lower recovery (e.g. 60% pH = 7.5) ACP precipitation is thermodynamically permitted and calcite is not, ACP nucleation will occur earlier in the retentate, promoting formation of ACP over calcite formation at higher recovery.

4.3. Estimation of operating expenses

A preliminary assessment of the major operating expenses was conducted for the new nanofiltration process and compared with the costs of chemical precipitation using ferric chloride (table 2). An average phosphorus concentration of 10 mgP/l was considered with a typical Fe/P molar ratio of 2 [39, 40]. The costs of ferric-chloride (635 USD/dry_ton) and sulfuric acid (131 USD/dry_ton) are taken from actual contracts made by US based towns or counties in 2017 for purchasing chemicals for wastewater treatment plants. The specific energy consumption (SEC) for the nanofiltration step was cal-

culated using

$$SEC(\frac{kWh}{m^3}) = P(bar) \frac{1(\frac{kWh}{m^3})}{36(bar)} \frac{1}{r} \quad (2)$$

, where P is the applied pressure (8 bars) and r is the recovery ratio (0.95). The energy expense was then calculated using the average cost of electricity to US industry, 0.07 USD/kWh. The sulfuric acid dose needed to decrease the pH from the original value (7.5) to 6.7 for preventing calcite formation was calculated using a PHREEQC [30] model of a high alkalinity (4.9 meq/l) secondary effluent [41].

Table 2: Main components of the operating expenses required for reducing phosphorus concentration in wastewater by >90%. Comparison between chemical precipitation (10 mgP/l and Fe/P molar ratio = 2) and nanofiltration (applied pressure = 8 bars and 95% recovery). Assumptions and calculations are explained in more detail in the main text.

Chemical Precipitaion Costs		Nanofiltration Costs	
FeCl ₃	0.067 \$/m ³	H ₂ SO ₄	0.0067 \$/m ³
		Energy	0.019 \$/m ³
Total	0.067 \$/m ³	Total	0.029 \$/m ³

As seen in table 2, the energy consumption was the main operational expense for the wastewater nanofiltration step. Nevertheless, the applied pressure and thus the energy consumption can be potentially reduced by 50% or more. This can be achieved with "loose" high-flux NF membranes, as opposed to the "tight" NF membrane used in this study. Pressure reduction is practical since the osmotic pressure of the effluent is low (0.1 bars) and the salt rejection is only partial, thus the trans-membrane osmotic pres-

sure is of little significance in the current case. Such loose NF membranes were previously developed by the authors [42] and are currently tested for phosphorus rejection. Expenses on acid for pH modifications were found to be insignificant, despite the fact that high alkalinity water was used for the calculation. This is due to the low buffer capacity of the carbonate system at the relevant pH range (7-8). Overall, the operational expenses were significantly lower for the NF scheme in the considered case, demonstrating its economical feasibility. It should be noted that for $P < 4 \text{ mg/l}$, the operational expenses for ferric chloride treatment are lower when using the same effluent and assumptions as above (8 bars, high alkalinity). However, the NF process has the additional benefits of removing pollutants (e.g. organic pollutants and heavy metals), decreasing salinity and enabling phosphorus recovery.

5. Conclusions

The analysis shown above introduces a new approach for the removal and recovery of phosphorus from diluted effluents. It comprises a low-pressure nanofiltration step followed by a Ca-P crystallization step applied on the retained solution. Frequent acid cleaning, enabled by the use of acid-durable membrane, is applied for restoring membrane performance and recover the Ca-P deposited on the membrane or the feed channel spacer. A commercial acid-durable membrane was found to provide high P rejection ($>97\%$) even at neutral pH. NaCl rejection by this membrane was also high (50-90%) making it ideal when salinity reduction of the effluent is desirable. In case salinity reduction is not required, low NaCl rejection is favoured for reducing energy consumption. A promising approach for achieving high $\text{H}_2\text{PO}_4^-/\text{Cl}^-$

selectivity, was previously demonstrated by [43] for nanofiltration membranes produced via layer by layer deposition of polyelectrolytes on a porous support. We currently test this type of membranes for their applicability in treating synthetic and real secondary effluents. Avoiding CaCO_3 precipitation during filtration was found to be critical for the technical feasibility of the suggested process. CaCO_3 competes with CA-P for Ca^{2+} ions, thus limits P recovery potential. Moreover, CaCO_3 forms a scaling layer on the membrane which rapidly reduces permeate flux, while Ca-P tends to precipitate in the bulk, allowing for more sustainable operation. A comprehensive thermochemical theoretical analysis, performed on model effluent, indicated that mitigating CaCO_3 precipitation, while maintaining high Ca-P supersaturation is achievable via pH adjustments. Acid cleaning was shown to recover membrane performance completely. A preliminary economical analysis demonstrated that in many cases the operational expenses of the suggested filtration scheme are lower than those for chemical precipitation with ferric chloride, a widely used method for P removal. Furthermore, the filtration method significantly improves other water quality parameters and enables P recovery. Overall our results suggest that low-pressure nanofiltration is a techno-economically viable alternative for P removal from dilute solutions. Moreover when acid-resistant membranes are used, Ca-P precipitation can turn from a limitation to an advantage.

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6. Graphical Abstract

