



Nanofiltration for the recovery of phosphorus – Development of a mass transport model[☆]



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HIGHLIGHTS

- Modelling approach for nanofiltration and mixtures of acids and salts was developed.
- The model was evaluated using synthetic mixtures and pre-treated sewage sludge.
- A nanofiltration separation process for phosphorus recovery was evaluated.
- The efficiency of the separation was analysed as function of the process conditions.

ARTICLE INFO

Article history:

Received 11 February 2014

Received in revised form 7 May 2014

Accepted 8 May 2014

Available online 29 May 2014

Keywords:

Nanofiltration

Mass transport modelling

Phosphorus recovery

ABSTRACT

Nanofiltration is a possible separation technology for phosphorus recycling from sewage sludge or sewage sludge ash. Nanofiltration can be applied for this purpose in combination with a low pressure wet oxidation or acidic hydrolysis of sewage sludge or leaching of sewage sludge ash. The feed of the nanofiltration in this application is in the pH range of 1.5 to 3 and contains phosphoric acid, sulphuric acid as well as metal ions which should be rejected. This paper presents experimental data and multi-ion transport modelling. The model is based on the solution diffusion model with permeability coefficients as the only input parameters. For several simplified synthetic solutions permeability coefficients could be successfully fitted. By interpolation of the parameters as functions of pH and concentration in the nanofiltration feed, retentions could be calculated for additional compositions. A validation with real solutions obtained from sewage sludge was performed.

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1. Introduction

Phosphate is a limiting nutrient in most ecological and especially agricultural systems. Today's agricultural productivity is achieved by using synthetic fertilisers originating from mineral phosphorus

Abbreviations: a , Debye Hückel coefficient, for 20 °C = 0.5042; $c_i(x)$, virtual concentration of component i at the position x in the membrane; c_i' , permeate concentration of component i ; c_i^f , feed concentration of component i ; F , Faraday constant; IS , ion strength ($= 0.5 \cdot \sum (z_i^2 \cdot c_i)$); J_v , permeate volume flux [$\mu\text{m/s}$] = [$\text{L}/(\text{m}^2\text{h}) \cdot 3.6$]; P_i , permeability of the component i ; R_g , gas constant; R_i , retention of the component $i = 1 - c_i'/c_i^f$; T , temperature; x , perpendicular distance from the membrane-feed interface (trans-membrane coordinate); z_i , charge of the component i ; $\gamma_i(x)$, activity coefficient of component i at the position x in the membrane; $\varphi(x)$, dimensionless electric potential at the position x in the membrane = $F\varphi^*(x)/(R_gT)$; $\varphi^*(x)$, electric potential at the position x in the membrane.

[☆] Most of the results of this publication were part of the dissertation "Nanofiltration for Phosphorus recycling from Sewage Sludge" by Claudia Niewersch, published by Verlagshaus Mainz GmbH, Aachen in 2013 [1].

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resources. The consumption rate of phosphorus rock exceeds by magnitudes the geological renewal rate. Phosphorus rock is located in few countries (more than 81% in Morocco and Western Sahara, China, US, Russia and Tunisia) [2]. The European countries are strongly depending on imports of phosphorus rock [3,4]. Some authors expect a depletion of economically available phosphorus resources in a time frame of less than 380 years [2,5,6]. The majority of the nowadays existing mining sites are sedimentary deposits. Due to their development they contain a large variety of elements, among which are numerous heavy metals, especially cadmium [7]. Hence it is expected that the quality of accessible phosphorus rock will decrease. Already in 2009, a large prize peak for phosphorus rock of 350 \$/t was observed. Similar prize peaks are likely to occur in the near future due to increasing scarcity and a low prize elasticity [8,9]. The phosphate shortage problem will be aggravated by a growing world population. The target of improving the nourishment situation in developing countries and the growing market for biomass for energy production will increase the demand for phosphate fertilisers.

According to these facts the development of alternative phosphate sources is presently of high relevance. Sewage sludge is a sink for more than 90% of the phosphate contained in waste water. In combination with a sludge pre-treatment with low pressure wet oxidation or an acidic, high pressure hydrolysis and ultrafiltration, nanofiltration can be used as refining process for phosphorus recovery. Due to the pre-treatment the nanofiltration feed has a low pH (around 1.5) and most part of the phosphate is in solution [10–13]. A similar feed is obtained by leaching of sewage sludge ash with sulphuric acid [14]. Important aims of a comprehensive phosphorus recycling process are to reduce the heavy metal load onto the soil and to provide a phosphate product with a high plant availability like magnesium ammonium phosphate instead of iron or aluminium salts. Due to the low pH, the nanofiltration membrane is positively charged and the phosphate is mainly not dissociated or one time dissociated phosphoric acid. The latter two compounds can pass the nanofiltration membrane relatively well under the given conditions. Hence a permeate containing purified phosphate is achieved which can be used for phosphate fertiliser production. For instance, it is possible to add magnesium oxide to precipitate magnesium ammonium phosphate.

To understand and optimise the separation process the mass transport through nanofiltration membranes needs to be quantified experimentally and mathematically described. In a previous experimental study it was concluded that relatively dense nanofiltration membranes like DL (GE Osmonics) or NF270 (DOW Filmtec) are suitable to achieve a high retention for metal cations [10–12,15]. According to several authors, for the description of ion flux through very dense nanofiltration membranes, for practical applications it is suitable to use a solution diffusion model without assuming an additional convective transport [16–18].

Several authors have shown successful application of nanofiltration modelling based on the solution diffusion model. Systems of two different ions were modelled [18] as well as solutions of non-charged components [19]. Furthermore, multi-ionic solutions were studied without taking into account the ion induced electric potential, i.e. neglecting the interaction between the ions in solution [20,21]. The role of electric interaction between charged solutes was studied in deep for systems of up to three different ions including the development of a rigorous solution of the sets of differential equations and successful experimental evaluation [22,23].

This study makes one step beyond these results by providing an approach for mass transport modelling in nanofiltration membranes including the effect of dissociation reactions and multi-ionic solutions containing up to nine different ion species.

2. Theory: modelling approach

We present a model and experimental evidence for a complex ionic solution quantifying the passage of phosphorus and the retention of metal ions as a function of pH, ion strength and flux. The transport equations used for this paper are based on the Nernst–Planck equation, but use the so-called virtual concentrations instead of real concentrations (see Eq. (1)). The virtual concentration is defined as the concentration in a free solution which is in thermodynamic equilibrium with a given cross-section at the relevant position inside the nanofiltration membrane [22,23]. Hence the permeability coefficients P_i presented in the equations are functions of the diffusion behaviour and of the partitioning behaviour of the components. The advantage of using virtual concentrations is that they provide continuous profiles across the membrane even at the transition feed-membrane and membrane-permeate.

$$J_v c_i'' = -P_i \left(\frac{dc_i}{dx} + c_i \frac{d(\ln \gamma_i)}{dx} + z_i c_i \frac{d\varphi}{dx} \right) \quad (1)$$

$$\wedge \sum_{i=1}^n (z_i c_i) = 0$$

These transport equations were presented by Yaroshchuk et al. [22, 23] in a similar way for cases, in which salt solutions are investigated and no chemical reactions between the components are taken into account. This paper presents an application on solutions containing acids and bases. It can be assumed that chemical reactions are taking place at the feed and permeate interfaces as well as in the membrane itself. Local chemical equilibrium was assumed as an approximation in the feed, permeate and in the membrane. The transport equations were developed for the relevant elements included in the nanofiltration feed. The transport equation for each element includes the fluxes for all components containing this element [24].

The strongest possible simplification of the disintegrated sewage sludge or sewage sludge ash after pre-filtration is a system containing phosphoric acid, sulphuric acid, one bivalent cation (e.g. magnesium) and one mono-valent cation (e.g. potassium). For this simplified system the validation of the nanofiltration model was done.

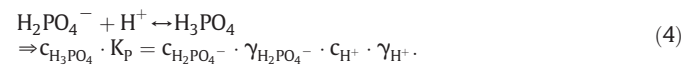
The dissociation of the acids and the reaction of magnesium with the dissociated acids lead to the following nine relevant components for a pH of 1.5–3: H^+ , $H_2PO_4^-$, H_3PO_4 , SO_4^{2-} , HSO_4^- , K^+ , Mg^{2+} , $MgSO_4$, and $MgH_2PO_4^+$ [24]. Hence transport equations were developed for the elements H, K, Mg, P and S. The following equation shows exemplarily the transport model for H:

$$\begin{aligned} & (c_{H^+}'' + 2 \cdot c_{H_2PO_4^-}'' + 3 \cdot c_{H_3PO_4}'' + c_{HSO_4^-}'' + 2 \cdot c_{MgH_2PO_4^+}'') \cdot J_v \\ &= -P_{H^+} \cdot \left(\frac{dc_{H^+}}{dx} + z_{H^+} \cdot c_{H^+} \frac{d\varphi}{dx} + c_{H^+} \frac{d(\ln \gamma_{H^+})}{dx} \right) \\ & - 2 \cdot P_{H_2PO_4^-} \cdot \left(\frac{dc_{H_2PO_4^-}}{dx} + z_{H_2PO_4^-} \cdot c_{H_2PO_4^-} \frac{d\varphi}{dx} + c_{H_2PO_4^-} \frac{d(\ln \gamma_{H_2PO_4^-})}{dx} \right) \\ & - 3 \cdot P_{H_3PO_4} \cdot \frac{dc_{H_3PO_4}}{dx} \\ & - P_{HSO_4^-} \cdot \left(\frac{dc_{HSO_4^-}}{dx} + z_{HSO_4^-} \cdot c_{HSO_4^-} \frac{d\varphi}{dx} + c_{HSO_4^-} \frac{d(\ln \gamma_{HSO_4^-})}{dx} \right) \\ & - 2 \cdot P_{MgH_2PO_4^+} \cdot \left(\frac{dc_{MgH_2PO_4^+}}{dx} + z_{MgH_2PO_4^+} \cdot c_{MgH_2PO_4^+} \frac{d\varphi}{dx} + c_{MgH_2PO_4^+} \frac{d(\ln \gamma_{MgH_2PO_4^+})}{dx} \right). \end{aligned} \quad (2)$$

The equations for the other elements are developed in an analogous way. The activity coefficients were approximated using the Davies equation [25].

$$\log \gamma_i = -a \cdot z_i^2 \cdot \left(\frac{\sqrt{I_S}}{1 + \sqrt{I_S}} - 0.3 \cdot I_S \right) \quad (3)$$

The influence of the pH-dependent dissociation was taken into account using the equilibrium equations. Exemplarily the equation is shown for the dissociation of phosphoric acid:



Together with the condition for electroneutrality this results in a set of differential equations containing the nine concentration gradients and the gradient of electric potential: five transport equations, four equations for chemical equilibrium, one equation for electric neutrality. The dissociation constants for free aqueous solutions are used as an approximation.

The only a priori unknown parameters in the system of differential equations are the permeability coefficients for each solute in solution. These parameters depend on the pH, the ion strength and to a lower extent on the concentration of the solute itself in the feed. The permeability coefficients have to be determined via fitting of experimental data. Once the permeability coefficients are determined, the equations

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