The Removal of Potassium Phosphate using Ceramic Nanofiltration

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Abstract

In the current study, the separation and rejection behavior of potassium phosphate salt using Nanofiltration membrane was done theoretically and experimentally. The extended Nernst Planck equation was used to describe the Nanofiltration separation behavior by using silver frost programming language using the version FTN95 model. Besides the modeling; an experimental work was done by preparing K_3PO_4 solution at concentration of 0.1 and 0.4 M. Where the rejections of K^{1+} and PO_4^{3-} ions were obtain at different TMP values ranging between 1 to 5 bars.

Keyword: Nanofiltration, membrane, potassium, phosphate, pore radius, rejection, volumetric flux.

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إزالة فوسفات البوتاسيوم باستخدام الترشيح النانوي الخزفي

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ملخص

في الدراسة الحالية، تم دراسة عملية فصل وسلوك رفض ملح فوسفات البوتاسيوم باستخدام غشاء الترشيح النانوي نظريًا وتجريبيًا. تم استخدام معادلة نرنست بلانك الموسعة لوصف سلوك فصل الترشيح النانوي باستخدام لغة برمجة الصقيع الفضي باستخدام نموذج FTN95. إلى جانب النمذجة؛ تم إجراء عمل تجريبي من خلال تحضير محلول K_3PO_4 بتركيز 0.1 و 0.4 مول/لتر . حيث تم الحصول على رفض أيونات K^{1+} و PO_4^{3-} أيونات عند قيم TMP مختلفة تتراوح بين 1 إلى 5 بار.

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Introduction

While Jordan boasts various water sources, including rainwater, groundwater, surface water, and others, the country faces multiple challenges contributing to its low annual per capita water allocation of around 150 cubic meters. Among these challenges, one of the most significant factors is the rapid population growth, which places increased pressure on water resources. Additionally, the substantial expansion of diverse economic activities that demand significant water resources exacerbates the situation..

"Membrane separation plays a significant role in chemical engineering, where membranes made from synthetic materials are widely employed. A membrane can be defined as a barrier that partially or completely restricts the passage of chemical species based on its unique characteristics. These processes encompass technologies primarily designed for physical or physical-chemical separation without necessitating a phase change. Typically, these membrane processes are combined with other unit operations to create industrial processes aimed at producing desired products (Ahsan & Imteaz, 2018).

Membrane process is a mechanical separation process, which implies the removal of solids from fluids using a filter medium which is the membrane, which permits the fluid to pass through but retains the solid particles. The process depends on the physical differences between the phases mainly the particle size and the particle shape. There are two main modes of liquid filtration, through-flow filtration where all of the feed pass through the filter medium, thereby separating all the suspended solids, and cross flow filtration where the feed flow is parallel to the medium, that can reduce the deposit and give higher sheer conditions, the fluid pass through by pressure difference as a driving force (Biron, 2018).

The particles unable to pass through the filter medium are termed "oversized," while the fluid that successfully traverses the medium is referred to as "permeate." These oversized particles can potentially form a filter cake, which has the potential to obstruct the passage of fluid through the filter medium (Bouranene, Fievet, & Szymczyk, September 1, 2009)..

The size of the targeted material to be separated controls the choice of the membrane to be used; Nanofiltration (NF) is used in separating organic materials with molecular weight over 400 and hardness ions such calcium and magnesium ions (Hilal, 2017).

Nanofiltration membrane

NF is a semi-permeable diffusion operated membrane, with pressure-driven process, its ability ranges between ultrafiltration and reverse osmosis. Reverse osmosis (RO) and NF have similar separation function, but NF has a higher permeate flux than RO with lower rejection abilities, in terms of dissolved salts. NF rejection abilities can be identified by a cut-off value - which is the molecular weight of the smallest molecule that can be 90% restricted by the top layer of the membrane in Dalton. NF membrane lies in the range of 150-2000 Dalton. In addition the molecular structure can also contributes to its rejection by NF (Biron et al, 2018), thus NF can filter more than 95 percent of multivalent ions, but it has limited rejection abilities of monovalent ion, there retention can range from 50 to 90 percent depending on the molecular weight and the ion radius (Murtomaki, 2021).

NF have different configuration such as tubular, hollow fibber, spiral-wound or flat (plate-and-frame). NF is used in many industries to treat saline surface water; brackish ground water and industrial process water also recycle wastewater. In addition NF is used in paper, dairy, and textile industries (Ahsan & Imteaz, 2018). NF is used in some applications which can be more efficient by using NF than using other membrane processes, desalination, desalting or total dissolved solids (TDS) reduction processes; thus NF can be considered as the primary application. Where NF is used in water softening, reducing the water hardness by separating divalent and multivalent ion, filtering inorganic contaminants such as nitrate, metals, arsenic, and radio-nuclides (radium, radon, and uranium), separating dissolved organic carbon, eliminating colour and turbidity elimination. Adding up, NF can remove viruses, bacteria, and other similar contaminants (Denver, 2nd edittion). The advantages of NF are its effective filtration; selectivity in rejection in comparison with other types of membrane which improve the effectiveness of separation. Also, NF process is energy

efficient, since NF has high rejection at low applied pressure in comparison with RO.

In this study the separation behaviour and selective rejection of potassium (K^{1+}) and phosphate (PO_4^{3-}) using tubular ceramic NF was investigated experimentally and theoretically. Understand the theory behind NF process by solving extended Nernst Planck equation, also run experimental work to show the effect of concentration, pressure, and flux on the separation mechanism. Ceramic membranes was considered in this study because it has higher thermal, chemical, and mechanical stability than polymeric and organic membranes, can treat acidic or basic feeds and tolerate pH values.

Potassium phosphate

Tri-potassium phosphate, also called tri-basic potassium phosphate with the molecular formula K_3PO_4 was used in this work. Tri potassium phosphate is a water-soluble white salt with a pH ranging between 11.5 and 12.3 (1% solution), with a milting point of 1380 ℃, density of 2.564 g/cm^3 at 17 ℃ and molar mass of 212.27 g/mol (Hilal, 2017).

Tri-potassium phosphate can be used as a base catalyst in the synthesis of organic compounds. K_3PO_4 has a high buffering capacity as a result it is used as a food preservative in frozen, packaged and dairy food products (Wadekar & Vidic, 2018). Also it is used in cosmetic products such as shampoos, conditioners, and bath products; as a buffering agent in order to shift pH of human skin and avoid the scalp.

One of the most important uses of potassium phosphate is the treatment of hypophosphatemia, which is a medical condition where blood has low levels of phosphorous; this condition can cause muscle weakness and pain, respiratory and heart failure, seizers, and coma. Also potassium phosphate is used in cleaning products and household care such as materials used in cleaning drains, control odours, clear blockages and removing grease (F. Mischel, 2022).

Theory

Nanofiltration (NF) ceramic membrane separation behaviour can be theoretically analyzed using non-equilibrium irreversible thermodynamics models that can illustrate the hydrodynamic and transport of ions behaviours through the membrane (Khulbe & Matsuura, 2021). Ions theoretical modelling is considered complex due to the interactions between the solution and the membrane, the interactions of the components of the feed solution itself, and the physical and chemical properties of the membrane such as membrane material, membrane surface charge, and pore size. Such conditions conclude that NF restricts material permeability's through the NF membrane media.

Model

In pressure driven membranes the applied pressure gradient should exceed the osmotic pressure difference across the membrane which is the minimum pressure needed to prevent inward transport of treated water back to the concentrated solution; where osmotic pressure depends on salts concentration. Thus to avoid osmotic pressure effects in NF process; then the feed is relatively diluted, which also prevents rapid fouling. Electrochemical effect encouraged by the membrane charge media can lead to a build-up of the opposed charged ions (attraction forces) at the membrane surface or in the pores, and a tiny amount by appear in the permeate, this alters the electrical potential across the membrane media (Ahsan & Imteaz, 2018). As a result, the model that represents the fluxes of the solutes and solvent of the system should represent all forces.

Physical-based NF models describe the interaction between the membrane and multi-ionic feed solutions. Generally speaking, membrane models yield permeate composition for specified feed concentration and operating conditions. The most successful NF models are those based in the combination of the Extended Nernst-Planck equation with the Donnan steric equilibrium (Krabbenhøft, 2008). In this work, the built model was used to predict the membrane performance and to give better understanding on the working mechanism.

Nernst -Planck equation is conservation of mass equation used to describe the motion of charged chemical species in a fluid medium. Nernst-Planck equation is a physical reformulation of Fick's macro-scale diffusion law, extended by the motion of charged particles. The equation was established and experimentally justified by Nernst, and theoretically elaborated by Planck; where it became significant when it was recognized as essential processes of life, such as cellular excitation and mitochondrial energy metabolism, depend on electro diffusion (Krabbenhøft, 2008).

The Nernst–Planck equation is applied in describing the ion-exchange kinetics in soils, and has been applied to membrane electrochemistry. A correlation for the non-linear potential gradient is derived from current density relation with fluxes. The boundary conditions are determined with the Donnan equilibrium at the membrane–solution interface, taking into account the convective flow. Nernst-Planck equation consists of the subsequent concepts which are concentration gradient, electrical potential gradient, and pressure difference across the membrane. Convection of ions is caused by the pressure difference across NF. Also concentration and electrical potential gradients causes ion diffusion across NF.

The extended Nernst-Planck equation is rewritten as the concentration gradient across the membrane separation active (Bouranene, Fievet, & Szymczyk, 1 September 2009) layer by assuming ideal steady state condition, the membrane effective charge to be constant positive charge, and the electro-neutrality condition in the bulk solution is assumed to be equal to zero (Santafé-Moros, 2008)

$$\frac{dc_i}{dx} = \frac{J_v}{D_{i,p}}\left(K_{i,c}c_i - C_{i,p}\right) - \frac{z_i c_i}{RT}F\frac{d\Psi}{dx} \tag{1}$$

where $(D_{i,p})$ is the hindered diffusivity (m²/s), (c_i) is the concentration in the membrane (mol/m³), (z_i) is the valence of ion (i), $(K_{i,c})$ is the hindrance factor for convection inside the membrane, (J_v) is the volume flux based on the membrane area (m/s), (R) is the universal gas constant (8.134 J/mol.K), (T) is the absolute temperature (K), (F) is Faraday constant (C/mol), (Ψ) is the electrical potential (V), $(C_{i,\,p})$ is the concentration of ion (i) in permeate (mol/m³), and x is the membrane active layer thickness (m).

Under the condition of electro-neutrality, then the Donnan equilibrium across a membrane, the differences of pressure and electrical potential would appear. If the non-permeating components are electrically neutral, only the pressure difference would have an effect on the rejection of ions (Biron, 2018). The Donnan equilibrium was assumed to apply at the feed/membrane interface and membrane/permeate interface; thus the electrical potential gradient as indicated in equation (1) is obtained (Wadekar & Vidic, 2018) as follow

$$\frac{d\Psi}{dx} = \frac{\sum_{i=1}^{n}\frac{z_i J_v}{D_{i,p}}\left(K_{i,c}c_i - C_{i,p}\right)}{\frac{F}{RT}\sum_{i=1}^{n} z_i^2 c_i} \qquad (2)$$

Donnan equilibrium was obtained by assuming a diluted solution and the activity coefficient is equal to unity; as a result, a relationship between the concentration inside the membrane active layer and the feed/permeate bulk solution would be given by equation (3) as follows

$$\left(\frac{c_i}{C_i}\right) = \phi\exp\left(-\frac{z_i F}{RT}\Delta\Psi\right) \qquad (3)$$

where $\Delta\Psi_D$ is the Donnan potential (V), C_i is the ion concentration in the feed and the permeate solution (mol/m³), and ϕ is the steric partitioning term. The applied boundary conditions across NF active layer are

$$at\ x = 0 \longrightarrow C_i = C_{i,f}$$
$$at\ x = \Delta x \longrightarrow C_i = C_{i,p}$$

where $C_{i,f}$ is the concentration of the ion in the feed (mol/m³). Ions rejection was obtained

$$R = 1 - \frac{C_{i,p}}{C_{i,f}} \qquad (4)$$

The concentration gradient equation (1) was used to calculate ion concentration inside the membrane. After that; equation (3) was used to obtain the ion concentration at the permeate side. As a result, equation (4) was used to calculate the ions rejection (Biron, 2018).

Numerical solution

Ion permeation through NF membrane was described by equations (1), (2), (3), and (4). Equations 1 and 2 were integrated across the membrane active layer thickness and the solute concentration in bulk feed. At the feed/membrane interface the solute concentration was $[C_{i,f}]$ and the initial ion concentration inside the membrane was $[c_{i,1}]$. At the membrane/permeate side the solute concentration inside the membrane was $[c_{i,N}]$ and ion permeate concentration was $[C_{i,p}]$.

Runge-Katta mathematical method was used to integrate equations (1) and (2). Equation (3) was used to calculate the initial ion concentration inside the membrane $(c_{i,1})$ at the feed bulk/membrane interface. By integrating equation (1) and (2), the final concentration insider the membrane $(c_{i,N})$ at the membrane/permeate bulk was obtained. Then equation (3) was used to calculate the permeate ion concentration $(C_{i,P})$ by the estimation of $(c_{i,N})$. In the end, the ion rejection was calculated using equation (4).

Integrating equation (1) in an iterative function using an initial guess for the value of the permeate concentration $(C_{i,p})$ to be equal to the feed concentration $(C_{i,f})$. The hindered diffusivity $(D_{i,p})$, the hindrance factor for convection inside the membrane $(K_{i,c})$ and the Donnan potential $(\Delta\Psi D)$ were calculated by using methods obtained from literature. Also the solution was assumed to be dilute; as a result the activity coefficient would be equal to unity (Biron, 2018).

The model was run for four different concentrations at different volume fluxes. The concentration values that were assumed to be 10, 100 and 1000 mol/m^3 concentration, and the volumetric flux per membrane surface area were assumed to be $1.0E^{-3}$ to $1.0E^{-6}$ m^3/m^2/sec. The membrane active layer thickness was assumed to equal $20.0E^{-6}$ m.
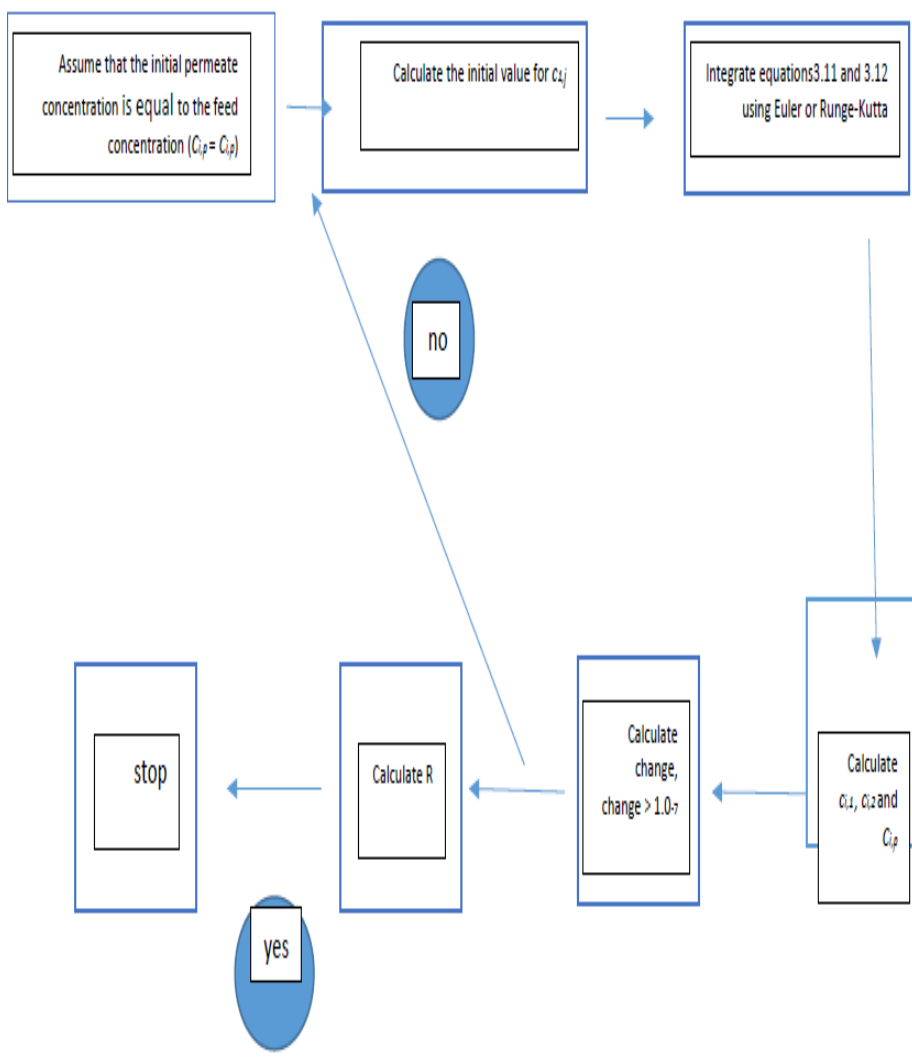
Figure 1. Schematic graph of Fortran module.

Experimental part

Two K_3PO_4 solutions at two different concentrations were prepared, were the concentrations were 100 mol/m^3 (0.1) and 400 mol/m^3 (0.4 mol/l). In the first stage, distilled water was used; where the distilled water was pumped through the membrane unit with a high-pressure pump, where Trans membrane pressure (TMP) changed from 1 to 5 bars. TMP is the membrane pressure gradient; where TMP is obtained by calculating the average value of the feed pressure and permeate pressure. The pressure was monitored using pressure gauges across the membrane unit and controlled by a control valve. The experiments were carried out at room temperature (25 °C) (Ahsan & Imteaz, 2018). For each TMP the permeate sample were collected for 20 minutes. For each TMP value; the feed pressure, permeate pressure, pH, and flux were monitored to ensure that the process is stable after removing all bubbles in the system. The volume and mass of each permeate sample were measured. The second stage experiment was run for K_3PO_4. After finishing the experiment; distilled water was used to wash the membrane several times to ensure removal of ions.

Finally distilled water experiment was run in order to compare distilled water passing through the membrane before and after K_3PO_4 solution was used. The comparison between the first stage and final stage would give a vision if fouling took place when using K_3PO_4 solution (Biron, 2018).

Results and discussion

Theoretical results

The module was run for three different concentrations which were 0.01, 0.1and 1.0 M. It was noticed that the rejection of K^{1+} and PO_4^{3-} increased as the volumetric flux through the membrane increased. Mean while the rejection of K^{1+} ions slightly increased as the feed concentration increased. Thus the volumetric flux per membrane surface area has a higher effect on the rejection of K^{1+} more than the effect of the ion concentrations figure 2. It was also noticed that the rejection of PO_4^{3-} ions increased as the feed concentration increased as shown in figure 3, (Hilal, 2017). The volumetric flux per membrane surface area (J_v) is related to TMP; as the applied

pressure was increased then permeate volumetric flux per membrane surface area would increases The optimum thickness of the active layer of the membrane was equal to 20 μm, the initial concentrations were (0.1 and 0.4) M, the pore radius of the membrane was 0.8 nm, and the volumetric fluxes ranged between was 2.5E-06 to 5E-07 m³/m².sec, obtained from Fortran program data.
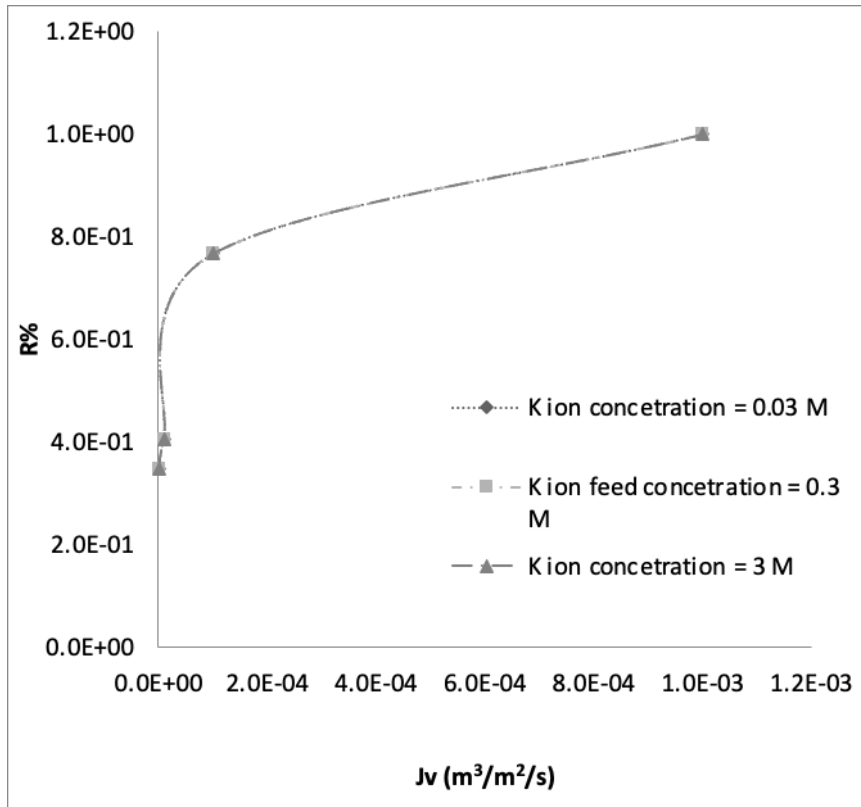
Figure (2)   Rejection of K^{1+} (R%) versus volumetric flux (m³/m²/s).
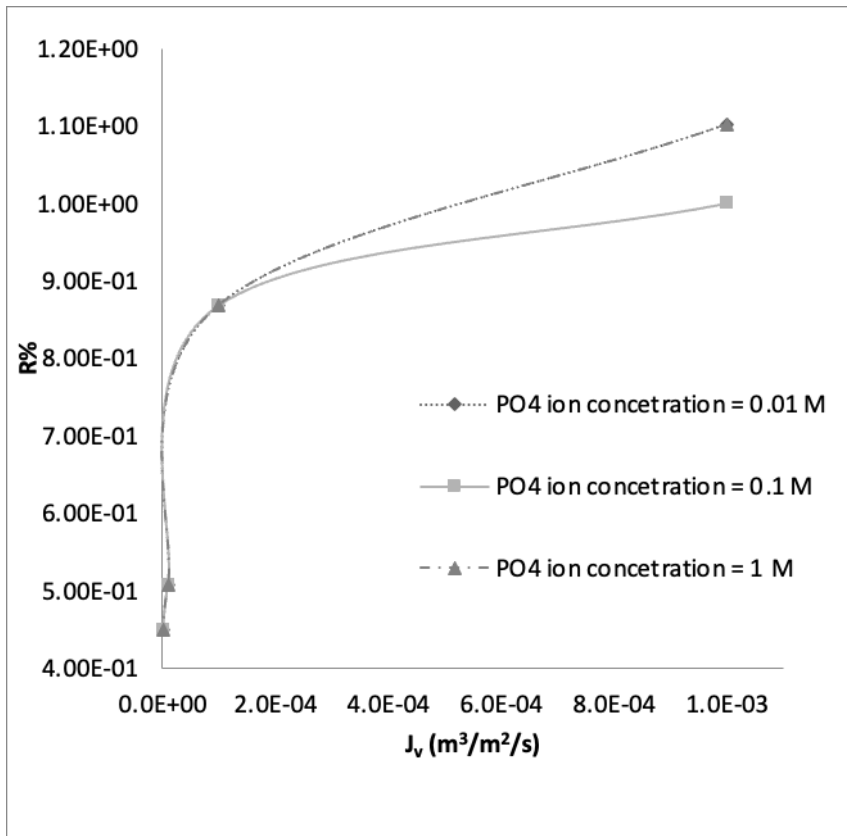
Figure (3) Rejection of $(PO_4)^{3-}$ (R%) versus volumetric flux ($m^3/m^2/s$).

It was noticed for both ions K^{1+} and PO_4^{3-} ions that the concentration of ions inside the membrane active layer increased as the volumetric flux increased. In addition, the ions concentration increased from the feed bulk side of the membrane to the permeate side of the membrane as shown in figures 4 and 5.
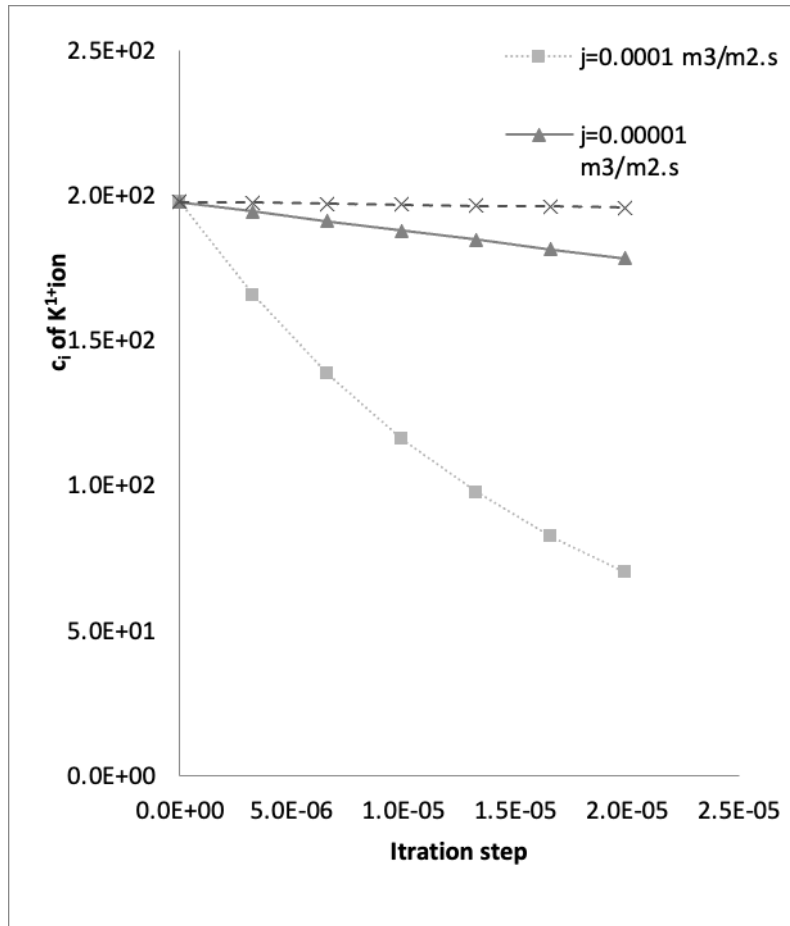
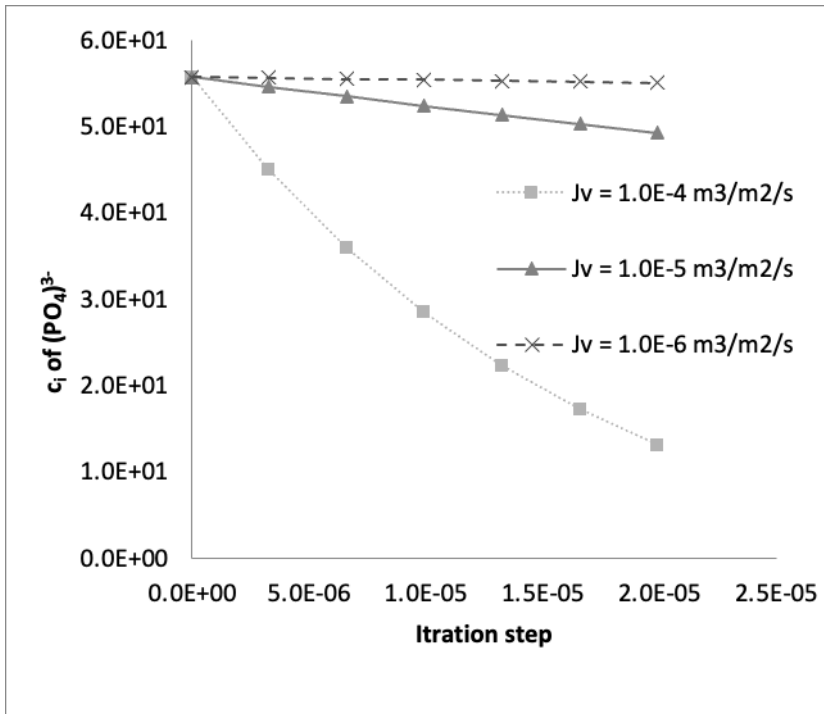**Figure (4) Concentration of K^{1+} ion inside the membrane active layer**

Figure (5) Concentration of $(PO_4)^{3-}$ ion inside the membrane active layer

Experimental results

From the experimental results; it was noted that the rejection of potassium ions (K^{1+}) at 0.1 M concentration was higher than the rejection at higher concentration which was 0.4 M, as shown in figure 5. It was noted that the rejection of K^{1+} at 0.1 M almost increased as the TMP increased. While the rejection of K^{1+} at 0.4 M decreased as the TMP increased.
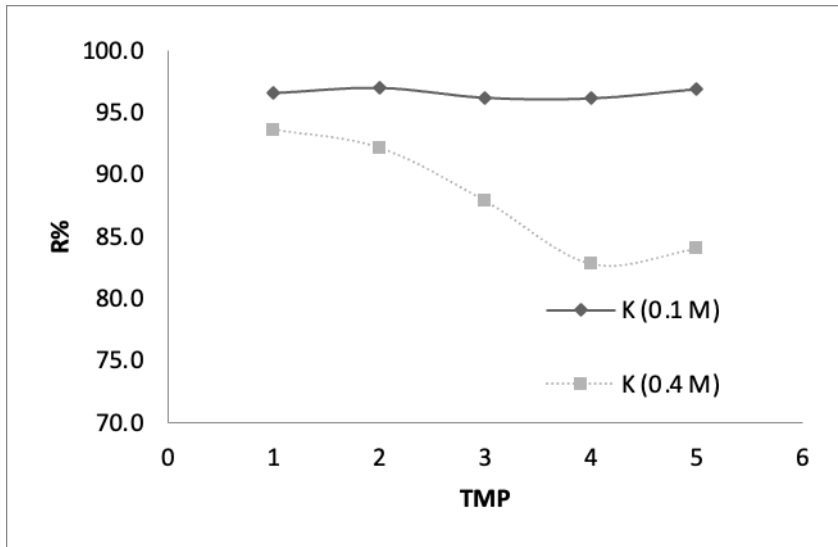
Figure (6) R% of K^{1+} ion versus TMP

Also it was noted that the rejection of phosphate ions (PO_4^{3-}) at 0.1 M concentration was higher than 0.4 M concentration as the TMP increased, as shown in figure 6. It was noted that the rejection of PO_4^{3-} at 0.1 M and 0.4 M increased as the concentration decreased. While the rejection of K^{1+} ions increased as the concentration decreased.
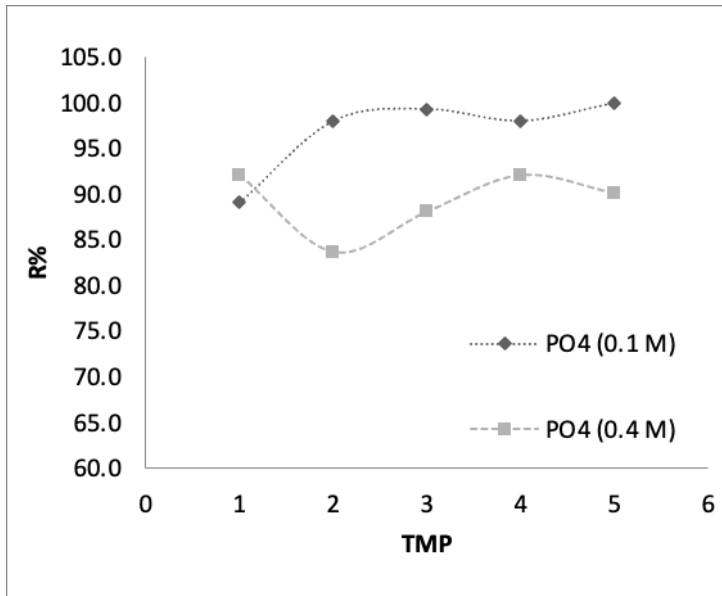
Figure (7) R% of PO_4^{3-} ion versus TMP

A distilled water experiment was run before starting K_3PO_4 solution experiment, and directly after K_3PO_4 solution experiment; before cleaning the membrane. It was noticed that the relationship between volumetric flux based on the membrane surface and TMP was lower than when the membrane was clean. Also the volumetric flux after higher concentration 0.4 M, was higher than the volumetric flux for solution with lower concentration 0.1 M. In the three cases the volumetric flux increased as TMP increased.
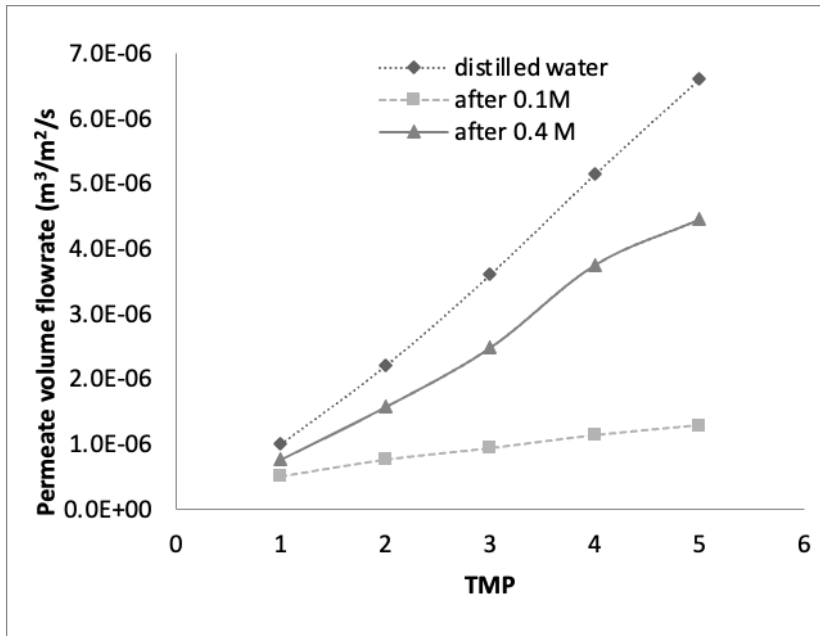
Figure (8) J_v versus TMP

Discussion

In this section the theoretical formulation and the experimental results were discussed. The theoretical development using Fortran programming after applying Runge-Kutta method were presneted. The effect of the change in ions concentration and volumetric fluxes on the rejection of K^+ ion and PO_4^{3-} ion were investigated; theoretically and experimentally.

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a) Theoretical results

It was clear from figures 2 and 3 that the rejections of K^{1+} and PO_4^{3-} ions increased as the feed concentration increased and volumetric flux increased. In addition, it was found that the concentration decreased inside the membrane separation active layer from the feed side to the permeate side of the membrane active layer. As well, the concentration inside the

membrane increased as the volumetric flux decreased which was obvious in figures 4 and 5 (Khulbe & Matsuura, 2021).

b) Experimental results

Experimental data were collected from the laboratory using ceramic NF membrane with pore size 0.8E-9 m. The selected concentrations were 0.1M and 0.4M; which were used to study the efficiency of ceramic NF membrane in the separation of K^{1+} ions and PO_4^{3-} ions. The data obtained from the experimental work were plotted using excel; it was found that by increasing the pressure from 1 bar up to 5 bars increases the volumetric flux. Moreover, the rejections of K^{1+} ions and PO_4^{3-} ion increased as TMP increased. It was found that when the feed concentration was 0.1 M and TMP with a value of 5 bars, the rejection of PO_4^{3-} was almost 100% and the rejection of K^{1+} was around 96%. When the feed concentration was 0.4 M; K^{1+} ions had a rejection of 100% at TMP 2, 3, 4 and 5 bars. High rejection of K^{1+} ions is due to repulsion between K^{1+} ion charge and the membrane surface positive charge; thus a repulsion would occur and not allowing the K^{1+} ions to pass through the membrane (Murtomaki, 2021). Meanwhile, the high rejection of PO_4^{3-} ions is due to attraction between the negative charge of PO_4^{3-} ions and the positive charge of the membrane active layer surface; where PO_4^{3-} ions remain in the bulk area at the membrane surface (Murtomaki, 2021).

Conclusion

In this study, the separation behaviour of potassium phosphate (K_3PO_4) using a ceramic NF membrane was investigated experimentally; through monitoring several variables such as pore radius, ions concentrations and volumetric flux. The extended Nernst-Planck equation was solved numerically by Runge-Kutta mathematical method and the module was written using Fortran language. The theoretical development of pertaining equations revealed that there is up to 100% rejection of K^{1+} and PO_4^{3-} ions under specific conditions (Murtomaki, 2021). For a condition where the initial concentrations were (0.1 and 0.4) M, the pore radius of the membrane was 0.8 nm, the membrane active layer thickness 20.0E-6 m; the best rejection of K^{1+} and PO_4^{3-} ions were at a volumetric fluxes ranging between

was 2.5E-06 to 5E-07 m³/m².sec, obtained from Fortran program data. From the experimental results; it was found the best rejection value for of PO_4^{3-} ions was at lower concentration and high TMP; which is supported by the theoretical results. And in the case of K^{1+} ion; the higher rejection values as the concentration increased and TMP increased (Wadekar & Vidic, 2018)

Nomenclature

j_i is the flux of ion (i) based on the membrane area (mol/m².s).

$D_{i,p}$ is the hindered diffusivity (m²/s).

c_i is the concentration in the membrane mol/m³.

z_i is the valence of ion (i).

$K_{i,c}$ is the hindrance factor for convection inside the membrane.

J_v is the volume flux based on the membrane area (m/s).

R is the gas constant (J/mol.K).

r_p is the effective pore radius.

r_i is the radius of component (i).

T is the absolute temperature (K).

F is Faraday constant (C/mol).

$C_{i,f}$ is the concentration of ion (i) in the feed (mol/m³).

$C_{i,p}$ is the concentration of ion (i) in the permeate (mol/m³).

C_i is the ion concentration in the solution (mol/m³).

$\Delta\Psi_D$ is the Donnan potential (V).

ϕ is the steric partitioning term.

TMP is trans-membrane pressure.

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