Permeability of P and K-nutrient through polystyrene membrane from aqueous solutions of urea + KH₂PO₄

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With the polymer-coated fertilizer as background, the permeability of P- and K-nutrient through a representative polymer membrane-polystyrene membrane were investigated by measuring their permeability in the solutions of KH_2PO_4-water and urea-KH_2PO_4-water at nominal temperature of 298 K using the Ussing chamber method. To analyze and interpret the variation of permeability with solute concentration, the solubility of permeate in polymer membrane were determined experimentally and the permeate diffusion coefficient were assessed by the measurements of density and apparent molar volume of the aqueous fertilizer solutions. An interesting "increase-decrease" trend for the permeability of both phosphorous (P)-nutrient, and potassium (K)-nutrient fertilizer with permeate concentration was observed, in which the increases in permeability at low concentrations of permeate could be attributed to the increase in solubility of KH_2PO_4 in polymer while the decreases in permeability at high concentrations was due to the decrease in diffusion coefficient of permeate in polymer membrane. Finally, the release kinetics of these nutrients from a PS-coated urea-KH_2PO_4 compound fertilizer granule was predicted using the Shaviv's model along with the permeability data of P- and K-nutrient generated.

Keywords: Permeability; polymer membrane; aqueous fertilizer solution; polymer-coated fertilizer.

INTRODUCTION

Even though it has been more than half a century since the first commercial polymer coated fertilizer (PCF) entered the market, the permeability of fertilizer nutrients through polymer membrane has not been systematically investigated. For a permeation process across polymer membrane, the permeability, also called permeation coefficient, is defined as ratio of mass flux to the concentration gradient of permeate across the membrane. The permeability of polymer membrane is of great importance for all slow/controlled release systems with polymer membrane as barrier material which governs the permeation of core material through the membrane such as fertilizers and drugs. The famous Ussing chamber method that were widely used in drug controlled release system[1, 2] and fuel cell[3, 4] can be used to measure the permeability, which was initially introduced by Ussing and Zerahn in 1951 to measure the transport of sodium ion in frog skin in epithelial ion transport physiology[5–7].

Recently, some researchers reported the permeability of fertilizer nutrients through various polymer membranes, as briefly summarized in the Table 1 including the information on the core fertilizer, polymer coating, characterizations, and source.

It is obviously that all the fertilizer nutrient permeability data reported are for nitrogen (N)-nutrient and there is no report on permeability of P-nutrient and K-nutrient so far. Furthermore, most of the N-nutrient permeabilities reported are isolated data points at certain concentration and temperature. The shortage and incompleteness of systematical permeability data of N-, P-, and K-fertilizer nutrient has been a serious hinder for the development of polymer-coated fertilizers. Therefore, series of studies were conducted to measure the permeability of N-, P-, and K-nutrient through various polymer membranes from various aqueous fertilizer solutions in our research group. In one of our previous studies[12], the permeability of N-nutrient fertilizer through polystyrene membrane from aqueous solutions of urea, urea + NaH_2PO_4, urea + $Ca(H_2PO_4)_2$, urea + KCl, urea + NaCl, and urea + KH_2PO_4 in wide composition range were reported. However, it was still of great necessity to measure the permeability of P- and K-fertilizer nutrient through polymer membrane for development of polymer-coated NKP compound fertilizer.

A variety of models have been proposed to analyze and interpret the permeation through a membrane including the "solution-diffusion" model[13] for non-porous membrane and "pore flow" model[14] for porous membrane. According to the "solution-diffusion" model the permeability (in the unit of cm^2/d) can be explained by,

$$P_s = SD \quad (1)$$

S and D are the solubility and diffusion coefficient of solute in membrane, representing the solute-membrane and solute-solution, solute-solute intermolecular interactions, respectively.

The aqueous fertilizer solutions generally consisted of N-, P-, and/or K-nutrient were interesting solutions with various intermolecular specific interactions such as hydrogen bond, ion-ion, and ion-molecule interactions. In our previous studies[12, 15], the variation of permeability with nutrient composition was interpreted with the solute

Table 1. Permeability of fertilizer nutrient through polymer membrane reported

Core fertilizer	Polymer coating	Concentration	Temperature [K]	Source
urea	polyurethane	500 g/L	298	[8]
urea	polyethylene	saturated	298	[9]
urea	long-alkane-chain modified N-phthaloyl chitosan	saturated	298	[10]
urea	latex	saturated	298	[11]

diffusion coefficient as well as its solubility in polymer membrane, in which the diffusion coefficient was related to the sizes of associated complexes resulted from the intermolecular specific interactions in the permeate solution and the possible configurations of these complexes were deduced based on the specific interactions that was reported in literature including urea-water, urea-K^+, urea-$H_2PO_4^-$, and so on[16–21]. Unfortunately, the deduction of solubility and diffusion coefficient was based on the indirect data of mathematical simulations and spectroscopic data from literature. Therefore, further study of providing direct supporting experimental data such as solubility of fertilizer nutrient in polymer membrane, and density and apparent molar volume of the aqueous fertilizer solutions for explanation was of great theoretical significance.

In the current study, with a polystyrene (PS) membrane made from solution casting as the model membrane, the urea ($CO(NH_2)_2$) and monopotassium phosphate (KH_2PO_4) as representative of N-nutrient, P-nutrient, and K-nutrient fertilizer, the permeability of P- and K-nutrient through the PS membrane from the aqueous solutions of KH_2PO_4 and $CO(NH_2)_2$ + KH_2PO_4 at different concentrations up to saturated concentration at nominal temperature of 298 K were measured using the Ussing chamber method. The solubility of KH_2PO_4 in PS membrane from its 1, 5, 10 wt.% solutions in water were determined experimentally using the absorption-desorption measurement coupled with the gravimetric measurement. And the density and apparent molar volume for the 5, 10, 20, 30 wt.% urea solutions in water and 1, 5, 10 wt% KH_2PO_4 solutions in mixed solvent of urea + H_2O were measured to interpret the permeability variation with solute concentration. It was worth noting that even though the PS selected in this study was not a biodegradable polymer, it could be used as polymer coating for PCFs in gardening and horticulture. Besides, the method demonstrated could be extended to membranes of biodegradable polymers that were suitable for agricultural applications.

EXPERIMENTAL

Chemicals

The chemicals and reagents used were listed in Table 2. All the chemicals were used without further purification.

Membrane preparation

The PS membrane was prepared using the solution casting method, in which 4.0 g of 5.0 wt.% polystyrene (PS) solution in dichloromethane (DCM) was typically cast on a flat dish with diameter of 9.0 cm at room temperature. The thicknesses of the membranes were measured using a micrometer.

Permeability measurement

The measurements for permeability of P- and K-nutrient through the polymer membrane have been described elsewhere[12]. Briefly, as shown in Figure 1, in a permeation experiment, the flux of solute J (in the unit of mg/cm^2) through the polymer membrane at pseudo-steady state could be described as,

$$J = \frac{V}{A}\frac{dC_R}{dt} = P_s \frac{C_D - C_R}{l} \qquad (2)$$

where V is the receptor volume, A is the membrane area, l is the membrane thickness, C_R and C_D are concentration of the solute in receptor and donor, respectively. The permeability could be calculated by,

$$P_s = \frac{V}{A}\frac{l}{C_D - C_R}\frac{dC_R}{dt} = \frac{Vl}{AC_D}\frac{dC_R}{dt} \qquad (3)$$
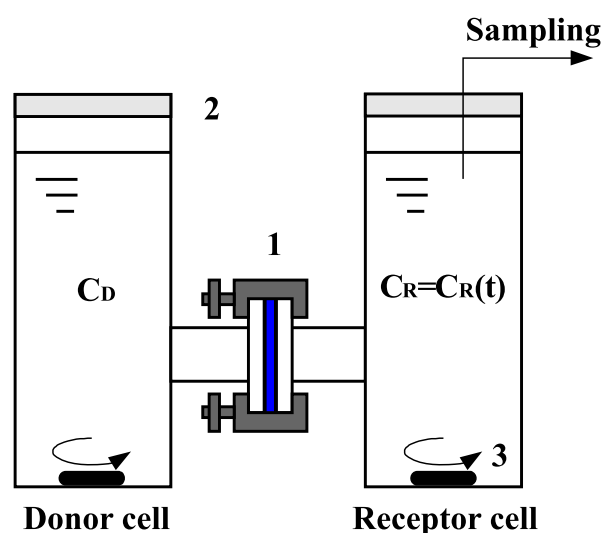
as $C_D \gg C_R \approx 0$.

Figure 1. Schematic diagram of the Ussing chamber method to measure the permeability of fertilizer nutrients through the polymer coating. 1 was the clamps to fix the polymer membrane, 2 was the covers to prevent water evaporation, 3 was the stirring bar.

The volumes of the cells were around 220 mL and the cross area of the connection part was 3.80 cm^2. Typically, the polymer membrane was first mounted to the connection part with the aid of two clamps before 200 mL of deionized (DI) water and test solution were filled into the two cells. The chambers were then immersed into a air bath with temperature of 298.2 ±1 K. The samples were taken from the receptor cell every 24 hours for 9 days and were characterized for the P- and K-nutrient concentration. After each sampling the same amount of DI water was added to keep the constant volume in the receptor cell.

Table 2. Chemicals and reagents used

Chemical & Reagent	Purity	Supplier
Polystyrene (PS)	Mw = 104 k, PDI = 1.3	Aladdin chemicals
Urea ($CO(NH_2)_2$)	≥ 99.0%	Sinopharm Chemical Reagent
Potassium phosphate monobasic (KH_2PO_4)	≥ 99.5%	Sinopharm Chemical Reagent
Hexammonium molybdate	≥ 99.0%	Shanghai Zhenqi Chemical Reagent
Antimony potassium tartrate	≥ 99.0%	Shanghai Chemical Reagent
Sulfuric acid	95.0–98.0%	Shanghai Chemical Reagent
Ascorbic acid (*L*)	≥ 99.7%	Shantou Xilong Chemicals

Determination of Phosphorus and Potassium element

The UV-Visible spectrometer (Shanghai Youke Instrumentation Co., Ltd.) was used to determine the P element concentration using Mo-Sb solution as chromogenic agent. The K element concentration was measured by a flame spectrometer (Beijing Beifen-Ruili Analytical Instrument Co., ltd).

Measurements for solubility of KH_2PO_4 and its aqueous solution in PS membrane

The solubility of KH_2PO_4 and KH_2PO_4 + H_2O solutions in PS membrane was measured using absorption-desorption method. The absorption of aqueous KH_2PO_4 solutions in the membrane was monitored by a suspended micro-balance. The solubility of KH_2PO_4 in the membrane was experimentally determined by measuring the conductivity of the desorption solution out of the saturated PS membrane that was dried in vacuum for 3 days after absorption. As shown in Figure 2, the suspended micro-balance was consisted of a balance (4), two magnets (3), a weighing cage (2), a thermocouple (5), and a container with jacket (1).
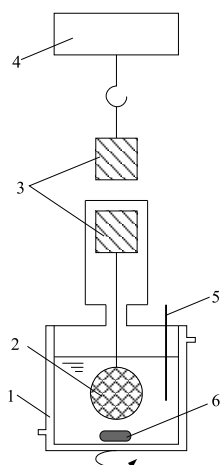
Figure 2. Schematic diagram of the suspended micro-balance. 1. container with jacket; 2. weighing cage; 3. magnet; 4. balance; 5. thermocouple; 6. stirrer

During a typical measurement, a piece of polymer membrane prepared by solvent casting from section 2.2 with mass known was loaded into the weighing cage (2) before the aqueous KH_2PO_4 solution was charged into the container with jacket. The reading on the balance was recorded at different time intervals. After about 3 days when the absorption equilibrium was reached, the polymer membrane was taken out of the cage and dried under vacuum for another 3 days. The dried membrane was then added to DI water with amount known for desorption, in which the conductivity of the desorbed solution was measured to determine the amount of KH_2PO_4 eluted. The comparison between the solubility of KH_2PO_4 in polymer membrane from the conductivity measurements and the solubility of aqueous KH_2PO_4 solution from the gravimetric measurements revealed the selectivity of water and KH_2PO_4 diffusion into the membrane.

Measurements for density and apparent molar volume

The Densities of solutions of KH_2PO_4 in water were measured by using a 25mL pycnometer with the equation of,

$$\rho = \frac{w}{w_{Water}} \rho_{Water} \tag{3}$$

The mass of w and w_{water} were determined using an electronic balance (Shanghai Yuepin Scientific instrument Co., FA10204B) with an accuracy of 0.0001 g. The volumes of the pycnometers were calibrated with deionized and double distilled water at 298, 308, and 318 K with repeatability of ±0.1 K.

The apparent molar volume were then calculated from the density data of solvent and solution using the equation,

$$V_\emptyset = \frac{M}{\rho} + \left(\frac{\rho_0 - \rho}{m\rho\rho_0}\right) * 1000 \tag{Eq-4}$$

where $V_\emptyset$ was the apparent molar volume, m (mol · kg⁻¹) was the number of moles of the solute per kilogram of solvent (molality). ρ(g · cm⁻³) and ρ_0 (g · cm⁻³) were the densities of solution and solvent, respectively. And M (g · mol⁻¹) was the molar mass of the solute.

RESULTS AND DISCUSSION

In this study, the concentrations of phosphorus element and potassium element that were measured to denote the concentrations of P-nutrient and K-nutrient were converted into concentrations of P_2O_5 and K_2O, which were common in fertilizer industry. The permeability of phosphorus nutrient as shown in P_2O_5 and potassium nutrient as shown in K_2O through the PS membrane were determined experimentally for binary aqueous solutions of KH_2PO_4, and ternary aqueous solutions of $CO(NH_2)_2$ + KH_2PO_4 at various compositions and at nominal temperature of 298 K, as shown in Table 3. To interpret the permeability data, the solubility of KH_2PO_4 in PS membrane from its aqueous solutions of 1, 2.5, 5, 10 wt.% were measured at nominal temperature of 298 K and the density and apparent molar volume for the solutions of urea + water and urea + KH_2PO_4 + water

Table 3. Permeability data of P- and K-nutrient through the PS membrane for the systems of KH_2PO_4_Water and KH_2PO_4_ Urea-Water

KH₂PO₄-Water System			
KH₂PO₄ Conc. [g/mL]	Permeability [cm²/d*10⁻⁵]		
	P₂O₅	K₂O	
0.0225	0.97	3.72	
0.0450	1.05	3.76	
0.6750	1.10	3.84	
0.0900	1.15	4.78	
0.2000	0.66	2.37	
KH₂PO₄- Urea-Water System			
KH₂PO₄ Conc. [g/mL]	Urea Conc. [g/mL]	Permeability [cm²/d*10⁻⁵]	
		P₂O₅	K₂O
0.0900	0.000	1.15	4.78
	0.125	1.38	55.72
	0.250	–	7.07
	0.375	2.25	6.40
	0.500	1.43	5.62
0.0225	0.500	0.16	1.99
0.0450		0.25	2.22
0.6750		3.33	6.63
0.0900		1.93	5.62

were determined experimentally to obtain information on the specific intermolecular interactions thus to assess the diffusion coefficient.

Error analysis

As shown in Table 4, The error analysis of the permeability, solubility, apparent molar volume, and density measurements was conducted using the equations of and their measurement accuracy was within ±3%, ±1%, ±2%, and ±1%, respectively[12]. (See the supporting information)

From the Figure 3(b), both the permeability of K_2O and P_2O_5 showed the similar "increase-decrease" trend with KH_2PO_4 concentration. According to the "solution-diffusion" model[13], the variation of permeability can be interpreted and attributed to the changes in solubility and diffusion coefficient of KH_2PO_4 in the PS membrane.

Solubility of KH_2PO_4 in PS membrane

The variation of conductivity with time for the aqueous desorption solutions of KH_2PO_4 from the PS membrane that was saturated with various KH_2PO_4 concentrations

Table 4. Error analysis of permeability, solubility, apparent molar volume, and density measurements

	Measuring equation	Error propagation equation	Accuracy
Permeability	$p_s = \left(\dfrac{dm}{dt}\right)\dfrac{I}{A\Delta C}$	$dp_s = \dfrac{\partial p_s}{\partial\left(\frac{dm}{dt}\right)} d\left(\dfrac{dm}{dt}\right) + \dfrac{\partial p_s}{\partial I} dI + \dfrac{\partial p_s}{\partial A} dA + \dfrac{\partial p_s}{\partial \Delta C} d\Delta C$	±3%
Solubility	$S_{KH2PO4-H2O} = \dfrac{m(\infty) - m_0}{m_0}$	$dS_{KH2PO4-H2O} = \dfrac{dm(\infty)}{m_0} - \dfrac{m(\infty)}{m_0^2} dm_0$	±1%
	$S_{KH2PO4} = \dfrac{V(ac+b)}{m_0}$	$dS_{KH2PO4} = \dfrac{(ac+b)}{m_0} dV + \dfrac{aV}{m_0} dc - \dfrac{V(ac+b)}{m_0^2} dm_0$	±1%
Apparent molar volume	$V_\varphi = \dfrac{M}{\rho} + \left(\dfrac{\rho_0 - \rho}{m\rho\rho_0}\right) * 1000$	$dV_\varphi = \dfrac{\partial V_\varphi}{\partial \rho} d\rho + \dfrac{\partial V_\varphi}{\partial \rho_0} d\rho_0 + \dfrac{\partial V_\varphi}{\partial m} dm$	±2%
Density	$\rho = \dfrac{w}{w_{Water}}\rho_{Water}$	$d\rho = \dfrac{\rho_{Water}}{w_{Water}} dw$	±1%

* $S_{KH2PO4-H2O}$ and S_{KH2PO4} are the solubility of aqueous solution of KH_2PO_4 and KH_2PO_4 in the polystyrene membrane, m_0 and m_∞ are the initial and final mass of the polymer membrane in the solubility measurement, a and b are the parameters of the calibration equation for KH_2PO_4 concentration against electrical conductivity c, V is the volume of eluted solution. In the equations related to apparent molar volume, m is the molarity while m is the mass of penetrant in the equations related to permeability.

Permeation in KH_2PO_4- water solutions

Permeability of K-nutrient

The variation of K_2O flux with time and the K_2O permeability with KH_2PO_4 concentration through the PS membrane was shown in Figure 3 (a) and (b), respectively. Similar to urea permeation in aqueous solutions that was reported in our previous study, the K_2O flux demonstrated linear increases with time at all the concentrations and its permeation rates increased with KH_2PO_4 concentration as expected. The K_2O permeability through the PS membrane fell into the range of $3.5-5\times10^{-5} cm^2/d$ and showed an intriguing trend of "increase-decrease" with KH_2PO_4 concentration in the range investigated, which was similar to the urea permeability through the PS membrane from the urea-water solution. Generally, for the Fickian diffusion behavior the permeability should be independent of permeate concentration, however, for the current system the permeation was seemed to be a non-Fickian behavior, which could be due to the interactions between the permeate solution with the polymer membrane[22–24].
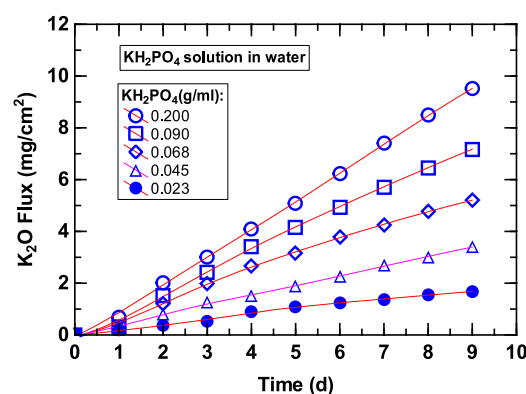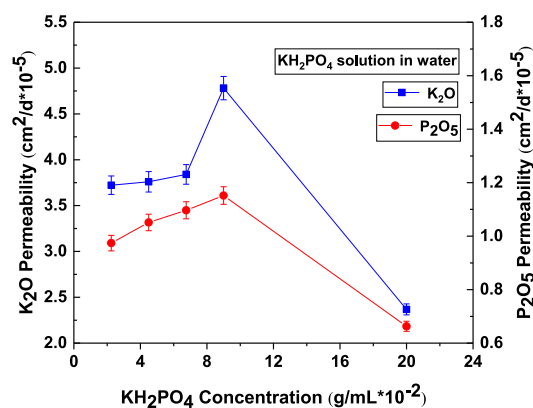
Permeability of P-nutrient

The variation of P_2O_5 flux with time and P_2O_5 permeability with KH_2PO_4 concentration through the PS membrane were shown in Figure 4 and 3(b), respectively. Similar to the K_2O as shown in Figure 3(a), the P_2O_5 flux demonstrated increases with time and its permeation rate increased with KH_2PO_4 concentration. Meanwhile the P_2O_5 permeability through the PS membrane was in the range of $0.75-1.25\times10^{-5} cm^2/d$. The permeability of P_2O_5 also showed an "increase-decrease" trend with KH_2PO_4 concentration.

(a)

(b)

Figure 3. Variation of K_2O flux through the membrane with time (a) and variation of K_2O permeability and P_2O_5 permeability with KH_2PO_4 concentration (b) for aqueous solution of KH_2PO_4 at concentrations of 0.023, 0.045, 0.068, 0.090, and 0.200 g/mL, respectively
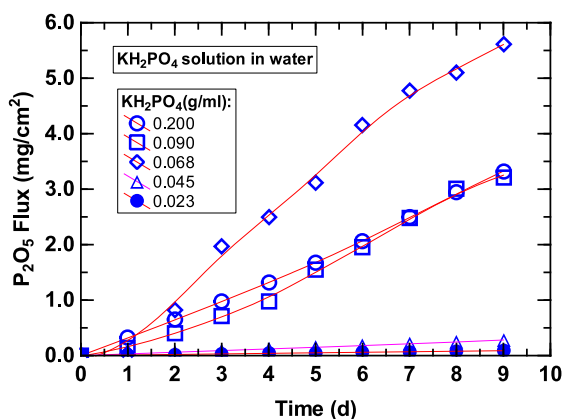
Figure 4. Variation of P_2O_5 flux through the membrane with time for aqueous solution of KH_2PO_4 at concentrations of 0.023, 0.045, 0.068, 0.090, and 0.200 g/mL

of 0.023, 0.068, 0.090, and 0.190 g/mL were shown in Figure 5(a). Combining with the calibration curve, the conductivity data at equilibrium were converted into solubility of KH_2PO_4 in PS membrane from aqueous solutions with different concentrations as shown in Figure 5(b). It could be found out that the solubility of KH_2PO_4 in the PS membrane increased with solution concentration.

The absorption of KH_2PO_4 solutions in water into the PS membrane were measured using a suspended micro-balance at KH_2PO_4 concentrations of 0.023, 0.068, 0.090, and 0.190 g/mL, as shown in Figure 5(c). From these absorption data, the solubility of the aqueous KH_2PO_4 solutions in the PS membrane were obtained and also presented in the Figure 5(b). The solubility of KH_2PO_4 solutions always showed higher values than those of KH_2PO_4 in PS membrane at all the concentrations, suggesting the presence of water molecule in the membrane. The solubility of water in the PS membrane from the KH_2PO_4 + water solutions were then calculated from the comparison between the solubilities of KH_2PO_4 and its aqueous solutions, as shown in Figure 5(b). It seemed that the presence of KH_2PO_4 increased the solubility of water in the PS membrane.

**Diffusion coefficient of KH_2PO_4 in PS membrane**

The increase in permeability of P- and K-nutrient with KH_2PO_4 concentration in the low concentration range could be explained by the increase in solubility of KH_2PO_4 with KH_2PO_4 concentration. However, the decrease in permeability in the high concentration range would be attributed to the decrease in diffusion coefficient of KH_2PO_4 in the PS membrane, which led by the formation of associated complexes resulted from the specific intermolecular interactions in the permeate solutions.

The KH_2PO_4-water solution is a complicated system with various specific interactions including the water-water (hydrogen bond), the hydration of K^+ and $H_2PO_4^-$ [20, 25],ionic pair of K^+ and $H_2PO_4^-$, and self-association of $H_2PO_4^-$ [26]. The hydration numbers of K^+ and $H_2PO_4^-$ ions were reported to be about 6 and 11 according to the previous studies on spectra and simulations[27, 28].
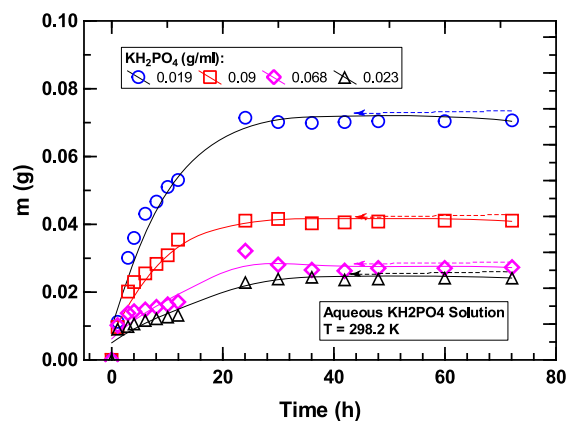
The cartoons in Figure 6 depicted the hydration complexes of $H_2PO_4^-$ ion (I), K^+ ion (II), and $H_2PO_4^-$- K^+ ion pair. At low KH_2PO_4 concentrations, the P- and K-nutrient penetrated the polymer membrane in the form
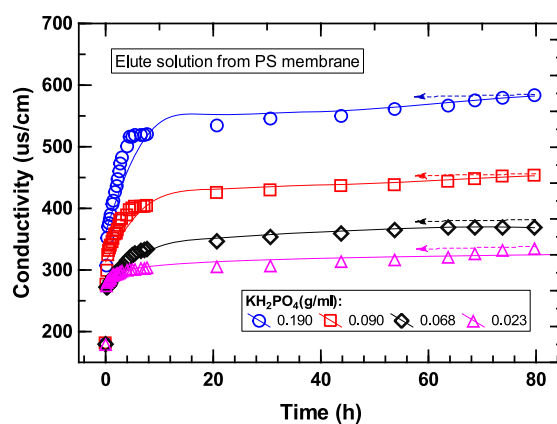
(a)
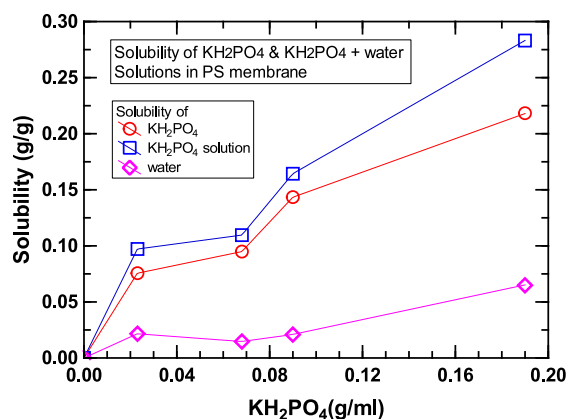
(b)

(c)

Figure 5. The variation of conductivity with time for the elute solution of KH_2PO_4 from the PS membrane to DI water (a), variation for solubility of KH_2PO_4, aqueous KH_2PO_4 solution, and water with KH_2PO_4 concentration (b), and variation of mass gain of the PS membrane with time in the absorption of aqueous KH_2PO_4 solutions at 0.023, 0.068, 0.090, and 0.190 g/mL (c).

of these hydration complexes. The larger size of the hydration complex of $H_2PO_4^-$ ion than K^+ ion suggested the lower permeability of P-nutrient than K-nutrient, which was confirmed by the experimental data shown in Figure 3(b). With the increase in KH_2PO_4 concentration, the solute-solute interactions of K^+- $H_2PO_4^-$ ion pair and self-association of $H_2PO_4^-$ ion were getting stronger

leading to the formation of ion pair and self-association of $H_2PO_4^-$ ion complexes with larger sizes than $H_2PO_4^-$ and K^+ ion hydration complexes, which reduced their diffusion coefficients through the membrane so that to suppress the permeation of these P- and K-nutrient, shown as decrease in their permeability at high KH_2PO_4 concentrations in Figure 3(b).
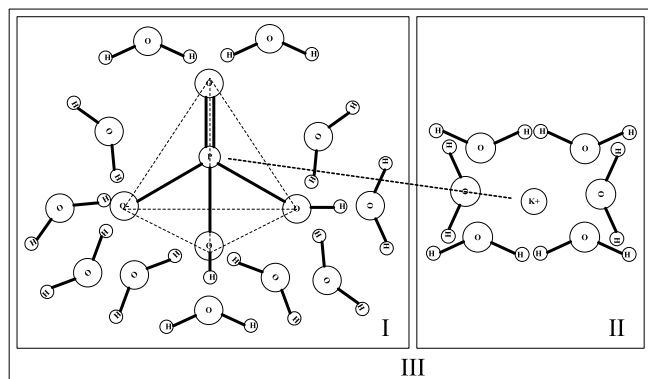

Figure 6. The possible configurations of $H_2PO_4^-$ and K^+ ion hydration complexes. (I) was the hydrated $H_2PO_4^-$ ion, (II) was the hydrated K+ ion, and (III) was the $H_2PO_4^-$- K^+ ion pair

Permeation in urea-KH$_2$PO$_4$-water solutions

In this section, the effects of urea concentration and KH_2PO_4 concentration on the permeability of P- and K- nutrient from the urea-KH_2PO_4-water solution were investigated. Furthermore, the variations were also be interpreted through the solubility of permeate in polymer membrane and specific interactions in the permeate solutions.
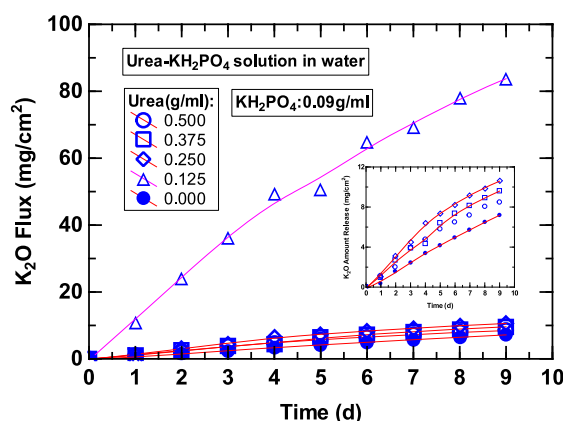
Effect of urea concentration on permeability

The variations of fluxes for P- and K-nutrient with time from the solutions of urea-KH_2PO_4 (0.090 g/mL)-water were shown in Figure 7(a) and (b), respectively. From these data, the effects of urea concentration on the permeability of P- and K-nutrient through the PS membrane were calculated and included in the Figure 7(c).

The permeability of P_2O_5 were in the rage of $1–2.5\times10^{-5}$ cm^2/d while the K_2O permeability were in a broader range of $3–60\times10^{-5}$ cm^2/d. Compared to the permeability data without urea addition, the addition of urea always increased both the P- and K-nutrient permeability at the KH_2PO_4 concentration of 0.090 g/mL, which was different from the addition effects of KCl and NaH_2PO_4 on the urea permeability in our previous study. At the same time, similar to the Figure 3(b), both the permeability of P- and K-nutrient demonstrated "increase-decrease" variations with the urea concentration. The increases in permeability at low urea concentrations could be attributed to the increases in solubilities of P- and K- nutrient in the polymer membrane upon addition of urea, while the decreases in permeability at high urea concentrations might originate from the decreases in diffusion coefficient resulted from formation of associated complexes with larger sizes due to the specific intermolecular and interionic interactions in the solution. The addition of urea into the KH_2PO_4 solution in water increased the complexity of the specific interactions in the solution since the urea molecule would not only interact with K^+ and
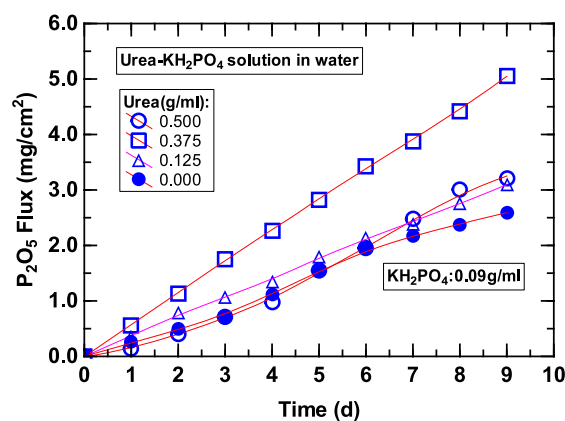
(a)

(b)
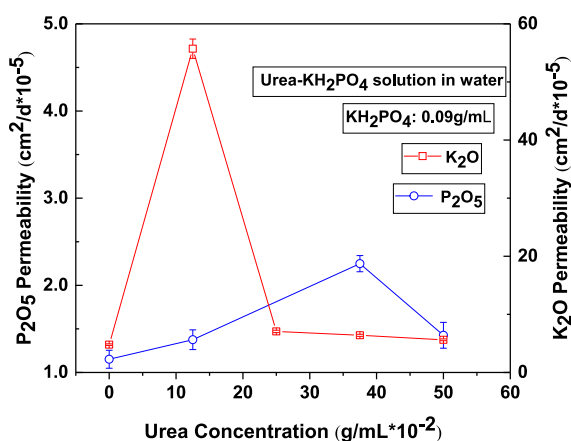
(c)

Figure 7. The variations of fluxes for P-nutrient (a) and K-nutrient (b) with time, and variations of permeability (c) with urea concentration through the PS membrane for aqueous solution of urea + KH_2PO_4. The KH_2PO_4 concentration was fixed at 0.090 g/mL and the urea concentrations were 0.090, 0.250, 0.375, and 0.500 g/mL

$H_2PO_4^-$ ions to form associated complexes but also alter the hydration of the ions either as a "structure breaker" or "structure maker" depending on the temperature and composition of the solution[27–29].

Apparent molar volume of KH₂PO₄ in mixed solvent of urea-water

To assess the solute-solute and solute-solvent interactions in the solutions with direct proof to interpret the variation of permeability of P- and K-nutrient through the PS membrane with solute concentration, the apparent molar volumes of KH_2PO_4 in the mixed solvent of urea-water were measured at the KH_2PO_4 molarities of around 0.10, 0.25, 0.50, 0.75, and 1.00 mol/kg and at the urea concentration of 0, 5, 10, 20, and 30 wt.%, which were shown in Figure 8. It should be pointed out that the solute was KH_2PO_4 while the solvent was mixture of water and urea in this treatment.

According to the Masson's equation[30, 31], the apparent molar volume could be correlated against molarity m with the equation of,

$$V\varphi = V_\varphi^0 + S_V * m \qquad (5)$$

where V_φ^0 was the partial molar volume, whose value equals to the infinite dilution volume of solute and showed the effects of interactions between solute and solvent molecules while S_V was the experimental interaction coefficient and reflected the interactions between solute and solute molecules[30]. From the apparent molar volume data shown in Figure 8, the variation of partial molar volume V_φ^0 and experimental interaction coefficient S_V with urea concentration at temperature of 298, 308, and 318 K were derived and illustrated in the Figure 9. The increases in partial molar volumes with urea concentration at these temperatures suggested the increases in solute-solvent interactions and thus the stronger ion-water and ion- urea interactions, in which the ions included the K^+ and $H_2PO_4^-$ ions. Meanwhile, the interaction coefficient S_v demonstrated an increase with urea concentration at relatively low temperature of 298 K while it displayed increases in the low urea concentration range (< 20 wt.%) and decreases at the urea concentrations greater than 20 wt.% at the higher temperature of 308 and 318 K, in which the increase in S_V represented the stronger solute-solute interactions, i.e., K^+-$H_2PO_4^-$ ion interaction. In all, the urea played a role of "structure making" in the current KH_2PO_4-urea-water solution, which would reduce the permeability of P- and K-nutrient through the polymer membrane by formation of associated complexes with enlarged sizes.
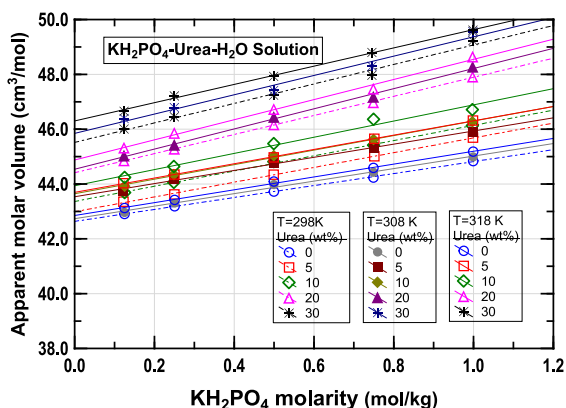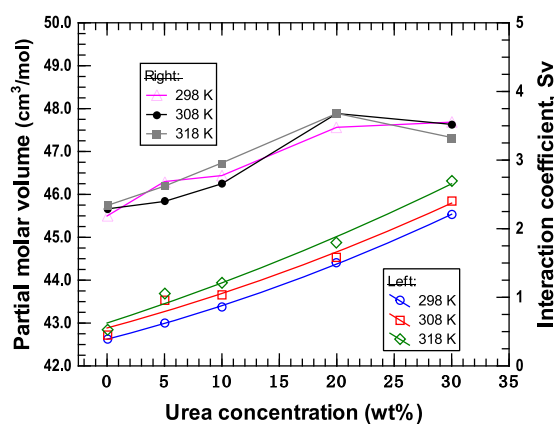

Figure 9. The variation of partial molar volume and interaction coefficient with urea concentration for the KH_2PO_4- -urea-water solutions at nominal temperatures of 298, 308, and 318 K

Effect of KH₂PO₄ concentration on permeability

The variations of fluxes for P-nutrient and K-nutrient through the membrane with time from the solutions of urea-KH_2PO_4-water with fixed urea concentration of 0.5 g/mL were shown in Figure 10 (a) and (b), respectively. From these data, the variations of P- and K-nutrient permeability with KH_2PO_4 concentration were calculated and also included in the Figure 10(c). The permeability of P- and K-nutrient from aqueous KH_2PO_4 solutions without addition of urea as shown in Figure 3(b) were also included as open circles and open squares in this figure for comparison. Once again, both the variations of P_2O_5 and K_2O permeability were observed to display the "increase-decrease" trends with KH_2PO_4 concentration, confirming the prevalence of solubility effect at low concentrations and the dominance of inter-molecular specific interactions at high concentrations.

The comparisons of the P- and K-nutrient permeability of the KH_2PO_4-urea-water solutions with the KH_2PO_4-water solutions revealed that the effects of the urea addition were KH_2PO_4 concentration dependent. At low KH_2PO_4 concentrations (0.023 and 0.045 g/mL), the addition of 0.5 g/mL urea lowered down the permeability, suggesting the decrease of KH_2PO_4 solubility in the PS membrane. In the range of relatively high concentrations (0.068 and 0.090 g/mL), the addition of urea raised the permeability greatly beyond the levels of the aqueous KH_2PO_4 solutions, which could be attributed to the competition of intermolecular interactions for the urea-K^+ ion and urea-$H_2PO_4^{2-}$ ion over the K^+- $H_2PO_4^{2-}$ ions.

Prediction of nutrient release

One of the most important mathematical models on release kinetics of nutrient from PCF granule was proposed by Shaviv and coworkers[32]. In this model, the release of fertilizer nutrients can be divided as three periods: lag period (I), constant-release period (II), and decaying release period (III) and the fractional release can be calculated, as shown in Figure 11 and Equations 6 through 10, respectively.

$$g(r,l,t) = 0, \quad t < t' \qquad (6)$$

$$g(r,l,t) = \frac{3P_s C_{sat}}{rl\rho_s}(t - t'), \quad t' \le t \le t'' \qquad (7)$$

Figure 8. The variations of apparent molar volume with the KH_2PO_4 molarity for the KH_2PO_4-urea-water solutions at nominal temperatures of 298, 308, and 318 K. The urea concentrations were 0, 5, 10, 20, and 30 wt.% in the solutions
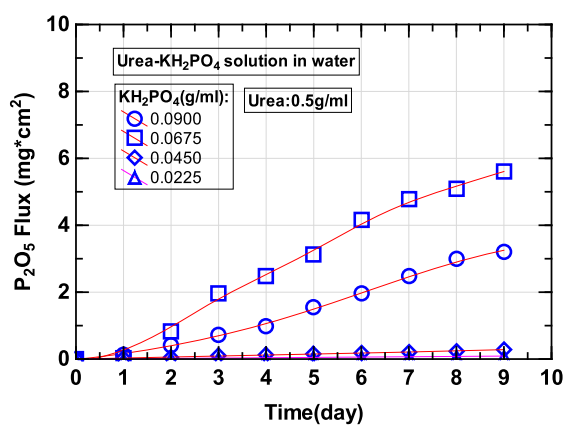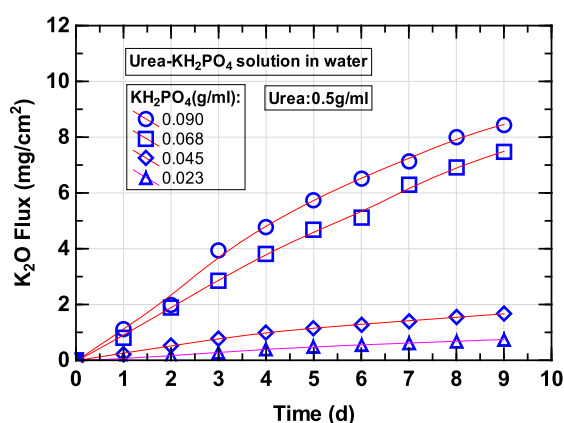
(a)

(b)
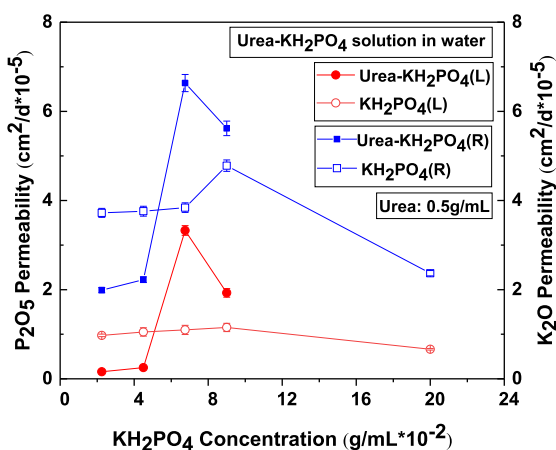
(c)

Figure 10. The variations of flux for P-nutrient (a) and K-nutrient (b), through the PS membrane with time and variations of permeability (c) with KH_2PO_4 concentration for aqueous solution of urea + KH_2PO_4. The urea concentration was fixed at 0.5 g/mL and the KH_2PO_4 concentrations were 0.023, 0.045, 0.068, and 0.090 g/mL
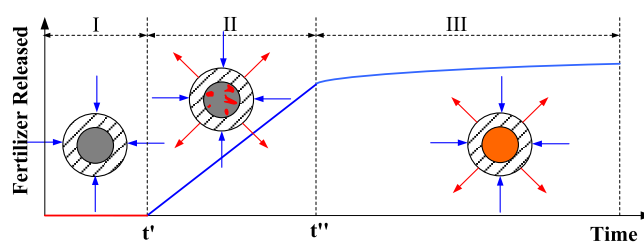

Figure 11. Three stages of the fertilizer release from the polymer-coated fertilizers. In stage I, the water in soil penetrates into the shell through the polymeric membrane to form saturated fertilizer solution. In stage II, from the saturated solution the fertilizer penetrates through the polymeric membrane to the soil with constant release rate. In stage III, the fertilizer was depleted and the fertilizer concentration in the solution decreases, leading to the decrease in its release rate.

$$g(r,l,t) = 1 - \frac{C_{sat}}{\rho_s} \exp[-\frac{3P_s}{rl}(t - t'')], \quad t > t'' \tag{8}$$

$$t' = \frac{\gamma rl}{3P_h \Delta P} \tag{Eq-9}$$

$$t'' = t' + \left(1 - \frac{C_{sat}}{\rho_s}\right) \frac{rl\rho_s}{3P_s C_{sat}} \tag{10}$$

where $g(r,l,t)$ was the fractional release, P_s and P_h were the permeability of fertilizer nutrient and water through the polymer membrane, respectively. C_{sat} was the nutrient concentration of the saturated solution, ρ_s was the density of fertilizer, r was radius of the PCF granules, l was thickness of the polymer coating. ΔP was the difference between vapor pressure of water and saturated fertilizer solution, and γ was the critical volume fraction of voids filled with water which was estimated around 0.05–0.1.

With the mathematical model and the permeability data of P- and K-nutrient from the urea-KH_2PO_4 aqueous solution presented previously, the release of P- and K-nutrient from a spherical PS-coated N-P-K compound fertilizer granule was predicted with regard to different fertilizer granule size r and PS coating thickness l, as shown in Figure 12. The parameters used in this prediction were listed in Table 5 including temperature T, permeability of water P_h, pressure difference ΔP, saturated concentration C_{sat}, density of the saturated solution ϱ_s, permeability of the P-nutrient P_s (P), and K-nutrient P_s (K). From this figure, the nutrient release kinetics predicted was sensitive to the parameters of r and l, and the increase in $r \times l$ would prolong the "constant release" period. More important, once the nutrients demand of crops were known, the predictions would help to select and screen the polymer coating and identify the thickness of the coating and size of the fertilizer granule.

However, it was worth noting that deviation of the predictions could originate from the differences in permeability of nutrient and water between the polymer coating membrane that was prepared by solution casting in this study and by coating techniques such as rotational coating and fluidized-bed coating in practice, which required further research.

Table 5. Parameters used in the prediction of P- and K-nutrient release from the PS-coated KH_2PO_4 fertilizer granule[12]

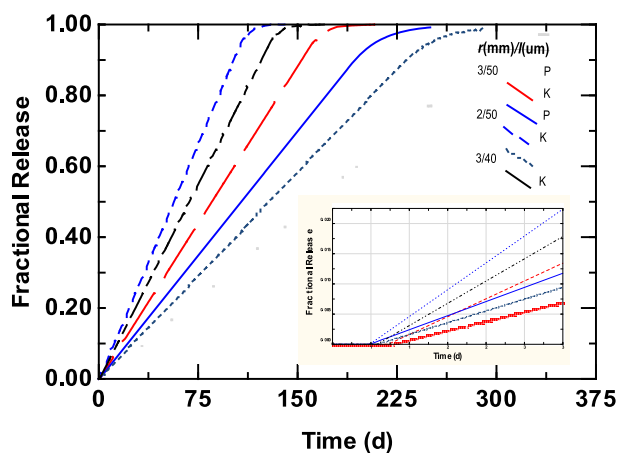| T [K]	P_h [cm^2 · Pa/d]	ΔP [Pa]	C_{sat} [g/mL]	ρ_s [g/cm^3]	P_s [P] [cm^2/d]	P_s [K] [cm^2/d]
298	1.09E-08	3169	0.09	1.71	1.92E-05	5.61E-05

Figure 12. Prediction for variation of fractional release of P- and K-nutrient with time from the granule of PS-coated compound fertilizer using the Shaviv's model along with the permeability data produced in this study

Conclusion

The K-nutrient always showed larger permeability than those of P-nutrient through the PS membrane from both solutions of KH_2PO_4-water and KH_2PO_4-urea-water. Both the P- and K-nutrient permeability demonstrated an "increase-decrease" trend with solute concentration for KH_2PO_4-water and KH_2PO_4-urea-water solutions. The initial increase in the permeability was due to the increase in solubility of KH_2PO_4 with solute concentration which had been confirmed by the experimental solubility data of KH_2PO_4 in PS membrane in the solutions of KH_2PO_4-water. The decrease in permeability at high solute concentrations could be attributed to the decrease in diffusion coefficient of permeate in polymer membrane resulted from the formation of K^+-water, H_2PO_4-water, and K^+-H_2PO_4 associated complexes with larger sizes led by the enhancement of specific intermolecular interactions such as solute-solvent and solute-solute interactions in the fertilizer solutions, which was assessed by the increases in apparent molar volume and S_V from experimental data of density for the solutions of KH_2PO_4-urea-water. By using the Shviv's model, the release kinetics of P- and K-nutrient from a PS-coated urea-KH_2PO_4 compound fertilizer granule could be predicted with the permeability data generated in this study.

ASSOCIATED CONTENT

Supporting Information

The calibration curves for concentrations of urea, phosphorus element and potassium element & the derivations of error analysis equation for measurements of density, solubility, apparent molar volume, and permeability were included.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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