

Diffusion Performance of Fertilizer Nutrient through Polymer Latex Film

Di An, Ling Yang, Boyang Liu, Ting-Jie Wang,*^{ORCID} and Chengyou Kan

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ABSTRACT: Matching the nutrient release rate of coated fertilizer with the nutrient uptake rate of the crop is the best way to increase the utilization efficiency of nutrients and reduce environmental pollution from the fertilizer. The diffusion property and mechanism of nutrients through the film are the theoretical basis for the product pattern design of coated fertilizers. For the coated fertilizer with a single-component nutrient, an extended solution–diffusion model was used to describe the difference of nutrient release rate, and the release rate is proportional to the permeation coefficient and the solubility of the nutrient. For the double- and triple-component fertilizer of N–K, N–P, and N–P–K, because of the interaction among nutrient molecules and ions, the release rates of different nutrients were significantly affected by the components in the composite fertilizer. Coating the single-component fertilizer (i.e., nitrogen fertilizer, phosphate fertilizer, and potash fertilizer) first and subsequently bulk blending is expected to be a promising way to adjust flexibly the nutrient release rate to meet the nutrient uptake rate of the crop.

KEYWORDS: coated fertilizer, polymer latex, nutrient, controlled release, diffusion

1. INTRODUCTION

Fertilizing controlled-release fertilizer with film coated is a promising way to increase the utilization efficiency of nutrients and reduce environmental pollution from the fertilizer.^{1,2} The nutrient release process of film-coated fertilizer consists of three stages:^{3,4} (1) Water vapors permeate through the film into the interior of the coated fertilizer and dissolve part of the fertilizer to form a saturated nutrient solution in the interior. The vapor pressure gradient across the film is the driving force in this stage. (2) The nutrient starts to release by the driving force of the concentration gradient across the film. The water constantly diffuses into the film to dissolve the fertilizer core at the same time, and the concentration of the internal solution remains saturated. (3) After the fertilizer in the core is dissolved completely, the concentration of the solution decreases as the release proceeds, and the release rate decreases accordingly. In the three stages, the second stage is the main stage of nutrient release from the film-coated fertilizer. Ideally, matching the nutrient release rate with the nutrient uptake rate of the crop can decrease the nutrient concentration in the soil, which reduces the loss of nutrient to water, volatilization to air, and the mineralization in soil, achieving the efficient use of fertilizer.³

For the coated fertilizer with the same film coating, the release rates of different nutrients are quite different. Huett and Gogel⁵ measured the release performance of coated compound fertilizer formulations of Osmocote (a brand of coated fertilizer produced by The Scotts Company, United States) and reported that the release rate was in the order of $N > K > P$. Broschat and Moore⁶ measured the release performance of polyolefin-coated fertilizer with the nutrient content of 13% N, 13% P_2O_5 , and 13% K_2O . The release rate obtained was in the order of $NO_3^- > NH_4^+ > K^+ > P$. Lu et al.⁷ measured the release property of thermosetting resin-coated fertilizer, and the release rate was in the order of $K > N > P$; the slow release rate of phosphorus is explained by its slow dissolution rate. Du et al.⁸

measured the release performance of polyurethane-coated fertilizer with the nutrient content 19% N, 6% P_2O_5 , and 13% K_2O and reported that the release rate was in the order $NO_3^- > NH_4^+ > K > P$, and the delay time of the phosphorus release is much longer. It was explained that the higher solubility of nitrogen and potassium resulted in their faster release rate, and when most of the nitrogen and potassium had released, phosphorus then began to dissolve and release. The different solubility of the nutrients is considered to cause the difference in nutrient release rates.^{5–8}

Besides the solubility of nutrients, the interaction between nutrients and the film also affects the nutrient release rate. Noppakundilograt et al.⁹ prepared coated fertilizer with acrylic acid–acrylamide copolymer and measured the release rates in the order of $NH_4^+ > P > K^+$. Although the NH_4^+ and K^+ have almost the same mobility in water and the same positive charge value, K^+ is smaller than NH_4^+ . Therefore, the K^+ has a higher surface area charge density to interact with the negatively charged carboxyl of the acrylic acid–acrylamide copolymer, resulting in the release rate of K^+ being lower than that of NH_4^+ .

The amount and rate of the crop's demand for nitrogen, phosphorus, and potassium nutrients are different, and it is desired for the release of nutrients in the coated fertilizer to match the crop's demand. Presently, although there are some relevant studies on the release properties of different nutrients in coated fertilizers, these studies lacked quantitative, systematic, and in-depth analysis. The polymer latex, of which the continuous phase is water, is free from toxic organic solvents, so it is an environmentally benign and promising material for producing film-coated fertilizer.¹⁰ The study of the diffusion

Received: September 10, 2017

Revised: November 19, 2017

Accepted: November 26, 2017

Published: November 27, 2017

Table 1. Amount of Component in $\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{K}_2\text{SO}_4$ and $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{K}_2\text{SO}_4$ Systems ($\text{N}:\text{P}_2\text{O}_5:\text{K}_2\text{O} = 1:1:1$)

$\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{K}_2\text{SO}_4$ (g)				$\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{K}_2\text{SO}_4$ (g)			
NH_4Cl	$\text{NH}_4\text{H}_2\text{PO}_4$	K_2SO_4	water	NH_4Cl	$(\text{NH}_4)_2\text{HPO}_4$	K_2SO_4	water
165.6	87.7	100	200	187.5	150	150	200

property and mechanism of different nutrients through the film, especially the polymer latex film, can provide a theoretical basis for the product and production process design of coated fertilizer, which is of great significance to achieve the precise release of the fertilizer.

In this work, the planar film was prepared using styrene-butyl acrylate-methyl methacrylate copolymer latex. The diffusion performance of different kinds of nutrient in different fertilizer across the polymer latex film was measured, and the diffusion mechanism was analyzed.

2. EXPERIMENTAL PROCEDURES

2.1. Materials. The chemical reagents used include urea, NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, KCl , K_2SO_4 , KNO_3 (Beijing Chemical Works, China), ethanol, *p*-dimethylaminobenzaldehyde, ammonium metavanadate, and ammonium molybdate (Sinopharm Chemical Reagent Co., Ltd., China), which are all analytical reagent grade. The copolymer latex of styrene-butyl acrylate-methyl methacrylate with 40% solid content was used to prepare the planar polymer film. The latex was synthesized via a semicontinuous emulsion copolymerization in the Department of Chemical Engineering, Tsinghua University. The water used in the experiment was ultrapure water; its resistivity was 18 $\text{M}\Omega\cdot\text{cm}$.

2.2. Film Preparation. A $250 \times 250 \text{ mm}^2$ rectangular area of a glass sheet was surrounded by medical tape with a thickness of 80 μm ; 8 g of polymer latex was diluted to 10 g with ultrapure water, and then the diluted latex was dropped onto the center of the rectangular area to produce a film by scraping with a glass rod. The glass sheet with latex coating was put in an oven at 120 $^\circ\text{C}$ for 1 h to remove the water in the latex and increase polymer cross-linking in the film. The formed film with uniform thickness was then cooled to room temperature and taken down from the glass sheet for subsequent permeability measurement.

2.3. Preparation of the Saturated Nutrient Solutions. In order to measure the diffusion performance of different nutrients in a single-component fertilizer through the film, the saturated solutions of urea ($(\text{NH}_2)_2\text{CO}$), NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, KCl , K_2SO_4 , and KNO_3 at 25 $^\circ\text{C}$ were prepared separately.

In the measurement of the diffusion coefficient of the nutrients in double-component fertilizer through the film, i.e., N-P and N-K composite fertilizer, the saturated solutions of urea-KCl and urea- $\text{NH}_4\text{H}_2\text{PO}_4$ at 25 $^\circ\text{C}$ were prepared separately according to the composition of the commercial fertilizer products. The saturated solutions for the double and triple components indicates that all of the components exist in both solid and liquid phases. In the preparation process, it is necessary to ensure that each component is saturated in the solution, that is, the quality of each component added exceeds the corresponding solubility when it exists alone in the solution.

The phase rule of multicomponent salt-water solutions under isothermal and isobaric conditions is expressed as¹¹

$$F = C - P_h \quad (1)$$

where F is the degree of freedom of each component concentration in the system, C the number of independent components, and P_h the number of coexisting phases in the system. For the urea-KCl saturated system, $C = 3$, and the system contains urea solid phase, KCl solid phase, and liquid phase, so $P_h = 3$. From eq 1, the degree of freedom of the system is $F = 0$. That is, the concentration of each component in the saturated solution is a fixed value and does not change with the amount of solid component added. The urea-

$\text{NH}_4\text{H}_2\text{PO}_4$ saturated solution has the similar case, and the degree of freedom of the system is $F = 0$.

In the measurement of the diffusion performance for the nutrients in the triple-component fertilizer, i.e., N-P-K composite fertilizer, the saturated solution of NH_4Cl -ammonium phosphate-potassium salt was prepared according to the composite of the commercial fertilizer products. Specifically, four groups of composite saturated solution, i.e., $\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{KCl}$, $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{KCl}$, $\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{K}_2\text{SO}_4$, and $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{K}_2\text{SO}_4$ at 25 $^\circ\text{C}$ were prepared separately, and in the preparation process, each excessive solid component compared to water was ensured. For the saturated solutions of $\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{KCl}$ and $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{KCl}$, $C = 4$, and the systems contain three solid phases and one liquid phase, i.e., $P_h = 4$, so $F = 0$; the concentration of each component is a fixed value. However, for the saturated solutions of $\text{NH}_4\text{Cl}-\text{NH}_4\text{H}_2\text{PO}_4-\text{K}_2\text{SO}_4$ and $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{HPO}_4-\text{K}_2\text{SO}_4$, $C = 5$ and $P_h = 5$, so $F = 0$; the concentration of each component is also a fixed value. Considering the most widely used nutrient ratio of $\text{N}:\text{P}_2\text{O}_5:\text{K}_2\text{O} = 1:1:1$, which is the most representative, its saturated solution was prepared as shown in Table 1.

2.4. Measurement of Film Permeability. The main stage of nutrient release of the film-coated fertilizers is the release of saturated nutrient solution from the interior of the film to the external water environment. Therefore, in order to simulate the release process, a Ussing chamber¹² was used to measure the diffusion performance of the nutrient through the polymer latex film, as shown in Figure 1. Both

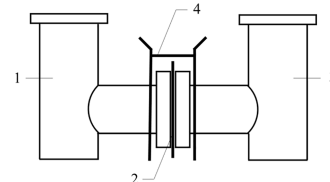


Figure 1. Schematic diagram of the Ussing chamber. 1, supply side, saturated solution; 2, film; 3, receiving side, ultrapure water; 4, clip.

sides of the Ussing chamber have a volume of 100 mL, and the connection neck has an inner diameter of 30 mm. The film was cut into a circular shape with a diameter of 40 mm, and its thickness was measured. Then the film was fixed in the middle of the Ussing chamber, clamped with a clip, and sealed with waterproof glue. The saturated nutrient solution was added to the supply side, and ultrapure water was added to the receiving side. Both sides were kept at the same height at the beginning. The Ussing chamber was sealed on top and placed into an incubator at 25 $^\circ\text{C}$. After a set time, the mass of nutrient diffusing into the receiving side was measured.

For single-component fertilizer, the concentration of urea was measured by ultraviolet-visible spectrophotometric methods using *p*-dimethylaminobenzaldehyde as chromogenic agent,¹³ and the concentrations of NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, KCl , K_2SO_4 , and KNO_3 were determined by measuring the conductivity of the solution in the receiving side. The concentrations of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ were measured by ion chromatography.¹⁴ For double- and triple-component fertilizer, the concentrations of NH_4^+ , K^+ , and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ in the solution of the receiving side were measured by ion chromatography.

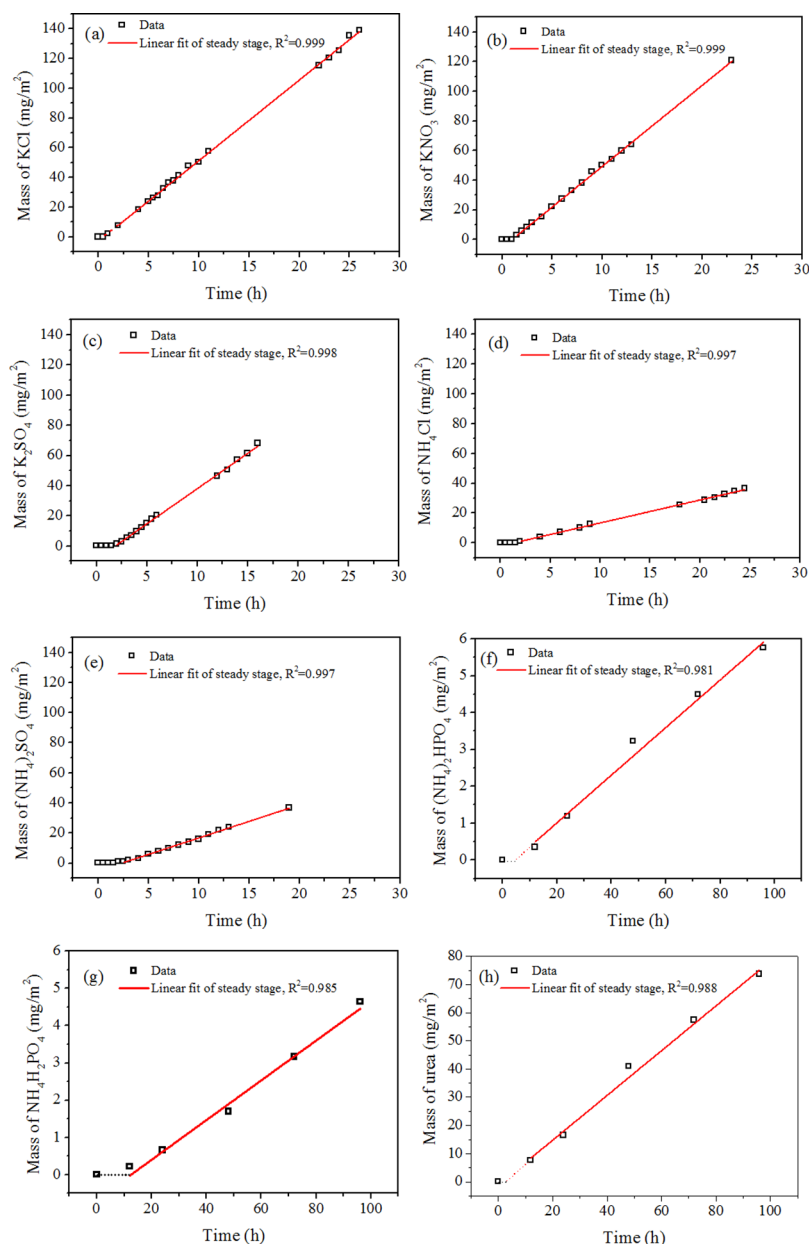


Figure 2. Mass of different nutrient diffused to the receiving side vs time: (a) KCl, (b) KNO₃, (c) K₂SO₄, (d) NH₄Cl, (e) (NH₄)₂SO₄, (f) (NH₄)₂HPO₄, (g) NH₄H₂PO₄, and (h) urea.

3. RESULTS AND DISCUSSION

3.1. Diffusion Property of Single-Component Fertilizer Solution. The change of different nutrient mass diffused to the receiving side with time is shown in Figure 2.

Figure 2 shows that the diffusion process of the nutrient through the film has two stages. In the first stage, the nutrient permeates through the film, and the mass of nutrient in the receiving side was almost zero. In the second stage, the diffusion was steady, and the mass of nutrient entering into the receiving side increased linearly with time, indicating that the diffusion flux of the nutrient is constant. As the concentration of the nutrient in the receiving side is much lower than that in the supply side, the concentration difference between both sides is regarded as the concentration in the film phase in the supply side, i.e., C_{m0} , is a constant. Therefore, the nutrient diffusions through the film are consistent with Fick's law, as shown in eq 2.

$$J = D \cdot \frac{dC_m}{dL} = D \cdot \frac{C_{m0}}{L} \quad (2)$$

where J is the diffusion flux, D the diffusion coefficient of nutrient in the film, dC_m/dL the concentration gradient of nutrient in the film phase, and L the thickness of the film.

The nutrient diffusion can be described by the solution–diffusion model.^{15,16} The permeation of nutrients in the model has three steps: (1) the partition of nutrients into the film phase in the supply side, (2) the diffusion of nutrients through the film, and (3) the partition of nutrients into the solution phase in the receiving side. Steps 1 and 3 are fast steps, and step 2 is the limiting step. Meanwhile, in the steady stage of diffusion, the diffusion flux of nutrients in the steady stage can also be expressed as

$$J = P_e \cdot \frac{C_{i0}}{L} = P_e \cdot \frac{C_s}{L} \quad (3)$$

Table 2. Parameters of Diffusion Performance for Each Nutrient through the Film

nutrient	L (μm)	θ (h)	D ($\times 10^{-13}$ m^2/s)	P_e ($\times 10^{-17}$ m^2/s)	K ($\times 10^{-3}$)
urea	50	1.40	0.83	51.9	6.3
KCl	50	0.62	1.86	25.1	1.3
KNO ₃	52	1.00	1.25	23.2	1.9
K ₂ SO ₄	70	1.90	1.19	79.9	6.7
NH ₄ Cl	60	1.34	1.24	8.26	0.67
(NH ₄) ₂ SO ₄	72.5	2.46	0.99	8.70	0.88
(NH ₄) ₂ HPO ₄	55	4.33	0.32	0.25	0.08
NH ₄ H ₂ PO ₄	60	12.5	0.13	0.22	0.16

where P_e is the permeation coefficient of nutrient across the film and C_{10} is the concentration in the solution phase in the supply side, which is the saturated concentration in the solution, C_s . The partition coefficient between the film and solution phase, i.e., K , is expressed as

$$K = \frac{C_{m0}}{C_{10}} \quad (4)$$

From eqs 2–4, it can be seen that

$$K = P_e/D \quad (5)$$

where P_e can be calculated according to eq 3 and D can be calculated by the time-lag method¹⁷

$$D = \frac{L^2}{6\theta} \quad (6)$$

where θ is the time it takes for the nutrient to reach the steady diffusion stage.

The parameters of diffusion performance for each nutrient were calculated and are reported in Table 2.

Table 2 shows the diffusion performance for different nutrients through the film. For nutrients with the same cation K^+ , the measured D was in the order $\text{KCl} > \text{KNO}_3 > \text{K}_2\text{SO}_4$. For nutrients with the same cation NH_4^+ , the measured D was in the order $\text{NH}_4\text{Cl} > (\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{HPO}_4 > \text{NH}_4\text{H}_2\text{PO}_4$. For nutrients with the same anion, the D of potassium salt is higher than that of ammonium salt. This can be explained by an extended solution–diffusion model.^{16,18} Based on the free volume model of the polymer,¹⁹ the volume of the polymer consists of two parts: one is the volume of the molecular chain itself, and the other is the free volume, that is, the volume among the molecular chains. The extended solution–diffusion model approximates the free volume with hypothetical cylindrical capillary pores having a mean average pore radius, and the D can be related to the diffusion coefficient of nutrient in infinite water D_w^∞ by hindrance factor $H(\lambda)$, which can be expressed as

$$D = H(\lambda) \cdot D_w^\infty \quad (7)$$

where λ is the ratio of the nutrient radius r_s to the capillary pore radius r_0 , that is, $\lambda = r_s/r_0$. $H(\lambda)$ represents the diffusion resistance of nutrients in the polymer film; it is negatively correlated with λ . The D_w^∞ of urea was reported to be 1.389×10^{-9} m^2/s ,²⁰ and the D_w^∞ of electrolyte nutrient can be calculated by the limiting molar conductivity in water of its dissociated ions. The formulas were shown as follows:²¹

$$D_j^\infty = \frac{RT\lambda_j}{|Z_j|Fa^2} \quad (8)$$

$$D_w^\infty = \frac{(|Z_i| + |Z_j|)D_i^\infty D_j^\infty}{|Z_i|D_i^\infty + |Z_j|D_j^\infty} \quad (9)$$

where D_j^∞ is the diffusion coefficient of the ion in infinite water, λ_j the limiting molar conductivity of the ion in water, z_j the charge value of the ion, R the ideal gas constant, Fa the Faraday constant, and T the temperature of the solution. The D_w^∞ of each nutrient at 25 °C was calculated, and the values are reported in Table 3. The radius value of each nutrient molecule and ion is reported in Table 4.^{22–24}

Table 3. Diffusion Coefficient of Nutrient in Infinite Water

nutrient	D_w^∞ ($\times 10^{-10}$ m^2/s)	nutrient	D_w^∞ ($\times 10^{-10}$ m^2/s)
urea	13.89	NH ₄ Cl	20.05
KCl	19.94	(NH ₄) ₂ SO ₄	15.43
KNO ₃	19.29	(NH ₄) ₂ HPO ₄	12.64
K ₂ SO ₄	15.35	NH ₄ H ₂ PO ₄	11.85

Table 4. Radius of Each Nutrient Molecule and Ion

nutrient	radius (Å)	nutrient	radius (Å)
urea	1.80	NO ₃ ⁻	1.89
K ⁺	1.38	SO ₄ ²⁻	2.15
NH ₄ ⁺	1.61	HPO ₄ ²⁻	2.30
Cl ⁻	1.81	H ₂ PO ₄ ⁻	2.38

Based on the parameters of each nutrient reported in Tables 3 and 4, the regularity of D of different nutrient can be explained. For nutrients with the same cation, as the radius of anion r_s increases, the $H(\lambda)$ of the nutrient decreases correspondingly, and the D_w^∞ of the nutrient also decreases. According to eq 7, the D decreases as radius of the anion increases. For nutrients with the same anion, the difference of D_w^∞ between potassium salt and ammonium salt can be neglected, while the radius of NH_4^+ is larger than that of K^+ , so the $H(\lambda)$ of ammonium salt is lower, and the D of ammonium salt is lower. It is shown that the larger the size of the nutrient molecules and ions are, the lower the diffusion coefficient of them in the film.

The results showed that the K of each nutrient is much lower than 1, which means the concentration of nutrient in film phase is much lower than that in solution phase. Among the nutrients, the K of urea and potassium salt are relatively higher, indicating that they have relatively higher solubility in the film. According to eq 5, the differences of D and K among different nutrients make the P_e of nutrients vary a great deal. The permeation coefficient across the film, P_e , is determined by the partition coefficients between the film phase and the solution phase, and the diffusion coefficient of nutrients in the film.

Table 5. Saturated Concentration of Each Nutrient in Urea–KCl and Urea–NH₄H₂PO₄ Composite Solutions^a

saturated solution	concentration of nutrient (g/L)		nutrient ratio
urea–KCl	urea: 601 (95% sat)	KCl: 168 (56% sat)	N:K ₂ O = 2.64
urea–NH ₄ H ₂ PO ₄	urea: 542 (87% sat)	NH ₄ H ₂ PO ₄ : 181 (53% sat)	N:P ₂ O ₅ = 2.46

^a“sat” indicates the saturated concentration of nutrient in the solution when it exists alone.

For the coated fertilizer with single-component nutrient, the release rate, i.e., the mass of nutrient released from coated fertilizer granular per unit time, can be expressed as follows:

$$\frac{dm}{dt} = \frac{P_e \cdot \Delta C \cdot S}{L} \quad (10)$$

where m is the mass of nutrient released and dm/dt is the release rate of coated fertilizer granular. ΔC is the concentration difference between the inside and the outside of the coated film. In the steady stage of nutrient release process, the concentration of nutrient solution inside the coated film is the saturated concentration C_s , which is much higher than that in the external water environment; therefore, $\Delta C = C_s$. S is the mass-transfer area for the spherical coated fertilizer granular with a radius of R , $S = 4\pi R^2$; L is the thickness of the coated film. Therefore, eq 10 can be re-expressed as follows:

$$\frac{dm}{dt} = \frac{P_e \cdot C_s \cdot 4\pi R^2}{L} \quad (11)$$

Eq 11 shows that the release rate of coated fertilizer is proportional to the P_e of the coated film and the saturated solubility of nutrients. Therefore, the release rate of coated fertilizer with a single component can be easily controlled by the film coating amount, according to the uptake rate of the nutrient by crops.

3.2. Diffusion Performance of N–K and N–P Double-Component Fertilizer Solution. The concentration of each nutrient in urea–KCl and urea–NH₄H₂PO₄ saturated solution was measured and is reported in Table 5. The results indicate that the saturated concentration of each nutrient in the double-component solution is lower than that when the nutrient exists alone in the solution, and the concentration of urea is higher than that of KCl and NH₄H₂PO₄ respectively. Specifically, for urea–KCl saturated solution, the mass of urea dissolved in the solution is 95% of that when urea exists alone, and for KCl, it is only 56%. The ratio of nutrient concentration in saturated solution is measured to be N:K₂O = 2.64. For urea–NH₄H₂PO₄ saturated solution, the mass of urea dissolved in the solution is 87% of that when urea exists alone, and for NH₄H₂PO₄, it is only 53%. The ratio of nutrient concentration in saturated solution is measured to be N:P₂O₅ = 2.46. This is because urea and water can easily form hydrogen bonds in the solution, which lowers the mobility of water molecules.^{25,26} Therefore, when the other nutrient is present, the saturated solubility of urea is not significantly reduced. However, because of the decrease in hydration and dissolution of KCl and NH₄H₂PO₄ by water molecules, the saturated solubility of KCl and NH₄H₂PO₄ significantly decreased.

The permeation coefficient P_e of each nutrient in different fertilizer solutions was measured and is reported in Table 6. In the urea–KCl saturated solution, the urea molecule interacts with K⁺ and Cl[−] to form complex molecules,²⁷ which have a relatively large size. A small proportion of the urea diffused through the film in the form of complex molecules, which have

Table 6. Permeation Coefficient of Each Nutrient in Different Fertilizer Solutions

saturated solution	permeation coefficient of nutrient (10 ^{−18} m ² /s)		
urea	urea: 519	–	–
KCl	–	KCl: 251	–
NH ₄ H ₂ PO ₄	–	–	NH ₄ H ₂ PO ₄ : 2.18
urea–KCl	urea: 323	KCl: 35.7	–
urea–NH ₄ H ₂ PO ₄	urea: 273	–	NH ₄ H ₂ PO ₄ : 1.27

a higher diffusion resistance and a lower permeation coefficient. A majority of the urea diffuses in the form of urea molecules. Therefore, the permeation coefficient of urea in composite solution is lower than that of the saturated urea solution. For the KCl solution, all of the K⁺ and Cl[−] diffuses through the film in the form of complex molecules, so the permeation coefficient of KCl in composite solution is much lower than that of the saturated KCl solution. In the urea–NH₄H₂PO₄ saturated solution, the urea molecules interact with H₂PO₄[−] to form complex molecules.²⁸ Therefore, the permeation coefficient of urea and NH₄H₂PO₄ in composite solution is lower compared with that when one component exists alone in the saturated solution. As a result, the release rate of N is much faster than that of K and P because of the interaction between nutrients.

The nutrient release rate ratio was determined by measuring the mass of nutrient in the receiving side and is reported in Table 7. Because of the difference in solubility and permeation

Table 7. Nutrient Release Rate Ratio in Urea–KCl and Urea–NH₄H₂PO₄ Saturated Solutions

saturated solution	nutrient release rate ratio
urea–KCl	N:K ₂ O = 23.6
urea–NH ₄ H ₂ PO ₄	N:P ₂ O ₅ = 486.4

coefficient of each nutrient, the release rates of different nutrients differ significantly. For the urea–KCl saturated solution, the nutrient release rate ratio is measured to be N:K₂O = 23.6. For the urea–NH₄H₂PO₄ saturated solution, the nutrient release rate ratio is measured to be N:P₂O₅ = 486.4. This means the release rate of N is much faster than that of K and P. That is, for the coated fertilizer with urea–KCl and urea–NH₄H₂PO₄ composition, after most of the urea released, KCl or NH₄H₂PO₄ would begin to release in large quantities.

3.3. Diffusion Performance of N–P–K Multicomponent Fertilizer Solution. The concentration of each nutrient in N–P–K saturated solution was measured and is reported in Table 8. The results indicate that the saturated concentration of each nutrient in the multicomponent fertilizer solution is lower than that when the nutrient exists alone in the solution, and because of the difference in affinity of different nutrients to water, the solubilities of different nutrients are different.

The nutrient concentration ratios in the N–P–K saturated solution and the release rate ratios of the nutrients through the film were measured and are reported in Table 9. It shows that among different solutions, because (NH₄)₂HPO₄ has a higher

Table 8. Saturated Concentration of Each Nutrient in N–P–K Composite Solution^a

saturated solution	concentration of nutrient (g/L)		
	NH ₄ Cl	NH ₄ H ₂ PO ₄ / (NH ₄) ₂ HPO ₄	KCl/K ₂ SO ₄
NH ₄ Cl– NH ₄ H ₂ PO ₄ –KCl	206 (66% sat)	54 (16% sat)	123 (41% sat)
NH ₄ Cl– (NH ₄) ₂ HPO ₄ – KCl	205 (65% sat)	130 (26% sat)	113 (37% sat)
NH ₄ Cl– NH ₄ H ₂ PO ₄ – K ₂ SO ₄	260 (83% sat)	60 (18% sat)	98 (85% sat)
NH ₄ Cl– (NH ₄) ₂ HPO ₄ – K ₂ SO ₄	243 (78% sat)	128 (26% sat)	88 (76% sat)

^a“sat” indicates the saturated concentration of nutrient in the solution when it exists alone.

Table 9. Ratio of Nutrient Concentration and Release Rate in N–P–K Saturated Solution

saturated solution	nutrient concentration ratio (N:P ₂ O ₅ :K ₂ O)	nutrient release rate ratio (N:P ₂ O ₅ :K ₂ O)
NH ₄ Cl– NH ₄ H ₂ PO ₄ –KCl	0.78:0.43:1	0.60:0.58:1
NH ₄ Cl– (NH ₄) ₂ HPO ₄ – KCl	1.14:0.98:1	30.9:0.52:1
NH ₄ Cl– NH ₄ H ₂ PO ₄ – K ₂ SO ₄	1.42:0.70:1	0.23:0.13:1
NH ₄ Cl– (NH ₄) ₂ HPO ₄ – K ₂ SO ₄	1.91:1.44:1	11.8:0.12:1

solubility and N content is higher than NH₄H₂PO₄, the solution taking (NH₄)₂HPO₄ as the source of phosphorus has relatively high contents of N and P compared with that of NH₄H₂PO₄. Because the solubility and permeation coefficient of different nutrients are different, there is a big difference among the release rates of different nutrients. For NH₄Cl–NH₄H₂PO₄–KCl saturated solution, the release rate was in the order K₂O > N > P₂O₅. It was analyzed that the highest concentration and smallest size of K⁺ resulted in the fastest release rate of K⁺. For NH₄Cl–(NH₄)₂HPO₄–KCl saturated solution, the release rate was in the order N > K₂O > P₂O₅. It was analyzed that (NH₄)₂HPO₄ can provide more NH₄⁺ in the solution; the enhancement in driving force derived from the concentration gradient means that the release rate of NH₄⁺ is faster than that of K⁺. In the case of solid nutrient ratio being N:P₂O₅:K₂O = 1:1:1, for the NH₄Cl–NH₄H₂PO₄–K₂SO₄ saturated solution, the release rate was in the order K₂O > N > P₂O₅, and for the NH₄Cl–(NH₄)₂HPO₄–K₂SO₄ saturated solution, the release rate was in the order N > K₂O > P₂O₅. In all solutions, as the concentration of phosphate is the lowest and its size is the largest, the release rate of P₂O₅ is the lowest. This shows that the selection of phosphorus source and potassium source has a great influence on the release rate of nutrients.

The diffusion performance of nutrients in the double- and triple-component fertilizer solutions indicated that there are significant differences among the release rate of different nutrients. In the double- and triple-component saturated solutions, the degree of freedom of the solution is 0, so the release rate of each nutrient is a fixed value; it is not possible to

change the release rate by adjusting the nutrient independently. Therefore the difference in the demands for N, P, and K of different crops can not be matched. Therefore, in order to meet the demands of different nutrients for crops, compared with fertilizing with coated compound fertilizer, coating the single-component fertilizer, i.e., nitrogen fertilizer, phosphate fertilizer, and potash fertilizer, and blending them according to the corresponding nutrient needs of the crops can adjust the nutrient release rate more flexibly.

AUTHOR INFORMATION

Corresponding Author

*Phone: +86-10-62788993. Fax: +86-10-62772051. E-mail: wangtj@tsinghua.edu.cn.

ORCID

Ting-Jie Wang: 0000-0003-4468-9498

Funding

This work was financially supported by the the National Key R&D Program of China (2017YED0200704).

Notes

The authors declare no competing financial interest.

REFERENCES

- Hanafi, M. M.; Eltaib, S. M.; Ahmad, M. B. Physical and chemical characteristics of controlled release compound fertilizer. *Eur. Polym. J.* **2000**, *36*, 2081–2088.
- Easton, Z. M.; Petrovic, A. M. Fertilizer source effect on ground and surface water quality in drainage from turfgrass. *J. Environ. Qual.* **2004**, *33*, 645–655.
- Shaviv, A. Advances in controlled-release fertilizers. *Adv. Agron.* **2001**, *71*, 1–49.
- Shaviv, A.; Raban, S.; Zaidel, E. Modeling controlled nutrient release from polymer coated fertilizers: diffusion release from single granules. *Environ. Sci. Technol.* **2003**, *37*, 2251–2256.
- Huett, D. O.; Gogel, B. J. Longevities and nitrogen, phosphorus, and potassium release patterns of polymer-coated controlled-release fertilizers at 30 and 40 °C. *Commun. Soil Sci. Plant Anal.* **2000**, *31*, 959–973.
- Broschat, T. K.; Moore, K. K. Release rates of ammonium-nitrogen, nitrate-nitrogen, phosphorus, potassium, magnesium, iron, and manganese from seven controlled-release fertilizers. *Commun. Soil Sci. Plant Anal.* **2007**, *38*, 843–850.
- Lu, P.; Zhang, M.; Li, Q.; Xu, Y. Structure and properties of controlled release fertilizers coated with thermosetting resin. *Polym.-Plast. Technol. Eng.* **2013**, *52*, 381–386.
- Du, C.; Zhou, J.; Shaviv, A. Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. *J. Polym. Environ.* **2006**, *14*, 223–230.
- Noppakundilongrat, S.; Pheatcharat, N.; Kiatkamjornwong, S. Multilayer-coated NPK compound fertilizer hydrogel with controlled nutrient release and water absorbency. *J. Appl. Polym. Sci.* **2015**, *132*, 41249.
- Lan, R.; Liu, Y.; Wang, G.; Wang, T.; Kan, C.; Jin, Y. Experimental modeling of polymer latex spray coating for producing controlled-release urea. *Particuology* **2011**, *9*, 510–516.
- Silcock, H. *Solubilities of Inorganic and Organic Compounds: Ternary and Multicomponent Systems of Inorganic Substances*; Pergamon Press: Oxford, U.K., 1979.
- Ussing, H. H.; Zerahn, K. Active transport of sodium as the source of electric current in the short-circuited isolated frog skin. *Acta Physiol. Scand.* **1951**, *23*, 110–127.
- Yang, L.; An, D.; Wang, T.; Kan, C.; Jin, Y. Swelling and diffusion model of a hydrophilic film coating on controlled-release urea particles. *Particuology* **2017**, *30*, 73–82.

(14) Skoog, D. A.; Holler, F. J.; Nieman, T. A. *Principles of Instrumental Analysis*; Saunders College Publishing, Harcourt Brace: Orlando, FL, 1998.

(15) Wijmans, J.; Baker, R. The solution-diffusion model: a review. *J. Membr. Sci.* **1995**, *107*, 1–21.

(16) Wang, J.; Dlamini, D.; Mishra, A.; Pendergast, M.; Wong, M.; Mamba, B.; Freger, V.; Verliefe, A.; Hoek, E. A critical review of transport through osmotic membranes. *J. Membr. Sci.* **2014**, *454*, 516–537.

(17) Garbarini, G.; Eaton, R.; Kwei, T.; Tobolsky, A. Diffusion and reverse osmosis through polymer membranes. *J. Chem. Educ.* **1971**, *48*, 226–230.

(18) Deen, W. Hindered transport of large molecules in liquid-filled pores. *AIChE J.* **1987**, *33*, 1409–1425.

(19) Sharma, J.; Tewari, K.; Arya, R. K. Diffusion in polymeric systems-A review on free volume theory. *Prog. Org. Coat.* **2017**, *111*, 83–92.

(20) Gosting, L. J.; Akeley, D. F. A study of the diffusion of urea in water at 25 °C with the gouy interference method. *J. Am. Chem. Soc.* **1952**, *74*, 2058–2060.

(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Dover Publications: New York, 1959.

(22) Schultz, S. G.; Solomon, A. Determination of the effective hydrodynamic radii of small molecules by viscometry. *J. Gen. Physiol.* **1961**, *44*, 1189–1199.

(23) Tansel, B.; Sager, J.; Rector, T.; Garland, J.; Strayer, R.; Levine, L.; Roberts, M.; Hummerick, M.; Bauer, J. Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. *Sep. Purif. Technol.* **2006**, *51*, 40–47.

(24) Collins, K. D. Sticky ions in biological systems. *Proc. Natl. Acad. Sci. U. S. A.* **1995**, *92*, 5553–5557.

(25) Ramondo, F.; Bencivenni, L.; Caminiti, R.; Pieretti, A.; Gontrani, L. Dimerisation of urea in water solution: a quantum mechanical investigation. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2206–2215.

(26) Rezus, Y.; Bakker, H. Effect of urea on the structural dynamics of water. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 18417–18420.

(27) Hong, J.; Capp, M. W.; Anderson, C. F.; Record, M. T. Preferential interactions in aqueous solutions of urea and KCl. *Biophys. Chem.* **2003**, *105*, 517–532.

(28) Palecz, B.; Grala, A.; Kudzin, Z. Calorimetric studies of the interactions between several aminophosphonic acids and urea in aqueous solutions at 298.15 K. *J. Chem. Eng. Data* **2014**, *59*, 426–432.