Potassium Chloride-Modified Urea Phosphate with Response Surface Optimization and Its Application Effect on Maize in Saline-Alkali Soil

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ABSTRACT: Urea phosphate (UP) is an acidic compound fertilizer, which significantly improves the low efficiency of P application caused by high pH in saline-alkali soil. In this study, urea phosphate potassium (UPK) was prepared by adding potassium chloride (KCl) to modify urea phosphate (UP) and the optimal combination of the synthetic process parameters was obtained using the response surface methodology at a four-variable, three-level experiment Box–Behnken design. Parameters such as the reaction temperature, KCl molar number, reaction time, and concentration of phosphoric acid were included for optimization. The thermostability, crystal structure, and microscopic morphology of UPK were measured by thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM), respectively. The fertilizer efficiency was validated in an experiment on maize grown in pots containing saline-alkali soil. The highest K2O content and UPK yield were obtained by using the following parameters: reaction time of 60 min, KCl of 0.32 mol, reaction temperature of 78 °C, and phosphoric acid concentration of 70%. Under optimal conditions, the predicted K2O value content and UPK yield were 3.51% and 69.8%, respectively. The experimental K2O content and UPK yield were 3.42 ± 0.35% and 67.58 ± 1.25%, respectively, which confirmed the strength of the predicted model. This model can be used as an effective tool to predict the K2O content and yield in UPK. Characterizations showed that KCl was uniformly distributed in UPK and its fluidity was effectively improved as observed in the angle-of-repose results. Compared to a conventional phosphorus fertilizer diammonium phosphate (DAP), the yield, total P use efficiency, soil available phosphorus content, and soil acid phosphatase activity of UPK increased significantly by 25.58, 174.5, 24.41, and 41.25%, respectively, and the soil pH on UPK treatments decreased by 3.98% significantly. In conclusion, this novel technology to modify UP by using KCl has an enormous potential for large-scale applications to satisfy the increasing demand for UP fertilizers on saline-alkali soil.

1. INTRODUCTION

Saline-alkali land is an important land resource. With increasing population pressure, the improvement, exploitation, and utilization of saline-alkali land have increased the attention toward it. Phosphorus (P) is an essential nutrient element for plant growth and development, which could directly affect the crop yield in agricultural production.1−2 The saline-alkali soil pH value is high, and phosphate fertilizers have the potential to quickly react with this soil’s components forming insoluble phosphate molecules that cannot be absorbed and utilized by plants.3−4 Studies have shown that, in saline-alkali soil under salt stress, the demand for P increases, and the application of a phosphate fertilizer promotes crop growth and development and improves salt tolerance.5 Therefore, improving the utilization rate of P in saline-alkali soil is of great significance.

At present, methods to improve P utilization in alkaline soil mainly include intercropping, application of microbial fertilizers, and other practices. However, low effects and high costs of these alternatives limit their promotion and use.6−9 Decreasing the soil pH improves solubility of secondary calcium (Ca) and P nutrients in soil and plays a crucial role in improving the effective utilization of P in alkaline soil. Urea phosphate (UP), (H3PO4·CO(NH2)2), is a highly acidic...
amino-structured complex prepared by the reaction of phosphoric acid with urea, which can be used not only as a feed additive for ruminants but also as a high-efficiency phosphorus fertilizer. The application of UP can reduce the pH value of soil and the fixation effect of soil on phosphorus. However, the nutrition element of UP is not balanced, containing only N and P, and it is only used as fertilizer additive in the market, which reduces the fertilizer efficiency and limits its promotion and application. Meanwhile, the crystalline fluidization of UP is low, and this is not favorable for industrial production.

Cocrystallization is a variation of solid matter with a eutectic state from steam and precipitation in the solution or melt; the process of the co-crystallization technique not only solves the problem of a solid product with low dispersion and low uniformity but also improves the product crystals' shape, fluidity, hygroscopicity, and stability. Mu et al. reported that KCl can be added in the crystallization process to make an NPK compound fertilizer, i.e., urea phosphate potassium (UPK). However, the mechanism of a KCl-improved crystal was not considered and its value for agricultural use was not validated. Factors influencing the UPK synthesis process (reaction time, temperature, phosphoric acid concentration, and others) by orthogonal and single-factor tests have been studied.

As only one variable can be optimized at a time in a single-factor test, the relative optimal solution of different variables and finite light combinations can be obtained by orthogonal design, and the second-order polynomial model between parameters and response values of all combined variables become not possible. Therefore, the response surface methodology (RSM), a mathematical and statistical analysis technique based on fitting a polynomial equation of experimental data, was used as an effective tool for optimizing the process. The RSM goal is to determine the factors that influence the synthesis process and the interactions between these factors to optimize the level of these variables to obtain the best response values.

The study objectives were to (1) determine the optimum technological conditions for UPK preparation by using the RSM, (2) identify the thermostability, crystal structure, and microscopic morphology of UPK by thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM), respectively, and (3) validate the UPK effect on the yield increment of maize in pots containing saline-alkali soil. The KCl-modified urea phosphate could provide an effective method for the efficient utilization of phosphorus in saline-alkali soil and contribute to improvement of saline-alkali land worldwide.

2. RESULTS AND DISCUSSION

2.1. Analysis of the Single-Factor Test of the UPK Synthesis Process. 2.1.1. Stirring Speed. To investigate the effect of the stirring speed on the yield of UPK, the synthesis process was carried out using different stirring speeds of 150, 200, 250, 300, and 350 r/min while keeping other synthesis parameters as the following constants: reaction time of 60 min, molar ratio of phosphate to urea of 1:1, concentration of phosphorus in the solution or melt of 60%, reaction temperature of 60 °C, KCl of 0.15 mol, and synthesis number of 3 times. The initial increase of
the stirring speed resulted in an obvious increase in the UPK yield, while a further increase had a negative effect on the UPK yield (Figure 1A). A possible explanation of this result is that a low stirring rate leads to uneven mixing of reaction reactants and an inadequate reaction, while an extremely high stirring rate hinders the crystallization process of UP. Therefore, a stirring speed of 300 r/min was considered suitable and used in the following experiments to study the effect of other factors on the UPK yield.

2.1.2. Molar Ratio of Phosphoric Acid to Urea. The effects of the molar ratio of phosphoric acid to urea (1:0.90−1:1.10) on the yield of UPK were studied (Figure 1B) keeping other synthesis variables as the following: stirring speed of 300 r/min, reaction time of 60 min, concentration of phosphate of 60%, reaction temperature of 60 °C, KCl of 0.15 mol, and synthesis number of 3 times. With the increase of the molar ratio of urea to phosphate, the yield of UP increased, reaching a maximum value when the ratio was 1:1, and decreased afterward. The reason may be that the solubility of UPK in the acidic environment increases when excess phosphate is present, and the synthesis of UPK was hindered when urea was excessive. Therefore, the optimal molar ratio of urea to phosphoric acid is 1:1.

2.1.3. Reaction Time. The effect of reaction time on the yield of UPK is shown in Figure 1C. Reaction times were set at 30, 40, 50, 60, and 80 min, while other synthesis parameters were the following: molar ratio of phosphoric acid to urea of 1:1, stirring speed of 300 r/min, concentration of phosphate of 60%, reaction temperature of 60 °C, and KCl of 0.15 mol. The yield of potassium urea phosphate increased with the prolongation of reaction time. However, longer reaction times will cause unnecessary energy consumption. Therefore, the reaction time was selected to be between 30 and 60 min.

2.1.4. KCl Molar Number. The molar numbers of KCl were set at 0, 0.05, 0.15, 0.25, 0.35, and 0.45 to investigate the effect of the KCl molar number on the yield (Figure 1D) and K2O content (Figure 2) of UPK. Other synthesis parameters were the following: molar ratio of phosphate to urea of 1:1, stirring speed of 300 r/min, concentration of phosphate of 70%, reaction temperature of 60 °C, KCl of 0.15 mol, and synthesis number of 3 times. With the increase of the molar number of KCl (Figure 2), but when the molar number of KCl exceeds 0.35, the content of K2O tends to be stable. Therefore, the molar number of KCl was selected to be between 0 and 0.35 mol.

2.1.5. Reaction Temperature. The effect of different reaction temperatures (50, 60, 70, 80, and 90 °C) on the yield of UPK (Figure 1E) was assessed, while other synthesis parameters were kept as follows: molar ratio of phosphate to urea of 1:1, stirring speed of 300 r/min, concentration of phosphate of 60%, reaction time of 60 min, and KCl of 0.15 mol. With the increase of temperature, the yield of UPK first increased and then decreased. The results indicated that the synthesis of the phosphate pulse was promoted by the increase of temperature, but because of the increase of temperature, urea was easily hydrolyzed and the yield of UPK was reduced. As a result, 80 °C was set as an appropriate synthesis temperature.

2.1.6. Concentration of Phosphoric Acid. In order to study the effects of the concentration of phosphoric acid on the yield of UPK, the concentration of phosphoric acid was set at 30, 40, 50, 60, 70, and 80% (Figure 1F); other synthesis parameters were as follows: molar ratio of phosphate to urea of 1:1, stirring speed of 300 r/min, reaction time of 60 min, KCl of 0.15 mol, reaction temperature of 60 °C. When the concentration of phosphate was between 30 and 40%, no crystallization precipitation of UPK was present at 20 °C. With the increase of the phosphate concentration, the yield increased rapidly. When the concentration of phosphate reached 80%, a portion of urea or KCl was not dissolved, and the yield could not be determined. However, the high concentration of phosphate also had adverse effects, such as the increase of viscosity, heat transfer in the reactor, and uneven mass transfer. Meanwhile, the decrease of the water mass fraction in the system and the increase of urea phosphate result in the increase of supersaturation of urea phosphate and raw urea. It is not favorable to the crystallization of UPK, which leads to separation of products and difficulty of purification, so the concentration range of phosphoric acid is 50−70%.

According to the single-factor study, the following conditions could be used for the following experiments: a molar ratio of phosphate to urea of 1:1, a stirring speed of 300 r/min, a reaction time of 30−60 min, a KCl of 0−0.35 mol, a reaction temperature of 70−90 °C, and a concentration of phosphoric acid of 50−70%.

2.2. Box–Behnken Design (BBD) and Analysis. 2.2.1. Statistical Analysis and the Model Fitting. BBD with four factors and three levels were carried out to optimize the mutual effect of four independent variables: the (C) reaction time, (D) KCl molar number, (E) reaction temperature, and (F) concentration of phosphoric acid on the K2O content and yield of UPK. Table 1 illustrates the design matrix and yield (Y1) and K2O content (Y2) of UPK. After these data were treated with the BBD, second-order polynomial equations reflecting the empirical relationship between the response variable (Y1 and Y2) and the independent variables (C, D, E, and F) are presented as the following:

![Figure 2. Changes of K2O content in UPK with the KCl molar number.](image)

The content of K2O gradually increases with the molar number of KCl, while the content of K2O tends to be stable. Therefore, the molar number of KCl was selected to be between 0 and 0.35 mol.
Table 1. BBD Matrix and Response Values for the Synthesis Yield (Y₁) and K₂O Content (Y₂) of Urea Phosphate Potassium (UPK)\textsuperscript{a}

| number | C (min) | D (mol) | E (°C) | F (%) | Y₁ (%) | Y₂ (%) |
|--------|---------|---------|--------|-------|--------|--------|
| 1      | 45      | 0.175   | 70     | 50    | 42.08  | 0.15   |
| 2      | 45      | 0.175   | 90     | 50    | 40.69  | 0.18   |
| 3      | 45      | 0.35    | 80     | 50    | 41.36  | 0.29   |
| 4      | 30      | 0.175   | 80     | 50    | 47.61  | 0.17   |
| 5      | 45      | 0       | 80     | 50    | 51.69  | 0      |
| 6      | 60      | 0.175   | 80     | 50    | 46.69  | 0.16   |
| 7      | 30      | 0.175   | 90     | 60    | 56.02  | 0.84   |
| 8      | 30      | 0.175   | 70     | 60    | 58.69  | 0.80   |
| 9      | 45      | 0.175   | 80     | 60    | 63.02  | 0.60   |
| 10     | 45      | 0       | 70     | 60    | 66.36  | 0      |
| 11     | 45      | 0.35    | 70     | 60    | 54.06  | 2.83   |
| 12     | 45      | 0.175   | 80     | 60    | 63.09  | 0.96   |
| 13     | 60      | 0.35    | 80     | 60    | 59.36  | 2.86   |
| 14     | 45      | 0.175   | 80     | 60    | 63.86  | 0.70   |
| 15     | 60      | 0.175   | 70     | 60    | 59.88  | 0.82   |
| 16     | 30      | 0.35    | 80     | 60    | 58.95  | 2.95   |
| 17     | 45      | 0.35    | 90     | 60    | 51.46  | 2.89   |
| 18     | 45      | 0       | 90     | 60    | 63.16  | 0      |
| 19     | 45      | 0.175   | 80     | 60    | 63.58  | 0.80   |
| 20     | 30      | 0       | 80     | 60    | 67.56  | 0      |
| 21     | 45      | 0.175   | 80     | 60    | 62.85  | 0.81   |
| 22     | 60      | 0.175   | 90     | 60    | 57.65  | 0.81   |
| 23     | 60      | 0       | 90     | 60    | 69.89  | 0      |
| 24     | 45      | 0       | 80     | 70    | 78.56  | 0      |
| 25     | 60      | 0.175   | 80     | 70    | 74.63  | 1.46   |
| 26     | 30      | 0.175   | 80     | 70    | 72.69  | 1.45   |
| 27     | 45      | 0.35    | 80     | 70    | 66.39  | 3.51   |
| 28     | 45      | 0.175   | 70     | 70    | 72.01  | 1.65   |
| 29     | 45      | 0.175   | 90     | 70    | 66.69  | 1.69   |

\textsuperscript{a}Note: (C) reaction time, min; (D) KCl molar number, mol; (E) reaction temperature, °C; and (F) concentration of phosphoric acid, %.

Y₁ = 63.28 + 0.5483C − 5.47D − 1.45E + 13.40F
− 0.4800CD + 0.1100CE + 0.7150CF + 0.1500DE
− 0.4600DF − 0.9825EF + 0.2238C² + 0.1213D²
− 4.88E² − 3.34F²

(1)

Y₂ = 0.7742 − 0.0186C + 1.28D + 0.0133E + 0.7440F
− 0.0230CD − 0.0160CE − 0.0250CF + 0.0143DE
+ 0.8060DF + 0.0035EF − 0.0998C² + 0.4614D²
+ 0.1277E² − 0.1015F²

(2)

Equation 1 relates the UPK yield with the molar ratio of phosphate to urea, concentration of phosphate, reaction temperature, and KCl molar number. The analysis of variance, goodness-of-fit, and adequacy of the regression model are summarized in Table 2. The F value of the eq 1 model was 259.89, and the p value was less than 0.0001, indicating that the model was highly statistically significant (eq 1). The F value and p value of the lack of fit were 5.57 and 0.0562, respectively, which confirmed the goodness-of-fit and suitability of the regression model.

With the interactive effects of the reaction time, concentration of phosphate, reaction temperature, and KCl molar number (independent variables) on the dependent variable, K₂O content, a quadratic regression equation was determined (eq 2). Correlation coefficients R² and adjusted R² were used to test the fit of the model; R² was 0.9633, indicating that the model predicted the response well. The value of the adjusted R² (0.9266) was also very high and indicated a satisfactory adjustment of the mathematical model to the test data indicating a very significant response model.

2.2.2. Optimization of Synthesis Parameters. The three-dimensional response surfaces were modeled based on eqs 1 and 2 (Figure 3). The response surfaces were based on the model, keeping two variables constant at the optimum level while varying the other two within the experimental range. The various effects of the independent variables on the K₂O content and yield of UPK can be graphically observed from the response surfaces and contours. In this study, changes in the reaction temperature or time did not significantly affect the levels of the UPK yield, while the molar number of potassium resulted in a significant adverse effect on the yield of UPK (Figure 3). It can be observed from the stereogram and contours of the response surface that the interaction between the concentration of phosphate and the reaction temperature was significant (Figure 3a). The surface demonstrated the interactive effects of the concentration of phosphate and reaction temperatures and suggested that the levels of yield of UPK increased with the increasing concentration of phosphate and increased first and then decreased with the increasing reaction temperature.

Based on the significant interaction between the KCl molar number and concentration of phosphate for a given concentration of phosphate, the levels of K₂O content of UPK increased with the increasing KCl molar number substantially. However, considering the concentration of phosphate, the K₂O content of UPK finally increased slowly (Figure 4). In this study, changes in the reaction temperature or time did not significantly affect the levels of K₂O content of UPK (Figure 4). Using 3D graphics can be done not only to represent interactions but also used to recommend the interpretation of models and experimental results and support these suggestions from other authors.

2.2.3. Verification of the Predictive Model. According to Figures 3 and 4, it could be deduced that the optimum reaction conditions when the K₂O content and yield of UPK were both the highest are as follows: reaction time (C) of 60 min, KCl molar number (D) of 0.32 mol, reaction temperature (E) of 78 °C, and concentration of phosphoric acid (F) of 70%. Under optimal conditions, the predicted values of the K₂O content and yield of UPK were 3.51 and 69.8%, and the experiment K₂O content and yield of UPK were 3.42 ± 0.35% and 67.58 ± 1.25%, respectively. The strong correlation between the predicted and actual results confirmed that the response model was adequate to reflect the expected optimization.

2.3. Characterization of UPK. Thermogravimetry (TG) curves of UP, UPS, UPK, and urea in this study are shown in Figure 5. The weight loss of urea at 36–345 °C was 100%. The weight losses within the temperature range of 36–800 °C were approximately 67.0 and 71.7% for UP and UPS, respectively. The TG curves of UP and UPS completely overlapped by heating from 36 to 630 °C. However, the weight loss of UP decreased by 4.7% compared with that of UPS from 630 to 800 °C, which may be due to the presence of trace metal ion impurities during the thermal process of phosphoric acid. The weight loss of UPK at 36–800 °C was 53.1%, which was 18.6%
lower than that of the UPS. It can be attributed to the melting point of KCl at 770 °C.

Compared with UP and UPS, the diffraction peak intensity of UPK decreased and the width increased, indicating that KCl induced shrinkage distortion (Figure 6). The lattice constant for both the UP and the UPS was 3.800 Å; however, it reduced to 3.796 Å after KCl was added, resulting in lattice distortion of the crystal. The morphologies of UPK, UP, and UPS were characterized using a microscope (Figure 7). The crystal shapes of UP and UPS were regular crystal structures, but the crystal structure of UPK was amorphous, and the aspect ratio of the crystals was reduced, which was consistent with the results of XRD.

The elemental spectrum of UP, UPS, and UPK are shown in Figure 8. There was no potassium in UP and UPS, only in UPK. By comparing with Figure 8I-d,f,II-d,f,III-d,f, energy-dispersive X-ray analysis confirmed that KCl was evenly distributed in UPK.

2.4. Determination of UPK Flowability. The angle of repose refers to the maximum angle that can be formed on the free surface of particle accumulation under a static state, and the smaller the angle is, the better the fluidity of particle is. Figure 9 illustrates the results of the repose angle of UP, UPS, and UPK. It was also found that the resting angles of UP and UPS were 24.1° and 23.9°, respectively, both of which were higher than those of UPK (angle of repose of 21.9°). Therefore, after being modified by KCl, a friction decrease and fluidity increase of the crystal occurred. Compared with UP and UPS, the repose angle of UPK was reduced by 2.2° and 2.0°, respectively. Combined with the microscope images (Figure 7) of crystalline granules, we can see that the addition of KCl changes the aspect ratio of the crystal, which reduces the repose angle of crystalline granules, thus increasing the fluidability of UPK.

2.5. Performance of UPK as a Fertilizer for Summer Maize Growth. Total P use efficiency of summer maize in DAP and UPK treatments were 10.00% and 27.45%, respectively (Table 2). ANOVAs for the Regression Models: (C) Reaction Time, min; (D) KCl Molar Number, mol; (E) Reaction Temperature, °C; and (F) Concentration of Phosphoric Acid, %
respectively (Table 3). The UPK had a significantly increased total P use efficiency by 17.45% over DAP. In this study, the UPK treatment achieved the maximum yield while PCK treatment achieved the lowest yield. Compared with DAP, the yield of UPK treatments increased significantly by 25.58%, and seeds per panicle increased significantly by 31.25%. The aboveground plant biomass (dry matter) was significantly affected by different P fertilizer treatments. The aboveground biomass of UPK treatments was 10.74% greater significantly than that of DAP.

The effect of different phosphorus applications on the soil available phosphorus content in different periods of maize was highly significant (Figure 10A), and the application of the phosphate fertilizer significantly increased the content of available phosphorus in soil. Compared with DAP treatment, the content of available phosphorus in soil treated with UPK was significantly increased by 37.38% during the 12-leaf stage of summer maize. From the 12-leaf stage to the mature stage of summer maize, the available nutrients in soil were transformed into crop biomass, which resulted in the decrease of the

Figure 3. (a–f) Response surface plots showing the interactive effects of the reaction time, KCl molar number, reaction temperature, and concentration of phosphoric acid on the yield of UPK. (a) Concentration of phosphoric acid and reaction temperature, (b) reaction temperature and KCl molar number, (c) reaction temperature and reaction time, (d) KCl molar number and reaction time, (e) concentration of phosphoric acid and KCl molar number, and (f) concentration of phosphoric acid and reaction time.
available nutrient content in soil. During the maturity stage, the soil available P treated with UPK was significantly higher than that treated with DAP by 24.41%. The pH value is an important index to measure the soil environment in saline-alkali land. The pH value of soil treated with UPK was significantly lower than that of other treatments (Figure 10B). During the harvest period, the soil pH value of UPK treatment was 3.98 and 3.46% lower significantly than that of DAP and PCK treatment, respectively, confirming that UPK significantly reduced soil pH and improved soil quality. Soil acid phosphatase can catalyze the hydrolytic cracking of ester phosphorus bonds of soil organophosphorus compounds, release the corresponding alcohol and inorganic phosphorus, and improve the effectiveness of soil phosphorus. For UPK treatments, soil acid phosphatase activity at the 12-leaf stage was increased significantly by 41.25% in comparison with the DAP (Figure 10C).

Overall, UPK reduced the soil pH, improved the microdomain environment of the maize rhizosphere and increased the activity of soil acid phosphatase in maize rhizosphere soil.

Figure 4. (a–f) Response surface plots showing the interactive effects of the reaction time, molar number of KCl, reaction temperature, and concentration of phosphoric acid on the K₂O content of UPK. (a) Concentration of phosphoric acid and reaction temperature, (b) reaction temperature and KCl molar number, (c) reaction temperature and reaction time, (d) KCl molar number and reaction time, (e) concentration of phosphoric acid and KCl molar number, and (f) concentration of phosphoric acid and reaction time.
further increasing soil available P and the yield of summer maize in alkaline soil.

3. CONCLUSIONS

UPK was prepared by the addition of KCl to modify UP successfully. A statistically based method using BBD was applied to develop a second-order regression model. The high adequacy of the model was proven by fitting the experimental and predicted values. Statistical analysis showed that the molar number of KCl and concentration of phosphoric acid presented significant positive effects on the yield and K$_2$O content of UPK, respectively. The optimal conditions obtained using BBD was as follows: reaction time (C) of 60 min, molar number of KCl (D) of 0.35 mol, reaction temperature (E) of 78 °C, and concentration of phosphoric acid (F) of 70%. Under optimal conditions, the predicted values of the K$_2$O content and yield of UPK were 3.51% and 69.8%, while the experimental K$_2$O content and yield of UPK were 3.42 ± 0.35% and 67.58 ± 1.25%, respectively. The addition of KCl changed the crystal shape of UP, reduced the aspect ratio of the crystal shape, and increased the crystal fluidity, which was conducive to industrial production. Compared with the conventional phosphorus fertilizer (DAP), UPK significantly reduced the soil pH and soil acid phosphatase activity and increased the soil phosphorus supply intensity and further increased the maize yield and the utilization rate of phosphorus in season.

Thus, the novel KCl-modified urea phosphate technology has a huge potential for large-scale applications to satisfy the increasing demand for urea phosphate on saline-alkali soil in the future, which can enhance the sustainability of agricultural systems and the environment.

4. EXPERIMENTAL SECTION

4.1. Materials. Urea (AR) and KCl (AR) were purchased from Tianjin Kaitong Chemical Industry Co., Ltd. (Tianjin,
China). Phosphoric acid (AR; w (P₂O₅) 85%) and urea phosphate standard (UPS) (AR) were purchased from Shanghai Macklin Co., Ltd.

4.2. Preparation of UPK. First, phosphoric acid with a concentration of 30−70% was poured into a three-neck flask and heated in a constant-temperature water bath to a temperature of 50−90 °C. Then, appropriate amounts of urea and potassium chloride (0−0.45 mol) were added and stirred at a speed of 150−350 r/min for 30−80 min. The molar ratio of phosphoric acid to urea ranges from 1:0.90 to 1:1.10. After the reaction, the solution was poured into a clean glass beaker and placed in an incubator at 5 °C for crystallization for 24 h. The crystals were filtered, washed with water, and dried to a constant weight (W1) at 60 °C in the drying box, and the yield was calculated according to eq 3 where W corresponds to the total mass of all the reactants.

\[
yield (\%) = \frac{W_1}{W}\tag{3}
\]

4.3. Characterizations of UPK. K₂O contents of UPK were determined by the sodium tetraphenylborate method. X-ray diffraction patterns were recorded using a Rigaku RINT 2200/PC diffractometer with Cu Kα radiation at 30 kV and 30 mA; the 2θ angle ranged from 15° to 35° with a scanning rate of 1°/min. Thermogravimetric analyses were conducted using NETZSCH STA 449 F3 Jupiter in an aluminum pan with a heating rate of 10 °C/min from room temperature to 800 °C under an air flow. The surface elemental compositions and distributions were measured with an energy-dispersive X-ray spectroscopy (EDX) detector attached to the SEM. The crystal morphology was observed with a microscope, and photographs were taken by a biomicroscope with a digital camera.

4.4. Measurement of Flow Performance. A volume of 100 mL of UP, UPS, and UPK particles was added to an angle-of-repose tester (FBS104, FURBS, China), and the angle of repose (ϕ) was determined by the particle accumulation height (h). The sample accumulation angles were calculated according to eq 4. This procedure was repeated five times, and the results were averaged.

\[
ϕ = \left(\arctan\left(\frac{h}{r}\right)\right) \times 180/\pi\tag{4}
\]

Figure 8. Elemental spectrum of UP (I), UPS (II), and UPK (III). (a) SEM image, (b) nitrogen distribution, (c) phosphorus distribution, (d) potassium distribution, (e) oxygen distribution, and (f) chlorine distribution.

Figure 9. Repose angles of UP, UPS, and UPK.

Table 3. Yield, Yield Components, Aboveground Biomass, and Total P Use Efficiency of Summer Maize under Different P Fertilizer Treatments

| treatment | grain yield (g/p) | yield increase vs DAP treatment (%) | aboveground biomass (g/p) | number of spikes (p⁻¹) | seeds per panicle (p⁻¹) | 100-grain weight (g) | total P use efficiency (%) |
|-----------|------------------|------------------------------------|---------------------------|------------------------|------------------------|------------------------|--------------------------|
| PCK       | 158.9c           | −22.28                             | 366.7bc                   | 13.75b                 | 33b                    | 30.68a                 | 10.00b                   |
| DAP       | 204.4b           |                                    | 390.8b                    | 14ab                   | 32b                    | 31.33a                 | 27.45a                   |
| UPK       | 256.7a           | 25.58                              | 432.8a                    | 15a                    | 42a                    | 31.68a                 | 27.45a                   |

“Means followed by the same letters within the same column were not significantly different by Duncan multiple range tests (p < 0.05). The total P use efficiency was calculated based on the following formula: [total P use efficiency (%) = (total plant P uptake from P treated plants) − (total P uptake from plants receiving no P fertilizer)/(total applied fertilizer P in the P treatment × 100)].

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4.5. Experiment Design. 4.5.1. Single-Factor Experiment. The yield of UPK depends on the reaction temperature, reaction time, KCl molar number, concentration of phosphoric acid, and molar ratio of phosphoric acid to urea. The effects of different factors on the yield of urea potassium phosphate were studied by a single-factor test, and the appropriate independent variables and levels were determined. The method of the single-factor experiment is to change one factor within a certain range so that all other factors remain unchanged. The operating conditions were as follows: stir speed (150, 200, 250, 300, and 350 r/min), reaction temperature (50, 60, 70, 80, and 90 °C), reaction time (30, 40, 50, 60, and 80 min), KCl molar number (0, 0.05, 0.15, 0.25, 0.35, and 0.45 mol), molar ratio of phosphoric acid to urea (1:0.90, 1:0.95, 1:1, 1:1.05, and 1:1.10), and concentration of phosphoric acid (30, 40, 50, 60, and 70%).

4.5.2. BBD and Statistical Analysis. Based on the results of single-factor experiments, independent variables that significantly influenced the yield and K2O content of UPK and the right levels were selected. Box–Behnken design (BBD) was a class of rotatable or almost rotatable second-order design based on incomplete factor design, which represents the level of variables in −1, 0, and 1. A four-factor and three-level Box–Behnken design was carried out. The number of experiments required to develop BBD (N) is defined as \( N = 2^k (2k - 1) + C_0 \) where \( k \) is a factor and \( C_0 \) is the number of central points. A total of 29 experiments \( (N = 29) \) were required for BBD with four factors \( (k = 4) \) and five central points \( (C_0 = 5) \). A statistical software package, Design-Expert (version 11.1.2.0), was used to analyze the BBD matrix, determine the regression coefficient of the second-order multiples according to experimental data, and represent the fitted polynomial equation in the form of a three-dimensional surface graph to illustrate the relationship between the response and the experimental level of each variable examined in this study. The statistical significance test of the model coefficient was determined by the application of ANOVA. In all analyses, \( p < 0.05 \) was considered significant and \( p < 0.01 \) was considered highly significant.

P. Use Efficiency. The influence of UPK on plant growth was investigated using summer maize (seed named “Zhengdan 958”). The experiment was carried out at the new fertilizer test station of Shandong Agricultural University (SDAU), Tai’an, Shandong, China, from June 13 to September 26, 2018. Each pot (diameter of 30 cm and height of 36 cm) was filled with 20 kg of soil. Soil samples were obtained from Wudi County in the Shandong Province, China (37.73N, 117.92E), at 0–20 cm in depth. The main properties of the soil are the following: pH 7.82, organic matter content of 7.69 g/kg, soil total N of 0.50 g/kg, soil total P of 1.83 g/kg, soil total K of 35.9 g/kg, NO3−-N of 75.0 mg/kg, NH4+-N of 10.6 mg/kg, available phosphorus of 14.0 mg/kg, and available potassium of 186.0 mg/kg. The soil is classified as Parasalic Ochri-Aquic Cambosols.

The three fertilizer treatments were no-fertilizer control (PCK) (treatment 1), traditional phosphate fertilizer (diammonium phosphate, DAP, N–P2O5–K2O, 18-44-0) (treatment 2), and urea phosphate potassium (UPK, N–P2O5–K2O, 14-42-4) (treatment 3). The same amount of N (5.40 g of N/pot) and potassium (3.6 g of K2O/pot) were applied to each pot as base fertilizers, while two P rates (0 and 1.80 g of P2O5 pot−1) were used. All fertilizers were applied in a single dose at the time when the seeds were planted. Diseases, pests, and weeds were well controlled by managers as needed.

Soil samples were collected from the root zone at the maize 12-leaf and maturity stage then air-dried and passed through a 2 mm sieve. Fresh soil samples were collected, and soil acid phosphatase was determined by enzyme-linked immunoassay (ELISA) in the maize 12-leaf period. The soil available phosphorus content (0.5 M NaHCO3) was determined by an automatic chemical discontinuity analyzer (AMS Smartchem 200, Italy). Soil pH values were measured by a pH meter (soil to water ratio of 1:2.5; PHS-3C, Precision Scientific Instrument Co, Shanghai, China). After plants were harvested, the plant dry biomass was determined by oven drying at 80 °C to a constant weight and then ground and passed through a 425 μm sieve. The plant sample was decomposed by a H2SO4/H2O2 method, and the total P concentration was measured using the automated chemistry analyzer (AMS Smartchem 200, Italy).

4.6. Statistical Analysis. All data were subjected to analysis of variance using SPSS software (SPSS 22, U.S.A.) followed by mean comparison using Duncan’s multiple range test \( (p < 0.05) \).

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Figure 10. Effect of different fertilizer treatments on the (A) soil available P at the 12-leaf and maturity stage, (B) soil pH at maturity, and (C) soil acid phosphatase at the 12-leaf stage. Note: Means followed by the same letters on the bar at each were not significantly different by Duncan multiple range tests \( (p < 0.05) \).
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