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Applying and Optimizing Water-Soluble, Slow-Release Nitrogen Fertilizers for Water-Saving Agriculture

Yanle Guo, Min Zhang,* Zhiguang Liu,* Chenhao Zhao, Hao Lu, Lei Zheng, and Yuncong C. Li

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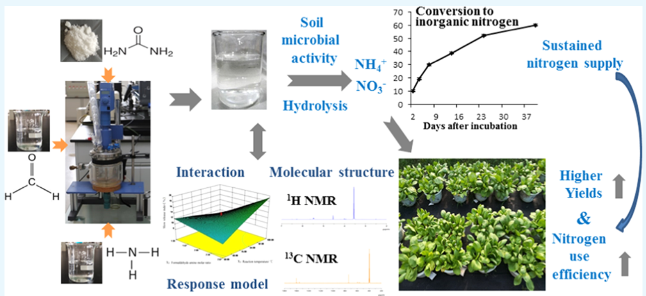
ABSTRACT: A novel, eco-friendly, water-soluble, slow-release nitrogen fertilizer was developed to enhance water solubility and nitrogen use efficiency. A test was performed to determine the interactive effects of process parameters using a central composite design and response surface methodology. The quadratic polynomial mode for slow-release nitrogen was determined and yielded differences ($p < 0.01$). The soluble, slow-release nitrogen fertilizers were analyzed using nuclear magnetic resonance, and the release characteristics of soil nitrogen from the fertilizer at 25 °C were also determined. The effects of the fertilizer on plant growth were determined using rape (*Brassica campestris L.*) outdoors. Conversion rates from the fertilizer to inorganic nitrogen were 30.0, 52.2, and 60.0% at 7, 24, and 40 days, respectively. This soluble, slow-release nitrogen fertilizer resulted in increased yields and nitrogen use efficiencies in rape plants compared with a standard urea fertilizer. The yields of rape plants treated with a mixture of the fertilizer and urea (BBW100%) were significantly higher than all of the other treatments. When the nitrogen application rate was reduced by 20%, the resulting "SSNF80%" and "BBW80%" treatments produced nearly the same yields as "UREA100%". Nitrogen use efficiencies for treatments with the study fertilizer ("SSNF") and the mixture bulk blend fertilizer ("BBW") were significantly higher than that with urea ("UREA") treatment by 37−52 and 42−43%, respectively. Hence, the fertilizer showed great potential for improving the production of rape and possibly other crops.



1. INTRODUCTION

Supplying good nitrogen levels is important for producing high-quality crops as nitrogen is the most important element for crop growth and yield.[1,2] However, low nitrogen use efficiency is a common problem worldwide,[3] resulting from improper fertilization, surface runoff, leaching, volatilization,[4] nitrification, and denitrification.[5,6] These issues may also lead to environmental problems such as water eutrophication, groundwater pollution, and excessive greenhouse gas emissions.[7] Controlled- or slow-release nitrogen fertilizers have been shown to increase nitrogen use efficiencies while being economical and eco-friendly.[8,9]

In general, vegetative plants like *Brassica campestris L.* are made up of 90−95% water. Water is critical to horticultural production and is required in large quantities for high crop quality.[10] However, most water is nonrenewable and scarcity of water is a worldwide issue.[11,12] To help alleviate these problems, considerable research attention has been recently focused on the development of water-efficient agricultural techniques such as the combined application of water and fertilizer.[13,14] Unfortunately, most of the slow-release nitrogen fertilizers developed for mixing with irrigation water were unsuitable for use in drip and sprinkling irrigation.[15] Many fertilizers are insoluble and coated with nitrogen[16] or are polymeric compounds such as urea formaldehyde,[17] which have very low solubility in water. Thus, developing water-soluble, slow-release, efficient, and environmentally friendly nitrogen fertilizers has become very important. Simultaneously, the rapid development of fertilizer manufacturing has created new opportunities to feasibly obtain and use soluble, slow-release nitrogen fertilizers.[18,19]

Liquid fertilizers based on urea formaldehyde and containing cyclic triazone structures have become widely used for providing slow-release soil nitrogen.[20] They have been produced by organic synthesis combining urea, formaldehyde, and amines under specific temperatures, reaction times, and molar ratios. The resulting products could be degraded by microorganisms; hence, they were environmentally friendly.[21] However, most of the research supporting these fertilizer characteristics were of single-factor or orthogonal design. The tests could not obtain second-order polynomials showing relationships between independent and dependent variables, and the resulting fertilizer solutions may not have been ideal (optimized) under synthetic conditions. During fertilizer

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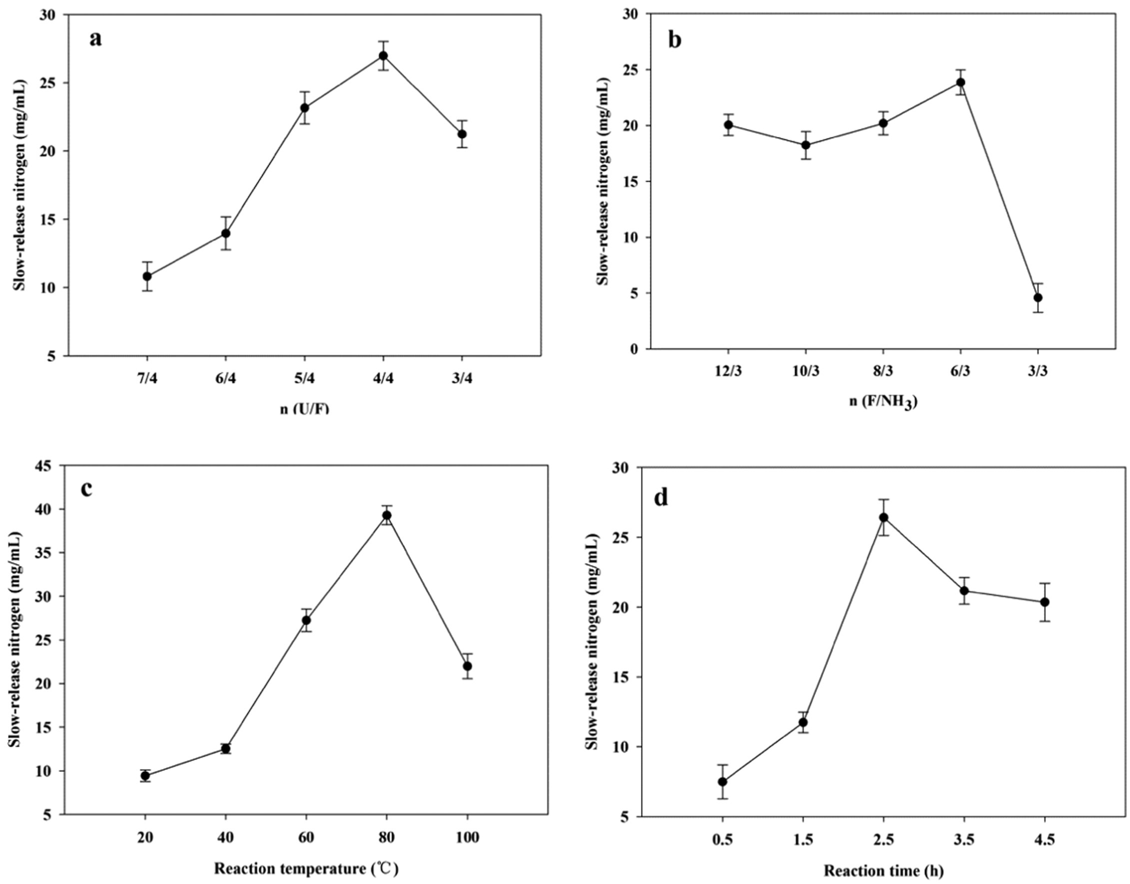

Figure 1. Effects of each reaction factor on the levels of slow-release nitrogen. (a) Effects of the urea/formaldehyde ratio on the levels of slow-release nitrogen; (b) effects of formaldehyde:amine ratio on the levels of slow-release nitrogen; (c) effects of reaction temperature on the levels of soil nitrogen; and (d) effects of reaction time on the levels of slow-release nitrogen.

manufacturing, different levels of polymerization result in different slow-release periods. This has rarely been reported, but it is essential for the manufacture of fertilizers with release periods targeted to specific crops and their growth periods. The response surface method has been proven helpful in addressing these problems.[22−24] But its use in optimizing and analyzing the interaction of liquid fertilizers with urea formaldehyde and with cyclic triazone structures has been rarely reported.

The objectives of this study involving the synthesis of soluble, slow-release nitrogen fertilizers were as follows: (1) to find the best manufacturing and production techniques using single-factor experiments and the response surface method; (2) to find the optimal molar ratios of urea/formaldehyde and formaldehyde/amine as well as ideal reaction temperatures and times; (3) to determine a quadratic, polynomial model if there are interactions between the two measured variables; (4) to determine the molecular structures and release characteristics of the fertilizers using nuclear magnetic resonance analyses and soil incubation; and (5) to find the effects of the fertilizers on the growth of containerized rape plants.

2. RESULTS AND DISCUSSION

2.1. Effects of Reaction Factors on the Slow-Release Nitrogen Fertilizers. At 60 °C and a 2.5 h reaction time, the slow-release nitrogen levels initially increased and then decreased with a reduction in the urea/formaldehyde ratio, with the minimum value of 7:4 and maximum values of 5:4 and 3:4 (Figure 1a). Hence, the optimal urea/formaldehyde ratio was between 5:4 and 3:4. The maximum slow-release nitrogen levels occurred when the formaldehyde/amine ratio was between 8:3 and 3:3 (Figure 1b). With increasing reaction temperature between 60 and 100 °C, the amount of slow-release nitrogen produced increased and then decreased, suggesting the maximum value (and most suitable reaction temperatures) was within this range (Figure 1c). Levels of slow-release nitrogen also initially increased and then decreased with time, suggesting maximum levels of slow-release nitrogen would occur within a reaction time of 1.5−3.5 h (Figure 1d).

2.2. Response Surface Method. The test involved using variables independent of urea/formaldehyde and formaldehyde/amine ratios, reaction time, and temperature. Analyses were performed with the Central Composite Design principle and Design-Expert 8.0.6 statistical software. Thirty combinations of independent variables were tested, and the results are determined (Table 1).

2.2.1. Effects and Significance of Reaction Factors on Slow-Release Nitrogen Fertilizers and on the Validity of the Models. As it is a chemically synthesized fertilizer, the release period was affected by the degree of polymerization. There has been previous research & development effort into this slow-release fertilizer, but the in-depth research of forecasting mathematical models was not enough.[25−27] To determine the effects of reaction factors on the dependent variable (slow-release nitrogen), regression analyses were performed (Table

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Table 1. Results of Using the Response Surface Method (equation 1)

	independent variables[a]			dependent variables[b]
run	AN (mg/mL)	UN (mg/mL)	TN (mg/mL)	SRN (mg/mL)
1	19.32	94.40	169.57	55.85
2	22.39	182.81	214.23	9.02
3	20.33	108.10	160.83	32.41
4	25.81	185.76	215.70	4.13
5	21.44	119.94	176.85	35.47
6	27.93	162.18	201.12	11.01
7	24.34	102.22	171.35	44.78
8	30.42	172.00	237.85	35.43
9	22.98	125.83	169.89	21.08
10	30.70	184.83	221.67	6.14
11	21.16	140.57	187.53	25.79
12	29.87	206.35	244.48	8.26
13	33.33	182.81	228.26	12.12
14	16.83	99.31	125.63	9.49
15	22.17	112.08	170.22	35.97
16	25.83	157.13	223.93	40.97
17	14.96	87.49	141.90	39.45
18	33.95	216.17	256.13	6.01
19	47.14	124.82	185.91	13.95
20	25.56	155.30	217.95	37.08
21	20.49	170.00	206.78	16.29
22	28.48	163.16	222.80	31.16
23	23.72	163.09	218.11	31.29
24	26.51	159.18	208.33	22.64
25	25.21	152.36	206.62	29.05
26	25.38	159.20	208.56	23.99
27	26.68	159.18	208.89	23.02
28	23.75	158.18	206.62	24.69
29	21.03	149.41	197.88	27.44
30	24.04	160.22	212.77	28.51

[a]Ammonium nitrogen (AN), urea nitrogen (UN), and total nitrogen (TN). [b]Slow-release nitrogen (SRN).

3). The regression model for slow-release nitrogen (Y_1) resulting from the ratios of urea/formaldehyde (X_1) and formaldehyde/amine (X_2), reaction temperature (X_3), and time (X_4) was calculated (eq 1).

$$\begin{aligned} Y_1 = {} & 283.601 - 158.908X_1 - 59.783X_2 - 1.613X_3 \\ & - 37.514X_4 + 14.437X_1X_2 + 0.952X_1X_3 \\ & + 19.704X_1X_4 + 0.516X_2X_3 + 5.296X_2X_4 \\ & + 0.037X_3X_4 - 14.844X_1^2 - 0.517X_2^2 \\ & - (1.699\text{E} - 3)X_3^2 + 0.131X_4^2 \end{aligned} \tag{1}$$

Correlation coefficients r^2 and adjusted r^2 were also determined with r^2 adjusted for the number of model parameters relative to the number of points in the test (eq 1).[28] For Y_1, r^2 was 96.97%, indicating a high correlation between predicted and experimental values (Figure 2).[29] The independent variables (X_1, X_2, X_3, and X_4) also resulted in very good correlations between the observed and predicted values for Y_1 as shown by the high adjusted r^2 (94.14%) (Table 2). The residuals tended to cluster around a diagonal line, representing the predicted result, which suggested that the assumptions of normality were correct (Figure 3).[30] Analysis of

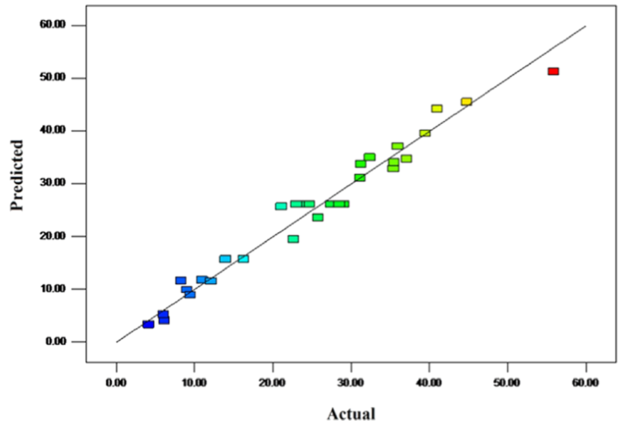

Figure 2. Correlation between predicted and actual values based on eq 1.

variance (ANOVA) results for the models of dependent variables were extremely significant for slow-release nitrogen (Y_1, Table 2). The lack-of-fit results for slow-release nitrogen (Y_1) were insignificant (p = 0.2606); hence, the model fit the data well.[31]

High values of F (low p values) for a term in the model often indicated that the term had a strong effect on the response variable and hence on the model.[32] Levels of significance for individual effects from linear, interaction, and quadratic sources or models were also examined. All of the linear and interaction terms were significant except for X_3X_4, and the significant terms had positive interactions (Table 2). Here, the most highly significant term was the urea/formaldehyde molar ratio. The following represents the "hierarchy" from most to least significant of the variables analyzed: urea/formaldehyde > formaldehyde/amine > reaction time > reaction temperature.

2.2.2. Interactive Analyses. In the response surface method, three-dimensional graphs (surfaces) show interactions, responses, and other effects produced by two independent variables and can greatly facilitate the interpretation of models and test results.[33] The present study successfully used the response surface method to illustrate and help interpret the results (Figure 5). Statistics for response surfaces indicated that the interactions between urea/formaldehyde (X_1) and formaldehyde/amine (X_2) on slow-release nitrogen (Y_1) and on X_1X_2 were significant (Figure 4). When X_1 remained unchanged, slow-release nitrogen (Y_1) increased with slightly increasing X_2 (Figure 4a). Here, with X_2 a constant (2.67), Y_1 increased gradually, while X_1 decreased to its minimum (0.75), where Y_1 was maximum. The interaction of X_1 and X_3 on Y_1 also was significant (Figure 4b). Here, at any constant X_3, low-release nitrogen (Y_1) increased gradually with decreasing X_1, but when X_3 was at its minimum (60 °C), Y_1 reached its maximum. At this minimum, also for X_1 (0.75), Y_1 decreased slightly with increasing X_3. With X_1 at its maximum (1.25), Y_1 increased slightly with increasing X_3. Based on the levels of slow-release nitrogen (Y_1), the interaction of X_1 and X_4 was also significant (Figure 4c). When X_4 was held at 1.5 h, Y_1 increased gradually with decreasing X_1 and reached its maximum value at X_1 = 0.75. At this minimum for X_1, Y_1 decreased with increasing X_4. But when X_1 was held at its maximum (1.25), Y_1 remained unchanged with changing values of X_4. A significant interaction occurred between X_2 and X_3 for Y_1 (Figure 4d). With X_2 = 2.67, Y_1 increased with increasing X_3 and reached its maximum value at X_3 = 100; with

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Table 2. ANOVA Results for Analyses by Response Surface Quadratic Models for the Slow-Release Nitrogen Fertilizer[a]

source	sum of squares	mean square	F	Df	p	significance
model (Y_1)[b]	4820.06	344.29	34.27	14	<0.0001	*
X_1	1766.41	1766.41	175.83	1	<0.0001	*
X_2	539.69	539.69	53.72	1	<0.0001	*
X_3	354.99	354.99	35.34	1	<0.0001	*
X_4	305.22	305.22	30.38	1	<0.0001	*
X_1X_2	93.57	93.57	9.31	1	0.0081	*
X_1X_3	362.39	362.39	36.07	1	<0.0001	*
X_1X_4	388.23	388.23	38.65	1	<0.0001	*
X_2X_3	763.9	763.9	76.04	1	<0.0001	*
X_2X_4	201.41	201.41	20.05	1	0.0004	*
X_3X_4	9	9	0.9	1	0.359	NS
X_1^2	23.61	23.61	2.35	1	0.1461	NS
X_2^2	1.48	1.48	0.15	1	0.7069	NS
X_3^2	12.67	12.67	1.26	1	0.2791	NS
X_4^2	0.47	0.47	0.047	1	0.8318	NS
residual	150.69	10.05	----	15	----	----
lack of fit	118.44	11.84	1.84	10	0.2606	NS
pure error	32.25	6.45	----	5	----	----
cor. total	4970.74	----	----	29	----	----

[a]Significant (*), not significant (NS), not available or applicable (----). [b]Y_1: r^2 = 0.9697, Adj-r^2 = 0.9414, pre-r^2 = 0.8534.

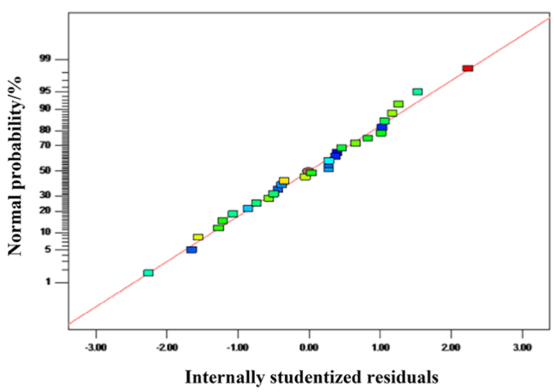

Figure 3. Slow-release nitrogen: probabilities for normal distributions of internally studentized residuals.

this value held constant, Y_1 decreased with decreasing X_2. When X_3 was at its minimum (60 °C), Y_1 remained unchanged with changing X_2 values. Significant interaction also occurred between X_2 and X_4 for slow-release nitrogen (Y_1) (Figure 4e). With X_4 held at 3.5 h, Y_1 increased with increasing X_2. When X_2 was held at its maximum (2.67), Y_1 remained unchanged with changing X_4 values. But with X_2 at its minimum (1.33), Y_1 increased with decreasing X_4. The interaction of X_3 and X_4 was not significant for Y_1, as suggested by the gentle slope on its response surface (Figure 4f). At each level of X_4, Y_1 increased with increasing X_3, and at each level of X_3, Y_1 increased with decreasing X_4.

2.3. Characterization and NMR Analyses. To further support findings such as the formation of slow-release fertilizer polymers, a sample from the response surface method test was subjected to ^1H NMR spectral analyses, and the molecular structure of the fertilizer was determined (Figure 5). The sample was chosen because it yielded the highest values for slow-release nitrogen (Y_1) and hence was considered the optimized fertilizer product. The total slow-release nitrogen of the optimized fertilizer product was 55.85 mg/mL, which was obtained using stable chemical substances with colorless transparent liquid and no mechanical impurities. This fertilizer was put forward as a new technology to solve the problem of low water and fertilizer use efficiency, and it was suitable for the combined applications of water and fertilizer. The ^{13}C NMR spectrum of the fertilizer revealed that it mainly contained carbon in alkyl and aliphatic molecules because all subsamples had peaks within resonance areas for these carbon forms (0−50 and 0−110 ppm, respectively) (Figure 6). The carbon atoms within alkyl molecules may have resulted from their simultaneous occurrence within aliphatic carbons in alkyl chains. Signals for aliphatic carbon atoms apparently replaced by nitrogen or oxygen were often observed within the *O*-alkyl C region (50−110 ppm).[34] For example, a signal within this region at 74.06 ppm indicated the presence of nitrogen and oxygen.

2.4. Nitrogen Release Characteristic of the Fertilizer. The release characteristics of soil nitrogen from the fertilizer at 25 °C were determined (Figure 7). Percentages of the fertilizer converted to inorganic nitrogen were 30.0, 52.2, and 60.0% at 7, 24, and 40 days, respectively. This indicated good nitrogen release and suitability for absorption by rape plants throughout the growing season. By contrast, as one of the solid slow-release fertilizers, the cumulative release of N from polymer-coated urea reached 88% after 140 days of submergence in 25 °C water,[35] and its characteristics were unsuitable for the rape plants and the combined applications of water and fertilizer. This mainly resulted from the polymer structure and biodegradability of the fertilizer.[36]

2.5. Field Tests of the Fertilizer on the Growth of Rape Plants. Yields, nitrogen use efficiencies, and nitrate values were effective indicators of rape plant growth (Table 3). Yields of rape plants treated with a mixture of the fertilizer and urea (BBW100%) were significantly higher than those of all of the other treatments (Table 3). However, there were no significant differences between the treatments “UREA100%” and the fertilizer, “SSNF100%”. When the nitrogen application rate was reduced by 20%, the resulting “SSNF80%” and “BBW80%” treatments produced nearly the same yields as

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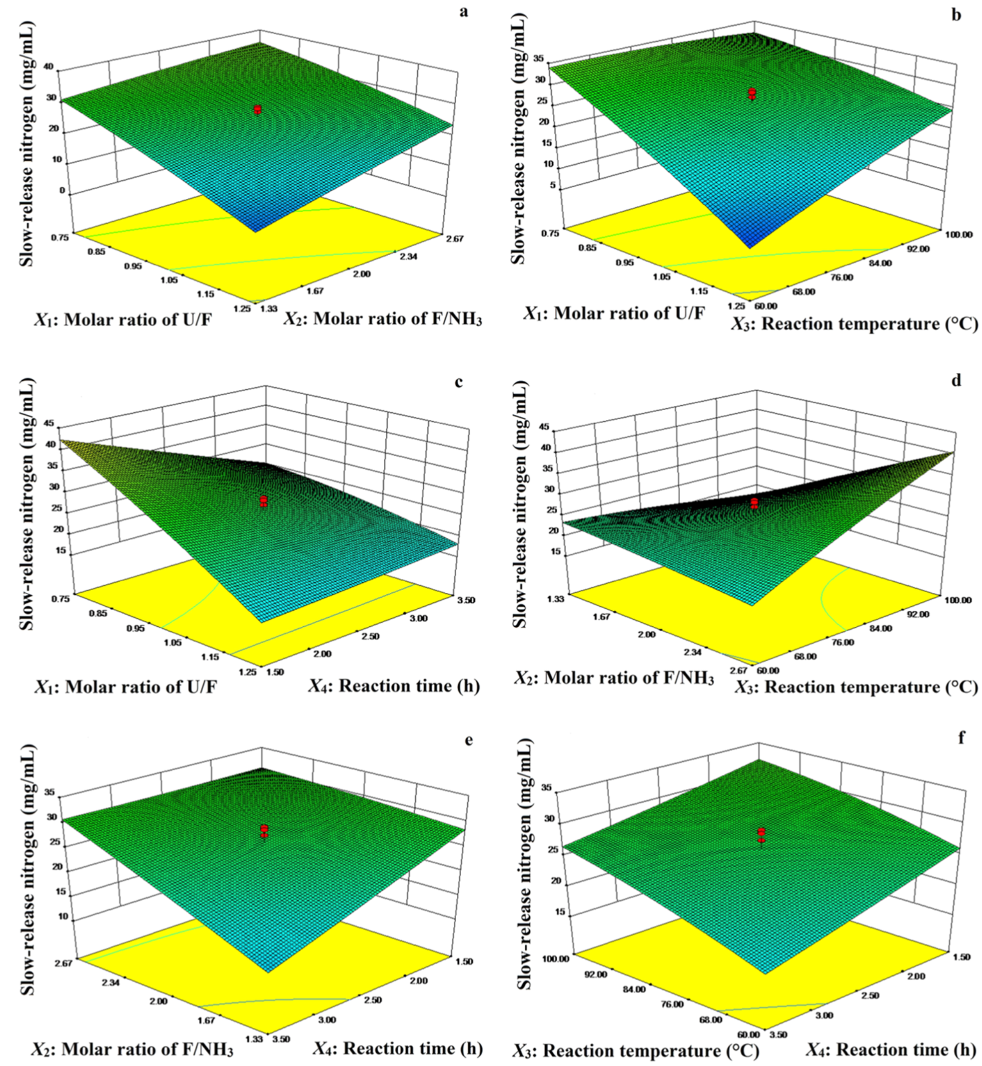

Figure 4. Response surfaces showing the effects of synthesis conditions on the levels of slow-release nitrogen. (a) Effects of urea/formaldehyde ratio and formaldehyde/amine ratio on slow-release nitrogen; (b) effects of urea/formaldehyde ratio and reaction temperature on slow-release nitrogen; (c) effects of urea/formaldehyde ratio and reaction time on slow-release nitrogen; (d) effects of formaldehyde/amine ratio and reaction temperature on slow-release nitrogen; (e) effects of formaldehyde/amine ratio and reaction time on slow-release nitrogen; and (f) effects of reaction temperature and reaction time on slow-release nitrogen.

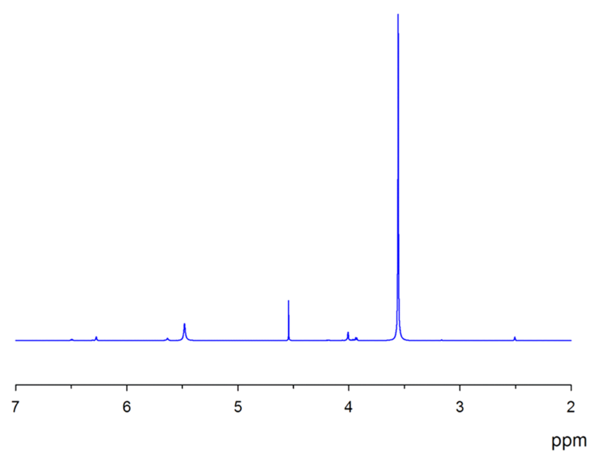

Figure 5. ^{1}H NMR spectrum for the soluble, slow-release nitrogen fertilizer.

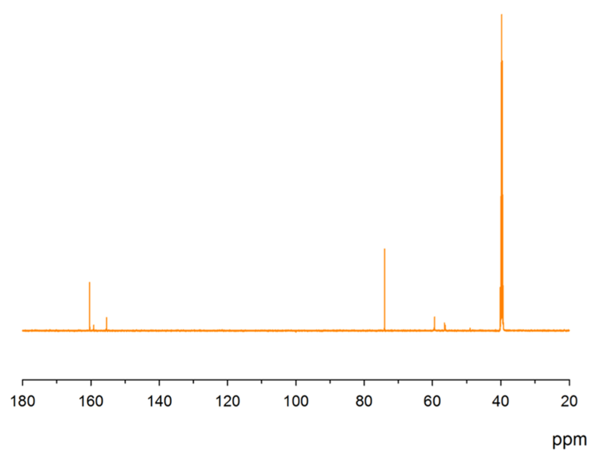

Figure 6. ^{13}C NMR spectrum for the soluble, slow-release nitrogen fertilizer.

UREA100%, though all three treatments produced significantly higher yields than the "UREA80%" treatment.

Nitrogen use efficiency has been found to effectively indicate the nitrogen recovery of crops.[37] We found that applying the

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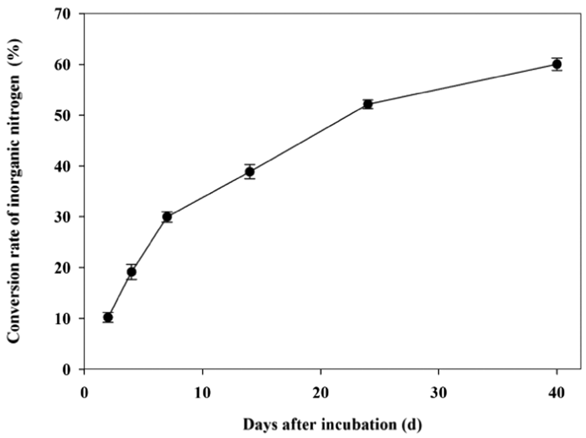

Figure 7. Rate of conversion from organic to inorganic nitrogen in 25 °C soil for the soluble, slow-release nitrogen fertilizer.

soluble, slow-release fertilizer can significantly increase the nitrogen use efficiency of rape plants. Nitrogen use efficiencies for the study fertilizer ("SSNF") and the mixture bulk blend fertilizer ("BBW") treatments were significantly higher than that for the urea ("UREA") treatment by 37–52 and 42–43%, respectively.

Nitrate contents of vegetable crops have been important in helping to evaluate product quality and safety, thereby affecting the health of consumers.[38] Excessive fertilization often results in levels of soil nitrogen too high for plants to completely absorb, which results in problems such as excessive weed growth, wasted fertilizer, and contaminated groundwater. By rational fertilization, the accumulation of excessive nitrate contents may be effectively curtailed. At each level of nitrogen fertilization, nitrate values for the SSNF100% and "BBW100%" treatments were significantly lower than that for the UREA100% treatment. At the 80% nitrogen rate, SSNF80% was significantly greater than UREA80%, which was significantly greater than BBW80%. The accumulation of excessive nitrate contents could be effectively curtailed using the SSNF fertilizer.

In the present study with rape plants, the soluble, slow-release nitrogen fertilizer significantly improved chlorophyll density (SPAD) by 4.4–10.9% on July 2, compared to urea fertilizer at the same nitrogen application rate (Table 4). Moreover, there were no differences between the study fertilizer and mixture treatments in the number of leaves and plant height. The SSNF treatments showed a steady supply of N throughout the rape growth period, and the SPAD value was higher compared to urea treatments at the initial stage.

Fertilization with the soluble, slow-release nitrogen fertilizer increased the soil inorganic nitrite content during the initial period. The following order shows that the hierarchy for soil nitrite increases from the most to the least effective treatments: SSNF100% (100% fertilizer) > BBW100% > BBW80% > SSNF80% (80% fertilizer) (Table 5). However, there were no significant differences between the treatments on July 10 and 18, 2017.

Soil contents of NH_4^+–N were significantly improved (18–19%) in combined fertilizer treatments compared to only urea at the same nitrogen application rates on July 18, 2017. However, there were no significant differences at other test periods.

All of the results showed that the soluble, slow-release nitrogen fertilizer had good release characteristics and promoted the growth of rape plants. This was shown by the increased yield, nitrogen use efficiency, chlorophyll density (SPAD), number of leaves per plant, plant height, and inorganic nitrogen levels.[35]

2.6. Cost Analyses. Synthesizing the soluble, slow-release nitrogen fertilizer mainly requires urea, formaldehyde, and ammonia: prices for these commodities were \$228/ton, \$240/ton,[39] and \$300/ton, respectively, with proportions of material used to make the fertilizer were 3:4:3. The production of soluble, slow-release nitrogen fertilizer does not consume any energy other than electricity in the chemical reactions. The finished fertilizer product costs about \$254/ton to produce.

3. CONCLUSIONS

Although synthesizing the fertilizer increased the cost per unit of nitrogen provided to plants, when combined with urea, the fertilizer improved the yields of rape plants and increased net profits. Conversion rates from the fertilizer to inorganic nitrogen were 30.0, 52.2, and 60.0% at 7, 24, and 40 days, respectively. Using the soluble, slow-release nitrogen fertilizer effectively increased yields and nitrogen use efficiencies and reduced the fertilizer production costs; hence, it has great potential for widespread use in agriculture.

4. MATERIALS AND METHODS

4.1. Materials. Formaldehyde (37% by weight, Tianli Chemical Reagent Co., Shanghai, China); ammonia water (26% by weight, Tianli Chemical Reagent Co., Shanghai, China); Urea, KOH, and hydrochloric acid solutions (Tianjin

Table 3. Yield, Nitrogen Use Efficiency, and Quality of Rape Plants[a]

treatment[b]	yield (g/container)	compared with UREA100% (%)	nitrogen content (mg/g)	nitrogen use efficiency (%)	compared with UREA100% (%)	nitrate (mg/kg)
control	245.33e	−24.36	32.61b			65.88e
UREA100%	324.33bc		44.59a	31.54b		125.73a
UREA80%	284.33d	−12.33	43.36a	30.22b	−4.20	97.42c
SSNF100%	339.00b	4.52	46.59a	43.34a	37.39	112.03b
SSNF80%	323.00bc	−0.41	44.06a	46.02a	45.88	130.98a
BBW100%	373.33a	15.11	42.53a	44.82a	42.08	105.41bc
BBW80%	307.33c	−5.24	43.91a	43.24a	37.06	80.30d

[a]Means within a column followed by different letters were significantly different based on one-way analyses of variance (ANOVAs) followed by Duncan tests for mean separation ($p < 0.05$). [b]Control (no fertilizer added), UREA100% or UREA80% (100 or 80% portions for urea), SSNF100% or SSNF80% (100 or 80% portions for water-soluble, slow-release nitrogen fertilizer), BBW100% or BBW80% (100 or 80% portions for a mixture of 70% SSNF and 30% urea).

Table 4. Analyses of Chlorophyll Density, Number of Leaves, Plant Height, and Variance of Rape Plants Subjected to Different Nitrogen Treatments[a]

treatment[b]	chlorophyll density (SPAD value)			number of leaves per plant			plant height (cm)		
	July 2	July 10	July 18	July 2	July 10	July 18	July 2	July 10	July 18
control	40.97d	33.17b	35.73d	6.00a	6.83c	7.00d	10.00d	15.97d	23.20b
UREA100%	44.57c	38.23a	40.97abc	7.00a	8.33b	9.00bc	11.03bc	18.13c	23.70b
UREA80%	45.33c	39.40a	43.60a	7.00a	8.67b	8.83c	11.40ab	17.77c	22.70b
SSNF100%	49.43a	39.97a	39.47bc	6.50a	9.33ab	10.33ab	10.13cd	21.23a	25.17a
SSNF80%	47.30b	38.87a	37.93cd	7.00a	9.00ab	10.00abc	11.00bc	20.10ab	23.83b
BBW100%	43.90c	40.03a	41.90ab	6.33a	10.00a	11.33a	10.17cd	17.77c	23.67b
BBW80%	45.23c	41.00a	39.00bc	7.00a	9.00ab	10.00abc	12.07a	19.00bc	23.17b

[a]Means within a column followed by different letters were significantly different based on analyses by one-way ANOVAs followed by Duncan tests for mean separation ($p < 0.05$). [b]Control (no fertilizer added), UREA100% or UREA80% (100 or 80% portions for urea), SSNF100% or SSNF80% (100 or 80% portions for water-soluble, slow-release nitrogen fertilizer), BBW100% or BBW80% (100 or 80% portions for a mixture of 70% SSNF and 30% urea).

Table 5. Levels of Soil Nitrogen Resulting from Nitrate and Ammonium Ions in Different Nitrogen Treatments[a]

treatment[b]	NO_3^- -N (mg/kg)			NH_4^+-N (mg/kg)		
	July 2	July 10	July 18	July 2	July 10	July 18
control	12.46d	22.75a	15.87a	8.17b	8.03ab	22.58c
UREA100%	15.45d	22.37a	17.51a	6.03b	7.62b	24.00c
UREA80%	13.67d	23.41a	17.15a	5.38b	8.75ab	24.52c
SSNF100%	76.81a	21.77a	17.68a	11.90a	8.90ab	25.76bc
SSNF80%	36.07c	21.95a	16.21a	5.26b	9.62a	24.45c
BBW100%	57.71b	23.62a	18.47a	7.08b	8.15ab	28.43ab
BBW80%	37.31c	22.58a	16.16a	7.38b	8.44ab	29.25a

[a]Means within a column followed by different letters were significantly different based on analyses by one-way ANOVAs followed with Duncan tests for mean separation ($p < 0.05$). [b]Control (no fertilizer added), UREA100% or UREA80% (100 or 80% portions for urea), SSNF100% or SSNF80% (100 or 80% portions for water-soluble, slow-release nitrogen fertilizer), BBW100% or BBW80% (100 or 80% portions for a mixture of 70% SSNF and 30% urea).

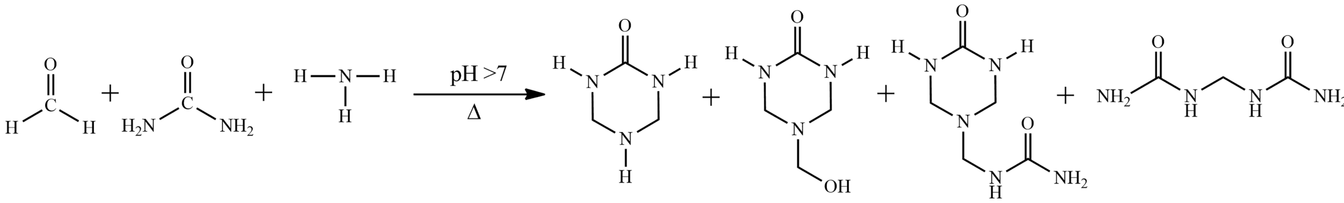

Figure 8. Synthesis of the soluble, slow-release nitrogen fertilizer (SSNF).

Kaitong Chemical Co., Tianjin, China) of analytical quality were used. All of the chemical synthesis, fertilizer samples, and soil analysis were carried out in a laboratory. The field experiment was conducted outdoors.

4.2. Preparation of the Soluble, Slow-Release Nitrogen Fertilizer. Initially, appropriate amounts of urea, ammonia, and formaldehyde solution were prepared and mixed into an aqueous solution, which was heated to 50 °C. The heated solution was added to a three-neck flask and mixed by a rotating mechanical agitator. After the urea dissolved, the solution was removed and ammonia solution was added to the mixture. Then, the solution was subjected to organic synthesis (Figure 8).

4.3. Single-Factor Test. The tests involved urea:formaldehyde molar ratios of 7:4, 6:4, 5:4, 4:4, and 3:4; formaldehyde:amine ratios of 12:3, 10:3, 8:3, 6:3, and 3:3; reaction temperatures of 20, 40, 60, 80, and 100 °C; and reaction times of 0.5, 1.5, 2.5, 3.5, and 4.5 h (Table S1). While one variable was being tested, the other conditions remained unchanged. For example, when optimizing the urea/formaldehyde molar ratios, the remaining conditions were fixed to a molar ratio of 0.3 for amine/urea with a reaction temperature of 60 °C and a time of 2.5 h. On optimizing the molar ratio for formaldehyde/amine (NH_3), the remaining conditions were fixed to 1.25 (urea/formaldehyde molar ratio), 60 °C (temperature), and 2.5 h (reaction time). Optimization of the reaction temperature involved fixing the remaining conditions to 1.25 (urea/formaldehyde), 2.67 (formaldehyde/amine), and 2.5 h (reaction time). When optimizing the reaction time, the other conditions were set at 1.25 (urea/formaldehyde), 2.67 (formaldehyde/amine), and 60 °C (reaction temperature).

4.4. Characterizing the Soluble, Slow-Release Nitrogen Fertilizer. The level of slow-release nitrogen (mg/mL, eq 2) was determined for the fertilizers. Components included slow-release nitrogen (SRN), total nitrogen (TN, mg/mL), urea nitrogen (UN, mg/mL), and ammonium nitrogen (AN, mg/mL). Part of the product solution was absorbed and tested by heating, digestion, and the Kjeldahl method for slow-release nitrogen, which involved using the colorimetric method of paradimethylaminobezaldehyde for urea nitrogen, or the Kjeldahl method for total and ammonium nitrogen. NMR spectra for ^{13}C NMR and ^{1}H in SSNF test fertilizers were

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determined using a Bruker AVANCE III at 500 MHz and dimethyl sulfoxide for a solvent.

$$SRN = TN - UN - AN \quad (2)$$

4.5. Response Surface Methods. Based on a single-factor test, ratios of urea/formaldehyde, formaldehyde/amine, and reaction temperatures, and times for the fertilizers were optimized using the response surface method and a central composite design based on Design-Expert software 8.0.6. Thirty combinations of factors were tested with ammonium, urea, and total nitrogen as independent variables, and slow-release nitrogen for dependent (response) variables (Table 6).

Table 6. Combinations of Compounds Tested and Their Reaction Temperatures and Durations

run	U:F[a] (molar ratio)	F:NH_3[b] (molar ratio)	reaction temperature (°C)	reaction time (h)
1	0.75	1.33	60	1.5
2	1.25	1.33	60	1.5
3	0.75	2.67	60	1.5
4	1.25	2.67	60	1.5
5	0.75	1.33	100	1.5
6	1.25	1.33	100	1.5
7	0.75	2.67	100	1.5
8	1.25	2.67	100	1.5
9	0.75	1.33	60	3.5
10	1.25	1.33	60	3.5
11	0.75	2.67	60	3.5
12	1.25	2.67	60	3.5
13	0.75	1.33	100	3.5
14	1.25	1.33	100	3.5
15	0.75	2.67	100	3.5
16	1.25	2.67	100	3.5
17	0.5	2	80	2.5
18	1.5	2	80	2.5
19	1	0.66	80	2.5
20	1	3.34	80	2.5
21	1	2	40	2.5
22	1	2	120	2.5
23	1	2	80	0.5
24	1	2	80	4.5
25	1	2	80	2.5
26	1	2	80	2.5
27	1	2	80	2.5
28	1	2	80	2.5
29	1	2	80	2.5
30	1	2	80	2.5

[a]Urea/formaldehyde ratio. [b]Formaldehyde/amine ratio.

These results were analyzed using the response surface method and eq 3.

$$Y = \alpha_0 + \sum_{i=1}^{n} \alpha_i X_i + \sum_{i=1}^{n} \alpha_{ii} {X_i}^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \alpha_{ij} X_i X_j \quad (3)$$

Here, the terms included the dependent variable slow-release nitrogen (Y) and independent variables (X_i and X_j), offset term (α_0), linear effect (α_i), first-order interaction effect (α_{ij}), and the squared effect (α_{ii}). ANOVAs, regression analyses, and plotting the surfaces representing dependent variables were performed to find the optimal conditions for the synthesis of the soluble, slow-release nitrogen fertilizers; $p < 0.05$ was considered significant.[40] Once the optimal reaction conditions were predicted, the test was repeated three times to check its reliability.[41]

4.6. Nitrogen Release Characteristics for the Optimized Nitrogen Fertilizer. The soluble, slow-release nitrogen fertilizer was mixed with water, resulting in a certain ratio by volume and making the 20 mL mixed solution into 100 g dry soil, which was kept in a Ziploc bag. This procedure was repeated 18 times at 25 °C. A control treatment with no fertilizer was also made. Three replications of the test were performed at 2, 4, 7, 14, 24, and 40 days after cultivation. Contents of NO_3^-−N and NH_4^+−N were subsequently measured by flow injection analyses, and the nitrogen release characteristics were measured by subtracting results from the control treatment.[42]

4.7. Field Experiment. The effects of optimized, soluble, slow-release nitrogen fertilizers on plant growth were determined using rape (*B. campestris L.*) "lvxiu91-1" (Qingdao International Seed Co., City, Province, China). The test was conducted in an open agricultural field with Typic, Hapli-Udic Argosols[26] at the New Fertilizer Test Station, Shandong Agricultural University, Tai'an, Shandong, China. Eight kilograms of dry soil was added to each of 28 plastic containers. The rape seeds were sown on June 7, 2017. On June 19, 2017 (12 days after planting), the emerged seedlings were transplanted into the containers, followed by thinning the seedlings to a maximum of seven per container. The experiment was performed in a factorial design with two fertilizer sources (optimized soluble, slow-release nitrogen and conventional urea fertilizers) and applied at three rates: 0, 2.21, and 2.76 total g/container applied, and three replicates. The same amounts of the following phosphorus and potassium fertilizers were also added to each container: 4.76 g of superphosphate and 1.82 g of potassium chloride. All fertilizers were added once before transplanting. Chlorophyll density (SPAD values) was measured with a Minolta SPAD-502 chlorophyll meter (Minolta Co., Tokyo, Japan). Soil samples were taken from a depth of 0−10 cm in the field at the New Fertilizer Test Station on July 2, July 9, and July 16, 2017 (25, 32, and 39 days after planting, respectively). Nitrate and ammonium nitrogen were measured in the samples by first adding 2 g of fresh soil to a 50 mL centrifuge tube along with 20 mL of calcium chloride solution (0.01 mol/L). After gyrating the solution for 1 h at 180 rpm in a mechanical shaker, it was passed through the solution for 10 min. Levels of nitrate and ammonium nitrogen in the filtrate were determined by an automatic chemical analyzer. The rape plants were harvested on July 21, 2017 (44 days after planting), cleaned, and then oven-dried at 75 °C, followed by passing the dried plant material through 425 μm sieves. Then, the dry matter quality and levels of nitrogen, phosphorus, and potassium within the plants were measured. Nitrogen use efficiency, rape plant yields, and nitrogen uptake were also calculated.[43] Standard agronomic planting and management practices were followed, for example, with irrigation, fertilization, and control of pests and weeds.

4.8. Statistical Analyses. Data analyses were carried out by Statistical Analysis Systems (Version 9.2 software SAS Institute, Cary, NC). Regression models were built and other data analyses were performed with Design-Expert software (Version 8.0.6, Stat-Ease Inc., Minneapolis, MN). ANOVAs, regression analyses, and plotting the surfaces representing dependent variables were performed to find the optimal

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conditions for the synthesis of soluble, slow-release nitrogen fertilizers; $p < 0.05$ was considered significant.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00303.

Photos of samples for the single-factor and response surface methodology tests (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Min Zhang − *National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China;* orcid.org/0000-0002-7838-3393; Phone: +86-538-8241531; Email: minzhang-2002@163.com

Zhiguang Liu − *National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China;* orcid.org/0000-0002-8844-1112; Email: liuzhiguang8235126@126.com

Authors

Yanle Guo − *National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China; College of Horticulture and Landscape Architecture, Jinling Institute of Technology, Nanjing 210038, China;* orcid.org/0000-0003-0134-377X

Chenhao Zhao − *National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China*

Hao Lu − *National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China*

Lei Zheng − *State Key Laboratory of Nutrition Resources Integrated Utilization, Kingenta Ecological Engineering Group Co., Ltd, Linshu, Shandong 276700, China*

Yuncong C. Li − *Department of Soil and Water Science, Tropical Research and Education Center, IFAS, University of Florida, Homestead, Florida 33031, United States;* orcid.org/0000-0001-6331-083X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00303

Notes

The authors declare no competing financial interest.

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