

Release Mechanisms and Kinetic Models of Gypsum–Sulfur–Zeolite-Coated Urea Sealed with Microcrystalline Wax for Regulated Dissolution

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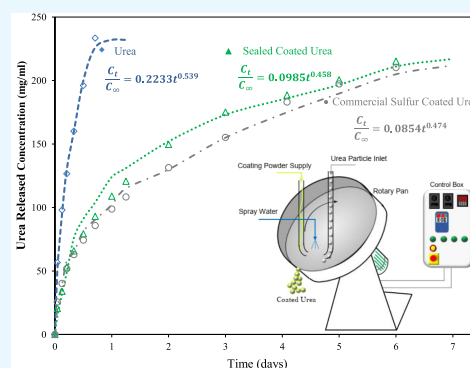


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ABSTRACT: In this study, a mineral-based coated urea was fabricated in a rotary pan coater using a mixture of gypsum/sulfur/zeolite ($G_{25}S_{25}Z_{50}$) as an effective and low-cost coating material. The effects of different coating compositions on the dissolution rate of urea and the crushing strength and morphology of the coated urea were investigated. A 25:25:50 (wt %) mixture of gypsum/sulfur/zeolite ($G_{25}S_{25}Z_{50}$) increased the coating effectiveness to 34.1% with the highest crushing strength (31.06 N). The effectiveness of coated urea was further improved to 46.6% with the addition of a microcrystalline wax (3%) as a sealant. Furthermore, the release mechanisms of various urea fertilizers were determined by fitting the release profiles with six mathematical models, namely, the zeroth-order, first-order, second-order, Higuchi, Ritger & Peppas, and Kopcha models. The results showed that the release mechanism of the uncoated urea and all other coated urea followed the Ritger & Peppas model, suggesting the diffusional release from nonswellable delivery systems. In addition, due to the increased mass-transfer resistance, the kinetic constant was decreased from 0.2233 for uncoated urea to 0.1338 for $G_{25}S_{25}Z_{50}$ -coated urea and was further decreased to 0.0985 when 3% Witcovar 146 sealant was applied.



INTRODUCTION

Urea is one of the world's most important nitrogenous fertilizers due to its high nitrogen content (46%), commercial availability, and low cost. However, two major drawbacks of using urea as a fertilizer include its high dissolution in water and its rapid hydrolysis,¹ which lead to an undesirable loss of nitrogen via leaching, ammonia volatilization, nitrification, and denitrification.² Approximately 40–70% of the applied nitrogen in urea is inaccessible to the plant³ but, instead, is easily run-off to the environment or chemically bound in the soil. This results not only in the uneconomical use of the fertilizer⁴ but also in the environmental problems associated with contamination of soil and water resources. To address these issues, fertilizers whose nutrient release kinetics has been altered such as slow-release fertilizers (SRFs) or controlled-release fertilizers (CRFs) have been developed to provide adequate nutrients for the plants over a longer time, allowing a remarkable decrease in the required fertilizer application rate.^{5,6}

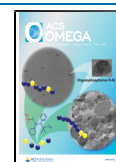
Although the terms CRF and SRF have sometimes been used interchangeably, they are different.⁷ CRFs are generally referred to as fertilizers in which factors dominating the rate, pattern, and duration of release are well known and controllable during CRF preparation.^{7,8} SRFs, on the other hand, are characterized by the nutrient release rate that is slower than that of a fertilizer in which the nutrient is readily available for plant uptake.

One way to produce CRFs/SRFs from urea is by coating the urea particles with suitable coating materials. The coating materials can generally be divided into the two main categories: polymer-based and mineral-based coating materials.⁹ Since they are not disturbed readily by soil microorganisms compared with mineral-based coating materials, most CRFs are produced with polymeric materials such as latex, polyethylene, polyurethane, and poly(vinyl alcohol), which allows a more precise rate of nutrient release.^{10,11} However, these materials are harmful to the environment since they are nondegradable and require toxic organic solvents during their processing. In recent years, biodegradable polymers made from different sorts of renewable natural resources, such as vegetable oils, starches, sodium alginate, hydrogels, and lignin are gaining interest in the production of CRFs.^{12–16} Nevertheless, the main drawback of polymer-coated fertilizers is their high manufacturing cost, making their use limited only to the cultivation of high-value crops in developed countries.⁶

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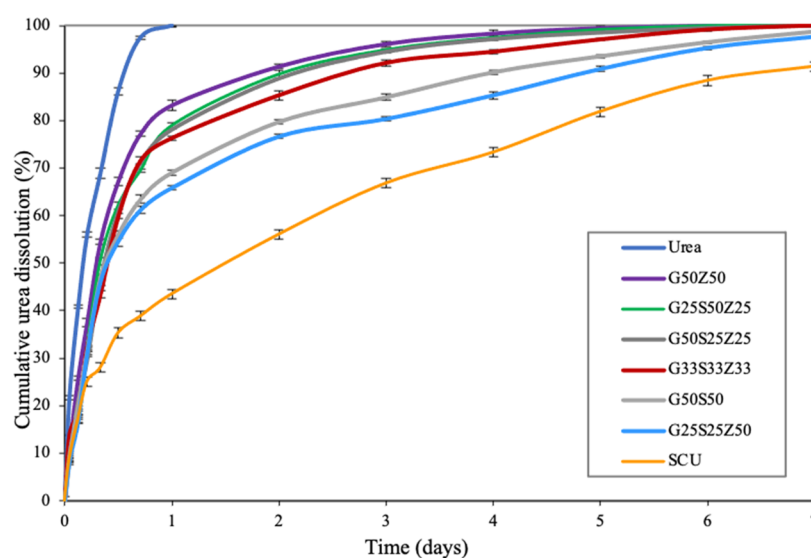


Figure 1. Effect of coating composition on urea dissolution. Error bars represent \pm standard deviation (SD).

Despite lower release longevity and controllability, which makes them classified as SRFs, urea coated with mineral coating materials is more widely used in most parts of the world, owing to its low cost. Sulfur is among the most widely used mineral coatings, and it provides an essential macronutrient required for proper plant growth.¹⁷ However, sulfur coatings are easily disrupted by microorganisms, leading to the appearance of cracks and imperfections and so a nonuniform nitrogen release rate.¹⁸ Mineral adsorbents such as zeolite, halloysite, montmorillonite, and bentonite nanoclays have also been investigated as coating materials due to high cation exchange property, which helps reduce nitrogen contamination of natural resources.^{19,20} Owing to high prevalence in sedimentary rocks and its unique physical and chemical properties, zeolite is among the most interesting natural mineral, and its role in agriculture as an ameliorant to improve soil properties and its use in SRFs have considerably attracted research attention.^{21,22} The pores in the crystalline structure of zeolite not only can hold nitrogen to a great extent but also improve the soil fertility by holding water in the root zone for subsequent availability to plants over time.^{20,21} In addition, compared with sulfur, zeolite is resistant to erosion and transformation by soil microorganisms.²²

Several coating technologies have been developed for the industrial production of coated fertilizer granules, which can be divided into two major approaches. The first uses pneumatic solid mixing, such as a spouted-bed²³ or Wurster fluidized bed,²⁴ while the second uses mechanical agitation, such as drums²⁵ and pans.²¹ Among these, the rotating drum and pan coaters are the simplest and most often employed due to their flexibility, large throughput, and ability to handle a wide range of products.²⁶ In the processing of coated SRFs, binders, either based on polymers (nondegradable or biodegradable) or minerals such as bentonite, gypsum, etc., are usually incorporated to provide a more homogeneous coating.^{27,28} In addition, sealing agents such as petroleum wax have been demonstrated to improve coating effectiveness and nutrient use efficiency.^{29,30}

Various coating materials, coating processes, and coating conditions have been evaluated for their effectiveness in forming slow-release coated urea.^{21,28,31–33} Mehmood et al.

compared the release of different urea fertilizer formulations, consisting of sulfur as a base coating, combined with gypsum, bentonite, or starch, using paraffin wax as a binder. A mixture of gypsum and sulfur was found to give the slowest urea release rate (i.e., 37%, as compared with uncoated urea). The scanning electron microscopy (SEM) image of the coated urea showed a uniform coating over the urea granules and had a minimum number of pores, suggesting that gypsum played an important role in enhancing the nitrogen utilization efficiency of the SRF.³⁰ In another recent study, zeolite-coated urea fertilizers using bentonite as a base binder, combined with one of the four different substances (i.e., white cement, corn starch, potato starch, or acrylic polymer) as another binder, were studied. Their results showed that the coated urea formulation with acrylic polymer gave the lowest urea release rate, suggesting the importance of the choice of binders to coating effectiveness.²¹

In this study, gypsum was used in all formulations as a low-cost mineral binder, together with sulfur and zeolite, for the fabrication of coated urea SRFs. The effects of different compositions of these coating materials and two types of microcrystalline waxes as sealants (Multiwax X-145 AH and Witcovar 146) on the release behavior of urea were systemically investigated. Furthermore, the slow-release kinetics was studied via a standard dissolution test in which the time course of the amount of urea released into a liquid media was monitored. Finally, to gain insights into the urea release mechanisms, six kinetics models (i.e., zeroth-order, first-order, second-order, Higuchi, Ritger & Peppas, and Kopcha models) were fitted to the experimental release data, from which the most appropriate model was proposed. The knowledge of the release kinetics and mechanisms of the SRFs allows better evaluation of the technical and economic feasibility for further application of such low-cost fertilizers to various field crops.

RESULTS AND DISCUSSION

Effect of G–S–Z Composition on Urea Dissolution and Crushing Strength. Figure 1 summarizes the time profiles of urea dissolution corresponding to the six compositions of the coated urea in comparison with the

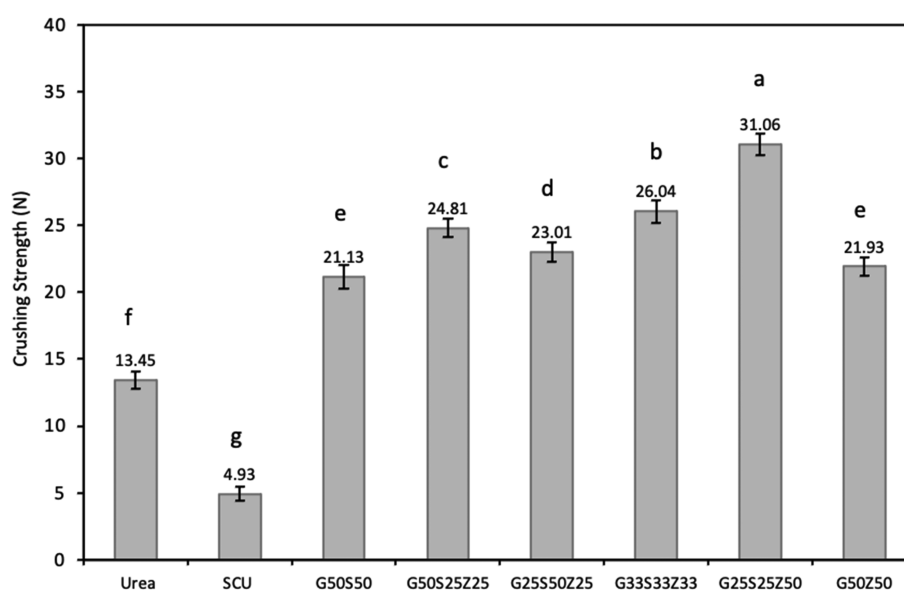


Figure 2. Crushing strength of coated urea using a mixture of gypsum, sulfur, and zeolite. Error bars represent \pm SD. Means within the same category with a different letter above them are significantly different.

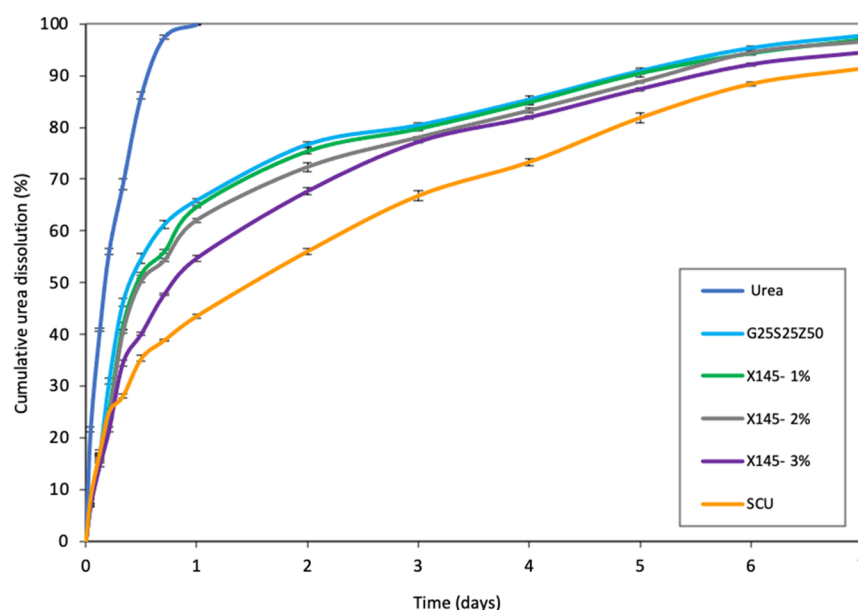


Figure 3. Effects of sealant (X-145) on urea dissolution. Error bars represent \pm SD.

uncoated urea and sulfur-coated urea (SCU). In all cases, the rates of dissolution were initially high followed by a gradual drop over time. The uncoated urea was completely dissolved within the first 24 h. The initial urea release rate (at the end of the first day) was higher for the 50:50 wt % gypsum–zeolite ($G_{50}Z_{50}$) coating, compared with 50:50 wt % gypsum–sulfur ($G_{50}S_{50}$) coating (83 vs 69%). This could be due to the zeolite's porous structure, leading to a higher diffusion of water into its interconnected pores. These results are consistent with those previously reported that urea coated with $G_{50}S_{50}$ exhibited a lower dissolution rate compared to that coated with $G_{50}Z_{50}$.²⁸

For the samples containing all three coating components, the urea dissolution rates were lower, compared with that containing gypsum and zeolite only. For the formulations with zeolite lower than 50%, as for 50% gypsum, 25% sulfur, and

25% zeolite ($G_{50}S_{25}Z_{25}$); 25% gypsum, 50% sulfur, and 25% zeolite ($G_{25}S_{50}Z_{25}$); and 33% gypsum, 33% sulfur, and 33% zeolite ($G_{33}S_{33}Z_{33}$), the initial urea dissolution rates varied from 69 to 83%, sitting between those of $G_{50}S_{50}$ - and $G_{50}Z_{50}$ -coated urea. On the other hand, for the coating formulation of 25% gypsum, 25% sulfur, and 50% zeolite ($G_{25}S_{25}Z_{50}$), the initial dissolution rate was lower than that of gypsum and sulfur only. Indeed, $G_{25}S_{25}Z_{50}$ was the most effective coating, in terms of sustained urea release, having the lowest initial dissolution rate of 66%. Although the underlying reason for these results is still unclear and remains to be investigated, the results suggest that there appeared to be some interactions between the components and their composition was an important factor affecting the coating effectiveness.

The results of the crushing strength tests for the different urea samples are shown in Figure 2. SCU exhibited the lowest

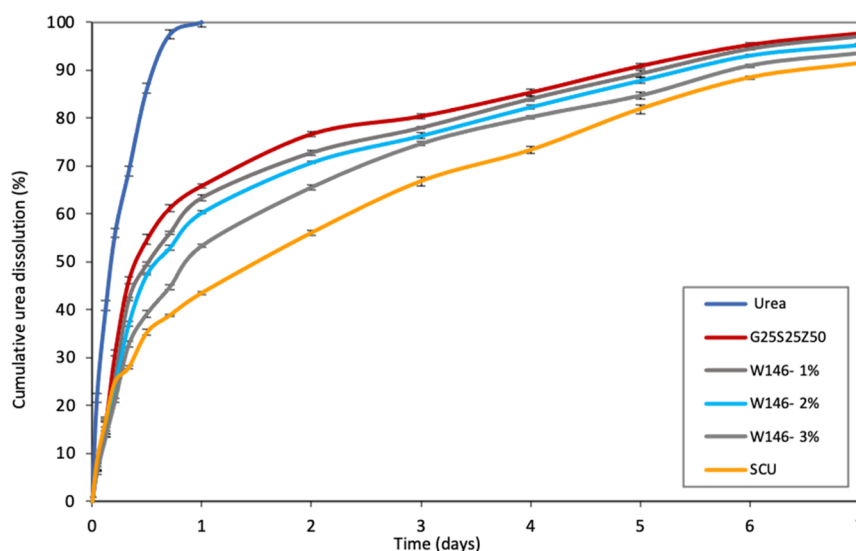


Figure 4. Effects of sealant (W-146) on urea dissolution. Error bars represent \pm SD.

strength, which was surprisingly even lower than uncoated urea. The low crushing strength of SCU is probably due to the fact that sulfur is friable, making the sulfur-coated shell susceptible to cracking.³⁴ On the other hand, all of the other coated samples demonstrated significantly higher crushing strengths. The presence of gypsum or zeolite in all coated urea samples was found to improve the crushing strength of the urea fertilizers, indicating their important roles in improving the structural characteristics of coated urea. By reacting with water, gypsum forms a hard substance, which can improve the strength of the coating mixture.³⁰ On the other hand, zeolite promotes the strength of the coating layer by the presence of Si in its structure.²⁸

The crushing strengths of GSZ-coated samples were significantly higher than those of $G_{50}S_{50}$ and $G_{50}Z_{50}$, exhibiting some degree of synergy between the three mineral coatings on the crushing strength. The highest strength of the GSZ-coated samples was observed to be associated with the $G_{25}S_{25}Z_{50}$ sample at 31.06 N, which could be due to the presence of the largest amount of silica in the zeolite structure. Based on the above, the $G_{25}S_{25}Z_{50}$ coating composition was selected for the subsequent studies to determine the effects of the sealing layer on urea dissolution and crushing strength.

Effect of Sealing Layer on Urea Dissolution Rate and Crushing Strength. Microcrystalline wax is commonly used in the preparation of SRFs. When it is used in the innermost layer of the fertilizer coatings, it acts as a binder to provide adhesion properties to coating materials so that the coating materials can bind to the surface of the urea granule.^{15,30} In this study, on the other hand, the molten microcrystalline wax (X-145 or W-146) was sprayed on the surface of the $G_{25}S_{25}Z_{50}$ -coated urea; the wax therefore acts as a sealant to close any cracks or imperfections and seal the flaws to reduce the rate of urea release.^{28,35} The urea dissolution of the X-145- and the W-146-sealed $G_{25}S_{25}Z_{50}$ -coated samples are shown in Figures 3 and 4, respectively.

The results in Figures 3 and 4 demonstrated that by applying either Multiwax X-145 or Witcovar 146 sealant as a top layer of $G_{25}S_{25}Z_{50}$ -coated urea, the rate of urea dissolution decreased. The hydrophobic character of either sealant could possibly prevent the disruption of the $G_{25}S_{25}Z_{50}$ -coated film and fast release of the urea fertilizer. In addition, increasing the amount

of applied microcrystalline wax from 1 to 3% improved the coating effectiveness. Similar trends have previously been reported, where the effectiveness of the controlled-release coating was improved when increasing the percentage of the applied hard wax.³⁶

While either Multiwax X-145 or Witcovar 146 coating reduced the urea dissolution rates compared with the unwaxed $G_{25}S_{25}Z_{50}$ -coated urea samples, coating with Witcovar 146 wax was more effective than that with Multiwax X-145. This could be due to the higher oil content of Witcovar 146 (Table 2). The coating quality was improved in the wax-sealed $G_{25}S_{25}Z_{50}$ -coated samples as the amount of the wax sealant was increased from 1 to 3%, as evidenced by the reduction in the urea dissolution from 66 to 53% at the end of the first day. The most effective sealant was 3% Witcovar 146, which resulted in the urea dissolution rate of 53% after 1 day, compared with 44% for SCU (Figure 4).

Figure 5 shows the coating effectiveness from the $G_{25}S_{25}Z_{50}$ -coated urea sealed with 3% microcrystalline Witcovar 146 wax. The application of the sealant enhanced the coating effectiveness of the sealed sample (as defined by eq 3) from

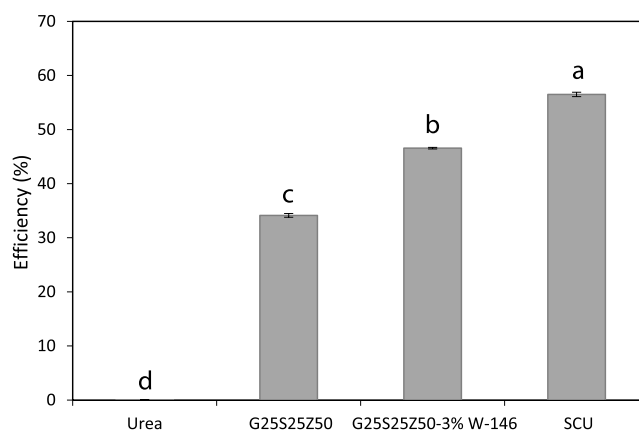


Figure 5. Coating effectiveness of $G_{25}S_{25}Z_{50}$ -coated urea and sealed-coated urea compared to that of commercial sulfur-coated urea (SCU). Error bars represent \pm SD. Means within the same category with a different letter above them are significantly different.

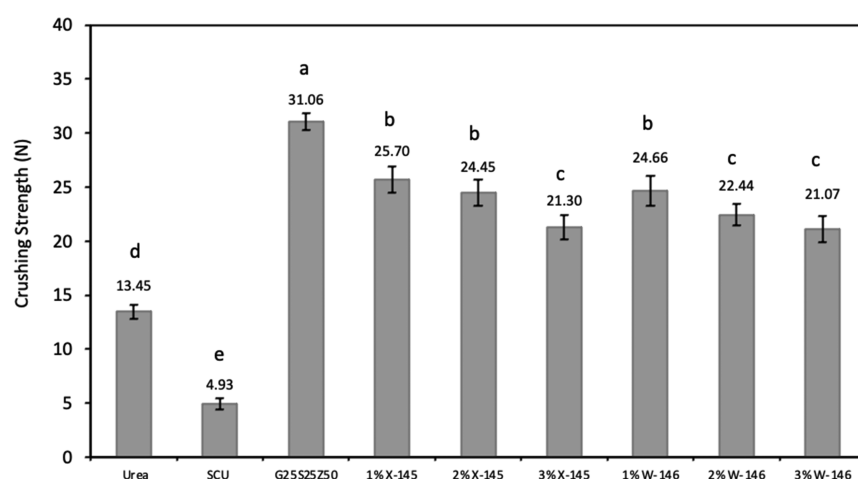


Figure 6. Effect of sealant (X-145 and W-146) on the crushing strength of coated urea. Error bars represent \pm SD. Means within the same category with a different letter above them are significantly different.

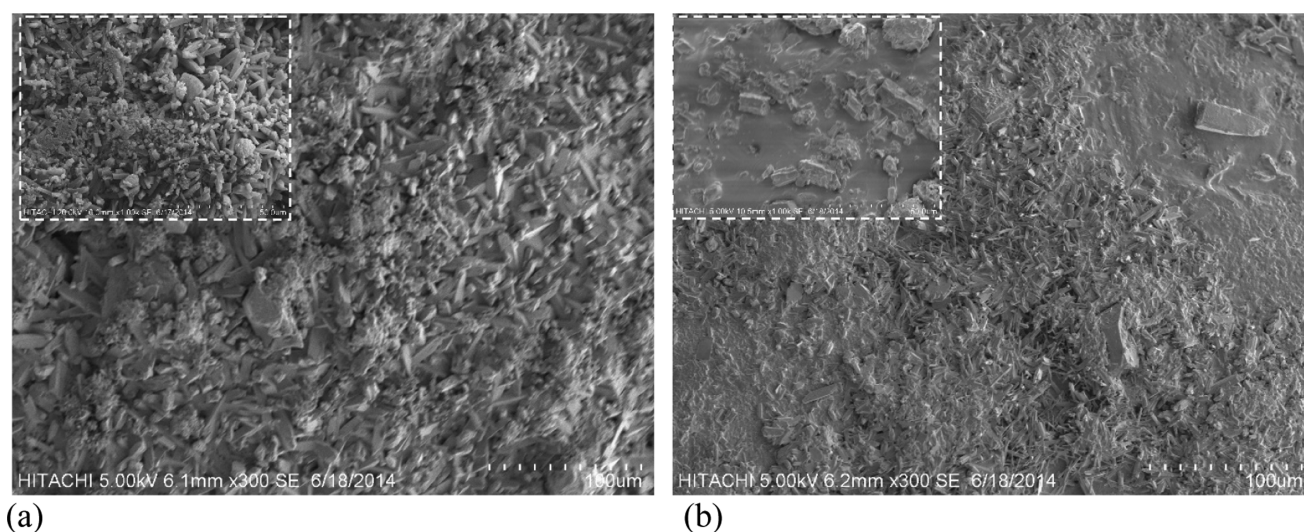


Figure 7. SEM images of (a) sealant-free and (b) sealed-coated urea with 3% W-146.

34.2 to 46.6% or approximately a 36% increase. An approximately 23.5% improvement in the coating effectiveness of 50:50% gypsum–ground magnesium lime-coated urea was previously reported when using polyol (1.1%) as a sealant.³²

The effect of Multiwax X-145 or Witcovar 146 wax sealants on the crushing strength is summarized in Figure 6. The average crushing strength of the G₂₅S₂₅Z₅₀-coated samples decreased with an increasing amount of the applied sealant from 1 to 3% from almost 31 N to approximately 21 N. Although this was considered a significant decrease, the crushing strengths of all of the sealed G₂₅S₂₅Z₅₀-coated urea samples were still significantly higher than that of SCU.

Surface Morphology of Coated Urea. As seen in the SEM images (Figure 7), although the particles dispersed in the coating layers were in the microsize range for both samples, the surface morphologies of the G₂₅S₂₅Z₅₀-coated samples without and with the sealant differed considerably. In G₂₅S₂₅Z₅₀-coated urea without the sealant, the surface roughness and small pores were apparent and various states, such as crystalline structures (rhombic and hexagonal shape crystals), were clearly seen on the sample surface (Figure 7a). These pores may contribute to water absorption into the matrix of the coated layer, leading to the relatively high urea dissolution, as previously observed. On

the other hand, by applying the sealant on the surface of G₂₅S₂₅Z₅₀-coated urea, good dispersion of the sealant on the pores and crack surface could cause a reduction in the microscopic pores and thus form a uniform coating layer over the urea particles, hence the appearance of a more compact structure (Figure 7b). This, in turn, led to a reduction in the water permeation and thus a decrease in the urea dissolution rate.

Kinetic Models of Urea Dissolution. To gain an insight into the release mechanisms, six kinetics models were used to fit the experimental concentration profiles for the studied samples (i.e., sealed G₂₅S₂₅Z₅₀-coated urea, unsealed G₂₅S₂₅Z₅₀-coated urea, uncoated urea, and SCU). For each studied kinetics model, the obtained k (release kinetic constant), n (release exponent), and R^2 (coefficient of determination) are listed in Table 1.

The Higuchi model, where the concentration of released urea is a linear function of $t^{0.5}$, gave the highest R^2 value (i.e., 0.997) for the uncoated urea, which might indicate the presence of a Fickian diffusion mechanism in the release process. Nevertheless, the Higuchi model of this form was derived based on Fickian diffusion of a solute from a planar matrix. Although the rectangular coordinate could reasonably

Table 1. Kinetic Parameters for Uncoated Urea, G₂₅S₂₅Z₅₀-Coated Urea, Sealed Coated Urea, and Commercial Sulfur-Coated Urea (SCU)

samples unit	zeroth-order		first-order		second-order		Higuchi		Ritger & Peppas		Kopcha	
	k ₀ (h ⁻¹)	R ²	k ₁ (h ⁻¹)	R ²	k ₂ (h ⁻¹)	R ²	k _H (h ^{-0.5})	R ²	n	k (h ⁻ⁿ)	R ²	k ₂ (h ⁻¹)
urea	0.0548 ± 0.0001	0.5941	0.0247 ± 0.0009	0.7162	0.0060 ± 0.0010	0.6192	0.2420 ± 0.0007	0.9968	0.539 ± 0.0074	0.2233 ± 0.0036	0.9953	0.0019 ± 0.0001
G ₂₅ S ₂₅ Z ₅₀	0.0062 ± 0.0000	0.2490	0.0027 ± 0.0001	0.3939	0.0005 ± 0.0000	0.7437	0.0922 ± 0.0001	0.7502	0.439 ± 0.0023	0.1338 ± 0.0010	0.8729	0.0149 ± 0.0001
1% X-145	0.0051 ± 0.0000	0.2010	0.0022 ± 0.0001	0.3991	0.0004 ± 0.0011	0.8192	0.0834 ± 0.0001	0.7519	0.437 ± 0.0041	0.1248 ± 0.0022	0.8825	0.0147 ± 0.0001
2% X-145	0.0043 ± 0.0000	0.1980	0.0021 ± 0.0000	0.4001	0.0004 ± 0.0012	0.8218	0.0764 ± 0.0000	0.7334	0.435 ± 0.0044	0.1232 ± 0.0022	0.8800	0.0138 ± 0.0001
3% X-145	0.0043 ± 0.0000	0.0507	0.0019 ± 0.0000	0.4523	0.0003 ± 0.0003	0.9137	0.0740 ± 0.0000	0.8331	0.448 ± 0.0022	0.1052 ± 0.0010	0.9213	0.0099 ± 0.0003
1% W-146	0.0051 ± 0.0000	0.1137	0.0023 ± 0.0001	0.4034	0.0004 ± 0.0027	0.8752	0.0826 ± 0.0001	0.7742	0.448 ± 0.0018	0.1174 ± 0.0008	0.8832	0.0140 ± 0.0002
2% W-146	0.0043 ± 0.0000	0.1060	0.0022 ± 0.0001	0.4640	0.0004 ± 0.0014	0.8857	0.0754 ± 0.0001	0.7686	0.440 ± 0.0044	0.1132 ± 0.0019	0.8881	0.0126 ± 0.0001
3% W-146	0.0042 ± 0.0000	0.1275	0.0020 ± 0.0000	0.4104	0.0003 ± 0.0001	0.9069	0.0728 ± 0.0001	0.8596	0.458 ± 0.0044	0.0985 ± 0.0027	0.9261	0.0088 ± 0.0002
SCU	0.0041 ± 0.0000	0.3481	0.0024 ± 0.0000	0.5240	0.0002 ± 0.0001	0.9156	0.0696 ± 0.0002	0.9304	0.474 ± 0.0029	0.0854 ± 0.0012	0.9539	0.0049 ± 0.0001

be assumed for some spherical systems (such as the system of thin coating layer), the Higuchi model could not be taken to reasonably describe the release profiles for most of the spherical coated SRFs in this study, as suggested by the relatively low R^2 values ($R^2 < 0.8$).

The Ritger & Peppas model, on the other hand, was the best-fitting model overall, owing to the high R^2 values (>0.99 , >0.87 , >0.88 , and >0.95 for uncoated urea, G₂₅S₂₅Z₅₀-coated urea, sealed G₂₅S₂₅Z₅₀-coated urea, and SCU, respectively). From this model, it is possible to establish a classification, according to the type of the observed behavior, based on the value of n (the diffusional exponent characteristic of the release mechanism), as follows: (i) Fickian model (case I, $n = 0.43$) and (ii) non-Fickian models (anomalous transport and case II, $0.43 < n \leq 0.85$).³⁷ For uncoated urea, n took the highest value of 0.539 compared with those for other coated SRFs, suggesting that release behavior from uncoated urea was relatively non-Fickian. On the other hand, the values of n for SCU, G₂₅S₂₅Z₅₀-coated urea, and sealed G₂₅S₂₅Z₅₀-coated urea fell between 0.474 and 0.435, which only slightly deviated from 0.43, indicating only a small degree non-Fickian (anomalous transport) release mechanism.

With regard to the rate of release, the kinetic constant (k) from the best-fitting Ritger & Peppas model was found to decrease from 0.2233 for uncoated urea to 0.1338 for G₂₅S₂₅Z₅₀-coated urea. This decrease can be attributed to the fact that the coated layer forms a protective layer on bare urea, slowing down the rate of urea release. For both types of sealants (Multiwax X-145 and Witcovar 146), the data revealed that the kinetic constant of sealed G₂₅S₂₅Z₅₀-coated urea decreased with increasing sealant dosage. There observed a gradual decline from 0.1248 to 0.1052 and from 0.1174 to 0.0985 when the amount of the applied sealant was increased from 1 to 3% for Multiwax X-145 and Witcovar 146-sealed G₂₅S₂₅Z₅₀-coated urea, respectively. The lower kinetic constant of sealed G₂₅S₂₅Z₅₀-coated urea compared with that of unsealed G₂₅S₂₅Z₅₀-coated urea suggested that the hydrophobicity nature of the sealant could resist the moisture penetration through the pinholes of the coated shell, thereby providing an additional control on urea release. This is in satisfactory agreement with the urea release behavior of sealed G₂₅S₂₅Z₅₀-coated urea (Figures 3 and 4). Table 1 also shows that the lowest kinetic constant (0.0854) was observed for SCU, suggesting the slowest nutrient (urea) release rate, in accord with the high efficiency of SCU (Figure 5).

CONCLUSIONS

Three different types of minerals (gypsum, sulfur, and zeolite) at various ratios were used as a coating material for urea. The optimal ratio was found to be a mixed coating of gypsum (25%), sulfur (25%), and zeolite (50%) based on obtaining the slowest rate of urea release in the dissolution analyses. By applying the G₂₅S₂₅Z₅₀ coating, the crushing strength was significantly improved. Additional application of Witcovar 146 wax as a sealant (3%) to G₂₅S₂₅Z₅₀-coated urea decreased the crushing strength compared to that of unsealed G₂₅S₂₅Z₅₀-coated urea, but the urea coating effectiveness was increased by 36%, making it a more efficient SRF. The effectiveness in delaying the urea release was improved to a comparable level to that of SCU, while the crushing strength remained significantly higher. The Ritger & Peppas model was found to best describe the kinetics, and so the release mechanism, of all samples: uncoated urea, SCU, G₂₅S₂₅Z₅₀-coated urea, and

sealed $G_{25}S_{25}Z_{50}$ -coated urea. All of the corresponding diffusional exponents were found to be only slightly higher than 0.43, indicating a small degree of anomalous (non-Fickian) transport. Based on the available nutrients (N from urea, Ca from gypsum, and S from sulfur and gypsum) and the longevity (approximately 92% of urea release in a solution in 7 days) of the sealed $G_{25}S_{25}Z_{50}$ -coated urea, the SRF could be applied to the cultivation of field crops such as rice. Further study on the effects of this SRF on the plant yield and nitrogen uptake in the controlled and field growing conditions, as well as the investigation into a possible mechanistic model that describes the nutrient release behavior of this SRF under these growing conditions, will be necessary.

EXPERIMENTAL PROCEDURES

Materials. Urea granules (about 1–4 mm diameter, 46% nitrogen content) were purchased from Petronas Agrenas. Gypsum was supplied by Siam Gypsum Plaster L.P. (Bangkok, Thailand), and sulfur was from the National Establishment for Agricultural and Industrial Sulfur, Saudi Arabia. The agriculture-grade zeolite (mordenite type) was provided by Khiazh Sdn. Bhd. (Subang Jaya, Selangor, Malaysia) under the brand name K2Zeo. Two microcrystalline waxes of low and medium melting points, Multiwax X-145 AH (X-145) and Witcovar 146 (W-146) (Table 2), were supplied by Sonneborn

Table 2. Properties of the Microcrystalline Waxes

properties	unit	method	specification	
			Multiwax X-145 AH (X-145)	Witcovar 146 (W-146)
color		ASTM D 1500	max 1.0	max 2.0
needle penetration at 25 °C	0.1 mm	ASTM D 1321	35–45	37–42
congealing point	°C	ASTM D 938	63–68	69–74
viscosity at 100 °C	mm ² /s	ASTM D 445	13–18	14–18
drop melting point	°C	ASTM D 127	64–69	78–83
flashpoint	°C	ASTM D 92	min 250	min 250
oil content	% wt	ASTM D 721		max 4.0

Refined Products. Acetonitrile (high-performance liquid chromatography (HPLC) grade) used in the preparation of the mobile phase for HPLC analysis of urea was obtained from Friendeman Schmidt (Australia).

Coating Process. The coating of urea particles was performed in a stainless-steel rotary pan of 60 cm diameter and 12 cm pan height (Scheme 1) at ambient conditions as previously described.³³ As shown in Table 3, six different coating formulations, consisting of combinations of gypsum, sulfur, and zeolite at various compositions, were studied. It should be noted that although each component has been used as a coating material for SRFs,^{30,38} in this study, gypsum plaster played another role as a binder, and it was therefore a base material in all formulations. Based on our preliminary trials, the amount of gypsum of at least 25 wt % of the coating materials would be required to hold the coating materials with the urea particles. In preparing each coated urea particle, the specified

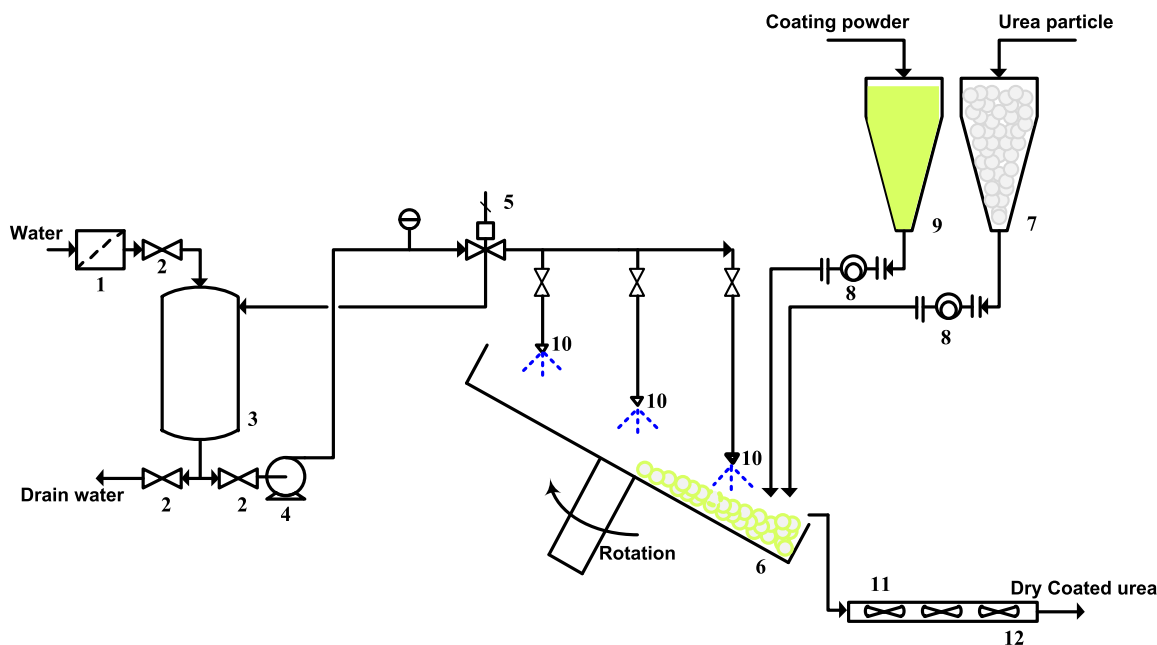
amounts of the three coating components were mixed, and the mixture was pulverized into a fine powder ($\leq 75 \mu\text{m}$ diameter particles). To produce coated urea with the optimal proportion of the coating of 25 wt % based on our previous study,²⁸ 1.25 kg of urea (ground and sieved to 2.8 mm in diameter) and 0.425 kg of the respective coating mixture were charged into the rotary pan (6) and then a water mist (25 g) was introduced over the surface of the pan (10). The pan was rotated for 17 min, during which time all of the urea and coating mixture were completely consumed. The coated urea granules were then transported to a vibrating tray (12), on which drying of the coated urea took place by means of a small electric fan (11). The dried coated urea granules were then collected for further studies. The other coating parameters and their corresponding values based on the previous study³³ are also summarized in Table 4.

When the sealant was applied, the molten microcrystalline wax (at 65 °C for X-145 and 80 °C for W-146) was spayed manually on the surface of the coated urea prior to drying. The different stages of commercial sulfur-coated urea (SCU) vs the coating process of this study are summarized in Table 5.

Analysis of Surface Morphologies. The surface morphologies of the sealant-free and sealed coated urea samples were studied under a scanning electron microscope (SEM; Model No. S3400N, Hitachi Co., Japan).

Analysis of Urea Dissolution. Dissolution tests of urea were conducted at three replicates to determine the effectiveness of the coatings in resisting moisture penetration. The urea dissolution study was conducted following the 7-day dissolution test developed by the International Fertilizer Development Centre and performed as previously described.³⁹ In this static dissolution test, 50 g of coated urea was placed in a bottle filled with 100 mL of distilled water and maintained at 30 °C by means of a water bath. To determine the percentage of urea dissolution, the concentrations of dissolved urea in 1 mL samples were measured six times during the first day and thereafter once a day for the following 6 days. The samples were analyzed via HPLC (Shimadzu LC20AT-Prominence, Japan) equipped with a LiChroCART 250-4,6 Pureser STAR column and a UV-vis detector following the method described in Eghbali Babadi et al.³² The SCU was used as the reference benchmark to compare the coating efficiencies, while raw urea granules were used as a negative control. It should be noted that the HPLC method and the conventional Kjeldahl method of measurement of nitrogen content gave similar results to those seen for the release of the nitrogen content of uncoated urea and SCU (Table S1).

The cumulative urea dissolution (%) was defined as the weight percentage of urea dissolved in the solution at a certain time.⁴⁰ In other words, this is the percentage of the weight of urea dissolved from any formulation, compared with that from uncoated urea, when it is dissolved entirely, given the same urea weight used. In this study, however, the same total weight of all fertilizers was used in all of the dissolution tests, in which 25% coating was applied to all of the coated formulations. Taken this fact into account, the amounts of urea in the coated samples must be adjusted by the division with the fraction $1 - \left(\frac{p}{100}\right)$. The cumulative urea dissolution for coated formulations is therefore expressed in terms of urea concentrations as

Scheme 1. Schematic of the Coating Process in the Rotary Pan³³Table 3. Coating Compositions Used in This Study^a

symbol	composition (%)			nitrogen content (%)	
	gypsum	sulfur	zeolite	theoretical	actual
G ₅₀ S ₅₀	50	50	0	36	35.93 ± 0.02
G ₅₀ S ₂₅ Z ₂₅	50	25	25	36	36.05 ± 0.01
G ₃₃ S ₃₃ Z ₃₃	33	33	33	36	35.89 ± 0.04
G ₂₅ S ₅₀ Z ₂₅	25	50	25	36	35.90 ± 0.03
G ₂₅ S ₂₅ Z ₅₀	25	25	50	36	36.01 ± 0.02
G ₅₀ Z ₅₀	50	0	50	36	35.85 ± 0.03

^aTotal coating materials: 425 g.

Table 4. Operational Parameters for the Urea-Coating Process

parameters	value
urea particle size (mm)	2.8
mass of bed (kg)	1.7
proportion of the coating (%)	25
rotation speed (rpm)	16
urea flow rate (g/min)	73
coating powder flow rate (g/min)	25
inclination of the pan (°)	37.5
spray water (%)	1.5
coating time (min)	17
temperature (°C)	30

$$\text{cumulative urea dissolution (\%)} = \left(\frac{C_{\text{cu},t}}{1 - \left(\frac{p}{100}\right)} \right) \times 100 \quad (1)$$

where $C_{\text{cu},t}$ is the concentration of dissolved urea (mg/L) from the coated sample at different times, t , C_u is the concentration of urea when uncoated urea is dissolved entirely, and p is the coating percentage (25%). In this study, the term “initial dissolution rate” (or release rate) refers to the change of urea release per unit time, evaluated at day 1. In other words, it is the dissolution percentage at day 1.

Table 5. Comparison between Coating Processes (Commercial Sulfur-Coated Urea vs Present Coated Urea)^a

coating process stages	commercial sulfur-coated urea ^b	present coating process ^c
(1) preheating of urea	✓	
(2) melting of coating materials	✓	
(3) granulation of coating materials on the surface of urea particles	✓	✓
(4) spraying wax on the coated urea	✓	✓
(5) cooling of coated urea	✓	
(6) drying of the coated product	✓	✓

^aCoating equipment. ^bRotary drum. ^cRotary pan.

The coating effectiveness is defined as the degree at which urea dissolution is retarded by coating the urea particles, relative to uncoated urea.³⁶ In terms of released urea concentrations, it is expressed at any time t , according to the following equation²⁹

$$\text{coating effectiveness (\%)} = \left(\frac{C_{\text{u},t} - C_{\text{cu},t}}{C_{\text{u},t}} \right) \times 100 \quad (2)$$

For this study, given that the uncoated urea is completely dissolved by day 1, the concentration of uncoated urea at day 1, $C_{\text{u},d1}$, is equal to C_w and the coating effectiveness (%) is defined at day 1. The expression for the coating effectiveness, after the correction for the different amount of urea used in dissolution tests for coated and uncoated samples by the fraction of $1 - \left(\frac{p}{100}\right)$, is given by eq 3

$$\text{coating effectiveness (\%)} = \left(\frac{C_u - \frac{C_{\text{cu},d1}}{1 - \left(\frac{p}{100}\right)}}{C_u} \right) \times 100 \quad (3)$$

where $C_{\text{cu},d1}$ is the concentration of dissolved urea (mg/L) from the coated urea at day 1 (24 h).

Table 6. Applied Dissolution Models^{a,b}

model	equation	plotting parameters		kinetic constant	assumption(s) of the model
zeroth-order	$\frac{C_t}{C_\infty} = k_0 t$	$\frac{C_t}{C_\infty}$ vs t	linear	k_0	the solute release rate is independent of its concentration ⁴⁷
first-order	$\frac{C_t}{C_\infty} = 1 - \exp(-k_1 t)$	$\ln \frac{C_t}{C_\infty}$ vs t	linear	k_1	the rate of the dissolution depends on the exposed surface, the structure of the surface, the temperature, the rate of stirring, and the arrangement of the apparatus ^{48,49}
second-order	$\frac{1}{C_\infty - C_t} = \frac{1}{C_\infty} + k_2 t$	$\frac{1}{C_\infty - C_t}$ vs t	linear	k_2	the dissolution process is not limited by diffusion ⁵⁰
Higuchi	$\frac{C_t}{C_\infty} = k_H \sqrt{t}$	$\frac{C_t}{C_\infty}$ vs $t^{0.5}$	linear	k_H	a "pseudo-steady-state" assumption was used in the diffusion region of a planar system ^{43,51,52}
Ritger & Peppas	$\frac{C_t}{C_\infty} = k t^n$	$\ln \frac{C_t}{C_\infty}$ vs $\ln t$	linear	k	applied to the systems with different geometries, to systems where one-dimensional diffusion cannot be assumed, and to systems where perfect sink boundary conditions are not maintained. ⁴² Sphere particle: $n = 0.43 \rightarrow$ Fickian diffusion; $0.43 < n < 0.85 \rightarrow$ anomalous (non-Fickian) transport; $n = 0.85 \rightarrow$ case II transport
Kopcha	$\frac{C_t}{C_\infty} = k_1 t^{1/2} + k_2 t$		nonlinear	k_1, k_2	the dissolution will not lead to altered physical states of the matrix ⁵³

^a C_t is the concentration of the dissolved solid in the medium at time t . ^b C_∞ is the concentration of the dissolved solid in the diffusion layer surrounding the solid at the infinite time.

Crushing Strength Analysis. The crushing strength of each of the uncoated and different composition coated urea samples was measured by a particle strength tester (dual-column table-top testing systems, 3365 INSTRON) following the method described in Eghbali Babadi et al.³² In measuring the crushing strength of each granule, the tester recorded the compressive force applied to the granule by a metal plunger, connected to the strength meter. The force at which the granule fractured was recorded as the measure of its strength. For each formulation of the SRFs, the crushing strength was taken to be the average strength of ten randomly selected granules. The significance of differences between the means of crushing strength data was evaluated using one-way analysis of variance (ANOVA) and posthoc Tukey's test using IBM SPSS statistical software. Significance was accepted at the $p < 0.05$ level.

Kinetic Models of Urea Dissolution. Describing the dissolution behavior with mathematical models simplifies the complex release processes and thus allows one to gain insights into the release mechanisms for a specific system.⁴¹ A number of mathematical models have been proposed, including Fickian and non-Fickian diffusion models. Based on Fickian diffusion, simple empirical equations have been derived, such as the power law⁴² and the Higuchi equations.⁴³ These equations have been widely used to study rehydration and dissolution processes, encompassing dehydration, as well as in the prediction of the release rates of active ingredients in pharmaceuticals.⁴⁴ Non-Fickian diffusion behavior, or the erosion of controlled-release matrix, has also been described by variations of kinetic models.^{45,46} In this study, the suitability of both Fickian and non-Fickian kinetic models (i.e., the zeroth-order, first-order, second-order, Higuchi, Ritger & Peppas, and Kopcha models) was evaluated to represent the urea release behavior. Table 6 summarizes the six kinetics models used in this study and their corresponding model parameters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c04353>.

Release of nitrogen content from uncoated urea and commercial sulfur-coated urea (SCU) determined by the HPLC method and the Kjeldhal method (PDF)

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Notes

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■ NOMENCLATURE USED

HPLC high-performance liquid chromatography
 SCU sulfur-coated urea
 SEM scanning electron microscope
 SRF slow-release fertilizers

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