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Research Article

Enhancing Biochar as Scaffolding for Slow Release of Nitrogen Fertilizer

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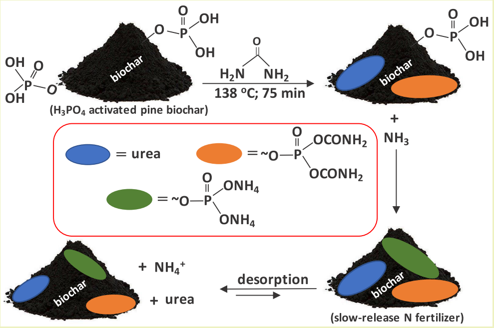
ABSTRACT: Nitrogen (N) is an essential macronutrient for plant growth; however, excessive use of N fertilizers and complexities of the N cycle in soil cause negative environmental impacts. This imposes several challenges in controlling the N availability timing and losses. The objective of this study was to develop a biochar-based slow-release fertilizer (SRF) to reduce N loss and increase N use efficiency in crop production. We provided a laboratory-based assessment of several H_3PO_4 activated (5 and 15%) biochar-based SRFs, produced from different combinations of biochar to urea (1:2, 1:3, 1:4, and 1:6), calcium lignosulfonate (5%), and paraffin wax (10%). Characterization analyses (SEM−EDS, XRD, FTIR, and XPS) of developed SRFs suggest successful urea grafting onto biochar through both the urea amine N and carbonyl C═O modes, without urea crystal structure disruption. The SRFs were more efficient than uncoated urea (control): (1) urea released in aqueous medium was 61−90% in 4320 min for the SRFs versus 99.6% in 12 min for the control; (2) cumulative N leached from soil columns was 68−71% after 41 leaching events for SRF versus 99.9% after four leaching events for the control; and (3) NH_3-N volatilization from soil was 0.2−0.9% for the SRFs versus 2% for the control. Inclusively, our results suggest that the developed SRFs are effective for reducing N loss from soil and provide larger quantities of NH_4^+-N to plants for a longer time (improved N use efficiency). We attribute this to that the developed SRFs are optimal for synchronizing with plant N uptake for providing better sustainability in modern agriculture.



KEYWORDS: *Biochar, Slow-release nitrogen fertilizer, Nitrogen use efficiency, Urea grafting, Sustainable agriculture*

INTRODUCTION

Although nitrogen (N) fertilizers have boosted crop production worldwide, significant N losses from agricultural fields (the main nonpoint source of N) due to leaching (NO_3^-), volatilization (NH_3), and denitrification (N_2 and N_2O) cause severe agronomic and environmental problems such as low N use efficiency by crop plants, water quality degradation, and ecosystem disruption. The primary cause for low N use efficiency in crop production is the lack of synchrony between the release of plant-available N from fertilizers and crop demand for N. Several best management practices (BMPs) and nutrient management practices have been developed to reduce the loss of N from soil;[1−4] however, identifying and adopting optimum BMPs across diverse soils, climates, and management systems is quite challenging. The ideal form of N would remain in the root zone long enough to be used by the growing crop. However, due to the complexity of the N cycle in soil, it is difficult to control the timing of N availability and losses. Hence, there is a pressing need for enhanced N management strategies to increase N use efficiency in crop production to improve soil health, improve water quality, and reduce greenhouse gas emissions.

Biochars are effective adsorbents of water and various nutrients and chemical contaminants as well as soil amendments for sequestering carbon and mitigating soil greenhouse gas (GHG) emissions.[5−9] Some biochars have also been shown to improve nutrient bioavailability and uptake by plants.[10−12] However, most biochars have few positively charged surface sites and, hence, limited anion exchange capacity[13] and ability to adsorb nutrient anions such as NO_3^-. Biochar surface modification has emerged as one of the major interests to expand environmental applications of biochar.[14,15] Phosphoric acid (H_3PO_4) activation of biochar surfaces is an effective way to increase meso- and nanoporosities; however, evaluation of the effect of H_3PO_4 activation on adsorption and desorption of NO_3^- and NH_4^+ is obscure.[16−19]

Several studies have explored the production of slow-release or controlled-release N fertilizer using urea[20−23] or have used urea−lignosulfonate binder[24] for high strength particulate composites. The concept of utilizing biochar and urea for this purpose is relatively recent,[25−28] and the effect of variation in

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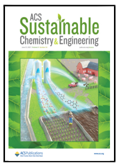

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biomass feedstocks on biochar-based slow-release fertilizer is not well-known. Moreover, in most cases, the N% in the resultant product is typically low, whereas farmers want fertilizer products with high N loadings to reduce the bulk of material that they must handle. Results from Maghsoodi et al.[29] show that the porous nature of a carrier like biochar reduces urea-N release from urea-impregnated biochar. The formation of hydrogen bonds between urea molecules and biochar functional groups reduces N loss from biochar-based slow-release fertilizer systems. Liao et al.[30] also reported that biochar-based slow-release N fertilizers can improve microbial activity, stimulate soil nitrification, and reduce denitrification by shifting the microbial communities toward the nitrifying bacteria as compared to a urea-only control. Enhanced nitrogen use efficiency and increased rapeseed (*Brassica napus* L.) yields were reported for controlled pot experiments.

Urea (46% N by weight), the dominant N fertilizer used worldwide, can be incorporated into pores of acidic biochars to stabilize the N from volatilization loss upon soil application. The pK_a of NH_4^+ is 9.2; hence, if the system pH increases further there will be substantial volatilization loss of NH_3. By keeping the system pH below 9.2, most of the NH_3 will be retained on the acidic surface as NH_4^+. Also, the use of lignosulfonate binder with urea is effective for forming coherent high strength urea fertilizer pellets.[24]

The overarching goal of this research was to develop a slow-release biochar-based N fertilizer with high loading of urea to reduce N loss and increase N use efficiency in crop production. We hypothesize that postpyrolysis treatment of biochar with H_3PO_4 creates more oxygenated functional groups for urea incorporation into the biochar and acidifies biochar surfaces to help stabilize urea and NH_4^+, thereby reducing volatilization loss of NH_3 upon soil application. We further hypothesize that the addition of lignosulfonate binder and paraffin will make biochar−urea fertilizer pellets physically stable and partially hydrophobic and inhibit rapid solubilization and release of urea. Objectives of this study include the following: (1) prepare and characterize various urea-infused biochar fertilizer formulations; (2) analyze the urea release from the prepared fertilizers in comparison with a conventional urea fertilizer in the aqueous phase; (3) compare leaching losses of urea, NH_4^+, and NO_3^- from soils fertilized with conventional urea and the various fertilizer formulations using soil columns; and (4) compare the loss of NH_3 to volatilization from soils fertilized with the biochar fertilizer formulations and the conventional urea fertilizer. These results are a preliminary (laboratory-based) assessment of the potential of the urea-infused biochar formulations to function as slow-release N fertilizers.

■ RESULTS AND DISCUSSION

Properties of the Developed SRFs. Properties of the developed SRFs are presented in Table 1. The N content of the SRFs was calculated based on the weight percentages of the biochar and urea and their respective N contents (%), assuming no N content for the calcium lignosulfonate (Ca-LS) and paraffin wax. The difference between predicted and measured total N contents is apparent for all developed SRFs, suggesting some N loss as volatilized NH_3 during the thermal infusion of urea into the biochar particles. The N loss ranges between 4.08 and 6.06% and between 4.37 and 7.12% for the 5 and 15% H_3PO_4 activated biochars, respectively. No consistent trend of N loss was found for different compositions; however, formulations with higher urea levels tended to have less N loss during the SRF development. The Mehlich III extractable phosphorus from the developed SRFs ranges between 0.19 and 0.39% and between 0.57 and 1.23% for the 5 and 15% H_3PO_4 activated biochars, respectively. This finding suggests that the 1 kg mass of developed SRFs is capable of providing 1.9−3.9 g and 5.7−12.3 g of elemental phosphorus for the 5 and 15% H_3PO_4 activated biochars, respectively. Moreover, the pH of the developed SRFs was mildly acidic to neutral range, which is beneficial for reducing N loss as NH_3 from the fertilizer upon application to the soil.

The FTIR spectra of the studied SRFs (lowest and highest urea levels) and uncoated urea are presented in Figure 1. The spectra show that the infusion of urea into the biochar changed the position of several peaks. The NH_2 stretching vibrations of urea (3430, 3330, and 3251 cm^{-1}) shifted to lower wavenumbers for both H_3PO_4 activated SRFs compared with urea, suggesting a decrease in binding energy, which is consistent with Kottegoda et al.[22] but not with Maghsoodi et al.[29] The relative broadening of the ~3200 cm^{-1} peaks suggest O−H/N−H valence vibration[31] (from H_3PO_4) with some possible H-bonding. There is an appearance of a small peak at 2942 cm^{-1} which can be attributed to the P−OH stretching vibrations of H_3PO_4;[32] however, the peak decreased in intensity with higher urea loading (1:2 versus 1:6 loading). This finding suggests the association of urea C═O with the P−OH group of H_3PO_4. The symmetric and asymmetric C−H stretching vibrations (2916 and 2848 cm^{-1}) in SRF samples are attributed to the added Ca-LS and paraffin wax. No peak shifting of the carbonyl C═O stretching vibration (1678 cm^{-1}) is observed; however, weakening of the peak is noticed which suggests the interaction of urea C═O group with the H_3PO_4. No significant differences in the NH_2 δ (1593 cm^{-1}) peak positions are observed for SRF samples as compared with urea. The urea phosphate characteristic peak[33] arises at 1652 cm^{-1} due to the amide I C═O stretching band (H-bonded) for both H_3PO_4 activated SRF samples. There is an increase in the amide II N—C═O symmetric stretching peak at 1626 cm^{-1} for SRF samples, suggesting the formation of more H-bonded amides. Moreover, a new peak at 1487 cm^{-1} is apparent for all urea-infused biochar samples due to N^+−H δ confirming the conversion of NH_3 to NH_4^+. This is anticipated for the acidic environment within the H_3PO_4 treated biochar particles to form ammonium phosphates. No significant peak shift appears for the 1463 cm^{-1} C−N−H δ; however, the intensity of the peak decreased for SRF samples relative to the urea. Slight changes in the 1000−1150 cm^{-1} region of the FTIR spectra were observed: the 1148 cm^{-1} peak shifted to 1154 cm^{-1} and the 1001 cm^{-1} peak shifted to 1013 cm^{-1} for both H_3PO_4 activated SRFs compared with urea. These peaks are assigned to symmetrical NH_2 rocking and symmetrical C−N stretching vibrations.[34,35] These changes in peak positions are attributed to the formation of complex or adduct of urea, with paraffin wax hydrocarbon (C_nH_{2n+2})[35] or due to the strong H-bonding between H_3PO_4 and urea.[36] These observations suggest possible H-bonding of urea to H_3PO_4 activated biochar, particularly between the N−H group of urea and the O atom of H_3PO_4, and the C═O group of urea and the O−H group of H_3PO_4.

XRD analysis of the urea, H_3PO_4 activated biochar, and the developed SRFs was used to identify the dominant mineral phases (Figure S1). XRD patterns of the developed SRFs have prominent urea peaks, without any peak shifting, that matches with those of pure urea (2θ deg of 22.2, 29.27, 24.58, 35.5,

Table 1. Physicochemical Properties of the Biochar and Slow-Release Fertilizers Used in This Study[a]

materials		elemental analysis (%)					
			N				
		C	predicted	measured	H	Mehlich III phosphorus (%)	pH (1:15)
5% H_3PO_4 activation	1:2	40.64 ± 3.3	26.74	25.12 ± 2.2	5.4 ± 0.5	0.39 ± 0.02	6.46 ± 0.23
	1:3	36.15 ± 1.9	30.06	28.2 ± 0.8	5.28 ± 0.2	0.35 ± 0.002	6.69 ± 0.07
	1:4	33.86 ± 1.1	32.05	30.62 ± 1.8	5.41 ± 0.2	0.21 ± 0.02	6.87 ± 0.12
	1:6	34.8 ± 0.3	34.32	32.9 ± 3.2	6.08 ± 0.8	0.19 ± 0.02	7.11 ± 0.014
15% H_3PO_4 activation	1:2	35.04 ± 1.7	26.74	24.8 ± 3	6.84 ± 0.9	1.23 ± 0.06	5.89 ± 0.07
	1:3	35.44 ± 0.8	30.06	28.7 ± 2.7	5.5 ± 0.3	1.14 ± 0.05	6.3 ± 0.14
	1:4	31.5 ± 0.8	32.05	30.4 ± 0.7	5.52 ± 0.2	0.64 ± 0.06	6.73 ± 0.21
	1:6	29.64 ± 0.3	34.32	32.8 ± 0.4	5.63 ± 0.2	0.57 ± 0.04	7.01 ± 0.32
pine biochar		67.95 ± 0.2	–	0.27 ± 0.05	2.45 ± 0.2	0.008 ± 0.0001	7.12 ± 0.52

[a] Average ± standard deviation; sample size = 3.

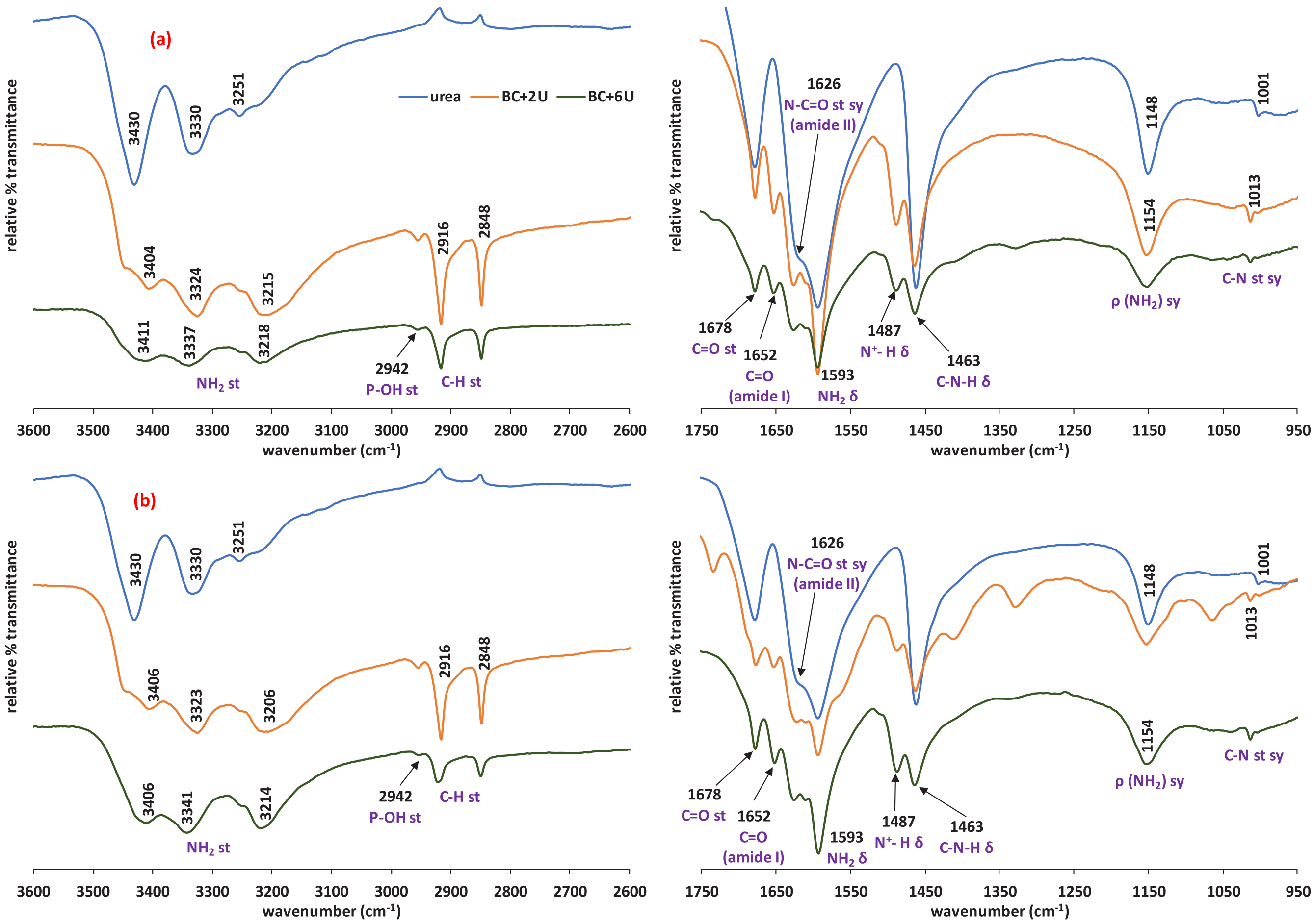

Figure 1. Fourier transform infrared spectra of the studied slow-release fertilizers prepared from 5 (a) and 15% (b) H_3PO_4 activated biochar. BC +2U = 1:2 biochar:urea and BC+6U = 1:6 biochar:urea.

41.52, and 31.6 which are attributed to the (110), (111), (101), (210), (102), and (200) crystal planes according to PDF card number ICDD 00-031-1979). Also, higher intensity for the (110) crystal plane urea peak was observed for the 1:6 composition compared with the 1:2 composition, which is consistent with the higher amount of urea infused into that sample. This finding suggests some urea infusion into the biochar particles without disruption of the urea crystal structure. We also noticed XRD peaks attributed to the polyethylene−urea complex (2θ deg of 21.6, 24.92, 26.27, 27.33, 20.35, and 12.42 which are attributed to the (110), (200), (201), (103), (102), and (100) crystal planes according to PDF card number ICDD 00-034-1766), suggesting the complex formation between urea and the added paraffin wax (consistent with our FTIR finding). No crystalline forms of either urea phosphate complex or ammonium phosphate were detected in the XRD patterns, suggesting the retention of the majority of urea in bulk forms on the H_3PO_4 activated biochar surface. Furthermore, no trace of biuret (PDF card number ICDD 00-011-0720) was found in any of the SRF samples. We conclude that urea did not undergo decomposition to form biuret for the operating condition employed in this study.

The above FTIR and XRD observations indicate the presence of four phases of N in the SRFs: bulk urea, urea interacting with the paraffin, urea bonded with the H_3PO_4 activated biochar surface, and NH_4^+. Thermal treatment converted part of the urea to NH_3, which was converted to NH_4^+ by abstracting H^+ from the protonated biochar surfaces.

SEM micrographs of the developed SRFs (lowest and highest urea levels) are shown in Figure S2. The micrographs show the porous nature of the biochar surface with urea infused into cavities and channels. The EDS analysis of the 5% H_3PO_4 activated biochars reveals the wide variation of atom percentage of N for the EDS analyzed spots for both 1:2 and 1:6 compositions (Figure S2a,b), which is consistent with urea being concentrated in pore spaces rather than uniformly coating all surfaces of the biochar. The P concentration also varies from spot to spot, ranging from 0.08 to 3.43%, again suggesting a nonuniform distribution of the P. However, this variation is not apparent for the 15% H_3PO_4 activated biochars (Figure S2c,d). We found relatively consistent C/N/P atom ratios for the spots studied. Sample size, however, is not large enough to discern whether this pattern is consistent or random.

The XPS N 1s spectra for pine biochar, urea, and the developed SRFs are presented in Figure S3 (lowest and highest urea levels). The N 1s core-level peak shifted from 402.1 eV for the pine biochar to a lower binding energy (399.6 eV) for urea, consistent with the more reduced condition of the N atom in urea. Moreover, small shifts in the N 1s core-level peak toward higher binding energy were observed for the developed SRFs (399.9 and 399.7 eV for the 1:2 and 1:6 compositions, respectively) compared with urea. This finding suggests the formation of a new bond between urea and acid-activated biochar in the developed SRFs through the urea N atom.

Urea Release Behavior in the Aqueous Phase. The rapid urea release study using three desorption steps shows significant urea mass loss from uncoated urea (99.5%), whereas the release of urea was slower for the developed SRFs (Table 2). There is no consistent trend between the urea loading rate and the urea release behavior for either the 5 or 15% H_3PO_4 activated biochar SRF. Overall, 19−37% and 23.6−44.6% of the added urea were released after three desorption steps for the 5 and 15% H_3PO_4 activated biochar SRFs, respectively. This result indicates that the urea rapidly released from the SRFs was substantially less than that from the uncoated urea. The reduction in the urea released from the SRFs relative to the control might be due to the blockage of biochar pores by paraffin and/or Ca-LS, which reduces the exposure of urea within the pores to water.[29] To elucidate the effect of paraffin wax in the SRFs, we conducted a rapid urea release study with the fertilizer pellets produced without the addition of paraffin wax (pellets prepared from only the lowest and highest urea addition samples). After the three desorption steps, the release of urea was slower from pellets (with no paraffin) than from the uncoated urea but faster than from the developed SRF pellets (with paraffin) (Table S1 and Table 2). This finding suggests that the addition of paraffin restricted the release of urea by 34.6−48.1% and 25.2−50.29% for 5 and 15% H_3PO_4 activated biochar SRFs, respectively.

Table 2. Cumulative Urea Desorption into Water after Three Washings from Urea and Slow-Release Fertilizers[a]

H_3PO_4 activation (%)	biochar (mass ratio)	urea (mass ratio)	urea dissolved (%)	total N dissolved (%)
5	1	2	33.12 ± 1.5	34.37 ± 2.1
	1	3	37.14 ± 2.1	40.28 ± 2.2
	1	4	19.08 ± 0.5	21.06 ± 1.1
	1	6	35.38 ± 0.8	38.42 ± 0.9
15	1	2	23.64 ± 1.2	26.34 ± 0.9
	1	3	44.64 ± 0.9	51.4 ± 1.1
	1	4	29.3 ± 1.8	34.5 ± 2.2
	1	6	30.74 ± 0.8	34 ± 0.5
urea control	0	1	99.5 ± 0.1	99.5 ± 0.1

[a] Average ± standard deviation; sample size = 3.

In the accelerated urea release test, a fast burst release of urea from uncoated urea is seen within the first 3 min of exposure to water (92.3%) (Figure 2). Moreover, 99.96% of the added uncoated urea was dissolved within only 12 min of exposure to water. A significantly slower release of urea was observed for the developed SRFs ($P < 0.05$). For instance, 36.5−59.3% and 56.7−68.7% of the added urea were released within 12 min for the 5 and 15% H_3PO_4 activated biochar formulations, respectively. After 12 min the urea release continued at a much slower rate. After 4320 min 65.2−81.2% and 61.2−90.2% of the added urea were released from the 5 and 15% H_3PO_4 activated biochar SRFs, respectively. The 1:4 composition of 5% H_3PO_4 activated biochar and the 1:2 composition of 15% H_3PO_4 activated biochar were the most effective, as only 65.2 and 61.2% of the added urea were released after 4320 min. No significant difference of urea release was found between different treatments ($P < 0.05$). This finding suggests that a significant fraction of the urea in the developed SRFs interacted with the biochar surfaces in a chemically stable form or was physically retained in inaccessible biochar pore spaces.

The release of urea from the developed SRFs was analyzed using Korsmeyer−Peppas and Higuchi kinetic models (Table S2). We noticed a two-stage urea release process from the SRFs: a rapid release of urea during the first 60 min (first phase; Figure 2a,c) and a relatively slower release rate that continued until 4320 min (second phase; Figure 2b,d). The linearized Korsmeyer−Peppas model ($\log M_t/M_\infty = \log a + n \log t$) gave the highest R^2 values for all samples (R^2 values range between 0.77 and 0.92 and between 0.8 and 0.88 for 5 and 15% H_3PO_4 activated biochar SRFs, respectively) (Table S1). This observation is consistent with Maghsoodi et al.[29] and Olad et al.,[37] who studied urea release from a series of urea impregnated materials including biochar. The exponent parameter, n, in the Korsmeyer−Peppas model for all samples is below 0.5, which suggests that the release of urea can be explained by one-dimensional Fickian diffusion.[38] This finding is important to understanding the behavior of the SRFs in soil environments and suggests that the slow release of urea is diffusion controlled.

Urea Release Behavior in the Column Leaching Study. The agricultural application of slow-release fertilizer involves the incorporation of the fertilizer into the top layer of soil. Purposefully, we designed the column leaching experiment to simulate the agricultural field scenario in which rainfall causes the leaching of the applied fertilizer and downward transport through the soil. The measured physicochemical properties of the Nicollet soil used in this study are tabulated in Table S3. The column leaching study using the developed SRFs and uncoated urea showed that the SRFs are effective in

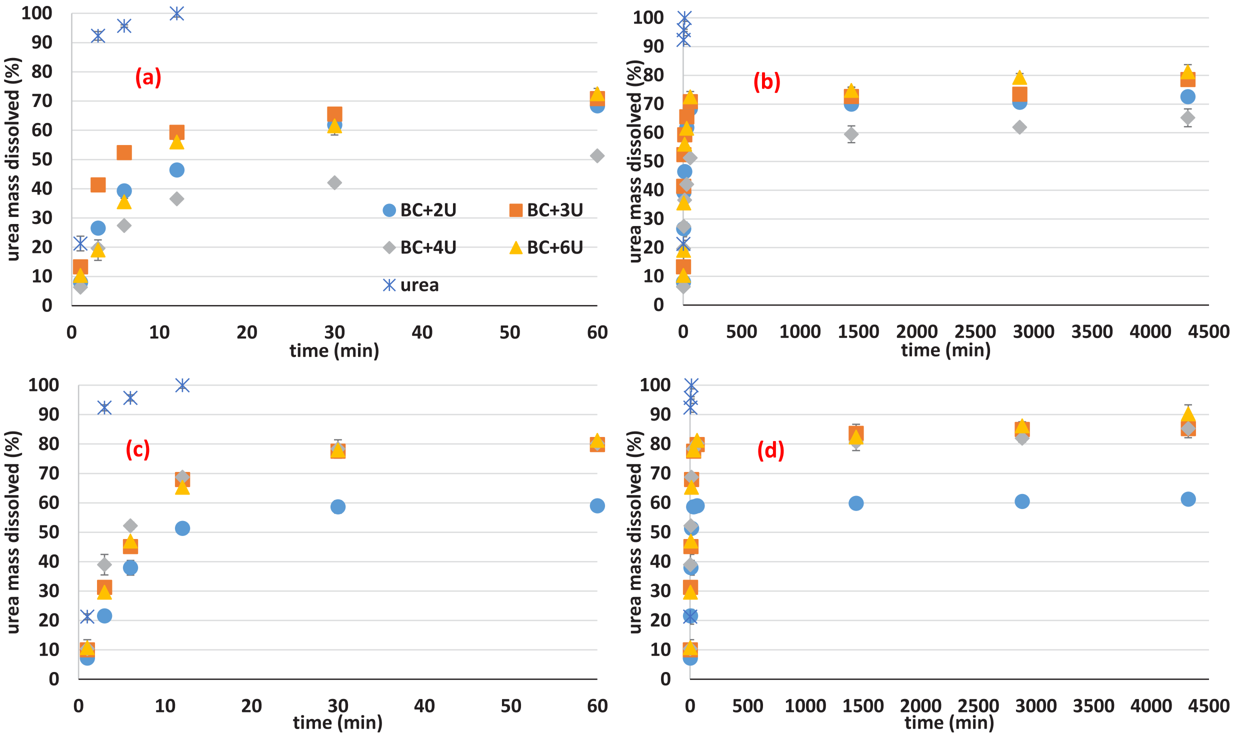

Figure 2. Accelerated urea release test for urea and the SRFs under saturated conditions. (a) and (b) are for the 5% H_3PO_4 activated biochar SRFs showing shorter (0−60 min) and longer (0−4320 min) time frames, and (c) and (d) are for 15% H_3PO_4 activated biochar SRFs showing shorter (0−60 min) and longer (0−4320 min) time frames, respectively. Error bars represent standard deviations of sample size = 3. Error bars that are not visible are smaller than the symbol. BC+2U = 1:2 biochar:urea, BC+3U = 1:3 biochar:urea, BC+4U = 1:4 biochar:urea, and BC+6U = 1:6 biochar:urea.

reducing leaching of urea (Figure 3a). The urea release profile from uncoated urea indicates the rapid release into the soil, as 99.5% of the added urea mass was lost after only four leaching events. The release rates of the SRFs are relatively slower ($P < 0.05$), as only 39.4−57.1% of the added urea mass was lost from the columns after the fourth leaching event. The release of urea from the soils receiving SRFs continued during subsequent leaching events. Overall, 65.4−84.25% of the added urea was leached after 17/18 leaching events from columns treated with SRFs. After 17 of the 18 leaching events, the urea concentration was below the detection limit. The 5% H_3PO_4 activated 1:4 and 15% H_3PO_4 activated 1:3 compositions showed the best results, significantly different from other treatments ($P < 0.05$) as only 65.4 and 66% of the added urea were released after 18 leaching events. However, these two treatments were not significantly different ($P < 0.05$) from each other. Moreover, the 1:2 composition of 5% H_3PO_4 activated biochar showed the highest urea release profile among all SRFs, suggesting a major portion of urea leached without being hydrolyzed to NH_4^+. In agreement with the urea release in the aqueous phase, the urea release from SRFs in the column study indicated a two-stage process: rapid release through seven leaching events followed by slower release during subsequent leaching events.

The highest NH_4^+-N concentration was observed for the fifth leaching event for uncoated urea (1.56 mg kg^{-1}), after most of the urea was leached out, and decreased gradually thereafter (Figure 3b). The SRF treated columns showed the highest NH_4^+-N concentrations for leaching events 4−7. Interestingly, concentrations of NH_4^+-N stayed several times higher for the SRF columns compared to those of the columns treated with uncoated urea, which suggests that the SRF preparation facilitated hydrolysis of urea to NH_4^+. It is noteworthy that the NH_4^+-N concentration decreased to less than 1 mg kg^{-1} after the fifth leaching event of the uncoated urea columns, whereas all but one (5% H_3PO_4 activated, 1:2 biochar to urea) of the SRF columns retained greater than 1 mg kg^{-1} even after the 41st leaching event. This result suggests that the developed SRFs can provide NH_4^+-N to the soil in larger quantities and for a longer period, which can potentially help increase the N use efficiency. Among the SRF treated columns, the 1:2 biochar to urea compositions for both H_3PO_4 activated biochars provided the highest NH_4^+-N (51.3 and 51.9 mg kg^{-1}) within five to seven leaching events, suggesting the rapid release of NH_4^+-N upon application of these SRFs. It should be noted that columns were saturated with water for 24 h and leached out before the columns were exposed to SRF and influent solution, so the NH_4^+-N must come primarily from the SRF.

In terms of cumulative N, the uncoated urea column released 99.6% of the total added N within four leaching events, whereas the SRF columns released between 40 and 59.6% during the first four leaching events (Figure 3c). After 41 leaching events, 68.8−92.5% of the added N was leached from the SRF columns. The 5% H_3PO_4 activated 1:4 biochar to urea and 15% H_3PO_4 activated 1:3 biochar to urea compositions had the lowest total N releases of 68.6 and 71.8%, respectively, significantly different from other treatments ($P < 0.05$). From the above observations, it is clear that the rate of N release was more than 12 times slower for the SRFs compared to uncoated urea, which supports its applicability as a slow-release N fertilizer for sustainable agriculture. We anticipate that the remaining 28−30% of the total N will be eventually released, although the time frame for

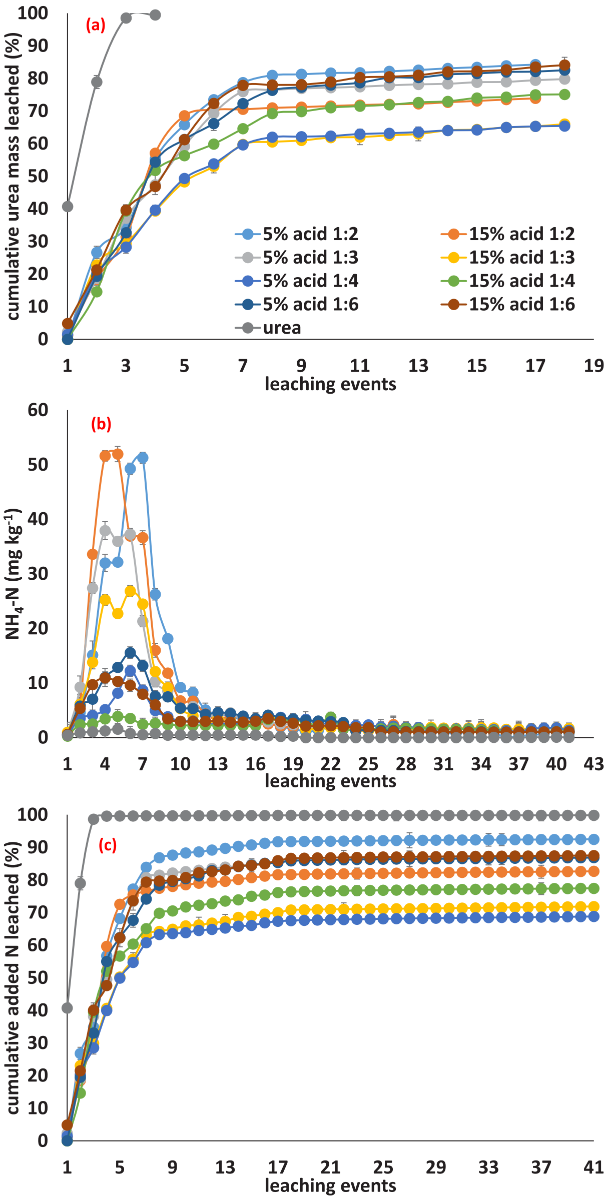

Figure 3. Soil column leaching study using different formulated fertilizers and uncoated urea: (a) release behavior of urea, (b) NH_4-N availability, and (c) total cumulative added N% leached after the 41 leaching events. Error bars represent standard deviations of sample size = 3. Error bars that are not visible are smaller than the symbol.

the release of the residual N is not clear and needs further evaluation.

Little or no NO_3^--N was detected in the leachate from the soil columns in this study, which may be due to the experimental design. Under field conditions with greater microbial activity, less frequent leaching events, and plant uptake of available N, nitrification will certainly influence N-use efficiency. For the control columns, the urea was rapidly leached before significant hydrolysis of the urea and nitrification could occur. For the SRF treated columns, the daily leaching events probably removed NO_3^- as rapidly as it was formed. The SRFs may have inhibited nitrification by slowing the release of urea and by adsorbing NH_4^+.[39] Also, pH of the SRFs falls in the acidic range, which may reduce the activity of nitrifying bacteria (*Nitrosomonas* and *Nitrobacter;* optimal pH levels ranging from 7 to 8.5).[40]

The N release rates for our developed SRFs are comparable to those reported previously: about 10 times slower N release from urea–montmorillonite composites than from urea[41,42] was observed versus about 12 times slower N release from urea–hydroxyapatite nanohybrid composites than from urea.[22] Liao et al.[30] reported 100% release of added urea N within 3 days, whereas their urea–biochar–bentonite composites released only 74.3% of N after 28 days.[30] The release pattern of N from our SRFs suggests that urea bonds strongly with the biochar surfaces and is protected within biochar pore spaces by Ca-LS and paraffin, which significantly reduces the release of urea.

NH_3 Volatilization from Soil Fertilized with SRFs.

Volatilization of NH_3 from soil fertilized with SRFs was significantly lower ($P < 0.05$) than from soils fertilized with uncoated urea during a 46 day greenhouse experiment (Figure 4a). The NH_3-N loss as percent of applied N was in the ranges of 0.4–0.78% and 0.27–0.41% for 5 and 15% H_3PO_4 activated biochar SRFs, respectively, whereas the NH_3-N loss was 2.24% for the uncoated urea. There is no definitive trend for the percentile NH_3 loss among the different SRFs; however, 15% H_3PO_4 activated 1:6 biochar to urea formulation has a relatively lower percent NH_3 loss than the 5% H_3PO_4 activated 1:6 biochar to urea formulation ($P < 0.05$; Figure 4a). Hence, the developed SRFs reduced NH_3 volatilization loss by 3–4 times compared with uncoated urea under the conditions of this experiment.

At the end of the 46 day greenhouse incubation, less than half of the added N (85 mg kg^{-1}) was extracted from the soils with 2 M KCl (Figure 4b). Most of the extractable N was present as NO_3^- in both the urea and SRF fertilized soils. The extracted NO_3^--N/NH_4^+-N from the uncoated urea fertilized soil was significantly higher/lower than compared with the SRF fertilized soils ($P < 0.05$). On average 42.1 mg kg^{-1} NO_3-N was extracted from the soils treated with uncoated urea, whereas 17.1–23.8 and 19.5–22.5 mg kg^{-1} NO_3-N were extracted from the soils fertilized with the 5 and 15% H_3PO_4 activated biochar SRFs, respectively. Only small amounts (0.39 mg kg^{-1}) of NH_4-N were extracted from the soils fertilized with uncoated urea, whereas 2.11–2.86 and 2.7–3.76 mg kg^{-1} NH_4-N were extracted from soils fertilized with the 5 and 15% H_3PO_4 activated biochar SRFs, respectively. Under conditions that promoted nitrification, these findings suggest that fertilization with the developed SRFs reduced the NO_3^- and increased the NH_4^+ concentrations in the soils relative to soils fertilized with uncoated urea. Losses of N to denitrification (N_2 or N_2O) were not measured during this study; however, as the soils were maintained at 60% water-filled pore space for the duration of the 46 day greenhouse incubation, we assume that denitrification was minimal.[43] Thus, most of the missing N was probably immobilized or, in the case of soils fertilized with the SRFs, was present as residual urea protected inside of biochar pores. This interpretation is supported by the results of the aqueous release and soil column leaching studies, which found that significant amounts of the N in the SRFs were not readily solubilized in water (Figure 2) or leached from soil (Figure 3), respectively. By reducing the pulse of NO_3^-, which typically follows fertilization of soils with urea, the SRFs are anticipated to reduce the risk of NO_3^- leaching. More research is needed to verify this interpretation under field conditions and to determine whether the missing N becomes plant available at a later date.

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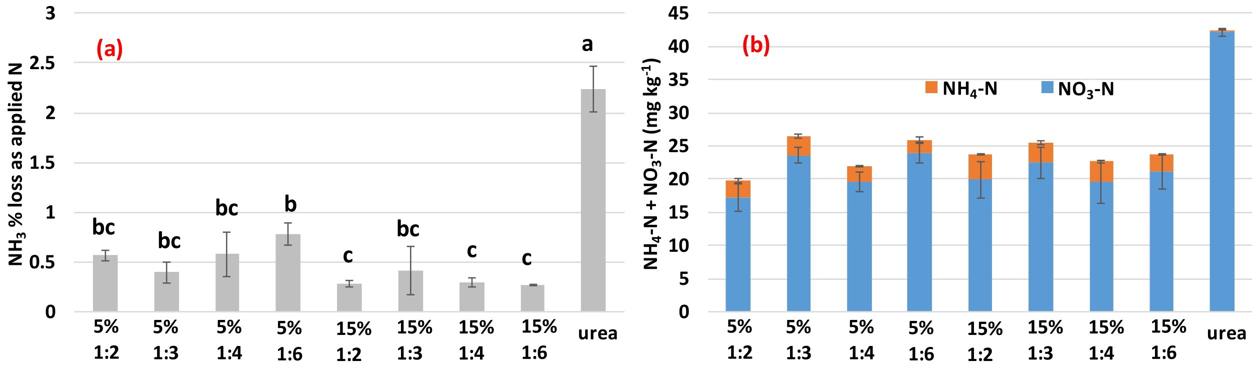

Figure 4. NH_3 volatilization test in the soil system using different formulated fertilizers and uncoated urea: (a) NH_3% loss as applied N (85 mg kg^{-1}) after the 46 day greenhouse experiment and (b) availability of total NH_4^+-N and NO_3^--N (mg kg^{-1}) extracted with 2 M KCl after the 46 day greenhouse experiment. Averages are for three replications; error bars represent standard deviations. Levels not connected by the same letter are significantly different.

The major pathway to NH_3 volatilization after urea fertilization is the conversion of urea into NH_4^+, then to ammonium carbonate, and finally to NH_3 under alkaline soil pH conditions. However, if the soil pH is neutral (6.5−7.5), the conversion of NH_4^+ to NH_3 occurs very slowly and NH_3 volatilization is very low. In the present study, the soil was neutral (pH 6.9) and the pH of the SRFs ranged from 6.3 to 7.11 (Table 1); hence, neither the soil nor the SRFs had pHs that promoted NH_3 volatilization. As a result, the NH_3 volatilization losses observed in our study were significantly lower than the 10−78% losses of applied urea N commonly observed in conventional agricultural systems.[44,45] It is noteworthy that we incorporated the urea/SRFs into the soil by "microtillage", which decreases NH_3 loss relative to leaving urea pellets on the soil surface.[46] Further research is needed to test the ability of the SRFs to reduce NH_3 volatilization loss on alkaline soils and when the fertilizer pellets are left on the surface and exposed to direct sunlight.

Mechanisms of Urea Retention on Biochar and Urea Release from SRFs. Both urea retention on and urea release from biochar surfaces largely depend on the biochar's surface properties including porosity, pH, and the nature and abundances of surface functional groups.[47,25] The melting stage used in the preparation of the SRFs allows the urea molecules to flow into biochar pores and to interact with surface functional groups within the pores. Finally, the selection of a low-ash feedstock (here southern yellow pine) yields low-ash biochar (ash content determined as 2.4% by the standard ASTM method; data not shown) and the H_3PO_4 treatments ensure that the pH of the biochar is neutral to mildly acidic, which reduces the rate of urea hydrolysis and helps stabilize any released NH_3 as NH_4^+.

Urea is stabilized within the SRF pellets through several mechanisms: (1) H-bonding between urea and phosphate groups grafted onto the biochar surfaces[25,29,47] (FTIR evidence, Figure 1); (2) complex formation between urea and the added paraffin wax (XRD evidence, Figure S1); and (3) physical trapping of urea within the biochar micro- and nanopores and protected from release by hydrophobic paraffin wax. Furthermore, urea and ammonium released after hydrolysis of urea are retained on biochar surfaces in three different forms: urea, urea phosphate complex, and ammonium phosphate complex. Our kinetics study suggests that the urea release from the SRFs in an aqueous medium is a multistage process, which is consistent with the multistage diffusion model proposed by Azeem et al.[48] and others.[22,47]

In preparation of the SRF pellets, we used both hydrophilic (Ca-LS) and hydrophobic (paraffin wax) agents. Any urea present on the exposed surfaces of the SRF pellets would be rapidly solubilized on exposure to water upon introduction into the soil. Urea that was retained within the biochar pores would be released more slowly depending on pore geometry and the amounts and distribution of urea, Ca-LS, and paraffin within the pore. We anticipate that the urea and Ca-LS will allow water to diffuse into the biochar pores and cause the buildup of osmotic pressure, which would facilitate the breakup of the SRF pellets and further release of urea. The presence of a paraffin wax layer, by contrast, would inhibit the diffusion of water into the SRF pellets. Thus, the proportions and distribution of urea, Ca-LS, and paraffin influence the stability of the SRF pellets and the release of urea-N. The neutral to mildly acidic conditions within the SRF pellets and chemical bonding of urea and NH_4^+ to functional groups on biochar surfaces provide a second mechanism for slowing the release of urea-N to the soil solution.

Economic Analysis and Environmental Implications. Techno-economic analysis at Iowa State University of fast pyrolysis biorefineries suggests a market price for biochar ranging between \$50 and \$100/metric ton.[49−51] Urea price ranges between \$377 and \$407/metric ton or between \$0.41 and \$0.44/lb of N in the U.S. agricultural market. The prices of paraffin wax and Ca-LS vary between \$600 and \$1,000/metric ton and between \$2,156 and \$2,256/metric ton, respectively. Using average values of these materials, the production of 1 metric ton of our 1:3 biochar to urea fertilizer composition (∼28% N; Table 1) will cost \$402−\$472 (\$0.72−\$0.84/lb of N), which is 1.75−1.9 times higher than the cost of uncoated urea. Therefore, to be economically competitive, the SRF must achieve substantially higher N use efficiency than uncoated urea. Given that 10−78% of urea-N is typically lost (40% on average),[44,45] the SRFs have good prospects for being economically viable. Additionally, the biochars in the SRFs are activated using H_3PO_4, which adds some extra cost. However, the P in the SRFs will be largely plant available and hence the extra cost will be offset by a reduced need for P fertilizer.

Because SRFs reduce the amount of N lost to runoff, they are expected to reduce eutrophication events in freshwater and marine environments. Because of the positive impacts of biochar on water and nutrient retention in soils, the use of SRFs will have positive impacts on soil health. Finally, because the carbon in biochar is recalcitrant over hundreds of years, the SRFs will provide a long-term role as carbon sequestration agents.[5,52]

■ CONCLUSIONS

This study demonstrates that N SRF pellets with high N loadings can be produced from urea and engineered biochar using Ca-LS and paraffin wax as binding and stabilizing agents, respectively. New contributions to science include (1) unique SRF formulations that include H_3PO_4 activation to increase biochar internal porosity, reduce the risk of NH_3 volatilization, and add P fertility; (2) demonstration of the production of SRFs with high N loading (24−32% N), which also provides 1.9−12.3 g kg^{-1} elemental P; and (3) evidence that the SRF pellets substantially slow the release of both urea and NH_4^+ to the solution and reduce NH_3 volatilization loss compared with uncoated urea. Of the various SRF formulations studied, the 1:4 biochar to urea composition with 5% H_3PO_4 activated biochar and the 1:2 and 1:3 compositions with 15% H_3PO_4 activated biochars were the most effective for increasing retention of urea (and total cumulative N) relative to uncoated urea. The developed SRFs reduced NH_3 volatilization and increased NH_4-N availability and reduced NO_3-N loss to leaching compared with uncoated urea. However, further work on optimizing SRF formulations and field studies designed to quantify N use efficiency and residual N are important as N release in subsequent years represents a potential reserve of slow-release N. The commercial prospects of SRFs will depend on the cost savings associated with higher N use efficiency offsetting the added expense of manufacturing them compared to urea fertilizer, a topic for future investigation.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c02267.

> Methodology section; cumulative urea desorption into water after three washings from slow-release fertilizers made without paraffin wax; kinetic models of urea release in aqueous medium; physicochemical properties of Nicollet soil used in this study; X-ray diffraction analysis of studied slow-release fertilizers prepared from 5 and 15% H_3PO_4 activated biochar; SEM−EDS analysis of studied SRFs prepared for 1:2 and 1:6 formulations from 5 and 15% H_3PO_4 biochars; XPS analysis for N 1s of pine biochar, urea, 15% H_3PO_4 activated 1:2, and 15% H_3PO_4 activated 1:6 formulations (PDF)

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Notes

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