

Lignite Scaffolding as Slow-Release N-Fertilizer Extended the SN Retention and Inhibited N Losses in Alkaline Calcareous Soils

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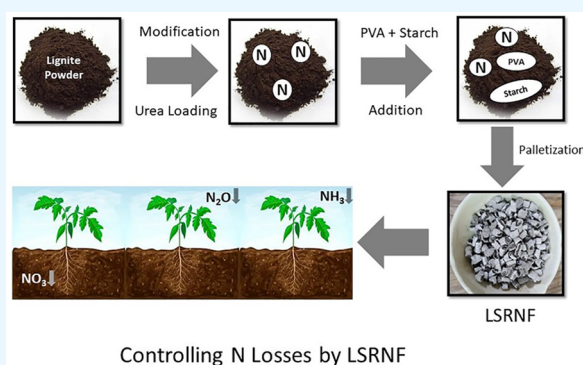
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ABSTRACT: Conventional nitrogen (N) fertilizers particularly urea mineralized quickly in soil. Without sufficient plant uptake, this rapid mineralization favors the heavy N losses. Lignite is a naturally abundant and cost-effective adsorbent capable of extending multiple benefits as a soil amendment. Therefore, it was hypothesized that lignite as an N carrier for the synthesis of lignite-based slow-release N fertilizer (LSRNF) could offer an eco-friendly and affordable option to resolve the limitations of existing N fertilizer formulations. The LSRNF was developed by impregnating urea on deashed lignite and pelletized by a mixture of polyvinyl alcohol and starch as a binder. The results indicated that LSRNF significantly delayed the N mineralization and extended its release to >70 days. The surface morphology and physicochemical properties of LSRNF confirmed the sorption of urea on lignite. The study demonstrated that LSRNF also significantly decreased the NH_3 -volatilization up to 44.55%, NO_3 -leaching up to 57.01%, and N_2O -emission up to 52.18% compared to conventional urea. So, this study proved that lignite is a suitable material to formulate new slow-release fertilizers, suiting to alkaline calcareous soils favorably where N losses are further higher compared to non-calcareous soils.



Controlling N Losses by LSRNF

1. INTRODUCTION

Loss of N fertilizers is one of the most critical challenge for sustainable crop production in modern agriculture. Consequently, the application of N fertilizers in excess to ensure sustainable crop production is a common practice. However, the plants do not utilize the excess N completely, and a considerable portion of applied N is lost as NH_3 -volatilization, NO_3 -leaching, and N_2O emissions result in the wastage of resources and money.¹ In addition, these losses lead to a decline in nitrogen use efficiency (NUE) and environmental pollution.² It has been reported that NUE in alkaline calcareous soils is much lower (15–23%)³ compared to non-calcareous soils (30–40%).⁴ High soil pH, temperature, and low cation-exchange capacity (CEC) and organic matter content are the main causes of lower NUE in alkaline calcareous soils.⁵ Besides, the very low NUE in alkaline calcareous soils, research studies encountering this issue are very limited. Therefore, finding an efficient solution to minimize N losses in alkaline calcareous soils is imperative.

Many research studies have proved that the addition of carbon-based amendments can reduce the NO_3 -N-leaching,⁶ NH_3 -volatilization,⁷ and N_2O emission⁸ and enhance the N retention in soil.⁹ Therefore, the declining NUE in alkaline

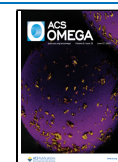
calcareous soils would require the maintenance of soil organic carbon to improve the NUE in a sustainable way.¹⁰ Therefore, there is strong evidence to hypothesize that integrating conventional N fertilizers like urea with carbon-based materials (lignite) as slow-release fertilizers (SRFs) could reduce fertilizer N losses and enhance the NUE. We know that the intervention of SRFs is an efficient option to delay the N hydrolysis and to ensure the N supply for a much longer period of time by matching the crop needs.¹¹ However, the high cost of SRFs is a major impediment to their general acceptance and widespread soil application. Recent research efforts are mostly focused on finding a suitable, affordable, and efficient carrier to synthesize the SRFs.

Lignite, often known as brown coal, is a widely available carbon-based material across the world. Predominantly the alkaline nature of biochar as a N carrier may not suit the

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alkaline calcareous soils. Lignite differs in its N retention behavior compared with biochar because, unlike biochar, lignite is generally acidic. Furthermore, the availability of biochar is limited, and relatively high cost of \$500–3000 per ton,¹² while lignite is readily available in many countries at lower costs.¹³ Therefore, lignite could be an alternative material with properties that make it appealing to use as a N fertilizer carrier for the development of novel and efficient lignite-based slow-release N fertilizer (LSRNF), especially for alkaline calcareous soils. Lignite has a greater number of functional groups (hydroxyl, carboxylic, ketone, etc.) than biochar, resulting in higher cation-exchange-capacity CEC.¹⁴ The complicated intra-particle pore structure, with abundant micropores, provides a great surface area with active sites having an extensive capacity for the adsorption of soil nutrients and other compounds.¹⁵ The deashing of lignite has the ability to remove the minerals and ash under 0.5% making it environment-friendly and further suitable for higher adsorption of N by enhancing microporosity and surface area. The acid leaching of lignite also removed the potential contaminants, including volatile organic compounds, polyaromatic hydrocarbons, heavy metals, etc.¹⁶ Moreover, lignite is pathogen free; therefore, it is not as potentially dangerous as a soil amendment instead it improves the physical, chemical, and biological properties of soil and increases water retention capacity.¹⁷ Many research studies have demonstrated that lignite is an effective soil amendment¹⁸ and soil conditioner because of its high humic-acid contents.¹⁹ Compared to previously developed SRFs, lignite as N-carrier for the development of new SRFs, have the capacity to extend many supplementary benefits such as carbon (C) sequestration, nutrients retention, soil structure improvement, reduction in greenhouse gases, delivery of humic substances, etc. Other SRFs, on the other hand, mostly use inert materials as carriers which do not have any additional benefits instead increase the cost of SRFs, while lignite due to many supplementary benefits saves the cost of crop production.

The mechanisms of minimizing the NH₃-volatilization, NO₃-leaching, and N₂O-emission by lignite could be due to the sorption of N via functional groups, high CEC, surface area, and abundant porosity.²⁰ Lignite as a novel N carrier needs extensive exploration because the literature regarding the use of lignite as a nutrient carrier is either not available or very limited. Therefore, it was hypothesized that lignite as an N-carrier to produce novel carbon-based LSRNF can result in a low-cost alternative to chemical fertilizers with improved environmental performance. It has also great potential to minimize the N losses and consequently enhance N retention in soil for crop uptake for the entire growing season after a single application. To counter the adequate knowledge gaps, a study was designed to prepare LSRNF and its evaluation to extend N release and control the N losses compared to conventional urea (CU).

2. RESULTS AND DISCUSSION

2.1. Characterization of Raw and Deashed Lignite.

The physicochemical properties of the raw lignite (RL) and deashed lignite (DL) are shown in Table 1. The results showed that deashing significantly decreased the pH of lignite by 3.65% and electrical conductivity (EC) by 31.65%. The deashing of lignite significantly increased the CEC by 10.40%. The volatile matter (VM) and ash (A) contents decreased significantly by 10.13% and 40.65%, respectively, while the fixed carbon (FC)

Table 1. Characteristics of Raw and Deashed Lignite

characteristics		raw lignite	deashed lignite
chemical	pH	3.84 ± 0.04	3.70 ± 0.04
	EC (d Sm ⁻¹)	0.79 ± 0.01	0.54 ± 0.01
	CEC (cmol ⁺ kg ⁻¹)	71.77 ± 0.24	80.10 ± 0.28
proximate	volatile matter (%)	49.37 ± 0.63	44.37 ± 0.92
	ash (%)	2.14 ± 0.04	1.27 ± 0.03
	fixed carbon (%)	48.49 ± 0.96	54.24 ± 1.07
structural	surface area (m ² g ⁻¹)	2.44 ± 0.04	13.11 ± 0.21
	pore volume (cm ³ g ⁻¹)	0.019 ± 0.00	1.33 ± 0.009

was enhanced by 10.60%. Similarly, deashing significantly increased the surface area and pore volume by 81.39 and 97.07%, respectively.

The modification of lignite by acid leaching significantly decreased the pH and EC of lignite because acid leaching removed the ash contents and alkaline minerals which is responsible for decreasing the pH and EC.^{21,22} In addition, acidic pH and low EC are attributed to the abundance of weak acidic oxygen-containing carboxylic and phenolic functional groups. The Fourier transform infrared (FTIR) of DL showed the abundance of acidic function groups in this study. The acid leaching also enhanced the CEC of lignite due to the insertion of new binding sites, the development of new pores, and the widening of the original pores.²³ These changes in the structure of lignite were confirmed during the characterization of lignite in this study.

The deashing significantly decreased the VM and A contents and increased the FC of lignite. During deashing, acid solubilized the inorganic compounds (ash) which were leached with sequential leaching. The removal of ash consequently increased the surface area and porosity as well. It was also reported that acid leaching presumably affects the Brunauer–Emmett–Teller (BET) values in two ways; first, inert mass (ash) was removed, resulting in an automatic increase in surface area per unit weight (because the weight decreased due to ash loss); second, the ash removed was probably blocking some of the pores otherwise available for N adsorption.²⁴ The increase in the surface area was due to the widening of existing pores or the creation of new pores.²⁵ The deashing might have loosened the structure so that the volatiles removal opened the micropores present in the structure by diffusing ash out from the inner zones.²⁶

2.2. X-ray Diffractometer, FTIR, and Scanning Electron Microscopy Characterization of Raw Lignite, Deashed Lignite, and LSRNF.

The X-ray diffractometer diffractograms (Figure 1) showed that the peaks appeared approximately at $2\theta = 49.42, 64.3,$ and 77.52° were common in RL, DL, and urea-loaded lignite, representing feldspar, quartz, and graphite. Similarly, other common peaks that appeared at $2\theta = 44.02$ and 69.14° were recognized as halite. However, the X-ray diffraction (XRD) pattern of urea-impregnated lignite displayed some new peaks attributed to the coating of urea. A sharp peak of urea was recognized at 2θ angle 22.0° and few other peaks of urea appeared at 2θ angle ($19.72, 24.36, 28.98, 31.48, 35.28,$ and 36.92°). The XRD patterns showed that the intensities of some mineral peaks either disappeared or were reduced due to the loss of minerals by acid leaching. The XRD pattern of urea-loaded lignite confirmed the presence of urea. The results, therefore, directed the formation of the complex of urea with lignite and binders. Almost similar results have been reported by Bakshi et al.²⁷ Liu et al.²⁸ found in his study that

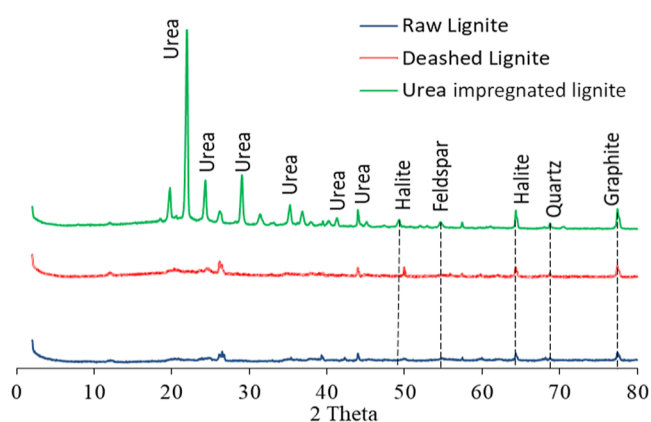


Figure 1. XRD patterns of raw lignite, deashed lignite, and urea-impregnated lignite.

urea reflection appeared at $2\theta = 22.61, 24.95, 29.65, 31.85, 35.91, 37.33, 45.73, 49.84, \text{ and } 55.24^\circ$ in the XRD patterns of biochar-based nitrogen fertilizer (BNF)-2 and BNF-4.

The FTIR patterns of RL, DL, and urea-loaded lignite are shown in Figure 2. The asymmetric stretching vibration of

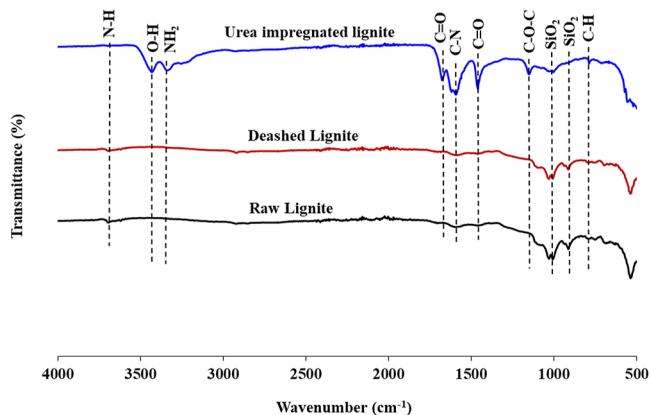


Figure 2. FTIR patterns of raw lignite, deashed lignite, and urea-loaded lignite.

silica (SiO_2) observed at 914 and 1000 cm^{-1} , at 1592 cm^{-1} deformation vibration of amide II band (C–N), at 3680 cm^{-1} amine (N–H) stretching were diagnosed in RL. There was no change in the distribution of functional groups in DL. However, a considerable change in functional groups occurred after impregnating the lignite with urea. The interaction of urea with the surface of lignite showed some additional stretching vibrations confirming the attachment of urea. A broad stretching vibration of the hydroxyl (O–H) functional group

was seen at 3431 cm^{-1} . At 3321 cm^{-1} aminoacidic (NH_2) group stretching, carboxyl functional group (C=O) at 1626 cm^{-1} , amide II band (C–N) at 1592 cm^{-1} , symmetric stretching vibration of the carboxylic (C=O) group at 1460 cm^{-1} , carbohydrate (C–O–C) vibration at 1148 cm^{-1} , silica (SiO_2) stretching at 1000 cm^{-1} , and aromatic (C–H) stretching at 787 cm^{-1} , respectively, were identified.

It was found that urea loading increased the intensity at both higher and lower wavenumbers of FTIR. At high-wavenumber region 4000–1600 cm^{-1} , urea-loaded lignite had higher intensity of peak stretches of O–H and N–H. Furthermore, the high intensity of carbonyl stretching (C=O) in the range of 1642–1652 cm^{-1} was attributed to amide groups. This suggested the reaction of C=O in adsorbents with NH_2 from urea. Barbosa et al.²⁹ investigated absorption band characteristics of urea at 3428.7–3253.3 cm^{-1} and the characteristics of primary amides in the NH_2 group after loading of biochar with urea. The band at 1675.8 cm^{-1} was characteristic of amide carbonyl; and the band at 1675.8 cm^{-1} was characteristic of amyl carbonyl. The peak at 1625.7 cm^{-1} was evidence of another common fold in primary amides, which is associated with the C=O bond of the urea molecule, and the bands at 1457.9 and 1149 cm^{-1} were related to C–N axial deformation.

The scanning electron microscopy (SEM) images of raw lignite (Figure 3a) showed that the RL was dense, irregular, and compact. However, there was a slight change in the structure of lignite (Figure 3b) after deashing. It was observed that sharp mineral edges found in the RL were obscured and smoothened, revealing a reduction in mineral particles from the lignite leading to the creation of micropores in the lignite structure. However, these micropores were filled with molten urea after urea loading as the SEM image of urea-loaded lignite (Figure 3c) showed that the surface got rough and covered with precipitated urea.

The SEM images showed that the abundance of meso- and micropores created after acid leaching of lignite allowed favorably to transport and store urea and water. Some urea particles filled into the pores and exposed cavities resulted due to leaching while some urea crystallized on the surface of lignite showing fissures and cracks in SEM images. The urea-loaded lignite exhibited a coarse and undulating surface which is attributed to the loading of urea.^{27,28}

2.3. N Release Patterns of LSRNF. The results (Figure 4a,b) showed that LSRNFs significantly delayed the N release in both soils compared to urea and C-SRF. It was noted that urea showed the fastest release rate, and 100% of N from urea was hydrolyzed within 24 h in both soils. The C-SRF, however, restricted the hydrolysis of N somewhat and lasted for 20 days in both soils. On the other hand, the N release from all formulations of LSRNF delayed N release significantly. It was noticed that LSRNF (1:1) released all N in 70 days in fine-

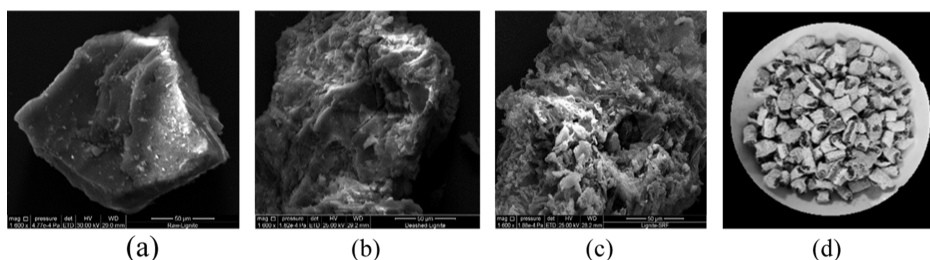


Figure 3. SEM images of (a) raw lignite, (b) deashed lignite, (c) urea-loaded lignite, and (d) digital image of granules of LSRNF.

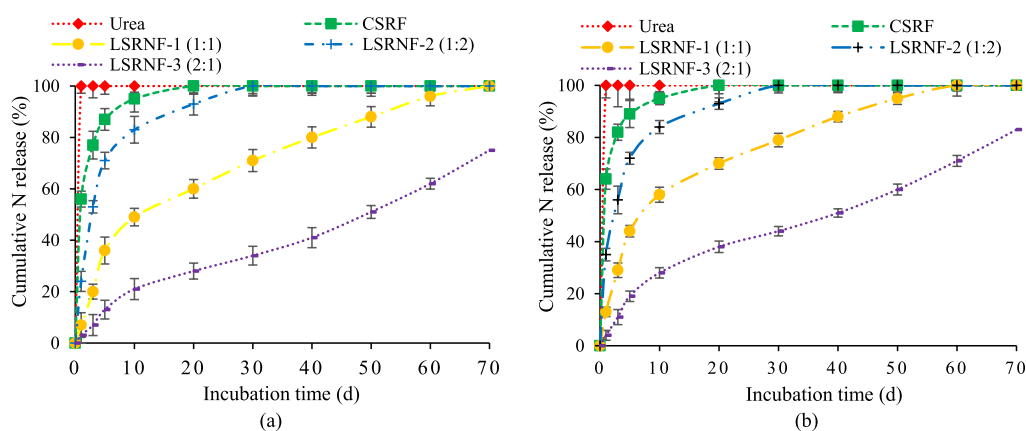


Figure 4. Cumulative N release (%) in (a) fine-textured soil and (b) coarse-textured soil after application of different N-fertilizers [urea, commercial slow-release fertilizer (C-SRF) and lignite-based slow-release nitrogen fertilizer (LSRNF-1, 2, and 3)]. Error bars represent the standard error of three replicates.

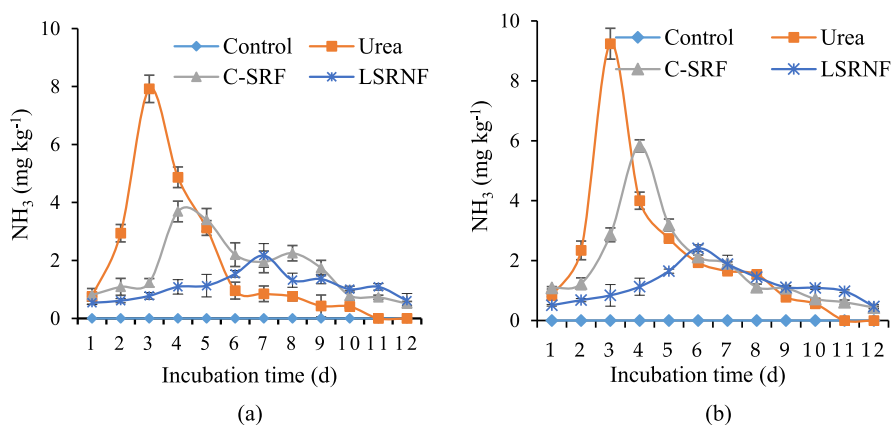


Figure 5. NH_3 -volatilization (mg kg^{-1}) in (a) fine-textured soil and (b) coarse-textured soil after application of different N-fertilizers (urea, C-SRF, and LSRNF). Error bars represent the standard error of three replicates.

textured soil and in 60 days in coarse-textured soil. All N from LSRNF (1:2) was released in 30 days in both soils. The N release from LSRNF (2:1) was 75% in fine-textured soil and 83% in coarse-textured soil during 70 days of the incubation period. So, on the basis of the N release pattern considering general crop needs, LSRNF-1 (1:1) was selected for further evaluation.

The extended N release from LSRNF into soils was due to the network structure of polyvinyl alcohol (PVA) and starch with lignite. Lignite can adsorb N to slow down its release rate, while the synergetic effects between binders further strengthen the slower release characteristics. Extended N retention by LSRNFs was also due to N adsorption on the surface of lignite. The urea first dissolved and then released through dynamic water exchange of adsorbed N via hydrogen bonding and surface complexation with oxygen-containing functional groups.⁴¹ Liu et al.²⁸ indicated that urea reacted with acidic functional groups or bound to specific sites on the surface of biochar.

2.4. NH_3 -Volatilization. The results (Figure 5) show that on all sampling days in fine-textured soil, NH_3 -volatilization from control (untreated), urea, C-SRF, and LSRNF ranged from 0.0–0.0, 0.41–7.92, 0.51–3.69, and 0.61–2.17 mg kg^{-1} , respectively. It was observed that there was a rapid increase in NH_3 -volatilization from the 3rd to 7th day in all treatments regardless of N fertilizers, and then, there was a decreasing

trend. On the 3rd day of incubation, urea emitted the maximum NH_3 -volatilization (7.92 mg kg^{-1}), followed by the C-SRF emitted 3.69 mg kg^{-1} NH_3 on the 4th day. However, LSRNF emitted the highest NH_3 (2.17 mg kg^{-1}) on the 7th day of incubation. It was further noticed that urea and C-SRF showed a sharp decline in NH_3 -volatilization after attaining the peak, whereas LSRNF demonstrated a slow decrease in NH_3 -volatilization after attaining the peak. Similarly, in coarse-textured alkaline calcareous soil, NH_3 -volatilization from urea and C-SRF ranged from 0.56–7.81 mg kg^{-1} and 0.43–5.83 mg kg^{-1} , respectively. The NH_3 -volatilization, on the other hand, from LSRNF ranged from 0.47–2.41 mg kg^{-1} . Beginning with a slow rise, NH_3 -volatilization significantly increased from day 3–6 after the application of urea and C-SRF, while in LSRNF, NH_3 -volatilization grew gradually until the 6th day and subsequently fell down following almost the same pattern. The maximum cumulative NH_3 -volatilization (23.02%) of applied N was recorded in urea, while it was decreased to 20.38% and 13.25% in fine-textured soil following the addition of C-SRF and LSRNF, respectively. Similarly, in coarse-textured soil, LSRNF significantly decreased the cumulative NH_3 -volatilization of applied N to 14.20% compared to 25.61 and 22.18% from CU and C-SRF, respectively (Figure 6).

The introduction of LSRNF, as opposed to CU, significantly reduced NH_3 -volatilization in alkaline calcareous soils. This was due to the complexation of N onto the surface of lignite.

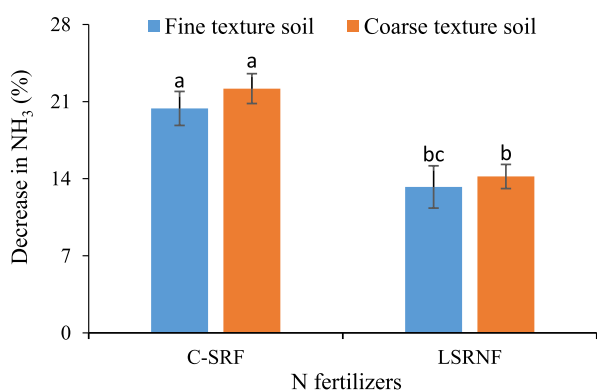


Figure 6. Decrease (%) in NH₃-volatilization after application of different N-fertilizers (urea, C-SRF, and LSRNF) in fine- and coarse-textured soils. Error bars represent the standard error of three replicates. Different letters within the same column indicate that the mean significantly differs according to Tukey's honestly significant difference test (Tukey's HSD) at $p < 0.05$.

The adsorption of urea was confirmed by SEM, XRD, and FTIR characterization of LSRNF. These results support the findings of other researchers who found that adsorption of urea with carbon-based materials reduced NH₃-volatilization by 23.1% in calcareous sandy loam soil.³⁰ In the present study, the lignite having acidic pH after urea adsorption and the introduction of acidic fertilizer reduced the soil pH and ultimately reduction in NH₃-volatilization. In addition, acidity (low pH), high CEC, and high hydrogen ion buffering capacity of lignite could have reduced the NH₃-volatilization in alkaline calcareous soils.³¹ The findings of this study back up Chen et al.,³² who found that adding lignite to soil decreased NH₃-volatilization from cattle manure by 60–68%.

2.5. NO₃-Leaching. The results (Figure 7) show that the application of LSRNF significantly decreased the NO₃-leaching compared to urea in both soils. It was also noticed that NO₃-leaching was higher at the start of the incubation period followed by a declining trend. It was further noticed that NO₃-leaching was higher in the first three leaching events in urea and C-SRF, while higher in LSRNF in the last four leaching events in both soils. Among all N fertilizers, urea showed the highest NO₃-leaching followed by C-SRF in both soils. This trend of NO₃-leaching clearly indicated a slow mineralization of N by LSRNF, compared to urea and C-SRF. In fine-textured soil, compared to urea, the percent decrease in cumulative

NO₃-leaching of applied N by C-SRF and LSRNF was 20.29 and 53.32%, respectively (Figure 8). Similarly, the percent reduction in cumulative NO₃-leaching by C-SRF and LSRNF of applied N in coarse-textured soil was 26.65 and 57.01% compared to urea, respectively.

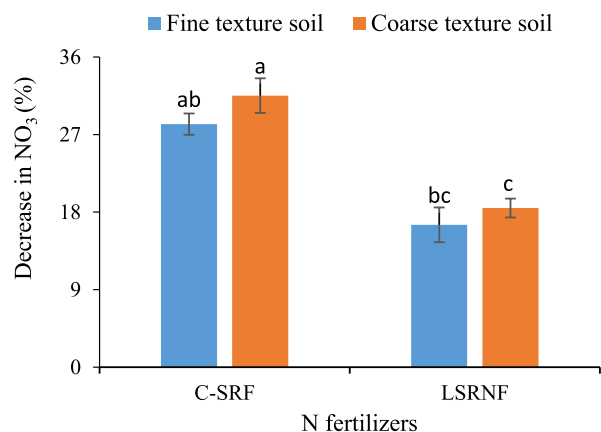


Figure 8. Decrease (%) in NO₃-leaching after application of different N-fertilizers (urea, C-SRF, and LSRNF) in fine- and coarse-textured soils. Error bars represent the standard error of three replicates. Different letters within the same column indicate that the mean significantly differs according to Tukey's HSD at $p < 0.05$.

Due to the potential of lignite to hold N and delay its mineralization, the addition of LSRNF significantly reduced the NO₃-leaching compared to CU. Joseph et al.³³ reported that NO₃-capture followed by pyrogenic C application could be due to a series of complex reactions involving the migration of urea to lignite pores, surface adsorption, and integration into an organo-mineral layer. The characterization of LSRNF in this study showed effective adsorption of urea on lignite which inhibited the fast release of urea in different soils and minimized its losses.

2.6. N₂O-Emission. The results showed that LSRNF significantly decreased the N₂O-emission compared to urea and C-SRF in both soils (Figure 9). In fine-textured soil, the maximum N₂O flux (296 and 209 $\mu\text{g kg}^{-1}$ soil day⁻¹) was measured on the 4th day in urea and C-SRF treatments which declined sharply after the 4th day. However, in LSRNF, the maximum N₂O flux (57 $\mu\text{g kg}^{-1}$ soil day⁻¹) was recorded on the 7th day, which declined slowly and gradually afterward,

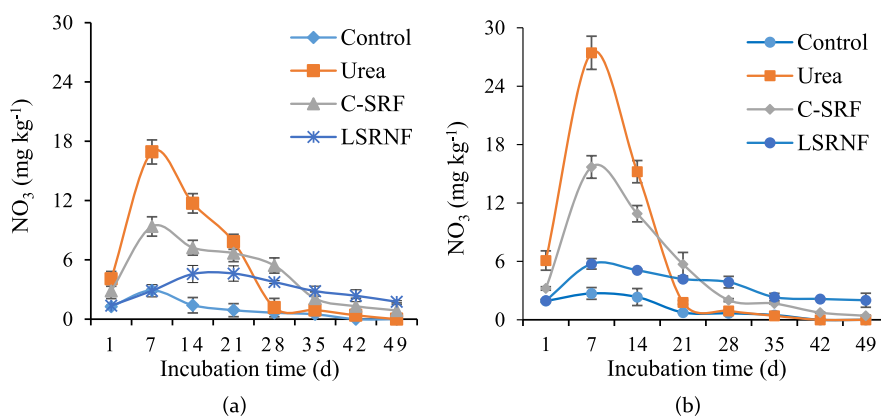


Figure 7. NO₃-leaching (mg kg^{-1}) in (a) fine-textured soil and (b) coarse-textured soil after application of different N-fertilizers (urea, C-SRF, and LSRNF). Error bars represent the standard error of three replicates.

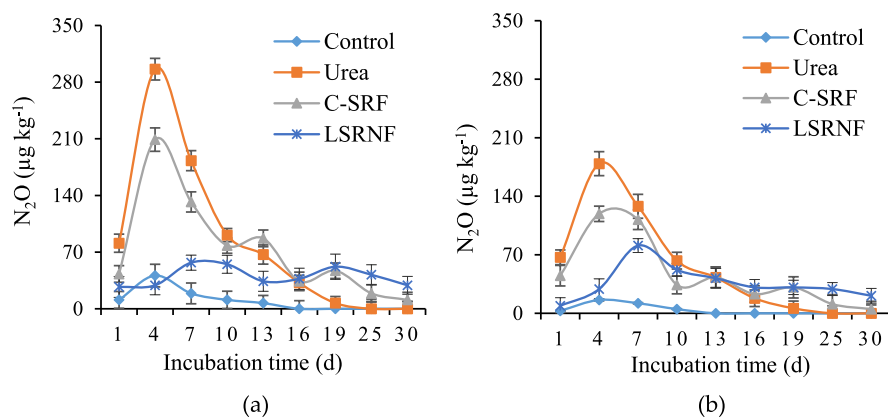


Figure 9. N₂O-emission in (μg kg⁻¹) (a) fine-textured soil and (b) coarse-textured soil after application of different N-fertilizers (urea, C-SRF, and LSRNF). Error bars represent the standard error of three replicates.

instead of a fast decline as it occurred in urea and C-SRF. The urea had the highest N₂O emission (757 μg kg⁻¹), which was about nine times greater than the control and significantly higher than the cumulative N₂O emission from all other treatments. In coarse-textured soil, urea had the highest N₂O flux (179 μg kg⁻¹ day⁻¹), followed by 119 μg kg⁻¹ day⁻¹ in C-SRF occurred on the 4th day. These values were 11 and 7 times greater than the control. N₂O flux in these treatments declined sharply after attaining this peak, while in control, N₂O-flux was quite low, never exceeding 16 μg kg⁻¹ soil day⁻¹. The highest N₂O emission (504 μg kg⁻¹) was recorded in urea following 423 μg kg⁻¹ in C-SRF. However, in LSRNF, the maximum N₂O flux (81 μg kg⁻¹ day⁻¹) was recorded on the 7th day. In fine-textured soil, compared to CU where 0.67% of applied N was lost as N₂O, the N₂O loss was decreased to 0.57 and 0.27% of the applied N in C-SRF and LSRNF treatments, respectively. In coarse-textured soil, 0.47% of applied N was emitted as N₂O in CU, but it was reduced to 0.39 and 0.29% of applied N by C-SRF and LSRNF, respectively (Figure 10).

The N₂O-emission was decreased significantly by LSRNF. The decrease in N₂O-emission could be due to slower N release and lower NO₃ availability during the incubation period. The reduction in N₂O emissions from the lignite-amended soil could be the result of the slower release of urea-

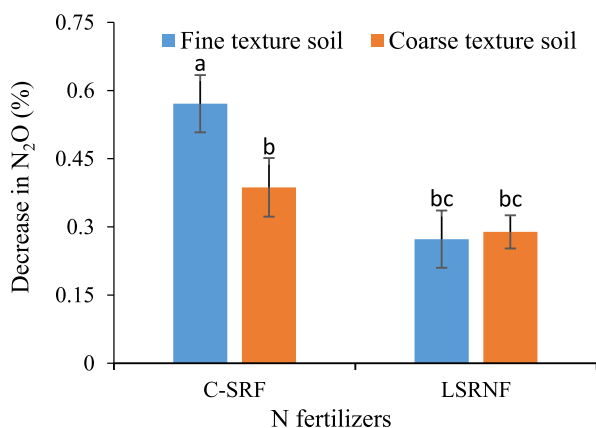


Figure 10. Reduction (%) in N₂O emission after application of different N-fertilizers (urea, C-SRF, and LSRNF) in fine and coarse-textured soils. Error bars represent the standard error of three replicates. Different letters within the same column indicate that the mean significantly differs according to Tukey's HSD at $p < 0.05$.

N and reduced availability of NO₃ during the incubation period.¹⁵

3. CONCLUSIONS

This research addressed the new LSRNF, using lignite as a N carrier. The lignite as a N carrier helped extend the N release period. It also offered a specific SRF to counter the N losses in alkaline calcareous soils which was missing earlier. The mechanisms that extended these benefits were extensive surface area, porosity, CEC, and diversity of functional groups of lignite which complexed the urea and enhanced N retention in soils. The LSRNF also significantly reduced the N losses (NH₃ by 45%, NO₃ by 57%, and N₂O by 52%) compared with CU. The acid leaching further enhanced the urea adsorption capacity of lignite by reducing the pH, EC, and ash contents while FC, surface area, CEC, and pore volume were enhanced. This research will offer a new N carrier for the synthesis of cost-effective and eco-friendly SRFs because lignite is widely available across the world.

4. MATERIALS AND METHODS

4.1. Materials. The lignite was collected from *Choa Saiden Shah Coal Mines*, Chakwal (Pakistan). All the chemicals used in this experiment were of reagent grade. The urea, boric acid, starch, and PVA were purchased from VWR International (USA), and C-SRF was purchased from Fatima Fertilizer Limited, Pakistan.

4.2. Characterization of Raw and Deashed Lignite and Urea-Loaded Lignite. The pH of RL, DL, and LSRNF was determined in a mixture (1:25, w/v) in deionized water using a digital pH meter. The samples were extracted to measure the EC using a digital EC meter.³⁴ The VM, A, and FC of RL and DL were measured following the standard procedure, developed by the American Society for Testing and Materials (ASTM).³⁵ The structural stability was identified by XRD. The BET surface area and pore volume were determined by the ASAP-2020 surface area and pore volume analyzer (Micromeritics, Norcross, GA, USA). The CEC was measured by the method described by Takaya et al.³⁶ The surface structure of RL, DL, and urea-loaded lignite was analyzed using an inspect S-50 scanning electron microscope (FEI, The Netherlands) at a magnification of 50 μm and HV 30,000 kv.

4.3. Preparation of LSRNF. Lignite was crushed and passed through a 0.5 mm sieve and leached by soaking in 0.1 M HCl for 24 h under continuous shaking to remove the

indigenous minerals.³⁷ After filtration through a 0.45 μm screen, sequential leaching with distilled water was carried out till the constant pH. The salient characteristics of RL and DL are presented in Table 1. The synthesis of LSRNF was carried out by mixing the DL and urea solution at the ratio of 1:1 (adsorbent: adsorbate) on a w/w basis under consistent shaking for 24 h.^{38,39} After urea loading, the material was dried at 65 $^{\circ}\text{C}$, and starch and PVA (1:1) were added at 10% (w/w basis) as binders to formulate the granules of LSRNF following the previously reported method.⁴⁰ The composition of LSRNF and other N fertilizers is presented in Table 2.

Table 2. Composition of N Fertilizers

fertilizers	N contents (%)	pH	C (%)
urea	46.0	7.22	
C-SRF	26.0	6.90	
LSRNF	21.0	6.47	31

4.4. Collection of Soil. A bulk soil (0–20 cm deep) was collected from two different locations: (i) Pindorian series, 33 $^{\circ}$ 55'55.4"N, 72 $^{\circ}$ 27'27.6"E (fine-textured soil) and (ii) Gujranwala series 33 $^{\circ}$ 56'06.4"N, 72 $^{\circ}$ 26'49.4"E (coarse-textured soil). The collected soils were air-dried and passed through a 2 mm screen, and a physicochemical analysis of both soils was carried out in the laboratory before using in experiments (Table 3).

Table 3. Physicochemical Properties of Soils Used in Experiments

soil parameter	unit	values					
		coarse-textured			fine-textured		
soil particle size distribution	%	sand	silt	clay	sand	silt	clay
		53	30	17	19	54	27
textural class	–	sandy loam			silty clay loam		
pH	–	7.7			7.6		
EC	d Sm^{-1}	1.02			1.11		
OC	%	0.34			0.41		
total-N	%	0.037			0.044		
$\text{NO}_3\text{-N}$	mg kg^{-1}	7.4			8.1		
$\text{NH}_4\text{-N}$	mg kg^{-1}	6.3			7.4		
available P	mg kg^{-1}	4.7			5.4		
extractable K	mg kg^{-1}	92			94		
CaCO_3	%	7.2			10.9		
CEC	$\text{cmol}^+ \text{kg}^{-1}$	11.3			13.1		

4.5. N Release Patterns of LSRNF. An incubation experiment was conducted at 25 \pm 2 $^{\circ}\text{C}$ to assess the N release behavior of N fertilizers in different soils. For this purpose, three different LSRNFs at a weight ratio of lignite and urea including LSRNF-1 (1:1), LSRNF-2 (1:2), and LSRNF-3 (2:1) were prepared. The treatments of the experiment were consisting of; (i) urea, (ii) C-SRF, (iii) LSRNF-1 (1:1), (iv) LSRNF-2 (1:2), and (v) LSRNF-3 (2:1), respectively. N contents equivalent to 1 g urea from each fertilizer were embedded into a polypropylene mesh bag (5 \times 5 cm) tied with a label showing the name of fertilizer. These mesh bags were buried beneath the 2–3 cm of soil surface into plastic containers filled with 150 g of soil. The diameter of the micro holes was 0.2 mm, and the distance between micro holes was 0.5 cm. The soil moisture contents were maintained at 60% of

field capacity by weighing and adding distilled water if necessary. The experiment was laid in a completely randomized design (CRD) having three replications in two different textured alkaline calcareous soils (coarse and fine texture). After 1, 3, 5, 10, 20, 30, 40, 50, 60, and 70 days of the incubation period, one mesh bag from each treatment was retrieved, and the total N was determined after being dried at room temperature to a constant weight. The loss in total N was subtracted from the initial contraction to assess the N release. This method was adopted by Wen et al.⁴¹ with some modifications. N was determined by the Kjeldahl method.⁴² The best-performing LSRNF out of three different formulations was selected and evaluated for further estimations.

4.6. NH_3 -Volatilization. The enclosure technique was adopted to trap and quantify the NH_3 -volatilization, as reported earlier by Liu et al.⁴³ The experiment was conducted with treatments including (i) control, (ii) urea, (iii) C-SRF, and (vi) LSRNF, respectively, with three replications arranged in the CRD layout. The application rates of different N fertilizers were 200 kg N ha^{-1} . Briefly, screw-lid plastic jars were filled with 500 g of soil. The treatments were mixed at the top 5 cm layer of each jar. About one-half of the space in the jars was left vacant for the production of NH_3 . Distilled water was slowly sprinkled on the surface of the soil to bring the soil moisture level up to 60% of water holding capacity, and a vial containing 10 mL of 4% boric acid, mixed with methyl red and bromocresol green indicators, was placed in every jar as NH_3 -trap and lids were screwed and airtight. All jars were incubated at 25 \pm 2 $^{\circ}\text{C}$. The experiment was repeated on two different textured alkaline calcareous soils. The experiment was executed soon after wetting the soil. The boric acid vials were removed and replaced daily until the color of the mixed indicator did not change, and the trapped NH_3 was measured by titrating with 0.01 M H_2SO_4 .

4.7. NO_3 -Leaching. An incubation experiment was conducted at 25 \pm 2 $^{\circ}\text{C}$ to evaluate the impact of LSRNF on NO_3 -leaching in two different alkaline calcareous soils. The experiment was conducted with treatments including (i) control, (ii) urea, (iii) C-SRF, and (vi) LSRNF with three replications arranged in the CRD layout. The application rates of different N fertilizers were 200 kg N ha^{-1} . The PVC columns 34 cm in height and 5 cm in diameter were fixed with polypropylene meshed cloth at the bottom, and then, columns were fixed on the plastic funnel having gravel in it. A layer of 3.0 cm of coarse sand was laid into every column to facilitate leachate movement. The columns were packed with soil, and a bulk density of 1.4 g cm^{-3} was maintained by gently tapping. A 4.0 cm from the top of every column was left open for ponding of distilled water. The apparatus was clipped on a wooden stand, and 500 mL leachate-receiving bottles were placed under each column to receive the leachate. The columns were saturated with distilled water, and a five pore volume of distilled water was leached for proper conditioning. Then, the treatments were mixed on top of every column, and one pore volume was leached on days 1, 7, 14, 21, 28, 35, and 42. Leachate was collected until it had totally leached out, and then, the leachate volume was recorded. The NO_3 concentration in the leachate was measured and the columns were covered with a polythene sheet to reduce evaporation, and the outlet was plugged till the next event of leaching. The method used in this experiment was adopted by Kanthle et al.⁴⁴ with some modifications.

4.8. N₂O-Emission. An incubation experiment was conducted at 25 ± 2 °C to evaluate the impact of LSRNF on N₂O emission in two different alkaline calcareous soils. The experiment was conducted with treatments including (i) control, (ii) urea, (iii) C-SRF, and (iv) LSRNF, respectively, with three replications arranged in the CRD layout. The application rates of different N fertilizers were 200 kg N ha⁻¹. Plastic jars having 7.5 cm diameter and 13 cm height, providing 250 mL headspace to a depth of 7 cm were filled with 500 g of soil. Soil moisture was kept at 60% of field capacity for 30 days. The jars were capped during the sampling and remained open for the rest of the time. All the treatments were mixed into the surface of the soil (2–3 cm deep). The N₂O measurements were made on 1, 4, 7, 10, 13, 16, 19, 25, and 30 days, at 0 h and 2 h for the initial and final time, after incubation using airtight 10 mL syringes. Gas samples were immediately analyzed for N₂O concentration using a gas chromatograph equipped with an electron capture detector. Total N₂O–N emission during 30 days was calculated by integration of actual N₂O emissions on sampling days. The method used in this experiment was adopted from a study by Majumdar et al.⁴⁵ with some modifications.

4.9. Soil Analyses. The analyses of soils used in experiments were conducted using following parameters, soil pH and soil EC,⁴⁶ organic carbon,⁴⁷ total nitrogen,⁴⁸ CaCO₃,⁴⁹ particle size distribution,⁵⁰ available-P,⁵¹ and NH₄ and NO₃.⁵²

4.10. Data Analysis. All data were reported as means and standard error of the means. Analysis of variance and Tukey's honestly significant difference test (Tukey's HSD) at *p* < 0.05 were used to determine the statistical significance of different treatment effects on N release, NH₃-volatilization, NO₃-leaching, and N₂O-emission.

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Notes

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