Controlled-Release Fertilizer with Lignin Used to Trap Urea/Hydroxymethylurea/ Urea-Formaldehyde Polymers

Gao-Jie Jiao,[a,b] Qiang Xu,[a,b] Sheng-Lei Cao,[c] Pai Peng,[c] and Diao She [a,b,*]

To improve nitrogen fertilizer efficiency and minimize the negative impact of nitrogen fertilizer on the environment, a novel three-dimensional network polymer material with slow release character was prepared based on hydroxymethylated lignin (HML) and urea/hydroxymethylurea/urea-formaldehyde polymers (U/HU/UF) through solution polymerization. The novel material (Lignin-U/HU/UF) was characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance spectra (^{1}H NMR), and distortionless enhancement by polarization transfer analysis (DEPT 135). The N release characteristics of the material were determined by soil leaching experiments under laboratory conditions. On this basis, the release profiles of total nitrogen and other nitrogenous compounds (NH_4^+ and NO_3^-) were investigated. The experimental data showed that lignin can be used as a majority component in material, which trapped polymers such as urea, hydroxymethylurea, and urea-formaldehyde to improve slow-release properties of fertilizer. The results indicated that the eco-friendly material (Lignin-U/HU/UF) with good controlled-release capacities potentially could be applied in agriculture and horticulture.

INTRODUCTION

The sustainable development of agriculture depends on the growing use of fertilizers to meet the need of a rapidly increasing world population. There are various types of natural and synthetic fertilizers for agriculture on the market in bulk quantities (Trenkel 1997). These fertilizers contain three elements, *i.e.*, nitrogen, phosphorous, and potassium. Urea ($CO(NH_2)_2$) is an important nitrogen fertilizer and a major source of plant nutrition (Baligar and Fageria 2015). Unfortunately, the practical use of conventional urea is not efficient due to its high water solubility. About 40% to 70% of nitrogen is lost to the environment by leaching and volatilization (Jansson and Thuvander 2004). The lost nitrogen results in marked inefficiency, less economic cultivation, reduced biomass production, and adverse environmental impact (Suherman and Anggoro 2011; Zarei and Ghaffarian 2013; Naz *et al.* 2014). Therefore, development of more efficient nitrogen fertilizers is extremely important (Wu *et al.* 2008). Controlled release fertilizer (CRF), a purposely designed manure, which releases active fertilizing nutrients at a pace that is synchronized with the nutritional demand of the plants, can retain

nutrients for a longer time and meet the sequential needs of plants for nutrients. Thus, an enhanced nutrient use efficiency and crop yield could be obtained (Shaviv 2005; Chien *et al.* 2009; Trenkle 2010).

There are three types of controlled-release fertilizers. In matrix-type formulations, diffusing nutrition elements spread slowly into the soil through the pores or channels. For example, modified rosin-paraffin wax resins prepared by mixing molten paraffin wax and molten modified rosin are controlled delivery systems. Potassium sulfate fertilizer is added and uniformly dispersed in this matrix. The potassium sulfate release is released through the pores of the matrix and gradually diffuses into the soil (Kakoulides and Valkanas 1994). A nitrogen-loaded slow release fertilizer based on the exfoliation of montmorillonite into a matrix of urea/urea-formaldehyde polymer has been produced by cold plastic extrusion (Yamamoto *et al.* 2016). The second type is by means of chemically or biologically controlled release, such as urea-formaldehyde fertilizer (Prasad *et al.* 1971). Urea-formaldehyde is formed by an acid-catalyzed reaction of urea with formaldehyde. Normally, linear and cross-linked urea-formaldehyde polymers of varying complexity result in varying slow-release cycles. Moreover, slow-release cycles are significantly influenced by the properties of soil such as pH, moisture, microbial activity, and soil texture. The third type is coating fertilizer. The release possibly depends on the physical properties of the coating material (Mulder *et al.* 2011). These materials can be divided into organic polymer and mineral-based inorganic coatings (Wang *et al.* 2013). The organic polymer coatings are based on resins and thermoplastic materials, such as polysulfone, wax, polyacrylonitrile, and cellulose acetate, whereas the mineral-based inorganic coatings are based on sulfur, phosphates, silicates, and other mineral materials (Hanafi *et al.* 2000; Jarosiewicz and Tomaszewska 2003). Coating fertilizer performs well for controlled release (Liang and Liu 2006; Jia *et al.* 2013). However, due to the high price, complex process, non-degradability of coating materials, and the non-recyclability of the organic solvents, coating fertilizer not only increases the costs of production, but also leads to environment issues (Yang *et al.* 2012; Azeem *et al.* 2014). These negative factors prevent the wide application of the coating controlled-release fertilizer in mainstream agriculture.

Lignin, one of the main components of lignocellulosic biomass, makes up 15% to 40% of dry matter of woody plants (Alekhina *et al.* 2015). It consists of three main phenylpropane units, namely guaiacyl alcohol (G), syringyl alcohol (S), and p-coumaryl alcohol (H) to form a complex three-dimensional randomized net linked to hemicelluloses. Due to its functional properties, low cost, and wide sources, lignin has good potential for preparing controlled-release fertilizers (Wilkins 1990; Ramirez-Cano *et al.* 2001). Acting as a humic acid precursor substance, lignin is a basic chemical substance for the formation of soil organic matter to influence the structure and the biological activity of soil (Stevenson 1994; Fischer and Schiene 2002). Lignin serves as a cheaper and biodegradable chelating agent to decrease the leaching of iron and zinc (Martín-Ortiz *et al.* 2009; Carrasco *et al.* 2012). At the same time, lignin, as a urease inhibitor, can reduce the nitrification rate of urea and enable urea to remain in the soil longer (Banta and Mendoza 1984).

There are two systems comprised of fertilizer and lignin. The first one is a fertilizer-lignin matrix. For example, lignin produces slow-release nitrogen fertilizers by ammoxidation (Meier *et al.* 1994; Ramírez *et al.* 2007). A hydrolyzed lignosulfonate-acrylonitrile graft copolymer matrix provides slow release solubility to urea (Detroit 1988). The second system is the coating system. The soluble fertilizer, such as urea or

phosphate fertilizer, is coated by the mixture of lignin and rosins (Ma *et al.* 1996, 1997). To improve coating properties, lignin also has been modified by physical and chemical methods, for example, steam explosion (Wang and Chen 2014), ammoxidation (Meier *et al.* 1994; Ramírez *et al.* 2007), Mannich reaction (Matsushita and Yasuda 2003), phenolation (Alonso *et al.* 2005; Hu *et al.* 2011), and hydroxymethylation (Alonso *et al.* 2004; Malutan *et al.* 2008), which improve its reactivity to cross-link other polymers.

Urea-formaldehyde fertilizers, the first group of products developed for slow release fertilizers, are typical condensation products, which are mainly comprised of urea-formaldehyde polymers having different degree of polymerization (Trenkel 2010). After application as fertilizers on soil, the short chain urea-formaldehyde polymers and unreacted urea show rapid release properties, whereas the long chain urea-formaldehyde polymers would release nitrogen in late stage of crop growth due to its low solubility and slow mineralization, which leads to nitrogen starvation of crops in early stage (Owen *et al.* 1952). Therefore, in order to meet the nutrient need of crop in early stage, it is essential to slow down the nitrogen release of the short chain urea-formaldehyde polymers and unreacted urea by certain measures.

Thus, in this study, a novel slow-release fertilizer based on lignin and urea/hydroxymethylurea/urea-formaldehyde was prepared by solution polymerization. The hydroxymethylated lignin (HML) made up a three-dimensional polymer network by condensation to trap free urea, hydroxymethylurea, and the short chain urea-formaldehyde polymers (UF). Lignin, an inexpensive and renewable material, trapped polymers such as urea, hydroxymethylurea, and urea-formaldehyde to improve the slow-release properties of fertilizer, and the three-dimensional polymer networks acted as a diffusional barrier against their dissolution to improve slow-release properties. Moreover, the availability of great quantities of technical lignin, a by-product in the chemical process of wood utilization, makes lignin a good candidate to prepare low cost slow-release fertilizer. In addition, urea-formaldehyde fertilizer provided extra nitrogen to accelerate the degradation of lignin due to its low C/N, which effectively enhanced the influence of lignin on soil. The product is expected to improve nitrogen fertilizer use efficiency and is beneficial to the ecosystem.

EXPERIMENTAL

Materials

Lignin extracted with mild alkaline solution from corncob residue after hydrolysis of hemicelluloses was supplied by the Longlive Biological Technology Co., Shandong, China. Its structural features and composition have been described previously (Yang *et al.* 2014). Regular urea prills with nitrogen content 46.5% and average primary particle size 0.5 mm to 2.0 mm were supplied by Shanghai Chemical Reagent Corp (China). All chemical materials were of analytical grade and used as received.

Preparation of Lignin-U/HU/UF

Hydroxymethylated lignin (HML) was synthesized as previously described (Wang and Chen 2014). Briefly, purified lignin (PL) and formaldehyde (FA) (PL/FA=8:1, w/w) were added to a three-neck flask equipped with a reflux condenser, thermometer, and motor-driven stirrer. Lignin was purified as described by Wang and Chen (2013). After adjusting the pH to 11.5 using 5 M NaOH, the solution was raised

gradually to 80°C. The PL was divided into three parts (50%, 30%, and 20%) and added into the system three times at intervals of 1 h. HML was collected by rotary evaporation and freeze-drying.

Formaldehyde solution was placed in a three-neck flask equipped with a reflux condenser, thermometer, and motor-driven stirrer. The pH was adjusted to 8.0 with 5 M NaOH. At the same time, the measured quantity of the urea was added and cooked at 90 $\pm$ 5 °C for 2 h. A certain amount of HML (1/10 w/w of HML to urea) was added into the hydroxymethylurea polymer solution (Table 1). The pH was adjusted to 5.3 after adding a desired volume of 20% CH_3COOH solution while stirring (400 rpm). After 2 h, 5 M NaOH was added to adjust the pH to 7.0. The supernatant (HML_S-U) and precipitant (HML_P-U) were collected by centrifuging at 5000 rpm for 5 min. The supernatant was obtained by rotary evaporation and freeze-drying, while the precipitant was only subjected to freeze-drying. The scheme for preparation of HML-U is presented in Fig. 1.
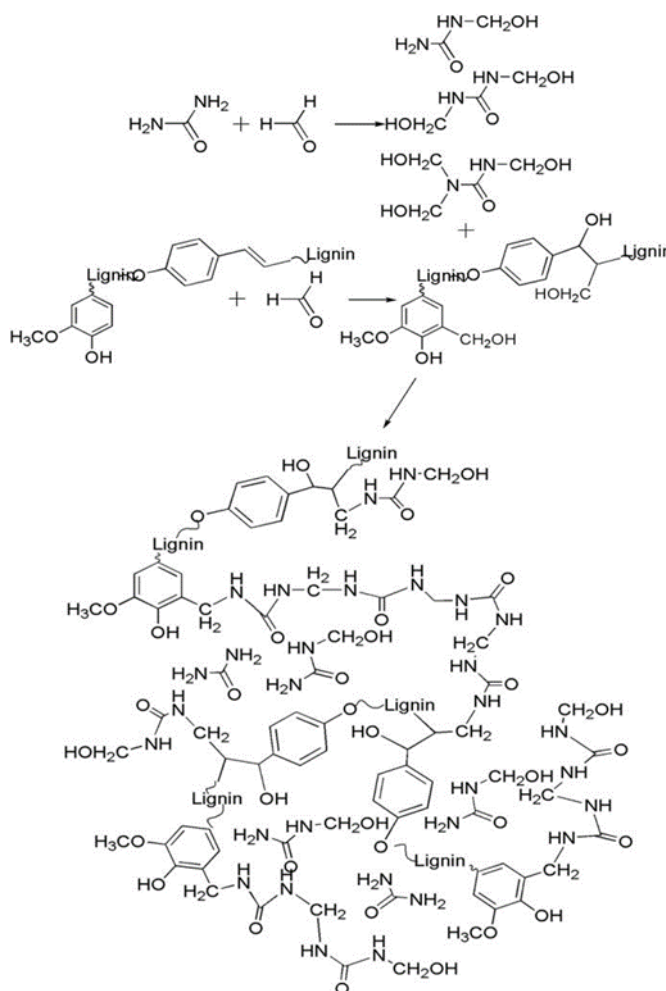
Fig. 1. Reaction of hydroxymethylurea polymer and hydroxymethylated lignin (HML) and formation of HML-U

Preparation of the Urea-Formaldehyde Fertilizers

Similar procedures to the methods above were repeated for the preparation of the hydroxymethylurea polymer solution. It should be noted that HML was not added into

the hydroxymethylurea polymer system at the polycondensation stage. The supernatant (HM$_S$-U) and precipitant (HM$_P$-U) were determined according to the above procedure. Finally, the resulting copolymers were dried, milled, and stored for further use. The resulting copolymers and their yields are listed in Table 1.

Table 1. Composition of Various CRFs

Samples	U/F[a] (molar ratio)	Lignin (g)	Yield (%)	Category
HML$_P$-U$_{0.8}$	0.8	2.5	55.85	
HML$_P$-U$_{1.3}$	1.3	2.5	19.83	precipitation
HML$_P$-U$_3$	3	2.5	5.97	
HM$_P$-U$_{1.3}$	1.3	—	31.69	
HML$_S$-U$_{0.8}$	0.8	2.5	27.14	
HML$_S$-U$_{1.3}$	1.3	2.5	68.93	supernatant
HML$_S$-U$_3$	3	2.5	91.55	
HM$_S$-U$_{1.3}$	1.3	—	53.88	

[a]U/F, urea / formaldehyde

Preparation of Lignin-U

In order to analyze the structure of Lignin-U/HU/UF, it was also necessary to analyze the structure of Lignin-U. A certain amount of urea, HML (3/1, w/w) and water were placed in three-neck flask equipped with a reflux condenser, thermometer, and motor-driven stirrer. The pH value was adjusted to 5.3 with 1 M HCl and stirring (400 rpm). After cooking at 90 ± 5 °C for 2 h, 6 M HCl solution was added to adjust the pH to 2.0 at ambient temperature. The precipitated lignin-U (LU) was recovered *via* filtration. This precipitate was repeatedly washed with distilled water and then freeze-dried.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were performed on a simultaneous thermal analyser (SDT Q600, TA Instrument, Selb, Germany) under a nitrogen atmosphere. Samples (3 mg to 6 mg) were heated from room temperature to 700 °C at a rate of 10 °C/min.

Fourier Transform Infrared (FT-IR) Characterization

FT-IR spectra of the samples were obtained using a Thermo Scientific Nicolet iN 10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI) equipped with a liquid nitrogen cooled MCT detector. Dried preparations were ground and their spectra were recorded in the range of 4000 cm^{-1} to 650 cm^{-1} at 4 cm^{-1} resolution and 128 scans per sample. Before data collection, background scanning was performed for correction.

^{1}H NMR and DEPT 135 Analysis

The solution-state ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (Karlsruhe, Germany) at 25 °C after 15 mg samples dissolved in 0.5 mL D$_2$O for PL and HML, respectively. The DEPT 135 spectra were obtained on a Bruker DRX-400 spectrometer (Karlsruhe, Germany) at 25 °C after 80 mg samples were dissolved in 0.5 mL D$_2$O (PL and HML) or DMSO-d$_6$ (LU and HML$_S$-U$_3$), respectively.

Nitrogen Release Behavior and Biodegradation in Soil

To study the nitrogen controlled-release behavior of the samples in soil, the following steps were performed. The soil (below 24 mesh) was taken from the surface

layer (0 cm to 20 cm depth) of meadow. The soil was dried at room temperature for 3 days after removing the roots of soil. The dried soil was sieved through a 2 mm sieve. Each sample (1 g) was mixed with the reference soil (50 g). Each soil incubation was added in the equipment (Fig. 2). The bottom part of the bottle was encapsulated with gauze. Throughout the experiment, all samples were incubated at 25 °C, and soil water content was adjusted to 30% by periodically adding water if necessary. The filtrates were collected at certain time intervals (1, 3, 5, 10, 15, 20, and 25 days) by adding 20 mL of tap water. The total N content of samples was determined by the Kjeldahl method (Bradstreet 1965). The ammonium (NH_4^+) or nitrate (NO_3^-) content was determined through agitated extraction. The ammonium (NH_4^+) and nitrate (NO_3^-) release rates were calculated as follows (Eqs.1 through 4),

$$NH_4^+\text{-}N = \alpha_{ppm} \times 10^{-3} \times d \times V_{bottle} \tag{1}$$

$$NO_3^-\text{-}N = \alpha_{ppm} \times 10^{-3} \times d \times V_{bottle} \tag{2}$$

$$TIN = NH_4^+\text{-}N + NO_3^-\text{-}N \tag{3}$$

$$TIN_{release} = TIN_{treatment} - TIN_{control} \tag{4}$$

where α_{ppm} is the result obtained in the flow injection (mg), d is the dilution, V_{bottle} is the total volume of the filtrate (mL), TIN is the total inorganic nitrogen content (mg).
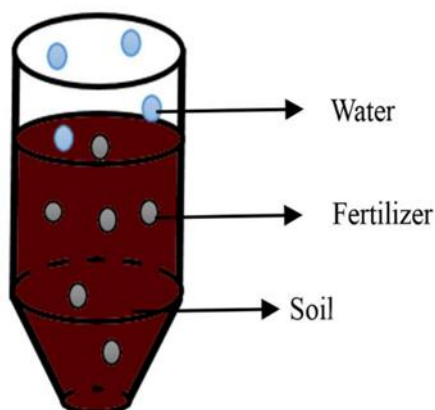

Fig. 2. Scheme of the equipment used in the study of controlled release

RESULTS AND DISCUSSION

FT-IR Analysis

The FT-IR spectra of the initial lignin (PL) and hydroxymethylated lignin (HML) are shown in Fig. 3. In the PL spectrum, peaks were observed at 3380 cm^{-1} (stretching vibration of O-H of R-OH and Ar-OH), 2941 cm^{-1} (methylene), 1699 cm^{-1} (stretching vibration of C=O of conjugated carboxylic acid and ketone groups), 1587cm^{-1}, 1505 cm^{-1} (aromatic skeletal vibrations), 1455 cm^{-1}(C-H deformation vibration in -CH$_3$ of methoxy groups), 1268 cm^{-1}, 1125 cm^{-1} (breathing vibration of syringyl and condensed guaiacyl, guaiacyl ring breathing with C=O stretching vibrations), 1217 cm^{-1} (C-C or C=O stretching vibrations), 1022 cm^{-1} (aromatic C-H in-plane deformation vibration), and 824 cm^{-1} (aromatic C-H out-plane deformation vibration), which are typical signals of lignin (Wen *et al.* 2013; Faix 1991).

For HML, there were some differences in the absorbance peaks. The obviously increased absorbances at 3380 cm^{-1} (stretching vibration of R-OH and Ar-OH) and 2941 cm^{-1} (caused by methylene) indicated that the methylolation increased the hydroxyl and methylene groups. The disappearance in the absorbance band at 1505 cm^{-1} (caused by breathing vibration of guaiacyl ring) indicated that formaldehyde was added into the aromatic C_5 position of G units. The absorbance at 824 cm^{-1} was assigned to aromatic C-H out-plane deformation vibration, which decreased obviously in the spectrum after methylolation.
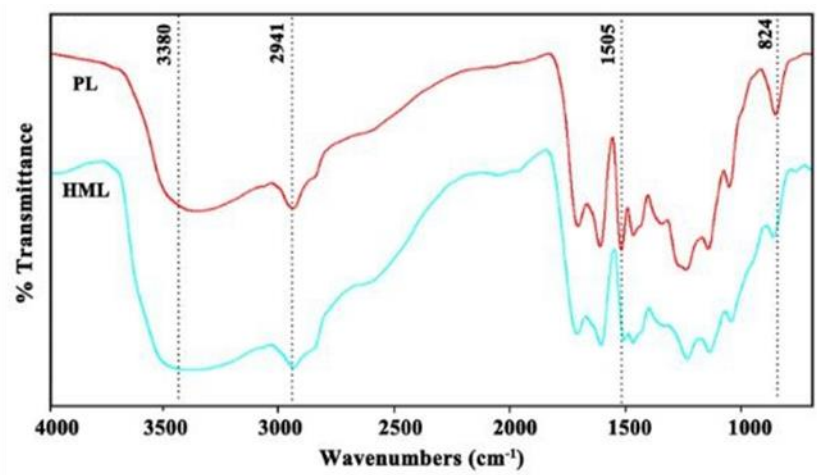

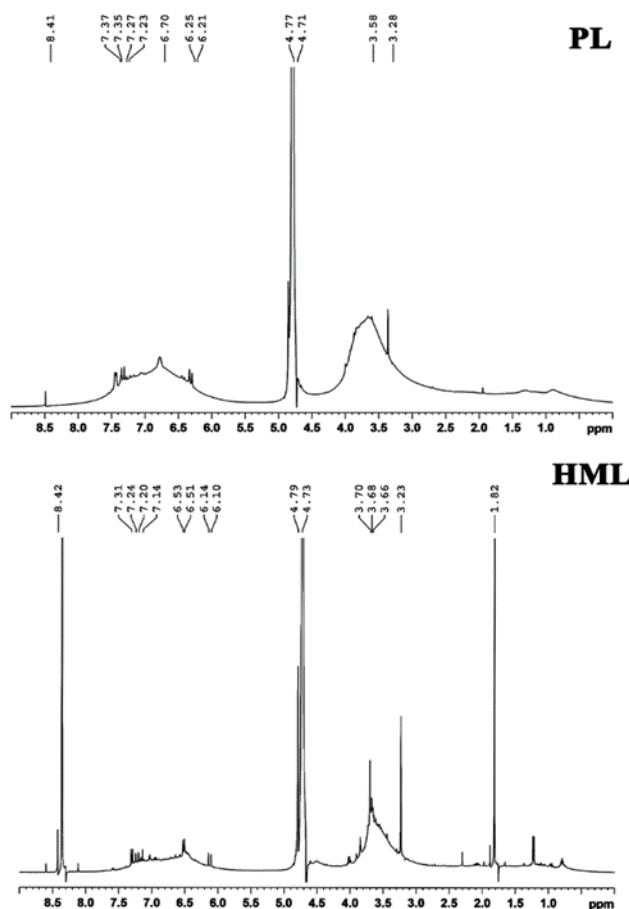**Fig. 3.** FTIR spectra of the PL and HML

bioresources.com


Fig. 4. ^{1}H NMR spectra of lignin and hydroxymethylated lignin

^{1}H NMR Analysis

The ^{1}H NMR spectra of lignin and hydroxymethylated lignin are shown in Fig. 4. Typical signals, *i.e.*, ~3.23 ppm for -CH$_2$ from hydroxymethyl groups, ~3.6 ppm for -OCH$_3$, ~4.79 ppm for solvent peak (D$_2$O), ~6.0 ppm, 6.5 ppm, and 7.0 ppm for Ar-H and ~8.42 ppm for formic acid were found in the spectrum of HML. The signal of -CH$_2$ linkages (3.23 ppm) in the hydroxymethyl chain of the lignin was strong in the HML spectrum but weak in the PL spectrum. Furthermore, the intensities of the Ar-H signals were weaker in the spectra of HML than those of lignin material. Therefore, the hydroxymethyl group was grafted on the lignin and changed its structure.

Distortionless Enhancement by Polarization Transfer (DEPT135) Analysis

The chemical shifts of DEPT 135 provided information on the chemical structure of the lignin-U/HMU/UF polymer (Fig. 5). In DEPT 135, all CH$_2$ signals face downward and CH or CH$_3$ signals face upward. Therefore, CH and CH$_3$ were distinguished from CH$_2$ by DEPT 135. In comparison with the spectrum of PL, it was clear that the new signals of HML appeared around at 61.3 ppm, which mostly probably be assigned to methylene CH$_2$ resonances of Ar-CH$_2$OH. The signals around at 68.5 ppm and 48.7 ppm might be due to CH resonances of C$_\alpha$ and C$_\beta$ from the Ar-CH(R)-CH(R)-CH$_2$OH unit of lignin, respectively. Anyway, these results suggested that the hydroxymethyl group was grafted on the lignin.
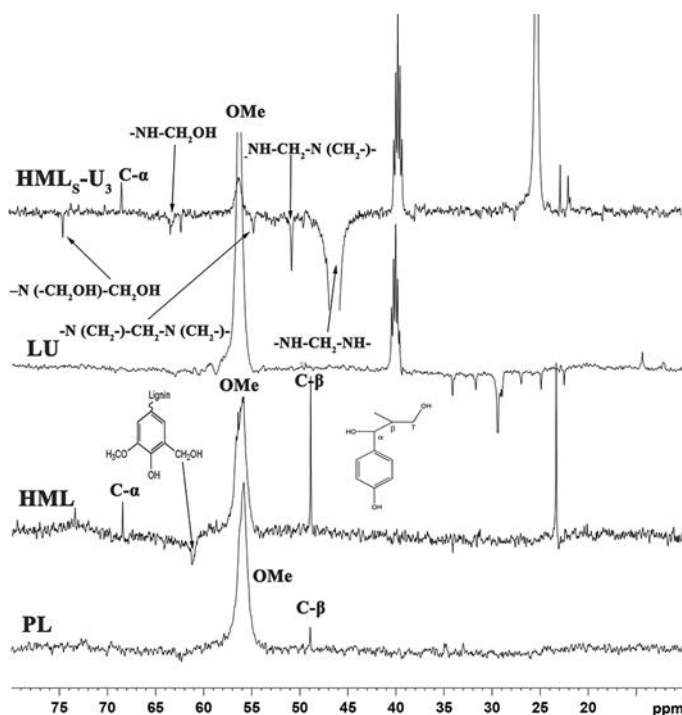
Fig. 5. DEPT 135 spectra of PL, HML, LU and HML$_S$-U$_3$

From the spectrum of LU, the signal around 61.3 ppm (methylene CH$_2$ resonances) disappeared. At the same time, some new signals around 21.9 ppm to 33.5 ppm appeared, which might be assigned to methylene CH$_2$ resonances of Ar-CH$_2$-NH- unit. This result suggested that hydroxymethylated lignin condensed into a three-dimensional polymer network. In the spectrum of HML$_S$-U$_3$, many new signals were assigned to methylene CH$_2$ resonances from HMU/UF. For example, the signals around 46.1 ppm, 50.6 ppm, and 54.7 ppm are assigned to CH$_2$ resonances of -NH-CH$_2$-NH-, -NH-CH$_2$-N(CH$_2$)- and -N(CH$_2$)-CH$_2$-N(CH$_2$)- unit, respectively. The signals around 62.1 ppm to 63.3 ppm and 74.4 ppm are due to CH$_2$ resonances of -NH-CH$_2$OH and -N(-CH$_2$OH)-CH$_2$OH units. The signals around 21 ppm to 26 ppm are assigned to the CH$_3$ resonances of CH$_3$COOH and CH$_3$CONHCONH$_2$. It is worth noting that the signals of lignin-U/HUM/UF in the spectra of HML$_S$-U$_3$ were difficult to assign due to their low solubility and complexity. However, through comparing with the spectra of PL, HML, LU, and HML$_S$-U$_3$, the structure of lignin-U/HUM/UF obtained in this study could be represented as shown in Fig. 1.

Thermogravimetric Analysis (TGA)

Thermal analyses show many details about the chemical composition of the various products, which are important for evaluating the slow-release property of products. In Fig. 6, the thermal stability of HML-U was better than that of urea and the HM-U, which was attributed to the addition of lignin, which increased the contents of thermostable macromolecules in these products. In addition, it is noteworthy that the "char residues" at 700 °C were 67.7% and 43.6% for HML and PL, respectively, indicating that more lignin with condensed structures, possessing a better thermal stability, were generated during the hydroxymethylation, which was beneficial for

bioresources.com

improving the slow-release properties of fertilizers. However, the thermo-decomposition rate of the HML was faster than that of PL at the beginning of decomposition, as presented in Fig. 6. This result was ascribed to the side chain oxidation of hydroxymethylated lignin (*i.e*., carbonylation/carboxylation of aliphatic hydroxyl group, side chain dehydrogenation) (Ke *et al.* 2011).

As shown in Fig. 7, urea presented two degradation stages. The maximum degradation rate occurred at 215 °C, resulting in 49% mass loss of urea, which was related to the release of NH_3 from the melting urea by volatilization. The polymerized fractions of urea were further degraded above 340 °C and decomposed completely at 400 °C. For HM-U, a shoulder peak was observed at around 290 °C, which resulted from the decomposition of urea-formaldehyde with low degree of polymerization, and the residues at 350 °C, nearly 23% of the total, might possess slow-release behavior in a longer term due to its high degree of polymerization. For HML-U, a same shoulder peak was found at 290 °C, indicating that those products contained a certain amount of urea-formaldehyde with low degree of polymerization (Fereidoon *et al.* 2013). At the same time, we noticed that similar to the DTG curve of urea, a small degradation peak appeared at 215 °C in the DTG curve of HML-U_3, while the peak was not found in other products such as HML-$U_{0.8}$ and HML-$U_{1.3}$. These results suggested there were a large amount of unreacted urea in the HML-U_3 matrix, which might be related to the high molar ratio of urea to formaldehyde (Yamamoto *et al.* 2016). Besides, it could be observed that after the temperature reached to 400 °C, DTG curves of all the samples became gradually flat and the mass loss of all the HML-U were much less as compared with HM-U. Based on the above analysis, it could be summarized that urea-formaldehyde with low degree of polymerization could be detected in all the products, while the unreacted urea appeared only in the HML-U_3, which was consistent with the results obtained by the leaching experiment.
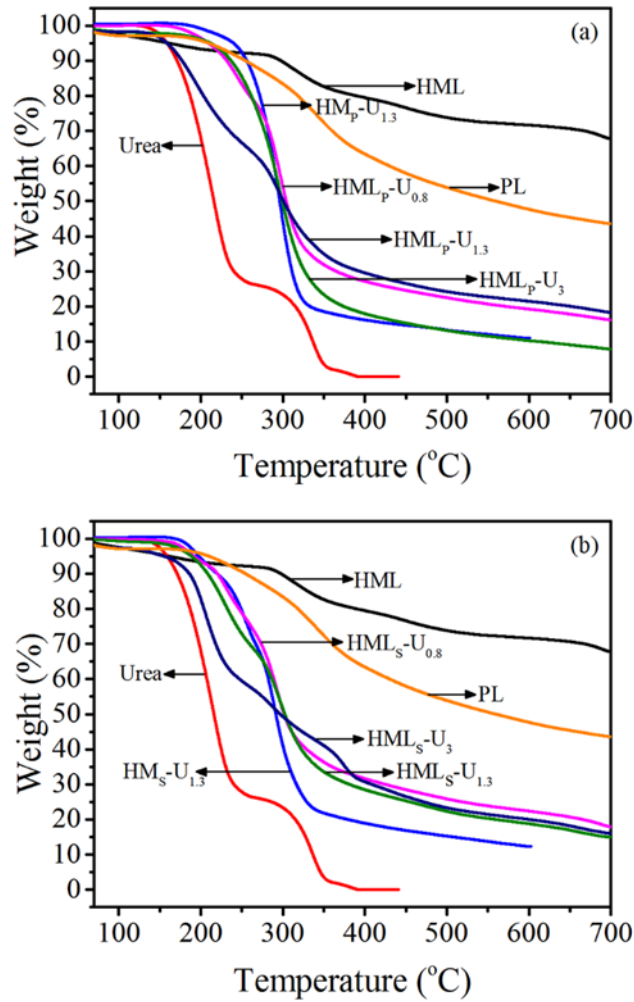
bioresources.com

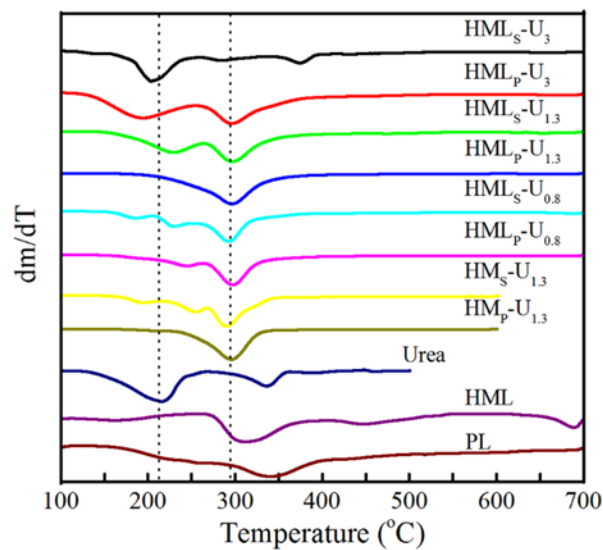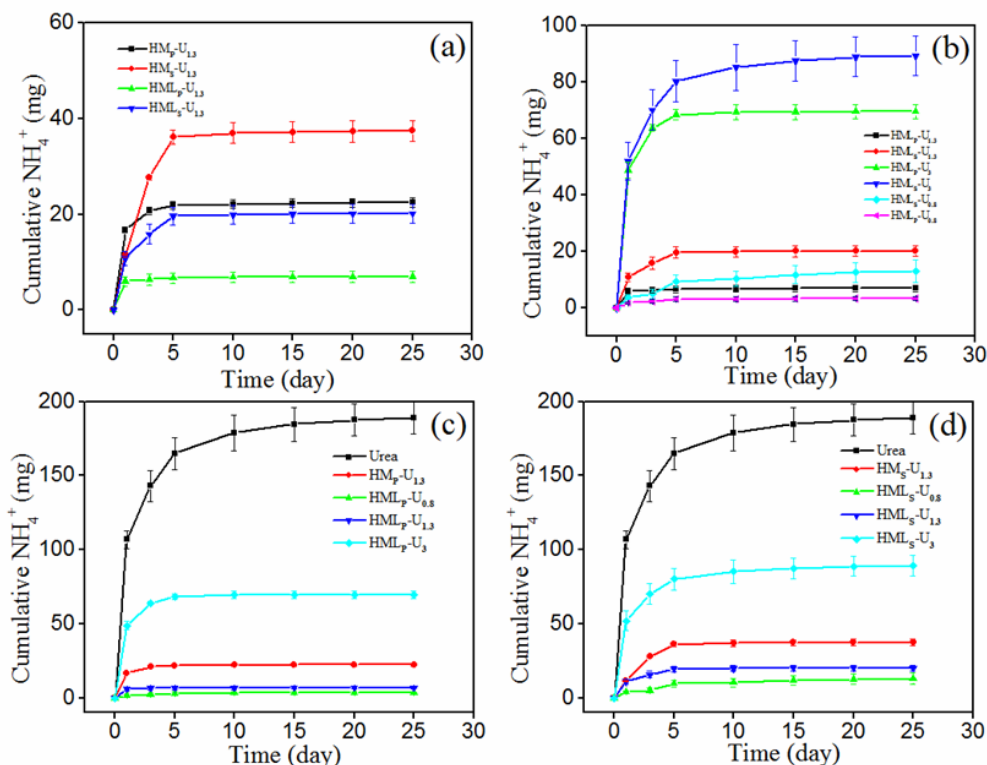**Fig. 6.** (a) TG curves of precipitated samples and (b) TG curves of supernatant samples


Fig. 7. DTG curves of lignin-U/HMU/UF formulations

Slow-Release Behavior of NH_4^+

Fig. 8. The release behavior of NH_4^+ obtained through soil incubation text

The NH_4^+ and NO_3^- are important plant-available nutrients. The cumulative release kinetics for NH_4^+ are shown in Fig. 8. It is worth noting that the release time and equilibrium value depended on the lignin, molar ratio of urea to formaldehyde, and derived form. In Fig. 8a, the cumulative NH_4^+ was 37.47 mg, 22.49 mg, 20.16 mg, and 6.9 mg for HM_S-$U_{1.3}$, HM_P-$U_{1.3}$, HML_S-$U_{1.3}$, and HML_P-$U_{1.3}$, respectively. Thus, lignin limited the formation of NH_4^+ and affected the nitrogen releasing properties. From Fig. 8b, the cumulative NH_4^+ of HML_P-U_3 and HML_S-U_3 were 69.53 mg and 89.23 mg, respectively, which were much more than the other samples. However, those of HML_P-$U_{0.8}$ and HML_S-$U_{0.8}$ were 3.39 mg and 12.90 mg, respectively. This indicates that the release behaviors were clearly influenced by the molar ratio of urea to formaldehyde. In the process of cross-linking polymerization reaction, the molar ratio of urea to formaldehyde affected both the degree of cross-linking and the molecular weight. The high molar ratio of urea to formaldehyde led to a low degree of polymerization and generated untreated urea and short-chain urea-formaldehyde. Conversely, the low molar ratio of urea to formaldehyde led to the high degree of polymerization and long-chain urea-formaldehyde, which was hard to decompose to supply the nutrient to the crops. As exhibited by HML_P-$U_{0.8}$ and HML_S-$U_{0.8}$, the release of NH_4^+ was very low. In Fig. 8c and 8d, the release behaviors of the precipitant were much slower than the supernatant, indicating that the precipitant may contain macromolecule polymers, such as long-chain formulations. The supernatant might contain small molecule substances, such as untreated urea, hydroxymethylurea, and short-chain formulations, which were easily degraded by microorganisms.

Slow-Release Behavior of NO_3^-

The NO_3^- is produced from available NH_4^+, meaning that the NO_3^- conversion is controlled by the total NH_4^+ content available. For all samples, the NO_3^- releasing trends followed the NH_4^+ evolution profile (Fig. 8 and Fig. 9). As shown in Fig. 9a through the contrast between HM-$U_{1.3}$ and HML-$U_{1.3}$, HML-$U_{1.3}$ had a slower release rate, indicating that lignin influenced the conversion of the available NH_4^+ to NO_3^-. In Fig. 9b, the NO_3^- release rate of high molar ratio of urea to formaldehyde samples, such as HML_P-U_3 and HML_S-U_3, was higher than that of low molar ratio of urea to formaldehyde samples (*i.e.*, HML_P-$U_{0.8}$ and HML_S-$U_{0.8}$). Figures 9c and 9d show the release profile of the precipitant and supernatant. The NO_3^- release rate of the precipitant was higher than that of the supernatant.
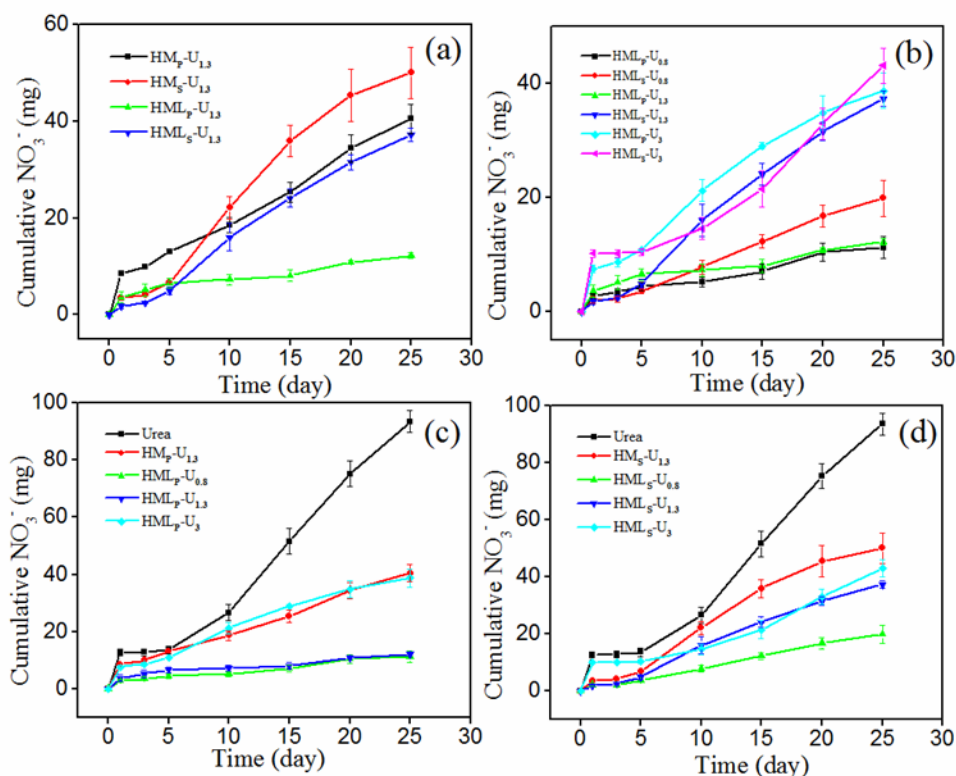
Fig. 9. The release behavior of NO_3^- obtained through soil incubation text

Slow-Release Behavior of Total Nitrogen

The slow release trends for total nitrogen of all samples are shown in Fig. 10. During this stage, about 95.3% of nitrogen from urea was released in the soil. However, other samples had a certain performance on controlled release capability. The amount of released nitrogen of the HM_P-$U_{1.3}$, HML_P-$U_{1.3}$, HM_S-$U_{1.3}$, and HML_S-$U_{1.3}$ were 37.9%, 23.4%, 49.2%, and 46.7%, respectively (Fig. 10a). Compared with the release behavior of HM-$U_{1.3}$, the amount of released nitrogen of HML-$U_{1.3}$ was less, indicating that lignin trapped urea or hydroxymethylurea to improve the slow-release capacity.

For those samples derived from the precipitated composition (*i.e.*, HML_P-$U_{0.8}$, HML_P-$U_{1.3}$, and HML_P-U_3), the amounts of released nitrogen were 15.7%, 23.4%, and 48%, respectively (Fig. 10b). It is worth noting that the amount of released nitrogen did not reach 50%. For the supernatant samples (*i.e.*, HML_S-$U_{0.8}$, HML_S-$U_{1.3}$, and HML_S-U_3), the amounts of released nitrogen were 37%, 46.7%, and 70%, respectively. It was

bioresources.com

remarkable that the amounts of released nitrogen were much more than these of the samples derived from the precipitant. The supernatant had a shorter slow release cycle due to its high release rate, and the precipitant had a longer slow release cycle. In the hybrid fertilizer, the large released nitrogen of the supernatant meets the needs of the early growth of crops, and the slow released nitrogen of the precipitant supports the late growth of crops. Therefore, this fertilizer can release nutrients continuously for the entire crop growth cycle.
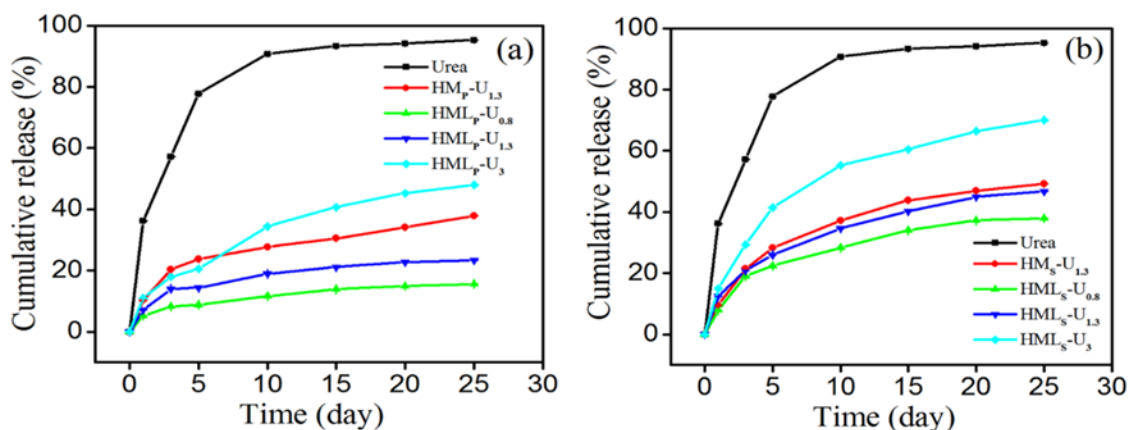

Fig. 10. The release behavior of total nitrogen obtained through soil incubation

CONCLUSIONS

1. A slow-release fertilizer based on a three-dimensional polymer network trapping urea/hydroxymethylurea/urea-formaldehyde polymers was prepared by condensation of hydroxymethylated lignin. The slow-release experiment demonstrated that the product had good slow release properties. The nitrogen released did not exceed 75% after being incubated in soil for 25 days.

2. The presence of lignin was essential to improve slow release properties of fertilizer because it trapped untreated urea, hydroxymethylurea, and urea-formaldehyde. This result indicated that lignin improved the slow-release capacity of fertilizer. In addition, the derived form impacted the extent of the slow-release capacity. These results suggest that this low-cost and eco-friendly compound fertilizer has great potential in agriculture and horticulture.

ACKNOWLEDGMENTS

bioresources.com

REFERENCES CITED

Alekhina, M., Ershova, O., Ebert, A., Heikkinen, S., and Sixta, H. (2015). "Softwood kraft lignin for value-added applications: Fractionation and structural characterization," *Industrial Crops & Products* 66, 220-228. DOI: 10.1016/j.indcrop.2014.12.021

Alonso, M. V., Oliet, M., Rodríguez, F., Astarloa, G., and Echeverría, J. M. (2004). "Use of a methylolated softwood ammonium lignosulfonate as partial substitute of phenol in resol resins manufacture," *Journal of Applied Polymer Science* 94(2), 643-650. DOI: 10.1002/app.20887

Alonso, M. A. V., Oliet, M., Rodríguez, F., García, J., Gilarranz, M. A., and Rodríguez, J. J. (2005). "Modification of ammonium lignosulfonate by phenolation for use in phenolic resins," *Bioresource Technology* 96(9), 1013-1018. DOI: 10.1016/j.biortech.2004.09.009

Azeem, B., Kushaari, K., Man, Z. B., Basit, A., and Thanh, T. H. (2014). "Review on materials & methods to produce controlled release coated urea fertilizer," *Journal of Controlled Release Official Journal of the Controlled Release Society* 181(1), 11-21. DOI: 10.1016/j.jconrel.2014.02.020

Baligar, V. C., and Fageria, N. K. (2015). "Nutrient use efficiency in plants: An overview," in: *Nutrient Use Efficiency: From Basics to Advances*, Springer India, New Delhi, India, pp. 1-14.

Banta, S., and Mendoza, C. V. (1984). *Organic Matter and Rice*, International Rice Research Institute, Manila, Philippines.

Bradstreet, R. B. (1965). "The Kjeldahl method for organic nitrogen," *Analytical Chemistry* 26(1), 169-234. DOI: 10.1016/B978-1-4832-3298-0.50008-4

Carrasco, J., Kovács, K., Czech, V., Fodor, F., Lucena, J. J., Vértes, A., and Hernandez-Apaolaza, L. (2012). "Influence of pH, iron source, and Fe/ligand ratio on iron speciation in lignosulfonate complexes studied using mössbauer spectroscopy. Implications on their fertilizer properties," *Journal of Agricultural & Food Chemistry* 60(13), 3331-3340. DOI: 10.1021/jf204913s

Chien, S. H., Prochnow, L. I., and Cantarella, H. (2009). "Recent developments of fertilizer production and use to improve nutrient efficiency and minimize environmental impacts," in: *Advances in Agronomy*, Elsevier Science & Technology, San Diego, USA, pp. 267-322. DOI: 0.1016/S0065-2113(09)01008-6

Detroit, W. J. (1988). "Controlled release formulation for fertilizers," U. S. Patent No. 4756738.

Faix, O. (1991). "Classification of lignins from different botanical origins by FT-IR spectroscopy," *Holzforschung* 45(s1), 21-28. DOI: 10.1515/hfsg.1991.45.s1.21

Fereidoon, A., Ahangari, M. G., and Jahanshahi, M. (2013). "Effect of nanoparticles on the morphology and thermal properties of self-healing poly(urea-formaldehyde) microcapsules," *Journal of Polymer Research* 20(6), 1-8. DOI:0.1007/s10965-013-0151-3

Fischer, K., and Schiene, R. (2002). "Nitrogenous fertilizers from lignins - A review," in: *Chemical Modification, Properties, and Usage of Lignin*, T. Q. Hu (ed.), Springer, Boston, USA, pp. 167-198.

Hanafi, M. M., Eltaib, S. M., and Ahmad, M. B. (2000). "Physical and chemical characteristics of controlled release compound fertiliser," *European Polymer Journal* 36(10), 2081-2088. DOI: 10.1016/S0014-3057(00)00004-5

Hu, L., Pan, H., Zhou, Y., and Zhang, M. (2011). "Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review," *BioResources* 6(3), 3515-3525. DOI: 10.15376/biores.6.3.3515-3525

Jansson, A., and Thuvander, F. (2004). "Influence of thickness on the mechanical properties for starch films," *Carbohydrate Polymers* 56(4), 499-503. DOI: 10.1016/j.carbpol.2004.03.019

Jarosiewicz, A., and Tomaszewska, M. (2003). "Controlled-release NPK fertilizer encapsulated by polymeric membranes," *Journal of Agricultural & Food Chemistry* 51(2), 413-417. DOI: 10.1021/jf020800o

Jia, X., Ma, Z. Y., Zhang, G. X., Hu, J. M., Liu, Z. Y., Wang, H. Y., and Zhou, F. (2013). "Polydopamine film coated controlled-release multielement compound fertilizer based on mussel-inspired chemistry," *Journal of Agricultural & Food Chemistry* 61(12), 2919-2924. DOI: 10.1021/jf3053059

Kakoulides, E. P., and Valkanas, G. N. (1994). "Modified rosin-paraffin wax resins as controlled delivery systems for fertilizers. 1. Fabrication parameters governing fertilizer release in water," *Industrial & Engineering Chemistry Research* 33(6), 457-460. DOI: 10.1021/ie00030a025

Ke, J., Singh, D., Yang, X., and Chen, S. (2011). "Thermal characterization of softwood lignin modification by termite *Coptotermes formosanus* (shiraki)," *Biomass & Bioenergy* 35(8), 3617-3626. DOI: 10.1016/j.biombioe.2011.05.010

Liang, R., and Liu, M. (2006). "Preparation and properties of coated nitrogen fertilizer with slow release and water retention," *Industrial & Engineering Chemistry Research* 45(25), 8610-8616. DOI: 10.1021/ie060705v

Ma, C. G., J. A. D., Vallejo, A., L. García, A., and Ma, C. C. (1996). "Use of kraft pine lignin in controlled-release fertilizer formulations," *Industrial & Engineering Chemistry Research* 35(1), 245-249. DOI: 10.1021/ie950056f

Ma, C. G., Vallejo, A., L. García, A., and Ma, C. C. (1997). "Manufacture and evaluation of coated triple superphosphate fertilizers," *Industrial & Engineering Chemistry Research* 36(3), 869-873. DOI: 10.1021/ie960153o

Malutan, T., Nicu, R., and Popa, V. I. (2008). "Contribution to the study of hydroxymetylation reaction of alkali lignin," *BioResources* 3(1), 13-20. DOI: 10.15376/biores.3.1.13-20

Martín-Ortiz, D., Hernández-Apaolaza, L., and Gárate, A. (2009). "Efficiency of a NPK fertilizer with adhered zinc lignosulfonate as a zinc source for maize (*Zea mays* L.)," *Journal of Agricultural & Food Chemistry* 57(19), 9071-9078. DOI: 10.1021/jf9017965

Matsushita, Y., and Yasuda, S. (2003). "Reactivity of a condensed–type lignin model compound in the mannich reaction and preparation of cationic surfactant from sulfuric acid lignin," *Journal of Wood Science* 49(2), 166-171. DOI: 10.1007/s100860300026

Meier, D., Zúñiga-Partida, V., Ramírez-Cano, F., Hahn, N. C., and Faix, O. (1994). "Conversion of technical lignins into slow-release nitrogenous fertilizers by ammoxidation in liquid phase," *Bioresource Technology* 49(2), 121-128. DOI: 10.1016/0960-8524(94)90075-2

Mulder, W. J., Gosselink, R. J. A., Vingerhoeds, M. H., Harmsen, P. F. H., and Eastham, D. (2011). "Lignin based controlled release coatings," *Industrial Crops & Products* 34(1), 915-920. DOI: 10.1016/j.indcrop.2011.02.011

Naz, M. Y., Sulaiman, S. A., Ariwahjoedi, B., and Shaari, K. Z. K. (2014).

"Characterization of modified tapioca starch solutions and their sprays for high temperature coating applications," *The Scientific World Journal* 2014(2014), 375206. DOI: 10.1155/2014/375206

Owen, O., Winsor, G. W., and Long, M. I. E. (1952). "The properties of some urea-formaldehyde materials in relation to their possible use as nitrogenous fertilizers," *Journal of the Science of Food & Agriculture* 3(11), 531-541. DOI: 10.1002/jsfa.2740031107

Prasad, R., Rajale, G. B., and Lakhdive, B. A. (1971). "Nitrification retarders and slow-release nitrogen fertilizers," *Advances in Agronomy* 23, 337-383. DOI: 10.1016/S0065-2113(08)60156-X

Ramírez-Cano, F., Ramosquirarte, A., Faix, O., Meier, D., Gonzálezalvarez, V., and Zúñigapartida, V. (2001). "Slow-release effect of n-functionalized kraft lignin tested with sorghum over two growth periods," *Bioresource Technology* 76(1), 71-73. DOI: 10.1016/S0960-8524(00)00066-3

Ramírez, F., Varela, G., Delgado, E., López-Dellamary, F., Zúñiga, V., González, V., Faix, O., and Meier, D. (2007). "Reactions, characterization and uptake of ammoxidized kraft lignin labeled with 15 N," *Bioresource Technology* 98(7), 1494-1500. DOI: 10.1016/j.biortech.2005.08.004

Shaviv, A. (2005). *Controlled release fertilizers, IFA International Workshop on Enhanced-Efficiency Fertilizers, Frankfurt,* International Fertilizer Industry Association, Paris, France.

Stevenson, F. J. (1994). "Humus chemistry: Genesis, composition, reactions," *Soil Science* 135(2), 129-130. DOI: 10.1021/ed072pA93.6

Suherman and Anggoro, D. D. (2011). "Producing slow release urea by coating with starch/acrylic acid in fluid bed spraying," *International Journal of Engineering & Technology*. 11(6), 77-80. DOI: 10.1166/asl.2017.8819

Trenkel, M. E. (1997). *Controlled-release and Stabilized Fertilizers in Agriculture*, Vol. 11, International Fertilizer Industry Association, Paris, France.

Trenkel, M. E. (2010). *Slow-and Controlled-release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*, IFA, International Fertilizer Industry Association, Paris, France.

Wang, G., Yang, L., Lan, R., Wang, T., and Jin, Y. (2013). "Granulation by spray coating aqueous solution of ammonium sulfate to produce large spherical granules in a fluidized bed," *Particuology* 11(5), 483-489. DOI: 10.1016/j.partic.2012.10.005

Wang, G., and Chen, H. (2013). "Fractionation of alkali-extracted lignin from steam-exploded stalk by gradient acid precipitation," *Separation & Purification Technology* 105(5), 98-105. DOI: 10.1016/j.seppur.2012.12.009

Wang, G. H., and Chen, H. Z. (2014). "Carbohydrate elimination of alkaline-extracted lignin liquor by steam explosion and its methylolation for substitution of phenolic adhesive," *Industrial Crops & Products* 53(1), 93-101. DOI: 10.1016/j.indcrop.2013.12.020

Wen, J. L., Xue, B. L., Xu, F., Sun, R. C., and Pinkert, A. (2013). "Unmasking the structural features and property of lignin from bamboo," *Industrial Crops & Products* 42(1), 332-343. DOI: 10.1016/j.indcrop.2012.05.041

Wilkins, R. M. (1990). *Controlled Delivery of Crop Protection Agents*, Taylor & Francis, Abingdon, Britain.

Wu, L., Liu, M., and Liang, R. (2008). "Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention,"

bioresources.com

Bioresource Technology 99(3), 547-554. DOI: 10.1016/j.biortech.2006.12.027

Yamamoto, C. F., Pereira, E. I., Mattoso, L. H. C., Matsunaka, T., and Ribeiro, C. (2016). "Slow release fertilizers based on urea/urea-formaldehyde polymer nanocomposites," *Chemical Engineering Journal* 287, 390-397. DOI: 10.1016/j.cej.2015.11.023

Yang, Y., Zhang, M., Li, Y. C., Fan, X., and Geng, Y. (2012). "Controlled release urea improved nitrogen use efficiency, activities of leaf enzymes, and rice yield," *Soil Science Society of America Journal* 76(6), 2307-2317. DOI: 10.2136/sssaj2012.0173

Yang, S., Wen, J. L., Yuan, T. Q., and Sun, R. C. (2014). "Characterization and phenolation of biorefinery technical lignins for lignin-phenol-formaldehyde resin adhesive synthesis," *RSC Advances* 4(101), 57996-58004. DOI: 10.1039/C4RA09595B

Zarei, A., and Ghaffarian, V. (2013). "Preparation and characterization of biodegradable cellulose acetate-starch membrane," *Polymer-Plastics Technology and Engineering* 52(4), 387-392. DOI: 10.1080/03602559.2012.752831