

pubs.acs.org/IECR

# Synthesis of Aminopropyl-Functionalized Mesoporous Silica Derived from Geothermal Silica for an Effective Slow-Release Urea Carrier

S. Silviana,\* Atikah A. Janitra, Afriza N. Sa'adah, and Febio Dalanta



**ABSTRACT:** An effective method to prepare slow-release urea was developed with aminopropyl-functionalized mesoporous silica (MS) to achieve enhanced urea adsorption and slow-release properties. As a novel study, mesoporous silica was developed using treated geothermal silica as the silica source, cetyltrimethylammonium bromide (CTAB) as the surfactant, and 3-aminopropyl trimethoxy silane (APTMS) as the surface modification agent. Mesoporous silica with the most desirable properties of uniform micro-morphology containing 38.55 wt % silica particles, 668.849 m<sup>2</sup>/g surface area, 149.33–353.28 mL/g adsorption–desorption range, and 0.26 mL/g adsorption pore volume was achieved using 0.05 mol of CTAB. The synthesized mesoporous silica showed type-IV hysteresis, which corresponds to mesoporous materials. Differential



scanning calorimetry (DSC)-thermogravimetric analysis (TGA) thermograms showed that mesoporous silica is more reactive, with peaks at 82.3 and 159.5 °C, has good thermal stability, and undergoes only 17.61% weight loss until 124 °C. Scanning electron microscopy (SEM) showed that functionalization and urea adsorption to mesoporous silica resulted in no significant morphological changes. In the Fourier transform infrared (FTIR) spectra, MS/APTMS/U26.74 was observed to have higher intensities of C==O, N-H, C-N, and C-H groups compared with other samples. The cumulative urea release during 7 days was 184.5 ppm (92.4%) for commercial urea and 124.6 ppm (64.4%) for MS/APTMS/U26.74. The Higuchi kinetic model yielded the best fit predicting MS/APTMS/U26.74 release kinetics, with an  $R^2$  of 0.9979 and a Higuchi constant of 24.4964%/day. Finally, MS/APTMS/U26.74 synthesized using geothermal silica, CTAB, and APTMS was noted to possess a potential composition for slow-release urea with enhanced efficiency.

# **INTRODUCTION**

Nowadays, urea is being widely used in fertilizers,<sup>1,2</sup> as a source of nitrogen in ruminants,<sup>3,4</sup> in pesticides,<sup>5,6</sup> for microbial growth,<sup>7,8</sup> and for various agriculture activities due to its rich nitrogen content, abundance, and cost-effectiveness. However, several studies reported that a high content of urea fertilizers is lost due to leaching and ammonia volatilization<sup>9</sup> upon application in soil, eventually generating severe environmental pollution, especially in soil and water sources.<sup>10–12</sup> Therefore, slow-release urea (SRU) development serves as a means to improve urea efficiency, enhance controllable usage, and minimize environmental pollution. Currently, SRU is commonly prepared by encapsulating or adsorbing a saturated urea solution to porous matrix media such as zeolites,<sup>13-15</sup> porous polymer composites,<sup>16–18</sup> or mesoporous materials<sup>19–24</sup> to control the urea release. Several polymers have been used as SRU matrix media, such as polyacrylonitrile,<sup>25,26</sup> polysulfone,<sup>10</sup> poly(vinyl chloride),<sup>27</sup> polyacrylic-rubber,<sup>28</sup> poly(vinyl ac-etate),<sup>29</sup> and polyurethane.<sup>30</sup> Sulfur-only-coated urea releases 83% urea after 7 days,<sup>10</sup> whereas impregnation on hydroxyapatite yields a release rate of 88% after 460 s.<sup>14</sup> Another study found that the use of bentonite in polycaprolactone or polyacrylamide hydrogel yields 75% urea release after 30 or 60 h.<sup>15</sup> Slow-release membrane-encapsulated urea yields 90% nitrogen release after the 5th day<sup>25</sup> and double-coated slowrelease fertilizers using ethyl cellulose (EC and starch-based superabsorbent polymer) yield 70% urea release at 96 h.<sup>23</sup> However, these polymers generate additional environmental issues due to the remaining nonbiodegradable polymer waste after they are used. Therefore, the application of biodegradable polymers has been carried out to solve the environmental

Received: February 4, 2022 Revised: May 28, 2022 Accepted: May 31, 2022

ACS Publications

Α

issues associated with the use of conventional polymers on SRU. Natural polymers have been applied as the matrix medium for SRU, including inorganics such as attapulgite<sup>31,32</sup> and organics such as cellulose,<sup>33</sup> chitosan,<sup>34</sup> aliginate,<sup>35,36</sup> starch,<sup>37</sup> and lignin.<sup>29</sup> Nevertheless, due to their natural characteristics, these natural polymers are easily attacked by fungi, bacteria, and other microorganisms, causing a lack of performance. Therefore, further investigations to develop a prominent matrix material for enhancing SRU characteristics and performance are still needed, and it remains a vast area of research.

Mesoporous silica (MS) has gained considerable attention because of its potential in various fields, including drug delivery,<sup>38-40</sup> catalysis,<sup>41</sup> adsorbents,<sup>42</sup> sensing,<sup>43</sup> and antibiotic-free antibacterial applications.<sup>44</sup> Due to the chemistry of silica, functionalizing and controllable tailoring of MS is easy, which allows it to be designed for the desired applications, including as the matrix medium for SRU. Many works have been conducted to synthesize MS with different structures, compositions, and pore properties to achieve desired and tunable characteristics.<sup>23,41,45,46</sup> The type of precursor, pH, reaction time, temperature, type and concentration of catalyst, cosolvent, and surfactant are the main influencers of the final properties of the synthesized MS.<sup>38,41,43</sup> Several synthesis procedures have been reported to develop MS with tunable and controllable properties, which are generally carried out in acidic and basic media.<sup>38,45,47</sup> Under both conditions, the effects of the reaction temperature, surfactant, cosolvent, and additive concentrations were observed, and numerous MS properties have been clearly explained.<sup>38,45,47</sup> A high specific surface area, high porosity, and tunable network framework structure can enable the generation of massive binding sites for urea in this matrix medium. However, it has also been reported that the thickness, hydrophilicity, and layer structure of the matrix medium strongly affect the release rate of SRU.<sup>28,30,34,47</sup> Consequently, to achieve a maintainable rate of urea release from the slow-release urea, further modification and/or functionalization of the SRU matrix medium is highly required.

Aminopropyl-functionalized materials have gained considerable interest due to their stronger absorption capability compared with several chemicals such as amines, phosphates, and nitrates. The presence of an amine group on aminopropylfunctionalized silica, which has an amine functional group similar to that of urea, causes the crystallization of urea by hydrogen bonding with other amine groups. This acts as a seed to initiate the crystallization of the urea network, thus enhancing the absorption of urea on the surface of aminopropyl-functionalized silica.<sup>24,48,49</sup> Various organometallic groups have been utilized to functionalize adsorption-based materials and enhance the capacity of adsorption and produce controllable kinetics.<sup>50,51</sup> Currently, the most investigated aminopropyl-functionalized material is biochar or activated carbon. Nevertheless, these materials preferably have welldeveloped surface morphology, but the micropore domination alters the adsorbate diffusion into the pores, causing a decrease in the adsorption capacity. Compared with biochar or activated carbon, MS has a high specific surface area, ordered pores, and relatively high pore volumes, indicating that it is a potential material for adsorbents with a controllable diffusion behavior.<sup>23,38</sup> Therefore, we was hypothesized the functionalization of MS as the SRU matrix medium to enhance the performance of SRU in terms of a high urea adsorption capacity and

controllable diffusion of urea from the synthesized SRU into the soil.

In this study, SRU with MS as the matrix medium was prepared from geothermal silica. Geothermal silica can be applied as the silica source to synthesize MS due to its high content of SiO<sub>2</sub>, which has been utilized in numerous applications. 52-57 The geothermal silica was purified using acid-leaching treatment before it was used. The purified silica was converted to sodium silicate as the precursor of silica source in MS preparation. Cetyltrimethylammonium bromide (CTAB) was used as the surfactant, and the mole amount of CTAB was varied to investigate its impact on the properties of the synthesized MS. The synthesized MS was further functionalized by covalently grafting aminopropyl groups on the MS surface using a 10% 3-aminopropyl trimethoxy silane (APTMS) solution to enhance the sorption capacity and slowrelease properties of the synthesized slow-release urea. The essential analyses, including morphology, chemical groups and compositions, surface area involving gas sorption, hysteresis behaviors, pore characteristics, and thermal properties, were comprehensively characterized using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectrometry, Xray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller and Barrett-Joyner-Halenda (BET-BJH) analyses, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The synthesized slow-release urea was experimentally tested in the soil to investigate the release characteristics and compared with commercial urea. The release kinetics of the synthesized slow-release urea were also studied by applying several appropriate kinetic models. Such a novel study of slow-release urea synthesis using aminopropylfunctionalized MS as the matrix, derived from geothermal silica as the silica source, and CTAB as the surfactant has not vet been reported.

### MATERIALS AND METHODS

**Materials.** The geothermal silica sample as the primary raw material for mesoporous silica synthesis was supplied by the geothermal power plant of PT Geo Dipa Energi, Dieng, Indonesia. Cetyltrimethylammonium bromide (CTAB, 99–101%) and 3-aminopropyl trimethoxy silane (APTMS, 99.8%) were purchased from Himedia and Sigma-Aldrich, Germany, respectively. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), sodium hydroxide (NaOH, 95%), and hydrochloric acid (HCl, 36.5–38%) used in purification treatments of geothermal silica were supplied by Mallinckrodt. Aqueous ammonia (NH<sub>4</sub>OH, 25%) and ethanol (C<sub>2</sub>H<sub>5</sub>OH, 96%) utilized in the preparation were purchased from Merck, Germany. Commercial urea (nitrogen  $\geq$ 46%) was supplied by PT Petrokimia Gresik, Indonesia. Distilled (DI) water was utilized in all experiments.

**Methods.** Purification Treatments of Geothermal Silica Samples. Geothermal silica contains contaminants. Therefore, it required a purification treatment to produce high-purity silica as the primary material to synthesize mesoporous silica.<sup>58-62</sup> There were two steps in the purification treatment, i.e., acid-leaching and a sodium silicate process. First, 250 g of the geothermal silica sample was dried in an oven at 110 °C for 12 h to reduce its moisture content. Then, the dried sample was crushed into a fine powder. This sample was then examined by X-ray fluorescence (XRF, Thermo Fisher Scientific) and X-ray diffraction (XRD, Thermo Fisher Scientific) to reveal its chemical composition and amorphous structure. Next, acid-leaching treatment was conducted based on the methods reported recently.<sup>58,59</sup> The treated geothermal silica (125 g) was carefully dispersed and constantly mixed in 500 mL of 20%  $H_2SO_4$  solution at 100 °C for 105 min. The acid processing by  $H_2SO_4$  is intended to remove the residual impurities on the sample, specifically the metal oxide content. After that, repeated washing and rinsing of the residue were performed to remove any unspent acid until a neutral pH was achieved. The residue was then placed in an oven at a temperature of 110 °C until completely dry. The treated silica from this step was analyzed using XRF and XRD.

The second purification step was conducted by filtering out the sodium silicate to further purify the treated silica of insoluble impurities. This procedure was conducted based on a method reported previously.<sup>55,59</sup> It was started by mixing 125 g of the treated silica sample with 600 mL of 4 M NaOH solution and was stirred and maintained at 90 °C for 60 min. After that, the mixture was filtered through a filter paper (Whatman No. 42) using a vacuum filter. The generated filtrate was sodium silicate, which was further applied as the precursor to synthesize mesoporous silica.

Synthesis of Mesoporous Silica. This step followed the modified Stöber method that was reported previously.<sup>59-61</sup> First, the primary solution was composed of 10 mol of ethanol, 22.4 mol of water, and 5.2 mol of NH<sub>4</sub>OH. The solution was constantly mixed at low speed (80-100 rpm) for 15 min. After that, CTAB as a surfactant was slowly added into the solution at concentrations of 0.015, 0.03, and 0.05 mol. Sodium silicate was prepared by dissolving 10 g of treated silica in 82.5 mL of 4 M NaOH. Next, 100 mL of the prepared sodium silicate solution was slowly added to the above solution. The solution turned opaque immediately, indicating that the reaction has started. The solution was continuously mixed and maintained for 2 h under room temperature conditions. After that, the solution was filtered to separate the solids as the generated mesoporous silica from the mixture through a filter paper (Whatman No. 42) using a vacuum filter. Subsequently, the solids were washed to remove any unspent solution. The solid was then calcined in a furnace burner at 550 °C to remove the remaining organic compounds, creating a mesoporous structure throughout the surface of the silica. The prepared mesoporous silica was characterized by scanning electron microscopy-energy-dispersive X-ray spectroscopy (Thermo Fisher Scientific), Brunauer-Emmett-Teller and Barrett-Joyner-Halenda (BET-BJH) analyses (autosorb IQ Quantachrome Instruments from Anton Paar Switzerland AG), thermal analysis of TG/DTA/DSC (Linseis STA 1600 Premium Series), and Fourier transform infrared spectroscopy (IRPrestige21, Shimadzu, Japan, by the transmittance mode of acquisition).

Purification Treatments of Geothermal Silica Samples. This procedure was based on previously reported studies.<sup>49,50</sup> In this method, APTMS was utilized as a silane coupling agent to modify the surface characteristics of mesoporous silica. First, calcined mesoporous silica was carefully mixed at 150 rpm with 10% APTMS solution at room temperature for 8 h. This step was performed to allow the surface modification reaction of mesoporous silica to yield the slow-release urea. It was then dried under atmospheric pressure at 40 °C. Finally, the modified mesoporous silica with APTMS was characterized using BET–BJH analysis and FTIR spectroscopy.

Next, 1 g of modified mesoporous silica/APTMS was added to the urea solution (U) at certain concentrations (6.74, 16.74,

26.74, and 36.74 wt %) with respect to 100 mL of aquadest. The mesoporous silica/APTMS with different urea compositions is presented in Table 1. The mixture was constantly

Table 1. Contents	of CTAB, APTMS,	and Urea i	n the
Preparation of the	Slow-Release Urea		

sample code	CTAB (mol)	APTMS solution (%)	urea solution (wt %)
MS	0.05	0	0
MS/APTMS	0.05	10	0
MS/APTMS/U6.74	0.05	10	6.74
MS/APTMS/ U16.74	0.05	10	16.74
MS/APTMS/ U26.74	0.05	10	26.74
MS/APTMS/ U36.74	0.05	10	36.74

stirred for 24 h at room temperature to allow the adsorption of urea into the mesoporous silica by hydrogen bonding.<sup>38</sup> Afterward, it was filtered, and the solids were dried in an oven at a temperature of 40 °C. Finally, the generated solids were characterized using FTIR spectroscopy.

Performance Test of the Prepared Slow-Release Urea. The slow-release urea performance was experimentally assessed by measuring the amount of urea present in the overflow liquid. The dissolved urea content in the groundwater was determined. Figure 1 depicts a schematic illustration of the



Figure 1. Schematic illustration of the apparatus for the slow-release urea performance test.

respective experiment. Initially, 1 g of slow-release urea was immersed in 25 g of soil in a plastic vase. Subsequently, 25 mL of DI water was used for watering the sample every day during 7 days of observation, and the overflow water from the vase was carefully collected. This test was repeated for three replications. The urea content in the overflow liquid was measured using a UV–vis spectrophotometer (Thermo Scientific GENESYS 10S). The measurement was performed at an optimum wavelength of 195 nm, which is close to the wavelength of 190 nm used in a previous research.<sup>62</sup>



Figure 2. (a) XRF results of the geothermal silica sample and purified silica after acid-leaching and (b) XRD patterns of geothermal silica and purified silica after acid-leaching.



Figure 3. SEM-EDX micrographs of the modified mesoporous silica using (a) 0.015 mol, (b) 0.03 mol, and (c) 0.05 mol of CTAB.

Study of Urea Release Kinetics. The mechanism of urea release from the slow-release urea was theoretically evaluated

by applying some kinetic models, such as the pseudo-firstorder, pseudo-second-order, Higuchi, and Hixson-Crowell

		MS-0	0.015 <sup>a</sup>	MS-	0.03 <sup>b</sup>	MS-	0.05 <sup>c</sup>
element	EDX recorded	weight (%)	atomic (%)	weight (%)	atomic (%)	weight (%)	atomic (%)
carbon	СК	25.16	33.59	27.94	27.66	11.42	17.36
nitrogen	N K	4.08	4.67	2.59	3.00	2.72	3.54
oxygen	O K	50.02	50.13	44.99	45.52	48.60	55.45
bromine	Br K	0.64	0.13	0.78	0.16	1.38	0.32
silicon	Si K	20.11	11.48	23.70	13.66	35.88	23.32

Table 2. Chemical Composition Data Extracted from EDX Spectra for Mesoporous Silica Using Three Different Amounts of CTAB

<sup>a</sup>MS-0.015 represents the mesoporous silica with 0.015 mol of CTAB. <sup>b</sup>MS-0.03 represents the mesoporous silica with 0.03 mol of CTAB. <sup>c</sup>MS-0.05 represents the mesoporous silica with 0.05 mol of CTAB.

models; the mathematical expressions of these models are represented by eqs 1-4.

Pseudo-first-order model<sup>63</sup>

$$\ln Q_t = \ln Q_0 - k_1 t \tag{1}$$

Pseudo-second-order model<sup>64</sup>

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_o^2} - \frac{t}{Q_o}$$
(2)

Higuchi model<sup>65</sup>

$$Q_t = K_{\rm H} t^{1/2} \tag{3}$$

Hixson–Crowell model<sup>63</sup>

$$Q_{o}^{1/3} - Q_{t}^{1/3} = K_{\rm HC}t \tag{4}$$

where  $Q_t$  is the amount of urea released at a certain time (%),  $Q_o$  is the initial amount of urea in the slow-release urea (%),  $k_1$  is the pseudo-first-order rate constant,  $k_2$  is the pseudo-second-order rate constant,  $K_{\rm H}$  is the Higuchi constant,  $K_{\rm HC}$  is the Hixson–Crowell constant, and *t* is time (day).

# RESULTS AND DISCUSSION

Properties of Purified Silica after Acid-Leaching Treatment. The sample of geothermal silica was subjected to acid-leaching treatment to remove the impurities, especially metal oxides. Figure 2a depicts the XRF results of geothermal silica and the purified silica after acid-leaching. The geothermal silica was found to consist of 86.3 wt % SiO<sub>2</sub>, with a fairly high content of metal oxides including CaO, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and MnO with concentrations of 3.21, 3.59, 0.07, 5.67, and 0.09 wt %, respectively. The presence of  $Cr_2O_3$  is a drawback of geothermal silica because it is not very reactive but dissolves in acid as hydrated chromium ions  $[Cr(H_2O)_6]^{3+}$ . This sample of geothermal silica was treated in 500 mL of 20% H<sub>2</sub>SO<sub>4</sub> solution at 100 °C for 105 min to dissolve the metal oxides into the sulfuric acid. The XRF analysis of the silica product after acid-leaching revealed that the sample consists of 95 wt % SiO<sub>2</sub>, leaving small amounts of metal oxides such as CaO, Cr<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and MnO with concentrations of 0.43, 0.42, 0.22, and 2.00 wt %, respectively. Based on this analysis, the acidleaching process significantly removed the metal oxides from the geothermal silica, resulting in a higher purity of the silica. The influence of the acid-leaching treatment was further evaluated by an XRD analysis.

Figure 2b represents the XRD patterns of geothermal silica and the purified silica after acid-leaching. The diffractogram pattern of geothermal silica shows a broad peak ranging from a  $2\theta$  of  $15-30^{\circ}$ , indicating the existence of amorphous SiO<sub>2</sub>. Three significant sharp peaks were found at 32.5, 46.3, and 49.8°, which correspond to Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and Cr<sub>2</sub>O<sub>3</sub> in the sample, respectively.<sup>38</sup> The purified silica after acid-leaching was also evaluated by XRD analysis. It can be clearly observed that the purified silica has a more significant broad peak at a  $2\theta$  of  $15-30^{\circ}$ , which indicates a higher amount of amorphous SiO<sub>2</sub> than that in the geothermal silica sample. Also, there are no other metal oxide peaks appearing in the diffractogram of the purified silica. Therefore, it can be reasonably concluded that the acid-leaching treatment successfully removed the metal oxides in the geothermal silica. Silica with higher purity ( $\geq$ 95%) can be utilized as the main material for synthesizing mesoporous silica with a higher Si content on its surface to react with surface-modifying agents.

Characterization of the Synthesized Mesoporous Silica. Surface Micrographs and Chemical Composition of the Synthesized Mesoporous Silica. In this study, the modified Stöber method was adapted for the synthesis of mesoporous silica. The reaction was conducted at room temperature using CTAB as the surfactant, aqueous NH<sub>4</sub>OH as the catalyst, ethanol as the cosolvent, and sodium silicate derived from geothermal silica as the silica source. For different formulations of material synthesis, the amount of NH<sub>4</sub>OH, ethanol, and sodium silicate were kept fixed, whereas the amount of CTAB was varied to 0.015, 0.03, and 0.05 mol. Hence, the effects of the mole amount of CTAB on mesoporous silica synthesis were experimentally investigated. It was found that different amounts of CTAB as a surfactant during synthesis have a significant effect on the micromorphology of the synthesized mesoporous silica, as clearly revealed by the SEM-EDX analysis shown in Figure 3 (with  $10.000 \times$  and  $20.000 \times$  magnifications). Figure 3a-c depicts the surface morphology images of mesoporous silica with 0.015, 0.03, and 0.05 mol of CTAB, respectively.

Different mole amounts of CTAB resulted in different shapes of mesoporous silica particles. When using 0.015 mol of CTAB (Figure 3a), the synthesized mesoporous silica had a randomized shape, fairly similar to that obtained with 0.03 mol of CTAB (Figure 3b), and showed a small increase in the number of mesoporous silica particles. Meanwhile, when using 0.05 mol of CTAB, the synthesized mesoporous silica had a more uniform particle shape. These findings suggest that the addition of CTAB tends to produce mesoporous silica particles. This phenomenon is in agreement with a previous study that an increasing amount of surfactant produces abundant interaction of two counter-charged surfactants, resulting in the growth of silicate particles.<sup>61</sup>

Further, an SEM-EDX analysis was carried out to reveal the chemical composition of the synthesized mesoporous silica with different loaded amounts of CTAB. Figure 3 shows the



Figure 4. Sorption isotherm of (a) geothermal silica, (b) purified silica after acid-leaching, and mesoporous silica products with CTAB variations of (c) 0.015 mol, <sup>68</sup> (d) 0.03 mol, and (e) 0.05 mol.

EDX spectra of the synthesized mesoporous silica with 0.015 mol (Figure 3a3), 0.03 mol (Figure 3b3), and 0.05 mol of CTAB (Figure 3c3). The quantification results of EDX are shown in Table 2, providing information about the chemical composition of the tested samples. The mesoporous silica synthesized with 0.015, 0.03, and 0.05 mol of CTAB were

found to consist of 20.11, 23.70, and 35.88 wt % Si, respectively. In the micrograph analysis, the mesoporous silica from 0.05 mol of CTAB was visualized as a white solid. According to previous research,<sup>66</sup> the CTAB surfactant undergoes a polar interaction with the silica precursor. It was observed that the hydrophilic head of CTAB was attached to

the surface of the silica, whereas the tail was oriented toward the polymer matrix. This phenomenon may be assumed to result from an interaction between the OH<sup>-</sup> ion on the silica surface and the N<sup>+</sup> ion of CTAB. In this step, ion exchange and aggregate formation can occur simultaneously. Furthermore, more mesoporous silica aggregates are released with a higher CTAB content. The aggregation of mesoporous silica is likely rectangular, as detected by the SEM analysis. Based on the BET-BJH analysis, a higher amount of CTAB resulted in a higher quality of mesoporous silica in terms of physical properties such as specific surface area, pore volume, and pore radius. Moreover, the Si content of mesoporous silica was detected to be higher at higher CTAB contents. Meanwhile, the components of C, N, and Br in EDX results were found to be from the residual amount of CTAB in the synthesized mesoporous silica after calcination to remove the CTAB. It can be assumed that the calcination operation conditions (at 550 °C for 3 h) did not completely decompose all of the CTAB. It can be concluded that using 0.05 mol of CTAB provided the best mesoporous silica with a high content of Si and a lower content of unreacted CTAB (based on the C content). These findings from EDX results are confirmed with SEM micrographs, as discussed previously.

Sorption Isotherm and Pore Properties of the Synthesized Mesoporous Silica. The pore properties and sorption isotherm of several samples were analyzed by a BET–BJH analysis of the N<sub>2</sub> adsorption/desorption patterns. Figure 4 represents the sorption isotherm of geothermal silica (Figure 4a), silica purified by acid-leaching (Figure 4b), and mesoporous silica synthesized with 0.015 mol (Figure 4c), 0.03 mol (Figure 4d), and 0.05 mol (Figure 4e) of CTAB. A type-IV sorption isotherm was developed for all samples, indicating mesoporous materials.<sup>67</sup>

A complete summary of the values of specific surface area, adsorbed-desorbed volume range, pore volume, and pore radius is presented in Table 3, and the pore size distribution of

Table 3. BET Analysis Results, Including Specific Surface Area, Pore Volume, and Pore Radius (Adsorption Isotherm) of Geothermal Silica, Purified Silica after Acid-Leaching, and Modified Mesoporous Silica with Different Amounts of CTAB<sup>68</sup>

sample	specific surface area (m²/g)	adsorbed–desorbed volume range (mL/g)	pore volume (mL/g)	pore radius (Å)
geothermal silica	40.899	18.61-86.79	0.11	19.83
purified silica after acid-leaching	178.063	37.62-158.62	0.62	17.07
mesoporous silica with CTAB 0.015 mol	582.454	102.35-485.75	0.62	19.11
mesoporous silica with CTAB 0.03 mol	511.946	103.47-346.11	0.39	15.31
mesoporous silica with CTAB 0.05 mol	668.849	149.33–353.28	0.26	17.04

the mesoporous silica product before and after APTMS introduction is shown in Figure 5. They show the variations of measured values upon an increased CTAB content. The specific surface area of geothermal silica was significantly increased from 40.899 to 178.063 m<sup>2</sup>/g in purified silica after acid-leaching. It could be possibly due to the removal of metal



Figure 5. BJH pore size distribution of mesoporous silica products with 0.05 mol of CTAB before and after treatment with APTMS.

oxides from the bulk body of silica, which produces more empty sites resulting in a higher measured surface area and higher adsorption ability. It was also found that the specific surface area considerably increased upon an increase in the mole contents of CTAB, which are 582.454, 511.946, and 668.849 m<sup>2</sup>/g for mesoporous silica synthesized with CTAB amounts of 0.015, 0.03, and 0.05 mol, respectively. This phenomenon indicates the greater generation of mesoporous structures upon an increase in the CTAB loading, resulting in a higher estimated surface area. This is in agreement with the SEM results showing that an increased loading of CTAB produces a more uniformly shaped particle, which possibly generates a higher surface area. At the same time, the initial intake adsorption-desorption volume was also found to increase from 18.61 mL/g (geothermal silica) to 102.35, 103.47, and 149.33 mL/g for mesoporous silica synthesized with CTAB contents of 0.015, 0.03, and 0.05 mol, respectively. However, the observed adsorption pore volume decreased upon the addition of CTAB from 0.62 mL/g for purified silica to 0.62, 0.39, and 0.26 mL/g for mesoporous silica synthesized with CTAB contents of 0.015, 0.03, and 0.05 mol, respectively. This can be explained by the increased growth of particles when a higher amount of CTAB was introduced, as evident from the SEM images. The uniform particle distribution can possibly produce a smaller void volume in the bulk body due to the smaller gaps between particles. Further, the measured pore radii were 19.83, 17.07, 19.11, 15.31, and 17.04 Å for geothermal silica, purified silica, and mesoporous silica with 0.015, 0.03, and 0.05 mol of CTAB, respectively. These pore radius values indicate that all of them can be classified as mesoporous materials.<sup>67</sup> Therefore, from these findings, synthesized mesoporous silica with 0.05 mol of CTAB showed the most desirable characteristics in terms of the adsorption isotherm specific surface area, adsorbed-desorbed volume, and pore radius, suggesting that it is a preferable matrix material for slow-release urea.

Thermal Analysis of the Synthesized Mesoporous Silica. To investigate the thermal characteristics of the synthesized mesoporous silica, DSC and TGA analyses were performed using an inert gas (nitrogen). Figure 6 shows DSC thermograms of three different samples, i.e., geothermal silica, mesoporous silica (best formulation using 0.05 mol of



Figure 6. DSC thermogram of geothermal silica, mesoporous silica, and pure CTAB.

CTAB), and pure CTAB. The DSC thermogram of geothermal silica shows no significant peaks that indicate the melting behavior of the sample. DSC was carried out by comparing the temperatures of the sample and reference material during temperature changes. The temperature of the reference material will be the same if there are no changes. Thermal phenomena such as melting can cause decomposition or changes in the amorphous structure of the sample. The DSC curve in Figure 6 shows two endothermic steps in mesoporous silica. The enthalpies measured were -69.2175 J/g (at 82.3 °C) and -10.0796 J/g (at 159.5 °C). The measured enthalpies in pure CTAB were -141.8772 J/g (at 115.4 °C) and -19.6368 J/g (at 272.4 °C).

The TGA analysis confirmed the weight loss behavior of geothermal silica, mesoporous silica, and pure CTAB at temperatures ranging from 30 to 500 °C. TGA thermograms of the three samples and a summary of the weight loss and degradation temperatures are shown in Figure 7 and Table 4, respectively. All samples experienced a gradual weight loss as a function of temperature. Generally, the degradation occurred in four steps for geothermal silica and mesoporous silica and in three steps for pure CTAB. The most significant weight loss in geothermal silica (Figure 7a) occurred at temperatures ranging from 30 to 135 °C, with 11.59% weight loss. This condition is possibly due to the evaporation of trapped and bonded water in the sample. Meanwhile, based on the TGA thermogram, mesoporous silica (Figure 7b) shows four regions of weight loss, which were 17.61% at 30-124 °C, 45.56% at 125-227 °C, 14.40% at 228–294 °C, and 5.72% at 295–500 °C. These are attributable to the evaporation of trapped water molecules in the first step, the degradation of organic compounds in the second step, degradation of CTAB in the third step, and degradation of the remaining long-chain organic compounds in the last step. In addition, the TGA thermogram of pure CTAB shows a significant weight loss of 87.45% at 227-287 °C, which was due to the degradation of organic chains in CTAB. A similar pattern was also observed in the TGA thermogram of mesoporous silica. This finding explains that the presence of CTAB in mesoporous silica interfered with the intermolecular interaction of CTAB and silica, and this interaction led to a



pubs.acs.org/IECR

**Figure 7.** TGA thermograms of (a) geothermal silica, (b) mesoporous silica, (c) pure CTAB.

change in the thermal degradation behavior of the synthesized mesoporous silica.

Characteristics of Slow-Release Urea with APTMS as a Surface-Modifying Agent. Based on previous discussions, synthesized mesoporous silica with 0.05 mol of CTAB shows the most suitable characteristics to be utilized as the matrix material for slow-release urea. Furthermore, to develop the desirable slow-release characteristic, surface modification of mesoporous silica was performed using a solution containing

Table 4. TGA Data Including Weight Losses at Certain Temperatures of Geothermal Silica, Mesoporous Silica, and Pure CTAB

sample	temperature range (°C)	weight loss (%)
geothermal silica	30-135	11.59
	136-236	4.32
	237-347	1.86
	348-453	1.05
mesoporous silica	30-124	17.61
	125-227	45.56
	228-294	14.40
	295-500	5.72
pure CTAB	30-226	6.75
	227-287	87.45
	288-500	5.45

10% 3-aminopropyl trimethoxy silane (APTMS). APTMS possibly undergoes an intermolecular interaction with the molecules of urea.<sup>48</sup> This interaction leads to a strong bonding between urea and the matrix of mesoporous silica; therefore, they can be combined to produce slow-release urea. However, the introduction of APTMS also created cross-linking between the APTMS molecules, which led to vertical polymerization and possibly pore blocking. This phenomenon affected the properties of mesoporous silica, especially its porosity, resulting in a lower value of the surface area, pore volume, and pore radius, as shown in Table 5.

Table 5. BET Analysis Results, Including Specific Surface Area, Pore Volume, and Pore Radius (Adsorption Isotherm) of Modified Mesoporous Silica Using 0.05 mol of CTAB before and after the Introduction of APTMS

sample	specific surface area (m²/g)	adsorbed-desorbed volume range (mL/g)	pore volume (mL/g)	pore radius (Å)
mesoporous silica with CTAB 0.05 mol before the introduction of APTMS	668.849	149.33-353.28	0.26	17.04
mesoporous silica with CTAB 0.05 mol after the introduction of APTMS	103.049	4.62–93.18	0.14	15.30

Figure 8 represents the SEM micrographs and EDX spectra of the synthesized slow-release urea. Based on Figure 8, it can be observed that all samples had a surface micromorphology similar to that of MS/APTMS. No significant changes in terms of the morphology occurred upon an increase in urea introduction to the slow-release urea. It can be reasonably concluded that the introduction of urea to MS/APTMS as the matrix did not influence the morphology of the generated slow-release urea. In addition, EDX results in Figure 8 reveal the spectra of the elements recorded in the tested samples. It was found that the major elements that appeared in all samples were Si, C, and O. A complete summary of the chemical composition of the synthesized slow-release urea is presented in Table 6. According to Table 6, introducing an increasing concentration of urea into the slow-release urea generates a higher content of N, corresponding to the quantity of urea in the slow-release urea. MS/APTMS has 3.81 wt % nitrogen, which gradually increased upon increasing the amount of urea introduced, which are 4.02, 4.63, 5.17, and 6.36 wt % for MS/

APTMS/U6.74, MS/APTMS/U16.74, MS/APTMS/U26.74, and MS/APTMS/U36.74, respectively. Therefore, the initial concentration of urea introduced significantly influenced the generated urea concentration in the synthesized slow-release urea.

FTIR analysis was performed to examine the bond interaction of urea in the matrix structure and the effect of APTMS on the synthesized slow-release urea. Figure 9 represents the FTIR spectra of different tested samples at wavenumbers of  $4000-500 \text{ cm}^{-1}$  (Figure 9a) and 2300-1300cm<sup>-1</sup> (Figure 9b).<sup>50</sup> From Figure 9a, it can be found that all tested samples displayed an intensely broad peak ranging from 1250 to 900 cm<sup>-1</sup>, indicating the vibration of Si-O-Si groups.<sup>49</sup> As shown in Figure 9b, further analysis of the formation of new functional groups upon the application of APTMS and the introduction of urea to the matrix was performed. It can be seen that the application of APTMS to the mesoporous silica generated a slightly higher recorded absorbance at 1556 and 1495 cm<sup>-1</sup>, which correspond to the vibrations of N-H and C-N groups, respectively.<sup>24</sup> This is explained by the formation of abundant N-H and C-N groups of APTMS on the mesoporous silica structure during the surface modification process.

On the other hand, the varied concentrations of urea introduced into MS/APTMS were also found to result in higher recorded absorbance intensities at several wavenumbers. Absorption bands at 2100 and 1636 cm<sup>-1</sup> indicate the stretching vibrations of N=C=O and C=O groups, attributed to the natural composition of urea and its cyanate impurities. Intense peaks recorded at 1556, 1495, and 1340 cm<sup>-1</sup> are related to the vibrations of N-H, C-N, and C-H groups, respectively.<sup>49,50</sup> On comparing the relative absorbance intensities of the tested samples, MS/APTMS/U26.74 was found to generate a higher intensity of C=O, N-H, C-N, and C-H groups. A higher intensity implies a higher content of the respective groups in MS/APTMS/U26.74 compared with other samples, suggesting the best formulation for the slow-release urea. Figure 9c depicts the proposed bond formations of the aminopropyl groups grafted from APTMS to the siloxane groups on the surface of the mesoporous silica, resulting in the aminopropyl-functionalized mesoporous silica. This functionalization is needed to effectively adsorb the urea and control its release. The amine groups from urea bonded with the amine sites of aminopropyl groups. This amine bond formation (N-H) was recorded and displayed on FTIR spectra. Furthermore, hydrogen bonding as another attractive intermolecular force can occur due to the abundance of highly electronegative atoms such as oxygen (O), nitrogen (N), and hydrogen (H). Therefore, it can allow a stronger bonding of urea groups on the surface of the functionalized mesoporous silica, thus resulting in an effective slow-release property.

Study of Release Kinetics of the Synthesized Slow-Release Urea. The performance of slow-release urea was determined by measuring the urea content in the overflow liquid (Performance Test of the Prepared Slow-Release Urea). The observed samples were MS/APTMS/U26.74, as the best formulation for slow-release urea discussed previously, and commercial silica, as the control variable. The initial urea content in each sample was set to 200 ppm. Figure 10a depicts the amount (ppm) of urea released during 7 days of observation from the sample to the overflow liquid. The highest overflow urea concentration was recorded on the second day for MS/APTMS/U26.74, with a value of 28.55 ppm, which was nearly constant on the

# Industrial & Engineering Chemistry Research

pubs.acs.org/IECR

## c:\edax32\genesis\genmaps.spc 15-Sep-2020 09:11:09 LSecs : 55 (a1) (a2) 726 SiKa 580 435 O Ka 290 145 CI Brl 7.00 9.00 1.00 2.00 3.00 4.00 5.00 Energy - keV 6.00 8.00 10.0 c:\edax32\genesis\genmaps.spc 15-Sep-2020 09:31:27 LSecs : 52 (b2) (b1)439-351 263 0 Ka 175 87 СК BrL 6.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 Energy - keV 4.00 4.50 5.00 5.50 c:\edax32\genesis\genmaps.spc 15-Sep-2020 10:29:25 LSecs : 94 (c2) 1.9 SiKa 1.5 1.2





Figure 8. continued

Article

pubs.acs.org/IECR



Figure 8. SEM–EDX micrographs and spectra of (a) MS/APTMS and the synthesized slow-release urea: (b) MS/APTMS/U6.74, (c) MS/APTMS/U16.74, (d) MS/APTMS/U26.74, and (e) MS/APTMS/U36.74.

# Table 6. Chemical Composition from EDX Analysis of the Synthesized Slow-Release Urea

sample code		СК	N K	O K	Br K	Si K
MS/APTMS	weight (%)	18.68	3.81	51.21	1.20	25.11
	atomic (%)	26.19	4.58	53.92	0.25	15.06
MS/APTMS/ U6.74	weight (%)	25.93	4.02	47.91	1.06	21.07
	atomic (%)	34.80	4.63	48.26	0.21	12.09
MS/APTMS/ U16.74	weight (%)	14.90	4.63	46.71	0.36	33.40
	atomic (%)	21.82	5.81	51.36	0.08	20.92
MS/APTMS/ U26.74	weight (%)	21.51	5.17	47.03	0.83	25.82
	atomic (%)	29.35	6.15	49.00	0.17	15.32
MS/APTMS/ U36.74	weight (%)	25.70	6.36	44.66	0.91	22.37
	atomic (%)	34.55	7.33	45.08	0.18	12.86

subsequent days. On the other hand, the highest overflow urea content was found on the third day, with a value of 52.65 ppm, which gradually decreased over the next few days. Subsequently, the performance of the synthesized slow-release urea was also evaluated by measuring the cumulative urea release, as presented in Figure 10b. MS/APTMS/U26.74 shows a linear trend of the cumulative urea release profile, with a total urea release of 124.6 ppm (64.4%) on the last day. In contrast, the commercial urea shows an exponential trend of the cumulative urea release profile, with a value of 184.5 ppm (92.4%) in total. This result indicates that APTMS/U26.74 can release urea more slowly than commercial urea. This can be partially due to the abundance of solid bonding interaction between urea molecules and MS/APTMS as the matrix of this slow-release urea, resulting in a relatively slower release of urea molecules.

To further understand the behavior of urea release, the kinetics of urea release was evaluated using several models, i.e., pseudo-first order (Figure 10c), pseudo-second order (Figure 10d), Higuchi (Figure 10e), and Hixson-Crowell (Figure 10f) models. Complete details of the fitted kinetic parameters and



Figure 9. FTIR results of the slow-release urea with different formulations: (a) FTIR results at a wavenumber of  $4000-500 \text{ cm}^{-1}$ ; (b) further evaluation of FTIR spectra at a wavenumber of  $2300-1300 \text{ cm}^{-1}$ ; and (c) proposed bond formation mechanisms of aminopropyl and urea groups on the synthesized slow-release urea.

the correlation coefficients are provided in Table 7. The pseudo-first-order model provided a reasonably good fit for commercial urea and MS/APTMS/U26.74, with  $R^2$  values of 0.8528 and 0.8395, respectively. The pseudo-first-order rate kinetic constant values were 0.3502 day<sup>-1</sup> for commercial urea and 0.2654 day<sup>-1</sup> for MS/APTMS/U26.74. In addition, the  $k_1$  value of commercial urea was recorded to be higher than that of MS/APTMS/U26.74, indicating that commercial urea has a

higher urea release rate per day than MS/APTMS/U26.74. This result indicates that the modified slow-release urea had a significantly reduced release rate. On the other hand, in this study, the pseudo-second-order kinetic model was seemingly unsuitable for modeling the urea release behavior, which is evident from the low correlation coefficients of only 0.3258 for commercial urea and 0.5703 for MS/APTMS/U26.74. The low value of  $R^2$  indicates that the model is less capable of being



Figure 10. Performance test results of the slow-release urea: (a) result of the measured urea concentration in the overflow liquid and (b) cumulative release of urea from commercial urea and MS/APTMS/U26.74. Curve fittings of the urea release kinetics for commercial urea and MS/APTMS/U26.74 using (c) pseudo-first-order, (d) pseudo-second-order, (e) Higuchi, and (f) Hixson–Crowell models.

Table 7. Model Parameters and Correlation Coefficients of Commercial Urea and MS/APTMS/U26.74 to Evaluate the Urea Release Kinetics Using Pseudo-First-Order, Pseudo-Second-Order, Higuchi, and Hixson–Crowell Models

		kinetic models						
	pseudo-firs	st order	pseudo-seco	nd order	Higuch	i	Hixson-Cro	well
sample	$k_1 ({\rm day}^{-1})$	$R^2$	$k_2$ (%/day)	$R^2$	$K_{\rm H}  (\%/{\rm day}^{1/2})$	$R^2$	$K_{\rm HC}  (\%^{1/3}/{\rm day})$	$R^2$
commercial urea	0.3502	0.8528	0.0037	0.3286	54.0668	0.9901	4.8308	0.9617
MS/APTMS/U26.74	0.2654	0.8395	0.0046	0.5703	24.4964	0.9979	2.3678	0.9772

used for data predictions. The Higuchi kinetic model yielded the best fit of urea release among all of the fitted models, with the highest  $R^2$  values of 0.9901 for commercial urea and 0.9979

for MS/APTMS/U26.74. The Higuchi constants were measured to be 54.0668%/day for commercial urea and 24.4964%/day for MS/APTMS/U26.74. The higher Higuchi

constant represents the higher diffusion rate of urea release from the sample.<sup>63</sup> Thus, the modification of MS/APTMS as the matrix medium has significantly improved the urea release rate by reducing the diffusivity of urea from the slow-release urea due to solid bonding interaction between the modified mesoporous silica and the urea molecules. The Hixson-Crowell model also showed an excellent urea release fit for both samples, with  $R^2$  values of 0.9617 and 0.9772 and Hixson-Crowell constants of 4.8308 and 2.3678%<sup>1/3</sup>/day for commercial urea and MS/APTMS/U26.74, respectively. This result suggests that the primary mode of urea release is a diffusion-controlled mechanism,<sup>67</sup> an indication similar to that of the Higuchi model discussed previously. Based on the studies and results, it can be reasonably suggested that the modification of mesoporous silica with APTMS has a significant impact on reducing the urea release rate by lowering the diffusivity of urea from the slow-release urea. Based on the findings and explanation, it can be reasonably concluded that slow-release urea has been synthesized successfully.

### CONCLUSIONS

In this work, a prominent slow-release urea fertilizer was developed with aminopropyl-functionalized mesoporous silica as the matrix to enhance the urea adsorption and slow-release property. It was developed by utilizing geothermal silica as the silica source, CTAB as the surfactant, and APTMS as the surface modification agent. Acid-leaching treatment using H<sub>2</sub>SO<sub>4</sub> was conducted to purify the geothermal silica sample and increase the SiO<sub>2</sub> content from 86.30 to 96.00%, which is feasible for mesoporous silica synthesis. The synthesized mesoporous silica was formulated with different mole amounts of CTAB. The mesoporous silica synthesized with the addition of 0.05 mol of CTAB possessed the most desirable properties of a fairly uniform surface micromorphology containing particles with 38.55 wt % silica content, a surface area of 668.849 m<sup>2</sup>/g, an adsorption-desorption range of 149.33-353.28 mL/g, and an adsorption pore volume of 0.26 mL/g. All synthesized mesoporous silicas showed a type-IV hysteresis, which corresponds to mesoporous-type materials, signaling the successful development of the mesoporous structure. The DSC results showed that the mesoporous silica becomes more reactive with recorded enthalpies of 69.2175 and -10.0796 J/gat temperatures of 82.3 and 159.5 °C, respectively, due to the addition of CTAB in the synthesis process. TGA thermograms show that the mesoporous silica has very good thermal stability and experienced only 17.61% weight loss at a temperature of up to 124 °C. These findings suggest the excellent potential of the synthesized mesoporous silica as a promising matrix material. Further, the functionalization of the aminopropyl group to the mesoporous silica using APTMS was performed. SEM results showed that the functionalization process and the adsorption of urea to the mesoporous silica resulted in no significant changes in the morphology of mesoporous silica. Meanwhile, significant changes were observed in the chemical functional groups generated after APTMS functionalization, resulting in some new groups including C=O, N-H, and C-N. From the FTIR spectra, MS/APTMS/U26.74 was observed to have a relatively higher intensity of C=O, N-H, C-N, and C-H groups among other samples, suggesting the higher content of the respective groups in MS/APTMS/U26.74. A comparative experiment and the kinetic study regarding the release property and kinetics between MS/APTMS/U26.74 as the best slow-release urea and commercial urea was conducted.

The cumulative urea release during 7 days of observation was 184.5 ppm (92.4%) for commercial urea and 124.6 ppm (64.6%) for MS/APTMS/U26.74. The abundance of strong bonding interaction between urea molecules and MS/APTMS as the matrix led to a relatively slower release of urea molecules. The Higuchi kinetic model yielded the best fit among the other models to predict the release kinetics of MS/ APTMS/U26.74 with an  $R^2$  value of 0.9979 and a Higuchi constant of 24.4964%/day<sup>1/2</sup>. The Higuchi constant of MS/ APTMS/U26.74 was smaller than that of commercial urea (54.0668%/day), indicating that the synthesized slow-release urea has a lower urea diffusivity out of the sample, thus resulting in a slower and controllable urea release. Finally, MS/ APTMS/U26.74 synthesized by utilizing geothermal silica, CTAB, and APTMS can be noted to have a potential composition for slow-release urea fertilizers to enhance the usage efficiency of urea.

#### AUTHOR INFORMATION

#### **Corresponding Author**

 S. Silviana – Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia; orcid.org/0000-0002-8831-0147; Email: silviana@che.undip.ac.id

#### Authors

- Atikah A. Janitra Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia
- Afriza N. Sa'adah Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia
- Febio Dalanta Department of Chemical Engineering, Faculty of Engineering, Diponegoro University, Semarang 50275, Indonesia

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.2c00424

## **Author Contributions**

S.S.: Conceptualization, methodology, supervision, funding acquisition, resources, and writing—original draft; A.A.J.: Methodology, investigation, and writing—original draft. A.N.S.: Project administration, software, and formal analysis. F.D.: Data curation, software, visualization, formal analysis, and writing—review and editing.

## Funding

This project was financially supported by the Ministry of Education, Culture, Research and Technology of the Republic of Indonesia through grant No. 225-54/UN7.6.1/PP/2020.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors are grateful to the community of Advanced Material Laboratory (AMaL) of Diponegoro University for all their support and discussion throughout the research.

#### ABBREVIATIONS

SRU	slow-release urea
MS	mesoporous silica
CTAB	cetyltrimethylammonium bromide
APTMS	(3-aminopropyl)trimethoxysilane

SEM	scanning electron microscopy
XRF	X-ray fluorescence
XRD	X-ray diffraction
FTIR	Fourier transform infrared
BET-BJH	Brunauer-Emmett-Teller and Barrett-Joyner-
	Halenda
TGA	thermogravimetric analysis
DSC	differential scanning calorimetry
HCl	hydrochloric acid
U6.74	urea 6.74 wt %
U16.74	urea 16.74 wt %
U26.74	urea 26.74 wt %
U36.74	urea 36.74 wt %

# REFERENCES

(1) Kay-Shoemake, J. L.; Watwood, M. E.; Kilpatrick, L.; Harris, K. Exchangeable Ammonium and Nitrate from Different Nitrogen Fertilizer Preparations in Polyacrylamide-Treated and Untreated Agricultural Soils. *Biol. Fertil. Soils* **2000**, *31*, 245–248.

(2) Saha, B. K.; Rose, M. T.; Wong, V.; Cavagnaro, T. R.; Patti, A. F. Hybrid Brown Coal-Urea Fertiliser Reduces Nitrogen Loss Compared to Urea Alone. *Sci. Total Environ.* **201**7, *601–602*, 1496–1504.

(3) Getahun, D.; Alemneh, T.; Akeberegn, D.; Getabalew, M.; Zewdie, D. Urea Metabolism and Recycling in Ruminants. *Biomed. J. Sci. Tech. Res.* **2019**, *20*, 14790–14796.

(4) Hailemariam, S.; Zhao, S.; He, Y.; Wang, J. Urea Transport and Hydrolysis in the Rumen: A Review. *Anim. Nutr.* **2021**, *7*, 989–996.

(5) Mehta, R.; Brahmbhatt, H.; Saha, N. K.; Bhattacharya, A. Removal of Substituted Phenyl Urea Pesticides by Reverse Osmosis Membranes: Laboratory Scale Study for Field Water Application. *Desalination* **2015**, *358*, 69–75.

(6) Berrada, H.; Font, G.; Moltó, J. C. Determination of Urea Pesticide Residues in Vegetable, Soil, and Water Samples. *Crit. Rev. Anal. Chem.* **2003**, 33, 19–41.

(7) Sasmal, S.; Roy Chowdhury, S.; Podder, D.; Haldar, D. Urea-Appended Amino Acid To Vitalize Yeast Growth, Enhance Fermentation, and Promote Ethanol Production. *ACS Omega* **2019**, *4*, 13172–13179.

(8) Santos, A. S.; Ferreira, L. M. M.; Martin-Rosset, W.; Cotovio, M.; Silva, F.; Bennett, R. N.; Cone, J. W.; Bessa, R. J. B.; Rodrigues, M. A. M. The Influence of Casein and Urea as Nitrogen Sources on in Vitro Equine Caecal Fermentation. *Animal* **2012**, *6*, 1096–1102.

(9) Li, Y.; Huang, L.; Zhang, H.; Wang, M.; Liang, Z. Assessment of Ammonia Volatilization Losses and Nitrogen Utilization during the Rice Growing Season in Alkaline Salt-Affected Soils. *Sustainability* **2017**, *9*, No. 132.

(10) Azeem, B.; KuShaari, K.; Man, Z. B.; Basit, A.; Thanh, T. H. Review on Materials & Methods to Produce Controlled Release Coated Urea Fertilizer. *J. Controlled Release* **2014**, *181*, 11–21.

(11) Jie, C.; Jing-zhang, C.; Man-zhi, T.; Zi-tong, G. Soil Degradation: A Global Problem Endangering Sustainable Development. J. Geogr. Sci. 2002, 12, 243–252.

(12) Liu, L.; Kost, J.; Fishman, M. L.; Hicks, K. B. A Review: Controlled Release Systems for Agricultural and Food Applications; American Chemical Society, 2008; pp 265–281.

(13) Espécie Bueno, S. C.; Filho, M. B.; de Almeida, P. S. G.; Polidoro, J. C.; Olivares, F. L.; Sthel, M. S.; Vargas, H.; Mota, L.; da Silva, M. G. Cuban Zeolite as Ammonium Carrier in Urea-Based Fertilizer Pellets: Photoacoustic-Based Sensor for Monitoring N-Ammonia Losses by Volatilization in Aqueous Solutions. *Sens. Actuators, B* **2015**, *212*, 35–40.

(14) Mihok, F.; Macko, J.; Oriňak, A.; Oriňaková, R.; Kovaľ, K.; Sisáková, K.; Petruš, O.; Kostecká, Z. Controlled Nitrogen Release Fertilizer Based on Zeolite Clinoptilolite: Study of Preparation Process and Release Properties Using Molecular Dynamics. *Curr. Res. Green Sustainable Chem.* **2020**, *3*, No. 100030. (15) Maghsoodi, M. R.; Najafi, N.; Reyhanitabar, A.; Oustan, S. Hydroxyapatite Nanorods, Hydrochar, Biochar, and Zeolite for Controlled-Release Urea Fertilizers. *Geoderma* **2020**, 379, No. 114644.

(16) Pereira, E. I.; da Cruz, C. C. T.; Solomon, A.; Le, A.; Cavigelli, M. A.; Ribeiro, C. Novel Slow-Release Nanocomposite Nitrogen Fertilizers: The Impact of Polymers on Nanocomposite Properties and Function. *Ind. Eng. Chem. Res.* **2015**, *54*, 3717–3725.

(17) Yamamoto, C. F.; Pereira, E. I.; Mattoso, L. H. C.; Matsunaka, T.; Ribeiro, C. Slow Release Fertilizers Based on Urea/Urea–Formaldehyde Polymer Nanocomposites. *Chem. Eng. J.* **2016**, *287*, 390–397.

(18) Shen, Y.; Zhou, J.; Du, C.; Zhou, Z. Hydrophobic Modification of Waterborne Polymer Slows Urea Release and Improves Nitrogen Use Efficiency in Rice. *Sci. Total Environ.* **2021**, *794*, No. 148612.

(19) Bortolin, A.; Aouada, F. A.; de Moura, M. R.; Ribeiro, C.; Longo, E.; Mattoso, L. H. C. Application of Polysaccharide Hydrogels in Adsorption and Controlled-Extended Release of Fertilizers Processes. J. Appl. Polym. Sci. **2012**, *123*, 2291–2298.

(20) Li, L.; Sun, Y.; Cao, B.; Song, H.; Xiao, Q.; Yi, W. Preparation and Performance of Polyurethane/Mesoporous Silica Composites for Coated Urea. *Mater. Des.* **2016**, *99*, 21–25.

(21) de Silva, M.; Siriwardena, D. P.; Sandaruwan, C.; Priyadarshana, G.; Karunaratne, V.; Kottegoda, N. Urea-Silica Nanohybrids with Potential Applications for Slow and Precise Release of Nitrogen. *Mater. Lett.* **2020**, *272*, No. 127839.

(22) Elhassani, C. E.; Essamlali, Y.; Aqlil, M.; Nzenguet, A. M.; Ganetri, I.; Zahouily, M. Urea-Impregnated HAP Encapsulated by Lignocellulosic Biomass-Extruded Composites: A Novel Slow-Release Fertilizer. *Environ. Technol. Innovation* **2019**, *15*, No. 100403.

(23) Vanichvattanadecha, C.; Singhapong, W.; Jaroenworaluck, A. Different Sources of Silicon Precursors Influencing on Surface Characteristics and Pore Morphologies of Mesoporous Silica Nanoparticles. *Appl. Surf. Sci.* **2020**, *513*, No. 145568.

(24) Yang, Y.; Wang, J.; Qian, X.; Shan, Y.; Zhang, H. Aminopropyl-Functionalized Mesoporous Carbon (APTMS-CMK-3) as Effective Phosphate Adsorbent. *Appl. Surf. Sci.* **2018**, 427, 206–214.

(25) Ghobashy, M. M.; Mousaa, I. M.; El-Sayyad, G. S. Radiation Synthesis of Urea/Hydrogel Core Shells Coated with Three Different Natural Oils via a Layer-by-Layer Approach: An Investigation of Their Slow Release and Effects on Plant Growth-Promoting Rhizobacteria. *Prog. Org. Coat.* **2021**, *151*, No. 106022.

(26) Guo, M.; Liu, M.; Zhan, F.; Wu, L. Preparation and Properties of a Slow-Release Membrane-Encapsulated Urea Fertilizer with Superabsorbent and Moisture Preservation. *Ind. Eng. Chem. Res.* **2005**, *44*, 4206–4211.

(27) Abdelghany, A. M.; Meikhail, M. S.; Asker, N. Synthesis and Structural-Biological Correlation of PVC\PVAc Polymer Blends. *J. Mater. Res. Technol.* **2019**, *8*, 3908–3916.

(28) Cui, Y.; Xiang, Y.; Xu, Y.; Wei, J.; Zhang, Z.; Li, L.; Li, J. Poly-Acrylic Acid Grafted Natural Rubber for Multi-Coated Slow Release Compound Fertilizer: Preparation, Properties and Slow-Release Characteristics. *Int. J. Biol. Macromol.* **2020**, *146*, 540–548.

(29) dos Santos, A. C. S.; Henrique, H. M.; Cardoso, V. L.; Reis, M. H. M. Slow Release Fertilizer Prepared with Lignin and Poly(Vinyl Acetate) Bioblend. *Int. J. Biol. Macromol.* **2021**, *185*, 543–550.

(30) Liu, J.; Yang, Y.; Gao, B.; Li, Y. C.; Xie, J. Bio-Based Elastic Polyurethane for Controlled-Release Urea Fertilizer: Fabrication, Properties, Swelling and Nitrogen Release Characteristics. *J. Cleaner Prod.* **2019**, *209*, 528–537.

(31) Ni, B.; Liu, M.; Lü, S.; Xie, L.; Wang, Y. Multifunctional Slow-Release Organic–Inorganic Compound Fertilizer. *J. Agric. Food Chem.* **2010**, *58*, 12373–12378.

(32) Ni, B.; Liu, M.; Lü, S.; Xie, L.; Wang, Y. Environmentally Friendly Slow-Release Nitrogen Fertilizer. J. Agric. Food Chem. 2011, 59, 10169–10175.

(33) Pang, L.; Gao, Z.; Zhang, S.; Li, Y.; Hu, S.; Ren, X. Preparation and Anti-UV Property of Modified Cellulose Membranes for Biopesticides Controlled Release. Ind. Crops Prod. 2016, 89, 176-181.

(34) Sathisaran, I.; Balasubramanian, M. Physical Characterization of Chitosan/Gelatin-Alginate Composite Beads for Controlled Release of Urea. *Heliyon* **2020**, *6*, No. e05495.

(35) Shan, L.; Gao, Y.; Zhang, Y.; Yu, W.; Yang, Y.; Shen, S.; Zhang, S.; Zhu, L.; Xu, L.; Tian, B.; Yun, J. Fabrication and Use of Alginate-Based Cryogel Delivery Beads Loaded with Urea and Phosphates as Potential Carriers for Bioremediation. *Ind. Eng. Chem. Res.* **2016**, *55*, 7655–7660.

(36) Wang, Y.; Liu, M.; Ni, B.; Xie, L. κ-Carrageenan–Sodium Alginate Beads and Superabsorbent Coated Nitrogen Fertilizer with Slow-Release, Water-Retention, and Anticompaction Properties. *Ind. Eng. Chem. Res.* **2012**, *51*, 1413–1422.

(37) Qiao, D.; Liu, H.; Yu, L.; Bao, X.; Simon, G. P.; Petinakis, E.; Chen, L. Preparation and Characterization of Slow-Release Fertilizer Encapsulated by Starch-Based Superabsorbent Polymer. *Carbohydr. Polym.* **2016**, 147, 146–154.

(38) Wanyika, H.; Gatebe, E.; Kioni, P.; Tang, Z.; Gao, Y. Mesoporous Silica Nanoparticles Carrier for Urea: Potential Applications in Agrochemical Delivery Systems. *J. Nanosci. Nanotechnol.* **2012**, *12*, 2221–2228.

(39) He, H.; Xiao, H.; Kuang, H.; Xie, Z.; Chen, X.; Jing, X.; Huang, Y. Synthesis of Mesoporous Silica Nanoparticle–Oxaliplatin Conjugates for Improved Anticancer Drug Delivery. *Colloids Surf., B* **2014**, *117*, 75–81.

(40) Yan, E.; Ding, Y.; Chen, C.; Li, R.; Hu, Y.; Jiang, X. Polymer/ Silica Hybrid Hollow Nanospheres with PH-Sensitive Drug Release in Physiological and Intracellular Environments. *Chem. Commun.* **2009**, *19*, 2718.

(41) Yang, D.; Fan, R.; Luo, F.; Chen, Z.; Gerson, A. R. Facile and Green Fabrication of Efficient Au Nanoparticles Catalysts Using Plant Extract via a Mesoporous Silica-Assisted Strategy. *Colloids Surf.*, A **2021**, *621*, No. 126580.

(42) Yin, F.; Xu, F.; Zhang, K.; Yuan, M.; Cao, H.; Ye, T.; Wu, X.; Xu, F. Synthesis and Evaluation of Mesoporous Silica/Mesoporous Molecularly Imprinted Nanoparticles as Adsorbents for Detection and Selective Removal of Imidacloprid in Food Samples. *Food Chem.* **2021**, *364*, No. 130216.

(43) Huang, R.; Shen, Y.-W.; Guan, Y.-Y.; Jiang, Y.-X.; Wu, Y.; Rahman, K.; Zhang, L.-J.; Liu, H.-J.; Luan, X. Mesoporous Silica Nanoparticles: Facile Surface Functionalization and Versatile Biomedical Applications in Oncology. *Acta Biomater.* **2020**, *116*, 1– 15.

(44) Kaya, S.; Cresswell, M.; Boccaccini, A. R. Mesoporous Silica-Based Bioactive Glasses for Antibiotic-Free Antibacterial Applications. *Mater. Sci. Eng.*, C 2018, 83, 99–107.

(45) dos Santos, S. M. L.; Nogueira, K. A. B.; de Souza Gama, M.; Lima, J. D. F.; da Silva Júnior, I. J.; de Azevedo, D. C. S. Synthesis and Characterization of Ordered Mesoporous Silica (SBA-15 and SBA-16) for Adsorption of Biomolecules. *Microporous Mesoporous Mater.* **2013**, *180*, 284–292.

(46) Policicchio, A.; Conte, G.; Stelitano, S.; Bonaventura, C. P.; Putz, A.-M.; Ianăşi, C.; Almásy, L.; Horváth, Z. E.; Agostino, R. G. Hydrogen Storage Performances for Mesoporous Silica Synthesized with Mixed Tetraethoxysilane and Methyltriethoxysilane Precursors in Acidic Condition. *Colloids Surf.*, A 2020, 601, No. 125040.

(47) Gil-Ortiz, R.; Naranjo, M. Á.; Ruiz-Navarro, A.; Caballero-Molada, M.; Atares, S.; García, C.; Vicente, O. New Eco-Friendly Polymeric-Coated Urea Fertilizers Enhanced Crop Yield in Wheat. *Agronomy* **2020**, *10*, No. 438.

(48) Cheah, W.-K.; Sim, Y.-L.; Yeoh, F.-Y. Amine-Functionalized Mesoporous Silica for Urea Adsorption. *Mater. Chem. Phys.* 2016, 175, 151–157.

(49) Luechinger, M.; Prins, R.; Pirngruber, G. D. Functionalization of Silica Surfaces with Mixtures of 3-Aminopropyl and Methyl Groups. *Microporous Mesoporous Mater.* **2005**, *85*, 111–118.

(50) Hicks, J. C.; Dabestani, R.; Buchanan, A. C.; Jones, C. W. Assessing Site-Isolation of Amine Groups on Aminopropyl-Function-

alized SBA-15 Silica Materials via Spectroscopic and Reactivity Probes. *Inorg. Chim. Acta* **2008**, *361*, 3024–3032.

(51) Burkett, S. L.; Sims, S. D.; Mann, S. Synthesis of Hybrid Inorganic–Organic Mesoporous Silica by Co-Condensation of Siloxane and Organosiloxane Precursors. *Chem. Commun.* **1996**, *11*, 1367–1368.

(52) Purnomo, A.; Dalanta, F.; Oktaviani, A. D.; Silviana, S. Superhydrophobic Coatings and Self-Cleaning through the Use of Geothermal Scaling Silica in Improvement of Material Resistance. *AIP Conf. Proc.* **2018**, No. 020077.

(53) Silviana, S.; Darmawan, A.; Subagio, A.; Dalanta, F. Statistical Approaching for Superhydrophobic Coating Preparation Using Silica Derived from Geothermal Solid Waste. *ASEAN J. Chem. Eng.* **2020**, *19*, 91.

(54) Silviana, S.; Darmawan, A.; Dalanta, F.; Subagio, A.; Hermawan, F.; Milen Santoso, H. Superhydrophobic Coating Derived from Geothermal Silica to Enhance Material Durability of Bamboo Using Hexadimethylsilazane (HMDS) and Trimethylchlorosilane (TMCS). *Materials* **2021**, *14*, No. 530.

(55) Silviana, S.; Ma'ruf, A. Silicon Preparation Derived from Geothermal Silica by Reduction Using Magnesium. *Int. J. Emerging Trends Eng. Res.* **2020**, *8*, 4861–4866.

(56) Silviana, S.; Sanyoto, G. J.; Darmawan, A. Preparation of Geothermal Silica Glass Coating Film Through Multi-Factor Optimization. *J. Teknol.* **2021**, *83*, 41–49.

(57) Tut Haklıdır, F. S.; Şengün, R.; Aydın, H. Characterization and Comparison of Geothermal Fluids Geochemistry within the Kızıldere Geothermal Field in Turkey: New Findings with Power Capacity Expanding Studies. *Geothermics* **2021**, *94*, No. 102110.

(58) Silviana, S.; Anggoro, D. D.; Salsabila, C. A.; Aprilio, K. Utilization of Geothermal Waste as a Silica Adsorbent for Biodiesel Purification. *Korean J. Chem. Eng.* **2021**, *38*, 2091–2105.

(59) Silviana, S.; Bayu, W. J. Silicon Conversion From Bamboo Leaf Silica By Magnesiothermic Reduction for Development of Li-Ion Baterry Anode. *MATEC Web Conf.* **2018**, *156*, No. 05021.

(60) Silviana, S.; Purbasari, A.; Siregar, A.; Rochyati, A. F.; Papra, T. Synthesis of Mesoporous Silica Derived from Geothermal Waste with Cetyl Trimethyl Ammonium Bromide (CTAB) Surfactant as Drug Delivery Carrier. *AIP Conf. Proc.* **2020**, *2296*, No. 020083.

(61) Silviana, S.; Sagala, E. A. P. P.; Sari, S. E.; Siagian, C. T. M. Preparation of Mesoporous Silica Derived from Geothermal Silica as Precursor with a Surfactant of Cethyltrimethylammonium Bromide. *AIP Conf. Proc.* **2019**, No. 020070.

(62) Silviana, S.; Sanyoto, G. J.; Darmawan, A.; Sutanto, H. Geothermal Silica Waste as Sustainable Amorphous Silica Source for the Synthesis of Silica Xerogels. *Rasayan J. Chem.* **2020**, *13*, 1692–1700.

(63) Shoaib, M. H.; Tazeen, J.; Merchant, H. A.; Yousuf, R. I. Evaluation of drug release kinetics from ibuprofen matrix tablets using HPMC. *Pak. J. Pharm. Sci.* **2006**, *19* (2), 119–124.

(64) Bullen, J. C.; Saleesongsom, S.; Gallagher, K.; Weiss, D. J. A Revised Pseudo-Second-Order Kinetic Model for Adsorption, Sensitive to Changes in Adsorbate and Adsorbent Concentrations. *Langmuir* **2021**, *37* (10), 3189–3201.

(65) Dash, S.; Murthy, P. N.; Nath, L.; Chowdhury, P. Kinetic modeling on drug release from controlled drug delivery systems. *Acta Pol. Pharm. - Drug Res.* **2010**, 67 (3), 217–223.

(66) Che Ismail, N. H.; Ahmad Bakhtiar, N. S. A.; Md Akil, H. Effects of Cetyltrimethylammonium Bromide (CTAB) on the Structural Characteristic of Non-Expandable Muscovite. *Mater. Chem. Phys.* **2017**, *196*, 324–332.

(67) Khoeini, M.; Najafi, A.; Rastegar, H.; Amani, M. Improvement of Hollow Mesoporous Silica Nanoparticles Synthesis by Hard-Templating Method via CTAB Surfactant. *Ceram. Int.* **2019**, *45*, 12700–12707.

(68) Silviana, S.; Darmawan, A.; Janitra, A. A.; Ma'ruf, A.; Triesty, I. Synthesized Silica Mesoporous from Silica Geothermal Assisted with CTAB and Modified by APTMS. *Int. J. Emerging Trends Eng. Res.* **2020**, *8*, 4854–4860.

# ■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was originally published ASAP on June 13, 2022. References 63–65 and 68 were revised, and the corrected version reposted on June 21, 2022.