


## Original Paper

# Development and characterization of a slow-release dual-purpose N and Zn fertilizer based on diatomite and nano-diatomite

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### Abstract

Leaching and volatilization of N from urea, and precipitation and fixing of Zn by commercial fertilizers, has led to excessive costs for farmers and problems for the environment. Incorporating fertilizers in a porous material such as diatomite can prevent these losses by slowing the nutrient release. A new fertilizer formulation, based on the urea-zinc (UZn) complex in the eutectic solution of salt-urea was prepared. In the following, UZn was incorporated into diatomite and nano-diatomite by using hydroxypropyl methylcellulose (HPMC) as a binder. The treatments included the following: U: urea; UZn: urea-Zn; UZn-D: urea-Zn-diatomite; UZn-ND: urea-Zn-nano-diatomite; UZn-D-B: urea-Zn-diatomite-binder; and UZn-ND-B: urea-Zn-nano-diatomite-binder. The slow-release urea fertilizers (SRUFs) were characterized using FESEM/EDS, FTIR, CHN, XRD, DLS, and zeta potential techniques. Urea slow-release behavior, kinetics in water, and available Zn and N-forms leaching in the soil column were evaluated compared with conventional urea and zinc fertilizers. The pattern of release of urea in water was sigmoidal and after 12 h, only 20% of urea was released from fertilizers containing diatomite and HPMC. The NO<sub>3</sub><sup>-</sup> release pattern in the soil started with a 12-day delay, and after that, the rate of NO<sub>3</sub><sup>-</sup> leaching decreased by two to three times in the application of fertilizers containing HPMC compared with urea. The Zn concentration in the leachates of columns supplied with SRUFs was 35% less than for those supplied with ZnSO<sub>4</sub>. The results showed that the SRUFs make N and Zn available in the soil and but reduce the rate of their release.

**Keywords:** ammonium; kinetic; leachate; nitrate; release behavior; urea-zinc complex

(Received: 17 May 2023; revised: 05 July 2023; accepted: 28 December 2023)

### Introduction

Urea is the primary source of mineral N (nitrogen) fertilizer used in agriculture worldwide due to its relatively low prices and large structural nitrogen percentage compared with other N fertilizers (Food and Agriculture Organization of the United Nations, 2008). Studies have shown that the global nitrogen demand increased by 1.4% per year until 2023, and global urea demand also increased by 1.2% and reached 184 Mt in 2023 (Heffer and Prud, 2019). A concern with urea fertilizers is the risk of N loss through NH<sub>3</sub> volatilization and NO<sub>3</sub><sup>-</sup> leaching, which reduces the N-use efficiency of fertilizers (Dawar et al., 2011). Nitrogen losses from urea could be ~42% via volatilization (Ahmad et al., 2021) or leaching (Wallace et al., 2020). The loss of fertilizer harms plant nutrition, increases process costs, and causes damage to the environment (Li et al., 2018). To overcome these challenges,

smart fertilizers such as slow release or controlled release fertilizers (SRF or CRF) are being produced and used to supply nutrients to plants in a slow and controlled manner (ME Trenkel, 2021). Research has shown that SRFs or CRFs can improve nutrient use efficiency in soils and minimize damage to the environment because these are environmentally friendly components with minimal pollution (Chen and Wei, 2018; Tian et al., 2021).

Usually, SRFs are produced by coating or encapsulating conventional water-soluble fertilizers; this results in permeable layers with low solubility forming on the fertilizer, and it is these layers which control water penetration and dissolution rate (Charoenchai et al., 2020; Gil-Ortiz et al., 2020). The release rate of these fertilizers depends on the number of coating layers and the characteristics of the coating material such as permeability and hydrophilic property.

Another type of SRF is the matrix-type formulation, in which nutrients are dispersed in a matrix made of polymers (Iftime et al., 2019) or minerals (Hermida and Agustian, 2019).

The trapping of nutrients in natural porous minerals or between layers of clay minerals is one of the methods used to develop SRFs by the matrix incorporation process (Hermida and Agustian, 2019). Diatomite (D) is a type of sedimentary rock that includes a frustule, a

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**Cite this article:** Mirbolook A., Rasouli-Sadaghiani M., Keshavarz P., Alikhani Moghadam M., & Sadeghi J. (2024). Development and characterization of a slow-release dual-purpose N and Zn fertilizer based on diatomite and nano-diatomite. *Clays and Clay Minerals* 72, e6, 1–14. <https://doi.org/10.1017/cmn.2024.11>

silicified hard diatomite shell, and minerals such as clay minerals and feldspar. Diatomite has unique physical and chemical characteristics including high porosity, large absorption capacity, suitable heat resistance, small particle size, and large specific surface area ( $10\text{--}30\text{ m}^2\text{ g}^{-1}$ ) (Fields et al., 2003). Diatomites are compounds the cation exchange capacity of which is large, and these properties make them suitable for use in the structure of SRFs (Pasković et al., 2018). Hydroxyl groups on the surface of diatomite are the main reaction sites. In addition to these, acid sites are also seen on the surface of diatomite and these are also suitable for surface reactions (Yuan et al., 2004).

The nano-clay minerals have a greater surface area and charge density than the micro-sized clay minerals (Anjum et al., 2019). Yuvaraj and Subramanian (2018) used a nano-zeolite as a carrier for Zn and observed that it took 1176 h to release the Zn from the nano-zeolite structure (Yuvaraj and Subramanian, 2018). Other research found that nano-bentonite can retain cadmium, chromium, and copper elements up to 74, 99.03, and 99.18% more than the normal ionic solution (Dehghani et al., 2016; Sirait and Manalu, 2018). Meanwhile, the adsorption efficiency in micro-bentonite for cadmium and chromium was reported as 82.4% and 55%, respectively (Barkat et al., 2014).

Zinc (Zn) is an essential micronutrient for plants because it acts in RNA and DNA synthesis and plays a significant role in carbohydrate metabolism (Umar et al., 2020). About one-third of the world's population, especially pregnant women and children, are exposed to a lack of Zn (Bouis and Saltzman, 2017). The cheapest and easiest way to overcome the malnutrition of Zn is the consumption of Zn fertilizers in agricultural products (Umar et al., 2020). In developing countries, due to a lack of awareness and reduction of production costs, micronutrients are not used much. Therefore, the simultaneous use of micro- and macronutrients in the fertilizer structure, especially with nitrogen fertilizers, is a suitable method in developed countries. In many studies, Zn with N has been used in fertilizer structures. Zn-coated urea has been synthesized in many types of research and the researchers have shown increasing use efficiency of both N and Zn (Irfan et al., 2018; Shivay et al., 2019; Dimkpa et al., 2020).

Various studies have been done on different binders to study the release process of macro- and micronutrients (Irfan et al., 2018). Compounds such as paraffin wax and palm oil (Azeem et al., 2014), chitosan (Vo et al., 2021), stearic acid (Umar et al., 2022), and hydroxymethyl cellulose (HPMC) (Mahdavi et al., 2014) have all been used as binders in urea fertilizers.

So far, diatomite has not been used as a porous structure in preparing urea-Zn slow-release fertilizers. Diatomite is a cheap raw material and could be an attractive component for slow release of nutrients in the structure of fertilizers. Also, this fertilizer supplies nitrogen and zinc to the plant at the same time, and if the structural features are confirmed, it could lead to economic savings for farmers. This research proposes to provide a simple method to make a urea slow-release fertilizer fortified by Zn based on the matrix incorporation method.

In this study, the urea was reacted with Zn in the form of molten salt and the ligand reaction between the metal cation and the urea molecule weakens the hydrogen bonds of the structure of the urea molecule. This leads to the formation of a bond between the urea and  $\text{Zn}^{2+}$  ion and the urea-Zn complex is formed. The urea-Zn complex in the melt can behave like a cation that is easily absorbable on charged surfaces. Therefore, the complex  $\text{Zn}(\text{urea})\text{-(UZn)}$  can be simply linked to the hydroxyl groups on the surface of diatomite, and the urea-Zn-diatomite complex (UZn-D) is formed. On the

other hand, the surface of diatomite can be increased with the help of the ball milling process. In the structure of nano-diatomite (ND), due to the smaller particle size and larger specific surface area, there is a possibility of increasing chemical reactions and then controlling the release of nutrients.

It was assumed that the binding of the urea-Zn complex on the porous surface of diatomite and nano-diatomite can reduce the rate of release of urea in the aquatic medium, and N and Zn in the soil medium. It is expected that the newly synthesized slow-release fertilizer will be very efficient at the retention of inorganic forms of N and available Zn in the soil.

The aims of this research were: (1) to synthesize and characterize urea-Zn (dual purpose) complex incorporated into diatomite and nano-diatomite as a slow-release fertilizer; (2) to develop and characterize slow-release UZn-D, and UZn-ND (urea-Zn-nano-diatomite complex) fertilizer which had hydroxymethyl cellulose as a binder (B); and (3) to evaluate the urea release characteristics in water and N-forms and available Zn in soil column from prepared slow-release fertilizers.

## Materials and methods

### Chemicals

Diatomite (density of  $= 2.35\text{ g cm}^{-3}$ ) was obtained from Tetra-Chem Company, Canada (supplier: Novin Taghiz, Iran). The results of the surface analysis are shown in Table 1. Hydroxypropyl methyl cellulose (gelation temperature:  $60\text{--}90^\circ\text{C}$ ) was obtained from Tetra-Chem Company, Canada (supplier: Novin Taghiz, Iran). Analytical-grade urea (46% N) and zinc chloride ( $\geq 97.0\%$ ) were purchased from Sigma-Aldrich Company, USA (supplier: dayexit, Iran). All reagents used were of high purity and double distilled water was used to make all the solutions.

### Preparation of slow-release urea-Zn fertilizers (SRUFs)

#### Preparation of UZn-D

For the synthesis of slow-release urea-Zn fertilizers, the reaction between urea (U),  $\text{ZnCl}_2$  (Zn), and diatomite (D) was done by two methods, as follows.

*Synthesis of urea-Zn (UZn) complex and then bonding to diatomite (UZn-D).* The eutectic solution of salt-urea was prepared from a mixture of urea ( $\text{CO}(\text{NH}_2)_2$ ) with zinc chloride ( $\text{ZnCl}_2$ ) at a molar ratio of six urea to one salt. The urea-Zn complex was obtained by heating a mixture of zinc chloride and urea in a beaker at a temperature of  $80^\circ\text{C}$  for 10 min in a water bath until a colorless liquid was formed. Diatomite was then added to the eutectic solution in a 1:1 ratio and thoroughly mixed for 4 h at  $105^\circ\text{C}$ . After the reaction was complete, the mixture of urea-Zn doped on diatomite was placed at room temperature to cool and dry. Finally, a white powder was formed (Park et al., 2004). To optimize the reaction, proportions of 1:1, 2:1, and 3:1 UZn:D (w/w) were prepared to reach the highest percentage of N and Zn in the synthesized slow-release fertilizer.

**Table 1.** Physical properties of natural diatomite

Sample	$S_{\text{BET}}$ ( $\text{m}^2\text{ g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{ g}^{-1}$ )	Average pore diameter (nm)
Diatomite	20.81	4.7808	5.47

**Table 2.** Nitrogen and zinc content (%) in SRUF formulations

SRUF formulation	Nitrogen content (%)	Zn content (%)
UZn-D (1:1)	6	0.4
UZn-D (2:1)	15	4
UZn-D (3:1)	15.66	4.2
DZn-U (1:1)	4.2	0.67
DZn-U (1:2)	6.3	0.58
DZnU (1:3)	7.2	0.52

UZn-D = urea-zinc-diatomite complex.

*Synthesis of diatomite-Zn (DZn) and then bonding to urea (DZn-U).* First, ZnCl<sub>2</sub> and diatomite were mixed in a weight ratio of 4:1 (zinc: diatomite) in a beaker. Deionized water was then added to the resulting mixture to form a suspension. The suspension was stirred at 80°C for 2 h. The collected supernatant was discarded and the solid part was dried in a vacuum drier and the DZn component was formed (Bhargavaramireddy and Subramanian, 2015). Finally, DZn was reacted with urea by the eutectic solution method mentioned above in 1:1, 1:2, and 1:3 DZn:U (w/w). The N and Zn concentrations in the structure of prepared fertilizers were determined using CHN and ICP-OES analysis, respectively (Table 2).

#### Preparation of UZn-ND

Nano-diatomite (ND) was prepared by ball milling (Fritsch-Pulverisette 7, Germany) for 6 h at a speed of 600 rpm. The resultant powdered nano-diatomite was used for this study. The reaction between ND and UZn was performed using the same method as used for D and UZn.

#### Preparation of UZn-D-B and UZn-ND-B

The UZn-D and UZn-ND (white powder) were mixed with an aqueous solution of 2.5 wt.% hydroxypropyl methylcellulose (HPMC) as a binder in the ratio of HPMC to UZn-D or UZn-ND of 1:10. The HPMC mixture with distilled water at room temperature underwent magnetic stirring for 20 min to form a gel composition. When completely mixed, the temperature of the mixture was raised slowly to 90°C, maintaining stirring for another 5 min to gelatinize the HPMC completely. The urea was thoroughly blended with the gel with a glass rod and was heated for 2 h at 90°C. Then the mixture was dried at 30°C in an oven and a shiny white powder was formed (Mahdavi, et al. 2014).

#### Characterization of SRUFs

A Perkin Elmer Fourier-transform infrared (FTIR) spectrophotometer was used to record the infrared spectra of KBr pellets at the standard ambient temperature in the 400–4000 cm<sup>-1</sup> region. The morphology of the diatomite, nano-diatomite, and SRUFs were evaluated using a Zeiss Company Sigma VP, field emission scanning electron microscope (FESEM) coupled with energy-dispersive spectroscopy (EDS) with preliminary gold coating. X-ray diffraction (XRD) of ND and UZn-ND were measured using a Philips PW1730 X-ray diffractometer using Cu (λ=1.540598 Å) and operated at 40 kV and 40 mA.

The hydrodynamic radius and zeta potential of SRUFs were measured using a dynamic light scattering (DLS)/zeta analyzer (Zetasizer, Malvern Panalytical). The surface area and pore size of

the diatomite was calculated by BET (ASAP 2020) with an accelerated surface area and porosity system. Thermo Finnigan Flash 1112EA was used to measure the element analyses (CHN). The Spectro Arcos-76004555 model of the inductively coupled plasma optical emission spectrometer (ICP-OES) was used to determine the amount of Zn in slow-release fertilizers. An atomic absorption spectrometer (AAS) was used to measure the amount of Zn in soil (Perkin Elmer 3030, USA).

#### Slow-release and kinetic study of urea from SRUF formulations in water

Release experiments were carried out at room temperature (25°C) as follows: 0.5 g of each SRUF compared with urea was placed into an Erlenmeyer 250 mL flask, 100 mL of distilled water was added, and the lid closed with paraffin. At 0, 1, 2, 4, 6, 8, 10, and 12 h of incubation, the containers were shaken, and 1 mL of supernatant was withdrawn from them and replaced with 1 mL of distilled water. The concentration of urea released at each time was determined by analysis in a UV-Vis spectrophotometer according to the methodology proposed by With et al. (1961) at a wavelength of 440 nm.

The mechanisms of urea release from the SRUFs that were assessed by four mathematical models were used for the evaluation of urea release kinetics; these models are described below (Gouda et al., 2017):

$$\text{First-order model: } \frac{M_t}{M_\infty} = 1 - e^{-k_1 t}, \quad (1)$$

where  $t$  is time,  $M_t/M_\infty$  is the released fraction of fertilizer at time  $t$ , and  $k_1$  is the first-order release constant.

$$\text{Higuchi model: } \frac{M_t}{M_\infty} = k_H t^{\frac{1}{2}}, \quad (2)$$

where  $t$  is time,  $M_t/M_\infty$  is the released fraction of fertilizer at time  $t$ , and  $k_H$  is the Higuchi dissolution constant.

$$\text{Hixson-Crowell model: } Q_0^{\frac{1}{3}} - Q_t^{\frac{1}{3}} = K_{HC} t, \quad (3)$$

where  $Q_0$  is the initial amount of urea in the fertilizer,  $Q_t$  is the remaining amount of urea in the fertilizer at time  $t$ , and  $k_{HC}$  is the Hixson-Crowell constant.

$$\text{Korsmeyer-Peppas model: } \frac{M_t}{M_\infty} = k_{KP} t^n, \quad (4)$$

where  $t$ ,  $k_{KP}$ , and  $n$  are time, diffusion content, and diffusion index, respectively.  $M_t/M_\infty$  is the released fraction of fertilizer at time  $t$ .

#### Slow-release behavior of SRUFs in the soil column

The soil used in this study was sandy and was collected from a field at the Khorasan Razavi Agricultural and Natural Resources Research Center, Mashhad, Iran, longitude 59.6°E and latitude 2.36°N, and passed through a 2 mm sieve after air drying. The soil organic matter (OM) was 0.8% (Walkley and Black, 1934), the pH (water) was 7.1, total nitrogen was 0.1% (Bremner and Mulvaney, 1982), available K (ammonium acetate extraction) was 95 mg kg<sup>-1</sup> (Shuman and Duncan, 1990), and Mehlich-III P was 8 mg kg<sup>-1</sup> (Mehlich, 1984). The soil cation exchange capacity was 10 cmol kg<sup>-1</sup> and the Zn concentration (DTPA-TEA extraction) was 0.2 mg kg<sup>-1</sup> (Lindsay and Norvell, 1978).

To evaluate the slow-release behavior of SRUF formulations in soil, these were applied to the PVC soil column with a 200-mesh screen at the bottom. The inner diameter and height of the soil column were 10 and 50 cm, respectively. One Whatman 42 filter paper was placed at the bottom of each column to prevent soil loss. The soil was filled in columns and a filter paper was placed on top of each column. The columns were immersed in a thin layer of deionized water so that the water capillary wetted the column. When the filter paper became wet on the soil surface, the columns were removed from the water, and the excess water was drained. After 48 h (field capacity – FC), SRUFs were applied at 10 cm of the soil surface; the N dose used was equivalent to 250 mg kg<sup>-1</sup>. Soil without any fertilizer was treated as C (control). NH<sub>4</sub>-N and NO<sub>3</sub>-N were documented at each leaching period. The amount of each N compound from the control was then withdrawn from all other treatments to emphasize the effect of treatments without interruption from the control. Each measurement was done in triplicate. The treatments consisted of the following: C: control; U: urea; UZn: urea-Zn; UZn-D: urea-Zn-diatomite; UZn-ND: urea-Zn-nano-diatomite; UZn-D-B: urea-Zn-diatomite-binder (the binder was HPMC); and UZn-ND-B: urea-Zn-nano-diatomite-binder. Deionized water (200 mL) was added to the top of the soil columns at intervals of 1, 3, 6, 9, 12, 18, 24, 33, and 45 days. Leachate from each column was collected and soil FC was maintained at a constant. NH<sub>4</sub>-N and NO<sub>3</sub>-N in leachates were determined with the Walter method (Walter, 1961). At the end of the experiment, soil samples were gathered from each column, mixed, and examined for total N and extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N.

### Statistical analysis

All the experiments were done in three replicates. Statistical analysis of data was done by one-way analysis of variance (ANOVA) with a confidence level of 95% ( $p < 0.05$ ). The significant effects between treatments were analyzed using Duncan's test. ANOVA analysis was performed by SPSS software, version 26.

## Results

### Optimizing molar ratio and formulating fertilizers

It is necessary to mix different compounds accurately to obtain the optimum percentage of nutrients in a fertilizer formula. Therefore, three diatomite-to-UZn ratios using two synthesis methods were tested to optimize the fertilizer formulation. The difference between N and Zn concentrations in synthesized SRUFs with various molar ratios and two different synthesis methods (numbers 1 and 2) is shown in Table 2. The highest concentrations of N and Zn were obtained with a 3:1 molar ratio of UZn to D and by synthetic method number 1.

Based on the results found, the final formulation of slow-release fertilizers is shown in Table 3.

### Characterization

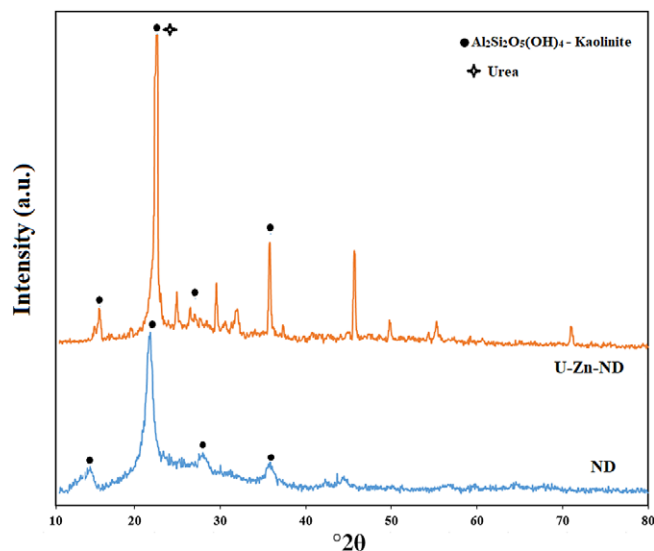
#### X-ray diffraction

The crystal structure and particle size of ND and UZn-ND compounds were determined by XRD patterns (Fig. 1). The peaks at 14.51°2θ, 21.79°2θ, 26.39°2θ, and 35.79°2θ corresponded to the diffraction peaks of kaolinite reported in JCPDS card no. 89-6538 (Pornaroonthama et al., 2015). The UZn-ND (Fig. 1) had

**Table 3.** The final formulations of the SRUFs

Type of fertilizer formulation	N (%)	Zn (%)
U	46	–
UZn	35	3.1
UZn-D (2:1)	15.66	4.2
UZn-ND (2:1)	15.66	4.2
UZn-D-B (2:1:0.1)	15.66	4.2
UZn-ND-B (2:1:0.1)	15.66	4.2

U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.



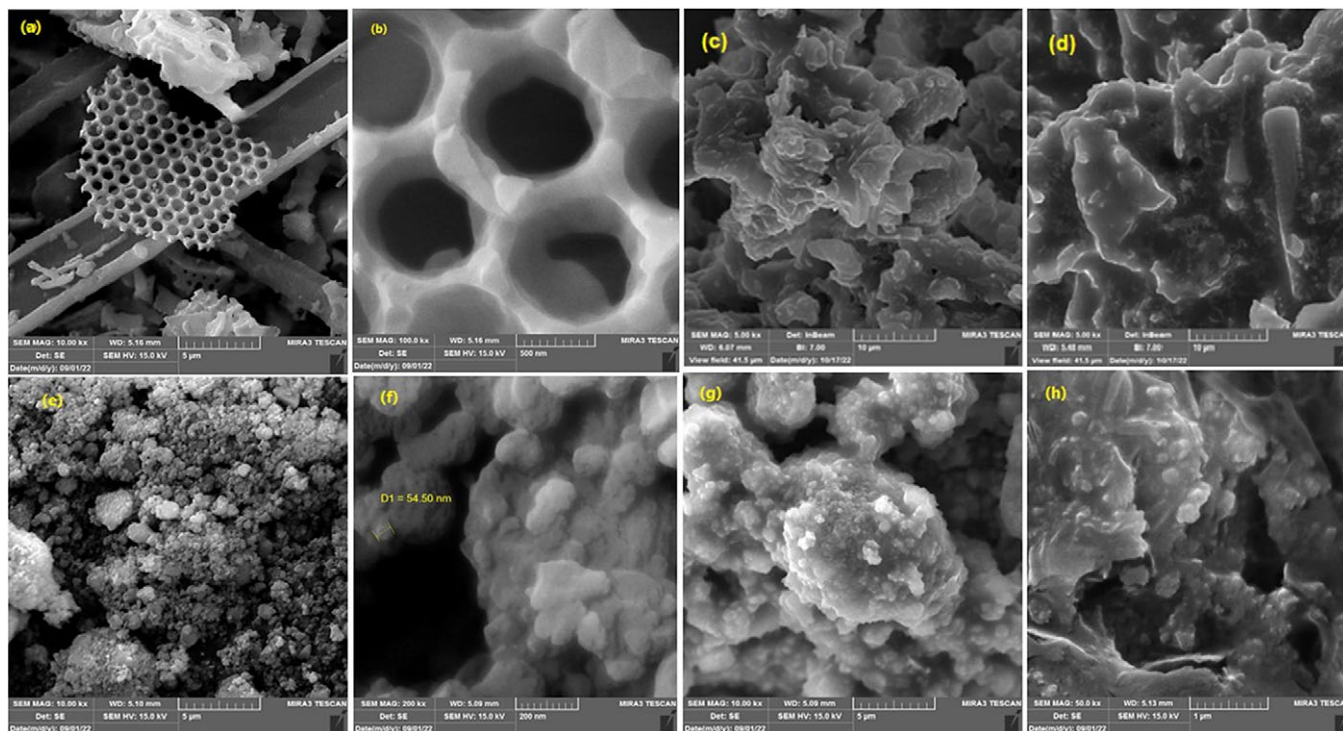
**Figure 1.** X-ray diffraction patterns for nano-diatomite (ND) and urea-Zn-nano-diatomite (UZn-ND).

characteristic shifted peaks at 15.99, 22.49, 24.89 and 35.74°2θ. The crystal sizes determined by the Scherrer equation (Hakimi and Alikhani, 2020) were 14.14 and 33.64 nm for ND and UZn-ND, respectively:

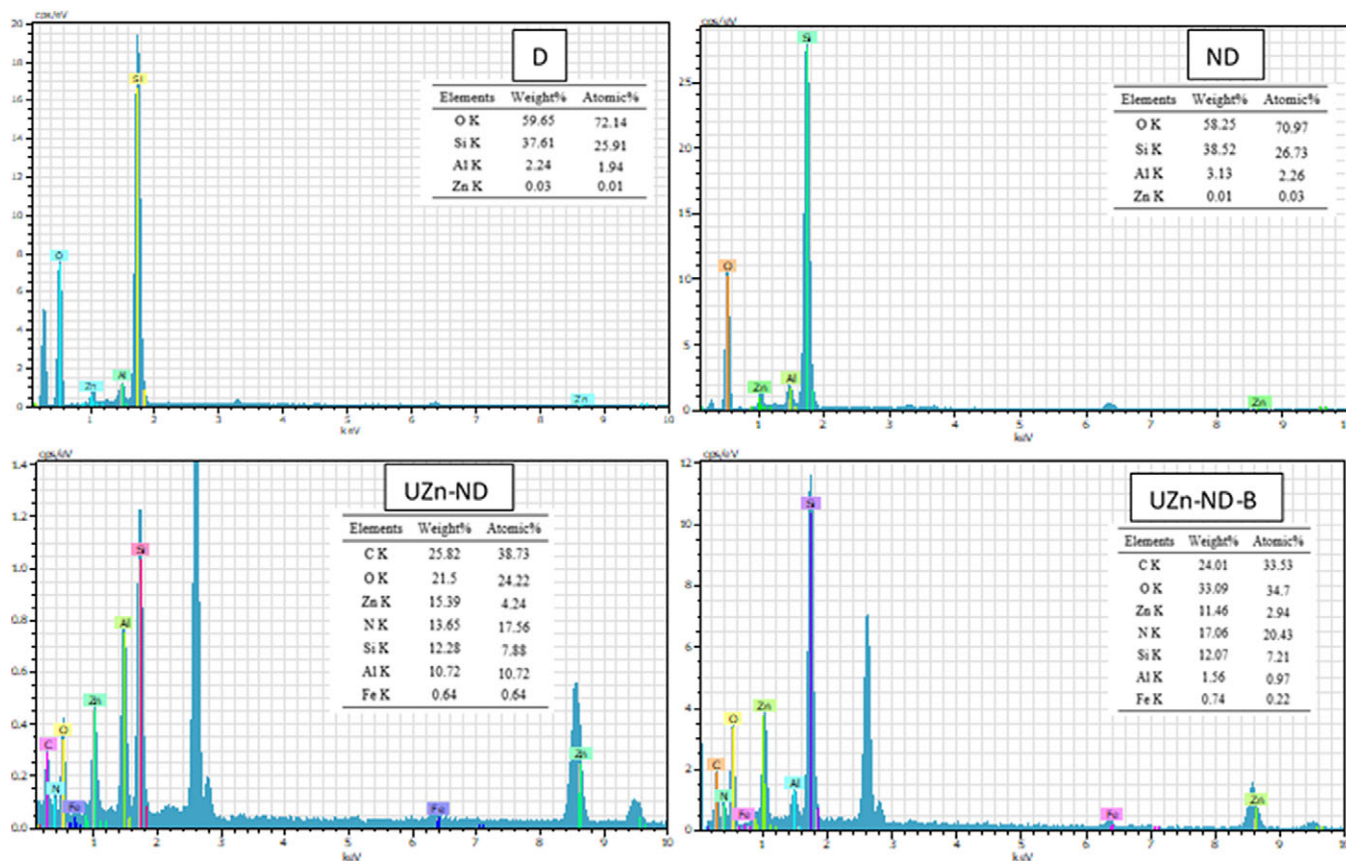
$$\text{Scherrer equation} : L = K\lambda / \beta \cdot \cos\theta, \quad (5)$$

where  $L$  is the nano-crystallite size, and  $\lambda$  is the radiation of wavelength (nm) from measuring the full width at half maximum of peaks ( $\beta$ ): full width at half maximum of peaks in radian located at any  $2\theta$  in the pattern.

The data obtained from XRD analysis showed that crystal structure was triclinic (Pornaroonthama et al., 2015). The diffraction peaks at 12.41, 21.41, 24.97, and 34.97°2θ were found to match those reported in JCPDS card no. 89-6538. The crystal structure of the kaolinite was determined to be triclinic, with lattice parameters of  $a = 5.1535 \text{ \AA}$ ,  $b = 8.9419 \text{ \AA}$ , and  $c = 7.3906 \text{ \AA}$ . Also, the peaks at 22.49°2θ correspond to the main characteristic peaks of urea, which shows that the plates of urea crystals have overlapped with the plates of diatomite (Loera-Serna et al., 2016). It is clear that in the XRD pattern of UZn-ND, the number of planes increased and the peak width also decreased. This may be due to the overlapping of planes of urea crystals and thereby a reorientation in the



**Figure 2.** Scanning electron microscopy images of: (a) diatomite; (b) high magnification image of diatomite; (c) urea-Zn-diatomite; (d) urea-Zn-diatomite-binder (binder was HPMC); (e) nano-diatomite; (f) high magnification image of nano-diatomite; (g) urea-Zn-nano-diatomite; and (h) urea-Zn-nano-diatomite-binder.



**Figure 3.** Energy-dispersive spectroscopy spectra of diatomite (D), nano-diatomite (ND), urea-Zn-nano diatomite (UZn-ND) and urea-Zn-nano-diatomite-binder (binder was HPMC) (UZn-ND-B).

structure, and this brings about a different morphology of the crystals themselves (Madhurambal et al., 2010).

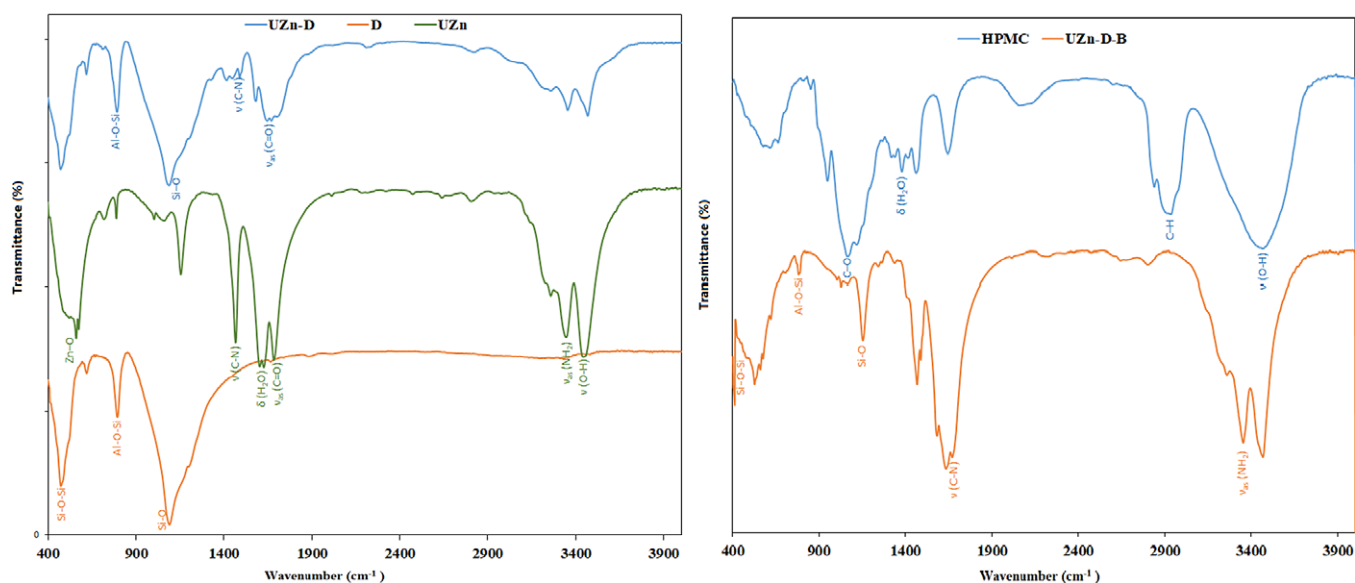
### FESEM/EDS

To study the surface morphology of diatomite (D) and nano-diatomite (ND) before and after urea-Zn (UZn) reaction, FESEM with energy-dispersive X-ray spectroscopy (FESEM-EDS) images were obtained, and are shown in Figs 2 and 3, respectively. Pure D shows a well-arranged porous structure; its surface is well-purified and there are no signs of contamination (Fig. 2a,b). In Fig. 2 (upper panels), the preparation of ND by the Ball mill method, in addition to making the particles smaller (<100 nm), changed the porous structure and turned them into spherical particles (Fig. 2e,f). The morphology of diatomite changed after the process of incorporating urea and the use of the HPMC binder. After modification with UZn, the surface of D showed UZn formation with spherical morphology, and the pores of D were almost covered with UZn (Fig. 2c). The morphology of ND incorporated in the HPMC hydrogel was investigated by FESEM (Fig. 2h). In Fig. 2h, the surface morphology of the UZn-ND was affected by the presence of the HPMC hydrogel. EDS analysis was also carried out to confirm the presence of expected elements as shown in Fig. 3.

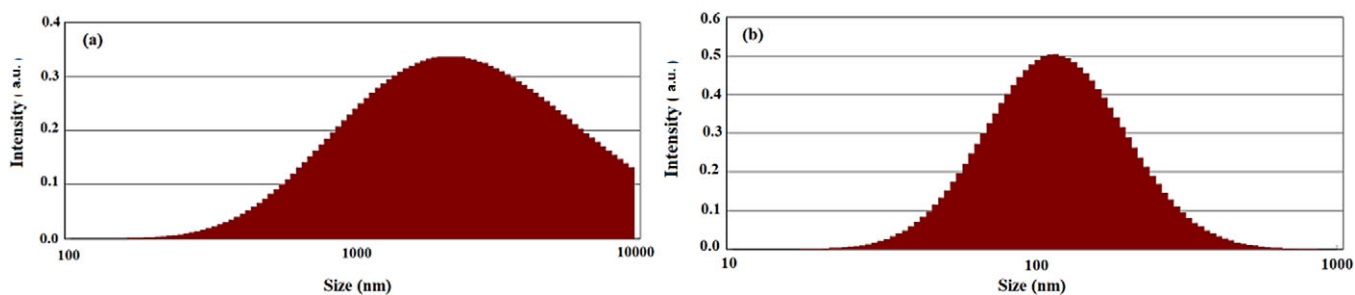
It is well established that silica and oxygen are the main constituents present in the D and ND. Subsequently, after surface modification with UZn, the presence of Zn, N, and C are noted, as expected, along with Si and O (Fig. 3).

### FTIR spectra

The FTIR spectrum of D (Fig. 4) shows typical bands at 1080 and 474  $\text{cm}^{-1}$ , corresponding to Si-O stretching and Si-O-Si bending, respectively, which were structural groups (Fu et al., 2016). Another stretching vibration at 799  $\text{cm}^{-1}$  was attributed to Al-O-Si (Caliskan et al., 2010; Caliskan et al., 2011). In the FTIR spectrum of the urea-Zn (UZn) complex, the band related to the stretching vibration  $\nu$  (O-H) of uncoordinated  $\text{H}_2\text{O}$  was observed at 3440  $\text{cm}^{-1}$ . In contrast, the corresponding bending motion of the uncoordinated water,  $\delta$  ( $\text{H}_2\text{O}$ ), was observed at 1626  $\text{cm}^{-1}$  (Mahdavinia et al., 2015). The characteristic stretching vibrations of the  $\nu_{\text{as}}$  ( $\text{NH}_2$ ),  $\nu_{\text{as}}$  (C=O), and  $\nu$  (C-N), were observed at nearly 3346, 1685, and 1466  $\text{cm}^{-1}$ , respectively (Ibrahim et al., 2012). In addition, metal-oxygen (Zn-O) stretching vibrations were observed at 559  $\text{cm}^{-1}$  (Beig et al., 2022). After surface D was functionalized with UZn, the weak band around 3354, 1670, and 1490  $\text{cm}^{-1}$  was observed in UZn-D, which was attributed to the UZn complex that



**Figure 4.** FTIR spectra of diatomite (D), urea-Zn (UZn), urea-Zn-diatomite (UZn-D), urea-Zn-diatomite-binder (binder was HPMC) (UZn-D-B) and HPMC (B).



**Figure 5.** Dynamic light scattering analysis of (a) diatomite and (b) nano-diatomite.

added to the spectrum of D (Liu et al., 2016). In the FTIR spectrum of HPMC (Fig. 4), the absorption band at  $3464\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  indicated the stretching and bending vibrations of the  $-\text{OH}$  groups, respectively (Jayaramudu et al., 2021). The bands at  $2929$  and  $1065\text{ cm}^{-1}$  represented the stretching vibration of  $\text{C}-\text{H}$  and  $\text{C}-\text{O}$  bonds, respectively (Mahdavinia et al., 2015). In the FTIR of UZn-D-HPMC (UZn-D-B), the presence of amide groups was confirmed by the appearance of the bands at  $3352$  and  $1670\text{ cm}^{-1}$ , which was indicative of stretching and bending  $\text{N}-\text{H}$  bonds of amide groups, respectively (Taghavi et al., 2021). In addition, the presence of D is confirmed by a band that appeared at  $1140\text{ cm}^{-1}$ , which was related to the  $\text{Si}-\text{O}$  stretching. Compared with the D, the  $\text{Si}-\text{O}$  band showed a shift of  $\sim 60\text{ cm}^{-1}$  to the higher frequency, showing the interaction between the clay and polymer functional groups (Morifuji and Nakashima, 2018).

#### Dynamic light scattering (DLS) and zeta potential

In this section, the average particle size of D and ND, as well as their polydispersity index (PI) (Fig. 5) and zeta potential (ZP) (Table 4) were investigated. The PI is a measure of the heterogeneity of a sample based on size. Polydispersity can occur due to size distribution in a sample or agglomeration or aggregation of the sample during isolation or analysis. Dynamic light scattering analyses (DLS) of D revealed particles with a mean diameter of  $1086\text{ nm}$  and a PI value of 1.71. On the other hand, ND had a mean diameter of  $111\text{ nm}$  and a PI of 0.296. Monodisperse nanoparticles

had a PI of  $<0.2$ , while polydisperse nanoparticles had a PI of  $>0.7$  (Khaledi et al., 2020).

The zeta potential was calculated at between pH5 and 10 for D, ND, UZn-ND, and UZn-ND-B (Table 4). The samples showed a negative charge on their surfaces at all pH levels studied. As pH increased, the degree of negative charge increased due to the deprotonation or dissociation of  $\text{H}^+$  from functional groups (Bernal et al., 2017). In addition, the results showed that the zeta potential value increased with the decrease in particle size. It should be noted that the zeta potential of UZn-ND was less than that of ND, which was probably due to the interaction between the Zn-Urea complex and ND.

#### Urea slow-release behavior and kinetics in water

The cumulative release rate of urea from SRUFs in water is shown in Fig. 6. The result indicated 87.2% and 80% release of U and UZn used as a control in water within 1 h. When urea was incorporated with diatomite, its release rate decreased. A cumulative release of  $\sim 34.5\%$  and  $21.8\%$  for UZn-D and UZn-ND, and 3% for UZn-D-B and UZn-ND-B, were observed in water at 1 h.

A cumulative release of  $\sim 3\%$ ,  $17.2\%$ , and  $24.3\%$  was observed for UZn-D-B and UZn-ND-B in water at 1, 6, and 12 h, while release of urea from UZn-D at 1, 6 and 12 h was  $34.5\%$ ,  $48.1\%$ , and  $54.4\%$ , and from UZn-ND was  $21.8\%$ ,  $28.8\%$ , and  $39.8\%$ , respectively, at the same time in the water. The intensity of urea release from fertilizers was as follows:

UZn-D-B  $\approx$  UZn-ND-B  $<$  UZn-ND  $<$  UZn-D  $<$  UZn  $<$  U.

Four different kinetic models (namely: first-order, Higuchi, Hixson-Crowell, and Korsmeyer-Peppas) were applied to study the cumulative release of urea in water. The correlation coefficient for fitting of the release data is presented in Table 5. In fertilizers containing diatomite and nano-diatomite (UZn-D and UZn-ND), the Higuchi model showed the best fit for urea release data with  $R^2$  of 0.76, and 0.93, respectively, and also UZn-D-B, and UZn-ND-B in water ( $R^2 > 0.93$ ).

#### Leaching of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ at 45-day intervals in the soil column

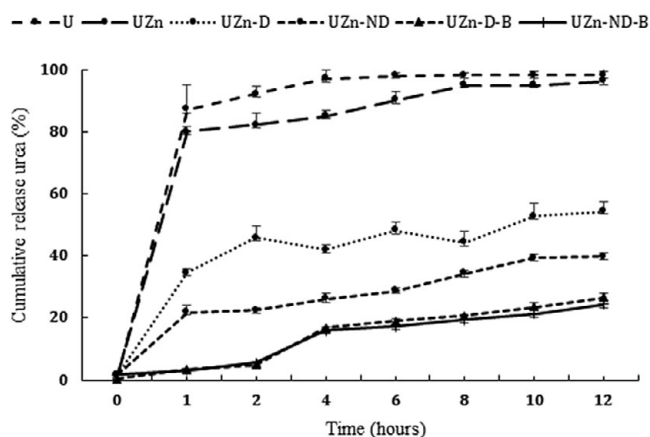
The effect of synthesized slow-release fertilizers on  $\text{NO}_3\text{-N}$  leaching over 45 days is shown in Fig. 7. During the five initial leaching periods (up to day 12), a low concentration of  $\text{NO}_3\text{-N}$  was recorded in the leachate. Although the leachate  $\text{NO}_3\text{-N}$  concentration increased from day 12 to day 24, with a peak on day 24, it then decreased for all treatments. The highest  $\text{NO}_3\text{-N}$  concentration was observed in the leachate of columns containing U. In the leachate of columns supplied with fertilizers including diatomite and also HPMC, the  $\text{NO}_3\text{-N}$  concentration decreased significantly, and even on day 24, lower peaks were observed compared with U and UZn application.  $\text{NO}_3\text{-N}$  concentrations in the leachate of columns applied by diatomite and nano-diatomite decreased by an average of 50%, and in columns containing diatomite and binder decreased by 70%.

The cumulative loss of  $\text{NO}_3\text{-N}$  in leachate during the experiment period in the soil columns is shown in Fig. 8. The cumulative loss of  $\text{NO}_3\text{-N}$  with the application of U treatment was the greatest ( $37.17\text{ mg kg}^{-1}$ ). Significantly, the lowest  $\text{NO}_3\text{-N}$  concentration was leached for UZn-D-B treatment ( $18.14\text{ mg kg}^{-1}$  compared with U). No significant difference was observed in the cumulative

**Table 4.** Zeta potential of D, ND, UZn-ND, and UZn-ND-B

Sample	Zeta potential (mV)			
	pH = 5	pH = 7	pH = 9	pH = 10
ND	-24.45	-28.86	-33.06	-36.14
D	-20.19	-28.56	-32.15	-34.67
UZn-ND-B	-17.08	-20.67	-25.70	-29.35
UZn-ND	-16.64	-20.39	-25.10	-28.60

D = diatomite; ND = nano-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-ND-B = urea-Zn-nano-diatomite-binder (binder was HPMC).

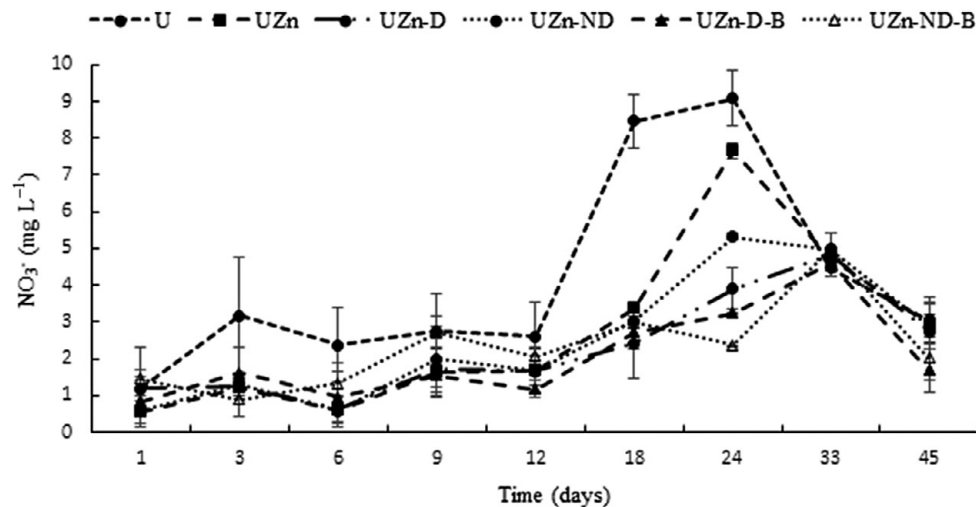
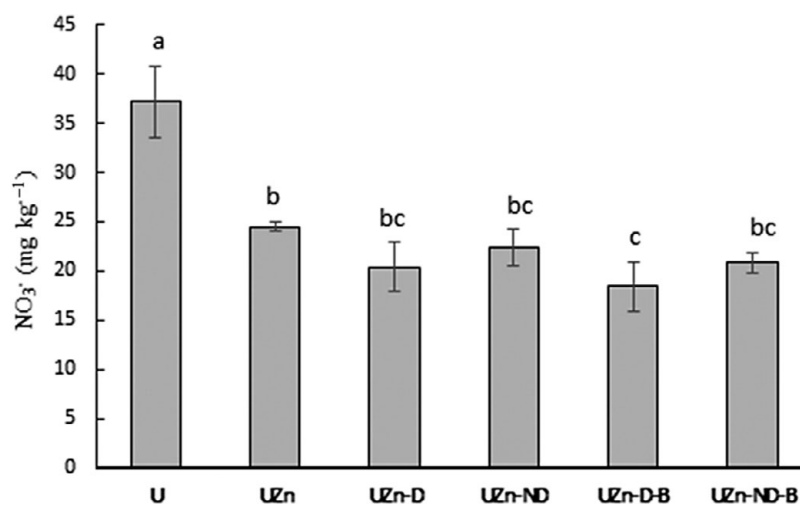


**Figure 6.** Effect of SRUFs formulations on the urea-release rate over time. U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.

**Table 5.** The correlation coefficient ( $R^2$ ) for fitting of the release data using different mathematical models

Models	Correlation coefficient ( $R^2$ )					
	U	UZn	UZn-D	UZn-ND	UZn-D-B	UZn-ND-B
First-order	0.671	0.824	0.591	0.858	0.934	0.998
Higuchi	0.591	0.677	0.764	0.939	0.943	0.932
Hixson-Crowell	0.528	0.677	0.583	0.823	0.927	0.921
Korsmeyer-Peppas	0.444	0.457	0.491	0.561	0.887	0.885

U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.

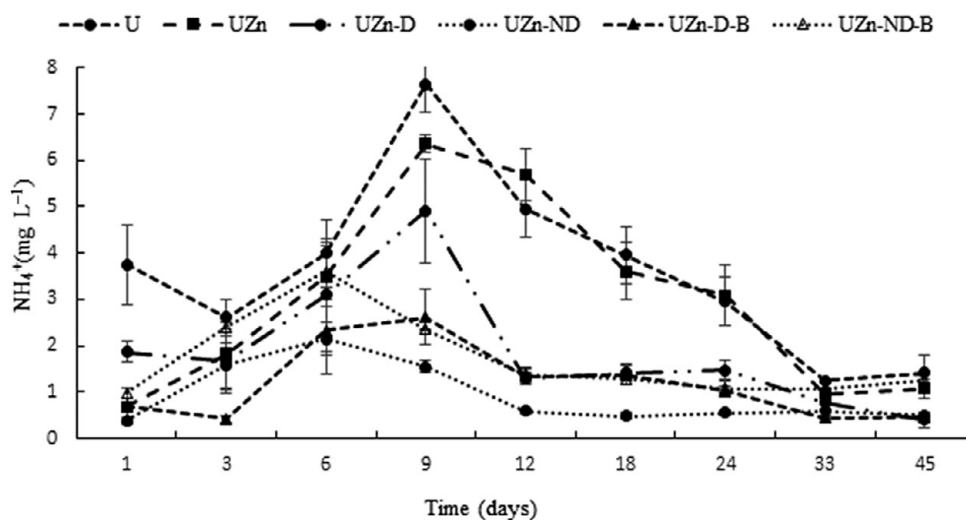
**Figure 7.** Effects of SRUFs formulations on  $\text{NO}_3\text{-N}$  leaching at different leaching intervals from soil columns. Error bars indicate the standard deviation of replicates ( $n = 3$ ). U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.**Figure 8.** Effects of SRUF formulations on cumulative losses of  $\text{NO}_3\text{-N}$  from soil columns. Means with different lowercase letters indicate significant differences among treatments by Duncan's test at  $P \leq 0.05$ . U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.

loss of  $\text{NO}_3\text{-N}$  in leachate in the application of slow-released fertilizers by diatomite and HPMC binder.

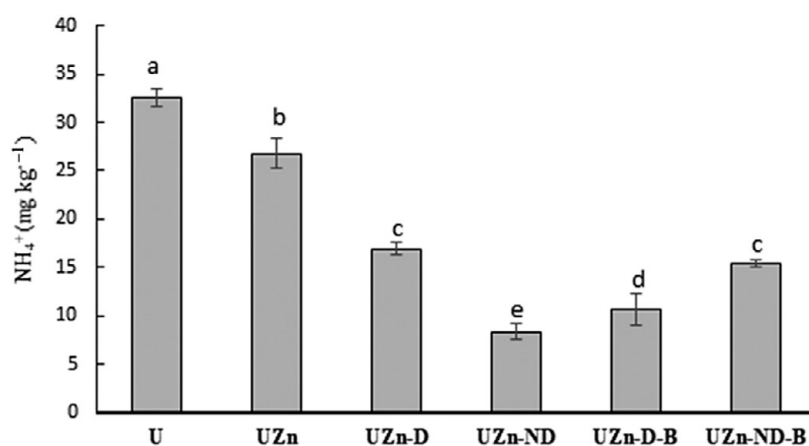
The effects of SRUF formulations on  $\text{NH}_4\text{-N}$  leaching at different leaching events in soil columns were compared with urea (Fig. 9). The concentration of  $\text{NH}_4\text{-N}$  in leachate was

largest in soil treated with urea, compared with that of all the others at day 9, and this increase continued for 45 days compared with other treatments. In the application of U, UZn, UZn-D, and UZn-D-B,  $\text{NH}_4\text{-N}$  leaching peaks occurred on day 9, and then the trend of  $\text{NH}_4\text{-N}$  concentration changes decreased until day 33 and

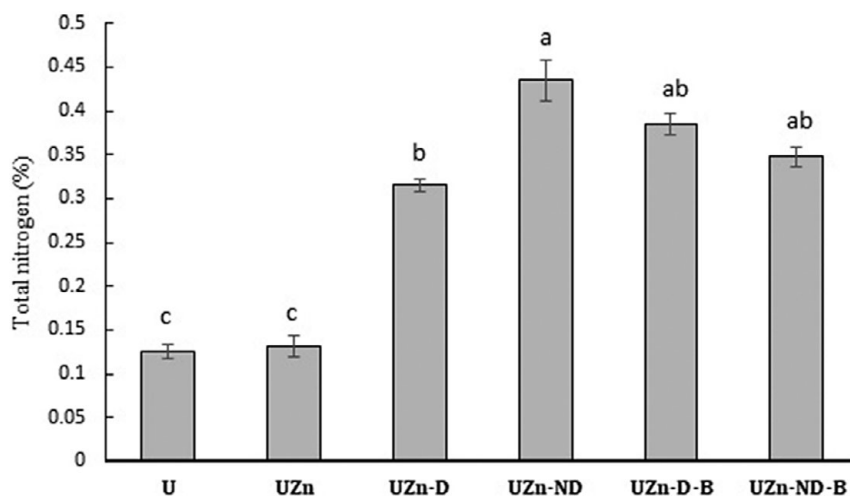




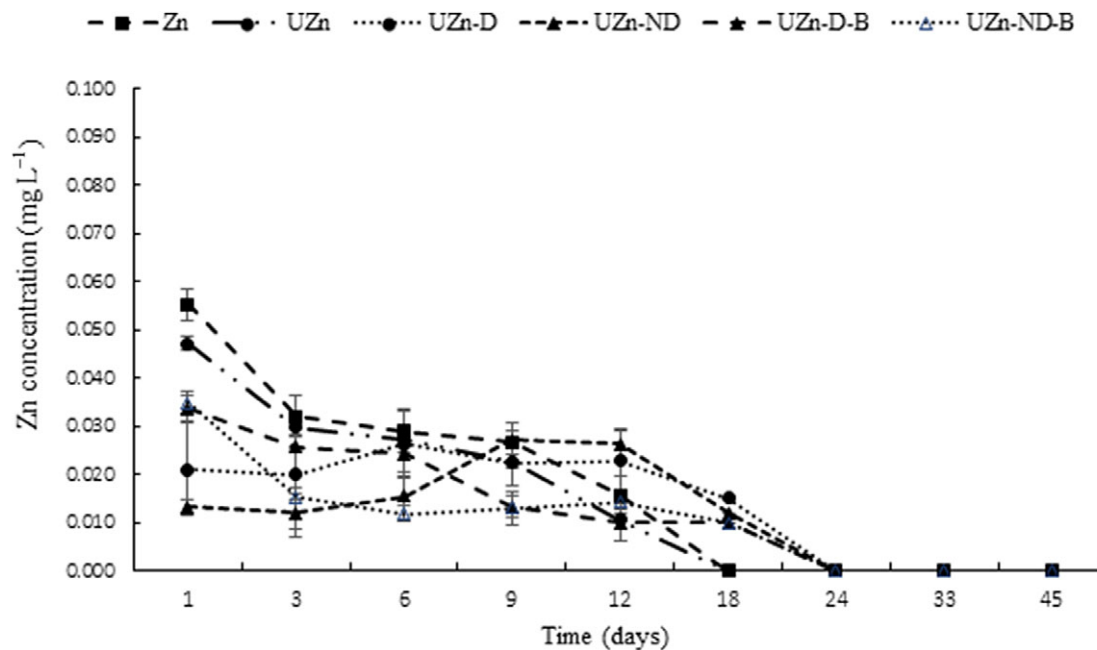
**Figure 9.** Effects of SRUF formulations on  $\text{NH}_4\text{-N}$  leaching at different leaching intervals from soil columns. Error bars indicate the standard deviation of replicates ( $n = 3$ ). U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.



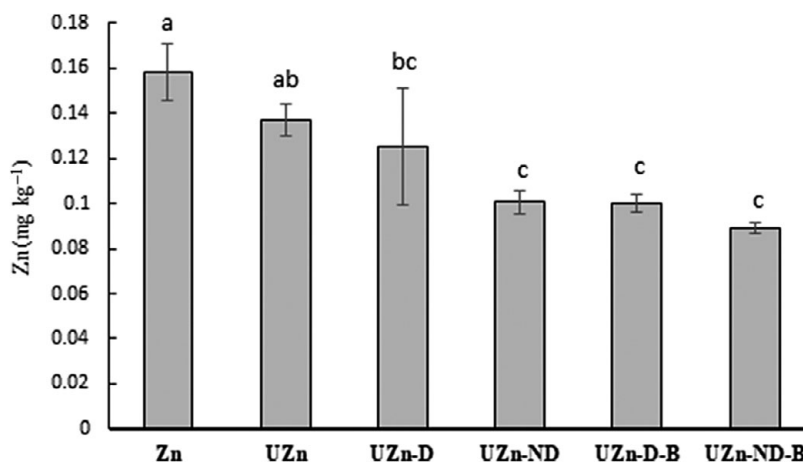
**Figure 10.** Effects of SRUF formulations on cumulative losses of  $\text{NH}_4\text{-N}$  from soil columns. Means with different lowercase letters indicate significant differences among treatments by Duncan's test at  $P \leq 0.05$ . U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.



**Figure 11.** Effects of SRUF formulations on total nitrogen retained in the soil at day 45 of leaching. U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.



**Figure 12.** Effects of SRUF formulations on Zn leaching at different leaching intervals from soil columns. Error bars indicate the standard deviation of replicates ( $n = 3$ ). U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.



**Figure 13.** Effects of SRUF formulations on cumulative losses of Zn from soil columns. Means with different lowercase letters indicate significant differences among treatments by Duncan's test at  $P \leq 0.05$ . U = urea; UZn = urea-Zn; UZn-D = urea-Zn-diatomite; UZn-ND = urea-Zn-nano-diatomite; UZn-D-B = urea-Zn-diatomite-binder (binder was HPMC); UZn-ND-B = urea-Zn-nano diatomite-binder.

was then stable until day 45. Leachate  $\text{NH}_4\text{-N}$  concentration in columns applied by UZn-D on day 9 was  $4.9 \text{ mg L}^{-1}$  and by UZn-D-B was  $2.39 \text{ mg L}^{-1}$ , which was reduced by 35.8% and 68.7%, respectively, compared with the U application. Application of UZn-ND and UZn-ND-B led to an increase in the  $\text{NH}_4\text{-N}$  concentration in soil column leachates on day 6, but the decline slope of  $\text{NH}_4\text{-N}$  concentration was relatively stable until day 45.

The cumulative concentration of  $\text{NH}_4\text{-N}$  determined in leachate over 45 days is shown in Fig. 10. The maximum  $\text{NH}_4\text{-N}$  was lost with U application at  $\sim 32.53 \text{ mg kg}^{-1}$ , and minimum with UZn-ND at  $8.39 \text{ mg kg}^{-1}$ . The UZn-ND was shown to be the most effective treatment to decrease the leaching of  $\text{NH}_4\text{-N}$  in soil columns. Leaching loss of  $\text{NH}_4\text{-N}$  was less in soils when diatomite and nano-diatomite formulations were applied.

#### Total soil nitrogen after the leaching experiment

The total soil N after the leaching experiment of SRUFs is shown in Fig. 11. The higher concentrations of total soil N in UZn-D (0.315%), UZn-ND (0.435%), UZn-D-B (0.385%), and UZn-ND-B (0.348%) than in U (0.125%) and UZn (0.131%) propose that both diatomite and HPMC (as a binder) ensured slower release of N. For UZn-ND, retention of total N was greater than in other treatments.

#### Leaching of Zn at 45-day interval

At the start of the experiment nutrient release pattern (Fig. 12), a maximum concentration of  $0.06 \text{ mg L}^{-1}$  Zn was observed in the leachate from  $\text{ZnSO}_4$  treatment (Zn). The data showed that the total

available Zn from Zn and UZn treatments was drained after 18 days, beyond which the Zn concentration was below detectable limits. However, the release of Zn from SRUFs continued for 24 days. The Zn concentration in the leaching with the application of SRUF was significantly smaller than Zn and UZn. The Zn concentration in the leachates of columns supplied with SRUFs was almost 35% less than Zn and UZn. In addition, a significant difference of ~24% between the release of Zn in the use of UZn-D and UZn-ND was observed.

The cumulative concentration of Zn determined in leachate over 45 days is shown in Fig. 13. The maximum Zn was retained with UZn-ND, UZn-D-B, and UZn-ND-B applications, and a statistically significant preservation of Zn was shown in all of the treatments compared with the ZnSO<sub>4</sub> application.

## Discussion

Urea and urea-based fertilizers are used as N fertilizers for agriculture and are susceptible to loss from volatilization and leaching after application to crops. Much research into slow-release fertilizers (SRFs) has been undertaken as the best way to develop novel N fertilizers. In this study, the SRUFs simultaneously supply N and Zn to the soil, synthesized by the reaction between U, Zn, and D by two methods. The result showed that the molar ratio of 3:1 UZn to D and synthesis method 1 was the best formulation and method for the preparation of SRUFs. The percentages of N and Zn in the final fertilizer formula were 15.66% and 4.2%, respectively.

Morphological studies of the compound's structure indicated that D has a porous structure and no pollution on the surfaces, and, after the binding of the UZn complex to D, its appearance changes, and becomes spherical particles. This indicates that the confinement of UZn into the pores of the D structure was due to molecular adsorption (Gnanamoorthy et al., 2014). The UZn particle agglomerates were uniformly distributed on the ND surface. Adding HPMC hydrogel to the structure of UZn-ND showed a more irregular and rough structure on the surface of the UZn-ND. The evaluating typical bands in the structure of the compounds with FTIR spectrum also confirmed the bond formation between the UZn complex with D and ND.

The result of the DLS analysis showed that the size dispersion of the nanoparticles produced in D (ND) is acceptable. The zeta potential of SRUFs confirms the ability of the diatomite structure to adsorb positive cations on the surface. The particle charge is a critical factor of HPMC performance, particularly regarding gelation for coating (Tundisi et al., 2021). The thermo-reversible property of HPMC is dependent on its behavior in the aqueous solution (Ghadermazi et al., 2019). Therefore, the surface charge may control swelling, dissolution, and dispersion of HPMC in the aqueous solution (Joshi, 2011). The pure HPMC solution has a negative charge, and its potential zeta range is  $-2.14$  to  $-3.4$  mV (Ghadermazi et al., 2019). In addition, presenting HPMC into a UZn-ND suspension can increase the total electric charge and move the solution to a high negative charge region. This leads to the repulsive forces between particles increasing, and HPMC stabilizes fertilizer structures (Lestari et al., 2015).

The main factor slowing down the urea release time was relation between pore structure of diatomite and water percolation. Percolation theory states that a material release is derived by the dissolution of the material within the capillary's composition of the material particle cluster and pore network (Holman and

Leuenberger, 1988). Besides, the interaction between diatomite and HPMC resulted in aggregation, leading to decreases in diatomite porosity. The HPMC might have formed a physical barrier in the form of membrane resistance of the matrix, causing a slower release by diffusion as a result of the concentration or pressure gradient, or both (Shen et al., 2018).

Synchronization between the supply of nutrients and their uptake by the plant can happen with the application of slow-release fertilizers. To achieve the best type of SRF, it is necessary to predict the release rate of nutrients from the fertilizer structure. A conceptual model for this development was presented by Shaviv (2005) and Shoji (1999), according to which the nutrient release pattern from the structure of SRF varies from parabolic release to linear release and sigmoidal release. They stated that linear and sigmoidal release patterns have the best synchronization with nutrient uptake. A sigmoidal release indicates that the release of nutrients only starts after a certain lag time. The release pattern of urea in water was sigmoidal for urea combined with diatomite and HPMC, but there was no lag for U alone or for the UZn complex. The application of HPMC in the fertilizer structure significantly reduced the rate of urea release, so that after 2 h from the start of urea release, U and UZn treatments released > 80% of urea in the water medium, but in UZn-D and UZn-ND the release rate was ~40% and 20%, respectively, and ~5% in the UZn-D-B and UZn-ND-B treatments. Research has shown that release from any loaded material from amorphous structures could be physically due to diffusion, degradation, and dissolution (Zhang et al., 2021; Emam and Shaheen, 2022).

The result of kinetic models indicates that their release rate was directly proportional to the amount of urea incorporated in the matrix (Wei et al., 2019). This result indicates that the prime mechanism of urea release from SRUFs is diffusion-controlled release (Paarakh et al., 2018). The Higuchi model states that the release of a compound from a matrix delivery system involves both dissolution and diffusion (Gouda et al., 2017). The urea was released by diffusion from the pores and channels of SRUFs. The HPMC binder acts as a barrier and slows down the process of solubility and diffusion of elements from the fertilizer structure. Hermida and Agustian (2019) used bentonite, HPMC, and starch to slow urea release. They reported that with the increase in binder concentration, the release rate of urea decreased and only 10% of urea was released from the fertilizer structure in 200 min in water. Furthermore, after 500 min, the fertilizer with 10% bentonite and 0.8% binder was the slowest compound to release urea in water.

The NO<sub>3</sub>-N leaching rate curve in the soil column also follows a sigmoidal pattern. Until day 12, there is a similar delay for all compounds, but after that, the rate of NO<sub>3</sub>-N leaching from urea treatment increases rapidly, while leaching is very slow in fertilizers containing diatomite and HPMC. The structure of diatomite can be trapped anions such as NO<sub>3</sub><sup>-</sup> in pores and channels and their release decreases. On the other hand, the porous structure of diatomite allows a large amount of water to penetrate the polymer network and may increase NO<sub>3</sub><sup>-</sup> leaching. Incorporating HPMC in the fertilizer structure can cover the surface and internal pores of the diatomite and lead to reduced nitrate solubility and leaching at a specified time (Bansiwali et al., 2006). Reactive sites such as hydroxyl groups on the diatomite surface can also adsorb NH<sub>4</sub><sup>+</sup> ions and increase their retention in the soil. The complex of UZn can form a stable eutectic system that acts like the cations that can adsorb on the negative surface sites. This leads to the stable binding of UZn to the surface of diatomite and nano-diatomite and reduces its losses as NH<sub>4</sub><sup>+</sup> (Park et al., 2004). These results have also been reported for

using compounds with similar silicate and clay structures (Zwingmann et al., 2009; Colombani et al., 2015). Eslami et al. (2018) displayed a decrease in  $\text{NH}_4\text{-N}$  losses, from 84% to 29% when the soil was treated with saturated clinoptilolite and chabazite. Similarly, Sempeho et al. (2015) reported the slow release of intercalated urea by kaolinite clay mineral. According to their results, it took around 150 h for the complete release in intercalated urea (Sempeho et al., 2015).

A significant difference was observed in the cumulative loss of  $\text{NH}_4\text{-N}$  concentration in the soil columns supplied with SRUFs in comparison with  $\text{NO}_3\text{-N}$ . More retention of  $\text{NH}_4\text{-N}$  than  $\text{NO}_3\text{-N}$  in the soil can be due to the unique characteristics of diatomite about the cation in their exchange surfaces and reactive edges (Yuan et al., 2004). The reduction of  $\text{NH}_4\text{-N}$  leaching in the application of SRUFs is due to the high affinity of diatomite for  $\text{NH}_4\text{-N}$  adsorption in the mineral lattices, whereas  $\text{NO}_3\text{-N}$  was absorbed into the pores of the diatomite. The principal action of the clay mineral in controlling the release of urea and decreasing  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  losses can be associated with two causes: (1) the layered or porous structure, such as in diatomite, can act as a physical barrier and prevent exposure to urea molecules and thus the rate of urea hydrolysis decreases; and (2) the retention by adsorption of  $\text{NH}_4^+$  as the silica surface of diatomite is covered by negatively charged reactive silanol (Si-OH) groups. The silanol group is an active one that leads reaction with numerous functional groups, causing minerals to absorb cation molecules ( $\text{NH}_4^+$ ) to balance the charge shortage, which therefore slows the release rate of nitrogen (Pereira et al., 2015). Clay minerals of nano-size keep a greater surface area and greater charge density than micro-sized clay minerals (Anjum et al., 2019). Research showed that nano-bentonite could remove 74% of chromium, 99% of cadmium, and 99.18% of mercury in solution. In contrast, the adsorption efficiency of micro-bentonite for cadmium and chromium is reported to be ~82% (Gu et al., 2013; Barkat et al., 2014).

The Zn leaching curve was divided into three stages. The first Zn levels decrease sharply until day 3 and stabilize then until day 12 (second stage). The result also showed that from day 12 to day 24, it follows the third stage. In this stage, Zn release was significantly reduced. The Zn release from SRUFs continued for 24 days. The controlled release of nutrients using clays (such as zeolite) had already been demonstrated for nutrients such as Zn. Yuvaraj and Subramanian (2018) reported that Zn release from the nano-zeolite substrate was prolonged for 49 days, while the Zn release from the mineral fertilizer of  $\text{ZnSO}_4$  finished within 9 days. The cumulative losses of Zn were also influenced by the presence of nano-diatomite and binder in the structure of SRUFs. Research by Hernández-Ávila et al. (2017) showed that diatomite is efficient at cationic exchange by metals and can be used in the absorption of cations due to the high retention capacity. The  $\text{Zn}^{2+}$  ion alone or in a complex with urea as a stable eutectic form (UZn) is a cation and is easily preserved in exchangeable sites of diatomite on its surface or active edges.

## Conclusions

In this study, new SRUFs were effectively synthesized through the incorporation of a stable eutectic system of urea-zinc (UZn) complexes into diatomite and nano-diatomite with the HPMC binder. The release of urea in water followed a sigmoidal pattern.

Approximately 40–50% of urea in UZn-D and UZn-ND were released after 12 h, while 20% of urea was released after 12 h for UZn-D-B and UZn-ND-B using HPMC. Conventional urea fertilizer dissolved completely in water after <1 h. The urea release kinetic model of SRUFs was associated with dissolution and diffusion mechanisms. The leaching  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the soil column were decreased in the soils supplied with SRUFs compared with urea alone. The retention of  $\text{NH}_4\text{-N}$  was greater than for  $\text{NO}_3\text{-N}$ . The maintenance of total N in the application of synthetic slow-release fertilizers was two to three times more than urea. In addition, the release of Zn from the structure of SRUFs was almost 35% less than for  $\text{ZnSO}_4$ . The application of diatomite and HPMC in a slow-release fertilizer structure reduced the release rate of N and Zn in the soil significantly compared with the common fertilizers of urea and zinc sulfate. These SRUFs can be viewed as a potential material for the slow and simultaneous releases of N and Zn in soil and for minimizing cost and environmental problems.

**Author contributions.** Atena Mirbolook: conceptualization, material processing, investigation, methodology, formal analysis, statistical, manuscript writing, review, and editing. Mirhassan Rasouli Sadaghiani: head of the lab, supervision of material processing, review, and editing. Payman Keshavarz: conceptualization, review, and editing. Mina Alikhani: methodology, review, and editing. Jalal Sadeghi: methodology.

**Acknowledgements.** The authors thank Urmia University, Iran, for financial support of this research under the grant agreement for a post-doc thesis.

**Financial support.** The authors acknowledge Urmia University, Iran, for financial support of this research.

**Competing interest.** The authors declare no competing interests.

**Data availability statement.** The data and code associated with this article can be accessed from Clay-D-23-00089R2 upon corresponding author's request.

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