



Slow-release urea fertilizer fabrication through the incorporation of raw bentonite and gelatin binder



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Abstract

Fertilization using slow-release fertilizers to prolong the availability of nutrients for plants and eliminate the diverse effects accompanied by conventional fertilization has become trendy. In this study, slow-release urea fertilizers were prepared through the recrystallization of urea with the addition of raw bentonite and using gelatin as a binder, to make use of the porous and layered structure of bentonite, these materials are inexpensive, biodegradable, and locally available. Various slow-release urea fertilizers were prepared with different portions of gelatin and bentonite to study their effect on the release of urea. Furthermore, the prepared fertilizers were ground for different periods to study the effect of mechanochemical activation on the pattern of urea release. These raw materials and the prepared fertilizers were characterized by FTIR, SEM, EDX, and XRD which all confirmed the incorporation of urea into the prepared fertilizers. Then they were tested for urea release, which showed that incorporating both bentonite and gelatin expands urea release time. The experiment results were then analyzed for kinetics. The results of this study indicated that the prepared fertilizers are biodegradable, eco-friendly, cost-effective, and can be used as slow-release fertilizers in sustainable agriculture.

Keywords: Fertilizers; Pollution; Slow release; Mechanochemical Activation

1. Introduction

With the global upsurge in population and rapid urbanization, come the problems of depletion of resources to feed these increasing numbers, the soil loss of fertility, and scarcity of agricultural land, with such exhaustion of resources the globe will soon collapse from hunger and poverty. These problems paved the route for the increase of fertilization, especially using urea ($\text{NH}_4(\text{CO})_2$) as the most common nitrogen fertilizer due to its high nitrogen content, hardly about 50%. For example, Egypt depends mainly on urea to fertilize most of its crops [1].

However, pollution is always connected with the excessive use of conventional urea fertilizers. Also, the majority of conventional fertilizers nutrients get lost before being used, only 30-50% of nitrogen from urea is recovered by plants and the rest is lost as nitrates (NO_3^-) in water or evaporated as nitrous oxide (N_2O) which cause air, soil, and water pollution [2]. The nutrient loss increases the demand for repetitive application of the same fertilizer through the plant's growth, increasing the economic loss for farmers and

countries. These problems have paved the route for creating a generation of fertilizers that prolonged the availability of nutrients for plants and reduce the loss of these fertilizers in leaching, evaporation, or else ways to decrease the pollution and increase the utility of nutrients by plants. Such generation includes slow-release fertilizers (SRFs), controlled-release fertilizers (CRFs), and using modern technologies such as nanotechnology in agriculture [3-5].

Slow release fertilizers (SRFs) are the easiest solution for the repetitive application of fertilizers, and the economic loss associated with it. However, all the available SRFs including urea-formaldehyde, isobutylidene-diurea, and sulfur or polymer-coated urea are based on synthetic chemical materials which have further complications such as burst release of nutrients when contact with water, accumulation of undegradable materials such as polymers or the manipulation of the soil ecosystem as acidity or salinity of the soil [6]

In this study, slow-release urea fertilizers (SRUFs)

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based on bentonite were fabricated with aim of using its layered porous structure to incorporate urea with gelatin as a binding material. These materials are biodegradable, readily available, and cost-effective. Utilizing these materials will decrease the cost of SRFs preparation and will increase the availability time of urea for plants, which will increase the nitrogen utilization efficiency (NUE) of urea. The technique used in the preparation is melting urea and then recrystallization after adding the bentonite and gelatin in different portions. The prepared slow-released urea fertilizers (SRUFs) were then subjected to mechanochemical grinding for further incorporation of urea into layers of bentonite, and then they were characterized and analyzed using various techniques after those SRUFs were tested for the urea release using a static release experiment.

In this manuscript urea, bentonite and gelatin were used as a slow release composite. In comparison with other formulae of slow release fertilizers, gelatin was used as a new binder as it plays an important role in retarding the solubility of the composite.

From an economic point of view, the materials used in the preparation of the proposed fertilizers are naturally available at a relatively low cost compared to the chemicals used for the preparation of other slow-release fertilizers. Furthermore, the preparation cost of the suggested fertilizers is considered low compared to the pollution problems and the effects produced by using traditional fertilizers.

In comparison with other formulae as urea-containing sodium alginate-g-poly(acrylic acid-co-acrylamide) superabsorbent-fertilizer hydrogel reinforced with carboxylated cellulose nanocrystals [7] and phosphate-coated fertilizer with poly(N-isopropyl acrylamide-co-acrylamide) [8]. These fertilizers have used synthetic polymeric undegradable materials, to hinder the solubility of fertilizers, which only focus on supplying chemical nutrients and neglect the biological fertility of the soil. During the current study we used urea, bentonite, and gelatin. These materials are all natural and benign

2. Experimental

2.1. Materials

Raw bentonite was collected from Moussa's eyes, Sinai, Egypt. Then it was ground to powder, screened, washed a couple of times, and then dried at 105 °C for 8 h before use. Gelatin pellets were purchased from a local source and were crashed before use. Urea was purchased from Sigma-Aldrich and was dried at 80 °C for 8 h before use.

2.2. Preparation of slow-release urea fertilizers (SRUFs)

The proposed method was performed according to (Hermida and Agustian, 2019) [9] with some modifications. 90 g of urea was melted at 130-135 °C

on a hot plate then 9.2-9.8 g of raw bentonite was added and mixed with the melted urea; the mixture was stirred for 5 min or until the full combination. 6 ml of distilled water was added to 0.2-0.8 g of gelatin and heated on a hot plate at 60 °C a viscous liquid was formed and added to the urea-bentonite mixture. The final mixture was stirred till the full combination. The SRUFs obtained were then dried for 8 h at 80 °C. Different composition of the material used to prepare various SRUFs is summarized in Table 1.

Table1. Composition of various SRUFs prepared

| Name | Urea (g) | Bentonite (g) | Gelatin binder (g) |
|-------|----------|---------------|--------------------|
| SRUF1 | 90 | 9.8 | 0.2 |
| SRUF2 | 90 | 9.6 | 0.4 |
| SRUF3 | 90 | 9.4 | 0.6 |
| SRUF4 | 90 | 9.2 | 0.8 |

Different batches of each SRUF were then subjected to the mechanochemical ground for different periods (0-30 min), for mechanochemical activation.

Table 2. Codes used for SRUFs samples subjected to grinding

| | Grinding time | Code |
|-------|---------------|---------|
| SRUF1 | 0 min | SRUF1-a |
| | 10 min | SRUF1-b |
| | 20 min | SRUF1-c |
| | 30min | SRUF1-d |
| SRUF2 | 0 min | SRUF2-a |
| | 10 min | SRUF2-b |
| | 20 min | SRUF2-c |
| | 30min | SRUF2-d |
| SRUF3 | 0 min | SRUF3-a |
| | 10 min | SRUF3-b |
| | 20 min | SRUF3-c |
| | 30min | SRUF3-d |
| SRUF4 | 0 min | SRUF4-a |
| | 10 min | SRUF4-b |
| | 20 min | SRUF4-c |
| | 30min | SRUF4-d |

2.3. Economical study

Urea fertilizer is the most used and fabricated solid fertilizer worldwide. During the commercial synthesis of urea involves the combination of ammonia and carbon dioxide at high pressure to form ammonium carbamate which is subsequently dehydrated by the application of heat, usually at 185-190 °C to form urea and water, this boiling water can be used to dissolve gelatin binder before addition to the composite. In urea fertilizer production operations, the final product is in either prilled or granular form. Production of either form from urea requires melting and recrystallization [14]. Knowing that the processing of fertilizer in this

study will not cost any additional costs for factories that already fabricate urea fertilizer.

The ton cost of commercially sold urea is about 740 US\$.

The cost of fertilizer per 1 ton is estimated in Table 3.

Table 3. The estimated cost of 1 ton of SRUFs

| Raw material | Price per 1 ton |
|-------------------|-----------------|
| Urea | 740 US\$ |
| Bentonite | 13 US\$ |
| Gelatin | 500 US\$ |
| SRUF4 as a sample | 671 US\$ |

Finally, we must point out that the relative cost and benefit of the proposed slow release fertilizer composite need more study in the field. But generally, it is well known that one of the main benefits of moving to a slow release fertilizer is that it lasts much longer than quick release fertilizer. If it cost US\$ 91.3 to fertilize one acre with quick fertilizer and it only last 4 weeks, that means it will cost US\$ 22.82 per week. While, if it cost US\$ 94.64 to fertilize one acre with slow-release fertilizer and it lasts about 9 weeks it will only cost about US\$ 10 per week.

2.4. Characterization

The prepared SRUFs were characterized by Fourier Transform Infrared (FTIR) spectra (FT/IR-4100typeA) to identify the organic function groups in the composition. Scanning Electron Microscopy (SEM) was done using (Scanning Electron Microscope model JEOL JSM 6510 lv) and images were used to identify the morphology of the samples. Energy Dispersive X-ray (EDX) was recorded by EDS Analysis for the SEM model Oxford X-Max 20) to confirm the elemental composition of SRUFs and X-Ray diffraction (XRD) was recorded using (Philips X'PERT-PRO diffract meter) to indicate the crystal structures of urea.

2.5. Static release experiment

This experiment was carried out according to

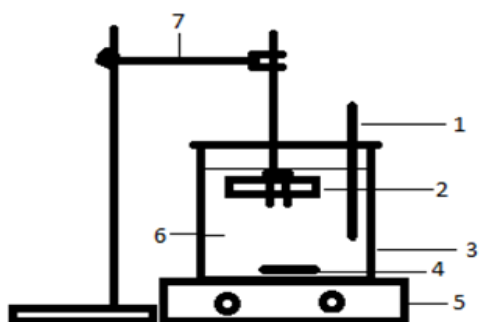


Fig. 1. Schematic representation of the used set up for determining the static release of urea in water (1: thermometer, 2: Wassermann tube, 3: glass beaker, 4: magnet, 5: hot plate magnetic stirrer, 6: distilled water 7: universal clamp).

procedures from (Higuchi, 1963) [11]. It was carried

out at room temperature, around 25-30 °C, to determine the release mechanism for urea and compare it to that of the prepared SRUFs. The experimental setup for determining the static release of urea in water is shown in Fig.1.

Generally, 3 g of urea or SRUF was put in a Wassermann tube with one end closed and the other end opened. Then this tube was immersed horizontally in a glass beaker containing 250 ml of distilled water to release urea. Then the stirrer was switched on and set at 100 rpm. After that, 0.5 ml of water was taken from two different points at the centre of the beaker every hour. The urea concentration in water samples was determined by spectrophotometry using UV-VIS spectrophotometer at 440 nm [12].

2.6. Urea release kinetics and mechanisms

Urea static release data were analyzed using Eq. (1) by (Peppas, 1985):[13]

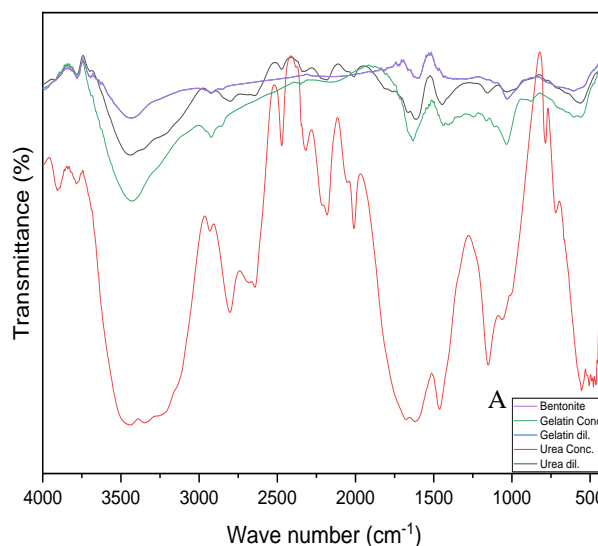
$$Q_t = Kt^n \quad \text{Eq. (1)}$$

Where Q_t is the fraction of urea released at time t , k is the kinetic constant, and n is the diffusion exponent which indicates the urea release mechanism.

3. Results and discussion

3.1. FT-IR spectra:

IR spectra of all the materials used in the preparation of SRUFs were induced in Fig.2.A and the IR spectra of the main four produced SRUFs were compared with that of urea in Fig.2. B.



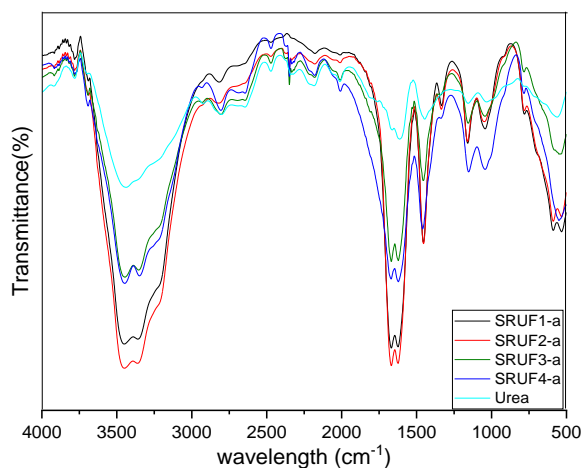


Fig.2 A. FTIR spectra of raw materials used in SRUFs preparation (urea, gelatin, and bentonite).

B. FTIR spectra of Urea, SRUF1-a, SRUF2-a, SRUF3-a, and SRUF4-a

IR spectra of SRUF ground with bentonite show

The spectra of urea showed bands at 3447 and 3362 cm^{-1} that were attributed to the stretching vibration of asymmetric and symmetric vibrations of the NH_2 group [2]. The bands assigned to amide I of gelatin lie in the region 3270-3370 cm^{-1} and overlap with that of urea. The incorporation of gelatin in the composite was confirmed by the band attributed to the proline side chain which appears at 1333 cm^{-1} [14].

The two strong bands at 1668 and 1633 cm^{-1} were attributed to ν (C=O) and δNH_2 of urea, respectively [2].

The existence of bentonite in the composite was confirmed by the existence of bands at 3690 cm^{-1} due to ν (OH) [15]. This band was shifted to a higher wavenumber due to the formation of hydrogen bonds with urea [16]. In addition to that, the band at 1044 cm^{-1} assigned to the vibration of Si-O supports the existence of bentonite in the composite [15]. The band at 1455 cm^{-1} was attributed to symmetric vibrations of the NH group.

From the above findings, it could be deduced that the three constituents (urea, bentonite, and gelatin) have no chemical interactions but only some physical ones.

As for the IR spectra of ground batches shown in Figs 3, 4, 5, and 6, it is observed that as we increase the grinding time the intensity of (C-N) vibrations at 720, 790, and 1155 cm^{-1} decreases as well as the intensity of (N-H) at 1456 cm^{-1} . The change in the intensity of these peaks can be explained by the intercalation of these molecules into the interlayer space of bentonite. [15].

From the above findings, it could be deduced that the three constituents (urea, bentonite, and

gelatin) have cooperated in forming composites and they were mechanochemically activated when the ground for different periods [17].

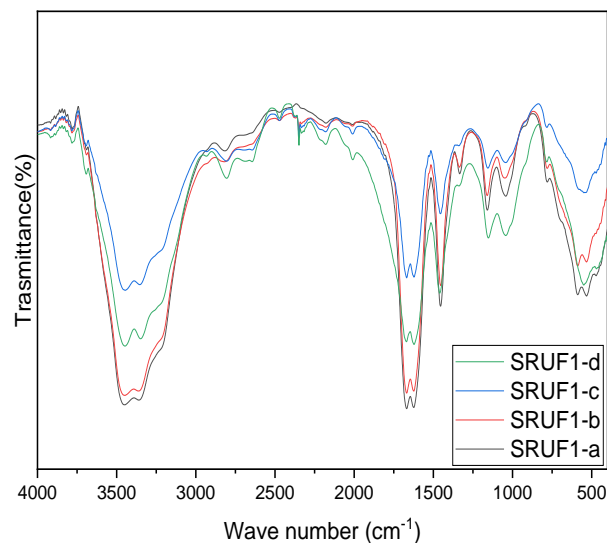


Fig.3. FTIR spectra of SRUF1-a, SRUF1-b, SRUF1-c, and SRUF1-d.

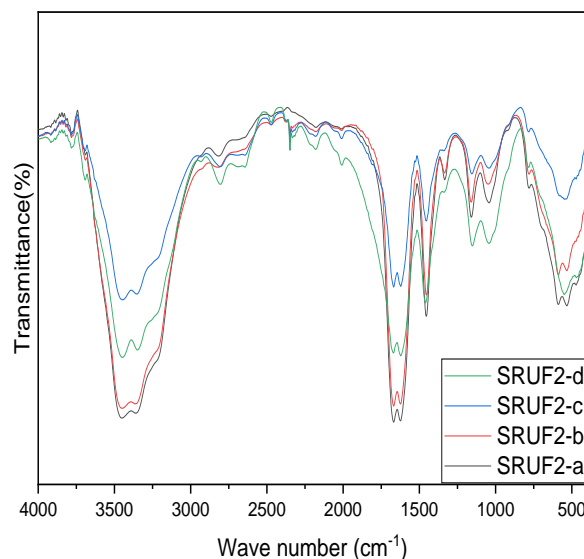


Fig.4. FTIR spectra of SRUF2-a, SRUF2-b, SRUF2-c, and SRUF2-d.

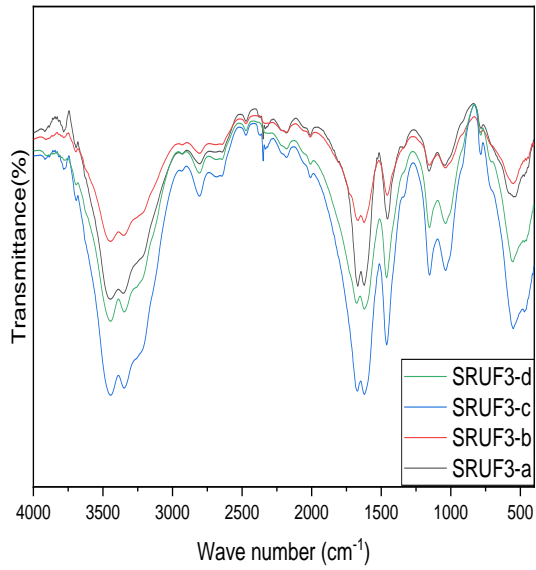


Fig. 5. FTIR spectra of SRUF3-a, SRUF3-b, SRUF3-c and SRUF3-d.

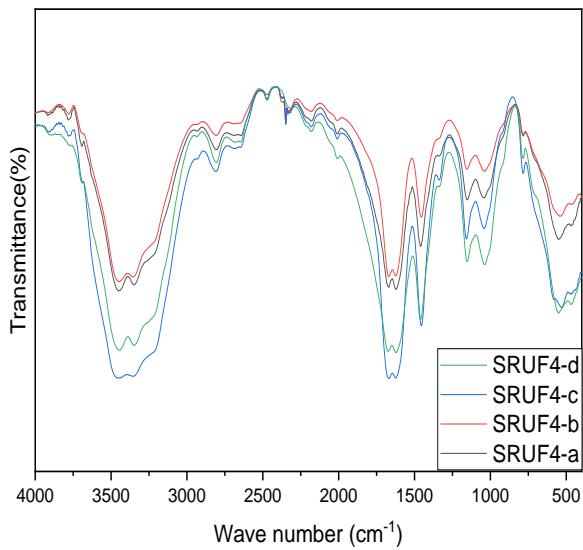
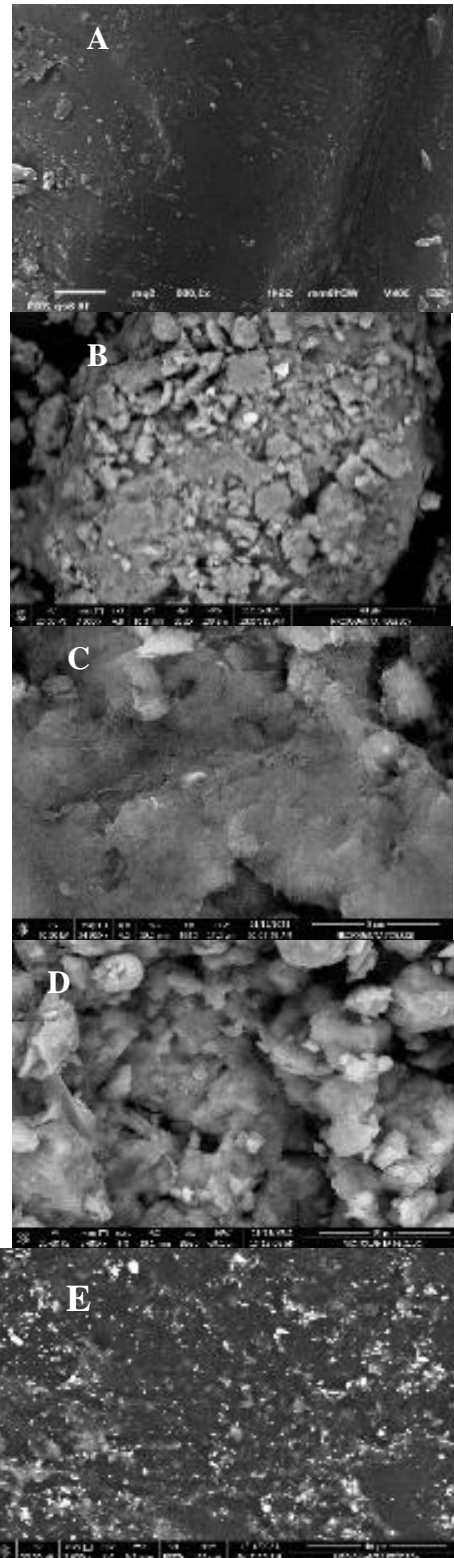


Fig. 6. FTIR spectra of SRUF4-a, SRUF4-b, SRUF4-c and SRUF4-d.

3.2. Morphology and chemical composition using (SEM) and (EDX)

Fig.7 illustrates the morphologies of unmodified urea and the prepared, SRUFs, composites. Fig.7.A shows a SEM image of the surface of conventional urea without any modifications at 5 μm resolution. This image can show that the surface of urea appeared as a smooth layer with some flakes or granules of traces and that can confirm that the urea molecules are well ordered and have a sediment rock appearance [2].



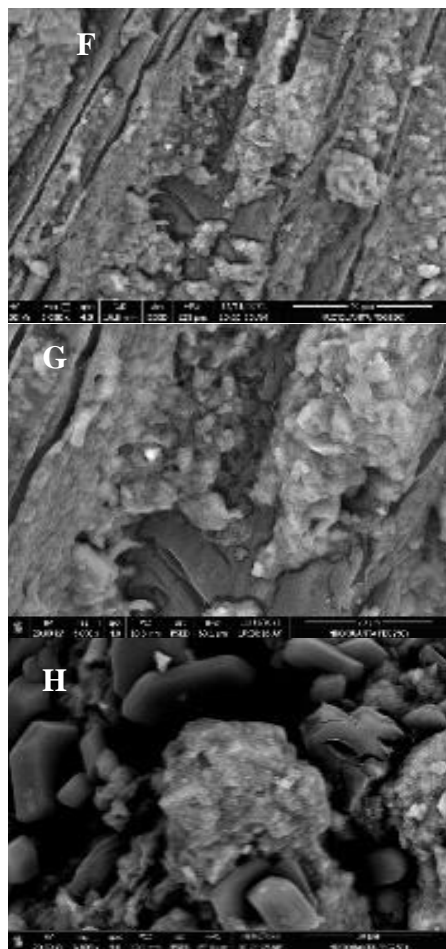


Fig.7. SEM images of (A) common urea, (B, C and D) raw bentonite, (E) Gelatin pellets, (F, G, H, and I) SRUF4-a at different magnifications.

The morphology of bentonite is shown in Fig.7.B, C, and D, in image B the structure of bentonite can be described as a rounded layered porous structure and that can be confirmed in images C and D where there are pseudo-globular structures between which there were some pores with the size range of (0.8-8 μm). As for gelatin pellets morphology it is shown in image E where there are some microcrystals and flacks that have a range size of (0.8-2.4 μm).

The morphology of the composites prepared by this technique was sampled by SEM images of SRUF4-a. They were characterized by a plate-like structure that was observed in Fig.7.F, G, H, and I, especially in images F and G, and that structure was not characteristic of any of the materials used in its preparation [17]. In image H there were some rod-like structures with a thickness range of (2-4 μm), as for image D, there were pseudo-globular crystals that appeared which were attributed to the recrystallized urea.

There were three main shades of colour in SEM images of fabricated SRUF which confirmed the hypothesis that urea and gelatin had been incorporated into the porous structure of bentonite.

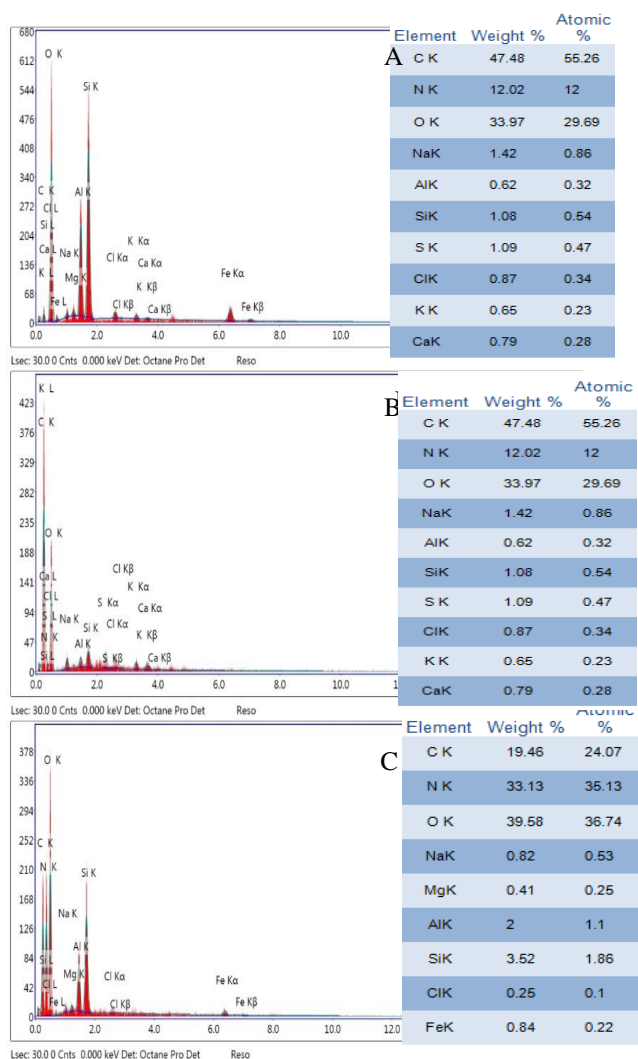


Fig.8. EDX elemental analysis of bentonite (A), gelatin (B), and SRUF4-A(C).

The elemental analysis of bentonite, gelatin, and SRUF4-A was provided in Fig.7. The elements are shown in Fig 7. A and B were also present in Fig.7.C; this can confirm the formation of a composite based on urea-bentonite incorporated with gelatin.

3.3. XRD and mechanochemical grinding

XRD of the raw material used and fabricated SRUFs were scanned in the range of 5-80 $^{\circ}$.

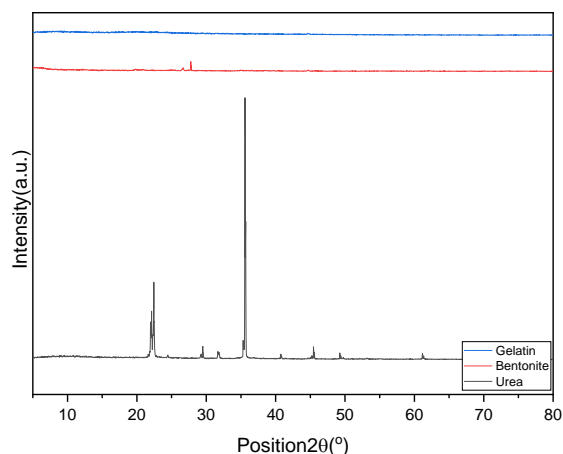


Fig.9. XRD pattern of urea, bentonite, and gelatin.

Urea has shown two main peaks at 22.5 and 35.6° corresponding to the planes (110) and (210). As for bentonite and powdered gelatin they were near the baseline with only minor peaks around 27°. To confirm the incorporation of urea with bentonite and gelatin the XRD of urea was compared to that of fabricated SRUFs without grinding as shown in Fig.10.

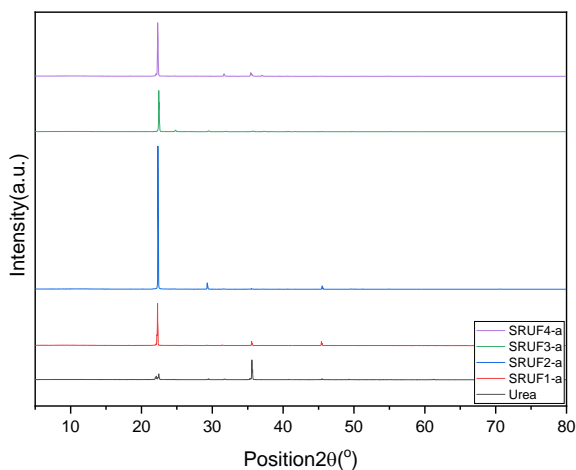
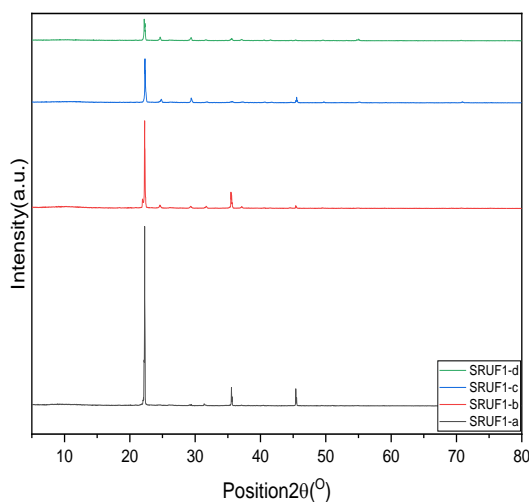


Fig. 10. XRD pattern of Urea, SRUF1-a, SRUF2-a, SRUF3-a, and SRUF4-a.

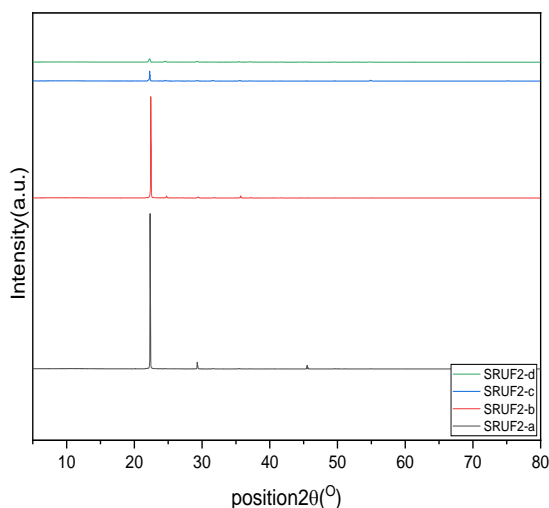
All samples show similar peaks at 22.5° with different higher intensities. However, urea without any modifications had shown a sharp peak at 35.6°, and a similar broad peak with a much lower intensity at 35.5° appeared in all prepared SRUFs, the change in intensity could be attributed to the adsorption of recrystallized urea between the planes and pores of bentonite [2].

To study the effect of mechanical activation by grinding, the ground samples were also scanned by XRD and compared to the ones that were not mechanically activated by grinding as shown in Fig.11

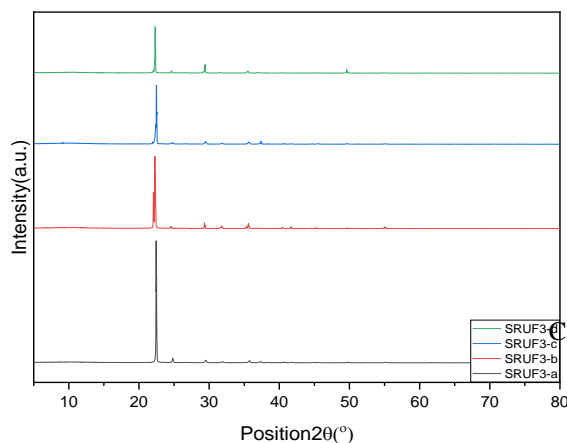
(A, B, C, and D). They all follow the same pattern where the sharp peaks of urea decrease in intensity and become border with the increase of grinding time, this can be taken as an indication of deformation of the crystal structure of urea and a decrease in the crystal size which directly affects the stability of fertilizer and releases time of urea.



A



B



C

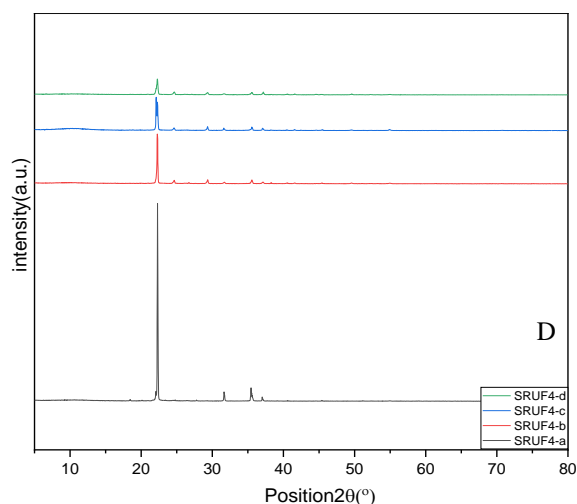


Fig.11. XRD pattern of (A)SRUFs1, (B)SRUFs2, (C)SRUFs3, and (D)SRUFs4.

3.4. Release rate of Urea and SRUFs

The static release experiment was done for each of the following samples: unmodified Urea and SRUFs of different proportions, to study the time of release and its relationship with the increase of gelatin binder Fig.12. Also, it was done on samples after mechanochemical activation with grinding to study the effect of grinding time on the release pattern and time of fertilizers Fig.13.

Table3. Urea concentrations in (mmol/L) were released by Urea, SRUF1-a, SRUF2-a, SRUF3-a, and SRUF4-a.

| Time (h) | Urea concentration (mmol/L) | | | | |
|----------|-----------------------------|---------------|--------------|--------------|--------------|
| | Urea | SRUF1-a | SRUF2-a | SRUF3-a | SRUF4-a |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 47.75 87 | 43.799 1 | 34.633 41 | 22.756 11 | 10.359 89 |
| 2 | 102.1 1324 | 50.058 63 | 39.196 58 | 26.657 44 | 14.201 96 |
| 3 | 133.1 735 | 59.686 96 | 44.124 79 | 30.753 99 | 17.567 28 |
| 4 | | 62.918 15 | 50.612 07 | 38.074 09 | 25.683 19 |
| 5 | | 66.831 93 | 55.242 31 | 40.935 93 | 21.679 93 |
| 6 | | 72.294 | 60.233 76 | 43.773 04 | 23.716 42 |
| 7 | | 91.802 15 | 67.937 99 | 50.508 16 | 26.149 15 |
| 8 | | 103.79 2 | 80.219 67 | 57.341 55 | 28.291 55 |
| 9 | | 114.68 176 | 83.657 53 | 72.324 71 | 32.871 82 |

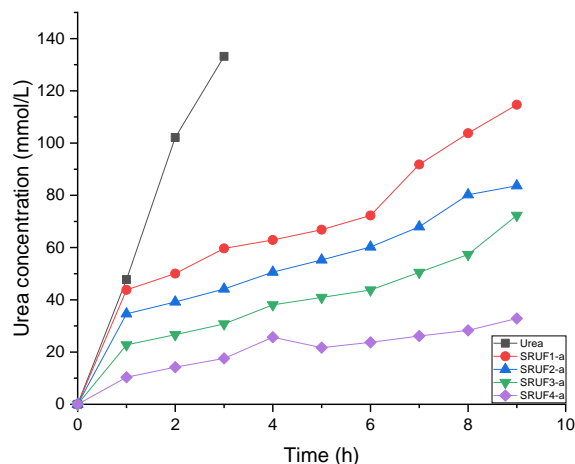


Fig.12. Release pattern of SRUF1-a, SRUF2-a, SRUF3-a, and SRUF4-a in comparison with urea.

The time-dependent results of urea in distilled water in (mmol/L) for each fertilizer indicated that common urea is readily soluble in water as expected and reaches a concentration of 133 mmol/L after 3 h, and by monitoring the release of synthesized fertilizers for 9 h it was indicated that they release urea continuously in this period by much lower dosage than conventional urea. This behaviour can be attributed to the physical connection between urea, bentonite, and gelatin as confirmed by FTIR results.

The static release results of other fertilizers such as organic polymer-urea (P-urea) and Bentonite-urea (B-urea), the complete release of P-urea was about 1h while the B-urea was hardly near 9 h [2]. While SRUFs continued releasing urea into the water for over 9 h. the release was faster at the beginning of the study and gradually decreased to almost constant values towards the end of the release experiment. We can exploit this behaviour in fertilizing plants that need more nitrogen in the growing stages and the stable supply of nutrients will help in accomplishing the later growth of crops.

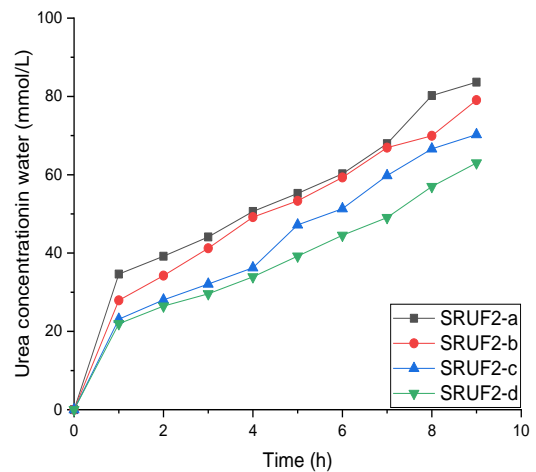
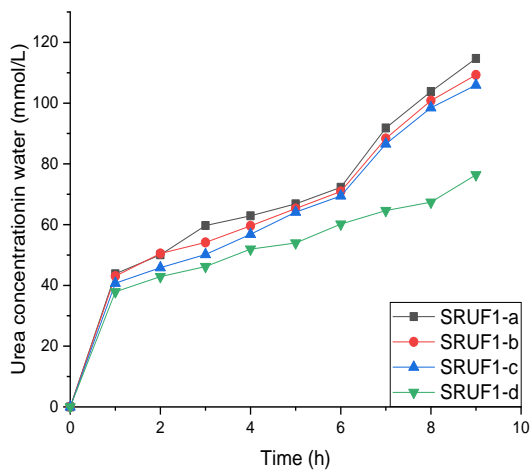
The hydrophobic (insolubility) nature of bentonite supports this suggestion. The dilation in the solubility, of urea modified with bentonite and gelatin, is suggested as follows: When melted urea, encounters bentonite a portion of urea runs into the intermolecular spaces of the bentonite structure which gives it some stability against water. Then, on the addition of the gelatin binder, it must coat the bentonite gaps filled with urea at the same time, the rest of the urea binds to the bentonite and coats with gelatin increasing the resistance of the prepared fertilizer to water solubility [18, 7].

Also, adding higher portions of gelatin binder slowed down the release rate of fertilizers as shown in Fig.12 and Table 3, this can be explained due to percolation theory as materials tend to produce pore

networks when dissolving into like materials; by adding more gelatin to the fabricated fertilizer it reduces the pore network generated by the dissolving fertilizers [19, 8].

Table 4 Urea concentrations in (mmol/L) were released by grinded samples SRUFs1, SRUFs2, SRUFs3 and SRUFs4

| Time (h) | Urea concentration (mmol/L) | | | | | | | | | | | |
|----------|-----------------------------|---------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | SRUF 1-b | SRUF 1-c | SRUF 1-d | SRUF 2-b | SRUF 2-c | SRUF 2-d | SRUF 3-b | SRUF 3-c | SRUF 3-d | SRUF 4-b | SRUF 4-c | SRUF 4-d |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 43.05 127 | 40.72 179 | 37.90 129 | 27.94 129 | 23.11 567 | 21.95 35 | 17.14 166 | 14.83 243 | 12.55 491 | 1.814 21 | 1.144 57 | 1.128 47 |
| 2 | 50.51 131 | 45.85 136 | 42.88 079 | 34.24 995 | 28.04 636 | 26.45 409 | 23.21 43 | 19.12 901 | 14.04 775 | 2.148 37 | 1.628 79 | 1.303 76 |
| 3 | 54.15 75 | 50.19 242 | 46.19 987 | 41.22 195 | 32.07 967 | 29.59 016 | 25.04 774 | 21.55 709 | 17.03 691 | 5.833 41 | 3.400 18 | 3.318 17 |
| 4 | 59.58 089 | 56.82 595 | 51.95 036 | 49.18 995 | 36.24 178 | 33.91 729 | 29.97 844 | 25.96 655 | 20.74 419 | 11.98 42 | 6.553 68 | 4.456 27 |
| 5 | 65.27 967 | 64.11 152 | 53.97 457 | 53.33 929 | 47.20 459 | 39.21 152 | 30.93 443 | 29.75 55 | 22.61 767 | 17.52 628 | 7.131 36 | 6.195 12 |
| 6 | 70.94 043 | 69.44 178 | 60.18 845 | 59.31 595 | 51.31 757 | 44.54 129 | 33.92 409 | 32.41 366 | 25.61 729 | 20.10 609 | 9.348 79 | 6.708 56 |
| 7 | 88.35 483 | 86.53 929 | 64.61 965 | 66.93 336 | 59.79 552 | 49.06 097 | 41.10 575 | 34.24 995 | 28.19 543 | 24.70 91 | 10.35 89 | 9.500 18 |
| 8 | 100.8 1529 | 98.47 352 | 67.38 172 | 69.94 244 | 66.61 995 | 56.98 083 | 42.15 769 | 37.71 752 | 31.42 795 | 25.87 442 | 12.80 059 | 12.07 816 |
| 9 | 109.2 773 | 105.9 4552 | 76.40 499 | 79.06 995 | 70.25 352 | 63.01 758 | 46.37 442 | 43.05 276 | 32.97 158 | 29.96 632 | 14.02 65 | 12.98 95 |



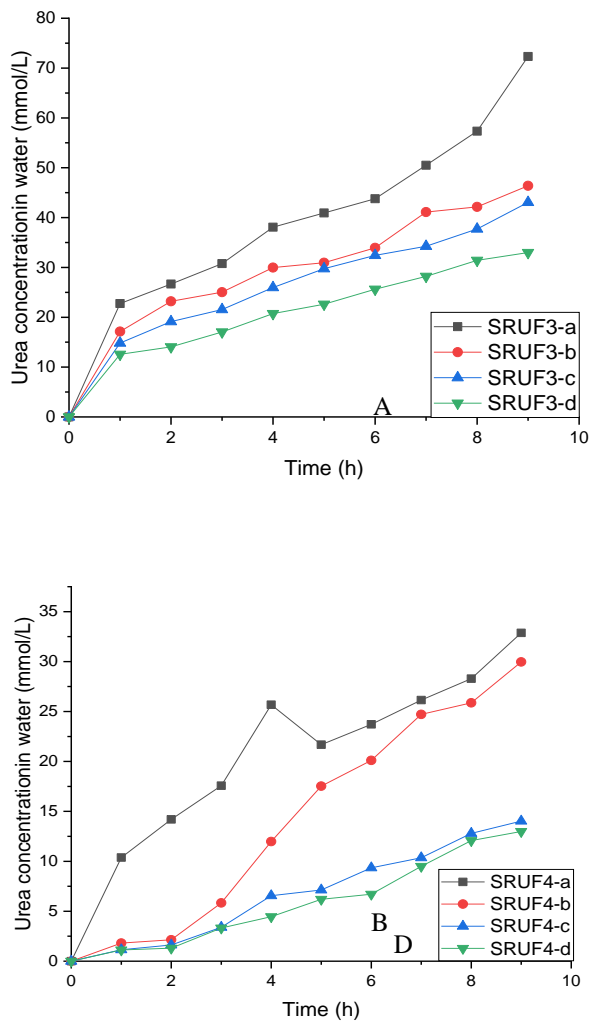


Fig.13. Release pattern of mechanochemical activated fertilizers SRUFs1 (A), SRUFs2 (B), SRUFs3 (C), and SRUFs4 (D).

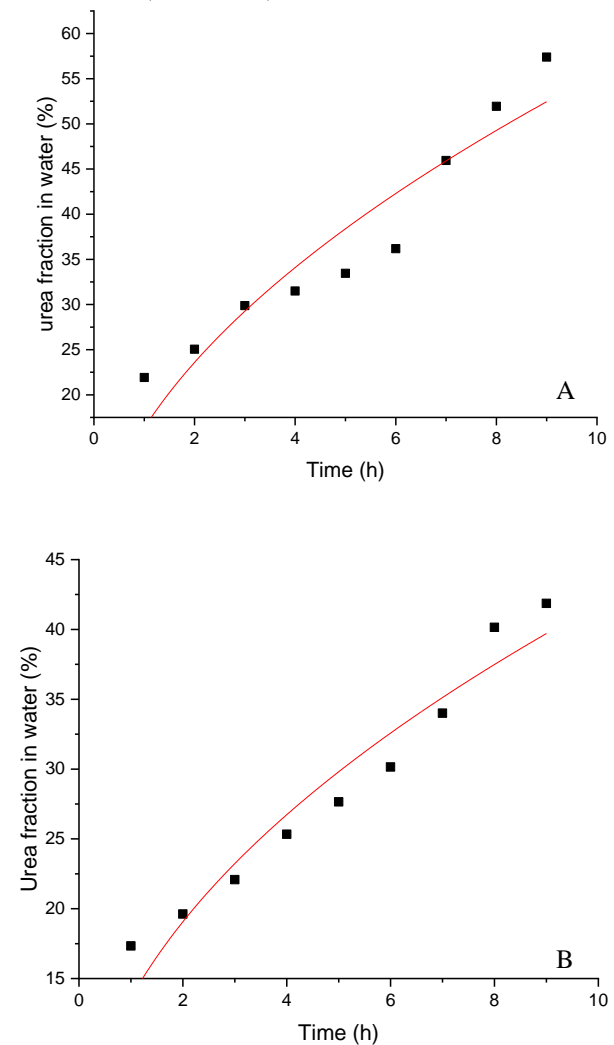
It is noticeable in Table 4 and Fig.13 that increasing the grinding time lowered the urea dosage released by the prepared SRUFs. This can be attributed to mechanochemical activation; which changes the physical and geometric properties of materials; fertilizers had become more hydrophobic or insoluble by increasing grinding time or increasing the mechanical activation [20-22].

3.5. Urea release statics

The Peppas equation was used for the analysis of static release data of SRUF1-a, SRUF2-a, SRUF3-a, and SRUF4-a. The kinetic constant (K) and diffusional coefficient (n) were calculated and used to identify the release mechanism of the prepared fertilizers [2]. These calculations were done by origin 2019 software, and they were shown in Fig.14.

For SRUF1-a, the kinetic constant (K) and diffusional coefficient (n) were 16.32568 and 0.53124 respectively, thus the release rate model of SRUF1-a was $Qt = 16.32568t^{0.53124}$, this can be used to explain the release mechanism as $R^2 = 0.87078$. According to (Hermida and Agustian, 2019) [9] when $0.45 < n < 1$, the urea release mechanism was known as non-fickian (anomalous) and that was the case for SRUF1-a.

While, for SRUF2-a, the kinetic constant (K) and diffusional coefficient (n) were 13.59131 and 0.48794, respectively, thus the release rate model of SRUF2-a was $Qt = 13.59131t^{0.48794}$, with $R^2 = 0.9219$. As for SRUF3-a, the kinetic constant (K) and diffusional coefficient (n) were 8.13524 and 0.61797, respectively, thus the release rate model of SRUF3-a was $Qt = 8.13524t^{0.61797}$, with $R^2 = 0.89382$. K and n constants were also calculated for SRUF4-a to be 5.31263 and 0.48669 respectively, thus the release rate model of SRUF4-a was $Qt = 5.31263t^{0.48669}$, with $R^2 = 0.9001$. According to the previous explanation, all SRUFs fabricated through this technique had shown a non-fickian (anomalous) urea release mechanism.



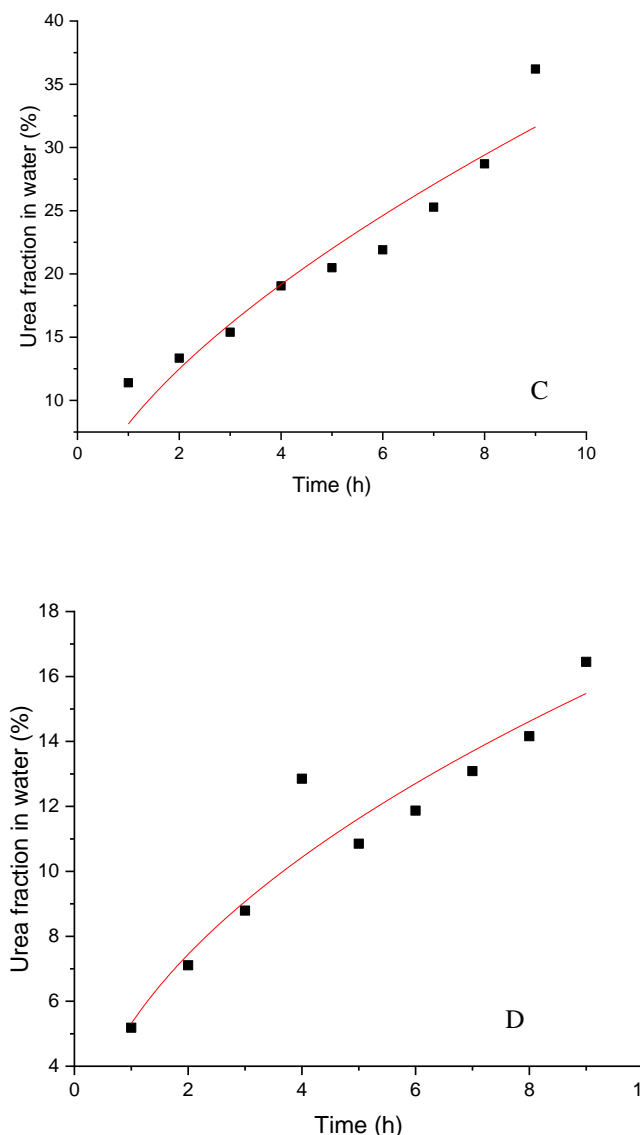


Fig.14. Urea release kinetics for (A) SRUF1-a, (B) SRUF2-a, (C) SRUF3-a, and (D) SRUF4-a.

4. Conclusion

various slow-release urea fertilizers (SRUFs) have been prepared through the incorporation of urea with natural and environmentally safe materials (bentonite and gelatin). They were tested for urea release using a static release experiment, which showed that prepared fertilizers have a slower urea release than common urea fertilizers. The release experiment showed that the release of urea also decreased as the gelatin portion increased in SRUFs. The kinetics of release calculations showed that the release mechanism of both fabricated fertilizers follows the non-fickian release (anomalous). The SRUFs were subjected to mechanochemical activation through grinding for different periods. The activated fertilizers had shown

that as the grinding time increases, the release of fertilizers decreases. Using mechanochemical activated urea, bentonite, and gelatin composite can present promising slow-release fertilizer prepared from natural, safe, and cheap materials that can reduce the repeated times of use of urea fertilizers and produced on large scale.

5. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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8. Arabic Abstract

تحضير سماد يوريا بطيئة التحرر من خلال خلطها بخام البنتونيت و الجلاتين كرابط

أصبح التسميد باستخدام الأسمدة بطيئة التحرر لإطالة مدة توافر العناصر الغذائية للنبات والتغلب على الآثار الجانبية للأسمدة العادية هو الاتجاه السائد. في هذه الدراسة، تم تحضير أسمدة يوريا بطيئة التحرر بطريقة إعادة تبلر اليوريا مع إضافة خام البنتونيت واستخدام الجيلاتين كمادة رابطة، وذلك بهدف الاستفادة من طبيعة البنتونيت المسامية والطبقية في الاحتفاظ بسماد اليوريا بداخله، وهذه المواد تعتبر غير مكلفة وقابلة للتحلل البيولوجي بالإضافة إلى توفرها محلياً. حيث تم تحضير العديد من أسمدة اليوريا بطيئة التحرر من خلال خلط نسب مختلفة من الجيلاتين والبنتونيت لليوريا بعد صهرها لدراسة تأثير كلا منهما على تحرر اليوريا. علاوة على ذلك، تم طحن الأسمدة المحضرة لفترات مختلفة لدراسة تأثير التنشيط الكيميائي الميكانيكي على نمط تحرر اليوريا. وقد تم توصيف كلا من المواد الخام والأسمدة بطيئة التحرر المحضرة باستخدام كلا من طيف الأشعة تحت الحمراء- FTIR والميكروسكوب الماسح الإلكتروني SEM و طيف الطاقة المتشتتة للأشعة السينية EDX و طيف حيود الأشعة السينية XRD والتي أكدت جميعاً وجود اليوريا في الأسمدة المحضرة. ثم دراسة هذه الأسمدة لمعرفة مدة تحرر اليوريا في الماء المقطر، وقد أظهرت النتائج أن وجود كل من البنتونيت والجيلاتين يساعد على إطالة مدة تحرر اليوريا. كما تم دراسة عملية التحرر للأسمدة محل الدراسة. وقد أشارت نتائج هذه الدراسة إلى أن الأسمدة المحضرة يمكن استخدامها كأسمدة بطيئة التحرر ويمكن الاستفادة منها عند تحضير كميات كبيرة منها في الزراعة المستدامة.