JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: B
CHEMICAL ENGINEERING

TURKISH CHEMICAL SOCIETY

Evaluation of the Nitrogen Release Properties of Chitosan-Bentonite Beads

Dilşad Dolunay ESLEK KOYUNCU* **Müjgan OKUR**, **Birsen TEMUÇİN**,
Selin Meliha ŞEN, **Esra ŞAHBAZ**, **Şule EROĞLU**, **Zeynep Sıla AKIN**,
Gonca TOPALOĞLU

Gazi University, Chemical Engineering, Ankara, 06570, Turkiye.

Abstract: In this study, chitosan-bentonite beads were prepared by using bentonite and chitosan as fertilizer carrier materials and urea as fertilizer components. The prepared samples were named BUC0.2, BUC0.4 and BUC0.6 based on the bentonite ratios of 0.2%, 0.4% and 0.6% (weight/volume). In the FT-IR and XRD results, it was seen that the characteristic peaks of the bentonite structure became evident in the BUC0.6 sample, while chitosan peaks were dominant in the BUC0.2 sample, as expected. As the amount of bentonite increased, the swelling ratio generally increased from 31.6% to 48.6. In the nitrogen release experiments, a very rapid nitrogen release occurred in the first hours of release. It was thought to be due to the rapid dissolution of urea in water. The cumulative release percentage showed a slightly decreasing trend in the days following the release experiment. When nitrogen release profiles of the samples containing different amounts of bentonite were compared, it was observed that the nitrogen release curves were quite close to each other due to the lower bentonite ratio. Release percentages of the samples containing different amounts of bentonite were obtained between 61.2-67.7. Observations supported the efficient degradation of fertilizers in the soil environment. As a result, it was evaluated that the prepared materials were promising as environmentally friendly nitrogen fertilizer.

Keywords: Bentonite, chitosan, urea, fertilizer, biodegradation

Submitted: February 10, 2024. **Accepted:** September 05, 2024.

Cite this: Eslek Koyuncu, D. D., Okur, M., Temuçin, B., Şen, S. M., Şahbaz, E., Eroğlu, Ş., Akın, Z. S., & Topaloğlu, G. (2024). Evaluation of the Nitrogen Release Properties of Chitosan-Bentonite Beads. *Journal of the Turkish Chemical Society, Section B: Chemical Engineering*, *7*(2), 185–194. https://doi.org/10.58692/jotcsb.1434727

***Corresponding author. E-mail:** deslek@gazi.edu.tr

1. INTRODUCTION

The increasing population increases the need for food in our country and in the world. However, land degradation occurs due to industrialization, urbanization, desertification, and floods, and as a result, arable land areas are decreasing day by day (Azeem et al., 2014). The necessity of increasing agricultural productivity to meet the increasing food demand necessitates the implementation of technological applications in the agricultural industry. Agricultural efficiency can be briefly defined as obtaining more product from less area. Some techniques are applied to increase agricultural efficiency. The most well-known of these methods include using high-quality seeds, leaving the soil fallow, ensuring that plant residues decompose in the soil without burning, and fertilizing (Azeem et al., 2014;Katip,2020). These techniques vary depending on land characteristics and soil type, and not every method can be applied to every land. Fertilization is one of the most practical and oldest known methods (Liu et al., 2019).

All natural or artificial substances containing the components plants need for their development are defined as fertilizers. The purpose of fertilization is not only to provide nutrients to the plant but also to maintain productivity by preserving the soil's physical, chemical, and biological properties. Fertilizers also prevent diseases and root pests and support the plant in taking nutrients from the soil. Fertilizers generally contain phosphate, nitrate, ammonium, and potassium salts, the components the soil needs most, and can be found in solid, liquid, and gas forms (Katip, 2020). Plants absorb approximately 90 different elements from air, water, and soil. About 20% of these elements are essential for the growth and development of the plant, while others contribute to growth and development. It is known that each element contributes to different functions of the plant. Figure 1 shows the classification of essential nutritional elements that must be present in the plant. Elements found in plants are classified as "macro" and "micro" nutrients according to their abundance. Of these elements, carbon, hydrogen, and oxygen, which constitute approximately 95% of the plant, can be taken from air and water in sufficient quantities, while other elements can be taken as anions, cations, or molecules. Apart from the elements given in Figure 1, Al, Co, Na, Si, and V elements must also be present in some plants (Bolat and Kara, 2017).

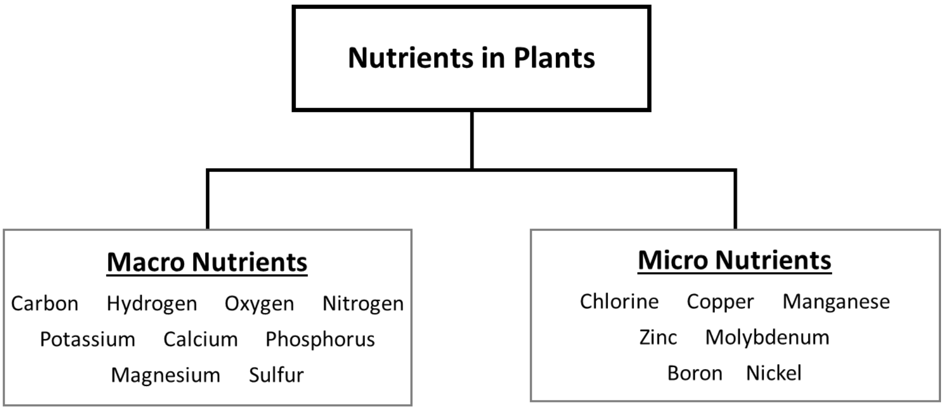

Figure 1: Classification of essential nutritional elements in plant.

Nitrogen (N), the primary nutrient required for plant growth, plays a role in the synthesis of protein and chlorophyll in the plant. Nitrogen, which is the basic building block of the plant cell wall, is also responsible for accelerating growth, stimulating roots, improving the quality of fruits, timely flowering, fruit formation, and seed formation (Bolat and Kara, 2017; Jayanudin et al., 2021). Nitrogen is transferred to the soil by the breakdown of organic matter in the soil over time, and in this way, plants can benefit from nitrogen. However, most of the world's soil is poor in nitrogen (Bolat and Kara, 2017).

The most crucial problem in increasing agricultural efficiency is the unsensible use of fertilizer. Although the use of fertilizer is an effective method to increase agricultural productivity, excessive use of fertilizer causes pollution of the environment and water resources. As a result of unsensible fertilization, the soil's salt content increases, the microorganisms' activity decreases, and as a result, product quality and productivity decrease. The long-term disadvantages of unsensible fertilization are significant environmental effects such as pollution of groundwater, increase in the amount of nitrate in water, erosion of the soil surface, increase in the amount of phosphate in streams and rivers, and the spread of nitrogen oxide into the atmosphere (Mushtaq et al., 2018).

With the development of controlled-release technology, efforts to reduce the adverse effects of traditional fertilization have gained importance in recent years. The controlled release provides a component's slow and long-term release into the desired environment. In recent years, this technology has shown promise in medicine, pharmacy, chemistry, agriculture, and veterinary. Controlled-release fertilizers are fertilizers prepared by coating plant nutrients with a slow-release ingredient. Synthetic organic polymers (acrylic resin, polysulfone, polyurethane, polyolefin, etc.), natural organic biopolymers (lignin, starch, cellulose, etc.), and inorganic components (silicas, phosphates, sulfur, etc.) can be used as coating materials (Mann et al., 2019; Tian et al., 2019). These fertilizers have attracted attention in recent years due to their advantages, such as reducing the accumulation of traditional fertilizer-derived components in the soil, reducing fertilizer consumption, and minimizing the harmful effects of chemical fertilizers on the ecosystem (Rahman et al., 2021). Controlled-release fertilizers provide slow release of nutrients into the soil, thus preventing nutrient leaching and nutrient loss. Since these fertilizers dissolve slowly in water, they also prevent groundwater contamination, especially in case of heavy rains and floods. In addition, their use on sloping, erosion-prone, and flow-prone lands provides significant benefits. Due to these advantages, controlled-release fertilizer production has accelerated in recent years. Studies have focused on fertilizer production with more environmentally friendly and lower-cost components.

The literature has determined that clays, hydroxyapatite materials, polymeric materials, and zeolites are used as support materials in controlled fertilizer release. Clays include double-layer hydroxides (Ureña-Amate et al., 2011; Berber and Hafez 2018; Bernardo et al., 2018), montmorillonite (Santos et al., 2015; França et al., 2018), kaolin (Liang et al., 2007; Mushtaq et al., 2018), bentonite (Daitx et al., 2019; Liu et al., 2019; Sarkar et al., 2021; Umar et al., 2022) are noteworthy. As polymeric materials, chitosan, which is a low-cost, non-toxic, natural, biodegradable biopolymer with swelling properties (Santos et al., 2015; França et al., 2018), cellulose (França et al., 2021), starch (Han et al., 2009; Perez and Francois, 2016; Giroto et al., 2020) are the most frequently used components.

There are a few studies in the literature using bentonite. Liu et al. (2019) prepared biochar fertilizers loaded with urea by hydrothermal method for controlled release using bentonite and polyvinyl alcohol. After 28 days of incubation in water, 61.3% was released, and after 98 days of incubation in soil, 54.6% was released. It has been evaluated that the water retention ability of the soil increases thanks to the water absorption properties of biochar and bentonite (Liu et al., 2019). In another study (Sarkar et al., 2021), diammonium phosphate fertilizer was prepared using starch, polyvinyl alcohol, and bentonite. Starch is an essential component used in encapsulated controlled-release fertilizers due to its adequate hydroxyl content, ease of access, biodegradability, and reactive compatibility with other molecules. It was stated that as the bentonite content increased, the relative crystallinity and density increased. It has also been stated that high bentonite content stabilizes the fertilizer structure, and encapsulation slows down N and P release. There are only a few studies in the literature on the preparation of fertilizer with chitosan and bentonite components. Haseena et al. (2016), bentonite-chitosan films were prepared and immersed in ammonium chloride solution, and their ability to retain NH_4^+-N was tested. As a result, it has been stated that these materials can be used as fertilizer (Haseena et al., 2016). Hamid et al. (2013) carried out water absorption, soil degradation, DSC, and FTIR analyses of urea fertilizers prepared using chitosan and bentonite. In the study, the effect of changing the chitosan ratio on the properties of the fertilizer by keeping the amount of urea constant was evaluated. As a result, it was stated that chitosan can be used in fertilizer as a biodegradable material (Hamid et al., 2013). Qudus et al. (2021) used vinasse and bentonite-chitosan matrix to prepare slow-release organomineral fertilizer. In the conducted study, vinasse was used as an NPK source. As a result, it was evaluated that the chitosan-bentonite matrix provides slow release effectively (Qudus et al., 2021). In another study (Piluharto et al., 2017), phosphate fertilizer was prepared with chitosan-bentonite beads, and low, medium, and high molecular weight types of chitosan were used. The release behavior of fertilizer materials was evaluated in different pH (3, 7, and 10) environments. It has been stated that chitosan polymer increases the water absorption capacity of fertilizer, and the most significant increase is observed with chitosan with high molecular weight. In addition, they have reported that the phosphate release decreased at decreasing pH values. There are no fertilizer studies in the literature that include chitosan, bentonite, and urea together. In this study, bentonite and chitosan were used as controlled-release fertilizer carrier materials and urea (nitrogen source) was used as the fertilizer component. Fertilizers were prepared in different bentonite contents (0.2%, 0.4% and 0.6% weight/volume). Prepared samples were characterized by FT-IR and XRD analyses. Swelling percentages of fertilizers, urea release behavior in water, and biodegradation in soil were determined.

2. EXPERIMENTAL

2.1. Preparation of the Chitosan-Bentonite Beads

In this study, bentonite and chitosan were used as controlled-release fertilizer carrier materials and urea (nitrogen source) was used as the fertilizer component. First, bentonite was added to 400 mL of distilled water at 0.2%, 0.4%, and 0.6% weight/volume ratios. Urea (Sigma-Aldrich, >99%, CAS No.: 57-13-6), a nitrogen source, was added in a ratio of 4% weight/volume and stirred at room temperature for 24 hours. Chitosan (medium molecular weight, Sigma-Aldrich, CAS No.: 9012-76-4) was added to the urea-bentonite mixture at a ratio of 2% weight/volume. Since the dissolution of chitosan requires acidic conditions, acetic acid (glacial, >99.5%, Isolab, CAS No : 64-19-7) was added to the mixture at 2% (volume/volume). The mixture was stirred at room temperature for 20 hours until chitosan dissolved. Using a Pasteur pipette, macro spheres were formed by dropping the prepared fertilizer mixture into a beaker containing 0.1 M sodium tripolyphosphate (ZAG, 94%). The materials prepared in this way were named BUC0.2, BUC0.4, and BUC0.6 based on the bentonite ratios of 0.2%, 0.4%, and 0.6%, respectively.

2.2. Characterization Studies

2.2.1. X-ray Diffraction (XRD)

X-ray diffraction patterns (XRD) were performed to determine the crystallite phase of the prepared spheres using a Rigaku Ultima-IV diffractometer (Cu Kα radiation with a wavelength of λ=0.15406 nm, at 40 kV and 30 mA) at a scanning rate of 2°/min.

2.2.2. Fourier Transform Infrared Spectrometry (FT-IR)

Fourier transform infrared spectrometry (FT-IR) analyses were carried out in a Jasco 4700 ATR/FT-IR spectrometer (in the medium infrared region of 4000-400 cm^{-1} with 4 cm^{-1} resolution, 128 scans) to evaluate chemical structures and structural bonds of the fertilizers.

2.2.3. Swelling Percentage

Exactly weighed spheres were soaked in distilled water for 48 hours until sufficiently swollen. It was then taken out, excess water removed, and the swollen spheres weighed to calculate swelling percentage (Eq.1).

$$Swelling\ \% = \frac{w_t - w_i}{w_i} \quad (1)$$

Here, w_t and w_i were the weight of the swollen sphere at time "t" and the initial dried sphere, respectively.

2.3. Nitrogen Release in Distilled Water

A certain amount of fertilizers was taken, put into the flask, and added 50 mL of pure water. The flasks were placed in a water bath at 30ºC. 5 mL samples were drawn at certain time intervals, and the same amount of purified water was added. Nitrogen analysis was performed for the samples taken to determine cumulative release. In the nitrogen release analysis, the reagent solutions were first prepared as follows.

0.01 g of $FeCl_3.4H_2O$ was placed into a 100 mL volumetric flask. 30 mL of pure water was added and mixed until dissolved. 10 mL of H_3PO_4 and 30 mL of H_2SO_4 were added, mixed thoroughly, and waited to cool (*Reagent 1*). 0.25 g diacetyl monoxime (DAM, Supelco, >99%) and 0.005 g thiosemicarbazide (TSC, Sigma-Aldrich, 99%) were weighed and placed in another volumetric flask. 50 mL of pure water was added and dissolved thoroughly (*Reagent 2*).

Then, 2 mL of *Reagent 1* and 1 mL of *Reagent 2* were added to 0.1 mL of the sample, shaken, and boiled for 5 minutes. It was cooled down to room temperature. Absorbance was measured at the wavelength of 526 nm in a UV spectrophotometer.

Each experiment was carried out in duplicate, and the cumulative nitrogen release percentage was calculated using the following equation (Eq.2) (Altunkaynak et al., 2022).

$$\text{Cumulative release }\% = \frac{(V_oC_n + \sum_{i-1}^{n-1} C_iV_i)}{W_o} * 100 \quad (2)$$

Here, V_o is the initial volume of the release solution in mL, V_i is the sample volume in mL, C_n and C_i are the nitrogen concentration (mg/L) at i and n sample times, and W_o is the weight of total fertilizer in the release medium.

2.4. Degradation in Soil

Approximately 50 mg of fertilizer sample was placed 3 cm below the soil surface in two different soil environments: Infertile garden soil (Soil1) and commercial soil (Soil2). The biodegradation behavior of fertilizers was observed by maintaining soil's moisture for 15 days.

3. RESULTS AND DISCUSSION

In this study, chitosan/bentonite beads containing urea were prepared and the urea-nitrogen release properties of these beads were examined. The FT-IR analysis results of the bentonite, chitosan, and prepared samples are given in Figure 2. In the FT-IR spectra of pure bentonite, the peaks at 445, 523, 790, and 1120 cm^{-1} were attributed to the presence of quartz in the bentonite structure (Chang et al., 2020; Atkovska et al., 2016). A high-intensity peak at 1009 cm^{-1} and a small peak that appeared at 1626 cm^{-1} were related to the amorphous SiO_2. A small shoulder at 619 cm^{-1} and a small peak at 672 cm^{-1} corresponded to the Al-O-Si-O bond (Zaitan et al., 2008; Atkovska et al., 2016). The presence of -OH^- groups was confirmed by the peaks at 912 (Al-Al-OH), 3410 (Si-OH) and 3608 cm^{-1} (Al-OH) (Chang et al., 2020; Atkovska et al., 2016). In addition, the peak at 1626 cm^{-1} was the indication of H-O-H bending and stretching vibrations of O-H bonds of water molecules in the silicate matrix (Elgarhy et al., 2022; Chang et al., 2020).

In the FTIR spectra of pure chitosan, the broad peak at 3200-3600 cm^{-1} indicated the stretching of -OH- groups. In this region, the -OH band and N-H stretching band overlapped. In the literature, the peaks at 3289 cm^{-1} and 3351 cm^{-1} were related to the N-H and O-H stretching and intramolecular hydrogen bonds. The peak at 2873 cm^{-1} belonged to the aliphatic C-H stretching. The peaks overlapped at 1593 and 1655 cm^{-1} and were assigned to the N-H bending of primary amine and C=O stretching of amide I, respectively. A small shoulder at 1327 cm^{-1} indicated the C-N stretching of amide III. At this region, bending vibrations of CH_2 (1417 cm^{-1}) and the symmetrical deformation peak of CH_3 (1374 cm^{-1}) were overlapped. The asymmetric stretching of C-O-C was observed at 1150 cm^{-1}. High-intensity peaks that overlapped at 1030 cm^{-1} and 1059 cm^{-1} were the indication of C-O stretching (Altunkaynak et al., 2022; Queiroz et al., 2015). In the BUC0.2, BUC0.4, and BUC0.6 samples, the characteristic peaks related to chitosan and bentonite structures were observed. It is seen in Figure 2-c that the characteristic peaks of the bentonite structure became evident in the BUC0.6 sample, which has a high bentonite ratio, while chitosan peaks were dominant in the BUC0.2 sample, as expected. It has been observed that the peaks belonging to SiO_2 and -CH in the chitosan/bentonite structure have shifted to high wavenumbers. In the studies conducted, it has been stated that the vibration bands of the interlayer Si–O– groups of bentonite in the chitosan/bentonite structure and the vibration bands of –CH in the –CH_2 and –CH_3 groups at 2888 cm^{-1} and 2942 cm^{-1}, have shifted to high wavenumbers, meaning that the reactive groups of chitosan interact with bentonite, respectively (Abdelkrim et al., 2020).

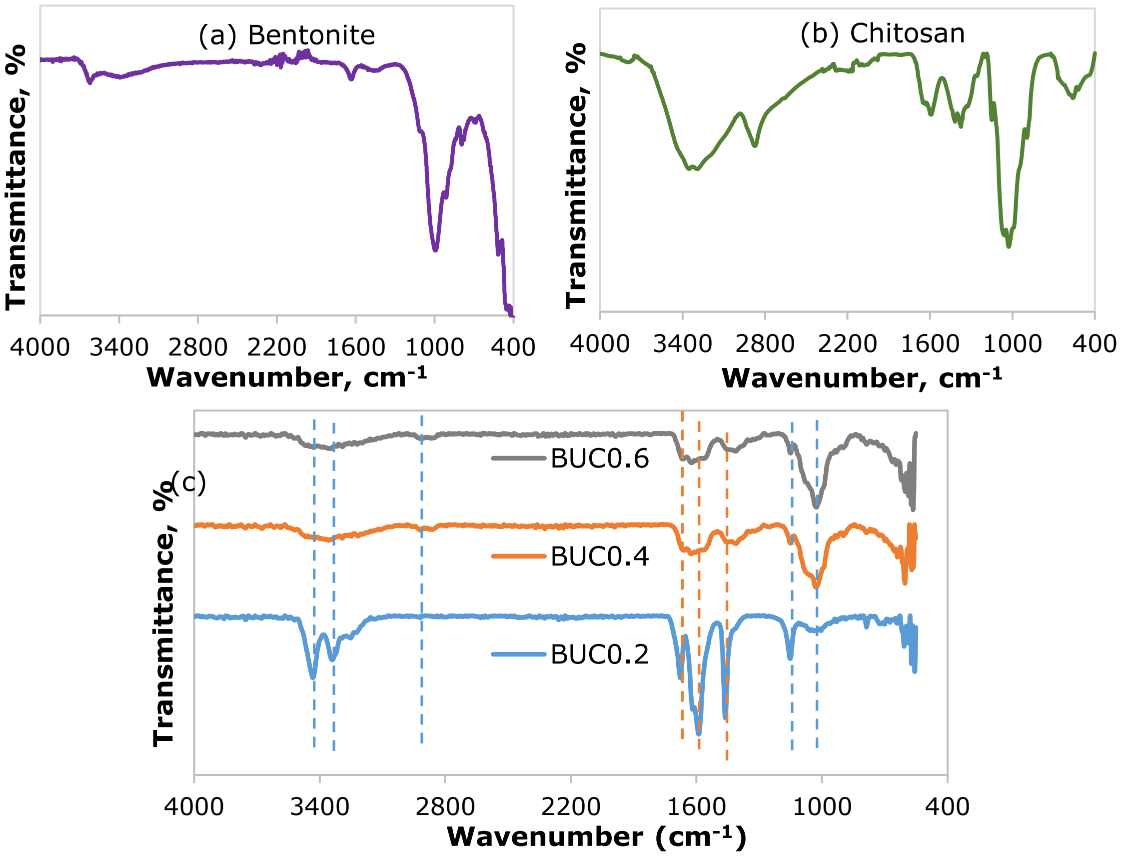

Figure 2: FT-IR spectra of (a) bentonite, (b) chitosan, and (c) prepared fertilizer samples.

The presence of bentonite and chitosan in the structure was also confirmed by the XRD patterns. XRD patterns of the prepared samples are given in Figure 3. It is seen that the materials exhibit an amorphous structure. In the XRD pattern of the BUC0.6 sample, which has a high bentonite ratio, the main peak of the bentonite structure became evident at 2θ= 6.9°, expectedly (Atkovska et al., 2016).

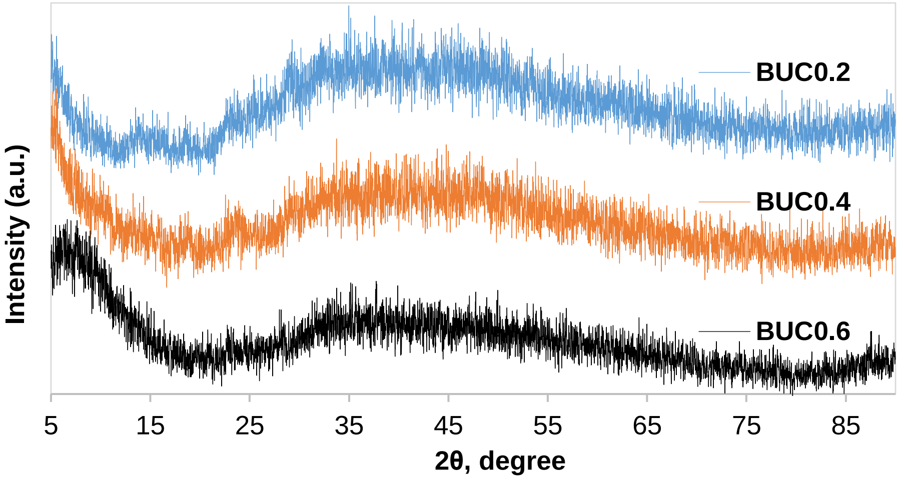

Figure 3: XRD patterns of the prepared fertilizer samples.

The degradation properties of fertilizer materials in soil are fundamental in terms of their environmental effects. For biodegradability analysis of the prepared fertilizers, this study used two different soil types: infertile garden soil (Soil1) and commercial soil (Soil2). Before the degradation tests, soil analyses were carried out for Soil1 and Soil2 samples, and the properties of soil types such as saturation in water, pH, conductivity, organic matter, phosphorus, potassium, calcium, and magnesium contents were compared (Table 1). It was observed that the water saturation, conductivity, organic matter, potassium, and calcium contents of the Soil1 sample were lower than those of Soil2.

Table 1: Properties of Soil1 and Soil2.

Property	Soil1	Soil2
Saturation with water (%)	78	177
Textural class	Clayey	Clayey
Electrical conductivity (dS/m)	0.92	2.82
Soil pH	7.06	6.66
Lime, $CaCO_3$ (%)	5.30	3.60
Organic matter (%)	6.03	25.26
Available P_2O_5 (kg/daa)	55.10	47.20
Available K_2O (kg/daa)	357.7	922.6
Available calcium (mg/kg)	5320	9060
Available magnesium (mg/kg)	849.5	969.0

In this study, the degradation properties of nitrogen-containing chitosan/bentonite samples were examined in soil. For this purpose, chitosan/bentonite was prepared as a film. The films were cut into 1 cm*1 cm dimensions and placed in the soil, and photographs were taken on the 15th day (Figure 4). It was observed that the films placed in Soil1 were slightly deformed after 15 days. The samples could not be weighed because they stuck to the soil. BUC0.6 was degraded in the soil. These observations visually show the deformation of films placed in soil. The films placed in Soil2 could not be observed at the end of the 15th day. This situation was thought to be related to the higher organic matter content of Soil2. Hamid et al. (2013) stated that chitosan films containing urea in soil appeared brittle and decreased in size on the 15th day (Hamid et al., 2013). Eddarai et al. (2022) stated that 21 days were sufficient for plasticized chitosan films to decompose in soil.

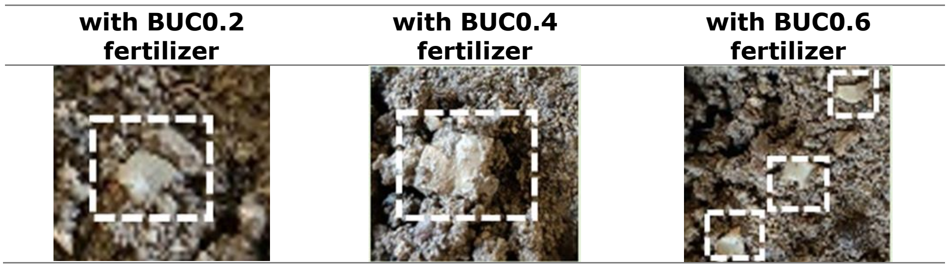
with BUC0.2 fertilizer
with BUC0.4 fertilizer
with BUC0.6 fertilizer

Figure 4: Degradation of the samples in soil 1.

The swelling percentages of BUC0.2-0.6 materials containing urea in an aqueous environment are calculated and given in Figure 5. The swelling percentage of the material containing 0.6 bentonite (BUC0.6) was found to be slightly higher than BUC0.2 and BUC0.4. As the bentonite ratio decreased, a decrease in swelling percentages was observed. The swelling percentages of materials containing 0.2 and 0.4 bentonite were found to be very close to each other. It was observed that the swelling rate was 31.6% with BUC0.2, 32.1% with BUC0.4, and 48.6% with BUC 0.6. The swelling test was followed for 120 hours, and it was observed that the swelling percentages fluctuated over time. This fluctuation may be due to nitrogen release during swelling experiments. Santos et al. (2015) stated that they observed a similar result in the release of phosphate from chitosan-montmorillonite microspheres. In their studies, fluctuations were observed in the swelling properties of chitosan-montmorillonite microspheres over time (Santos et al., 2015). In another study, Chitosan-based urea fertilizer was prepared by Hamid et al. (2013). The water absorption percentages of these fertilizers were found between 10 and 20%. Piluharto et al. (2017), investigated the phosphate-release properties of chitosan-based composite beads. The water absorption by chitosan and chitosan-bentonite composite beads was measured, and it was reported that water absorbance increases with chitosan molecular weight increase. Additionally, it was found that adding chitosan/bentonite composite beads resulted in lower water absorbance when compared to the chitosan addition.

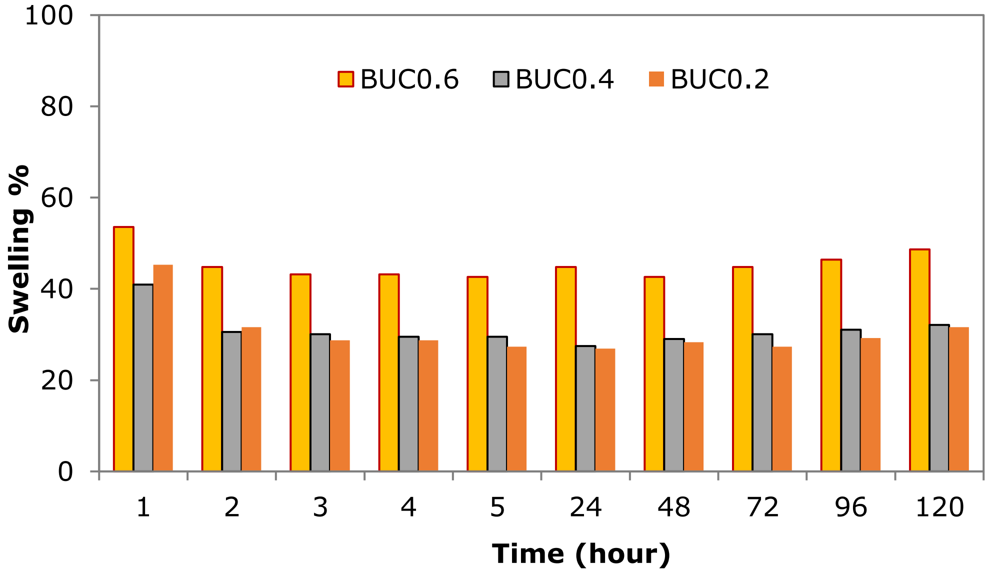

Figure 5: Swelling properties of the prepared fertilizer samples.

Figure 6 shows the nitrogen release profile from beads in water. Release experiments were followed for 32 days. It was observed that a very rapid nitrogen release occurred in the first hours of release in all three release profiles. This was thought to be due to the rapid dissolution of urea in water. It was observed that the cumulative release % showed a slightly decreasing trend in the following days of the release experiment. This meant that the amount of nitrogen in the release medium decreased over time. When nitrogen release profiles from spheres containing different amounts of bentonite were examined, it was observed that the nitrogen release curves were quite close to each other. The reason for the rapid release of nitrogen from the chitosan/bentonite structure at the beginning of the release experiments can be attributed to the sudden diffusion and dissolution of urea in the solution due to its weak hydrogen bonding to the outer surface of chitosan/bentonite (Arafa et al., 2022). Qudus et al. (2021) compared the nitrogen release properties of vinasse-based slow-release of organo-mineral fertilizer (SR-OMF) and vinasse organo-mineral fertilizer (OMF). SR-OMF fertilizer was prepared by mixing OMF with chitosan-bentonite matrix, and it was found that chitosan-bentonite matrix decrease the nitrogen release about 10 %.

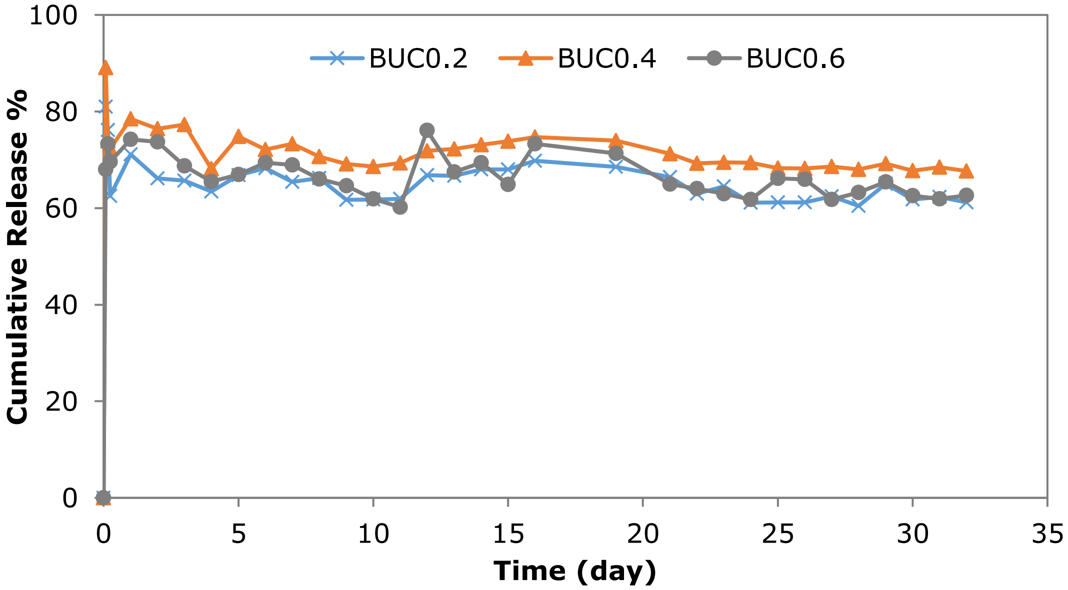

Figure 6: Cumulative nitrogen release % from the prepared fertilizer samples.

4. CONCLUSION

In this study, chitosan/bentonite beads containing urea were prepared, and the urea-nitrogen release properties of these beads in distilled water were examined. The FT-IR and XRD analyses confirmed the presence of bentonite and chitosan in the prepared fertilizer samples. It was seen that the characteristic peaks of the bentonite structure became evident in the BUC0.6 sample, which has a high bentonite ratio, while chitosan peaks were dominant in the BUC0.2 sample, as expected. It was observed that as the amount of bentonite increased, the swelling ratio generally increased. In the nitrogen release experiments, a very rapid nitrogen release occurred in the first hours of release for all three samples. This behavior was thought to be due to the rapid dissolution of urea in water. When nitrogen release profiles of the samples containing different amounts of bentonite were compared, it was observed that the nitrogen release curves were quite close to each other. The observations supported the degradation of fertilizers in soil environment. As a result, it was evaluated that the prepared materials were promising as nitrogen fertilizer.

5. CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

6. ACKNOWLEDGMENTS

“Gazi University Research Fund” (Grant No: FHD-2022-8277) and “Scientific and Technological Research Council of Turkey” (TUBITAK-2209/A, No: 1919B012221923) are gratefully acknowledged.

7. REFERENCES

Abdelkrim, S., Mokhtar, A., Djelad, A. Bennabi, F., Souna, A., Bengueddach, A., Sassi, M. (2020) Chitosan/Ag-Bentonite Nanocomposites: Preparation, Characterization, Swelling and Biological Properties. *Journal of Inorganic and Organometallic Polymers and Materials,* 30, 831–840. https://doi.org/10.1007/s10904-019-01219-8.

Altunkaynak, F., Okur, M., & Saracoglu, N. (2022). Controlled release of paroxetine from chitosan/montmorillonite composite films. *Journal of Drug Delivery Science and Technology, 68,* 103099. https://doi.org/10.1016/j.jddst.2022.103099

Arafa, E.G., Sabaa, M.W., Mohamed, R.R., Kamel, E.M., Elzanaty, A.M., Mahmoud, A.M., & Abdel-Gawad, O.F. (2022). Eco-friendly and biodegradable sodium alginate/quaternized chitosan hydrogel for controlled release of urea and its antimicrobial activity, *Carbohydrate Polymers, 291,* 119555. https://doi.org/10.1016/j.carbpol.2022.119555

Atkovska, K., Bliznakovska, B., Ruseska, G., Bogoevski, S., Boskovski, B., & Grozdanov, A. (2016). Adsorption of Fe(ii) and Zn(ii) ions from landfill leachate by natural bentonite, *Journal of Chemical Technology and Metallurgy, 51*(2), 215-222.

Azeem, B., KuShaari, K., Man, Z. B., Basit, A., & Thanh, T. H. (2014). Review on materials & methods to produce controlled release coated urea fertilizer. *Journal of Controlled Release, 181*, 11–21. https://doi.org/10.1016/j.jconrel.2014.02.020

Berber, M. R., & Hafez, I. H. (2018). Synthesis of a new nitrate-fertilizer form with a controlled release behavior via an incorporation technique into a clay material. *Bulletin of Environmental Contamination and Toxicology, 101,* 751–757. https://doi.org/10.1007/s00128-018-2454-x

Bernardo, M. P., Guimarães, G. G. F., Majaron, V. F., & Ribeiro, C. (2018). Controlled phosphate release from layered double hydroxide structures: Dynamics in soil and application as smart fertilizer. *ACS Sustainable Chemistry & Engineering,* 6, 5152–5161. https://doi.org/10.1021/acssuschemeng.7b04806

Bolat, İ., & Kara, Ö. (2017). Bitki besin elementleri: Kaynakları, işlevleri, eksik ve fazlalıkları. *Bartın Orman Fakültesi Dergisi, 19,* 218–228. https://doi.org/10.24011/barofd.251313

Chang, Y. S., Au, P. I., Mubarak, N. M., Khalid, M., Jagadish, P., Walvekar, R., & Abdullah, E. C. (2020). Adsorption of Cu(II) and Ni(II) ions from wastewater onto bentonite and bentonite/GO composite. *Environmental Science and Pollution Research, 27,* 33270–33296. https://doi.org/10.1007/s11356-020-09423-7

Daitx, T. S., Giovanela, M., Carli, L. N., & Mauler, R. S. (2019). Biodegradable polymer/clay systems for highly controlled release of NPK fertilizer. *Polymers Advanced Technologies, 30*, 631–639. https://doi.org/10.1002/pat.4499

Eddarai, E.M., El Mouzahim, M., Boussen, R., Bellaouchou, A., Guenbour, A., & Zarrouk, A. (2022). Chitosan-kaolinite clay composite as durable coating material for slow release NPK fertilizer. *International Journal of Biological Macromolecules, 195*, 424–432, 2022.

Elgarhy, A. H., Mahran, B. N. A., Liu, G., Salem, T. A., ElSayed, E. E., & Ibrahim, L. A. (2022). Comparative study for removal of phosphorus from aqueous solution by natural and activated bentonite. *Scientific Reports, 12,* 19433. https://doi.org/10.1038/s41598-022-23178-w

França, D., de Barros, J. R. S., & Faez, R. (2021). Spray-dried cellulose nanofibrils microparticles as a vehicle for enhanced efficiency fertilizers. *Cellulose, 28,* 1571–1585. https://doi.org/10.1007/s10570-020-03609-5

França, D., Medina, Â. F., Messa, L. L., Souza, C. F., & Faez, R. (2018). Chitosan spray - dried microcapsule and microsphere as fertilizer host for swellable - controlled release materials. *Carbohydrate Polymers, 196,* 47–55. https://doi.org/10.1016/j.carbpol.2018.05.014

Giroto, A. S., Garcia, R. H. S., Colnago, L. A., Klamczynski, A., Glenn, G. M., & Ribeiro, C. (2020). Role of urea and melamine as synergic co-plasticizers for starch composites for fertilizer application. *International Journal of Biological Macromolecules, 144*, 143–150. https://doi.org/10.1016/j.ijbiomac.2019.12.094

Hamid, N. N. A., Mohamad, N., Hing, L.Y., Dimin, M. F., Azam, M. A., Che-Hasan, M. H., Ahmad, M.K.S.M., & Shaaban, A. (2013). The effect of chitosan content to physical and degradation properties of biodegradable urea fertilizer. *Journal of Scientific and Innovative Research, 2* (5), 893-902.

Han, X., Chen, S., & Hu, X. (2009). Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. *Desalination 240*, 21–26. https://doi.org/10.1016/j.desal.2008.01.047

Haseena, P. V., Padmavathy, K. S., Krishnan, P. R., & Madhu, G. (2016). Adsorption of ammonium nitrogen from aqueous systems using chitosan-bentonite film composite. *Procedia Technology, 24,* 733–740. https://doi.org/10.1016/j.protcy.2016.05.203

Jayanudin, Lestari, R. S. D., Kustiningsih, I., Irawanto, D., Bahaudin, R., Wardana, R. L. A., Muhammad, F., Suyuti, M., & Luthfi, M. (2021). Preparation of chitosan microspheres as carrier material to controlled release of urea fertilizer. *South African Journal of Chemical Engineering, 38,* 70–77. https://doi.org/10.1016/j.sajce.2021.08.005

Katip, A. (2020). Kimyasal gübre tüketiminin değerlendirilmesi: Bursa ili örneği. *Uludağ Üniversitesi Mühendislik Fakültesi Dergisi, 25* (3) 1271–1286. https://doi.org/10.17482/uumfd.782633

Liang, R., Liu, M., & Wu, L. (2007). Controlled release NPK compound fertilizer with the function of water retention. *Reactive & Functional Polymers, 67*, 769–779. https://doi.org/10.1016/j.reactfunctpolym.2006.12.007

Liu, X., Liao, J., Song, H., Yang, Y., Guan, C., Zhang, Z. (2019). A biochar-based route for environmentally friendly controlled release of nitrogen: Urea-loaded biochar and bentonite composite. *Scientific Reports, 9,* 1–12. https://doi.org/10.1038/s41598-019-46065-3

Mann, M., Kruger, J. E., Andari, F., McErlean, J., Gascooke, J. R., Smith, J. A., Worthington, M. J. H., McKinley, C. C. C., Campbell, J. A., Lewis, D. A., Hasell, T., Perkins, M. V., & Chalker, J. M. (2019). Sulfur polymer composites as controlled-release fertilisers. *Organic & Biomolecular Chemistry, 17,* 1929–1936. https://doi.org/10.1039/c8ob02130a

Mushtaq, A., Jamil, N., Rizwan, S., Mandokhel, F., Riaz, M., Hornyak, G. L., Malghani, M. N., & Shahwani, M. N. (2018). Engineered silica nanoparticles and silica nanoparticles containing controlled release fertilizer for drought and saline areas. *IOP Conf. Series: Materials Science and Engineering, 414,* 012029. https://doi.org/10.1088/1757-899X/414/1/012029

Perez, J. J., & Francois, N. J. (2016). Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers. *Carbohydrate Polymers, 148,* 134-142. https://doi.org/10.1016/j.carbpol.2016.04.054

Piluharto, B., Suendo, V., Maulida, I., & Asnawati. (2017). Composite beads of chitosan/bentonite as a matrix for phosphate fertilizer controlled-release. *Journal of Chemical Technology and Metallurgy, 52,* 1027–1031.

Qudus, N., Kusumaningtyas, R. D., Syamrizal, Z., Hartanto, D., & Zakaria, Z. A. (2021). Vinasse-based slow-release organo-mineral fertilizer with chitosan-bentonite matrix. *Jurnal Bahan Alam Terbarukan, 10(1),* 1–8.

Queiroz, M. F., Melo, K. R. T., Sabry, D. A., Sassaki, G. L., Rocha, H. A. O. (2015). Does the Use of Chitosan Contribute to Oxalate Kidney Stone Formation?, *Marine Drugs, 13,* 141-158. https://doi.org/10.3390/md13010141

Rahman, M. H., Haque, K. M. S., Khan, M. Z. H. (2021). A review on application of controlled released fertilizers influencing the sustainable agricultural production: A cleaner production process. Environmental Technology & Innovation, 23, 101697. https://doi.org/10.1016/j.eti.2021.101697

Santos, B. R., Bacalhau, F. B., Pereira, T. D. S., Souza, C. F., & Faez, R. (2015). Chitosan-montmorillonite microspheres: A sustainable fertilizer delivery system. *Carbohydrate Polymers, 127,* 340–346. https://doi.org/10.1016/j.carbpol.2015.03.064

Sarkar, A., Biswas, D. R., Datta, S. C., Dwivedi, B. S., Bhattacharyya, R., Kumar, R., Bandyopadhyay, K. K., Saha, M., Chawla, G., Saha, J. K., & Patra, A. K. (2021). Preparation of novel biodegradable starch/poly(vinyl alcohol)/bentonite grafted polymeric films for fertilizer encapsulation. *Carbohydrate Polymers, 259,* 117679. https://doi.org/10.1016/j.carbpol.2021.117679

Tian, H., Liu, Z., Zhang, M., Guo, Y., Zheng, L., & Li, Y. C. (2019). Biobased polyurethane, epoxy resin, and polyolefin wax composite coating for controlled-release fertilizer. *ACS Applied Materials & Interfaces, 11*, 5380–5392. https://doi.org/10.1021/acsami.8b16030

Umar, W., Czinkota, I., Gulyás, M., Aziz, T., Hameed, M. K. (2022). Development and characterization of slow-release N and Zn fertilizer by coating urea with Zn fortified nano-bentonite and ZnO NPs using various binders. *Environmental Technology & Innovation, 26*, 102250. https://doi.org/10.1016/j.eti.2021.102250

Ureña-Amate, M. D., Boutarbouch, N. D., Socias-Viciana, M. M., & González-Pradas, E. (2011). Controlled release of nitrate from hydrotalcite modified formulations. *Applied Clay Science, 52,* 368–373. https://doi.org/10.1016/j.clay.2011.03.018

Zaitan, H., Bianchi, D., Achak, O., & Chafik, T. (2008). A comparative study of the adsorption and desorption of o-xylene onto bentonite clay and alumina, *Journal of Hazardous Materials, 153*, 852-859. https://doi.org/10.1016/j.jhazmat.2007.09.070