RESEARCH PAPER

Preparation of a Mesoporous Ceramic Adsorbent Based on Iranian Domestic Kaolin to Utilize as Slow-Release Urea Fertilizer Medium

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Abstract: *Overusing nitrogen fertilizer causes some serious problems for water resources, soil, and agriculture products. Researchers have been trying to develop effective means which may use less amount of fertilizers containing nitrogen. In this work, cost-effective ceramic granule adsorbent was prepared to be used as a fertilizer carrier of controlled release behavior. A mixture of 70 wt.% domestic kaolin and 30 wt.% gibbsite was used to produce the granules. By utilizing thermal analysis of raw granule, the calcination temperatures were obtained and the effect of various calcination temperatures of 500, 600, and 700 ˚C on the water adsorption was studied. The characteristics of granules were investigated by XRD, BET, FTIR, and SEM analyses. The results showed that by increasing the calcination temperature, the crystal structure of the granules was transformed into a dehydrated form and by calcination, at 600°C the specific surface area of granules increased from 7.50 to 53.45 m^2/g. The granules were soaked in a 500 g/L solution of urea, where they adsorbed about 10 wt.% urea. The dried urea-loaded granules were placed in water where the release of urea was measured by UV-vis spectrophotometry. Finally, different portions of urea-loaded granules were evaluated as fertilizer in the growing bed of corn plant where the height and the stem diameter of samples were compared with a control sample as well as a sample fertilized by urea directly. The results showed that by using the loaded granules, the urea consumption can be reduced by 50%.*

Keywords: *Ceramic adsorbent, Clay, Gibbsite, Nitrogen fertilizer, Calcination, Slow-Release fertilizer.*

1. INTRODUCTION

Nowadays fertilizers have an important role in agriculture and there are many agrochemical manufacturers which are producing different kinds of them. Fertilizers are added to soil to release essential nutrients for plant growth [1]. The utilization of chemical fertilizers especially nitrogen fertilizers has increased considerably in the world and it is expected to reach 130-150 million tons a year up to 2050 [2]. As an example, a corn plant which is a widely used agriculture product needs about 8 g urea for a period of growth, which is 360 kg in a hectare. However, about 40-70% of nitrogen of the applied normal fertilizers is lost to the environment which brings about not only enormous economic and resource losses but also hazardous environmental pollution [3]. Moreover, conventional nitrogen fertilizers cause nitrate accumulation in crops which is one of the key factors of diseases such as cancer [4].

One technique to effectively decrease the nutrient components losses and environmental pollution is utilizing slow-release fertilizers [3,5] which can be categorized in three groups including (1) slightly soluble materials, such as urea-formaldehyde; (2) materials for deep placement, such as urea super granules; as well as (3) coated fertilizers [6]. Although controlled released fertilizers are mostly made of polymers [3–8], eco-friendly polymer controlled-release fertilizer has been reported [9]. In polymer-coated fertilizers, the solubility of nitrogen is temperature-dependent which limits their application [10]. Furthermore, the fabrication of these fertilizers is expensive and requires advanced technology [11].

In recent decades, clay minerals have been introduced as cost-effective, eco-friendly, and simply accessible candidates for the application of primary material in controlled-release fertilizers [12–15]. Interestingly, urea can intercalate into the layers of clays easily and the releasing process is not temperature-dependent [16]. Moreover, great adsorption ability, as well as the possibility of modifying its surface, made clay minerals promising structure for the slow-release fertilizer medium application [17]. Hansen et al. [18] developed a new method to make phosphate fertilizer by using activated alumina obtained from the gibbsite precursor. The phosphorus granules have 1 to 20 wt.% PO_4^{3-} and a specific surface area of 120 m^2/g to 380 m^2/g. In novel research, Zhao et al. [19] synthesized a ceramic adsorbent using Kanuma and Akadama clay and studied the adsorption of ammonia by the ceramic adsorbent from wastewater. Due to high ammonium nitrogen content, cost-effective, and environmentally degradable starting material, the granules were expected to be reused as a nitrogen controlled released fertilizer. In another investigation, Golbashi et al. [11] prepared an eco-friendly slow-release fertilizer via montmorillonite and aqueous suspension technique. The FTIR and XRD analyses confirmed the intercalation of the urea into clay lamellae which resulted in such a good slow-release behavior; however, its precursors were pure and expensive. Zenoz kaolin is a domestic and relatively low-cost clay in Iran. As far as the authors know, the synthesis of fertilizers-loaded ceramics made from Zenoz kaolin has not been reported yet. In this work, a ceramic adsorbent, which has high adsorption capacity was developed utilizing domestic clay and gibbsite. The main purpose of this study was to produce a granular ceramic adsorbent, evaluate its physical properties, as well as investigate the feasibility of using the granular ceramic adsorbent as a nitrogen fertilizer for corn plants.

2. MATERIALS AND METHODS

Zenoz kaolin (SiO_2 63±1%, Al_2O_3 24±1%, Fe_2O_3 0.55±0.1%, TiO_2 0.04±0.01%, CaO 1.2±0.2%, MgO 0.55±0.06%, Na_2O 0.4±0.1%, K_2O 0.3±0.1%, and L.O.I of 10%) from Zenoz mines in Iran was used as the starting material

with the particle size and the specific surface area of 20 μm and 7.50 m^2/g, respectively. Gibbsite powder (Gahar Ceram Co, Iran) with the particle size and the specific surface area of 75 μm and 2 m^2/g was added to the kaolin. To determine the range of calcination temperatures, thermal analyses including differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (PerkinElmer Pyrifdiamond TG/DTA, rate 10 ˚C/min, N_2 atmosphere) were used for kaolin and gibbsite. Zenoz kaolin was mixed with gibbsite at the weight ratio of 7 to 3. Deionized water was then added to the mixture to produce a paste. Thereafter, the paste was granulated into spherical shapes with diameters of 5-8 mm (Fig. 1). In the next step, the granules were dried at 120˚C for 2 h and followed by calcination in the air atmosphere at the temperatures of 500, 600, and 700 °C for 2 h.

Fig. 1. *Calcined granules (70% kaolin, 30% gibbsite).*

Phase analysis was conducted by XRD (PW3710, Philips, Netherlands) using Cu Kα radiation (wavelength 0.154 nm). The microstructure of the granules was evaluated by SEM (VEGA\\ TESCAN-LMU, Czech Republic). Also, specific surface area, pore size, and pore size distribution were measured using BET analysis (Belsorp mini II, Japan).

Raw granules were calcined at 500, 600, and 700 ˚C for 2 h and after cooling they were soaked in water for 3 h. Then, their mass increase was measured to study the effect of calcination temperature on the water adsorption. Thereafter ,the granules were placed in a commercial urea solustion (70% nitrogen content) in the ambient temperature at a concentration of 500 g/L for 1 h to absorb the maximum amount of urea (averagely

10wt.%), the loaded granules were then dried. To investigate the urea release rate, a certain amount of the urea-loaded granules (1 g) was placed in 300 mL of distilled water and the solvent concentration was measured at regular intervals (60 minutes) for 420 minutes by a UV-vis spectrophotometer (Rayleigh, UV-1800). Besides, Fourier transform infrared spectroscopy (FTIR) (BRUKER, Tensor 27 FTIR, mid-IR) of granules was evaluated to track the adsorbed urea through recognition of functional groups. In the following, 40 and 80 g of loaded granules were added to 10 liters of the growing bed of corn plant. Moreover, both zero (control sample) and 8 g fertilizer were added to the growing bed to compare the results better. Finally, stem diameter and plant height were measured after two months by a digital caliper and a ruler, respectively to investigate the effect of the granules on corn growth.

3. RESULTS AND DISCUSSION

3.1. Thermal Analysis

The dehydroxylation of kaolin is a complex process because it can be affected by impurities as well as the crystalline quality of kaolinite mineral. The main step of dehydroxylation occurs between 450-650 °C due to the transition of the kaolinite to metakaolin which will result in about 10% weight loss in Zenoz kaolin (since the L.O.I of used kaolin is 10%). If the calcination continues until further temperatures (1100 °C) then crystalline structures like mullite and spinel will be obtained [20,21]. On the other hand, gibbsite contains more hydroxyl functional groups than kaolin so it would lose much more mass during calcination. The main step of gibbsite mass loss occurs at about 200-300 °C and then continues until 700 °C with about a total of 35% weight loss to produce a dehydrated structure with a high surface area. According to the thermal analysis of the raw granule (Fig. 2), about 9 wt.% mass loss occurred at about 200-300 °C due to removing of some pores and surfaces OH⁻ groups of gibbsite. Therefore, the weight loss trend is continued to 700 °C with roughly 18 wt.% mass loss, and the dehydroxylation process has finished. It is worth not-

ing that just about 7% of this mass reduction is because of kaolin while it made 70% of the granule content; hence, gibbsite plays a crucial role in mass loss (about 11%) due to dehydroxylation and enhances the surface area significantly.Besides, the reactions would continue in further temperatures to obtain a high crystalline phase of mullite; however, there was no need to proceed with the process to that point. The results of these analyses were also in good agreement with other research studies [22,23]. The calcination temperatures for granules were therefore chosen as 500, 600, and 700 °C since the most mass loss has occurred in this range of temperatures.
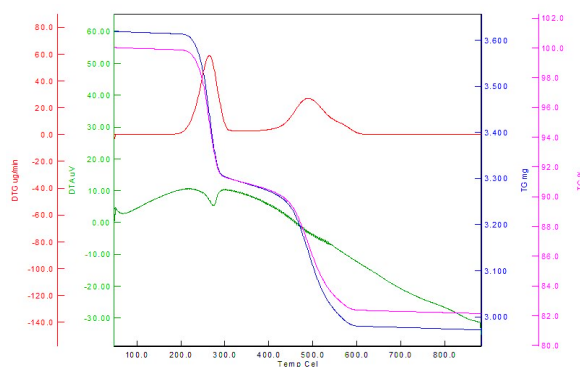

Fig. 2. Thermal analysis of raw granule (70% kaolin-30% gibbsite).

3.2. Phase Analysis

The XRD patterns of the green (before heat treatment) and calcined granules containing 30 wt.% gibbsite are shown in Fig.s 3a and b, respectively. Kaolinite, quartz, and gibbsite are present in the raw granule as their reflections are marked in Fig. 3a. Quartz is a natural impurity in kaolin and gibbsite. By the calcination of granules at the mentioned temperatures the peak intensity of kaolinite and gibbsite phases have diminished significantly such that all of them except quartz have completely disappeared which is in agreement with the results of other researchers [22, 24–27]. This is due to the dehydroxylation of kaolinite and gibbsite which have been transformed into the metakaolin and transition phase of alumina, respectively. Indeed, the crystalline structures of kaolinite and gibbsite have collapsed by heat treatment.
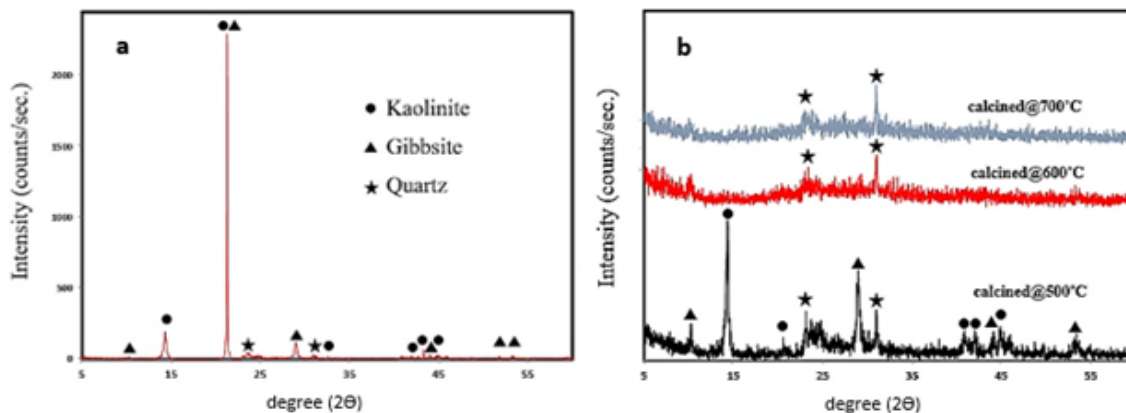
Fig. 3. XRD pattern of (a) raw granules, (b) calcined granules at 500, 600, and 700˚C

3.3. Microstructural Analysis

A flake-like microstructure can be seen in Fig. 4a. As kaolin is the major composition (70 wt.%) of the green mixture, this appearance can be attributed to the layered structure of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) which is the main constituent mineral of kaolin. According to the SEM micrographs (Fig.s 4b-d), the calcined samples have demonstrated more porous structures than the green mixture, as the destruction of the raw materials, structures have occurred by losing the hydroxyl groups during heat treatment at 500 to 700 °C which has consequently caused the formation of the metakaolin and activated alumina.

Also, SEM micrographs depict that the urea adsorbed granules are less porous which is because of the urea adsorption (Fig. 4e). As it is demonstrated by the EDS analysis, adsorbed urea is homogeneously dispersed in the volume of the granules (Figs. 4f and g). In this Fig., green points indicate carbon and red points indicate nitrogen atoms which are correlated to the presence of urea molecules ($(NH_2)_2C=O$).
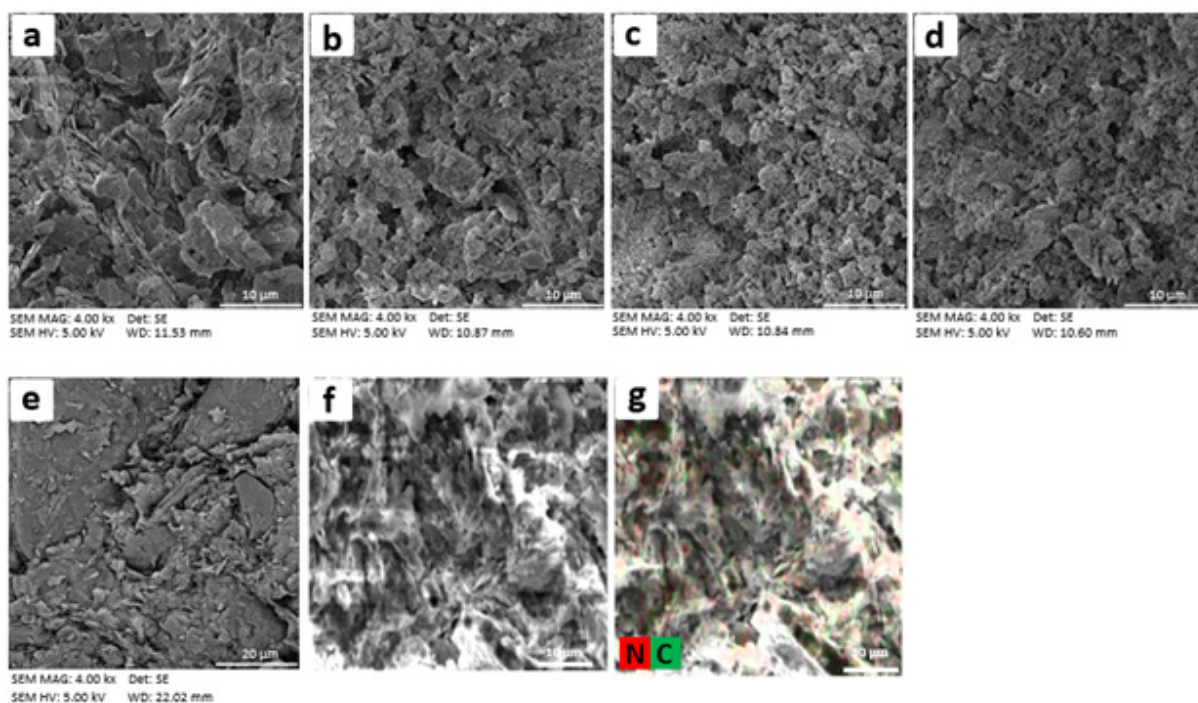

Fig. 4. SEM micrograph of (a) raw granule, (b) calcined granule at 500˚C, (c) 600˚C, (d) 700˚C, and (e) calcined granule at 600˚C after absorption of urea. (f) granule before urea absorption, and (g) its MAP after urea absorption.

3.4. The Effect of Calcination Temperature on Water Adsorption

As it is illustrated in Fig. 4, by increasing the calcination temperature, water adsorption has also increased slightly. However, the water uptake of granules calcined at 700 °C is grown just 1% in comparison with the calcined sample at 600 °C which is not so tangible. In contrast, the water uptake of the granules which calcined at 600 °C is grown 4% in comparison with 500 °C. The temperature of 600 °C was therefore chosen as the optimum temperature. On the other hand, granules calcined at 500 °C did not possess sufficient mechanical strength.
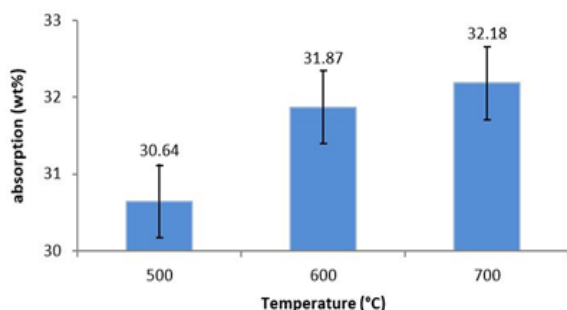

Fig. 5. The effect of temperature on water absorption of granules (70% kaolin, 30% gibbsite).

3.5. BET analysis of the calcined granules

The isotherm adsorption and desorption curves of BET analysis of the sample have formed a hysteresis (Fig. 6a) similar to the curve type IV according to the IUPAC classification [28]. Therefore, the size of pores was in the meso range and the obtained granule is classified as a mesoporous adsorbent.

The specific surface area, the volume of pores, and the average of pores diameter of the samples measured by the BET method were 53.45 , 0.14 , and 10.73 nm, respectively (Fig. 6b).

Compared to the specific surface area of green powder of granules (7.50 m^2/g for kaolin and 2 m^2/g for gibbsite), heat treatment has increased the specific surface area over 7 times. In similar researches, Hansen et al. [18] reported the specific surface area of 120-380 m^2/g by utilizing pure gibbsite. Zhao et al. [19] reported the specific surface area of 33.59 m^2/g

by the application of a Japanese domestic clay. It is worthy to note that Japanese domestic clay contained about 14% more Al_2O_3 content than Iranian clay (Zenoz). So it must have more kaolinite mineral which is responsible for obtaining a high specific surface area substance due to calcination. As a result, calcined granules in this study had a significantly higher specific surface area than the calcined Japanese domestic clay owing to the existence of gibbsite. In other words, the utilization of gibbsite positively influenced the characteristics of the granules.
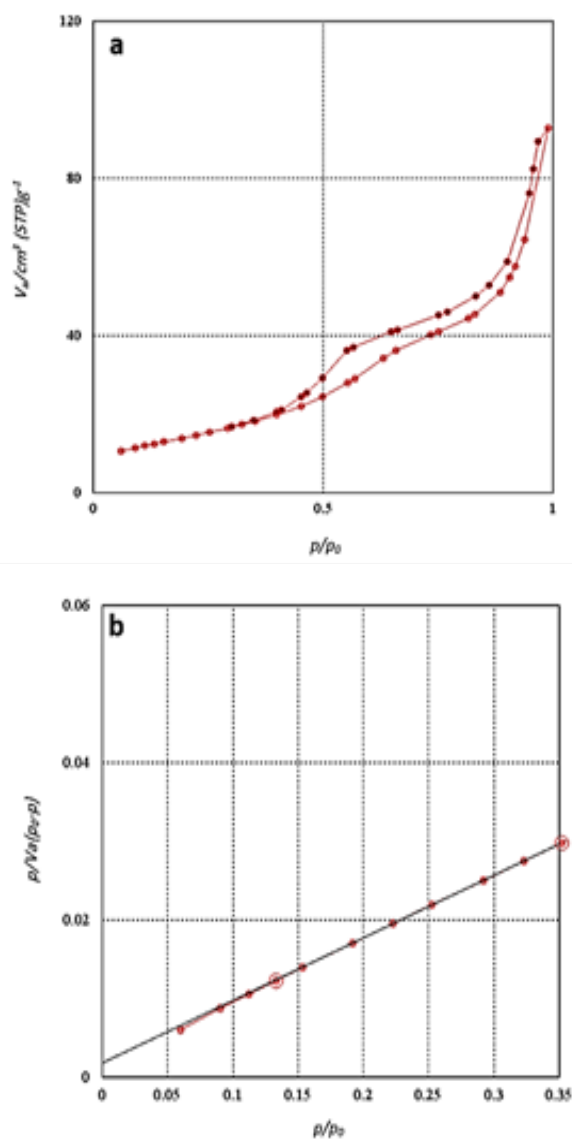

Fig. 6. (a) Absorption and desorption isotherm of calcined granule at 600˚C and (b) BET diagram of calcined granule at 600˚C.

3.6. Adsorption and Desorption of Urea

After calcination, the granules were put in the urea solution to adsorb the maximum amount of urea and FTIR analysis was used to reveal the presence of urea in granules after drying. According to Fig. 7, the presence of peaks at about 471, 804, and 1065 cm^{-1} are related to stretching vibrations of Si-Si, transitional vibration of Si-O-Al, and vibration of Al-O bonds, respectively. Also, the appeared peaks at 1463, 1676, as well as 3354 cm^{-1} can be attributed to the stretching mode of N-H and C=O groups of urea, as well as the interaction of hydrogen atoms of urea with the surface of kaolinite through the NH group [11, 29] which suggest the presence of urea in the calcined granules. Besides, there is a peak at 3454cm^{-1} which is the result of the vibration of hydroxyl groups. The adsorption phenomenon in calcined granule is a physio-chemical process by which the presented ions in water are adsorbed on the surface of granules with an ion exchange process [30]. Another part of the adsorption corresponds to the electrostatic attraction of specific surface areas which happens after removing hydroxyl groups by the remaining acidic and basic active sites [31]. Indeed, the molecule of urea ($(NH_2)_2C=O$) contains amine functional groups that are naturally basic [32], so by increasing the acidic sites in granules the urea adsorption tendency will be enhanced.
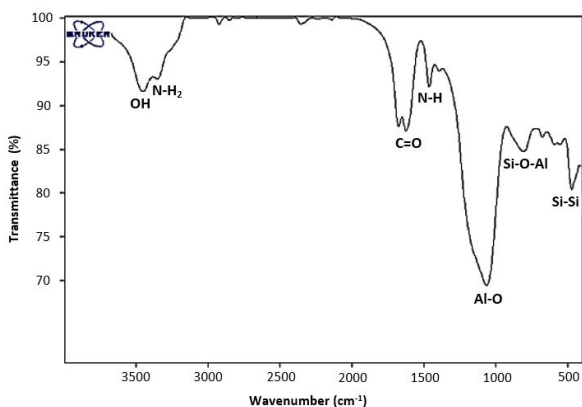
As time passed, the concentration of urea in water increased. Since the mechanism of desorption of urea in water is a concentration gradient, the rate of desorption decreases with time. The release rate of urea from granules and the solution rate of free urea in water are demonstrated in Fig.s 8a and b, respectively. The release rate was faster in the first 100 minutes and then decreased gradually. According to Fig. 8a, the release rate of urea decreased with a constant rate due to a decreasing concentration gradient. It should be considered that the dissolution experiment was performed in a harsh condition because the granules immersed in water completely, while in the real condition of growing bed it is not like that. So it seems the release rate would be much slower in the real situation. Based on Fig. 8b, urea fertilizer was completely solved in an aquatic environment in 25 minutes and after that with passing time, urea concentration in water remained constant. The urea release rate from the granules is slower in comparison with conventional urea fertilizer and gradually provided necessary nutrients for the plant.
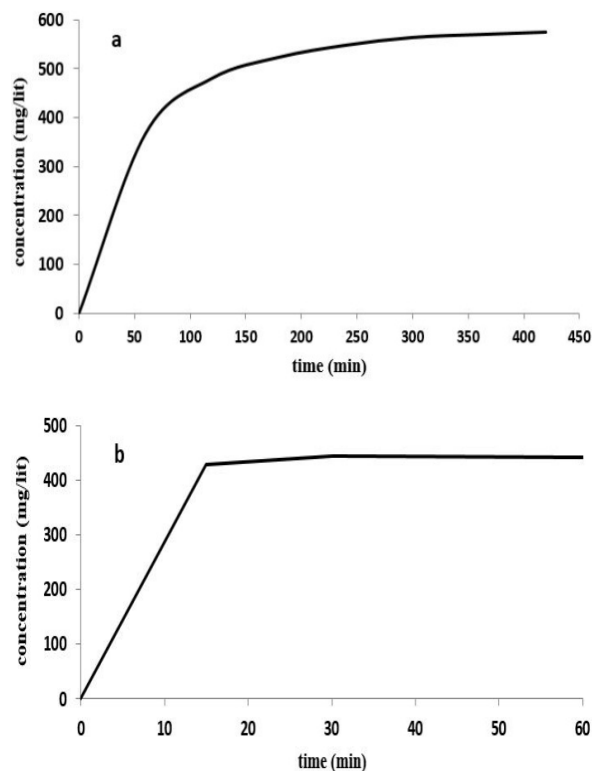

Fig. 8. (a) The concentration-time diagram of urea desorption from charged calcined granule at 600˚C, and (b) the concentration-time diagram of urea solution in water (without granule).
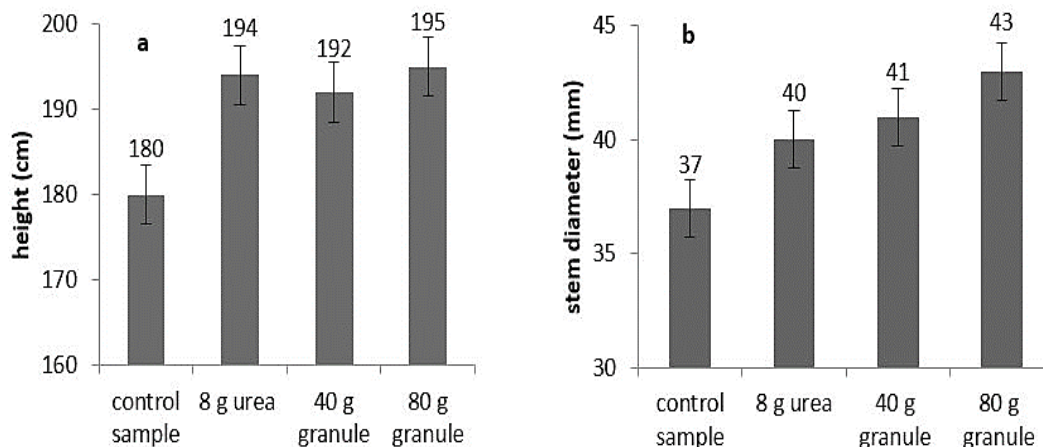

Fig. 7. The FTIR spectrum of the calcined charged granule with urea

Fig. 9. (a) The heights and (b) stem diameters of plants in different fertilizing condition

3.6. Measuring the Height and Stem Diameter of Transplants

Figs. 9a and b compare the height and stem diameter of different samples including the control sample, fertilized with traditional urea, 40 g granule, and 80 g granule. Although all fertilized samples had grown better than the control sample which was not fertilized, they did not show a significant difference in height and stem diameter. Their heights were measured to be 180, 194, 192, and 195 cm, and their stem diameters were measured to be 37, 40, 41, and 43 mm for the control sample, fertilized with traditional urea, 40 g granule, as well as 80 g granule, respectively. Nevertheless, from an environmental point of view, using 40 g granules, containing 4 g urea, had the same results as using 8 g urea directly. This means that by utilizing the half amount of needed urea, the corn plant grows efficiently. Thus, it is possible to reduce the amount of urea by using these kinds of granules by 50% which can ensure the reduction of negative environmental and health consequences.

4. CONCLUSION

A cost-effective and easily accessible ceramic adsorbent was fabricated from Zenoz domestic clay by adding 30 wt.% gibbsite and was applied as a nitrogen slow-release fertilizer. The granules were calcined at 500, 600, and 700 ˚C and their water adsorption was compared. Then the granules were characterized by XRD, BET, FTIR, as well as SEM analyses. According to these analyses, by increasing the calcination temperature the crystal structure of granules was destroyed and the specific surface area of granule was increased from 7.5 to 53.45 m^2/g after heat treatment at 600 ˚C. The calcined granules were charged by 500 g/L solution of urea which led to about 10 wt.% adsorption. Then Ⓒ 40 and 80 g charged granule were used as fertilizers in the growing bed of corn plant and their heights and stem diameters were compared with a control sample and a sample which was fertilized with 8 g urea directly. The results demonstrated the amount of urea that corn plant needed has decreased by 50% utilizing these ceramic granules. So, they could be used as a reliable controlled-release fertilizer.

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