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Rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites with controlled release of fertilizer nutrients

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Abstract

Superabsorbent nanocomposites of rice straw-g-poly(acrylic acid)/nano-zeolite NaX were prepared using ammonium persulfate as an initiator, methylene bisacrylamide as a cross-linker, rice straw as a cellulosic backbone, and nano-zeolite NaX as a slow-release absorbent matrix. The structure and morphology of the superabsorbent nanocomposites and evidence of grafting and component interactions were investigated using Fourier-transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. The water absorbency of the nanocomposite was investigated, and its potential application was verified through the study of nitrogen, phosphorus, and potassium fertilizer release from the as-prepared sample. The results showed that nano-zeolite NaX caused an ion-exchange interaction between the porous material and fertilizer and enhanced the desired slow-release property of the fertilizer in water and soil. The as-synthesized product with efficient water retention, slow-release capacity, nontoxicity in water and soil, high economic value, and eco-friendliness is expected to find useful application in agriculture.

1. Introduction

Fertilizers are chemical compounds used to promote plant growth and yield. They are usually applied on the soil for uptake by plant roots or supplied by foliar feeding for uptake through leaves. Fertilizers can also be applied to aquatic environments (ocean fertilization). Artificial fertilizers consist of inorganic compounds combined in appropriate concentrations, and they provide three main nutrients: nitrogen, phosphorous, and potassium (N, P, and K, respectively) for various crops and growing conditions. N promotes leaf growth and is required to form proteins and chlorophyll. P contributes to root, flower, and fruit development, and K contributes to stem and root growth and protein synthesis [1, 2].

However, about 40–70% of N, 80–90% of P, and 50–70% of K of the applied fertilizers cannot be absorbed by plants and are lost to the environment, causing not only substantial economic and resource loss but also leading to significant environmental pollution [3, 4]. Recently, the use of controlled slow-release fertilizers has become a trend to reduce fertilizer consumption and minimize environmental pollution [5, 6]. This has led to the development of encapsulated fertilizers in which NPK is incorporated into polymer networks in nano- or micro-particles of inorganic materials such as montmorillonite [7-9], kaolin [10, 11], mica [12], sercite [13], bentonite [14], taponite clay [15], natural zeolite, [16] and synthetic zeolite [17, 18]. The incorporation of these substances not only reduces cost but also improves the properties of fertilizers, such as their swelling ability, gel strength, mechanical stability, and thermal stability besides altering their liquid absorption-retention and slow release [18]. Superabsorbent polymers and cross-linked hydrogels have attracted considerable attention due to their versatile fluid absorption-release characteristics and controlled-release matrix properties. These polymers have been found to be useful in improving the physical properties of soil, such as its water-holding capacity, permeability, and infiltration rates; and in improving plant growth, particularly in drought-prone areas [19, 20]. Superabsorbent composites have attracted attention in recent years because of their unusual and superior characteristics over conventional hydrogels [21]. However, the application of superabsorbents in the field has substantial problems, such as a high production cost, weak salt resistance, and poor biodegradability [22]. In this study, crop residues were introduced to mitigate these problems. The utilization of crop residues as a basic material is expected to significantly reduce the production cost. Rice straw, a byproduct of rice production, has the advantages of being cheap, abundantly available, renewable, and biodegradable. The main components of rice straw are cellulose, hemicellulose, and lignin. It has various functional groups such as hydroxyl, carboxyl, phosphate, ether, and an amino group. The existence of these functional groups is beneficial for its use in the preparation of superabsorbent composites [23]. Nano-zeolite NaX is a highly versatile molecular sieve from the faujasite family of zeolites whose 7.4-Å three-dimensional pore structure and solid acidity make it useful as a catalyst, adsorbent, and membrane [24-27]. Nano-zeolite NaX is a porous material with a high cation exchange capacity, making it a potential candidate for ensuring the slow release of plant nutrients in water and soil. The combination of a superabsorbent with a fertilizer results in slow release as well as water retention properties. This combination is added to a reaction mixture and polymerized in situ, and the fertilizers are entrapped in the superabsorbents.

This study focuses on two points: (1) synthesis of superabsorbent hydrogel nanocomposites using rice straw, acrylic acid, and nano-zeolite NaX, and (2) absorption and controlled release of NPK fertilizers in water and soil.

2. Material and Methods

2.1. Materials

Acrylic acid (AA, Merck, 99%) was distilled at reduced pressure before use (to remove the polymerization inhibitor) and stored in a freezer. Ammonium persulfate (Qrec, 98%), N, N-methylene-bis-acrylamide (NMBA, Merck, 98%), potassium hydroxide (Qrec, 85%), ammonium nitrate (Ajax, 99%), fumed silica (7 nm, Sigma-Aldrich), sodium hydroxide (Volchem, ≥ 98%), sodium aluminate (Sigma-Aldrich), ammonium nitrate (Ajax, 99%), ammonium dihydrogen orthophosphate (Loba, 99%), potassium sulfate (Qrec, 99%), and other reagents were used without further purification. Rice straw (RS), collected between October and November, was obtained from Amphoe Mueang Lampang, Lampang, Thailand. It was chopped and washed several times using distilled water to remove soluble impurities and surface dirt; it was then dried in an oven at 100 °C for 48 h and sieved to keep the 200 mesh fraction.

2.2. Preparation of nano-zeolite NaX

Nano-zeolite NaX was prepared by hydrothermal crystallization in a temperature-controlled shaker. Aluminosilicate gel was prepared by mixing freshly-prepared aluminate and silicate solutions in a molar ratio of $5.5Na_2O:1.0Al_2O_3:4.0SiO_2:190H_2O$ [26]. Finally, hydrothermal crystallization was performed in a 250 mL plastic bottle.

2.3. Preparation of rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites

A uniform suspension of 132 mL deionized water and 20 g rice straw was prepared in a 500-mL batch reaction using a mechanical stirrer at 250 rpm. The suspension was then heated to ~85–95 °C using a heater band. The suspension was maintained at this temperature for approximately 30 min, and then allowed to cool to 60 °C and purged with nitrogen. Next, a solution of 37 mL acrylic acid and 28 mL deionized water was prepared in a 500-mL beaker. Using 23.3 mL 50% potassium hydroxide solution, partial neutralization was obtained by stirring and cooling. The solution was cooled to ~18–22 °C. Thereafter, the neutralized acrylic acid solution was added to the RS suspension and the resulting mixture was stirred for approximately 5 min. Then, a suspension of fertilizers—ammonium nitrate (20 g dissolved in 20 mL of deionized water), ammonium dihydrogen orthophosphate (20 g dissolved in 20 mL of deionized water), potassium sulfate (20 g dissolved in 20 mL of deionized water)—and 10 g of nano-zeolite NaX were added to the suspension, and the resulting mixture was stirred for approximately 5 min. Methylene bis-arylamide (1 g dissolved in 20 mL of deionized water) was then added to the suspension, and the resulting mixture was further stirred for approximately 5 min. Lastly, ammonium persulfate (1 g dissolved in 3.3 mL of deionized water) was added to the suspension and heated to approximately 80 °C for 15 min while being continuously stirred. The resulting product was dried in an oven at 40 °C to a constant weight and milled using a pulverizer before use.

2.4. Slow release behavior of rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites in water and soil

The slow-release experiment of the NPK fertilizer in water was performed by immersing 25 g of the rice straw-g-poly(acrylic acid)/nano-zeolite NaX sample in 1000 mL of distilled water. After a certain time interval, 150 mL of the solution was sampled for fertilizer evaluation, following which 150 mL of distilled water was added to the beaker to maintain a constant volume of the solution. All the release experiments were carried out twice, and their mean values were used for plotting. The N-content was estimated by the Kjeldahl method (AOAC, 1990) while the content of P was determined by vanadium molybdate colorimetry and that of K was determined using an atomic absorption spectrophotometer. The cumulative release was obtained from Eq. (1) below:

$$E = \frac{V_E \sum_1^{n-1} C_i + V_0 C_n}{m_0} \text{ x } 100 \qquad (1)$$

where E is the cumulative release (%) of fertilizer, V_E is the sampling volume, V_0 is the initial volume of the release medium, C_i and C_n are the fertilizer concentrations (mg.mL^{-1}), i and n are the sampling times, and m_0 is the mass of the fertilizer in the formulation samples.

The slow-release experiment of the NPK fertilizer in soil was performed by mixing 2 g of dried rice straw-g-poly(acrylic acid)/nano-zeolite NaX with 200 g of dry sandy soil (below 25 mesh). The mixture was filled into custom-made graduated glass columns with ceramic membranes and 90 mL of water was added to the soil column until it reached the soil–water saturation point. The moisture content during the study period was determined by adding water (90 mL). After a certain time interval, 10 mL of the soil water was collected and the NPK content of the solutions were tested.

2.5. Characterization and measurement techniques

Powder X-ray diffraction data was collected by a Bruker D5005 diffractometer operating in Bragg–Brentano geometry with Cu Kα (35 kV and 35 mA) radiation and secondary monochromator. The samples were measured in scan mode with steps of 0.3°/0.02 s. Phase identification was performed by searching through the database of the International Centre for Diffraction Data using the Joint Committee on Powder Diffraction Standards files for inorganic compounds. Fourier transform infrared (FTIR) spectroscopy was employed to study the structure. FTIR spectra were obtained using a Shimadzu 8900 FTIR spectrometer in the 4000 to 1400 cm^{-1} region using the KBr pellet technique. The spectra were obtained using an average of 45 scans with 8 cm^{-1} resolution. Prior to measurement, the samples were dried in vacuum till they reached a constant weight. The dried samples were mixed with KBr powder and then compressed to make a pellet for FTIR characterization. The morphologies of the rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites were analyzed by scanning electron microscopy (SEM). The samples were coated with a layer of gold and observed using a JSM-5410V scanning electron microscope. To obtain rice straw-g-poly(acrylic acid)/nano-zeolite NaX samples for water absorbency measurements, 0.1 g of the sample was immersed in 250 mL of distilled water at ambient temperature (25–30 °C) for 24 h in order to reach equilibrium swelling. The residual water was removed by filtration through an 80 mesh stainless steel screen and the super absorbent nanocomposite (SAC) was left on the screen for more than 1 h to drain off the additional unabsorbed water. During this period, the screen was gently shaken at an alternate lined angle of 15–20 °C to ensure that most of the unabsorbed water was separated. This water, which was held by capillary force in the free spaces between the SAC particles due to variation in particle size, had to be excluded. After weighing the swollen and dried superabsorbent nanocomposite, the water absorption was determined using the equation below:

$$\text{Water absorbency } (\text{g.g}^{-1}) = \frac{W_1 - W_o}{W_o} \qquad (2)$$

where W_o is the weight of the dried superabsorbent sample and W_1 is the weight of the swollen superabsorbent sample.

3. Results and discussion

3.1 Preparation of nano-zeolite NaX

Nano-zeolite NaX was successfully prepared by hydrothermal technique at 90 °C. As shown in Figure 1, the X-ray diffraction (XRD) pattern of the faujasite zeolite indicated its crystalline structure.

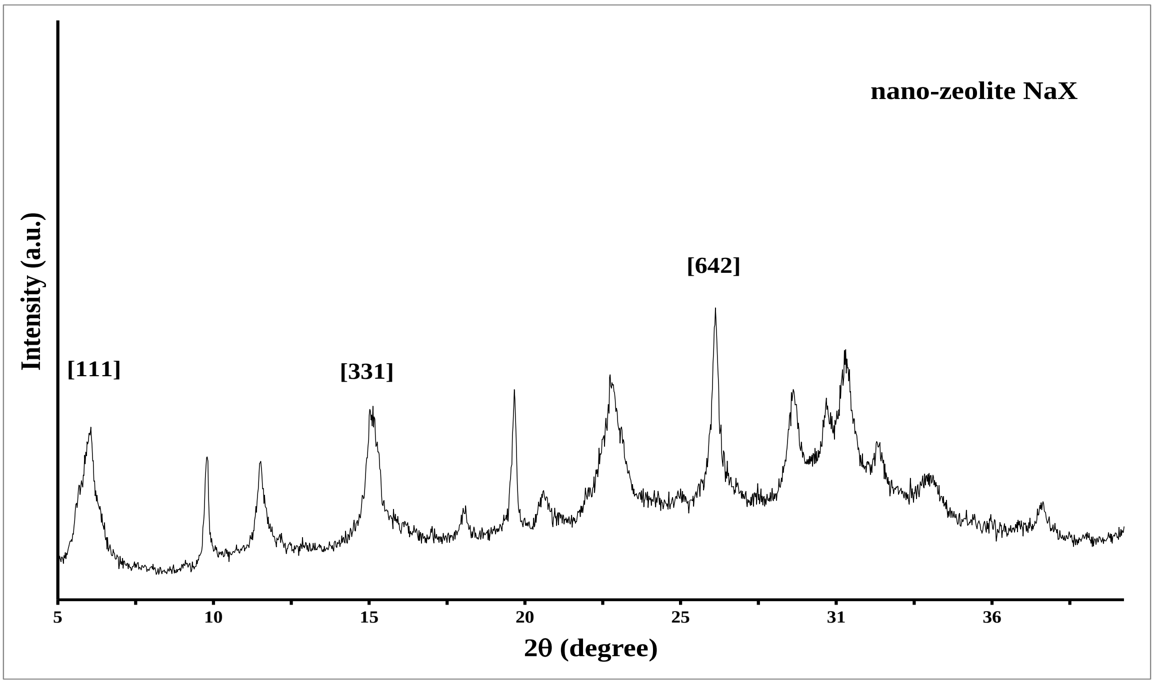

Figure 1: XRD pattern of nano-zeolite NaX

Nano-zeolite NaX is highly hydrophilic with entrance pores of approximately 74 Å. An average crystal dimension of 105±9 nm was calculated using Scherrer's equation from the 2θ diffraction peaks at 6° [111], 15° [331], and 26° [642]. The molecular band of the nano-zeolite NaX appeared as two bands at 608 and 559 cm^{-1}, similar to that of a typical faujasite zeolite; furthermore, a symmetric band, double-ring vibration, and silanol (Si–OH) bending was observed at 566, 750, and 860 cm^{-1}, respectively. The weak absorption band observed around 608 cm^{-1} is presented in Figure 2. As reported in a previous study by Li et al. [28], this absorption band only appeared on nano-zeolite NaX.

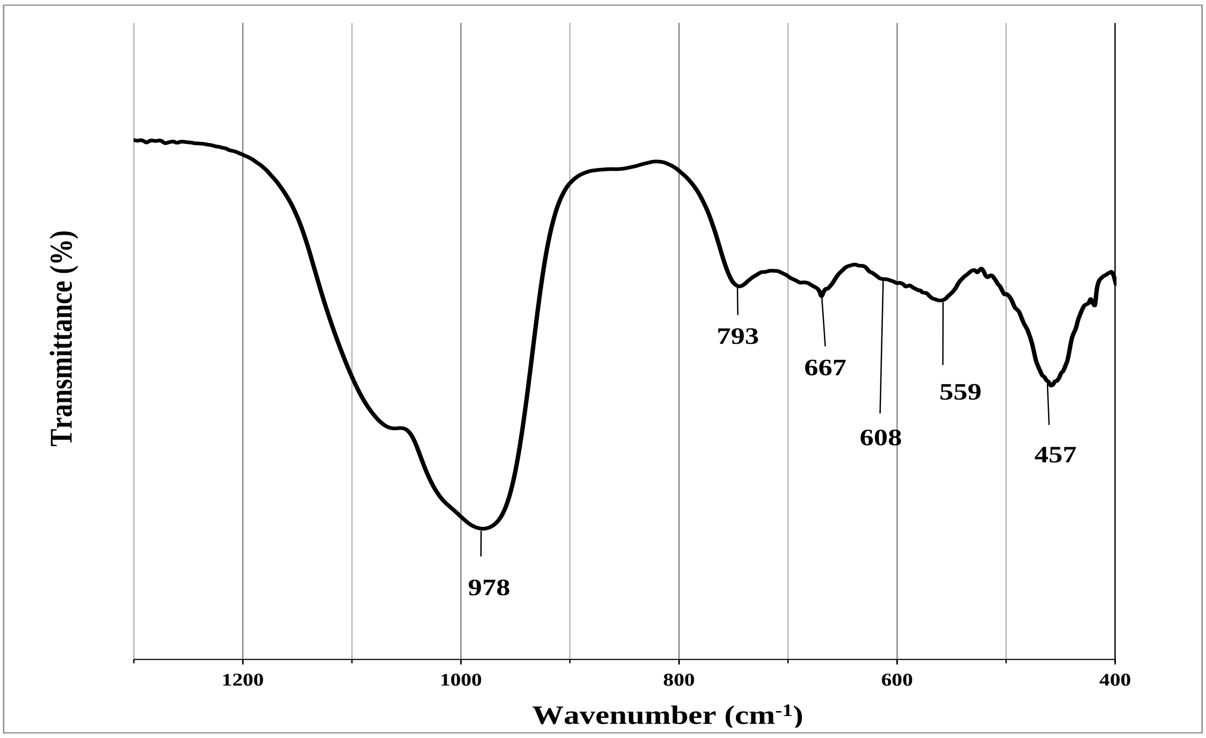

Figure 2: FTIR spectrum of nano-zeolite NaX

3.2. Synthesis and mechanistic aspects

The rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites were synthesized by graft polymerization of a monomer onto a rice straw (a carbohydrate) in the presence of an initiator to form a rice straw graft copolymer. The nano-zeolite NaX was dispersed in a solution containing a rice straw graft copolymer to form a reaction mixture and fertilizer nutrients were added to this mixture. Then methylene bis-acrylamide was added so as to crosslink and adjust the pH of the rice straw grafted copolymer. The proposed mechanism for the preparation of rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposite is outlined in Figure 3.

3.3 Characterization of rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites

The chemical structure of the NPK fertilizers—(RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK—which were incorporated into rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites was analyzed using FTIR. Their spectra are shown in Figure 4. The broad band at 3411 cm^{-1} is due to O–H stretching groups of rice straw (α-cellulose), while C–H stretching appears at 2900 and 894 cm^{-1} [28]. The band at 617 cm^{-1} is an external vibration associated with the sensitive tetrahedral structure of zeolite (external symmetric vibration) [29].

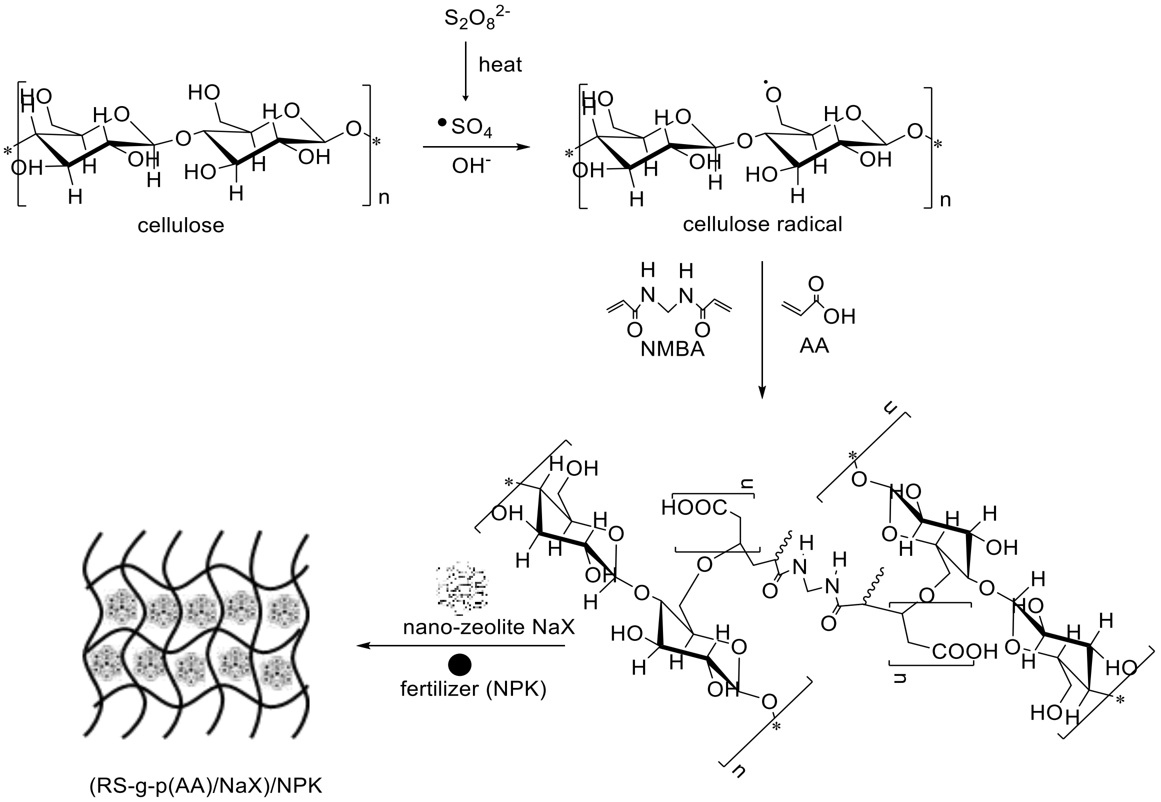

Figure 3: Proposed reaction mechanism for synthesis of (RS-g-p(AA)/NaX)/NPK superabsorbent nanocomposite

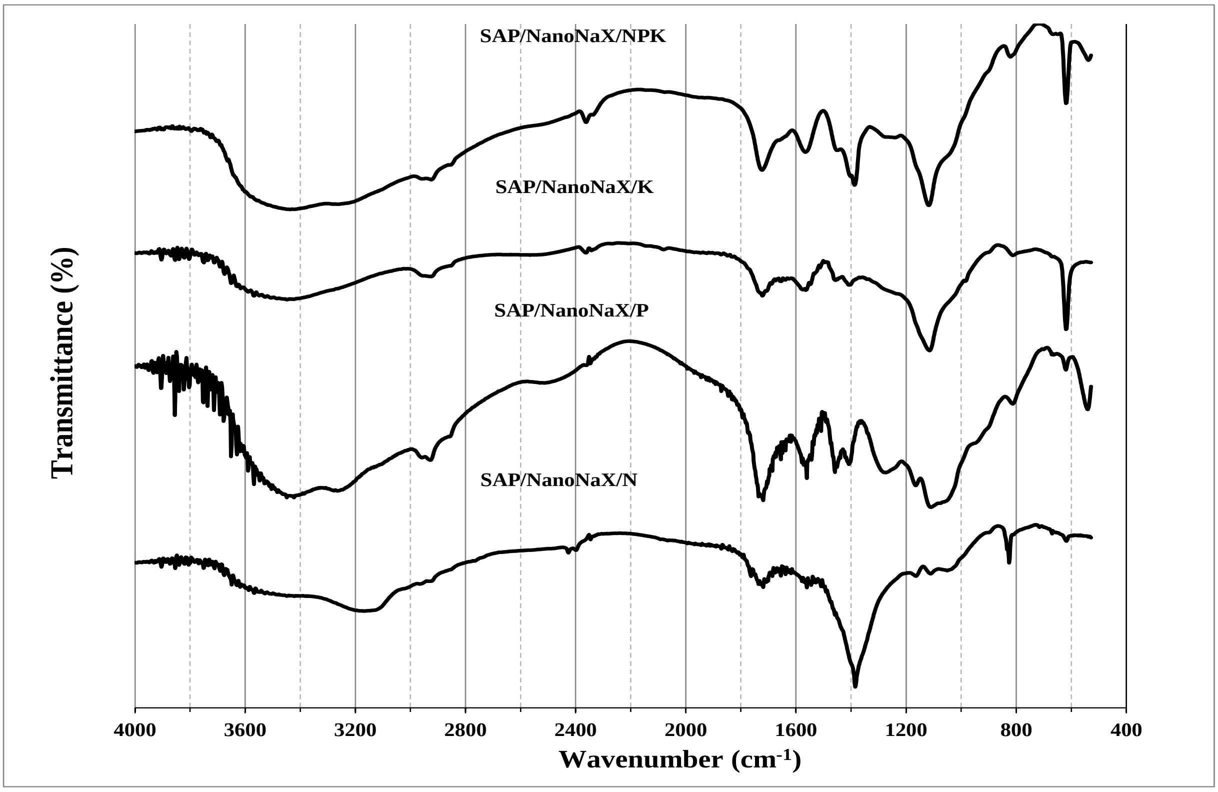

Figure 4: FTIR spectra of (RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK

In addition, the absorption peak at 1118 cm^{-1} indicates the formation of an ether group –O– between N-hydroxymethyl and hydroxyl groups of rice straw (cellulose) and the graft copolymerization of vinyl and rice straw. The other peaks show that the synthesis of the superabsorbent nanocomposite occurred between 1720–1653 and 1280–1051 cm^{-1}. These peaks indicate the presence of a carbonyl group (C=O) and C–O or C–N [30, 31]. Based on the FTIR analyses, it can be concluded that a cross-linked copolymer of acrylic acid and rice straw was formed. In addition, there was a characteristic weak absorption peak of the nano-zeolite NaX tetrahedral structure. A 619 confirmed the incorporation of nano-zeolite NaX into the hydrogel network.

XRD patterns of nano-zeolite NaX, (RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK are shown in Figure 5. Figure 5(a) shows the XRD patterns of pristine nano-zeolite NaX. The characteristic peaks of nano-zeolite NaX appeared at 2θ=6°, 15°, and 26°. For (RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK, these patterns almost disappeared, implying that nano-zeolite NaX dispersed (intercalated) and constituted the inner part of the superabsorbent. However, the presence of crystalline reflections of NH_4NO_3 (N) in the superabsorbent at 2θ=19° and 29°, $NH_4H_2PO_4$ (P) in the superabsorbent at 2θ=16.5° and 24°, K_2SO_4 (K) in the superabsorbent at 2θ=21°, 31°, 37°, and 44°, and NPK in the superabsorbent at 2θ=19°, 29°,16.5°, 24°, 21°, 31°, 37°, and 44° are clearly seen and can be indexed as Figures 5(b), 5(c), 5(d), and 5(e), respectively [32-34].

The surface morphologies of (RS-g-p(AA)/NaX)/N and (RS-g-p(AA)/NaX)/NPK products were examined by SEM and are shown in Figures 6(a) and (b). The SEM micrograph of (RS-g-p(AA)/NaX)/NPK, shown in Figure 6(b), reveals that an NPK fertilizer compound has been finely dispersed on the surface and in the pores of nano-zeolite NaX within the superabsorbent nanocomposite. Moreover, the surface morphology was coarse and porous, indicating that after the reaction, the monomers were grafted onto the rice-straw skeleton, which resulted in a broad network and an increased porous structure on the surface of the product.

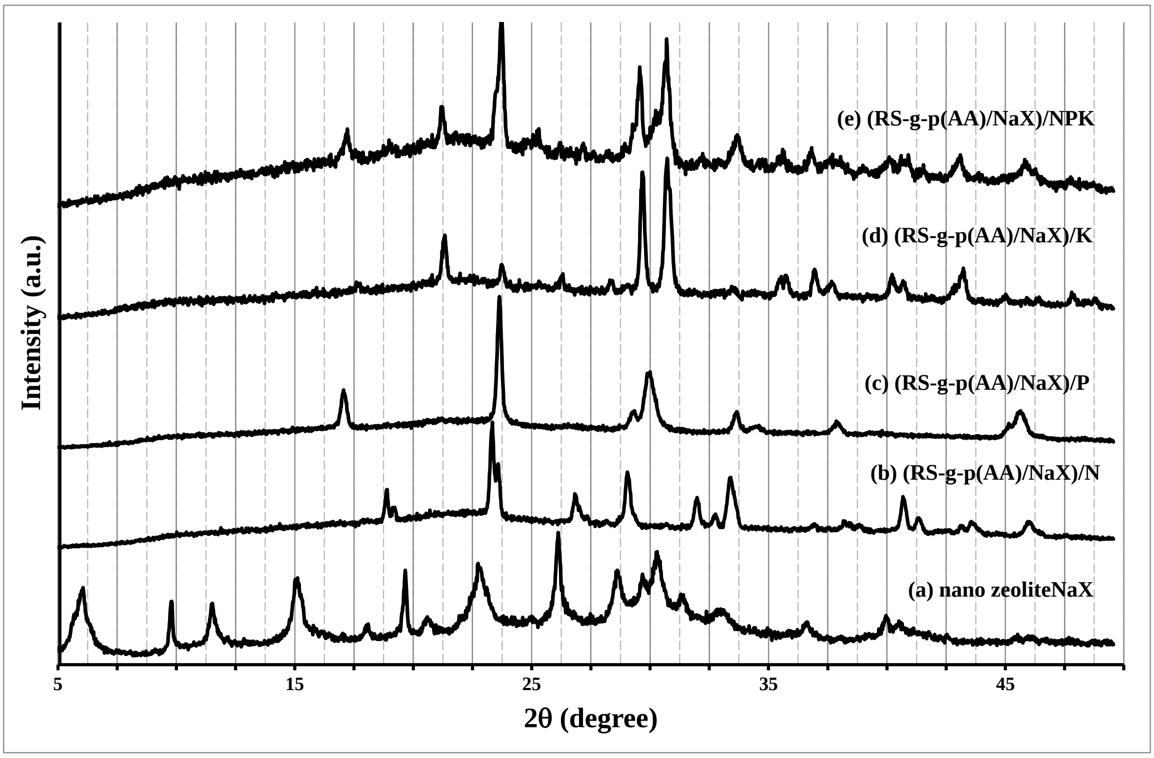

Figure 5: Powder XRD patterns of nano-zeolite NaX, (RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK

The water absorbency of the superabsorbent nanocomposites incorporated into different fertilizer components in distilled water are shown in Figure 7. The swelling of the superabsorbents followed the following sequence: N (NH_4NO_3) > K (K_2SO_4) > NPK (NH_4NO_3, $NH_4H_2PO_4$, and K_2SO_4) > P ($NH_4H_2PO_4$). High swelling was observed in (RS-g-p(AA)/NaX)/N, whereas the swelling in (RS-g-p(AA)/NaX)/K, (RS-g-p(AA)/NaX)/NPK, and (RS-g-p(AA)/NaX)/P were 37.96, 29.59, 16.66, and 15.04 (g.g^{-1}), respectively. This was because of the presence of an ionic group that was released in water. These ions prevented water molecules from diffusing into the superabsorbents due to the high to low parameters of diffusion performance: NH_4NO_3 (1.24), K_2SO_4 (1.19), and $NH_4H_2PO_4$ (0.31), thus decreasing the swelling capacity of the superabsorbent.

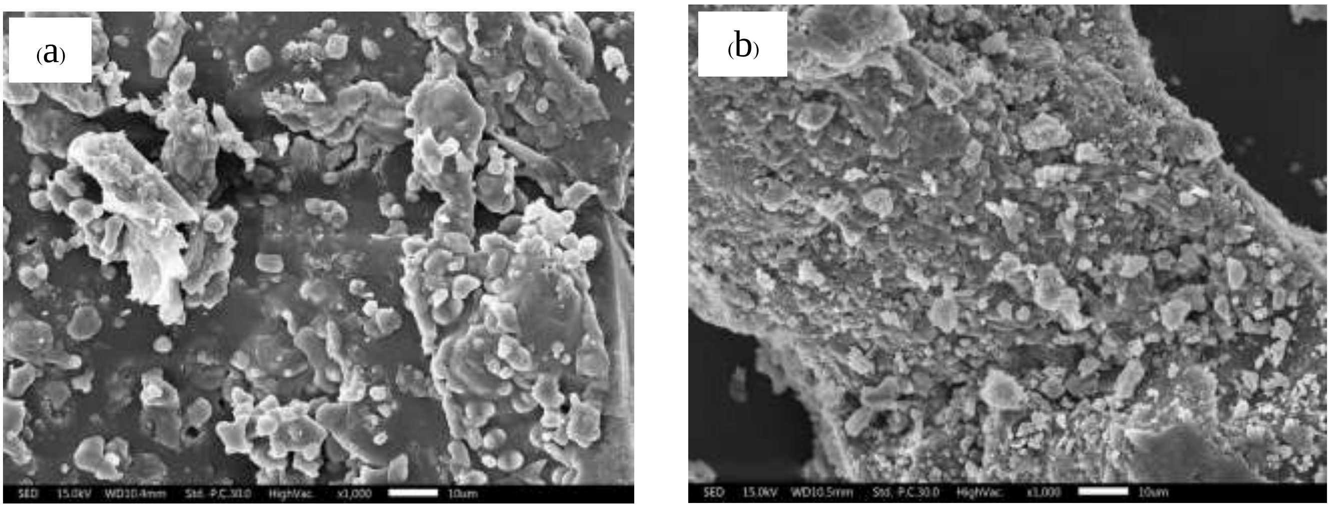

Figure 6: SEM images of (a) (RS-g-p(AA)/NaX)/N and (b) (RS-g-p(AA)/NaX)/NPK

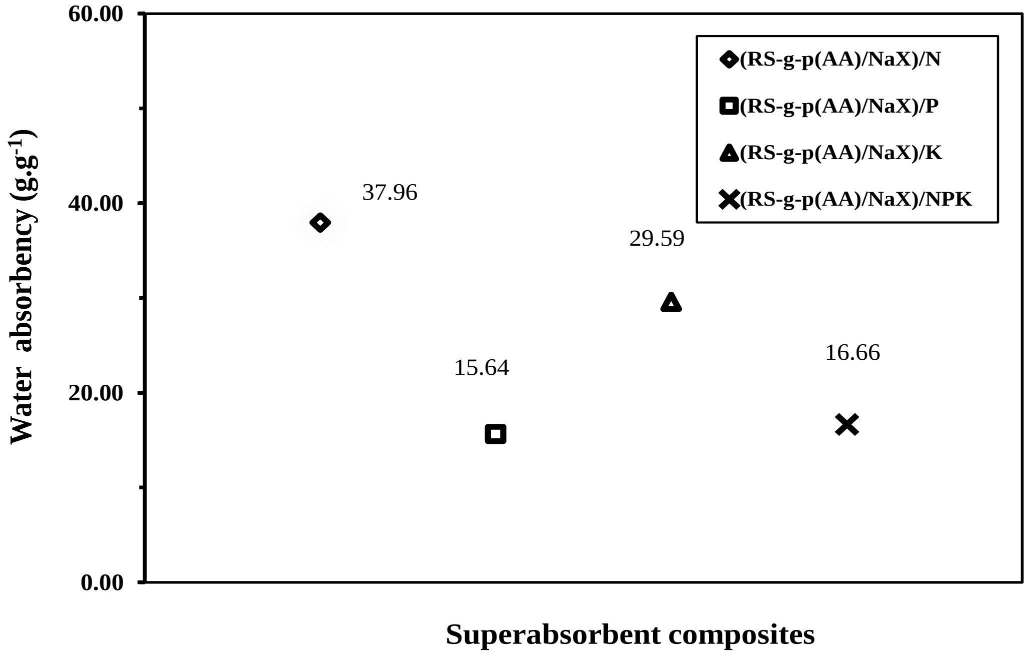

Figure 7: Water absorbency of (RS-g-p(AA)/NaX)/N, (RS-g-p(AA)/NaX)/P, (RS-g-p(AA)/NaX)/K, and (RS-g-p(AA)/NaX)/NPK

3.4. Slow-release NPK behaviors of rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposites in water and soil

Figure 8 shows the slow release of N, P, K, and NPK superabsorbent nanocomposites in deionized water. The N, P, and K contents released from each of the corresponding superabsorbent nanocomposites were 40.00%, 1.25%, and 73.63%, respectively, after 30 days, and those from the NPK fertilizer were 15.71%, 1.29%, and 53.01%, respectively. The low P-release in both cases indicates that the present fertilizer is a good slow-release P fertilizer. Moreover, the release time of N and K from the superabsorbent nanocomposites also conforms to the standard of slow-release fertilizers of the Committee of European Normalization [35].

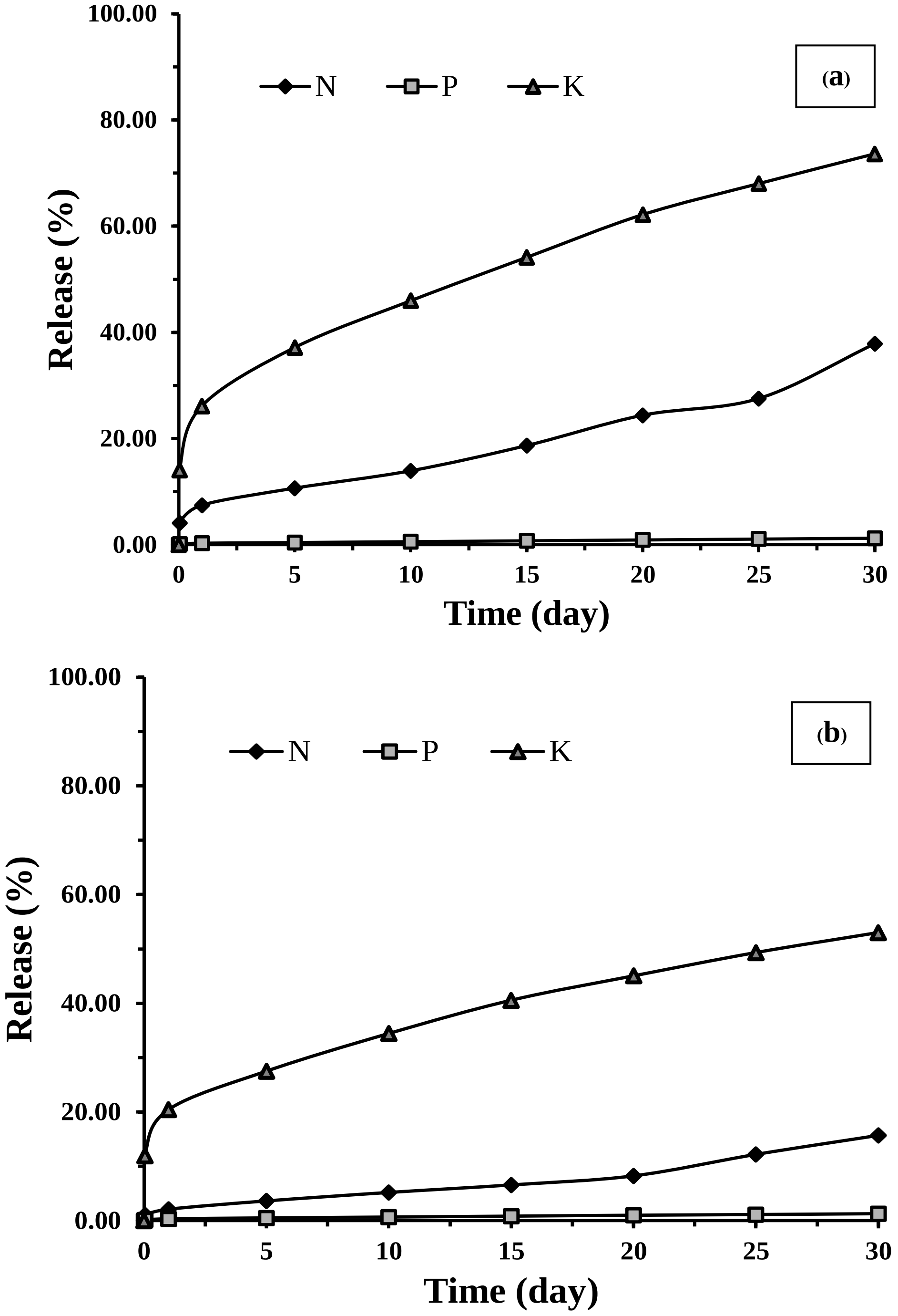

Figure 8: Release behavior of (a) N, P, K, and (b) N/P/K from superabsorbents in distilled water

It is known that N, P, K, and NPK compound fertilizers are highly water-soluble; thus, they quickly run out after being added to the soil. However, the superabsorbent nanocomposites added to fertilizers have a macromolecular structure that is difficult to dissolve in cool water. The slow release of fertilizer from these nanocomposites might be related to their highly porous structure, surface area, and ion exchange. NPK fertilizers encapsulated in superabsorbent nanocomposites can be released slowly due to the nano-sized zeolite NaX which retains and retards the release of fertilizer through the superabsorbent nanocomposite medium. The addition of nano-zeolite NaX to the pure superabsorbent not only causes a porous and ion exchange structure in the superabsorbent nanocomposite but also controls the release of fertilizer from it. Figure 9 shows the slow-release behavior of N, P, K from superabsorbent nanocomposite in soil at room temperature. The release rate of nitrogen is higher than those of potassium and phosphorus.

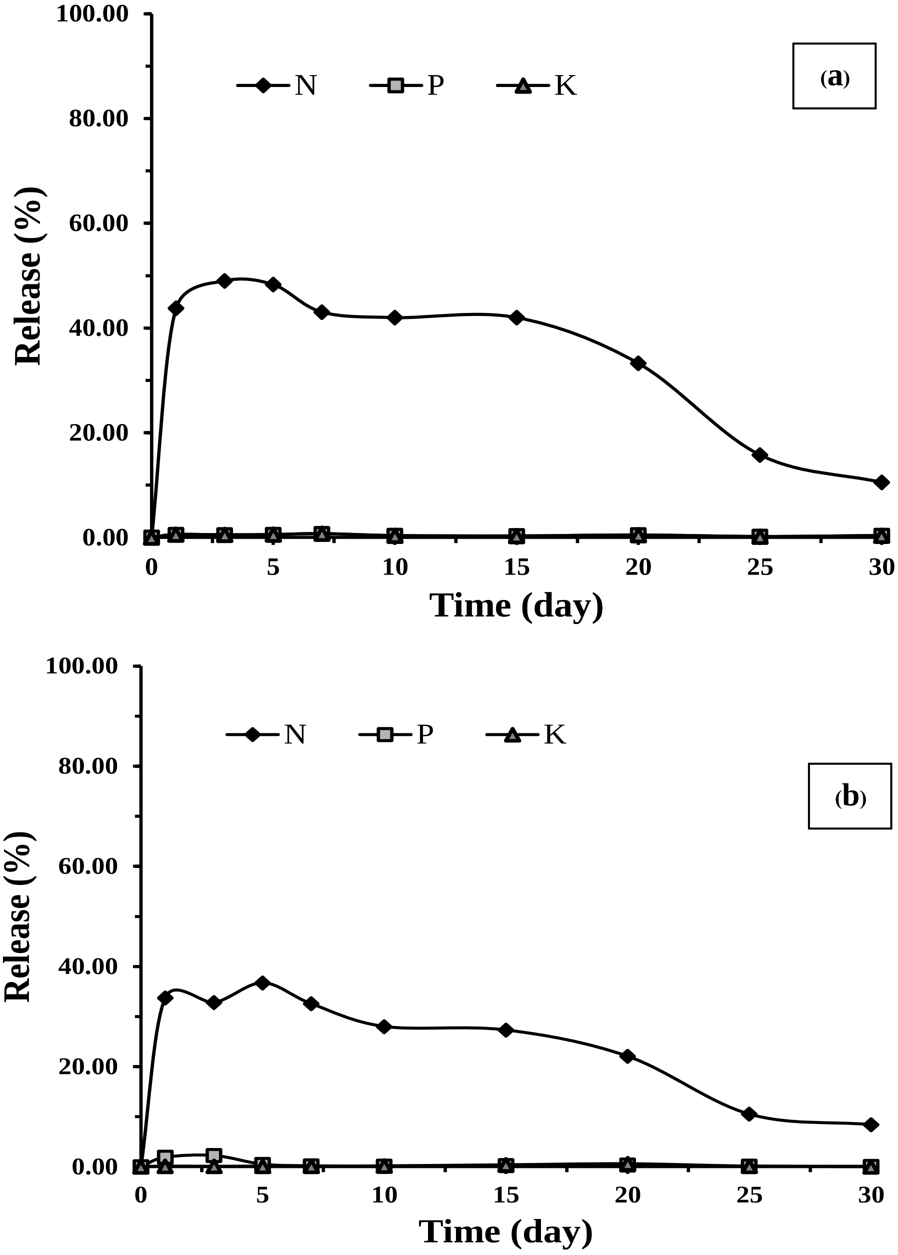

Figure 9 : Release behavior of (a) nitrogen (N), phosphorus (P), potassium (K), and (b) nitrogen (N)/phosphorus (P)/potassium (K) of superabsorbents in soil

The nitrogen quickly dissolves in the soil solution after being immersed in soil. In contrast, phosphorus and potassium release rate of superabsorbent nanocomposite is lower. The rapid release in the early stage (in 5 days) can be mainly ascribed to the dissolution of NH_4NO_3, $NH_4H_2PO_4$, and K_2SO_4 that were filled physically in the superabsorbent composite cores. The release rate after 5 days is low. This is mainly due to the physical barrier of the inner and outer superabsorbent nanocomposites. Moreover, the high ion exchange capacity of nano-zeolite NaX slowly releases nutrients. As mentioned earlier, nano-zeolite NaX has a high surface area and ion exchange, and many parallel channels in its lattice.

When water diffuses into the superabsorbent composite cores, part of the nutrients are absorbed by nano-zeolite NaX, which consequently slows the release rate of nutrients. The reasons for the slower release rate in soil than in water may be due to the existence of several kinds of ions in the soil solution and the lower degree of swelling of the superabsorbent in soil than that in distilled water, making the diffusion of fertilizer in soil difficult and thus decreasing the release rate of fertilizer. Moreover, when N passed through the soil column, the absorption and de-absorption processes of the fertilizer molecules and soil granules also contributed to the slower fertilizer release rate of soil [36].

Conclusion

An innovative rice straw-g-poly(acrylic acid)/nano-zeolite NaX superabsorbent nanocomposite was synthesized through a graft copolymerization reaction of rice straw and acrylic acid in aqueous solution. The highest water absorbency was obtained by loading nitrogen into the as-prepared nanocomposite. The FTIR spectra revealed the successful incorporation of the nano-zeolite NaX within the superabsorbent matrix. The nano-zeolite NaX structure of the superabsorbent nanocomposite was observed by XRD. The highly porous structure of the superabsorbent was formed by the addition of nano-zeolite NaX to the pure superabsorbent. Furthermore, the slow-release properties of superabsorbent nanocomposites in water and soil were investigated in detail. It was found that the amount of nutrients (N, P, and K) released in water and soil were lower than 75% on the 30th day; the release of fertilizer from superabsorbent nanocomposites in soil was slower than that in water. This study demonstrated a method of utilizing crop residues, such as rice straw, in the production of superabsorbent materials. The introduction of superabsorbents into these residues is expected to significantly reduce production cost and improve environmental-friendliness, which is crucial in the application of superabsorbents in agriculture.

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