



## Influence of chitosan addition on the properties and characteristics of acrylic acid-chitosan based superabsorbent prepared through gamma irradiation technique and its application for urea loading

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### ABSTRACT

Superabsorbent can be used as a carrier for urea-fertilizer which can release urea slowly and can be used as a dry soil moisturizer. The main goal of the current study was to investigate the influence of adding chitosan grafted onto acrylic acid as a superabsorbent base material on the properties and characteristics of the resulting superabsorbents. The method used to prepare the superabsorbent was the gamma irradiation technique. Acrylic acid was neutralized by adding KOH, and then chitosan was added. The mixture was put in a plastic container, followed by irradiation with gamma rays. The formed superabsorbent was washed and dried in an oven, then the dry superabsorbent was analyzed for its properties and characteristics. The results showed that superabsorbent properties such as swelling ratio (from 49.38 g/g to 49.38 g/g), water retention (0.43%-0.89% after 7 days), and urea loading (86.75% to 96.4%) were affected by the amount of chitosan added. However, adding too much chitosan can reduce the superabsorbent properties. The characterization of the superabsorbent revealed a smooth surface with a porous structure, and FTIR analysis showed that chitosan was grafted onto acrylic acid.

### ABSTRAK

Superabsorben dapat digunakan sebagai pembawa pupuk urea yang dapat melepaskan urea secara perlahan dan sebagai pelembab tanah kering. Tujuan penelitian ini adalah mempelajari pengaruh penambahan kitosan yang dicangkokkan pada asam akrilat sebagai bahan dasar superabsorben terhadap sifat dan karakteristik superabsorben yang dihasilkan. Metode yang digunakan dalam pembuatan superabsorben adalah teknik iradiasi sinar gamma. Asam akrilat dinetralisasi menggunakan KOH kemudian ditambahkan kitosan. Campuran tersebut dimasukkan ke dalam wadah plastik kemudian diiradiasi dengan sinar gamma. Superabsorben yang terbentuk dicuci dan dikeringkan di dalam oven, kemudian dilakukan analisis terhadap sifat dan karakterisasinya. Hasil penelitian menunjukkan bahwa sifat superabsorben seperti *swelling* (mulai dari 49,38 g/g sampai 49,38 g/g), retensi air (0,43%-0,89% setelah 7 hari), dan pemuatan urea (86,75% sampai 96,4%) dipengaruhi oleh jumlah kitosan yang ditambahkan. Akan tetapi, penambahan kitosan yang terlalu besar dapat menurunkan sifat-sifat superabsorben tersebut. Analisa karakteristik superabsorben menunjukkan permukaan yang halus dengan struktur pori dan analisa FTIR menunjukkan bahwa kitosan tercangkok di dalam asam akrilat.

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## 1. Introduction

Conventional urea fertilizer is easily soluble in water, but plants can only utilize nitrogen from the urea fertilizer 30-35% and the remaining nitrogen is lost due to the flowing water or due to washing by rain [1,2]. The low efficiency of fertilizer use causes the use of large amounts of fertilizer by adding fertilizer repeatedly to increase crop yields. Such conditions can burden farmers because they require high costs to buy urea fertilizer. In addition, such conditions can pollute the environment because excessive nitrate, nitrite and ammonia content in the environment can disturb human health [3,4]. Environmental damage caused by residual nitrogen that is not absorbed by plants includes ecosystem eutrophication, downstream water quality degradation, global greenhouse gas effects, and other ecosystem disturbances [1,2].

Several innovations have been developed to improve the efficiency of fertilizer use, one of them is to develop a slow-release fertilizer. This fertilizer type can improve the efficiency of absorption of nutrients by plants because this fertilizer can release urea slowly [5]. The principle of the slow-release fertilizer is that water pushes urea out from the fertilizer-polymer barrier to the soil-polymer barrier. The polymer serves as a barrier with a certain thickness. The stages of fertilizer release are (1) solid dispersion/inflammation, (2) damage to the urea layer, and (3) layer rupture, water penetration and finally dissolution [6]. Methods for making slow-release fertilizers have also been developed, such as immersion techniques, rotary pan coating, fluidized bed [7], and encapsulation process where fertilizers are coated with polymeric materials physically or chemically [8].

Another technology that can be used for the slow release of fertilizers is using superabsorbent hydrogel. The superabsorbent hydrogel has the ability to hold water so it can function as soil moisturizers. In addition, the superabsorbent hydrogel can absorb large amounts of urea with high concentrations. The superabsorbent hydrogel method for the slow release of urea is chemical and physical cross-linking [9]. Superabsorbent hydrogels are hydrophilic polymers having crosslinked networks, so they have the capability for absorbing and retaining aqueous solutions up to 100-fold of their own weight. Most of the superabsorbent hydrogels are generated using synthetic materials, for example, acrylic acid and acrylamide which are naturally unrefined [10]. Therefore, the development of superabsorbent hydrogels based on natural materials continues to be carried out, where natural materials include cellulose, starch, dextran, guar gum, and chitosan [10]. However, as superabsorbent materials, natural materials have low mechanical properties and absorption capability. Hence, they are usually combined with synthetic materials.

The preparation of superabsorbent hydrogels with chemical cross-links has a disadvantage because most of the chemicals used are toxic. Therefore, this study used a physical method, namely cross-linking with gamma irradiation. This method is easy to conduct and environmentally friendly, leaves no residue, and does not require an initiator, catalyst and crosslinker because ionizing radiation is very strong. The synthesis of a superabsorbent hydrogel using a mixture of chitosan and acrylic acid has been carried out by Ismail et al. [10] by comparing the volume of acrylic acid with chitosan and irradiated with various doses. Meanwhile, Barleany et al. [11] conducted the synthesis process of acrylic acid-based superabsorbents mixed with chitosan at various weights and irradiation doses. The mixing of synthetic and natural polymers is called the hydrophilic monomer grafting process. In this study, superabsorbents were made from chitosan grafted with acrylic acid using the irradiation method. Then, the superabsorbent hydrogel was applied as a slow-release fertilizer by loading the hydrogel with urea fertilizer. Therefore, the main goal of the current study was to study the influence of chitosan weight on the properties and characteristics of the hydrogel.

## 2. Research Methodology

### 2.1. Preparation of superabsorbent hydrogels

First, distilled water as much as 85 mL was put in a 250-mL-beaker glass. Furthermore, 15 mL acrylic acid was neutralized using 50% KOH solution, and then was added to the beaker glass. Furthermore, chitosan was added at various weights of 0.5 g, 1 g, and 2 g, and then homogenized using an overhead stirrer. Then, the mixture was packed in a plastic container with a seal and then irradiated using gamma rays at a dose of 5 kGy to form a gel. The hydrogel was separated from the plastic container and dried at 60°C until its weight was constant. The dried hydrogel was then cut and pulverized.

### 2.2. Swelling Ratio

As much as 0.5 g of dry superabsorbent hydrogel was placed in a tea bag. Furthermore, the tea bag was fully immersed in 250 mL of water under room conditions until the swelling equilibrium was reached. The swollen samples were taken and then let stand for a while to remove water on the surface of the samples. The samples were weighed and the swelling ratio was determined by Equation 1.

$$\text{Swelling Ratio (g/g)} = \frac{W_s - W_d}{W_d} \quad (1)$$

Where:

$W_d$  = weight of the dry sample (g)

$W_s$  = weight of the swollen sample (g) (g)

### 2.3. Water retention

The swollen samples were weighed and stored at room temperature for 0.5, 1, 2, 3, 4, 5, 6, and 7 days. After that, they were weighed again. Water retention can be calculated using Equation 2.

$$\text{Water retention (\%)} = \frac{W_t - W_d}{W_i - W_d} \times 100 \quad (2)$$

Where:

$W_i$  = initial weight of the swollen superabsorbent (g)

$W_t$  = weight of the swollen superabsorbent at a time "t" (g)

$W_d$  = weight of the dry superabsorbent (g)

## 2.4. Reusability

As much as 0.5 g of dry superabsorbent was soaked in 250 mL of distilled water and then the swelling equilibrium was measured. After weighing, the swollen superabsorbent was dried in an oven under 60°C and weighed. Then, the superabsorbent was soaked again in the water. These processes were repeated up to 5 times. The reswelling ratio can be calculated using Equation 3.

$$\text{Reswelling ratio} = \frac{W_s - W_d}{W_d} \quad (3)$$

Where:

$W_d$  = weight of the dry sample (g)

$W_s$  = weight of the swollen sample (g)

## 2.5. Urea loading

Urea loading was carried out by soaking 0.5 g of dry superabsorbent hydrogel in a 10% w/v urea solution during 1 day (24 hours). The sample containing urea was filtered to remove water, and then weighed. Weighing was carried out until a constant weight was obtained. Urea loading can be calculated using Equation 4.

$$\% \text{ Urea loading} = \frac{W_1 - W_0}{W_1} \times 100\% \quad (4)$$

Where,  $W_1$  and  $W_0$  are the weight of the dry gel loaded with urea and the weight of the empty gel (without urea loaded)

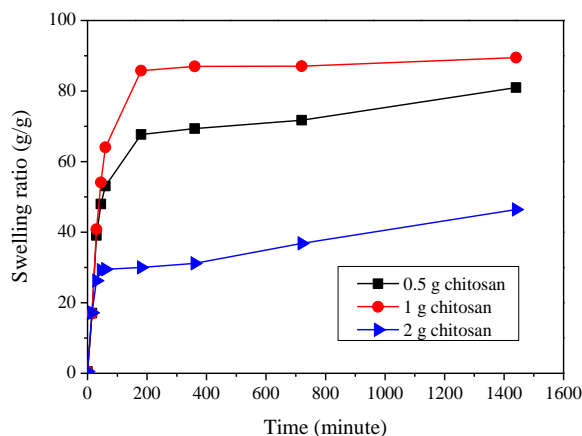
## 2.6. Characterization of Superabsorbent Hydrogels containing urea using SEM, FTIR, and XRD

Hydrogel samples containing urea were coated with platinum and analyzed for morphology using SEM with a high vacuum (HV) resolution of 3.0 nm (30 kV), with a low vacuum of 4.0 nm (30 kV). FTIR analysis was conducted using the Shimadzu IR spectrophotometer type using KBr pellets. XRD analysis was conducted using the Shimadzu 7000 Maxima-X. Samples were analyzed using Cu-Kalpha radiation with the scan rate of 2°/min at 2θ from 2° to 90° with a step size of 0.02°

## 3. Results and Discussion

### 3.1. Swelling ratio

Swelling is the most important factor of superabsorbent. It shows the capability of superabsorbent to absorb and retain large amounts of liquid in its matrix structure. In the swelling process, the interaction between the liquid and the matrix causes the matrix to expand and absorb the liquid into the polymer network. Figure 1 shows the influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the swelling ratio.



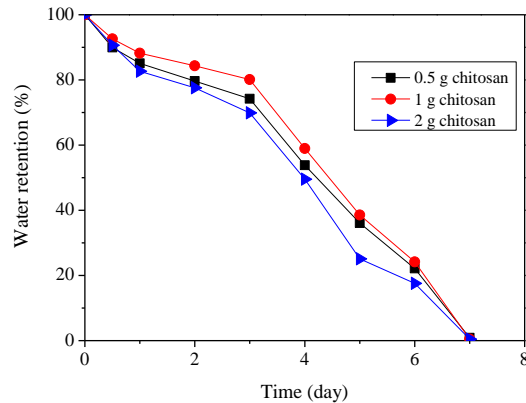
**Figure 1. The influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the swelling ratio**

Figure 1 shows the change in weight of chitosan added to acrylic acid as a basic ingredient for making superabsorbent. The highest swelling ratio was 89.5 g/g when 1 g chitosan was added and the lowest swelling ratio was 49.38 g/g when 2 g chitosan was added at an absorption time of 1440 minutes (24 hours). An increase in chitosan weight decreased the amount of liquid absorbed in the superabsorbent. The same results were reported by Erizal and Wikanta, [12] reporting that an increase in chitosan addition can reduce the diffusion of water to the superabsorbent. Chitosan can increase water absorption because chitosan is hygroscopic so the chitosan addition can improve the absorption capacity of the superabsorbent [10].

Based on Figure 1, the results of this study indicated that increasing the amount of chitosan until 1 g in the superabsorbent can increase water absorption, but further chitosan addition (more than 1 g) can reduce the capacity of water absorption so that the value of the swelling ratio decreased. These phenomena were due to the steric effect of overcoming the potential for bonding of functional groups due to an increase in the viscosity of chitosan [4].

### 3.2. Water retention

Water retention is the capability of the absorbent material to retain water that has been absorbed in its matrix structure. Water retention is used as a measure to show the effectiveness of superabsorbents in retaining liquid that has been absorbed without experiencing leakage. Figure 2 shows the ability of acrylic acid-chitosan based superabsorbents to retain water from the evaporation process.



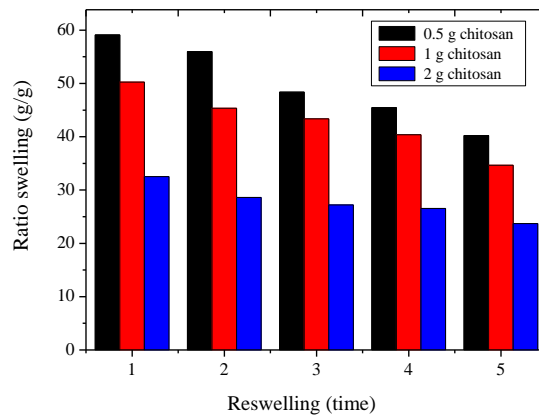
**Figure 2. The influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the water retention**

Figure 2 shows that the difference in chitosan weight influenced the evaporation rate of water in the superabsorbent. The chitosan addition of 2 g generated a lower water retention value than that of 0.5 and 1 g. On the 7th day, all superabsorbents had the almost same water retention values, namely 0.43%, 0.89%, and 0.45% for the chitosan addition of 2 g, 0.5 g, and 1 g. Therefore, the addition of 1 g of chitosan was able to retain water better than the addition of 2 and 0.5 g of chitosan.

The addition of chitosan influenced the water retention because chitosan has a chemical structure and its interactions with water molecules. The hydrophilic group adsorbs immobilized water molecules in three-dimensional cross-links. The addition of chitosan can retain water better, prevent leakage, and improve overall performance in water-based applications [13].

### 3.3. Reusability

The analysis of superabsorbent reusability is intended to determine the ability of the superabsorbent after it is used to absorb water.

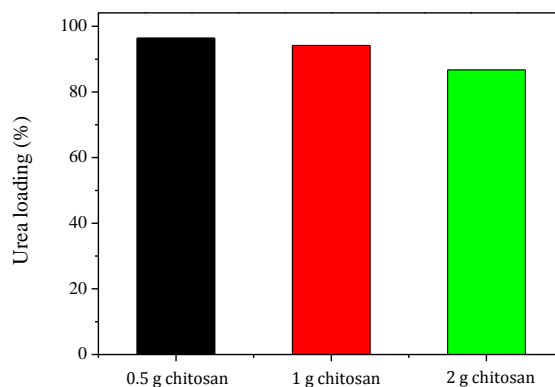


**Figure 3. The influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the reusability of superabsorbents**

Analysis of the reusability was done by reswelling the superabsorbent, where the superabsorbent was used to absorb water, and then it was dried and soaked back into the water. This process was carried out 5 times and the results are presented in Figure 3. Figure 3 presents that there is a decrease in the swelling ability of the superabsorbent. After the swelling analysis was carried out 5 times, the superabsorbents only experienced a decrease in the swelling ability of around 27–32 g/g. This showed that the resulting superabsorbent was still able to absorb water even though its swelling ability decreased. The damage to the superabsorbent polymer network causes a decrease in swelling ability. The function of this reusability analysis is that the superabsorbent that has been used can be reused so it can reduce the superabsorbent replacement cost. Also, if the superabsorbent can be used many times, it can reduce the environmental pollution load due to the use of superabsorbents [14].

### 3.4. Urea loading

Superabsorbents can be used in agriculture to increase soil moisture, increase the absorption capacity of sandy soil used for agriculture, and release nutrients/fertilizers slowly. The ability of the superabsorbent to load urea affects the amount of urea adsorbed in the superabsorbent matrix. Figure 4 shows the influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the loading of urea.



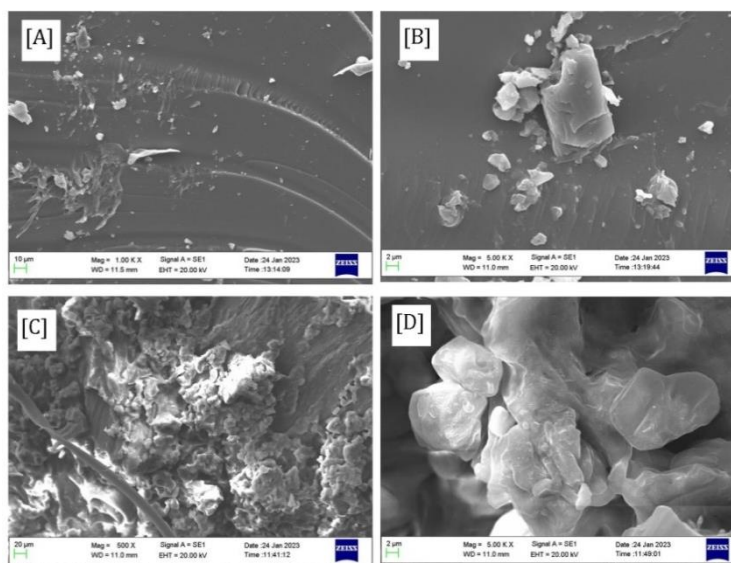
**Figure 4.** The influence of chitosan weight in the acrylic acid-chitosan based superabsorbent on the urea loading

Figure 4 shows that the superabsorbent ability to load urea was very good, which can reach 86.75% to 96.4%. Increasing the amount of chitosan in the superabsorbent based on acrylic acid-chitosan decreased the loading of urea. The addition of 0.5 g of chitosan was able to contain urea 96.4%. The increase in the amount of chitosan in the superabsorbent can increase the cross-linking thereby reducing the absorption capacity of fluids. This condition caused a decrease in the amount of urea that can be loaded in the superabsorbent. The high urea loading value in this study showed that the acrylic acid-chitosan based superabsorbent can be utilized as a carrier to release urea slowly.

### 3.5. Characterization of superabsorbent based on acrylic acid-chitosan

#### 3.5.1. Scanning Electron Microscope (SEM)

Surface morphology analysis of the superabsorbent made from acrylic acid-chitosan was carried out using SEM instrumentation. The superabsorbents before and after being loaded with urea fertilizer were analyzed. The results of the SEM analysis are shown in Figure 5.

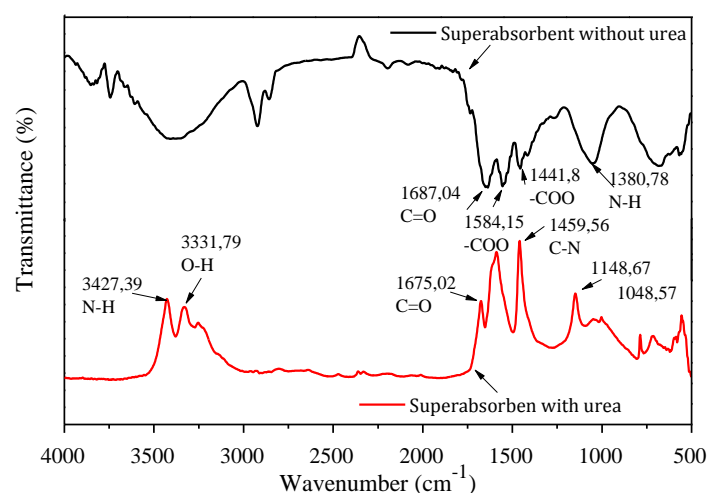


**Figure 5.** Morphological analysis of superabsorbents before and after loading with urea at various magnifications; [A] superabsorbent before loading urea with urea at 1000× magnification; [B] superabsorbent before loading urea at 5000× magnification; [C] superabsorbent after loading urea at 500× magnification; [D] superabsorbent after loading urea at 5000× magnification

Figure 5 shows the differences in the morphological analysis of the superabsorbent surface before and after loading urea. The surface of the superabsorbent before loading urea has a smooth surface as shown in Figures 5A and 5B., even though at a magnification of 5000×, the surface of the superabsorbent still looks smooth. On the other hand, based on Figures 5C and 5D, the superabsorbent surface is visible flakes that stick to the surface and are indicated as urea attached to the superabsorbent surface. The urea not only enters the superabsorbent but also presents on the surface. Fang et al. [15] reported that superabsorbents have a smooth surface and a porous structure. The capacity and rate of water absorption can both be increased by the linked pore structure.

#### 3.5.2. Fourier Transform Infrared (FTIR)

FTIR analysis is used for qualitative or quantitative analysis of functional groups in a compound. Figure 6 shows the FTIR analysis results of superabsorbents before and after loading urea fertilizer.



**Figure 6.** FTIR analysis for superabsorbent before and after loading urea fertilizer

The FTIR spectrum in Figure 6 for the superabsorbent loading urea fertilizer shows that the C=O stretching frequency appears at  $1675.02\text{ cm}^{-1}$ . The N–H stretching frequency appears at  $3427.39\text{ cm}^{-1}$ . The C–N stretching frequency appears at  $1459.56\text{ cm}^{-1}$ . The FTIR spectrum of the chitosan-graft poly-acrylic acid shown in Figure 6 contains several functional groups analyzed such as: stretching the carbonyl (C=) of amide I at  $1687.04\text{ cm}^{-1}$ , and two other bands assigned to asymmetric and symmetric stretching of  $-\text{COO}-$  groups at  $1584.15$  and  $1441\text{ cm}^{-1}$ . In addition, the band used for strain vibration and bending of the C–N bond in the amide III band is at  $1380.78\text{ cm}^{-1}$ . Absorption bands resulting from raw chitosan could not be found, which confirmed that  $-\text{NH}_2$ ,  $-\text{NHCO}$  and  $-\text{OH}$  of chitosan took part in the graft reaction with acrylic acid [15].

#### 4. Conclusion

Superabsorbents made from acrylic acid-chitosan were successfully prepared with various chitosan weights for grafting onto acrylic acid. The weight of chitosan influenced the superabsorbent properties such as swelling ratio (49.38 g/g to 49.38 g/g), water retention (0.43%–0.89% after 7 days), reusability (reswelling), and urea loading (86.75% to 96.4%). Increasing the amount of chitosan added can improve the superabsorbent properties, but adding too much chitosan can reduce the superabsorbent properties. The loading of urea in the superabsorbent was quite high so this superabsorbent can be used as a carrier to release urea slowly. Based on the SEM analysis, the superabsorbent had a smooth surface and a porous structure. Furthermore, based on the functional group analysis, it can be concluded that chitosan was grafted onto the acrylic acid chain.

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