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The Preparation of Controlled Release Fertilizer Based on Gelatin Hydrogel Including Ammonium Nitrate and Investigation of its Influence on Vegetable Growth

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Abstract: A controlled release fertilizer (CRF) systems based on gelatin hydrogel was prepared to improve fertilizer use efficiency and minimize its negative impact on environment. Gelatin hydrogel was synthesized by using glutaraldehyde (GA) as crosslinker and its swelling/degradation behaviors were investigated. Ammonium nitrate (AN) was loaded into the gelatin hydrogel and its releasing was followed. Release of AN from gelatin beads versus time was followed, and it is found that the release gently increased at first and then complied between 40-50 h. The releasing date shows that the prepared AN/gelatin hydrogel system could be named as a CRF. The efficiency of gelatin hydrogel beads including AN were examined on the vegetable growing using cucumber seeds. Plant growth and stem elongations measurements presents the formed hydrogel beads could be successfully used as a CRF system. It can be concluded that the CRF system produced in this study is much promising in utilizing a natural resource like gelatin in the production of matrix material, which could significantly reduce the production costs and offer a quite environmental friendly alternative technique.

Keywords: Gelatin, Controlled release fertilizer, Ammonium nitrate, Plant growth, STEM elongation

Introduction

Fertilizer and water are essential factors that limit agricultural production. The main purpose of fertilizer application is to provide nutrients to plants in order to increase the yields. So it is very important to improve the utilization of water resources and fertilizer nutrients [Ni et all, 2007]. However, about 40-70% of nitrogen and 80-90% of phosphorus of the applied normal fertilizers cannot be absorbed by plants. They are released to the environment which causes not only large economic and resource losses but also a very serious environmental pollution [Corradini et all., 2010].

Researchers and fertilizer producers have attempted to discover advanced techniques for fertilizer usage that can improve nutrient use efficiency and minimize environmental impacts. One possible way to overcome this problem is controlled released fertilizer (CRF) usage. CRFs are broadly defined as products that release nutrients to soil for plant uptake at a pre-determined time and rate (Trenkel, 2007). Compared to the conventional type, CRFs have many advantages such as (1) decreasing fertilizer loss rate, (2) supplying nutrients sustainable, (3) lowering application frequency and (4) minimizing potential negative effects associated with over dosage [Al-Zahrani, 1999].

CRFs can be divided into 3 categories based on their coating and nutrient composition. (1) Uncoated, nitrogen-based fertilizers are the oldest class of CRF that consist of chemically-bound urea and the release rate is determined by particle size, available water, and microbial decomposition e.g. (2) Coated, nitrogen-based fertilizers – Sulphur-coated urea is one of the first CRF. Thickness of sulphur coating controls the nitrogen discharge. (3) Polymer-coated or polymer matrix multi-nutrient fertilizers. All principal classes of polymers, i.e.

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plastics, coatings, elastomers, fibers and soluble polymers are presently utilized in applications that include the controlled release of nutrients [Chandra and Rustgi, 1998]. In this type of CRF, thicknesses, porosities and swelling behaviors of polymers control the release of nutrients.

Hydrogels have been extensively studied and preferred for a large number of applications in much kind of industrial fields [Pulat and Asıl, 2009; Pulat et all., 2011]. Because of their excellent characteristics, hydrogels can also be used for controlled release of agrochemicals and nutrients in agricultural and horticultural applications [Rafaat et all, 2012].

Most of the synthetic polymers used to prepare hydrogels causes some problems because of their long degradation times and degradation products. Natural polymers are a good choice to overcome this issue. Gelatin is a biodegradable natural polymer with extensive industrial, pharmaceutical, and biomedical uses that has been employed for coatings and microencapsulating various drugs, and for preparing biodegradable hydrogels [Pulat and Akalın, 2013]. Since it is soluble in aqueous solutions, the materials for long-term applications must be submitted to crosslinking, which improves both thermal and mechanical stability of gelatin. Among the chemical crosslinking agents, glutaraldehyde (GA) is by far the most widely used due to its high efficiency of collagenous materials stabilization [Bigi et al, 2001].

In recent years, our studies focused on gelatin hydrogels as a controlled-release material. Based on our pervious works about hydrogels and controlled-release systems, in this study it is intent to develop a CRFs based on gelatin hydrogel (Pulat et al., 2014). The swelling/degradation behaviors of the hydrogel were determined and ammonium nitrate (AN) was chosen as fertilizer to be controlled of release. The objective of this study was to investigate the effect of AN loaded gelatin hydrogels on the germination rate and early development of tomato and cucumber seedlings.

Methods

Preparing and Characterization of Gelatin Hydrogel

In this study, gelatin (Fluka, Type B, 280-Bloom, from pig skin) hydrogel was prepared by mixing 10% of aqueous gelatin solutions with 25% of GA (Aldrich, 25% aqueous solution). Gelatin/GA mass ratio is arranged as 1/0.5. Crosslinking reaction was preceded for 24 h at room temperature in a glass tube. The fresh hydrogel rods were taken from the tube and were cut into pieces 0.5 cm long. After the discs were left overnight at room conditions, they were washed several times with distilled water to remove unreacted chemicals.

Gravimetric tests were carried out, and the formula given below was used to determine hydrogel formation (HF) percentage [Chen et al, 2005]. Dried and weighed samples were placed in water for 48 h to extract the unreacted monomers and then dried.

$$HF(\%) = \frac{m}{m_0} \times 100 \qquad (1)$$

where m and mo are the weights of the dried hydrogel after and before extraction, respectively.

Swelling test of hydrogel sample was gravimetrically carried out. First, the dried hydrogel sample were left to swell in the Britton-Robinson buffer (BRB) (pH = 7.0) at 30˚C. Swollen gel was taken from the swelling medium at regular intervals, and dried with filter paper, weighed, and placed into the same bath. Measurements were performed to constant weight and the percentage swelling (S%) values were calculated using the equation given below [Chen et al, 2005]:

$$S(\%) = \frac{mw - md}{Md} \times 100 \qquad (2)$$

where mw is the wet weight of the sample, and md the dry weight of the sample before swelling.

Degradation test of hydrogel samples were carried out at pH 7.0 and 30°C. Dried hydrogel discs were left to swell in BRB solution. At the end of 48 h, swollen gels were dried and weighed. Then the hydrogels placed into the same bath and the procedure was repeated until they completely degraded. The degradations were determined using the following formula:

$$\text{Degradation } (\%) = \frac{Mm - Mt}{Mm} \times 100 \qquad (3)$$

where Mm and Mt are the weights of hydrogel at the maximum swollen stage and at time t.

Loading of AN and Release Studies

In this study, fertilizer-entrapped hydrogel samples were prepared by adding particular amounts of AN (Merck) (53 mg per disc) into the gelatin-GA mixture during crosslinking reactions (Bajpai and Giri, 2002). AN release was followed spectrophotometrically at a wavelength of 305 nm for 60 h. AN-entrapped samples were placed into 100 mL of water. At different times, aliquots of 0.2 mL were drawn from the medium to follow the AN release: a maximum of 30 aliquots were taken, so the volume could be considered constant. The AN release always maintained sink conditions. The cumulative release of AN was calculated by using the equation given below:

$$\text{Release } (\%) = \frac{W_t}{W_{total}} \times 100 \qquad (4)$$

where Wt is the weight of the released fertilizer in the releasing medium at any time, and Wtotal represents the initial total weight of the fertilizer entrapped into the gel system.

Effects of AN loaded Discs on Vegetable Growth

Effect of the hydrogels containing AN on vegetable growth was investigated by following germination and shooting periods. The test conditions were summarized into Table 1.

Healthy and uniformly sized tomato and cucumber seeds were selected and sown into the prepared soil pots. Seeding depth was 3 cm. Seed germination experiments were carried out with 4 sets. First pot set doesn’t contain any AN disc. 3, 6 and 9 discs were placed in other pot sets at 1.5 cm depth. Watering schedule is given in Table 1. A series of photographs were taken during experiment days. The seed germination percentage (SG) was calculated from the following formula (Jayarambabu et al. 2016):

$$SG\ (\%) = \frac{Sg}{S} \times 100 \qquad (5)$$

Where, Sg is number of germinated seeds and S is total number of seeds.

Height of stems was measured using ruler starting from the base to the tip of the plant. Stem elongation yields (E%) were calculated using following formula:

$$E\ (\%) = \frac{Hs - Hc}{Hc} \times 100 \qquad (6)$$

Where, Hs and Hc are the stem height of the sample and control.

Table 1. Growing test procedure

Sets	**AN-3 :** 3 discs in one pot **AN-6:** 6 discs in one pot **AN-9**: 9 discs in one pot **C** : Control, not includes fertilizer.
Specification of Soil	Torf (Gertengold), 4 L per pot. pH: 6 - 7 ; %0.4-1.0 N; 150-300 ppm of F; 600-1200 ppm of K.
Seeds	Cucumber (*Cucumis sativus* L.,Fento Tohumculuk) Tomato (*Solanum lycopersicum*, Fento Tohumculuk)
Seeding procedure	4 L torf per pot. 50 tomato seeds per pot 10 cucumber seeds per pot, seeding depth are 3 cm.

	Depth of hydrogel discs are 1.5 cm.
Watering schedule	0.5 L per pot every other day during first 15 days (germination period). After two weeks, same amounts for each day (growing period).

Results and Discussion

Characterization of Gelatin Hydrogel

Gelatin hydrogel discs were produced as described in the methods. HF was calculated via Equation 1 and the result was given in Table 2. The primary purpose of this study is to obtain high efficiency for hydrogel preparing. 94% value is a very satisfactory result.

Swelling behavior was followed at a regular temperature 30 ºC and calculated vis Equation 2. S% increased with time initially, and then remained constant at close to 48 h. and the maximum value was reached as 218%. Swelling profile of a hydrogel is an important parameter and directly affects the release behavior. On the other hand, degradation time should be compatible cumulative fertilizer release. The time of 100% degradation of prepared hydrogel was found as 60 days. The results presented in Table 2 are very satisfying.

Table 2. HF, maximum swelling (MS) and time of 100% degradation (DT)

HF (%)	MS (%)	DT (day)
94	218	60

AN Release

The release profile of AN from gelatin hydrogel is calculated via Equation 4 and presented in Figure 1. As seen from this figure, AN release gently increased at first and then complied near 50 h. Full of the loaded fertilizer were released at the end of the release time. Release behavior of the hydrogel was similar to swelling profiles.

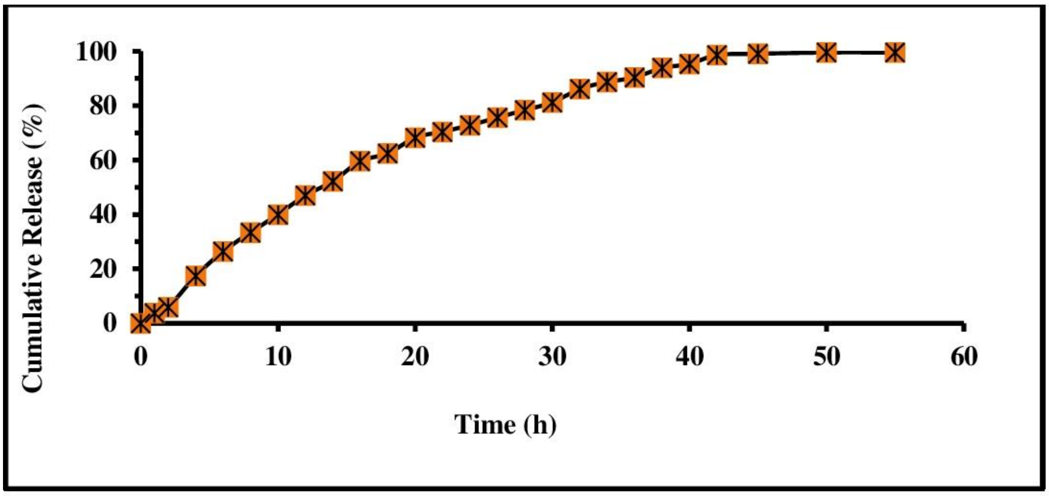

Figure 1. Cumulative release of AN through gelatin hydrogel

The results of the present work indicate that the gelatin hydrogels are good support materials for controlled release of AN with their excellent swelling/degradation capability.

Effects of AN loaded Hydrogel Discs on Vegetable Growth

Seed germination and plant growth of vegetables were followed as described above by taking photographs. As seen from Figures 2-3, the maximum growth was observed for the samples containing 9 hydrogel discs per pot. The less germination and elongation were obtained for control groups.

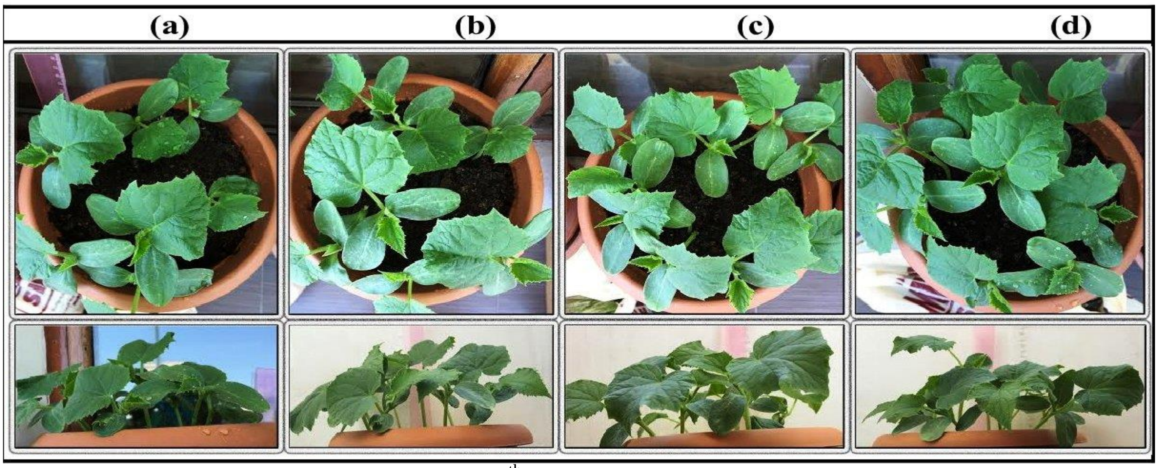

Figure 2. Cucumber growths at 35th day. (a) Control (b) AN-3 (c) AN-6 (d) AN-9

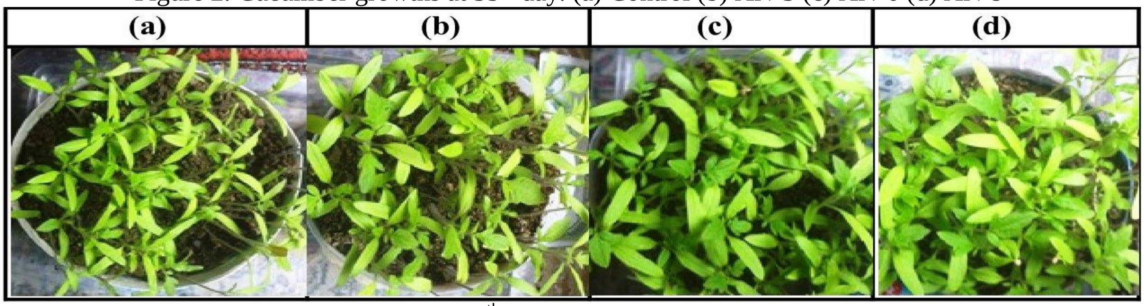

Figure 3. Tomato growths at 35th day. (a) Control (b) AN-3 (c) AN-6 (d) AN-9

The variations of vegetable germination by time were presented in the Figures 4-5. As seen from these figures, the germination was nearly completed at 15 days. The less value was obtained for control groups. The maximum germination was reached for the sample containing 9 hydrogel discs.

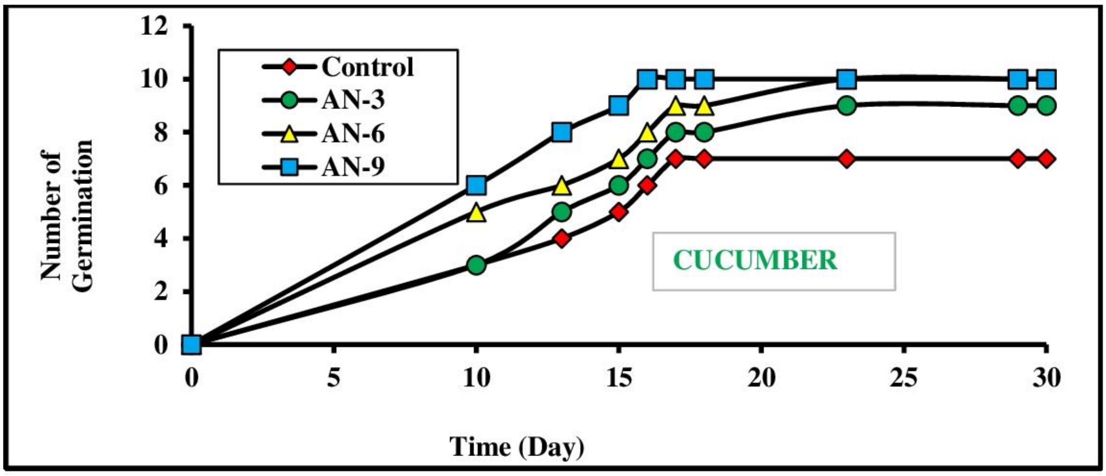

Figure 4. Variation of cucumber germination by day

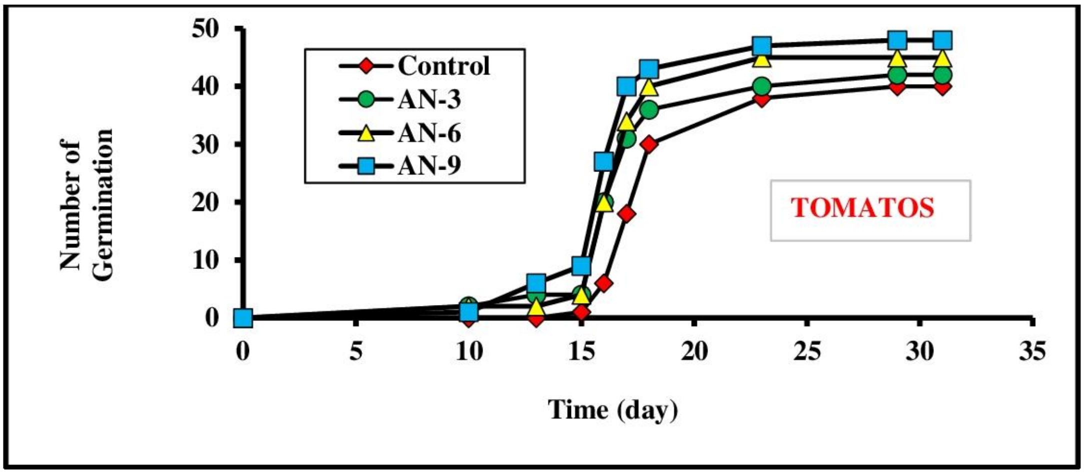

Figure 5. Variation of tomato germination by day

SG (%) values were calculated using Equation 5 and presented in Table 3. The percentage values changed from 70 to 100 for cucumber and from 76 to 94 for tomatos. It is clear that AN included hydrogel discs positively affect the seed germination for all samples.

Table 3. SG (%) and E (%) values of vegetables

Seed	SG (%) at 23th day				E (%) at 35th day			
	Control	AN-3	AN-6	AN-9	Control	AN-3	AN-6	AN-9
CUCUMBER	70	100	100	90	-	7	29	42
TOMATOS	76	90	94	80	-	8	25	41

Stem elongation of cucumber and tomato were followed in every day and the variations were presented in Figure 6-7. As seen from these graphs, stem elongation of control groups is less than the samples included AN/hydrogel discs.

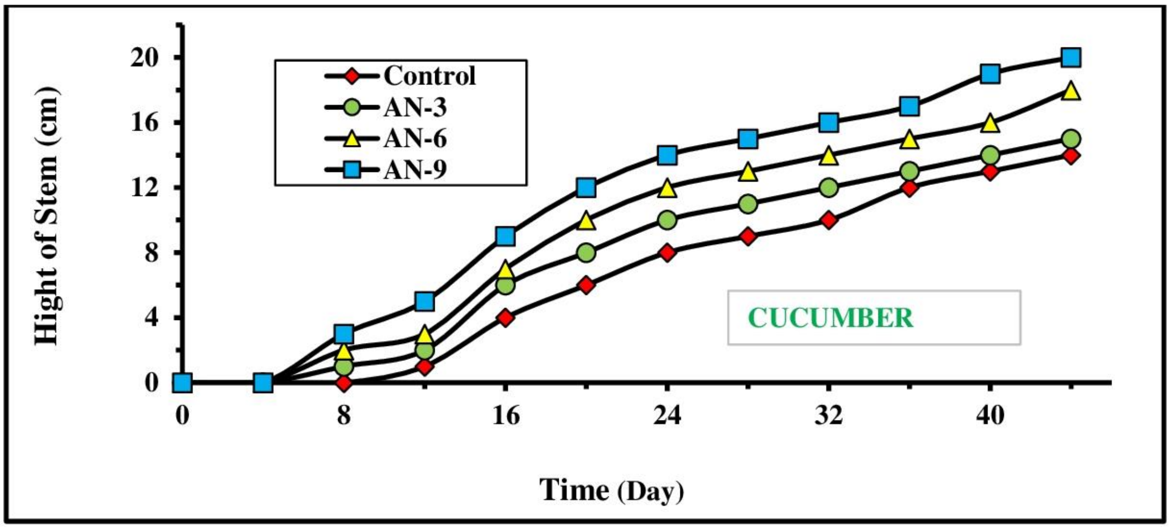

Figure 6. Stem elongation of cucumber

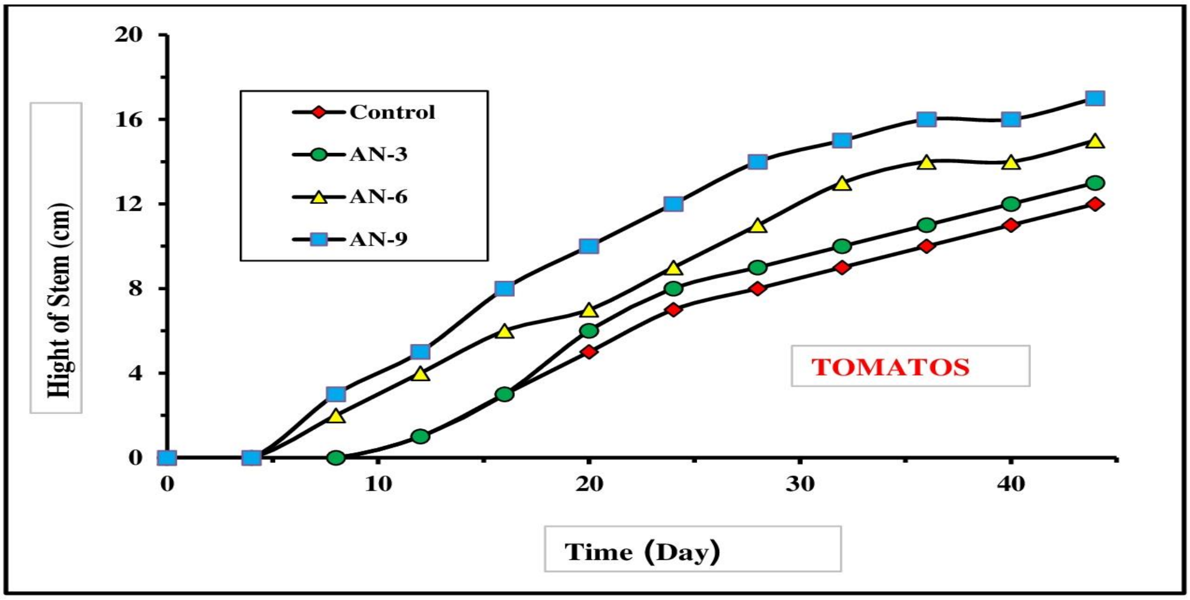

Figure 7. Stem elongation of tomato

Conclusion

It can be concluded that the CRF system produced in this study is much promising in utilizing a natural resource like gelatin in the production of matrix material, which could significantly reduce the production costs and offer a quite environmental friendly alternative technique.

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