Original Research Article

SYNTHESIS OF COATED UREA AND ITS RELEASE PATTERN

.

ABSTRACT

The main aim of this paper is to develop three different type of urea fertilizer coating with ethyl cellulose and starch- super absorbent polymer and to study its effectiveness in the slow release of nitrogen. The synthesis and characterization of the coated fertilizer was carried out in Department of Nanoscience and Technology, *TNAU, Coimbatore-03, India. A column experiment was also set up at Radioisotope Laboratory in TNAU Coimbatore-03, India for a period of 30 days.* The column experiment consists of 5 treatments and 3 replications with a Completely Randomized Block (CRD) design. The treatments consist of control, uncoated urea, Ethyl cellulose (EC), Starch-Super absorbent polymer (SAP) and EC+Strach-SAP coating. Double coated urea (EC+Starch-SAP) shows best nitrogen slow-release pattern among the three coating types with a release of only 40% of nitrogen in the first day of incubation and shows release of nitrogen till the 20th day.

Keywords: Ethyl cellulose, Super Absorbent polymer, Potato starch, Hydrogels, slow release fertilizer

1. INTRODUCTION

Fertilizer of any form is an indispensable part and one of the highest impacting inputs in crop production. According to the UN, Department of Economy and Social Welfare, the world population is estimated to reach 9.6 billion by the year 2050. With the growing population in the country and around the world and the task of feeding millions, there is a growing demand for foods and other agro-products. This often resulted in larger amount of fertilizer application so as to procure a higher yield for crops. The three primary nutrients, nitrogen (N), phosphorus (P) and potassium (K), since are required in higher quantity by plants, are often supplied by chemical fertilizers in a larger quantity. Urea is one of the most extensively used fertilizer source for nitrogen all over the world. To fulfill supply and demand, around 200 million tons of urea fertilizer are produced globally at the moment. However, due to inefficiency, a quarter of the urea applied to soils is lost to the environment [1].

Urea has the highest solubility in water. In comparison to other nitrogenous fertilizers, urea supplies higher nitrogen to plants and soil due to its high nitrogen concentration. Urea fertilizer has a high nitrogen content of 46% by dry weight but however the nitrogen use efficiency ranges from 20-30 %. This is due to the loss of nitrogen through volatilization and leaching to a great extent. It can also cause high environmental risks and pose a serious threat to the marine life such as eutrophication in water bodies, degrades soil fertility, implications for human and ecosystem health, greenhouse gas balances and biological diversity [2]. Controlled and slow-release fertilizers (CSRF) approach is the main strategy adopted to delay nutrients dissolution according to the plant's needs [3]. Numerous researches have been done in the field of coated fertilizers where various coating materials have been explored. The coating of fertilizer can be of a single layer or even coated with a double layer for a further slow-release behavior in various cases.

Ethyl cellulose is a water-insoluble cellulose ether that is extensively used in pharmaceutical film coating [4]. Food grade ethyl cellulose is among the few water-insoluble non-toxic films and thickeners. Super absorbent polymers are known to have of a three-dimensional network with a high capacity to absorb and hold a large amount of water. They swell and absorb water to a great extend to the point where they can absorb up to hundred times their own dry weight and hardly removable under a certain pressure [5]. In an attempt to develop novel dual-layer slow-release fertilizers, different starch materials which are obtained from plants have also been tested for their slow-release behavior. The three main starch sources largely studied were maize, cassava and potato [6].

In the present paper, urea granules are coated with a layer of Ethyl Cellulose, Starch-Superabsorbent polymer and as a double layer where Ethyl Cellulose acts as the inner coating and Starch- Superabsorbent polymer acts as the outer coating. The starch source in for the starch-SAP is potato starch. Potato starch has a high-water imbibing capacity compared to other plant-based starch sources [7]

2. MATERIAL AND METHODS

2.1 Materials

The Chemicals used for the synthesis of the coating materials were all procured and supplied from Prassad Associate, Coimbatore. The chemicals ethyl cellulose, stearic acid and acrylamide were manufactured by Nice Chemicals (P) Ltd. from Kochi, Kerela, India. Ceric ammonium nitrate was manufactured by S. D. Fine Chemicals limited in Mumbai, India. The N,N'-methylene-bisacrylamide, or N,N'-MBA were obtained from Sisco Research Laboratories Pvt. Ltd., Maharashtra, India. Every other chemical used in the current work is of the reagent grade and is readily available commercially.

2.2 Preparation of Ethyl Cellulose and Starch-Super Absorbent Polymer

Ethyl Cellulose solution was prepared by mixing 9-part Ethyl Cellulose and 1-part Stearic acid in a 6.25% Ethanol. Since Ethyl cellulose is highly hydrophobic, they are not readily soluble in water. After the mixture is mixed thoroughly, the urea granules are then sprayed with the ethyl cellulose solution so as to evenly coat the urea granules in a tray. The urea granules after coating with the ethyl cellulose were then left to dry in room temperature.

The starch-superabsorbent polymer was prepared by mixing 12 g starch in 45 ml of distilled boiling water. After which 18 g acrylamide and 0.14 g N,N'-methylene-bisacrylamide, or N,N'-MBA was added to the mixture. This was allowed to mix at a magnetic stirrer at a rate of 80 rpm for 10 minutes. After mixing for 10 minutes, the solution begins to gelatinize. 0.75 g of Ceric ammonium nitrate (CAN) was dissolved in a boiled water. The temperature was then decreased to 60^{o} C before adding Ceric ammonium nitrate (CAN) solution into the mixture. This was then allowed to mix again for 10 minutes at 80 rpm. After a few minutes from adding the Ceric ammonium nitrate (CAN) solution, the mixture begins to gelatinize even more. In this reaction Ceric ammonium nitrate (CAN) acts as the initiator while N,N'-MBA acts as the crosslinker. Crosslinking reagents (or crosslinkers) are those molecules that have a reactive side of two or more that are able to bind themselves or attach themselves to a specific functional group on a protein or other molecule [8].10 g of Sodium hydroxide (NaOH) dissolved in 20 ml distilled water was added to the mixture. Sodium hydroxide (NaOH) acts as a saponification agent. Wash the product with methanol successively so as to remove any free polymer which may be present in the mixture. Methanol also acts as a dewatering solvent. The final starch-super absorbent polymer were then dried to keep them in a constant weight in a hot air oven at $60\text{-}70^{o}$ C. The products were then grinded and pulverized to a fine powder. The final coating of urea fertilizer are given in figure 1.

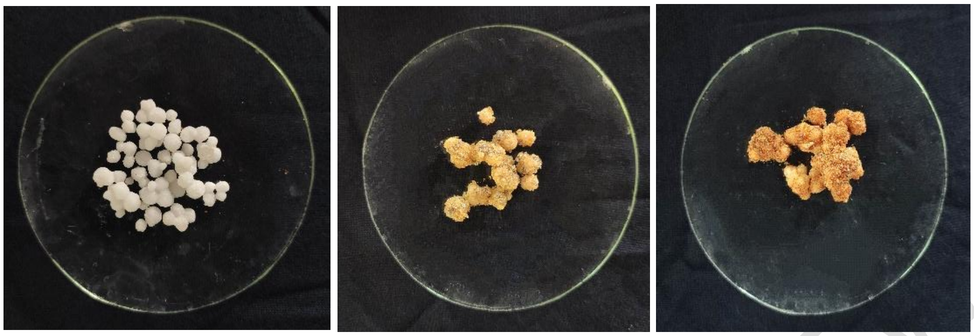


Figure 1: (a) Ethyl Cellulose (EC) coating (b) Starch-Super absorbent polmer (SAP) coating (c) EC + Starch-SAP coating

2.3 Characterization

2.3.1 Scanning Electron Microscopy (SEM)

The morphology of the coated fertilizers was observed using the Scanning Electron Microscopy, Techno FEI (SEM) in Department of Nanoscience and Technology, TNAU, Coimbatore. Sputter coating is done for all the samples before running the sample in the instrument. Sputter coating for SEM is the process of applying an ultra-thin coating of electrically-conducting metal – such as gold (Au), gold/palladium (Au/Pd), platinum (Pt), silver (Ag), chromium (Cr) or iridium (Ir) onto a non-conducting or poorly conducting specimen [9].

2.1.2 Fourier transform infrared spectroscopy (FTIR):

The ethyl cellulose and starch-SAPs' infrared spectra were obtained using FT/IR-6800 type A model which is DTGS (deuterated triglycine sulphate) detector-equipped from Department of Nanoscience and Technology, TNAU. The spectra were collected at a resolution 4 cm^{-1}.

2.1.3 Water absorbent capacity (WAC):

One of the basic requirements for a polymer to be specified as an SAP is that dry polymeric substances must absorb twenty times or more of their original weights from water, saline, or physiological solutions [10]. The SAPs were measured for their water absorbent capacity by putting 0.5 grams of the SAPs into a mesh cotton cloth bag. The bag was then allowed to be immersed into a pool of distilled water in a beaker for approximately 1 hour at room temperature. After the bag was taken out, the surface of the bag was lightly taped dry so that the excess water was removed. Each water absorbed starch-SAP was weighed in terms of its net weight. The water absorbent capacity was calculated using the formula:

$$WAC(g/g) = (M_1 – M_2)/M_2$$

where M_1 (g) is the weight of swelling starch SAPs and M_2 (g) is the weight of dried starch SAPs, respectively. All of the results are averages of three replicates.

2.4 Column Experiment

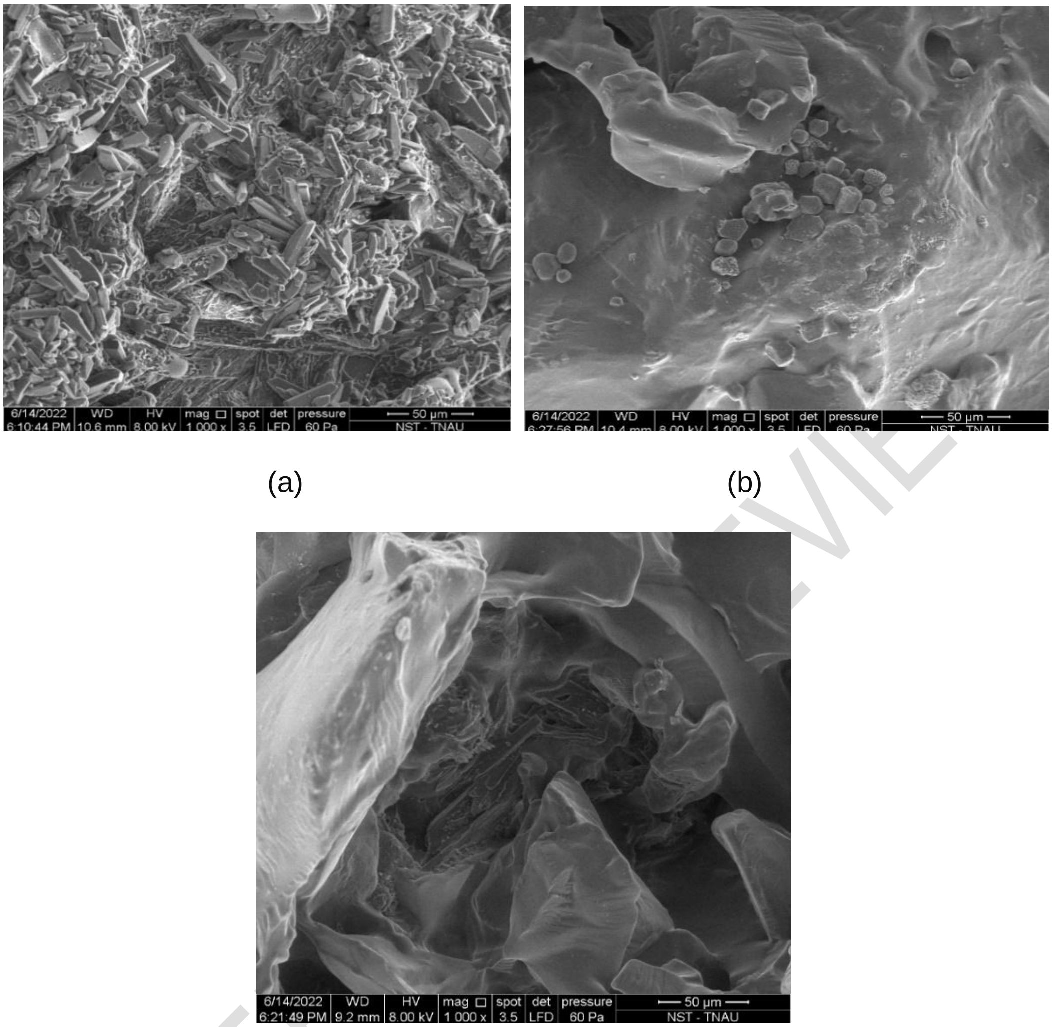
A column experiment was set up to study the leachate from the coated fertilizer and to study their release patterns. The columns were set up in the Radioisotope laboratory, TNAU, Coimbatore. The column experiment consists of 5 treatments and 3 replications with a Completely Randomized Block (CRD) design. Each columns were filled with approximately 500 g of soil collected from Vaiyampalayam, Tamil Nadu with 11.1356° N, 77.0035° E coordinates. The type of soil in use for this experiment was black calcareous soil and has a sandy clay loam texture. The soil physicochemical properties were analysed before carrying out the column experiment. The available nitrogen was found to be low (213 kg/ha) [11], the available P is in a medium range (18 kg/ha) [12] and available K is found to be high (543 kg/ha) [13]. It has a medium availability of organic carbon with 0.56 % [14]. The soil pH is 8.30 which is slightly alkaline in nature and the EC of the soil is 0.95 dSm^{-1}.

The leachate was collected at different intervals on 1,2,3,4,10,15,20 and 30 days. The columns were filled with water to their field capacity. The leachates were collected and analyzed for their ammonium-N (NH_4^+-N) and nitrate-N (NO_3^--N). Ammonium was distilled using magnesium oxide, and nitrate was reduced to ammonium using a ball-milled Deverda alloy [15]

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

The SEM micrograph of Ethyl Cellulose and SAP coatings are shown in Figure 2. The EC membrane does not swell and is compatible with a wide range of plasticizers and pore-forming chemicals [16]. The pore spaces which can be seen in the SEM images show the potential locations for penetration of water. The swelling process involves the following actions: solvent molecules permeate the polymeric network structures. Simultaneously, the molecular chains between the cross-linked sites stretch, lowering their enthalpy values. This new molecular network structure has elastic contractive pressures, which amplifies the networks' contraction tendency [17]. Starch-SAP absorbed a substantial amount of water due to the hydrophilicity of $–COO^-$ groups and the associated osmotic pressure. Because the starch-SAP molecular chains (glucan and polyacrylamide) crosslinked by N-MBA created strong grid walls, a significant fraction of water could be trapped in the grids, which were analogous to the superporous hydrogel's interconnected pores [18].



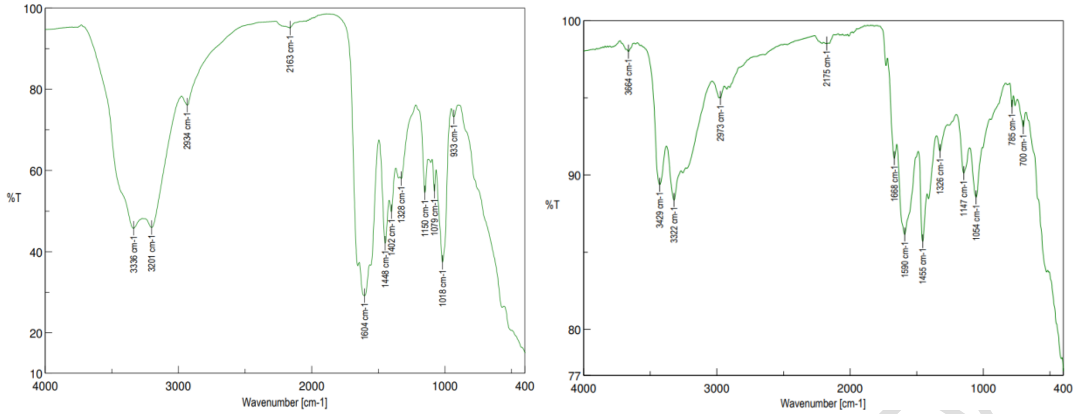
(a) (b)

(c)

Figure 2: SEM images of EC, SAP and EC+SAP coated urea.

3.2 Fourier transform infrared spectroscopy (FTIR):

The Starch-SAPs when analyzed shown in figure 3 (a) a typical IR bands which includes a strong band of N-H stretching adsorption (1604 cm^{-1}), C-N stretching was also observed (1402 cm^{-1}) and C-O stretching can be attributed to the bands at 1150 cm^{-1} [19]. The bands for the ethyl cellulose sample in figure 3 (b) show a $C=CH_2$ type of bond with the adsorption peak of 2973 cm^{-1}. The bands at 3322, 2175, 1590, and 1054 cm^{-1} can be attributed to O-H, C-H, C=O and C-O stretchings respectively [20].



(a) SAP coating (b) EC Coating

Figure 3: FTIR images of (a) SAP coating (b) EC Coating

3.3 Water absorbent capacity (WAC)

The Water absorbent capacity (WAC) of the starch-SAP was approximately 70 times its initial weight or dry weight (0.5 g) (Figure 4). SAPs may hold over absorbed fluids under pressure because of their loosely cross-linked structures and hydrophilic nature, which allows the hydrophilic groups to be hydrated in an aqueous environment, resulting in a hydrogel structure. Therefore, the starch-SAP can hold and imbibe a large amount of water in it before slowly releasing it to its surrounding.

Surface-cross-linked particles kept their forms during the swelling process. This results in a less tightly packed gel bed with air gaps, allowing fluid to flow freely in a high permeability pattern. This is related to the micron-scale grid size and the nanoscale fractal gel characteristics. For instance, the smaller grid size caused by shorter polyacrylamide (PAM) chains may boost capillary forces in the micro-porous structure and improve the availability of the hydrophilic groups to water during hydration due to a greater specific surface area [21].

Figure 4: (a) Dried starch-SAP (0.5 g) (b) Swelled starch-SAP

3.4 Column experiment

The uncoated urea has the highest amount of leaching in the first four days of incubation which is a typical release pattern for uncoated urea. The urea coated with Ethyl Cellulose releases 58% of the cumulative nitrogen and gradually increases till the 10th day. The slow release pattern of Ethyl cellulose coated urea fertilizer can be due to the inert property and hydrophobicity of the ethyl cellulose [22]. For the case of urea coated with Starch-SAP alone, the release of nitrogen in the first day is comparatively higher than EC coating. This can be attributed to the fact that the Starch-SAP has the ability to imbibe large portion of the water applied. Urea was dissolved in the water retained by the Starch-SAP network and diffused outwards through the network due to the osmotic gap between the network's inner and outer walls [23]. The double coated urea (EC+SAP) showed the highest slow release pattern with a release of only 40% of nitrogen in the leachate. The release pattern was the longest which shows a release upto 20 days. Water could constantly travel through the EC layer as the starch-SAP layer swelled, gradually dissolving the fertilizer core. The pace at which the dissolved nutrient diffused from the fertilizer core into the soil would be substantially influenced by the starch-SAP barrier permeability.

The NH_4^+-N was found to be higher in the initial leachate collected from all the 5 different columns. There is then a gradual decrease in the NH_4^+-N content from the 4th day in the leachates. The decrease in NH_4^+-N leaching might be attributed to the loss of NH_3 (ammonia) through volatilization or the transformation of NH_4^+-N to NO_3-N through nitrification [24]. An increase in NO_3-N in the leachate from the controlled-release fertilizers towards the end of the leaching trial shows that urea must be released from the coating for further hydrolysis and nitrification over a prolonged duration of time [25].

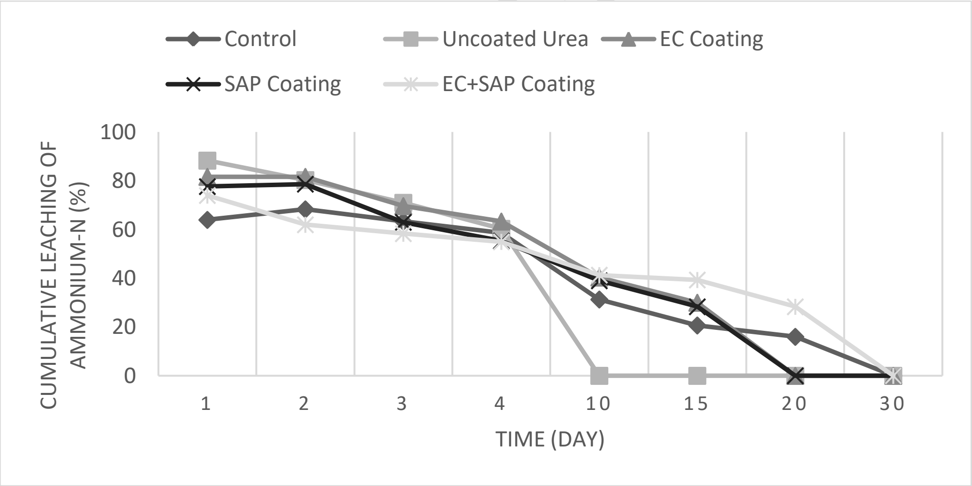


Figure 5: Effect of time in cumulative leaching of Ammonium-N

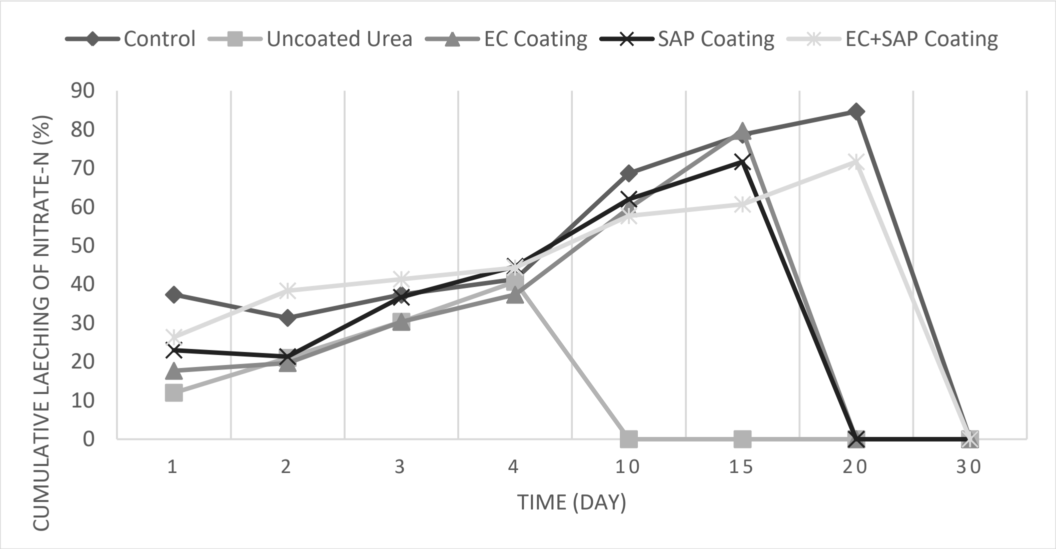


Figure 6: Effect of time in cumulative leaching of Nitrate-N

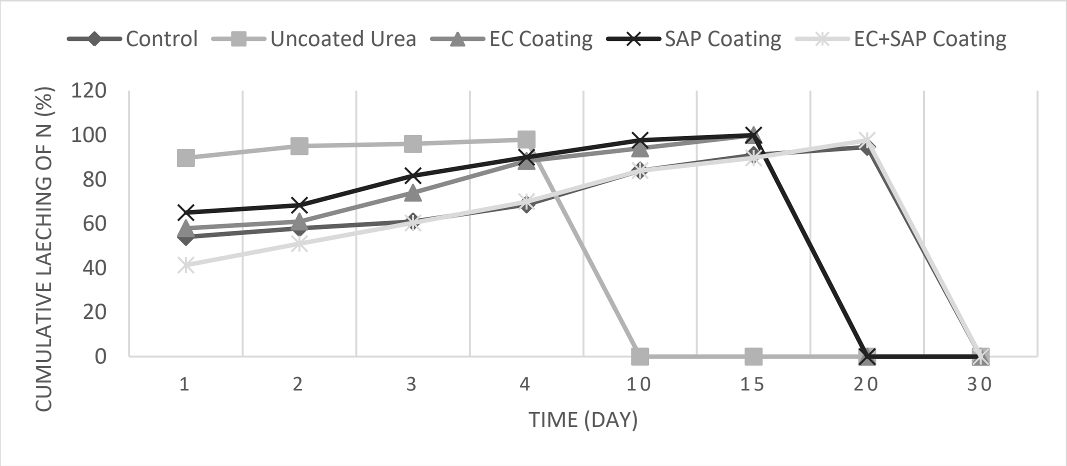


Figure 7: Effect of time in cumulative leaching of Nitrogen

4. CONCLUSION

To summarize, in the present study, the preparation and synthesis of Starch-Super absorbent polymer from potato starch was demonstrated. The water absorbent capacity (WAC) of Starch-SAP was also examined where it can hold 70 times its dry weight. Coating of urea fertilizer with three types of coating, namely with EC, Starch-SAP and EC+Starch-SAP was synthesized and release pattern was studied. From the column experiment conducted, the release rate of the different coating of urea was determined. Of the three different type of coatings, double coated urea (EC+Starch-SAP) shows the best slow-release pattern for nitrogen.

REFERENCES

1. Beig, Bilal, Muhammad Bilal Khan Niazi, Zaib Jahan, Arshad Hussain, Munir Hussain Zia, and Muhammad Taqi Mehran. "Coating materials for slow release of nitrogen from urea fertilizer: A review." *Journal of plant nutrition* 43, no. 10 (2020): 1510-1533
2. Cui, Yanjun, Yongsheng Xiang, Yumei Xu, Jia Wei, Zhifang Zhang, Li Li, and Jing Li. "Poly-acrylic acid grafted natural rubber for multi-coated slow release compound fertilizer: Preparation, properties and slow-release characteristics." *International Journal of Biological Macromolecules* 146 (2020): 540-548.
3. Davidson, Drew, and Frank X. Gu. "Materials for sustained and controlled release of nutrients and molecules to support plant growth." *Journal of agricultural and food chemistry* 60, no. 4 (2012): 870-876.
4. Hyppölä, Riikka, Isabelle Husson, and Franciska Sundholm. "Evaluation of physical properties of plasticized ethyl cellulose films cast from ethanol solution Part I." *International journal of pharmaceutics* 133, no. 1-2 (1996): 161-170.
5. Yu, Yeli, Yong Zhang, Xiaogang Yang, Hongyi Liu, Lan Shao, Xiumei Zhang, and Juming Yao. "Biodegradation process and yellowing mechanism of an ecofriendly superabsorbent based on cellulose from flax yarn wastes." *Cellulose* 22, no. 1 (2015): 329-338
6. Qiao, Dongling, Hongsheng Liu, Long Yu, Xianyang Bao, George P. Simon, Eustathios Petinakis, and Ling Chen. "Preparation and characterization of slow-release fertilizer encapsulated by starch-based superabsorbent polymer." *Carbohydrate polymers* 147 (2016): 146-154
7. Grommers, Hielko E., and Do A. van der Krogt. "Potato starch: production, modifications and uses." In *Starch*, pp. 511-539. Academic Press, 2009.
8. Hermanson, Greg T. *Bioconjugate techniques*. Academic press, 2013.
9. Ramalho, Jéssica Reais. "Heparin functionalization of fibrin hydrogels for tissue engineering." PhD diss., Instituto Superior de Engenharia de Lisboa-Escola Superior de Tecnologia da Saúde de Lisboa, 2017.
10. ZOHOURIAN, MEHR MJAD, and Kourosh Kabiri. "Superabsorbent polymer materials: a review." (2008): 451-447.
11. Bremner, J. M. "Determination of nitrogen in soil by the Kjeldahl method." *The Journal of Agricultural Science* 55, no. 1 (1960): 11-33.
12. Olsen, Sterling Robertson. *Estimation of available phosphorus in soils by extraction with sodium bicarbonate*. No. 939. US Department of Agriculture, 1954.
13. Stanford, George, and Leah English. "Use of the flame photometer in rapid soil tests for K and Ca." (1949).
14. Walkley, Aldous, and I. Armstrong Black. "An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method." *Soil science* 37, no. 1 (1934): 29-38.

15. Akratanakul, Wanee. "The effect of soil temperature and soil moisture stress on S-urea mineralization and ryegrass yield." (1971).
16. Kaur, Gaganjot, Jasleen Grewal, Kiran Jyoti, Upendra K. Jain, Ramesh Chandra, and Jitender Madan. "Oral controlled and sustained drug delivery systems: Concepts, advances, preclinical, and clinical status." In *Drug targeting and stimuli sensitive drug delivery systems*, pp. 567-626. William Andrew Publishing, 2018
17. Braihi, A. "Superabsorbent polymers." *Univ Babylon* (2017).
18. Chen, Jun, and Kinam Park. "Synthesis and characterization of superporous hydrogel composites." *Journal of controlled release* 65, no. 1-2 (2000): 73-82.
19. Zou, Wei, Long Yu, Xingxun Liu, Ling Chen, Xiaoqing Zhang, Dongling Qiao, and Ruozi Zhang. "Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers." *Carbohydrate polymers* 87, no. 2 (2012): 1583-1588.
20. Hospodarova, Viola, Eva Singovszka, and Nadezda Stevulova. "Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials." *American journal of analytical chemistry* 9, no. 6 (2018): 303-310.
21. Kiatkamjornwong, Suda. "Superabsorbent polymers and superabsorbent polymer composites." *ScienceAsia* 33, no. 1 (2007): 39-43.
22. Zhang, Manxian, and Jisheng Yang. "Preparation and characterization of multifunctional slow release fertilizer coated with cellulose derivatives." *International Journal of Polymeric Materials and Polymeric Biomaterials* 70, no. 11 (2021): 774-781
23. Xiao, Xiaoming, Long Yu, Fengwei Xie, Xianyang Bao, Hongsheng Liu, Zhili Ji, and Ling Chen. "One-step method to prepare starch-based superabsorbent polymer for slow release of fertilizer." *Chemical Engineering Journal* 309 (2017): 607-616
24. Paramasivam, S., and A. K. Alva. "Leaching of nitrogen forms from controlled-release nitrogen fertilizers." *Communications in Soil Science and Plant Analysis* 28, no. 17-18 (1997): 1663-1674.
25. Wang, F. L., and A. K. Alva. "Leaching of nitrogen from slow-release urea sources in sandy soils." *Soil Science Society of America Journal* 60, no. 5 (1996): 1454-1458.