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Synthesis and Performance Evaluation of Cellulose-based Slow-release Fertilizer: A Review

Dhyna Analyes Trirahayu[1]✉, Ridwan P. Putra[2], Achmad Syarif Hidayat[3],
Muhammad Iqbal Perdana[4], Erwina Safitri[5]

[1)]Department of Chemical Engineering, Politeknik Negeri Bandung, Jalan Geger Kalong Hilir, Bandung, 40559, Indonesia
[2)]Graduate School of Engineering and Science, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo, 135-8548, Japan
[3)]Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[4)]Department of Science, Faculty of Science and Technology, Prince of Songkla University Pattani Campus, 94000, Pattani, Thailand
[5)]Department of Food and Agriculture Product Technology, Faculty of Agricultural Technology, Universitas Gadjah Mada, Jalan Flora 1, Bulaksumur, Yogyakarta, 55281, Indonesia

Abstract. Cellulose-based materials are attractive candidates for the fabrication of sustainable and eco-friendly slow-release fertilizers. The ability of the cellulose structure to be modified and functionalized makes it promising as a scaffold backbone in the development of advanced agricultural materials. In this review, different synthesis techniques of cellulose-based slow-release fertilizers are discussed. Crucial parameters in the design of the slow-release fertilizers (i.e., slow-release behavior, water retention properties, and biodegradability) are presented. The applications of cellulose-based fertilizers in enhancing the growth of agricultural and horticultural commodities are provided. To date, solution polymerization is more widely employed in the preparation of cellulose-based slow-release fertilizers due to its low cost and simple operation, with no solvent recovery required. Esterification tends to be the most typical reaction during the synthesis of the fertilizers because of its high substrate solubility and more straightforward product purification. This review can be used as a reference to develop other efficient cellulose-based slow-release fertilizers that can be utilized to delay the release of fertilizers and prevent the overuse of fertilizers.

Keywords: *slow-release fertilizer, cellulose, polymerization, water retention, biodegradability*

Abstrak. Material berbasis selulosa merupakan kandidat yang menarik dalam pembuatan pupuk lepas lambat yang ramah lingkungan dan berkelanjutan. Kemampuan struktur selulosa untuk dimodifikasi dan dimanfaatkan membuat material ini menjanjikan sebagai kerangka utama dalam pengembangan bahan pertanian maju. Dalam ulasan ini, beberapa teknik yang dapat digunakan untuk mensintesis pupuk lepas lambat berbasis selulosa dibahas. Parameter penting dalam desain pupuk lepas lambat (sifat retensi air, kinerja lepas lambat, dan biodegradabilitas) disajikan. Aplikasi pupuk berbasis selulosa dalam mempercepat pertumbuhan komoditas pertanian dan hortikultura disediakan. Hingga saat ini, teknik polimerisasi larutan lebih banyak digunakan dalam pembuatan pupuk lepas lambat berbasis selulosa dikarenakan oleh biayanya yang rendah dan pengoperasiannya yang sederhana, tanpa memerlukan pemulihan pelarut. Esterifikasi merupakan reaksi yang paling umum pada sintesis pupuk jenis ini dikarenakan kelarutan substratnya yang tinggi dan pemurnian produk yang lebih mudah. Tinjauan ini dapat digunakan sebagai referensi untuk mendukung pengembangan pupuk lepas lambat berbasis selulosa yang dapat digunakan untuk mengontrol pelepasan pupuk dan mengurangi penggunaan pupuk secara berlebihan.

Kata kunci: *pupuk lepas lambat, selulosa, polimerisasi, retensi air, biodegradabilitas*

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✉ Corresponding author
E-mail: dhyna.analyes@polban.ac.id

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INTRODUCTION

Cellulose-based materials have been widely used in various applications. In the paper industry, cellulose serves as a raw material due to its fibrous suspensions that cause fibrillation, hydration, and shortening of fibers. The transformation of cellulose fibers induces the rise of external fibrillation and flexibility that results in the enhanced linking potential and mechanical properties of the papers (Chaussy et al., 2011). The high tensile strength of natural cellulosic fibers and their antimicrobial properties make them potential in biomedical and textile applications (Guna et al., 2019). The capability of nanocrystalline cellulose to bind a substantial amount of ionizable water-soluble antibiotics can be implemented as a drug delivery excipient for solo use or in combination with other medicines (Jackson et al., 2011). As food ingredient, cellulose can be utilized as a source of dietary fiber with an excellent ability to absorb oil that can help maintain body weight, reduce cholesterol levels, and stimulate the digestive system (Yan et al., 2018). Cellulose derivatives are promising candidates for energy-efficient and sustainable building materials because of their strong mechanical strength and superior robustness (Sun et al., 2021).

The strong mechanical strength of cellulose has been associated with its decent chemical and physical properties. Cellulose contains carbon, oxygen, and hydrogen atoms that act as the skeleton of the material, confirmed using energy dispersive X-ray analysis (Krishnan et al., 2013). Another study on the crystalline cellulose reveals the presence of pockets within the cellulose structure (Williams et al., 2021). The pockets can be employed to accommodate and encapsulate various chemicals to protect them from degradation and loss before use. This potential property of cellulose motivates the implementation of the material in agricultural sectors to capture chemical fertilizer that is highly required to simultaneously foster the intensification of agriculture in the form of slow-release fertilizers.

Slow-release fertilizers are known as conventional fertilizers coated with macromolecule materials that delay the release of fertilizer to the soil that can efficiently supply the nutrients to the crops (Felix et al., 2015 & Blouin et al., 1967). These macromolecules can be either in the form of natural or semi-natural materials (Dos Santos et al., 2021 & Liu et al., 2020). The slow-release fertilizers offer a practical approach to achieving sustainable productivity that can simultaneously address various problems regarding agricultural sustainability and overuse of fertilizer (Guo et al., 2021).

Many materials have been developed as slow-release fertilizers. Graphene oxide films were utilized to encapsulate KNO_3 pellets as a slow-release fertilizer. The slow-release properties of the fertilizer can be significantly improved upon the reduction of graphene oxide on the KNO_3 pellets, with a prolonged 8 h fertilizer release when immersed in water (Zhang et al., 2014). Hydrogel/clinoptilolite nanocomposite was also introduced to prepare a new core-shell slow-release fertilizer to coat commercial NPK fertilizer. The study indicates that the nanocomposite layer induces the release of nutrients in a more controlled mode and possesses good water-retention properties (Rashidzadeh et al., 2015). Yang et al. (2011) investigated the prospect of a slow-release fertilizer based on dolomite phosphate rock for crop growing and landscapes to reduce the leaching loss of water-soluble fertilizers. The results show that the dolomite phosphate rock fertilizers are excellent for ryegrass growth in terms of dry-matter products and nutrient absorptions in the plant. Nevertheless, despite their good properties in retarding the release of fertilizers, the materials still suffer from environmental issues and resources depletion that prompt researchers to look for more biodegradable and sustainable materials.

Recently, cellulose-based materials are emerging as an attractive and promising candidate for fabricating environmentally friendly and sustainable slow-release fertilizers. A new slow-release fertilizer prepared from wheat straw cellulose semi-interpenetrating polymer networks exhibits slower nitrogen nutrient release in neutral condition and achieve an enhanced controlled-release performance in larger particle size (Li et al., 2016). With the encapsulation using nanocomposite based on carboxymethyl cellulose, the release of NPK fertilizer can be decelerated and the encapsulation can improve fertilizer utilization in agricultural and horticultural applications (Olad et al., 2018). Therefore, this review focuses on the synthesis methods, properties, and application of cellulose-based slow-release fertilizers. The most important properties in the design of slow-release fertilizers comprise water-retention properties, slow-release behavior, and biodegradability. To the best of our knowledge, no comprehensive review on cellulose-based slow-release fertilizer has been published to date.

SYNTHESIS METHODS OF SLOW-RELEASE FERTILIZER

The methods to prepare cellulose-based slow-release fertilizers are categorized into synthesis methods based on the reaction phase and type of reaction, as depicted in Figure 1.

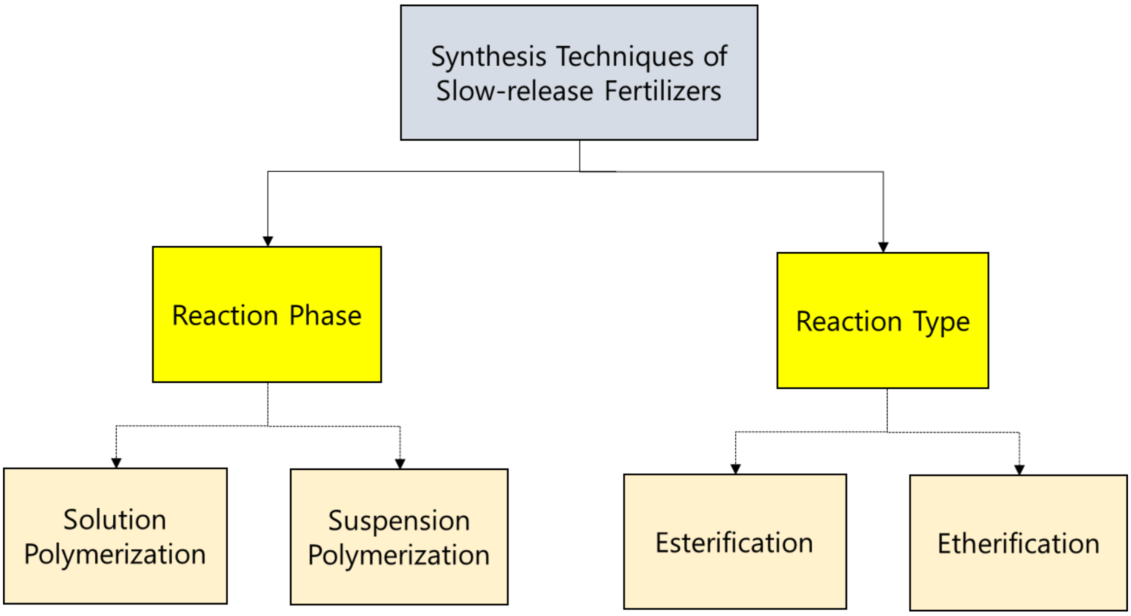

Figure 1. Diffferent techniques used to synthesize cellulose-based slow-release fertilizers.

Table 1. Slow-release fertilizers prepared using various techniques from the literature.

	Technique	Material	Ref.
Reaction Phase	Solution Polymerization	Semi-interpenetrating carboxymethyl cellulose-potassium-*g*-polyacrylic acid/polydimethylurea-potassium-phosphate (CMCK-*g*-PAA/PDMUP) polymer network fertilizer	Wang et al., 2021
		Slow-release fertilizer hydrogel based on coco peat-*g*-poly(acrylic acid)/NPK	Ramli et al., 2019
	Suspension Polymerization	Hydrogels based on poly(acrylic acid-*co*-acrylamide)/cellulose nanofibrils nanocomposites	Mahfoudhi et al., 2016
		Cellulose-based hydrogel produced from rice straw pulp	Abou-Baker et al., 2019
Type of Reaction	Esterification	Hydrogel based on cellulose acetate and ethylenediaminetetraacetic dianhydride (GEDTA)	Senna et al., 2015
		Slow-release fertilizer based on ethyl cellulose/starch phosphate carbamides (EC/SPC based SRU)	Zhang et al., 2020
	Etherification	Absorption resin based on acrylic acid-*co*-methyl cellulose-*g*-maleic anhydride (AA-*co*-MC-*g*-MA)	Li et al., 2020
		Slow-release fertilizer based on carboxymethyl cellulose immobilized microspheres (CFM)	Qi et al., 2019

According to the reaction phase of the reaction media, the commonly used technique include solution polymerization and suspension polymerization. Meanwhile, based on the type of reaction, the slow-release fertilizers are frequently prepared using esterification and etherification techniques to form macromolecules. The summary of the slow-release fertilizer synthesis studies using these techniques obtained from the literature is presented in Table 1.

Solution Polymerization

The solution polymerization method is performed by dissolving and reacting all reactants and chemical initiators in water (Figure 2a). This technique is widely used in the polymer industry (Galukhin et al., 2021). Wang et al. (2021) proposed a synthesis route of slow-release fertilizer composite obtained from waste straw. In their study, potassium hydroxide solution is added to the cellulose extract obtained from corn straw to attain CMC-K. Formaldehyde and urea are mixed separately to produce dihydroxyl-methyl-urea (DMU). The DMU is further mixed with potassium dihydrogen phosphate to produce polydimethylurea potassium phosphate (PDMUP). The polymerization reaction is performed by mixing CMC-K, acrylic acid, PDMUP, and N, N-methylenebis acrylamide (MBA) to obtain CMCK-*g*-PAA/PDMUP particles with phosphorus, nitrogen, and potassium content of 11.06%, 18.58%, and 11.29%, respectively.

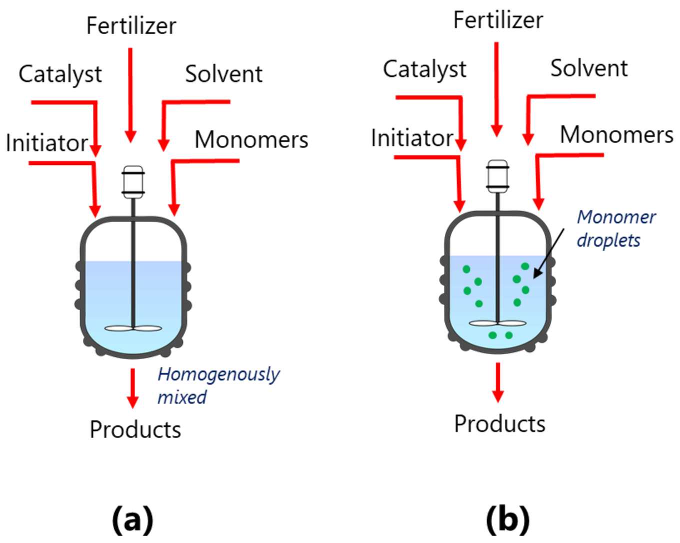

Figure 2. Scheme of (a) solution polymerization and (b) suspension polymerization reactions.

In another study, a slow-release fertilizer hydrogel of coco peat-*g*-poly(acrylic acid)/NPK [CP-*g*-P(AAc)/NPK] was synthesized by graft-copolymerization of coco peat fiber onto acrylic acid monomers with the addition of NPK 15-15-15 fertilizer (Ramli et al., 2019). The coco peat fiber contains lignocellulose as the major component, which comprises 43% cellulose, 8% hemicellulose, and 49% lignin (Thakur et al. 2015). A neutralized acrylic acid solution is initially mixed with MBA, fertilizer solution, and coco peat fiber. Ammonium persulphate solution, as a chemical initiator, is subsequently added to gel up the mixture. The final product is then dried and ground to 2 mm in size (Ramli et al., 2019).

Suspension Polymerization

Different from solution polymerization, suspension polymerization uses a monomer suspension kept under vigorous stirring during the reaction, with the formation of beads as the final products, as illustrated in Figure 2b (Zhang et al., 2011). This technique is widely utilized for the preparation of microsphere and microcapsules that the products can be recovered by simple filtration (Rattanasaikaew et al., 2020 & Ballard et al., 2017). Mahfoudhi et al. (2016) introduced a new technique to prepare hydrogels based on poly(acrylic acid-*co*-acrylamide)/cellulose nanofibrils nanocomposites. Fibers are initially pre-treated by a mediated oxidation technique to accelerate the disintegration process and produce cellulose nanofibrils (CNF) with a high yield. The nanocomposite is prepared by mixing neutralized acrylic acid with acrylamide and MBA to attain a clear solution. An appropriate amount of CNF suspension is combined with the mixture, followed by the addition of potassium persulphate chemical initiator under a nitrogen atmosphere. The reaction is run in a water bath, and the product is subsequently dried until a constant weight of the hydrogel is attained.

In 2019, Abou-Baker et al. studied the alteration of lignocellulosic biomass to a cellulose-based hydrogel. The graft polymerization reaction is conducted via vinyl polymerization of the rice straw pulp. Some lignin in the rice straw pulp is reduced using KOH solution under mechanical stirring. This treatment is also used to generate active sites on the cellulose chains. Afterwards, the resulting fibers are filtered and introduced with potassium persulphate and acrylic acid. The product suspension is then rinsed with ethanol and dried in an oven. To compare with the solution polymerization technique, the advantages and disadvantages of these two methods are summarized in Table 2.

Table 2. Advantages and disadvantages of solution polymerization and suspension polymerization.

Technique	Advantages	Disadvantages	Ref.
Solution Polymerization	• Straightforward • Low-priced • Relatively safe • Convenient • Solvent recovery is unnecessary	• High product viscosity • Prone to gel formation • Difficulty to produce highly concentrated and large polymer • Drying process requires energy • More susceptible to agglomeration	Zhang et al., 2002 Wang et al., 2010
Suspension Polymerization	• Cost-effective • Excellent heat reaction control • Simple • Wide design latitude	• Large particle sizes of the products (2-4000 µm) • Small number of water soluble monomers • Low productivity • Buildup of polymer on the reactor surfaces • Non-continous production	Chen & Fang, 2011 Alehosseini et al., 2019 Mahabadi et al., 1996 Yuan et al., 1991

Esterification

The esterification process involves acid and alcohol to form ester and water molecules (Nanthagopal et al., 2016). This process is catalyzed by Brønsted acids, e.g., sulfonic, sulfuric, and hydrochloric acids (Schuchardt et al., 1998). A typical esterification reaction is written in Equation (1). With R_1OH as the molecule with an alcohol functional group, R_2COOH as the molecule with a carboxylic functional group, and R_2COOR_1 is the ester product in the form a single-molecule.

$$R_1OH + R_2COOH \rightleftharpoons R_2COOR_1 + H_2O \qquad (1)$$

When the reaction is a polymerization esterification, the reaction is shown in Equation (2). With HOR_1OH as the molecule with two alcohol functional groups, $HOOCR_2COOH$ as the molecule with two carboxylic functional groups, and $-(R_2COOR_1)_n-$ is the ester product in the form of a polymer chain. The R_1 and R_2 can be equivalent.

$$HOR_1OH + HOOCR_2COOH \rightleftharpoons -(R_2COOR_1)_n- + H_2O \qquad (2)$$

Senna et al. (2015) studied the synthesis of hydrogel generated from cellulose acetate as a coating agent for slow-release NPK fertilizer via esterification. The hydrogels are prepared from cellulose acetate solubilized in dimethylformamide crosslinked with ethylenediaminetetraacetic dianhydride. The esterification crosslinking reaction is catalyzed by trimethylamine with a neutralization of carboxylic acid moieties using aqueous $NaHCO_3$ to increase the affinity of water. Subsequently, the final product is purified, washed with distilled water and ethanol, dried, and sieved to yield a white granular product.

Table 3. Advantages and disadvantages of esterification and etherification.

Technique	Advantages	Disadvantages	Ref.
Esterification	- Thermodynamically more favorable than hydrolysis - High substrate and product solubility in organic solvents - Simple product isolation and purification - Mild reaction media	- Expensive - Stringent operating conditions - Long technological processes - The formed water (as a by-product) induces hydrolysis reaction of the ester product - Water removal is very important during the reaction	Kumar et al., 2016 Seo et al., 2021 Karakhanov et al., 2018 Ning et al., 2014 Zhao et al. 2011
Etherification	- The conversion is less sensitive to temperature - More likely to proceed at a lower temperature - More effective and typical strategy for regioselective substitution - Ether bond is more stable than ester bond	- Less favorable for long-chain alcohols - More unreacted alcohols are present after the reaction - Reduces the acid strength as the catalyst - Prone to dimerization	Di Girolamo et al., 2001 Haugaard et al., 2001 Friis-Pedersen et al., 2008 Fox et al., 2011 Pourchez et al., 2006

Zhang et al. (2020) developed esterification modified starch by urea and phosphates using a solvothermal technique as a urea slow-release fertilizer. Here, the starch phosphate carbamides (SPC) are employed as outer coating substance, along with ethyl cellulose as the inner coating layer. The SPC was synthesized using a facile alcohol solvothermal technique from corn starch, urea, monosodium phosphate, and disodium phosphate. The materials were poured into an autoclave containing an ethanolic and water mixture. Carbamoylation and phosphorylation of starch enhance the yield of starch products because of the reaction of the hydroxyl groups in the isocyanic acid and /or phosphate with the hydroxyl moieties of the starch. The final product was rinsed and dried in a vacuum oven.

Etherification

In the etherification process, a reversible chemical reaction of alcohols is carried out to generate ether with acid as a catalyst (Yee et al., 2014). In comparison with the esterification reaction, the advantages and disadvantages of these two methods are summarized in Table 3. A typical etherification reaction is written in Equation (3). With R_1OH as the first molecule with an alcohol functional group, R_2OH as the second molecule with an alcohol functional group, and R_1OR_2 is the ether product in the form of a single-molecule.

$$R_1OH + R_2OH \rightleftharpoons R_1OR_2 + H_2O \qquad (3)$$

When the reaction is a polymerization etherification, the chemical reaction is stated in Equation (4). With HOR_1OH as the first molecule with two alcohol functional groups, HOR_2OH as the second molecule with two alcohol functional groups, and $-(R_1OR_2)_n-$ is the ether product in the form of a polymer chain. The R_1 and R_2 can be identical.

$$HOR_1OH + HOR_2OH \rightleftharpoons -(R_2OR_1)_n- + H_2O \qquad (4)$$

Li et al. (2020) introduced a UV polymerization technique to prepare maleacylated methyl cellulose acrylic acid absorbent resin via etherification, methyl cellulose modification, and acrylic acid grafting. The synthesis is performed with the modification of methyl cellulose using maleic anhydride and acrylic acid. In the study, the etherification process takes place during the preparation of methyl cellulose from the cellulose of waste cotton stalks.

In 2019, Qi et al. proposed a synthesis route of carboxymethyl cellulose microspheres with fertilizer excellent release behavior. The carboxymethyl cellulose is mixed with β-cyclodextrin and NaOH in deionized water. Epichlorohydrin as a crosslinking agent is then poured into the system to produce the microspheres. Characterization of the microspheres using Fourier transform infrared spectroscopy verifies the formation of a new ether bond that is formed during crosslinking process.

PROPERTIES OF SLOW-RELEASE FERTILIZER

Water-retention Properties

Water-retention properties are of key importance in the design of effective slow-release fertilizers in agriculture applications (Olad et al., 2018). The materials work by gradually releasing water when the soil is too dry due to humidity drop in the soil. These parameters indicate the correlation of moisture content, saturation degree, void ratio, and total unit weight with respect to the negative water pressure in the pores (Pineda Jaimes et al., 2020). The water retention properties are investigated by mixing a certain amount of slow-release fertilizer with soil (Olad et al., 2018). The fertilizer is initially mixed with soil. Distilled water is subsequently added into the mixture and weighed (W_o). The exact amount of soil and distilled water, without the addition of slow-release fertilizer, was mixed as control (W). The mixture is then maintained at room temperature and weighed on a daily basis (W_t). The water retention is calculated using Equation (5).

$$\text{WR (\%)} = \frac{W_t - W}{W_o - W} \times 100 \qquad (5)$$

Durpekova et al. (2021) developed a biopolymer hydrogel from cellulose derivatives and acid whey to improve the water retention capacity of the soil. The hydrogels are prepared by mixing carboxymethyl cellulose and hydroxyethyl cellulose with a 3:1 weight ratio. Citric acid with a concentration of 5, 10, 15% (w/w), respectively, is subsequently introduced into the corresponding mixture to form H5CA, H10CA, and H15CA, respectively. The variation is aimed to produce hydrogels with various degrees of crosslinking. The results indicate that soil samples treated with the hydrogel show a significant humidity increase due to enhanced water uptake capacity. Among all materials used in this study, H15CA tends to exhibit the highest water retention and exceeds the water retention of pure soil (almost 30%) as shown in Figure 3.

Using cellulose nanocrystals-filled polyvinyl alcohol nanocomposites (PVA@CNC), Kassem et al. (2021) prepared waterborne coating materials used for NPK fertilizer with excellent water retention behavior. The materials are prepared from cellulose nanocrystals produced from raw hemp stalks via hydrolysis using sulfuric acid. The nanocrystals are subsequently mixed with polyvinyl alcohol and sonicated to yield PVA@CNC nanocomposite. The study shows that the nanocomposite exhibits excellent water retention capacity compared with uncoated fertilizer. The CNC-filled PVA coating layers are generated by ingenuous CNC and PVA blending without chemical grafting or crosslinking of synthetic superabsorbents. From the study, it was obtained that untreated soil shows 46% water holding capacity, while soil treated with various concentrations of PVA@CNC from 6-14.5% exhibits 49.86-51.58% water holding capacity. Similar results were also observed in our previous studies on the water holding capacity of polymer materials. The water holding capacity tends to be affected by the hydrophobicity of the polymer materials (Putra et al., 2020 & Putra et al. 2021).

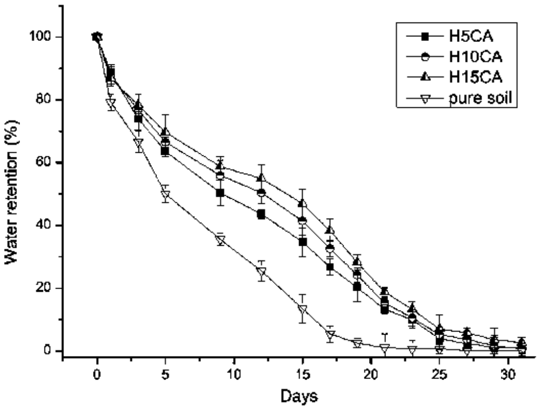

Figure 3. Water retention capacity (%) of soil mixed with H5CA, H10CA, and H15CA. Reprinted under Creative Commons license CC BY 4.0 from Durpekova et al. (2021).

Slow-release Behavior

Slow-release behavior indicates controlled fertilizer release of the material. The slow-release behavior of cellulose-based slow-release fertilizers can be determined using a soil leaching column. A typical soil leaching column is shown in Figure 4. This behavior is investigated by pouring water into the column filled with the treated soil sample. The filtrate will flow through the bed and subsequently be collected in a bottle. The filtrate can be analyzed further using conventional chemical procedures, chromatography, and spectrophotometry techniques.

Zhang et al. (2021) studied a multifunctional slow-release fertilizer prepared from urea, ethyl cellulose, thiourea, and cellulose-based superabsorbent polymer incorporating biochemical inhibitors dicyandiamide. The study indicates that the nitrogen rate release in the material decreases significantly compared with uncoated urea. The release rate observed is 0.2, 15.1, and 58.6% measured on the 4th, 7th, and 15th day, respectively. This implies that the material possesses excellent slow-release properties, which can prevent nutrient losses due to delayed release of the fertilizer.

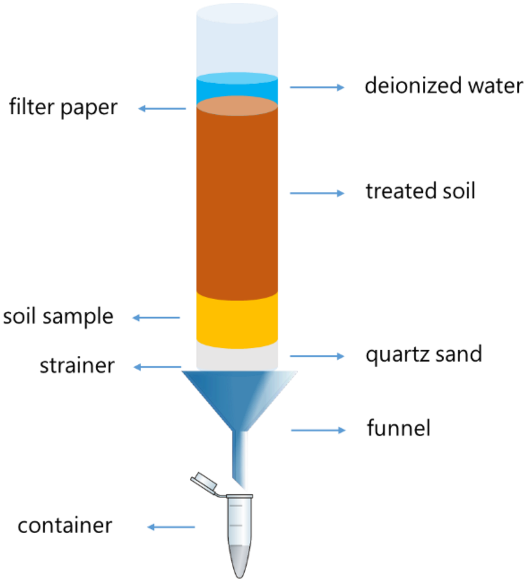

Figure 4. A typical soil leaching column used to investigate the slow-release behavior of slow-release fertilizers.

In another study on the synthesis of a superabsorbent based on corn straw cellulose with slow-release properties, corn straw cellulose, acrylic acid, polyvinyl alcohol, and ammonium polyphosphate were crosslinked to produce CSC-*g*-AA/PVA-APP (Wang et al., 2020). The study shows that the control groups with ammonium polyphosphate exhibit an increased leaching rate, with a single N leaching loss of 42.33% occurring at the first leaching cycle. Meanwhile, the N leaching loss is significantly reduced in CSC-*g*-AA/PVA-APP groups, with a single leaching loss value of 10.05% happening at the fourth leaching cycle. The study reveals that the treated samples showed decreased and delayed N leaching due to the presence of chemical bonds in the polymer chain. The adsorption and steric hindrance hamper the nutrient diffusion due to enlarged hydrogel.

Biodegradability

The biodegradability of slow-release fertilizers is an important aspect that determines the extent and time frame of the material in the soil decomposed by biological agents (Pischedda et al., 2019). Slow-release fertilizers with high biodegradability are required in agricultural applications that can prevent environmental pollution and other negative impacts on living organisms caused by chemical agents. This property is investigated using a soil burial degradation test (Salimi et al., 2020). Some amount of the slow-release fertilizer is wrapped (W_o) and buried under a soil surface inside a container. The soil moisture content is kept at a specific value by frequently adding deionized water. At every certain time interval, the sample is taken out and dried. The dried slow-release fertilizer (W_f) is used to calculate the percentage of degradation rates as justified in Equation (6).

$$DEG\ (\%) = \frac{W_0 - Wf}{W_o} \times 100 \qquad (6)$$

Pushpamalar et al. (2018) proposed eco-friendly smart hydrogels as a slow-release fertilizer that can improve the quality of soil and control fertilizer release. The hydrogels are prepared using electron beam irradiation on carboxymethyl sago pulp (CMSP). The sago pulp is transformed into CMSP with various degrees of substitution (DS). The soil burial tests carried out for 4 months revealed that the degradation of CMSP hydrogel with a DS of 0.4 was the fastest among all of the hydrogels tested in this study. The results show that these materials can be completely degraded within 3 months. The deterioration of the materials is more severe in the materials with a DS of 0.6 than 0.8. The biodegradability of the materials is also affected by the glass fiber content (%GF) in the hydrogels, with the material with a %GF of 25% showing the highest biodegradability rate.

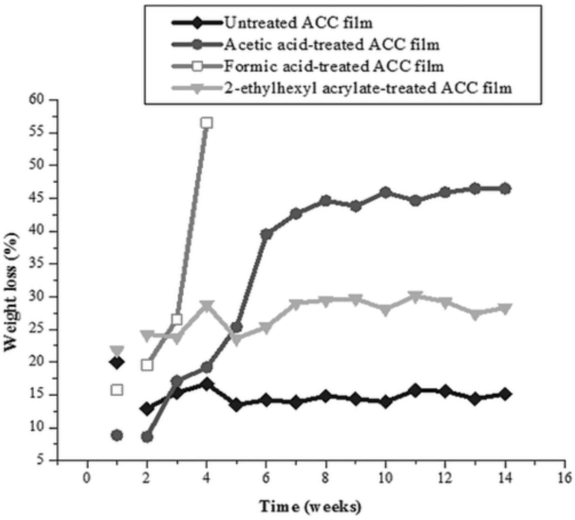

Figure 5. Biodegradatility rate of untreated and treated ACC films buried in the soil. Reprinted under Creative Commons license CC BY 4.0 from Zailuddin et al. (2020).

Zailuddin et al. (2020) introduced all-cellulose composite (ACC) films from oil palm empty fruit bunch. The ACC films are synthesized from the oil palm empty fruit bunch and microcrystalline cellulose treated with different chemical treatments, i.e., acetic acid, formic acid, and 2-ethylhexyl acrylate. The biodegradability rate of the materials was investigated by burying the materials into the soil and measuring the percentage of weight loss. The results indicate that the chemically treated ACC films exhibit higher degradation rates compared to the untreated films (Figure 5). This is likely due to higher moisture absorption values of the treated ACC films that promote the microorganism growth and accelerate film decomposition.

In another study, acid whey and cellulose derivatives-based biopolymer hydrogel as a slow-release fertilizer also exhibited excellent biodegradability (Durpekova et al., 2021). The study showed that the hydrogels were degraded by microorganisms in the soil for around 55.4% after 5 days and 95.2% after 20 days. Characterization using scanning electron microscopy (SEM) also indicated the formation of cavities in the hydrogel structure (Figure 6). As can be seen, the structure started to collapse after 20 days. The study reveals that a hydrogel with natural antimicrobial substances is likely to enhance the sustainability of the material in the environment.

APPLICATIONS OF SLOW-RELEASE FERTILIZER TO FOSTER PLANT GROWTH

Cellulose-based fertilizers have been implemented in various agricultural sectors to enhance the production of agricultural and horticultural commodities. In 2006, Abed et al. introduced the synthesis of four polymeric matrixes from hydroxyethyl cellulose. To investigate the performance of the materials as slow-release fertilizers, biological experiments were conducted. As much as 100 mL of the materials are mixed with 4 kg air-dried soil and fifty barley seeds are planted in the medium. The results show that polymeric fertilizers improve the seeds germination from 93% to 100%. The fresh weight of the plant shoot part also increases from 5.2 g/medium (without polymeric fertilizer) to a maximum of 15.47 g/medium (with the employment of polymeric fertilizer).

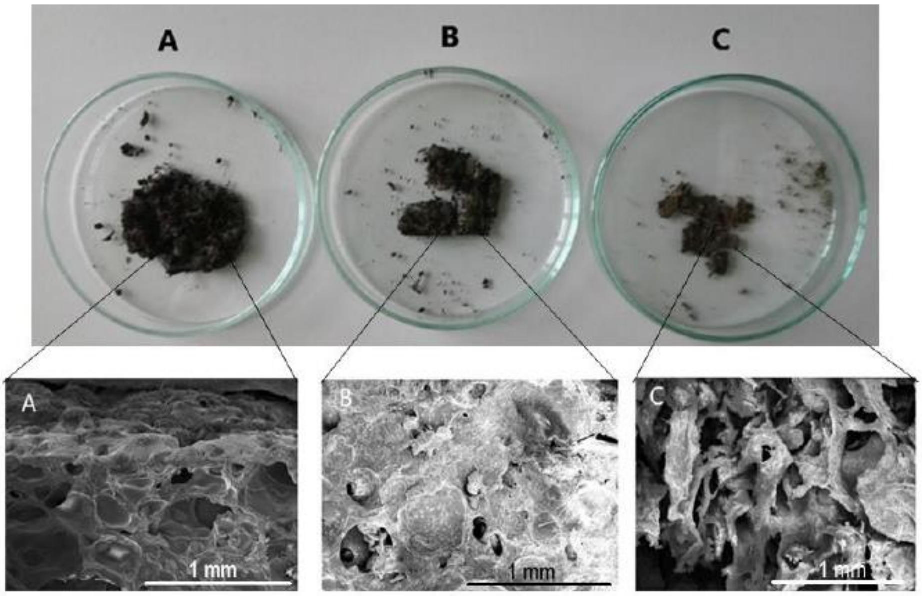

Figure 6. Physical appearance and SEM images of H15CA hydrogel in soil after 5 days (a), 10 days (b), and 20 days (c). Reprinted under Creative Commons license CC BY 4.0 from Durpekova et al. (2021).

Mohammadbagheri et al. (2021) introduced a novel superabsorbent from modified cellulose with slow-release urea fertilizer. The glucose compounds in polymeric structure of cellulose are transformed into 2,4-dihydroxy-3-(1-hydroxy-2-oxoethoxy) butanal, followed by condensation to form 5,7-dihydroxy-6-((1-hydroxy-4-oxopent-2-en-1-yl)oxy) hept-3-en-2 one unit (CCDEUs). The CCDEUs are further grafted and mixed with other materials to yield an environmentally-safe CCDEUs-*g*-poly(AA)/urea superabsorbent material. Growth test performance is performed by preparing two clay pots consisting of 200 g of soil blended with the material (CCDEUs-*g*-poly(AA)/urea) and 200 g of soil mixed with the material with no urea (CCDEUs-*g*-poly(AA)). Three pinto bean seeds of the same size are put in each clay pot, and distilled water is subsequently poured to saturate the soil. According to the study, the CCDEUs-*g*-poly(AA)/urea significantly influences plant growth. The results indicate that the seeds placed in the soil added with CCDEUs-*g*-poly(AA)/urea germinate, and the shoots reach 3, 19.8, and 22 cm, respectively, after 10 days. Meanwhile, only two seeds in the CCDEUs-*g*-poly(AA) treated soil germinate with a lower shoot length of 2 and 10.2 cm, respectively. This implies that the urea incorporated in the network structure of the coating material is gradually released into the water that can be implemented in the agricultural sector as an effective slow-release fertilizer.

CONCLUSIONS

In summary, numerous cellulose-based slow-release fertilizers have been widely developed to control the release of fertilizers and prevent the overuse of fertilizers. Based on the reaction phase, the synthesis methods of the slow-release fertilizers include solution polymerization and suspension polymerization. Meanwhile, the synthesis techniques are categorized into esterification and etherification reactions according to the reaction type. Based on the literature, solution polymerization is more broadly utilized in the synthesis of cellulose-based slow-release fertilizers because of its low cost and simple operation, with no solvent recovery required. Esterification is found to be the most typical reaction during the preparation of the fertilizers due to its high substrate solubility and more simple product purification. The studies show that cellulose-based slow-release fertilizers possess excellent water retention properties, slow-release behavior, and material biodegradability. The materials have been implemented in various agricultural applications to enhance the growth and production of agricultural and horticultural commodities. Further research is required to obtain highly effective slow-release fertilizers that can be produced and commercialized on a large scale.

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