BIODEGRADABLE POLYMER LAYERS FOR PRODUCTION OF SMART UREA FERTILIZER BY COATING PAN SYSTEM

NGHIÊN CỨU MÀNG POLYMER PHÂN HỦY SINH HỌC ĐỂ SẢN XUẤT PHÂN URE THÔNG MINH BẰNG THIẾT BỊ BỌC DẠNG ĐĨA

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ABSTRACT

This paper presents the results of synthesis of biodegradable polymer layers from modified starch, coated urea technology by coating pan system and evaluates the efficiency of smart urea fertilizers (SUFs) experimentally. The results indicate that graft copolymers of polymer photsphated starch crossed linked with polyvinyl alcohol and polyacrylic acid helps slowing the release of urea through the layer into the environment. SUFs were produced by a coating pan has diameter 0.2 m, speed is 50 rpm, angle of inclination 40°, dry temperature 60°C. Release efficiency of SUF with the synthetic layer is evaluated by the time that 70% of urea was released, was up to 360 minutes and more than 60 times the uncoated urea fertilizer. The paper also presents the results of urea concentration of SUFs released in soil environment and the release rate is 8.5 ppm/day. They are the basis for the production and use of SUFs in green agricultural production.

Keywords: *coating pan system; green agricultural production; modified starch; release; smart ureafertilizer.*

TÓM TẮT

Bài báo trình bày kết quả tổng hợp các loại màng polymer phân hủy sinh học từ tinh bột biến tính, công nghệ bọc phân urê bằng thiết bị bọc dạng đĩa và đánh giá hiệu quả các loại phân urê thông minh (SUFs) bằng thực nghiệm. Kết quả xác định được màng bọc đồng polymer giữa tinh bột biến tính phot phat liên kết ngang với polyvinyl alcol và polyacrylic acid, giúp làm chậm quá trình khuếch tán urê qua màng vào môi trường. Phân urê thông minh được tạo trong thiết bị bọc đĩa quay có đường kính 0.2m, tốc độ 50 vòng/phút, góc nghiêng 40°, nhiệt độ sấy 60°C với thời gian bọc 30 phút và thời gian sấy 15 phút. Hiệu quả khuếch tán của phân urê thông minh với màng tổng hợp được đánh giá bằng thời gian khuếch tán 70% chất dinh dưỡng lên đến 360 phút, gấp hơn 60 lần so với urê không bọc. Đồng thời, bài báo cũng xác định được hàm lượng Urê khuếch tán của phân bọc trong môi trường đất và tốc độ khuếch tán đạt 8,50 ppm/ngày, đây là cơ sở cho việc sản xuất và sử dụng phân urê thông minh trong sản xuất nông nghiệp xanh.

Từ khóa: *hệ thống bọc hạt đĩa quay; nông nghiệp xanh; phân urê thông minh; khuếch tán; tinh bột biến tính.*

1. INTRODUCTION

Fertilizers are increasingly used in agricultural production, help increase crop yields[1]. However, the use of fertilizer currently still has much problems, the fertilizer use efficiency is low, the crops is only absorbed about 30% ÷ 50% nitrogen (N), 10% ÷ 15% phosphorus (P) and 50% ÷ 60% potassium (K) of the total applied conventional fertilisers are used [1, 2]. Therefore, a large amount of fertilizer has not

been usedand lost to the environment, polluting, affecting health and consuming resources [3,4].

Enhanced fertilizer use efficiency in agricultural production, the International Plant Nutrition Institute (IPNI), The Fertilizer Institute (TFI) and the International Fertilizer Industry Association (IFA) suggested 4R Nutrient Stewardship for fertilizer: Right source, Right rate, Right time and Right place [1], that is the concept of smart fertilizer. The smart fertilizer provide sessential nutrients at the right time, just enough to meet each type of plant demand. It helps to enhance fertilizer use efficiency, reduce the use of resources, the impact on the environment during production and use of fertilizers in agriculture. In which, the researchs on coating materials and technologyis directed towards producing controlled release fertilizers having a barrier layer [5].

Based on mechanism of nutrient release from coated fertilizers (see Figure 1), the release time and nutrient concentration depend on property, structure and thickness of the layer. They are affected by coating materials and technology [6].

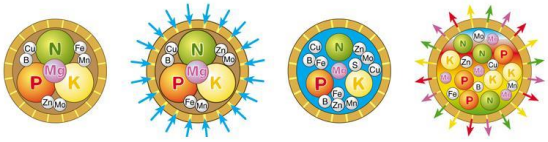

Figure 1. *Mechanism of nutrient release through the layer into the environment: a) The nutrients are coated by the layer; b) Water moves through the layer; c) The nutrients dissolve in water; d) The nutrients release through the layer into the environment.*

It has been shown that for the production of smart fertilizers in this direction, it is first necessary to synthesize coating materials and have the appropriate coating technology to create a suitable layer, ensuring the "4R" requirement.

At present, there are many various researchs on coating materials to produce SUFs: 1) mineral materials (e.g. sulfur, liquid glass); 2) synthetic polymers (polyolefines, polyacrylic, polyacrylamide, polysulfonate, polyurethane, polyvinyl chloride, polystyrene, polylactide, polyvinyl acetate and polyvinyl alcohol); 3) natural polymers (e.g. cellulose, lignin, chitosan, alginate, wheat gluten, rubber, latex and starch) [5]. Synthetic polymers, which are often expensive, difficult to degrade or degradation time is long, that affect the environment. In particular, the coating materials are made from starch are low cost, biodegradable and environmentally friendly are proposed [7].

2. MATERIALS AND METHODS

2.1. Materials

Modified starch such as: Cationic Starch (Ca. St.), Acetylated starch (A. St.) and Photsphate Starch (Ph. St.) are provided by Vedan Company, VietNam. Polyvinyl alcohol, PVA (99%) and p-dimethyl aminobenzaldehyde (99%) are purchased from HiMedia, India. Sodium tetraborate ($Na_2B_4O_7.10H_2O$), pure Urea (99%) are purchased from Guangdong, China. Polyacrylic acid (PAA) is pure acrylic emulsion, Nuplex Resins company, VietNam. Granular Urea (46.3% nitrogen, particle size 2.0 ÷ 4.5 mm, moisture 0.5%) is product of Ca Mau Fertilizer Plant, VietNam.

2.2. Synthetic biodegradable polymer layers

Dissolve 5 grams of cationic, acetatylated and phosphate modified starches with 100 mL distilled water at 80^{o}C, stirred for 30 minutes with speed 300 rpm. Then, 0.05g sodium tetraborate ($Na_2B_4O_7.10H_2O$) and 2g PVA are added slowly to the mixture and continue stirring for 30 minutes [8, 9,10].

Mix 70mL PAA emulsion and 30mL polymer phosphate modified starch horizontal link with PVA for 20 minutes to form a copolymer solution.

The solutions after synthesis are carried out to measure their density by hydrometer and viscosity by technical viscometer Prona RV-2, Taiwan. Then, adjust viscosity with distilled water (about 0.035 ÷ 0.04Pa.s) to achieve the appropriate viscosity forspray process to form coating layer.

2.3. Particle coating process to produce smart urea fertilizers

Scheme of the particle coating pan system as shown in Figure 2.

Weigh 50g of granular urea have been classified by sieve (diameter 3±0.2 mm) put into a coating pan has diameter 0.2 m, speed is 50 rpm, angle of inclination 40°, dry temperature 60°C. The solution is used to form coating layer is applied to the nozzle Prona R51 – F, its diameter is 0.5 mm, injection pressure 0.1 MPa, spray flow 0.5 mL/min. The coating time is 30 minutes, the dry time after coating is 15 minutes.

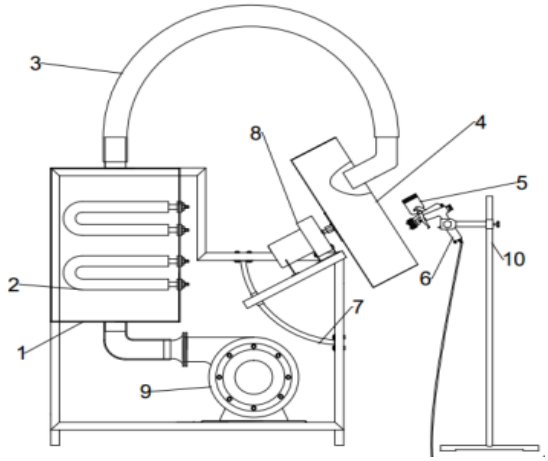

Figure 2. *The particle coating pan system*

1- Air heater; 2- Resistor; 3- Dry air tube; 4- Pan; 5- Nozzles; 6- Air inlet; 7- Ruler angle adjustment; 8- Motor; 9- Fan; 10- Carrier

2.4. Determining concentration of released urea fertilizer

Take 0.5g of granular urea (uncoated) and coated urea put in 250mL glass cup containing 100mL of distilled water, then take samples with the appropriate marking times for each type of fertilizer [6]. Urea concentration of samples is determined by spectrophotometric method (VIS), based on standards TCVN 6600:2000 [11], on the spectrophotometer GENESYS 20 (Thermo Scientific, USA).

The ratio of release urea is determined by the formula:

$$\%Release = \frac{C_i}{C^*} \quad (1)$$

In which: $C_i$is urea concentration at the marking times; $C^o$is urea concentration when totally released, it is determined by taking 0.5 g those urea fertilizers put in 250 mL glass cup containing 100 mL of distilled water, stirred at 100 rpm for 30 minutes to totally release and take the sample.

Mix 2.5g of those urea fertilizers with 100g of soil, take samples and white samples (without fertilizer) to determine urea concentration in soil. The specimens are stored in the container is kept confidential and take samples determine urea concentrationdaily, the soil moisture is stabilized by 20%. Urea concentration in soil is determined by: take 1g of sample dissolve 100mL of distilled water, stirred at 100 rpm for 15 minutes; then take the mixture to vacuum filter; the filtrate is analyzed to determine urea concentration by spectrophotometric method as above.

3. RESULTS AND DISCUSSION

3.1. Release efficiency of urea through the layer

The various coated urea fertilizers are produced by the particle coating pan system show in Figure 3

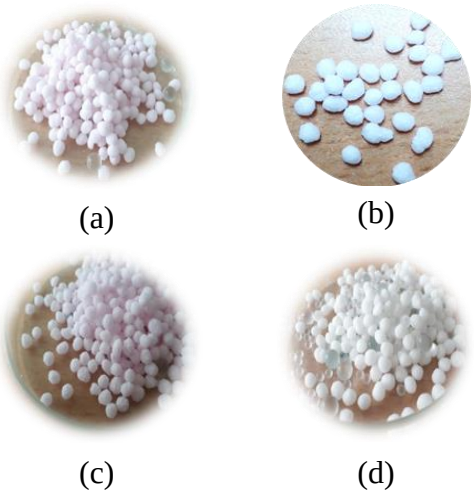

Figure 3. *The coated urea fertilizers with coating material is*
(a) cationic starch–g–PVA,
(b) acetylated starch–g–PVA,
(c) photsphatestarch–g–PVA,
(d) copolymer of photsphatestarch–g–PVA and PAA

Their surface linkage structure is described by SEM image (Vietnam academy of science and technology, Ho Chi Minh city) is shown in Figure 4.

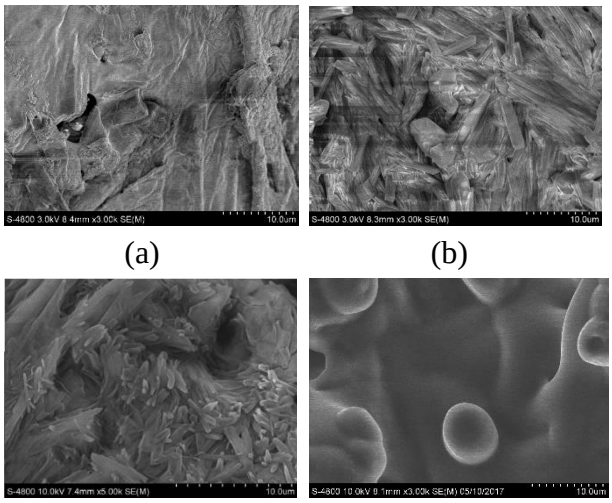

Figure 4. *Surface SEM image of coated urea fertilized with coating material is*
(a) cationic starch–g–PVA,
(b) acetylated starch–g–PVA,
(c) photsphatestarch–g–PVA,
(d) copolymer of photsphatestarch–g–PVA and PAA

The SEM image shows that copolymers of polymer photsphate starch horizontal link with PVA (photsphatestarch–g–PVA) and PAAcreate a layer has good bonding structure, uniformity and good compression. These reduce the possibility of swelling, ability to break the layer, the release rate, increases the release time of the particle.

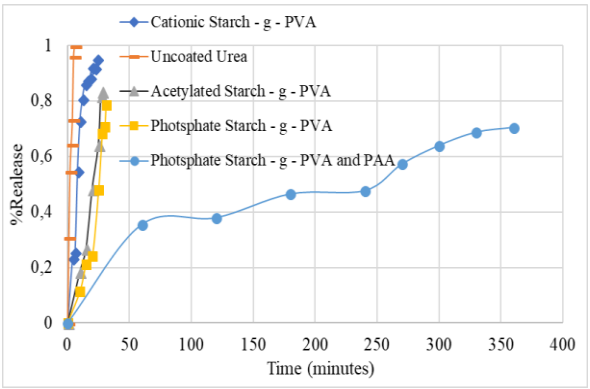

Figure 5. *The ratio of release urea for each type of fertilizer over time*

The result of the ratio of release urea for each type of fertilizer is shown in Figure 5.

Figure 5 shows that the release time of the urea fertilizer, are coated by polymer modified starch horizontal link with PVA, is longer than that of uncoated ureaabout 5 ÷ 6 times. However, the other is coated by copolymer of polymer photsphate starch horizontal link with PVA (photsphatestarch–g–PVA) and PAA has release time to be greater than, the time that 70% of urea was released, is up to 360 minutes and more than 60 times the uncoated urea fertilizer. In addition, its urea concentration changes slowly, stability. So, it is easy to adjust the release rate and efficiency, reduce nutrient loss into the environment.

3.2. Changes of urea concentration of SUFs released in soil environment

Result of urea concentration of SUFs released in soil environment are shown as Figure 6.

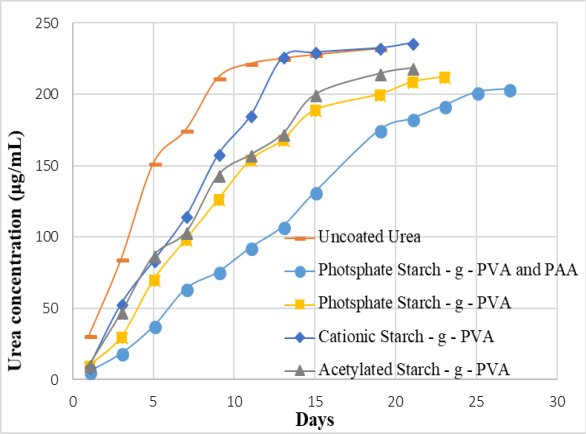

Figure 6. *Urea concentration of SUFs released in soil environment*

Figure 6 shows that uncoated urea fertilizer has release time totally on 9th day, threlease time totally of SUFs are coated by polymer cationic starch–g–PVA is 13 days, photsphate or acetylated starch–g–PVA is 19 days. The other is coated by copolymer has release time until the 25th day. Its urea concentration released in soil also low, so the crops can be absorbed slowly, avoid rooting toxicity due to high concentration. The time that the urea concentration is preserved in soil, is longer and more stable, so it does not

need to add fertilizer, reduce the amount of fertilizer used.

The release rate of urea fertilizers in soil environmentare calculated and shown in Table 1.

The results in Table 1 shows that the release rate of the coated ureais less than the uncoated urea. In which, the one is coated by copolymer has the release rate is at least.

4. CONCLUSSIONS

SUF is produced by the particle coating method with the coating material is copolymers of polymer photsphate starchhorizontal link with PVA and PAA. The coating process is performed in the coating pan, at a speed of 50 rpm, angle of inclination 40°, dry temperature 60°C, the coating time 30 minutes, the dry time coating 15 minutes.

Table 1. *The release rate of Urea fertilizers in soil environment*

	Uncoated Urea	Ph. St. - g - PVA and PAA	Ph. St. - g - PVA	Ca. St. - g – PVA	Ac. St. - g - PVA
Rate release ($\mu g.mL^{-1}.day^{-1}$)	25,34	8,50	13,23	17,19	14,09

The SUF has time that 70% of urea was released, is up to 360 minutes and more than 60 times the uncoated Urea fertilizer in water.

The release of SUFs in the soil environmentis also performed. In particular, the coated urea by a layer from copolymers has release time until the 25^{th} day, and the release rate is 8.50 $\mu g.mL^{-1}.day^{-1}$(ppm/day)

The study shows that, the use of SUF with the appropriate coating material will enhance fertilizer use efficiency, reduce the loss of nutrients into the environment, the use of resources, the impact on the environment and assuring a green agriculture. This study is also the basis for the research, development and application of smart fertilizers into modern agriculture.

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