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Boric acid modified starch polyvinyl alcohol matrix for slow release fertilizer

Abstract: The slow release urea fertilizer was prepared by the boric acid crosslinked starch/polyvinyl alcohol (SPB) matrix as biodegradable carrier material. Using a two level factorial design of experiment, a comprehensive understanding of the concentration of boric acid, reaction time and heating temperature in the preparation of SPB matrix was obtained. The swelling ratio, release profile of urea in water, and crushing strength were selected as the response. The interaction between the variables and response was analyzed using the ANOVA model. The system was confirmed using the constant determination, R^2 with values above 0.99. The high concentration of boric acid with a prolonged reaction time at high temperature gave relative good results of swelling ratio, dissolution rate of urea and crushing strength. In the 28-day soil incubation experiment, the retention of exchangeable ammonium ion (NH_4^+) was significant higher in SPB urea as compared to pure urea. There was a potential for SPB matrix to improve nitrogen efficiency by increasing the accumulation of exchangeable NH_4^+ and decreasing the dissolution rate of urea in the flooded condition.

Keywords: ammonium ion; boric acid; slow release; tapioca starch; urea.

1 Introduction

The rapid growth in global population and food demand increase the application of fertilizer to accelerate plant growth. Urea is one of the most popular nitrogenous fertilizers among farmers due to its high nitrogen content, 46% by weight, which has surpassed other nitrogenous fertilizer. When urea fertilizer inputs to the soil system exceed the crop needs, there is a possibility that half of the applied fertilizer escapes to the environment due to leaching, surface runoff, decomposition and ammonium volatilization in soil as only a fraction is actually absorbed by plants. Apart from its economic and resource losses to the growers, nitrates losses through the soil runoff cause issues of groundwater and surface water resources pollution. In situations where the soil is high in pH, volatilization of ammonia may occur and its loss to the atmosphere cause the problem of air pollution (1, 2).

The slow release fertilizer arises as a new generation environmentally-friendly fertilizer which attracts the interest of researchers around the world. The slow release technology was applied on urea fertilizer to release the nutrient contents gradually and to coincide with the utilization efficiency of plant uptake. The slow release fertilizer can be physically prepared by encapsulating the fertilizers with various material matrixes that reduce their dissolution rate (3). Research has shown that slow release technology could effectively sustain supply or minerals for a prolonged time, lower the frequency of application in accordance with normal crop requirements, and minimize economic loss and adverse effects on the environment (3–7).

Starch has been recognized as a renewable, low cost, and fully biodegradable polymer, which blended with the synthetic polymer polyvinyl alcohol (PVA) to develop starch based products for conserving the petrochemical resources and reducing environmental impact. The additional chemical crosslinking approaches can be employed to improve the structural integrity of the blend (8). It can be effectively used as a polymer matrix for the mechanism of release elements from chemical substance after derivatization and crosslinking (9). The matrix will provides an effective control over the fertilizer for a relatively long period of time in heavy water environments.

In this work, the boric acid crosslinked starch/polyvinyl alcohol (SPB) was used as the matrix and the urea was used as the fertilizer base to prepare a slow release urea fertilizer. The objective of this work is to evaluate

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the effectiveness of SPB matrixes improving sustainable release properties as well as to investigate the ability of retaining NH_4^+ in soil. Various SPB matrixes were prepared under different processing parameters such as boric acid concentration, reaction time and heating temperature, and their swelling power and release rate of urea were characterized. This finding was promising because, if effective, slow release fertilizers could be easily made, environmentally safe and relatively inexpensive as compare to coated urea.

2 Experimental

2.1 Materials

The commercial tapioca starch was purchased from Cap Kapal ABC (Thailand). Fully hydrolyzed polyvinyl alcohol (PVA), with average molecular weight of 60,000 and the degree of hydrolysis ≥98% was obtained by Merck (M) Sdn Bhd (Malaysia). Glycerol with 99.5% purity was supplied by Systerm ChemAR (Malaysia) and boric acid with 99.8% purity was provided by local reagent supplier (Malaysia). The analytical grade urea with 99.5% purity was supplied by QReC (Malaysia).

2.2 Methods

2.2.1 Preparation of SPB film

The PVA (5.0 g) was dissolved in 50 ml deionized water at 90°C. The starch/PVA matrix was prepared by stirring starch (5.0 g), dissolved PVA and glycerol in 50 ml deionized water at 80°C for 2 h. Subsequently, a quantitative amount of boric acid was dissolved in the mixture and continued heating according to the values fixed in Table 1. The SPB matrix was cast in a Teflon-coated Petri dish and was dried in an oven at 60°C until constant weights were achieved. The cast films of approximately 0.3 mm thickness was conditioned at 23°C and 50% relative humidity for swelling characterization.

2.2.2 Preparation of SPB urea

The urea particles were thoroughly mixed with the SPB matrix with a glass rod for 10 min. The mixture was poured onto Teflon-coated glass plates and dried in an oven at 60°C until constant weights were achieved. The pellets were prepared by compressing 1.0 g SPB urea at 4.5 metric ton with a hydraulic press. The pure urea and SPB urea pellets were 13 mm in diameter and 6 mm in height and stored in sealed glass bottle for further characterization.

2.2.3 Dissolution of urea in water

The analysis of dissolution of urea was carried out according to the procedure mentioned in previous literature (4, 10) with some modification. A 1 g of SPB urea pellet was immersed in 100 ml distilled water in an Erlenmeyer flask and sealed. The Erlenmeyer flask was placed in an incubator shaker for 300 min at 30°C with the rotation speed set to 100 rpm. A quantity of 0.1 ml of solution was taken out to estimate for the contents of urea-nitrogen after a certain interval. According to diacetylmonoxim (DAM) colorimetric method (11), the amount of released urea from the extracted samples was measured at 527 nm using a UV-Vis spectrophotometer (UV-1700, Shimadzu). All the experiments were done in three replications, and their results were averaged. The concentration of released

Table 1: Overview of the results – responses from variation of the selected factors.

Code	Concentration of boric acid (X_1) (%)	Reaction time (X_2) (h)	Reaction temperature (X_3) (°C)	Swelling ratio (Y_1)	Slow release efficiency (Y_2) (%)	Crushing strength (Y_3) (kN)
SPB1	1	1	60	5.49	26.19	3.02
SPB2	4	1	60	5.82	15.23	3.96
SPB3	1	4	60	5.53	26.38	3.21
SPB4	4	4	60	5.28	31.37	3.76
SPB5	1	1	90	4.52	34.66	3.18
SPB6	4	1	90	4.10	42.39	3.47
SPB7	1	4	90	3.78	46.88	3.45
SPB8	4	4	90	2.12	50.74	3.58
SPB9	2.5	2.5	75	4.33	39.85	3.91

urea was reported by the percentage based on the primary concentration of urea in each sample. The matrixes slow release efficiency is a comparison of the dissolution rate of the SPB urea pellet against pure urea at the fifth hour and is calculated based on the formula:

$$\text{Efficiency (\%)} = \frac{C_{PU} - C_{SPB}}{C_{PU}} \times 100$$

where C_{PU} is the concentration of pure urea released at the fifth hour, and C_{SPB} is the concentration of SPB urea released at the fifth hour.

2.2.4 Soil incubation

The nitrogen mineralization characteristic of the SPB urea in the flooded condition was determined using procedures as outlined previously (12) with minor modification. The acid soil with pH 3.52 used in the 28-day incubation experiment was taken from a paddy field located in Ayer Molek, Melaka. The soil was air-dried and gently ground to pass through a 2 mm mesh sieve. A 1 g SPB urea pellet was applied on the 20 g soil flooded with 30 ml distilled water in a plastic vial (300 ml) to make four sets of soil samples. Each set of soil samples contain 27 samples treated with nine different treatments with three replications. The vials with treatments were sealed with a parafilm and incubated for 4 weeks at room temperature. At each week of incubation, one set of soil samples were analyzed for exchangeable ammonium ions (NH_4^+), and available nitrate ions (NO_3^-) contents using the Keeney and Nelson method (13).

2.2.5 Swelling power

The swelling power of various SPB films in deionized water was determined according to Yin et al. (14) with slight modification. The SPB film was immersed in 50 ml deionized water for 24 h at 30°C until the film had reached the equilibrium state of swelling. The swollen film was weighted immediately after removing residual water on its surface. The wet weight of the film (W_w) was recorded. The swollen SPB film was then dried in an oven at 60°C for up to 24 h or until a constant dry weight (W_d) was obtained. All experiments were conducted in duplicate. The swelling ratio of the SPB film was calculated according to Equation [1].

$$\text{Swelling ratio} = \frac{W_w - W_d}{W_d} \qquad [1]$$

where W_w and W_d are the wet and dry weight of the film, respectively.

2.2.6 Attenuated total reflectance-fourier transform infrared (ATR-FTIR) spectroscopy

The FTIR spectra was generated using a Fourier Transformed Infrared Spectrometer (JASCO FT/IR-6100, accessory ATR PRO450-S) with an average of 128 scans and measured in the range of 400–4000 cm^{-1} wavenumbers at a resolution of 4 cm^{-1}. The spectra of SPB urea pellet and SPB matrix were obtained and compared.

2.2.7 Crushing strength

The crushing strength of urea pellets was determined using a Universal Testing Machine (Shimadzu AG-1/100 kN). The pellet underwent compression loading with force speed of 1 mm/min and stroke set for 2 mm. The force at which the pellet fractured was obtained as a measure of strength.

2.2.8 SEM

The surface features of the SPB film and SPB urea pellet were observed using a scanning electron microscope (Zeiss Model EVO-50) at a voltage of 10 kV. The samples were placed onto aluminum stubs and sputter coated with gold palladium.

2.2.9 Two-level factorial design experiment

Design experiments were carried out using Design Expert software (Statistics Made Easy, version 6.0.10, Stat-Ease, Inc., Minneapolis, MN, USA). A two-level factorial design experiment was used to show the statistical significance of the concentration of boric acid, reaction time, and reaction temperature for the urea encapsulation efficiency. A 2^3 factorial design for three independent variables with three replications at the center points was employed with a total of 11 sets of experiments carried out in this study (Table 1). From the experimental findings, the effects of the independent variables on the swelling ratio, dissolution of urea and crushing strength were studied and analyzed with analysis of variance (ANOVA) to determine the adequacy of the model.

3 Results and discussion

3.1 Crushing strength

The compilation of response of the experiments and results can be seen in Table 1. The sample was loaded in compression mode up to deformation of structure. Based on the average values, a force around 1.69 kN was required for pure urea pellet to reach failure. From the crushing strength perspective, it is satisfactory to note that the SPB urea had better strength compared to pure urea to withstand the operational handling. The highest crushing strength obtained was SPB2, which was 3.96 kN, whereas the lowest strength was SPB1, which was 3.02 kN. It was obvious that the crush resistance was improved when using the SPB matrix on urea pellet compared to pure urea.

3.2 Dissolution of urea

The dissolution rate of urea was used to indicate the SPB matrixes efficiency upon their immersion in water. The comparison between the SPB urea and pure urea was used to provide a general indication of the performance for encapsulating the urea into SPB matrixes in retarding urea release and thus superior matrixes efficiency. It was found that the pure urea pellet dissolves in water entirely within 60 s. At the end of the eight hour, all the SPB urea pellets were dissolved completely in water. The shells of SPB urea pellets were retained at the bottom of flask. The dissolution patterns of all the SPB urea pellets were monotonically increasing. It was noteworthy that

the rate of urea release had evidently been slowed down by the SPB matrixes as shown in Figure 1. The SPB2 urea had the highest rate of urea release and dissolved around 10% urea into the water during the first hour; after 5 h the nitrogen content of urea had been released completely. Conversely, the SPB8 urea had the slowest rate of urea release and dissolved around 50 wt% urea only after 5 h, indicating the apparent high efficiency slow release behavior of SPB8 urea amongst all the SPB urea. The urea dissolution in water at the fifth hour was used as the benchmark to indicate SPB matrixes efficiency as listed in Table 1. In terms of efficiency, SPB2 was the lowest at 15.23%. SPB8 had the highest slow release efficiency of 50.74%.

3.3 Swelling power

The swelling power of various SPB film is presented in Table 1. The water uptake was directly correlated to the crosslink density of a polymer network chain, whereby less water penetrated through the membrane indicating higher crosslink density (15). It can be observed that the water uptake for SPB8 was the lowest among the SPB film, which clearly reflected their difference in structure and crosslink density. The water uptake is directly correlated to the crosslink density of a polymer network chain, whereby less water penetrated through the membrane indicating higher crosslink density. This could be reasonably attributed to the increased crosslinking interaction between starch and PVA with the presence of boric acid. The crosslinking density increased and thus hindered the penetration of water into the SPB molecular network as there were less open chains and gaps between SPB molecules. This observation is in line with the results as previously reported by Yin et al. (14).

The urea release rate was reduced significantly by the SPB matrix, which is consistent with the results of the swelling study. The SPB membrane is hard to swell, thus the diffusion through this membrane is the rate limiting step for swelling and urea release. The pellets with the smaller swelling ratio provides less interfacial surface between the water and urea, causing harder penetration of water inside the pellets and hence releasing less urea. Most of urea could not be released until the SPB matrix became swollen enough and in the swollen state, the urea has a comparable diffuse and release rate. The urea in the swollen SPB matrix can diffuse rapidly and can be released quickly due to weak interaction between urea and SPB matrix membrane. These results agreed with works of Chen et al. (4).
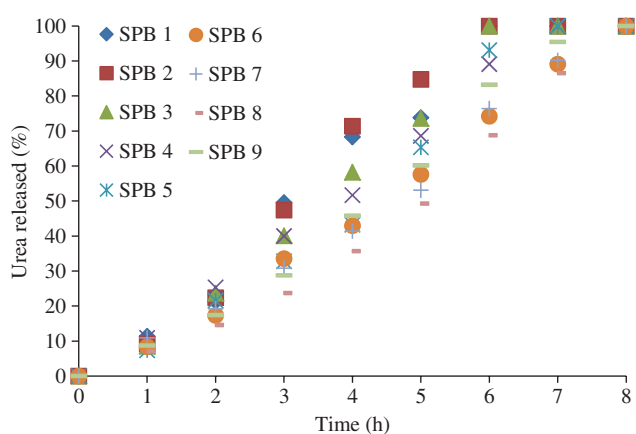

Figure 1: The release curves of urea from SPB urea.

3.4 Soil incubation

The weekly exchangeable NH_4^+ were recorded during the experiment was shown in Figure 2. The accumulation of soil exchangeable NH_4^+ was significantly higher in the SPB urea than pure urea after 4 weeks soil incubation. The higher concentration of soil exchangeable NH_4^+ was partly due to increase in the pH of the soil as mineralization of organic N to NH_4^+ is enhanced by the higher pH (16). In the first week, it was found that the amount of available NH_4^+ of the pure urea was lower than the SPB urea because the pure urea had been dissolved totally in soil during the urea hydrolysis.

The retention of soil exchangeable NH_4^+ in SPB urea during hydrolysis could be attributed to the electrostatic attraction of the partially negative charged SPB matrixes in flooded conditions and the homeotropic anchoring effect (17). The SPB matrix was characteristically electron deficient with an incomplete octet of electrons around the central boron atom (18). The negative sites due to ionization of SPB matrixes (19) might have improved NH_4^+ retention thus it reduces the ammonia volatilization. The higher concentration of boric acid in the SPB urea produces a more negative site around the matrix to accumulate the NH_4^+ in soil. Retardation of nitrification also may have occurred due to the SPB matrixes chemically protect NH_4^+ against microbial nitrification. The effect of SPB matrixes on total soil available NO_3^- was not significantly different from pure urea (Figure 3). The NO_3^- was generally low in the flooded soil after 28 days of incubation.

3.5 FTIR

The SP and SPB matrix have similar peaks in Figure 4, except the bands at 3257 cm^{-1} of SP film showed an apparent
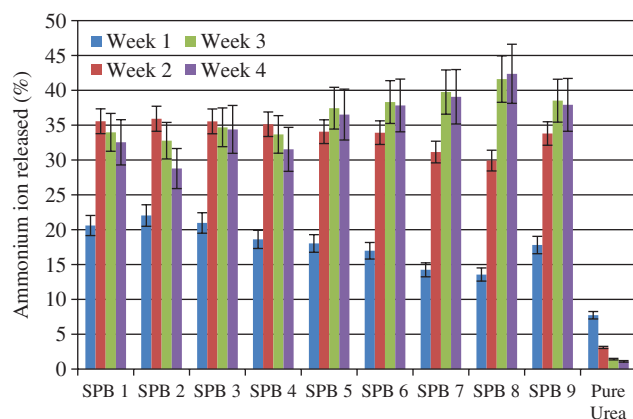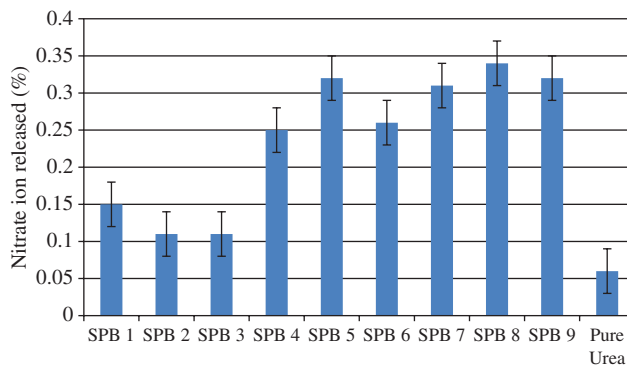

Figure 3: Total soil available nitrate ion NO_3^- after the 28 days of soil incubation.

shift to higher wavenumbers 3273 cm^{-1} after crosslinking with boric acid. The band at 3257 cm^{-1} is ascribed to the hydrogen bonding O-H stretching. The band shift to a lower frequency indicated the intensity of the -OH band decreases upon crosslinking of polymer chain to form the oxygen-boron complex (20). The FTIR characteristic peaks of the C-H stretching absorption at 2927 cm^{-1}, the C-C stretching vibration at 1419 cm^{-1}, the O-H stretching vibration at 3273 cm^{-1} were observed in the SPB film. The new characteristic band composed of 3428 and 3300 cm^{-1} appeared in the SPB urea pellet which was assigned to the stretching of N-H bond corresponding to primary amine. Another two bands observed at 1672 and 1587 cm^{-1} were attributed to the C=O group and vibrational stretching of the N-H group. The result indicates that the urea is present in SPB matrix. A similar observation has been reported by Castro et al. (21).

3.6 SEM

The surface of the pure urea and SPB urea could be observed under SEM in Figure 5. The long pointy crystals and gaps were clearly seen throughout the surface of the pure urea (Figure 5A and C). For the SPB urea, the long pointy crystals of urea were tightly cemented on the surface of the SPB matrix (Figure 5C). There was no visible sign of gaps and cavities observed on the surface of SPB matrix (Figure 5D). It was concluded that the urea was entrapped successfully in the SPB matrix.

3.7 Interaction between variables for swelling characteristic and crushing strength of the SPB matrix

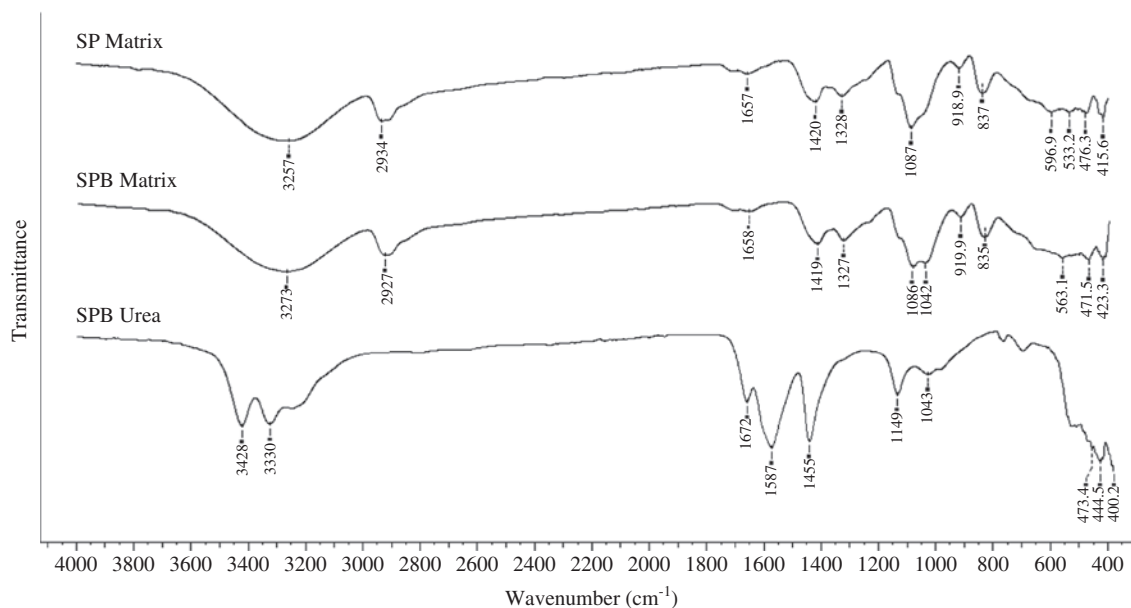The regression model for each response is presented in Table 2. All the variables are included in each equation.

Figure 2: The weekly soil exchangeable ammonium ion NH_4^+ during the 4 weeks' soil incubation.

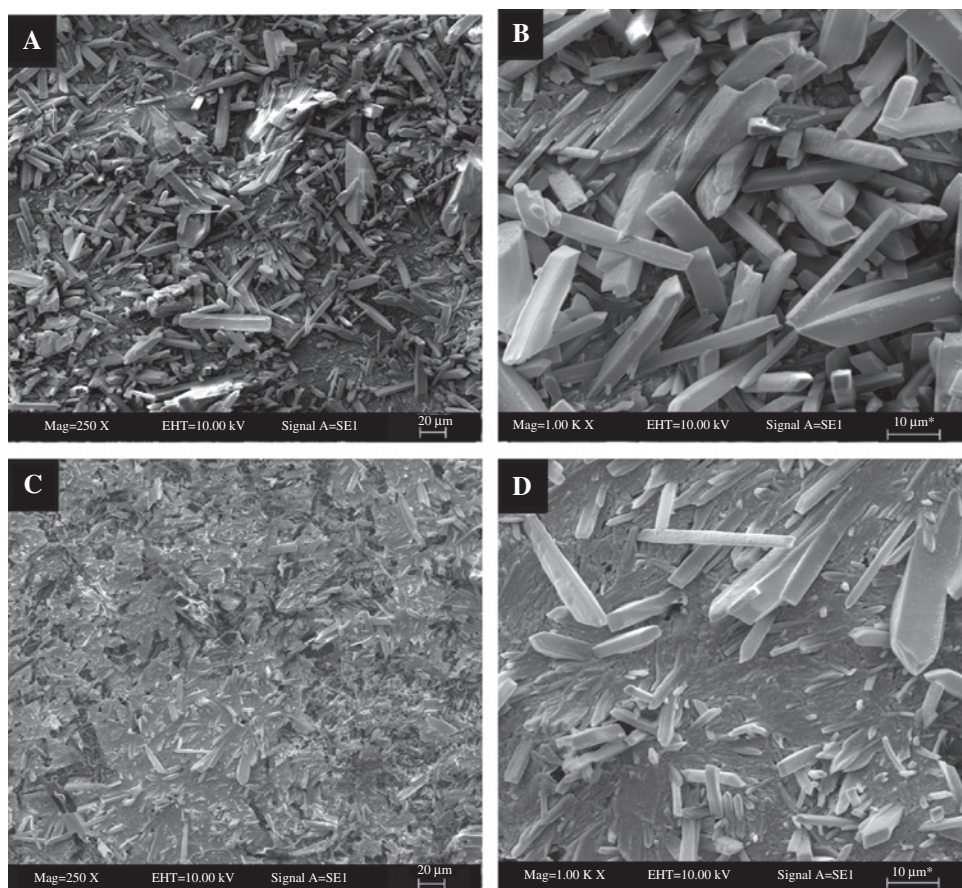**Figure 4:** FTIR spectra of (A) SPB matrix (B) SPB urea.

Figure 5: SEM images of the pure urea (A) at magnification 250× and (B) 1000× and SPB urea (C) at magnification 250× and (D) 1000×.

This regression equation represents the quantitative effects of the independent variables and their interaction effects to the response. The positive signs indicate effects that lead to optimization of response whereas negative signs reflect opposite effect on the response. This regression model is accurate and can be used to navigate the design

Table 2: Regression equations for different responses.

| Responses	R^2	Equation of the models
Swelling	0.9999	$Y_1 = 6.347 + 0.535X_1 + 0.457X_2 - 0.0175X_3 + 0.0814X_1X_2 - 0.060X_1X_3 - 0.0063X_2X_3 - 0.0024X_1X_2X_3$
Slow release efficiency	0.9988	$Y_2 = 39.50 - 22.29X_1 - 14.13X_2 - 0.132X_3 + 6.177X_1X_2 + 0.281X_1X_3 + 0.207X_2X_3 - 0.073X_1X_2X_3$
Crushing strength	0.9999	$Y_3 = 1.849 + 0.841X_1 + 0.104X_2 + 0.0125X_3 - 0.0944X_1X_2 - 0.0081X_1X_3 + 0.00004 X_2X_3 + 0.00085X_1X_2X_3$

space because it shows a high R^2 range of 0.9994–0.9999; it implies that almost 100% of variance for the response is attributable to the independent variables tested.

In this study, reaction temperature is the temperature at which the boric acid is crosslinked with starch and PVA to form a workable SPB matrix. At a lower temperature, apparently the kinetic probability of the starch and PVA to be crosslinked by boric acid is too low as well, so the rate of crosslinking reaction is low. Therefore, the values of swelling ratio and crushing strength obtained at temperature 60°C is lower than at 90°C. There was a correlation between swelling power and slow release efficiency, with the matrix of higher swelling powers showing lower slow release efficiency of urea. A reaction time of 4 h appeared to be more effective than the shorter period of 1 h. At a shorter reaction time, the boric acid has inadequate time to crosslink the starch and PVA, thereby producing the SPB matrix that has higher swellability. Boric acid appeared to have a higher reactivity with a longer reaction time. The concentration of boric acid has a significant effect on the swelling ratio and crushing strength. The lower swelling ratio and higher crushing strength are obtained at the 4% concentration of boric acid. At the high level of concentration of boric acid, the chance of boric acid to crosslink with starch and PVA is larger as well.

The generated regression model can be utilized to optimize boric acid concentration and processing parameters for producing the SPB matrix at maximization of the slow release efficiency. According to the response surface plot in Figure 6, the slow release efficiency of SPB urea is maximized at 50.74% simply with the corresponding optimum concentration of boric acid, reaction time and reaction temperature are 4%, 4 h and 90°C, respectively. This was shown in the SPB8 urea fertilizer.

4 Conclusion

The various SPB urea fertilizers were prepared and the release behaviors of urea were examined and compared to each other. The dissolution rate experiment revealed a dramatic decrease in urea release after encapsulating
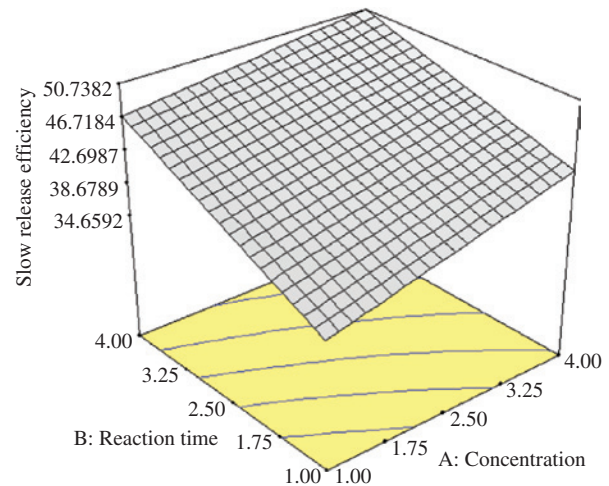
Figure 6: Response surface plot showing variation in slow release efficiency.

urea with the SPB matrix. The experimental results also showed that by increasing the concentration of boric acid with a prolong reaction time at high temperature, the swelling ratio of matrix decreased whereas the crushing strength increased. The SPB matrix has the ability to accumulate the NH_4^+ in soil after 28 days incubation experiment. It can be concluded that the SPB matrix can be used as an effective material for slow release urea fertilizer.

References

1. Qiu X, Zhu D, Tao S, Chen C, Ren X, Hu S. 1-naphthylacetic-acid-functionalized polyacrylate-coated urea with dual controlled-release properties. J Appl Polym Sci. 2013;129(2):559–67.
2. Roshanravan B, Mahmoud SS, Mahdavi F, Abdul RS, Khanif YM. Preparation of encapsulated urea-kaolinite controlled release fertilizer and their effect on rice productivity. Chem Speciation Bioavailability. 2014;26(4):249–56.

3. Ibrahim KRM, Babadi FE, Yunus R. Comparative performance of different urea coating materials for slow release. Particuology. 2014;17:165–72.

4. Chen L, Xie Z, Zhuang X, Chen X, Jing X. Controlled release of urea encapsulated by starch-g-poly (L-lactide). Carbohydr Polym. 2008;72(2):342–8.

5. Han X, Chen S, Hu X. Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating. Desalination. 2009;240(1):21–6.

6. Riyajan SA, Sasithornsonti Y, Phinyocheep P. Green natural rubber-g-modified starch for controlling urea release. Carbohydr Polym. 2012;89(1):251–8.

7. Zhong K, Lin ZT, Zheng XL, Jiang GB, Fang YS, Mao XY, Liao ZW. Starch derivative-based superabsorbent with integration of water-retaining and controlled-release fertilizers. Carbohydr Polym. 2013;92(2):1367–76.

8. Uslu I, Daştan H, Altaş A, Yayli A, Atakol O, Aksu ML. Preparation and characterization of PVA/Boron polymer produced by an electrospinning technique. e-Polymers. 2007;7(1):1568–73.

9. Onofre FO, Mendez MG, Wang YJ. Sustained release properties of crosslinked corn starches with varying amylose contents in monolithic tablets. Starch – Stärke. 2010;62(3):165–72.

10. Babadi FE, Yunus R, Rashid SA, Salleh MAM, Ali S. New coating formulation for the slow release of urea using a mixture of gypsum and dolomitic limestone. Particuology. 2015;23:62–7.

11. Douglas LA, Bremner JM. Colorimetric determination of microgram quantities of urea. Analyt Letters. 1970;3(2):79–87.

12. Ono SI. Nitrogen mineralization from paddy and upland soils under flooded and nonflooded incubation. Soil Sci Plant Nutri. 1989;35(3):417–26.

13. Keeney DR, Nelson DW. Methods of Soil Analysis Part 2 Chemical and Microbiological Properties. 2nd ed. Madison, WI: ASA and SSSA; 1982. 643 p.

14. Yin Y, Li J, Liu Y, Li Z. Starch crosslinked with poly (vinyl alcohol) by boric acid. J Appl Polym Sci. 2005;96(4):1394–7.

15. Pang SC, Chin SF, Tay SH, Tchong FM. Starch–maleate–polyvinyl alcohol hydrogels with controllable swelling behaviors. Carbohydr Polym. 2011;84(1):424–9.

16. Omar L, Ahmed OH, Majid NMA. Improving ammonium and nitrate release from urea using clinoptilolite zeolite and compost produced from agricultural wastes. Sci World J [Internet]. 2015 Jan [cited 2015 Nov 16]; 2015(574201). Available from: http://dx.doi.org/10.1155/2015/574201.

17. Marin L, Ailincai D, Paslaru E. Monodisperse PDLC composites generated by use of polyvinyl alcohol boric acid as matrix. RSC Adv. 2014;4(72):38397–404.

18. Chattopadhyay AK. "Boring" Boron and Adhesives. Adhes Seal Ind. 2014;21(9):32.

19. Zittle CA, Harris TN. The antigenic structure of hemolytic streptococci of lancefield group A X. The purification and certain properties of the group-specific polysaccharide. J Bio Chem. 1942;142(2):823–33.

20. Melo AD, Borges DL, Debacher NA, Curtius AJ. Synthesis and bharacterization of poly (vinyl alcohol)-boric acid beads from PVA with several hydrolysis degrees. e-Polymers. 2007;7(1):1650–61.

21. Castro EDD, Rodríguez FF, Ramírez WB, Torres CPI, Castillo OMM, Rodríguez FDE, Ledesma OAI. Preparation, characterization and release of urea from wheat gluten electrospun membranes. Materials. 2012;5(12):2903–16.