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Carbonaceous microsphere-based superabsorbent polymer as filler for coating of NPK fertilizer: Fabrication, properties, swelling, and nitrogen release characteristics

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ABSTRACT: Recently, the use of controlled release fertilizers in agriculture has resulted in huge benefits in plant growth and cultivation. Superabsorbent polymer (SAP)-coated fertilizers have the added advantage in retaining water in soil after irrigation and also reduce the nutrient release rate from soil in a controlled manner. This study aimed to produce a nitrogen–phosphorus–potassium (NPK) fertilizer coated with superabsorbent carbonaceous microspheres polymer (SPC) by inverse suspension polymerization method with water-retention and controlled release properties. Two sets of experiments were conducted: (1) three different weight percentages and (2) different materials. NPK coated with SPC showed increasing water-retention ability with respect to carbon microsphere percentages and retains >80% water at the 30th day of experiment compared with pure NPK and NPK coated with SAP. The slow release behavior of all samples was investigated by induced coupled plasma mass spectrometry spectrometry and results showed that NPK coated with SAP and SPC has a low release rate with <50% nutrient release compared with uncoated NPK at the 30th day. The release mechanism kinetics of NPK coated with SAP and SPC were studied based on the Kosmeyer–Peppas model. The mechanisms approached Fickian diffusion-controlled release as the n value for both samples was less than 0.5. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 48396.

KEYWORDS: controlled release fertilizer (CRF); hydrothermal carbonization (HTC); superabsorbent carbonaceous microsphere polymer (SPC); superabsorbent polymer (SAP)

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INTRODUCTION

Water is clearly a key factor that improves agricultural growth. The higher the temperature, the higher the amount of water required for agricultural growth. But owing to drought conditions and water scarcities, conditions have not been ideal for world agricultural development. The farmers are thus looking for rainfall dependability so that they can choose the most suitable crops for the area. According to assessments, around 84% of the farm land in the 1.44 million acres of the world's land that is suitable for cultivation is under dry condition. The stunted agricultural growth due to drought conditions and water scarcities annually costs more than the amount of losses due to the other factors[1,2]; therefore, it is vital and obligatory to utilize the water resources efficiently.

The study of superabsorbents (SAs) as water management resources for agricultural as well as horticultural applications has received cumulative interest in the past few years.[3,4] Practical applications have shown that superabsorbent polymers (SAPs) exhibit a promising future of increasing the existence rate and at the same time easing the effects of drought stress on the crops in arid and semiarid regions.[5–7] SAPs are a type of polymers that can absorb and retain large amounts of pure water, saline water, or physiological solutions typically more than traditional absorbent material and they are also three dimensional cross-linked, hydrophilic in nature.[8–10] The crosslinked structure of SAPs allows them to maintain a stable network, even in its swollen state. During the early years, the SAPs were synthesized from chemically modified starch, cellulose, and polymers such as polyvinyl alcohol and polyethylene oxide.[11,12] At present, the SAPs are commonly produced from partially neutralized and lightly crosslinked polyacrylic acid, polyacrylamide, and other polyacrylates to form high-performance superabsorbent materials, which have also proved to exhibit the best performance versus cost ratio.[11,13]

SAPs have been used in a various range of applications, that is, forestry, agriculture, industry, chemical industry, personal care, and drug delivery systems.[14–16] In particular, in the agricultural field, the SAPs play a significant role to reduce the frequency of irrigation, improve soil water-retention capacity, improve plant survival rate, reduce pesticide residue, and also improve microbial activities in the soil.[17–21] SAPs used in soil directly influences the water penetrability, soil structure, and texture, also the water evaporation and infiltration rates.[21,22] SAPs made from synthetic polymers possess exceptional characteristics; therefore, observation and comparison between SAP-based synthetic polymer and SAPs natural-based polymers are significant. Although the SAPs have been broadly studied, enhancing their properties, progressing the theory of the superabsorbent hydrogel, and improving their structural property controllability are some of the main concerns. Simultaneously, improving the environmentally friendly characteristics of the SAPs is a hot research area.[23] Slow release nitrogen–phosphorus–potassium (NPK) fertilizer may influence in succeeding these goals of effective fertilizer nutrient management and lowered environmental effect.

The other factors that limit the yield and growth of crops are the nutrients.[24] Nitrogen is the main element in crop nutrition and affects the crop yield greatly. The consumption rate of nitrogen based fertilizers is comparatively small and accounts for merely around 30–50%.[25] Incompetent nitrogen absorption raises growers' input cost and causes numerous environmental problems. Despite the environmental problems, conventional NPK fertilizers are still preferred fertilizers in agriculture as nutrients resources to the crops.[26] But due to unreliable water flowing, the NPK fertilizers tend to fast release their nutrients to the soil environment.[27] The excessive usage of NPK fertilizers would damage crop growth and also cause soil pollution due to leaching. Therefore, it is vital to make sure that nutrient release can be controlled to improve the economic feasibility and environmental sustainability of fertilizer consumption.[28]

Carbon is an important material and usually produced from the interactions of natural processes. Carbon can improve the physical properties, by expanding the water holding capacity and cation-exchange capacity of the soil. Hence, the carbonaceous microspheres are used as fillers in order to improve the interfacial adhesion between carbon fillers and SAPs, which turns them into superabsorbent carbonaceous microspheres polymer (SPC). Carbon has been a raw material for several thousands of industrial products and their production from various bioresources is an active area of research.[29] During last one decade, carbon has been used as a filler in a wide range of applications, such as in urea-formaldehyde resin in order to reduce the formaldehyde emission and in wood composites.[30–32] These carbon materials are either synthesized by pyrolysis or by hydrothermal carbonization process (HTC) methods which are simple, versatile, and commercially scalable methods. The advantage of HTC is that they have the ability to transform high moisture material into carbonaceous solids at relatively high yields. It also eliminates the need for an energy-intensive drying before or during the process. This opens up the field of potential feedstock's to a variety of nontraditional sources: agricultural waste, wet animal manures, sewage sludge's, municipal solid waste (MSW), as well as aquaculture and algal residues.[33–37] HTC process is an exothermal process that lowers both the oxygen and hydrogen content of the feed by mainly dehydration and decarboxylation. The common operating temperatures of HTC process is between 180 and 350 °C in a mixture of biomass and excess water at saturated pressure for hours of duration.[37] The carbon filler combined by means of hydrothermal carbonization method[38] using an oil palm empty fruit bunch as a feedstock into the SAP composite will help the hydrogel to decompose itself when it is applied on the soil.

In this work, the hydrothermally carbonaceous microspheres were used as filler in SAP in order to improve the efficiency of NPK fertilizers in the soil by using inverse-suspension polymerization method. In this study, the controlled release behavior, water retention of NPK coated with SAP and SPC, kinetic study on controlled release mechanism, and surface morphology of NPK coated with pure SAP and SAP with carbonaceous microspheres will be discussed.

MATERIALS AND METHODS

Material

Acrylic acid (AA) and sodium hydroxide (NaOH) were obtained from Merck, Germany, with purity over 99%. NPK fertilizer and starch were obtained from local store, Kuantan, Pahang. These NPK fertilizers are spherical shape, light red-colored fertilizers. N,N'methylenebisacrylamide (NNMBA), sorbite anhydride monostearic acid ester (Span-80), and ammonium persulfate (APS) were obtained from Sigma Aldrich (Missouri, USA) with purity over 99%.

The carbonaceous fibers were produced from Kenaf fiber through the HTC by same method as reported by Tuan Zakaria *et al.*[39]

Synthesis of SAP and Superabsorbent SPC

The SAP was prepared by mixing 306 mL of cyclohexane and 34 mL Sorbite Anhydride Mono Stearic Acid Ester (Span-80) in a three-neck flask using a hotplate. The mixture was continuously stirred and heated at 55 °C in the presence of nitrogen gas for 15 min. This mixture acted as the continuous phase in the process. In another beaker, a mixture of dispersed phase, which contains 8 mL of partially neutralized AA, 4 g of acrylamide, 3.4 g of APS, and 0.34 g of NNMBA, was prepared. The mixture was then added slowly to the first mixture in a three-neck flask and the reaction was held at 65 °C for 3 h time with a stirring speed of 300 rpm. The preparation of SPC was similar to that of SAP except a 0.04 wt % of carbonaceous microspheres from the total weight of AA and was added in SAP mixture in the continuous phase solution with a stirring speed of 300 rpm for 10 minutes. The resulted mixture solution was filtered, then washed with distilled water, and oven-dried.

Coating of NPK Fertilizer with SAP and Superabsorbent SPC

The coating process starts with sieving the NPK fertilizer to below 2-mm particle size. The starch was then added to NPK as an adhesive to ensure the NPK is coated homogeneously with SAP and SPC. Starch of 10 g was mixed with 5 g of NPK in a beaker with continuous spray of distilled water (approx. 10–15 mL) until NPK fertilizer was fully coated with starch. The beaker was constantly rotated to ensure uniform distribution of water onto the NPK and starch, which helps to prevent the agglomeration of the starch. Then, NPK coated with starch was put on a sieve to remove the excess starch before being coated with SAP and SPC. SAP of 5 g was taken in a petri dish for final coating process and then starch-coated NPK fertilizer was rolled in a petri dish until they are fully coated. The same process was repeated for SPC also, and finally, the NPK fertilizer coated with SAP and SPC was oven-dried at 105 °C for 24 h time and then kept in an airtight container for testing.

Sample Characterization

Water Retention in Soil. Water-retention tests were carried out to determine the retention of water retention in the soil containing NPK, NPK coated with SAP, and NPK coated with SPC. Soil of 50 g was oven-dried at 105 °C for 24 h and then sieved into below 2-mm particle size. Two sets of experiments were conducted: (1) in the first set, three different weight percentages, that is, 1, 3, and 5 of NPK is coated by SPC and (2) in the second set, pure NPK, 5 wt % of NPK coated by SAP, and 5 wt % of NPK coated by SPC. All these weight percentages are calculated from the weight of soil (50 g) used.

Distilled water of 50 mL was slowly added to the samples (soil + NPK, soil + NPK coated by SAP, and soil + NPK coated by SPC) without reaching the soil surface. The beakers were left at room temperature for 30 days and weighed every day. The water retention in the soil was calculated by using eq. (1).

$$R = \frac{m_i}{m_0} \tag{1}$$

where R is the water retention after 30 days, m_i is the final weight after 30 days, and m_o is the initial weight of the sample.

Slow Release and Kinetics of CRF

The slow release behavior of controlled release fertilizer (CRF) in soil was investigated by the following methods:

50 g of sieved dry soil was mixed homogeneously with 2.5 g of NPK fertilizer, NPK coated with SAP, and NPK coated with SPC, respectively, before being placed in a 100-mL pot complete with saucer and incubated. Throughout the experiment, the soil was maintained at 30 wt % water holding capacity by weighing daily and adding distilled water (if necessary). The excess water collected from the saucer was taken to determine the N, P, and K contents by induced coupled plasma mass spectrometry (ICP-MS, model 7500, Agilent) method. Results collected from the spectrometry analysis were analyzed using an empirical equation (eq. (2)) to estimate the values of n and k:

$$\frac{M_t}{M} = kt^n \; or \log\left(\frac{M_t}{M}\right) = \log(k) + n\log(t) \tag{2}$$

where Mt/M is the release fraction at time t, n is the release exponent, and k is the releasing factor. From the slope and intercept of the plot of log (Mt/M) versus log t and the kinetic parameters, n and k were calculated.

Then, the initial diffusion coefficient (D) was calculated using eq. (3):

$$\frac{M_t}{M} = 4\left(\frac{Dt}{\pi l^2}\right) \tag{3}$$

where l is the thickness of hydrogel polymer.

Scanning Electron Microscope

The surface morphology of NPK fertilizer, outer layer & adhesive in CRF and cross section of CRF were studied using a scanning electron microscope (SEM; EVO 50, Zeiss). Samples were adhered onto double-sided electrically conducting carbon adhesive tapes mounted on small aluminum stubs and coated with platinum by a sputter coater.

RESULTS AND DISCUSSION

Physical Characteristic of NPK Coated with SAP and SPC

The average water absorbency of the SAP is 40.61 ± 2.75 g/g, while the SPC is 55.28 ± 1.32 g/g in distilled water. The additions of carbonaceous filler in the SPC indirectly increase the carbon content from 36.5 to 56.7 wt % as well as the water absorbency ability of the outer layer material. The SAP particle size ranged between 135 and 690 µm, while for the SPC particle size ranged from 93 to 444 µm.[40]

Water Retention of NPK Coated with SAP and SPC (CRF) in Soil

Different Weight Percentage. The water retention of CRF in soil was first observed for NPK coated with SPC samples for 30 days at different weight percentages (1, 3, and 5 wt %) in order to find out the optimal amount of CRF in soil to enhance the water retention in the soil. The water-retention percentage of each samples was calculated using eq. (1). Figure 1 shows the water-retention percentage of NPK coated with SPC at different weight percentages. SPC + NPK 1, SPC + NPK 3, and SPC + NPK 5 represents sample with 1, 3, and 5 wt %, respectively, for CRF.

The rate of water retention in soil increases with increasing amount of CRF used. At the 15th and 30th day, the SPC + NPK 1 recorded 87.32 and 78.1%, SPC + NPK 3 recorded 94.2 and 85.24%, and SPC + NPK 5 recorded 95.47 and 88.28% water retention in the soil, respectively. The overall evaporation rate of water after 30 days was 21.9% for sample SPC + NPK 1, 14.76% for sample SPC + NPK 3, and 11.72% for sample SPC + NPK 5. These results indicated that the amount of water retained in the soil remained above 50% even after 30 days of experiment,

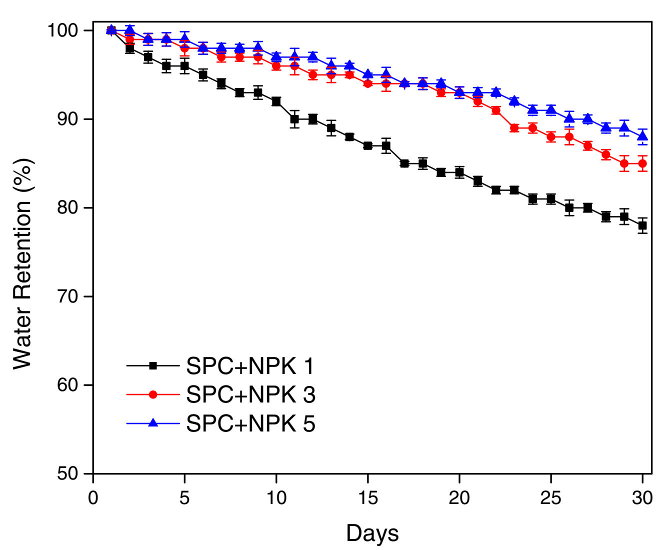


Figure 1. Water retention percentage of NPK coated with SPC at different weight percentages. [Color figure can be viewed at wileyonlinelibrary.com]

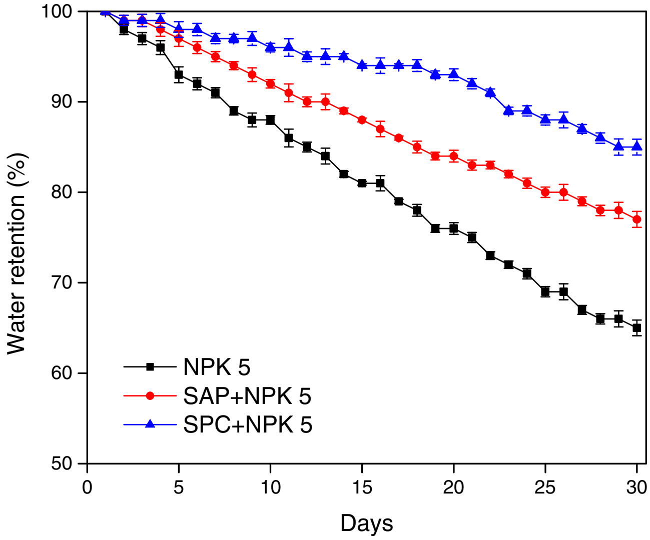


Figure 2. Water retention of different coating-type CRFs at constant weight percentage. [Color figure can be viewed at wileyonlinelibrary.com]

indicating that CRF has the ability to retain water in a soil for a longer duration; the higher the amount of CRF, the better is the water-retention capacity. In general, the results show that SPC polymer clearly improved the features of CRF and enhanced its performance with the soil environment.

Different Coating Materials. In this study, the water retention in soil by CRFs with different type of coating materials (NPK 5, SAP + NPK 5, and SPC + NPK 5) was investigated. The raw NPK 5 was chosen only to compare it with SAP- and SPC-based fertilizers. The water-retention percentage of each samples was also calculated using eq. (1). This parameter was chosen to discover the effect of SAP and SPC as a coating material and to study the effect of carbon filler on the water-retention ability of CRFs. Figure 2 illustrated water-retention percentage of different coating-type CRFs at constant weight percentage (5 wt %).

The raw NPK fertilizer showed the lowest rate of water retention as compared with CRF with SAP and SPC coatings. NPK fertilizer recorded 81.06 and 65.25% of water-retention percentage at the 15th and 30th days, respectively, whereas the SAP + NPK 5 recorded 88.43 and 77.65% and SPC + NPK 5 recorded 94.21 and 85.5% water retention at the 15th and 30th days, respectively. The NPK coated with SPC recorded the highest water-retention percentage as compared with other two materials. These results are better comparatively than the montmorillonite-based superabsorbent nanocomposite based on maize bran; for example, the water retention recorded at the 10th and 15th days is 31.2 and 16.8%, respectively.[41] As shown in Figure 2, there is a clear gap between the three samples, and therefore, it is concluded that carbon microspheres in the SPC has aided the CRF toward higher water-retention ability.

Slow Release Behavior of NPK Coated with SAP and SPC (CRF) in Soil

CRFs were traditionally designed to release nutrients continuously in a controlled manner. In order to investigate the slow

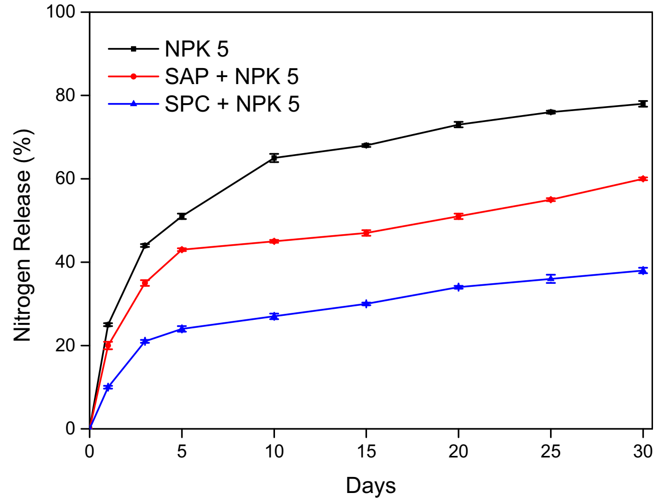


Figure 3. Percentage of nitrogen release behavior from NPK, SAP with NPK, and SPC with NPK. [Color figure can be viewed at wileyonlinelibrary.com]

release behavior of the CRF, NPK and NPK coated with SAP and SPC are produced in this study. The presence of N, P, and K in the samples was detected using ICP-MS for 30 days, as shown in Figures 3–5. The percentages of N, P, and K released into the soil over time were measured.

Figure 3 shows the percentage of nitrogen release for 30 days. NPK 5 recorded the highest percentage nitrogen release, that is, 51, 68, and 78% nitrogen at the 5th, 15th, and 30th days, respectively, as compared with NPK coated with SAP and SPC samples. NPK coated with SAP samples recorded percentage of nitrogen release are 43, 47, and 60% at the 5th, 15th, and 30th days, respectively, whereas, NPK coated with SPC sample recorded the lowest release of nitrogen, that is, 24, 30, and 38% at the 5th, 15th, and 30th days, respectively.

Figure 4 shows the percentage of phosphorus release over 30 days. At the 5th, 15th, and 30th days, NPK released 63, 70,

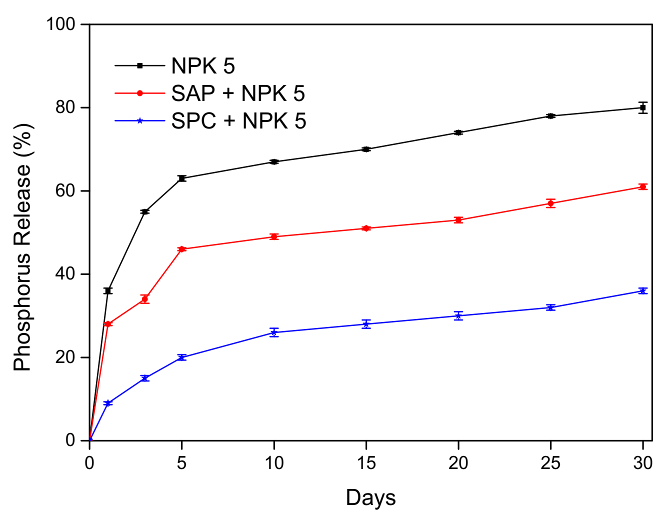


Figure 4. Percentage of phosphorus release behavior from NPK, SAP with NPK, and SPC with NPK. [Color figure can be viewed at wileyonlinelibrary.com]

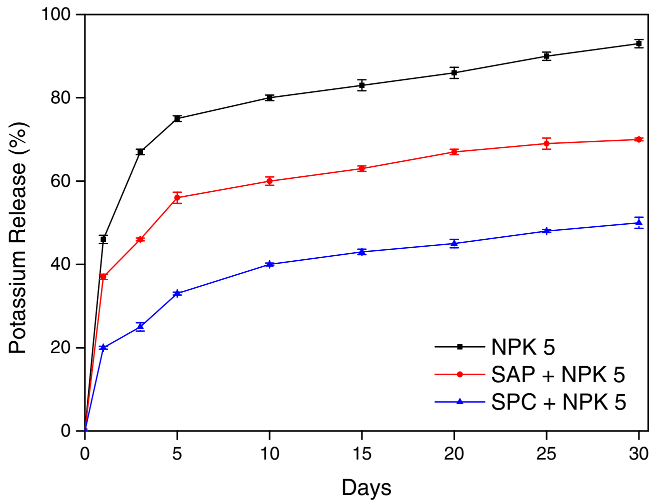


Figure 5. Percentage of potassium release behavior from NPK, SAP with NPK, and SPC with NPK. [Color figure can be viewed at wileyonlinelibrary.com]

and 80% of phosphorus, NPK coated with SAP released 46, 51, and 61%, and NPK coated with SPC released 20, 28, and 36%, respectively. The amount of phosphorus released in terms of percentage is highest for pure NPK while it is lowest for NPK coated with SPC.

Figure 5 shows the percentage of potassium release over 30 days. The same trend can be observed from the samples as shown in both nitrogen and phosphorus release. At 5th, 15th, and 30th days, NPK sample released 75, 83, and 93% of potassium, NPK coated with SAP sample released 56, 63, and 70% of potassium, and NPK coated with SPC sample released 33, 43, and 50% of potassium, respectively.

As observed in Figures 3–5, the release rate of N, P, and K by raw NPK fertilizer was more than 50% within 5 days. The NPK coated with SPC, however, showed that the lowest release rate, that is, less than 50% of N, P, and K, was found at the 30th day. The results of nutrient release demonstrated that NPK coated with SAP and SPC possessed slow release properties, as both samples released less than 75% of nutrients into the soil by the 30th day; this definition is based on the European Committee for Standardization.[42] The addition of carbonaceous microspheres into SAP and then associating them further with NPK fertilizer have shown positive outcomes on slow release behavior of the fertilizer. Figure 6 shows the mechanism of nutrient release of CRF in the soil.

The polymeric quality in SAP is hydrophilic *viz.* "water adoring" in light of the fact that it contains water-cherishing carboxylic acid (— COOH) groups. At the point when water is added to SAP, there is a polymer/solvent interaction; hydration, and the development of hydrogen bonds.[43] When SAP came in contact with the water, it absorbs water and swell. So when the NPK was encapsulated by SAP or SPC, the easily melted NPK stays inside and it does not burst out immediately into the soil. The swollen SAP or SPC holds the nutrients in NPK fertilizer and slowly releases the nutrients into soil while also releasing water that it retains, which makes it a CRF.

Kinetic Study of Controlled Released Fertilizer

In order to gain deeper insights into the controlled release characteristics of NPK fertilizer coated with SAP and SPC, a semiempirical model known as the Korsmeyer–Peppas model (eq. (2)) was selected to study the kinetics of the release mechanism of the samples. Figure 7 shows the plot of log (Mt/M) versus log *t*.

The kinetic parameters of n and k were calculated based on the slope and intercept of the graph plotted in Figure 7 using eq. (2), where Mt/M is the released fraction at time t, n is the release exponent, and k is the release factor. According to the Korsmeyer–Peppas model developed in 1983, a value of n of ≤ 0.5 implies that the fertilizer release mechanism approaches a Fickian diffusion-controlled release, n = 1.0 signifies that the fertilizer release mechanism approaches Case II transport, which is zero

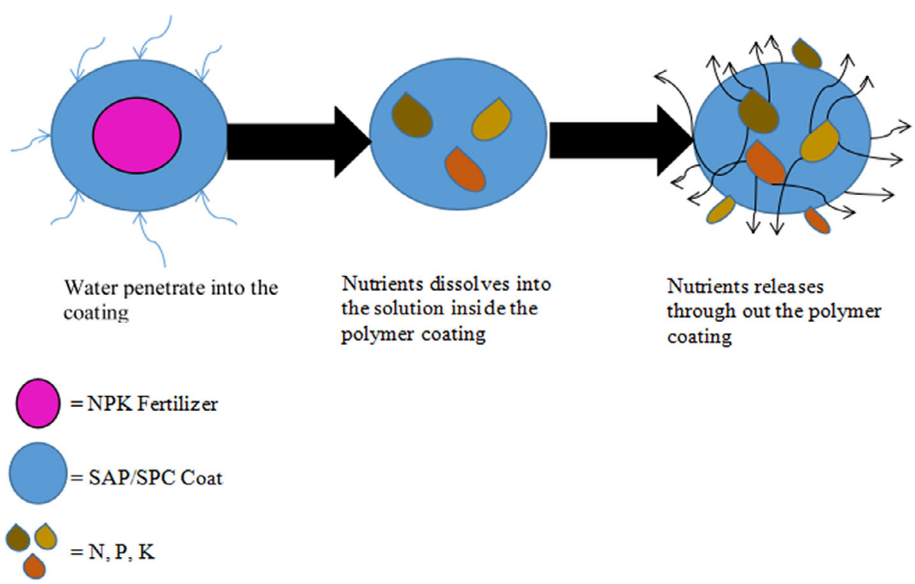
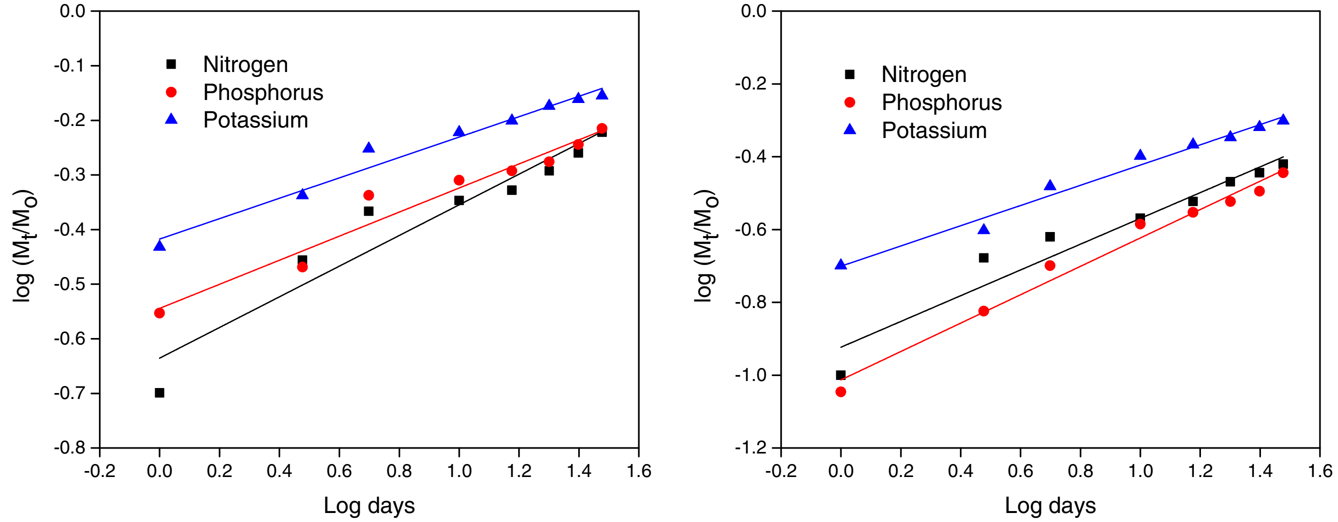


Figure 6. The nutrient release mechanism. [Color figure can be viewed at wileyonlinelibrary.com]



(a) SAP coated NPK fertilizer vs time **(b)** SPC coated NPK fertilizer vs time

Figure 7. (a) Plot of release fractions of SAP coated NPK fertilizer versus time. (b) Plot of release fractions of SPC-coated NPK fertilizer against time. [Color figure can be viewed at wileyonlinelibrary.com]

order release, whereas n = 0.5–1.0 indicates that the fertilizer release mechanism is anomalous transport, also known as non Fickian diffusion.[44–46] Table I summarizes the values for N, P, and K release from NPK coated with SAP and NPK coated with SPC in soil.

As shown in Table I, n values for NPK coated with SAP and SPC are below 0.5 for both, which implies that the release mechanism of these fertilizers approaches Fickian diffusion-controlled release. This mechanism signifies that the nutrients are released by the combined mechanisms of pure diffusion-controlled and swelling-controlled release.[47] The value of initial diffusion coefficient, D of both samples is affected by the chemical structure and the surface area of the polymer, where the value of D for NPK coated with SAP is higher than NPK coated with SPC. This shows that the incorporation of carbonaceous microsphere filler into the polymer aids in controlling the release rate of the nutrients into soil; the nutrients are released slower from NPK coated with SPC than NPK coated with SAP.[44,46,47]

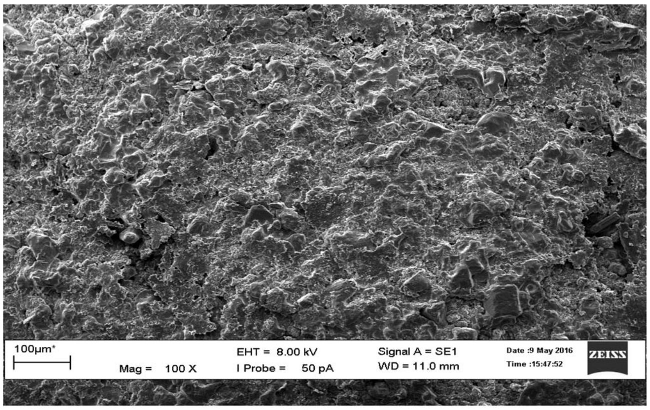
Surface Morphology of NPK Coated with SAP and SPC

The surface morphology of controlled released NPK fertilizer was studied using SEM. The morphology of these samples was observed in order to distinguish between the inner core (NPK fertilizer), the adhesive (starch), and the outer coat (SAP/SPC). Figure 8 shows the morphology of NPK fertilizer and CRFs.

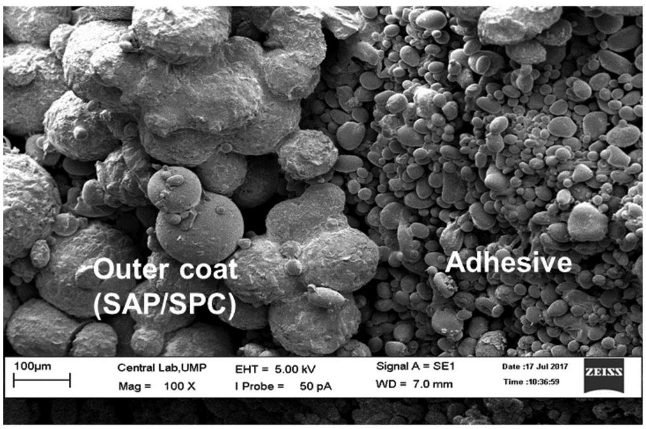
Figure 8(a) illustrates the morphology of NPK fertilizer, and naturally, this fertilizer produced spherical shape with light pink in color. It may appear hard when dry, but when it is associated with water, it becomes soft and is easily dissolved. As shown in Figure 8, the surface of NPK fertilizer is porous, which makes it easy for water to penetrate into it, leading to fast release of nutrients into the soil during the irrigation process. The purpose of the SAP and SPC polymers in NPK fertilizers is to counter this problem by covering the fertilizer wholly and preventing the nutrients from releasing too fast into soil. As shown in Figure 8(b), the adhesive was successfully integrated with the polymer and covered the NPK fertilizer. This helps in preventing the NPK fertilizer from being released into soil too fast during and after the irrigation process. The SAP and SPC polymers act as an outer shell protecting the fertilizer, absorbing water and restoring large amount of water while aiding the release of nutrients in controlled manner. Figure 8 (c) depicts the morphology of the cross-sectional area of the NPK coated with SAP and SPC (CRF). Evidently, as shown in the figure, SAP and SPC are the outer layers, the adhesive is the middle layer, and NPK fertilizer is the inner core of this CRF.

Table I. The Release Factors (k), Release Exponent (n), Determination Coefficient (r^2) and Initial Diffusion Coefficient (D) Following Linear Regression of Release Data of Nutrients from NPK Coated with SAP and NPK Coated with SPC

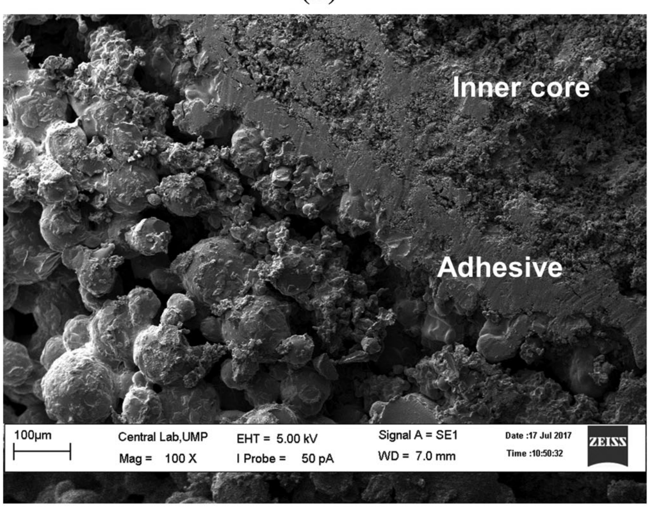
Types of fertilizer	Nutrients	n	k	r^2	D (cm^2/s)
NPK coated with SAP	N	0.28	0.53	0.91	1.4565×10^{-11}
	P	0.22	0.58	0.95	6.6394×10^{-11}
	K	0.18	0.66	0.97	6.5884×10^{-11}
NPK coated with SPC	N	0.35	0.40	0.93	5.3700×10^{-12}
	P	0.38	0.36	0.98	6.0706×10^{-12}
	K	0.27	0.50	0.98	2.9815×10^{-12}



(a)



(b)



(c)

Figure 8. (a) SEM morphology of NPK fertilizer; (b) SEM morphology of outer layer and adhesive in CRF; and (c) SEM morphology of cross-sectional area of CRF.

CONCLUSION

This study was conducted to investigate the efficiency of SAP and SPC polymers as coating material in the CRFs. Measurement of water retention in soil showed that NPK coated with SPC had the highest water-retention rate compared with raw NPK and NPK coated with SAP, with more than 80% of water remaining in the soil at the 30th day, indicating that carbonaceous microsphere filler enhances the water-retention ability of the CRF. The effect of amounts of CRF in the soil on the water retention was also investigated, and it was found that the higher the amount of CRF, the better the water retention. The slow release behavior of NPK coated with SAP and SPC in soil was observed using ICP-MS for 30 days. Based on the observations, NPK coated with SPC possesses better slow release behavior than NPK coated with SAP. NPK coated with SPC had released less than 50% of nutrients into the soil at the 30th day. The kinetic study of NPK coated with SAP and SPC (CRF) was carried out to gain deeper insights into the release mechanisms of the samples. The nutrient release mechanisms of both NPK coated with SAP and with SPC followed the Fickian diffusion-controlled release as the n value for all nutrients from both samples was below 0.5. The initial diffusion coefficient (D) value for NPK coated with SPC was lower than for NPK coated with SAP, indicating that addition of carbonaceous microspheres filler into the polymer aids the controlled release of the CRF, as the nutrients were released more slowly and in a more controlled manner. The morphology of the CRFs showed that the SAP and SPC polymers had integrated with the adhesive, hence acting as the outer layer of the fertilizer, wholly covering it and protecting it from dissolving too fast, and absorbing and restoring a large amount of water while aiding the release of nutrients in a controlled manner.

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REFERENCES

1. Carrao, H.; Naumann, G.; Barbosa, P. *Glob. Environ. Chang.* **2016**, *39*, 108.
2. Cheng, D.; Liu, Y.; Yang, G.; Zhang, A. *J. Agric. Food Chem.* **2018**, *66*(23), 5762.
3. Seetapan, N.; Wongsawaeng, J.; Kiatkamjornwong, S. *Polym. Adv. Technol.* **2011**, *22*(12), 1685.
4. Ni, B.; Liu, M.; Lü, S.; Xie, L.; Wang, Y. *J. Agric. Food Chem.* **2010**, *58*(23), 12373.
5. Wei, J.; Yang, H.; Cao, H.; Tan, T. *Saudi J. Biol. Sci.* **2016**, *23*(5), 654.
6. Witono, J.; Noordergraaf, I.; Heeres, H.; Janssen, L. *Carbohydr. Polym.* **2014**, *103*, 325.
7. Guo, L.; Ning, T.; Nie, L.; Li, Z.; Lal, R. *Eur. J. Agron.* **2016**, *75*, 118.
8. Feng, E.; Ma, G.; Wu, Y.; Wang, H.; Lei, Z. *Carbohydr. Polym.* **2014**, *111*, 463.

9. Zhang, M.; Cheng, Z.; Zhao, T.; Liu, M.; Hu, M.; Li, J. *J. Agric. Food Chem.* **2014**, *62*(35), 8867.
10. Zohuriaan-Mehr, M.; Omidian, H.; Doroudiani, S.; Kabiri, K. *J. Mater. Sci.* **2010**, *45*(21), 5711.
11. Ullah, F.; Othman, M. B. H.; Javed, F.; Ahmad, Z.; Akil, H. M. *Mater. Sci. Eng. C.* **2015**, *57*, 414.
12. Ahmed, E. M.; Aggor, F. S.; Awad, A. M.; El-Aref, A. T. *Carbohydr. Polym.* **2013**, *91*(2), 693.
13. Spagnol, C.; Rodrigues, F. H.; Pereira, A. G.; Fajardo, A. R.; Rubira, A. F.; Muniz, E. C. *Carbohydr. Polym.* **2012**, *87*(3), 2038.
14. Liu, J.; Wang, Q.; Wang, A. *Carbohydr. Polym.* **2007**, *70* (2), 166.
15. Liu, T.; Qian, L.; Li, B.; Li, J.; Zhu, K.; Deng, H.; Yang, X.; Wang, X. *Carbohydr. Polym.* **2013**, *94*(1), 261.
16. Hussien, R. A.; Donia, A. M.; Atia, A. A.; El-Sedfy, O. F.; El-Hamid, A. R. A.; Rashad, R. T. *Catena*. **2012**, *92*, 172.
17. Pathak, V. M.; Kumar, N. *Data Brief*. **2017**, *13*, 291.
18. Wilske, B.; Bai, M.; Lindenstruth, B.; Bach, M.; Rezaie, Z.; Frede, H.-G.; Breuer, L. *Environ. Sci. Pollut. Res.* **2014**, *21*(16), 9453.
19. Feng, D.; Bai, B.; Wang, H.; Suo, Y. *J. Agric. Food Chem.* **2017**, *65*(29), 5896.
20. Wu, L.; Liu, M.; Liang, R. *Bioresour. Technol.* **2008**, *99* (3), 547.
21. Yang, Y.; Wang, H.; Huang, L.; Zhang, S.; He, Y.; Gao, Q.; Ye, Q. *J. Hazard. Mater.* **2017**, *328*, 70.
22. Montesano, F. F.; Parente, A.; Santamaria, P.; Sannino, A.; Serio, F. *Agric. Agric. Sci. Procedia*. **2015**, *4*, 451.
23. Chen, Y.; Tang, H.; Liu, Y.; Tan, H. *J. Taiwan Inst. Chem. Eng.* **2016**, *59*, 569.
24. Li, S.-X.; Wang, Z.-H.; Malhi, S.; Li, S.-Q.; Gao, Y.-J.; Tian, X.-H. *Adv. Agron.* **2009**, *102*, 223.
25. Spiertz, J. *Agron. Sustain. Dev.* **2010**, *30*, 43.
26. Chaudhary, S.; Dheri, G.; Brar, B. *Soil Tillage Res.* **2017**, *166*, 59.
27. Chen, S.; Yang, M.; Ba, C.; Yu, S.; Jiang, Y.; Zou, H.; Zhang, Y. *Sci. Total Environ.* **2018**, *615*, 431.
28. Klutse, A. R.; Bationo, A.; Mando, A. Socio-economic determinants and trends on fertilizer use in West Africa. In Improving the Profitability, Sustainability and Efficiency of Nutrients through Site Specific Fertilizer Recommendations in West Africa Agro-Ecosystems: Volume 1; Bationo, A.; Ngaradoum, D.; Youl, S.; Lompo, F.; Fening, J. O., Eds., Springer International Publishing: Cham, **2018**. p. 253.
29. Ahmed Khan, T.; Kim, H.-J.; Gupta, A.; Jamari, S. S.; Jose, R. *J. Chem. Technol. Biotechnol.* **2019**, *94*(5), 1374.
30. Khan, T. A.; Gupta, A.; Jamari, S. S.; Jose, R.; Nasir, M.; Kumar, A. *BioResources*. **2013**, *8*(3), 4171.
31. Tanveer Ahmed Khan, A. G.; Jamari, S. S.; Jose, R. *Int. J. Eng. Technol. Sci.* **2015**, *3*(1).
32. Tanveer Ahmed Khan, A. G.; Jamari, S. S.; Poddar, P. *Asian J. Appl. Sci.* **2014**, *2*(6), 916.
33. Stemann, J.; Putschew, A.; Ziegler, F. *Bioresour. Technol.* **2013**, *143*, 139.
34. Reza, M. T.; Rottler, E.; Herklotz, L.; Wirth, B. *Bioresour. Technol.* **2015**, *182*, 336.
35. Álvarez-Murillo, A.; Román, S.; Ledesma, B.; Sabio, E. *J. Anal. Appl. Pyrolysis*. **2015**, *113*, 307.
36. Lin, Y.; Ma, X.; Peng, X.; Yu, Z.; Fang, S.; Lin, Y.; Fan, Y. *Fuel*. **2016**, *181*, 905.
37. Fang, J.; Zhan, L.; Ok, Y. S.; Gao, B. *J. Ind. Eng. Chem.* **2018**, *57*, 15.
38. Jamari, S. S.; Howse, J. R. *Biomass Bioenergy*. **2012**, *47*, 82.
39. Ezzah, M.; Zakaria, T.; Norlirabiatuladawiyah, C. A.; Saidatul Shima, J.; Suriati, G.; Khan, T. A.; Ali, M. F. B. *Aust. J. Basic Appl. Sci.* **2016**, *10*(17 Sp.), 122.
40. Zakaria, M. E. B. T.; Jamari, S. S. B.; Ghazali, S. *J. Mech. Eng. Sci.* **2017**, *11*(3), 2794.
41. Olad, A.; Gharekhani, H.; Mirmohseni, A.; Bybordi, A. *Adv. Polym. Technol.* **2018**, *37*(6), 1682.
42. Trenkel, M. E. Controlled-Release and Stabilized Fertilizers in Agriculture; International Fertilizer Industry Association: Paris, France, **1997**.
43. Buchholz, F. L.; Graham, A. T. Modern Superabsorbent Polymer Technology; John Wiley & Sons, Inc.: New York, NY, **1998**. p. 279.
44. Irfan, S. A.; Razali, R.; KuShaari, K.; Mansor, N.; Azeem, B.; Versypt, A. N. F. *J. Control. Release*. **2018**, *271*, 45.
45. Ritger, P. L.; Peppas, N. A. *J. Control. Release*. **1987**, *5* (1), 37.
46. Olad, A.; Zebhi, H.; Salari, D.; Mirmohseni, A.; Tabar, A. R. *Mater. Sci. Eng. C.* **2018**, *90*, 333.
47. Jamnongkan, T.; Kaewpirom, S. *J. Polym. Environ.* **2010**, *18* (3), 413.