Available online at www.sciencedirect.com

ScienceDirect

Materials Today: Proceedings 5 (2018) 21911–21918

materialstoday: PROCEEDINGS

www.materialstoday.com/proceedings

The 3rd International Conference on Green Chemical Engineering Technology (3rd GCET_2017): Materials Science

Impact of sap-biochar incorporation on controlled release water retention fertilizer (CRWR) towards growth of okras (*Abelmoschus Esculentus*)

Nureen Noordin*, Suriati Ghazali, Najahusna Adnan

Faculty of Chemical Engineering and Natural Resources, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia

---

Abstract

The preparation of SAP-biochar as the CRWR coatings material was carried out via solution polymerization technique with introduction of biochar as fillers, in the aim to observe its effect towards Okras. Studies between SAP with and without incorporation of biochar was done for comparison. SEM imaging shows the incorporation of biochar contributes to a porous structure of the SAP hydrogel. The highest WR% and growth height achieved was observed at CRWR SAP-biochar at 75% and 22.3cm respectively. SAP-biochar also showed the lowest percentage of total potassium release of 21.59%. From the results, shows that incorporation of SAP-biochar contributes to a positive effect towards Okras.

Selection and/or Peer-review under responsibility of The 3rd International Conference on Green Chemical Engineering and Technology (3rd GCET): Materials Science, 07-08 November 2017.

Keywords: Superabsorbent polymer; biochar; solution polymerization, nutrient release; controlled release water retention fertilizer; water retention.

---

* Corresponding author. Tel.: +609-4245000 ; fax: +609-4245055
E-mail address: nureennoordin92@gmail.com

Selection and/or Peer-review under responsibility of The 3rd International Conference on Green Chemical Engineering and Technology (3rd GCET): Materials Science, 07-08 November 2017.

1. Introduction

Okra, (*Abelmoschus esculentu*) is is a vegetable crop that were typically grown in tropical and subtropical regions across the world [1]. Okra has been found to be a rich source of vitamins A and C, calcium, thiamine, riboflavin and also very rich in iron [2]. Apart from its medicinal properties, Okra's plants are regularly consumed as a delicacy in Malaysia. NPK (15-15-15) fertilizer were often used at the early stages of Okras growth [3]. Like any other types of conventional fertilizers, NPK-fertilizers are soluble in water and were often leached off during watering. This could lead to excessive usage due to multiple application as to provide the nutrients for plants. The utilization of excessive fertilizer in crop production for nutrient supply can lead to many environmental issues such as agricultural pollution and [4].

Controlled release water retention (CRWR) fertilizer is a type of controlled release fertilizer which uses superabsorbent polymers (SAPs) as its coating [5]. The use of SAPs as a coating benefits both in controlling nutrient release rate of fertilizer as well as retaining water content. It is most advantageous in the application on drought land as it will maintain the soil moisture content at a longer period of time. Compared to other types of coatings, CRWR proves to give the best nutrient release control as the SAPs creates barrier around the fertilizer, preventing it to dissolve immediately [6]. As fertilizers are known to be soluble in water and dissolved easily during watering, the nutrient would have first dissolved through the SAPs, then to the soil. In determining the quality of CRWR production, the nutrient release rate and pattern must be studied and observe. Rate refers to the total quantity of nutrient released over the entire time period while pattern refers to the periodic distribution of nutrient release at a specific time intervals towards the designated release period. A good commercialized CRWR fertilizer releases nutrients as soon as the starting application and provide consistent flow of nutrient throughout the designated of the release period [7].

In forest tree nurseries, nutrients were preferable to be released in an exponentially increasing manner to better match the supply demand of plant. The same could be applied in agricultural field. The release mechanism of CRWR depends highly on the properties of SAPs as coatings. Better polymerization of the hydrogel formed results to a better controlled release manner of nutrient into the soil. During watering, upon contact with water, the SAPs coating surrounding the fertilizer granules will expand, absorbing water, turning into hydrogel. This happen due to difference concentration gradient caused by the osmotic pressure. Over time, a dynamic exchange between the free water in the hydrogel and the water in solution will develop [8]. The fertilizer granules will be dissolved in the hydrogel network, and the nutrient from the granules will slowly diffuse out through this dynamic water exchange, hence reducing the 'burst effect'. Burst effect happens when the nutrient undergoes a rapid release in large amount, and was washed or leached away during watering.

CRWR fertilizers are expected to be designed to provide good control over release in soil and to match plant demand to provide high use efficiency and minimize adverse effects on the environment. The SAPs coating of CRWR fertilizer were known to be poorly degradable and are less favourable for the application in agriculture. In solving this problem, organic fillers were introduced which fit perfectly in the current trend to develop an environmentally friendly alternative to superabsorbent hydrogels [9]. In light of this, the introduction of biochars as fillers can be a novelty as it both helps the polymers to biodegrade easily and contributes many benefits in agricultural application. Moreover, it provides an alternative to reuse agricultural waste as a soil enhancer. Solution copolymerization of Acrylic Acid and Acryl Amide were commonly used in synthesizing an environmental friendly hydrogel. Ammonium persulfate (APS) as an initiator were often used with the presence of methylenebisacrylamide (MBA) as a crosslinker [10]. The incorporation of filler usually acte as covalently bound and multifunctional cross-linkers to the polymer, which leads to mechanical toughness, high tensile modules, and rapid swelling [11]. The palm oil milling process in Malaysia produces oil palm solid wastes such as shell, fiber, and EFB, which are considered insignificant materials [12].

The application of biochar has a number of specific function in the natural environment as it is beneficial to prevent global warming and increases the functionality of soils. Hence, incorporation of biochar into the SAP polymeric chain not only are a way in utilizing waste, the carbon particles in biochar also helps enhance the structure of SAP as well. When filler dispersed in SAP, the porous structures bring about and thus increase the surface area and capillary effect of SAP [13]. The significance outcome from this study is to observe the effect of SAP-biochar incorporation as a coating for CRWR fertilizer towards Okras. Moreover, this study also suggested an alternative towards the environmental problem regarding the pollution and low cost products that directly produce the green products. The application of carbon based CRWR is very important in agriculture to reduce cost such as reduce watering frequency and help to retain nutrient from fertilizer.

2. Materials and Methods

2.1. Preparation of SAP-biochar CRWR fertilizer

CRWR fertilizer were produced by coating NPK fertilizer granules with SAP-biochar synthesized via solution co-polymerization method. Materials used are Acrylic Acid (98% purity) as monomer and Acryl Amide (98% purity) as co-monomer. N,N-methylene-bis-acrylamide (MBA) with purity of 99%, Ammonium persulphate (APS) with purity of 98% and sodium hydroxide pellets with purity of 99% which used as neutralization purpose during polymerization process. The SAP was synthesized by mixing an amount of Acryl amide and Acrylic Acid in a 250 mL three neck flasks. The solution was then neutralized with 5M NaOH until pH of 5.5. After that, 0.4% weight of biochar were then added and stirred for at least 5 minutes using a magnetic stirrer. The mixture was then connected with a condenser, nitrogen line and thermometer. MBA, which acts as a cross-linker agent was added and the mixture solution was stirred at room temperature until the MBA was completely dissolved. The flask then immersed in a water bath and heat up to 70 °C and then APS initiator was added to the solution with continuing stirring. The reaction mixture was left to stir for 2 hours until gel point with high viscosity of mixture. In the preparation of CRWR fertilizer, starch was used as an adhesive material for coating process [14]. The resulting hydrogel then were dried overnight in oven at 60 °C until the sample was at constant weight. After that, the dried SAPs were then proceeded to be ball-milled and sieved at 50ηm. The commercial fertilizer granules were dipped in starch solution and then immediately place on SAPs powder and shaken. Then, the fertilizer was later dried in oven at 60 °C to obtain the final product which is CRWR fertilizer. The method was repeated without the addition of biochar to produce SAP coated CRWR fertilizer for comparison.

2.2 Scanning Electron Microscopy (SEM)

The surface and cross-section morphologies of SAP and SAP-biochar at swollen state was analysed by scanning electron Microscopy (SEM) as a comparison to study the morphology of both hydrogel. After immersing both the SAP and SAP-biochar in distilled water, both swollen samples were frozen in liquid nitrogen and then were cut in half to obtain cross sections. Samples were then coated with a gold layer prior to testing to avoid sample charging for SEM observation [15].

2.3 Water retention Of CRWR fertilizer in soil

To study the water retention ability of SAP-biochar incorporation as coatings, 0.3g of SAP-biochar CRWR fertilizer granules were mixed with 250g of soil in a beaker. 0.3g SAP CRWR fertilizer sample was also prepared by the same method for comparison. A soil sample without any mixture was set as a control to observe the water retention of empty soil without any influence of SAP or SAP-biochar CRWR fertilizer. Then 120 mL of distilled water was slowly added into all the sampled beaker and weighed (W) as initial weight and maintained at room temperature. The beakers were weighed every day (W_n) over a period of 7 days. The water retention ratio (WR %) of soil was calculated using the following Equation 1 [5].

$$WR\% = \frac{W}{Wn} \times 100 \tag{1}$$

2.4 Nutrient release behavior

Pot-in-pot trials were conducted following methods by [16] Simonne et al., (2005) and [1] Uka et al., (2013) to study the rate of nutrient release of fertilizer. 4 samples were taken into measure and the samples condition were as shown in Table 1. NPK fertilizer (15-15-15) were used in this study and was applied at a rate of 0.3g per 250g soil. The pots were perforated at the base to allow excess water to drain out and a container was placed at the bottom to collect drained water. The treatment were done with three replications for each sample. Approximately every 3 days, for a period of 30 days, 400ml of deionized water were added to the top of each pot and were allowed to drain into the bottom container for 24 hours. A removable plastic cover were placed around the pot to eliminate the pots from rainfall and reduce evaporative losses. The drained water or leachates were collected and analyzed for its nutrient release.

Table 1. Samples condition for nutrient release study.

Samples	Conditions
Controlled	NPK fertilizer without Okra
NPK-granules	NPK fertilizer with Okra
CRWR SAP	CRWR coated SAP with Okra
CRWR SAP-biochar	CRWR coated SAP-biochar with Okra

To study the nutrient release pattern, leachate that were collected were sent to Central Laboratory in Universiti Malaysia Pahang, where the determination of potassium or elemental K, were done using Flame AAS.

2.5 Effect of coating layer towards the growth of Okras

To study the effect of coating layer on the growth of Okras, another experiment were implemented. Three samples were prepared with three replication each, following the conditions as shown in Table 2.

Table 2. Samples condition for effect of SAP-biochar coating towards growth of Okra.

Samples	Conditions
NPK-granules	NPK fertilizer with Okra
CRWR SAP	CRWR coated SAP with Okra
CRWR SAP-biochar	CRWR coated SAP-biochar with Okra

In each sample, 0.3g of CRWR coated SAP and CRWR coated SAP-biochar were mixed with 250g of soil respectively. Control sample were prepared for comparison where 0.3g of NPK-fertilizer were used instead. 100ml of distilled water were added to the top of each pot every five days and the average height of the Okras were tabulated.

3. Result and Discussions

3.1. Morphological structure of SAP-biochar incorporation

Addition of biochar particles into the polymeric chain of SAP gives an observable effect on the morphology structure of the hydrogel when observed under SEM imaging. In this study, the samples were compared on its morphological structure of SAP with and without the presence of biochar as a filler at swollen state. Figure 1(a) shows the SEM imaging of the SAP surface without any biochar filler (SAP) while Figure 1(b) shows the structure of SAP-biochar. Both swollen state sample of (a) and (b) were observed under magnification of 600 µm. As observed, the surface of SAP-biochar at (a) gives a smother surface without any visible pores. When compared to the swollen sample of SAP-biochar at 0.4% incorporation in (b), the addition of biochar creates pores on the SAP structure. As explained earlier in the methodology, the biochar used were produced using EFB waste that undergoes pyrolysis method which converted the EFB materials into microporous structure with very high surface area. Introducing biochar particles to the polymeric chains, changes the structure of SAP hydrogel by increasing the formation of pores which enhances water absorbency of the SAP.

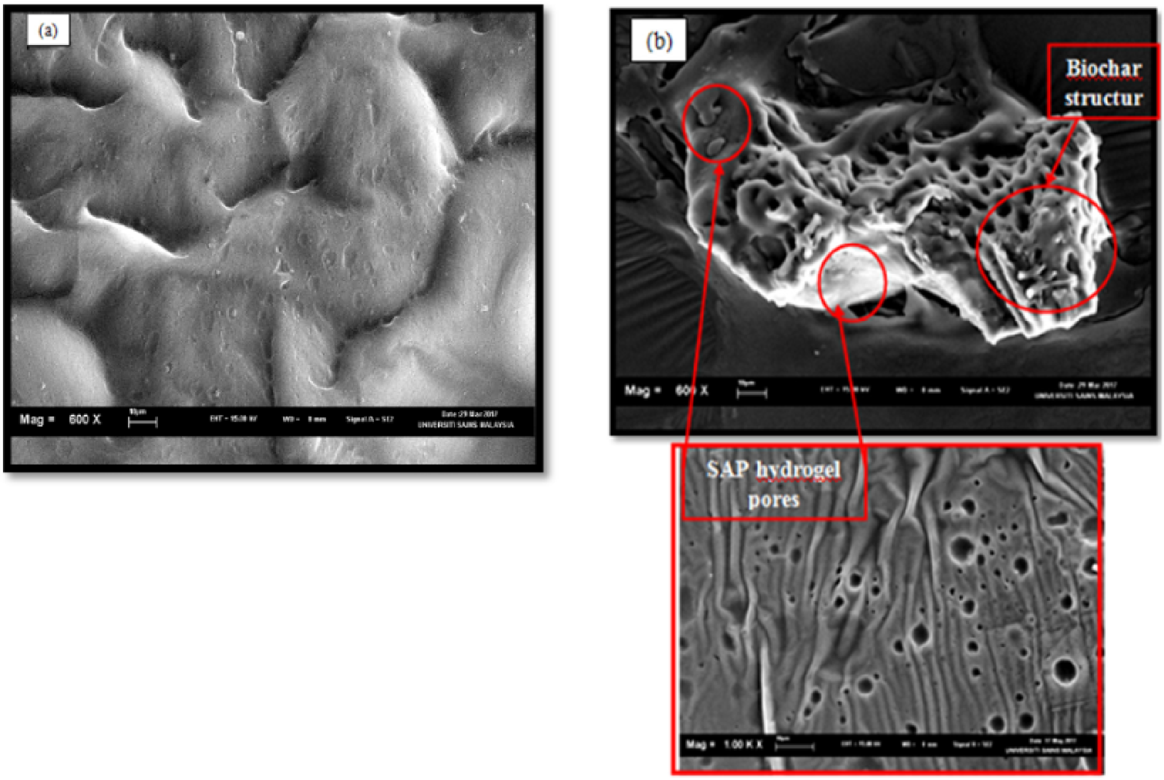

Fig. 1. FESEM imaging swollen surface of (a) SAP hydrogel; (b) SAP-biochar incorporation hydrogel.

Biochar particles enhances water absorbancy and water retention due to the binding of polymeric chains with the biochar particles, creating a rigid formation of hydrogel during the polymerization process. Water diffusion in porous networks depend on the porous structure of SAP, which means that water molecules tend to be more mobile with larger pores. This explains why the SAP-biochar appears to have higher water absorbency compared to SAP without biochar incorporation. During the polymerization, it appears that the morphology of hydrogel undergoes some transformations accompanied by the formation of larger pores and probably the densification of polymer-rich domains [17].

3.2. Water Retention of CRWR in soil

The study on water retention of CRWR fertilizer in soil were done on three samples over the period of 7 days as observe in Figure 2. WR% shows the percentage of water content of the three samples labelled 'soil' which contains mainly the soil; SAPs and SAPs-biochar, which contains mixture of soil and CRWR coated with SAP and SAP-biochar materials respectively. As shown in the figure, all WR% trends shows a decrease pattern, with sample 'soil' having the lowest WR% at 30% by the end of day 7. For SAPs and SAPs-biochar coatings sample, reached 59.4% and 75.7%. All decreasing trends of WR% represents water loss of each samples.

Water loss can occur due to factors such as evaporation, plant water uptake and irrigation [18]. Since in this study, the WR% for each samples were conducted inside a beaker and without any plant, water loss can be assume due to evaporation to surroundings. As explained earlier, SAPs can absorb and hold water molecules for a long period of time. Its application in agriculture can help retain water content in soil, preventing water loss in the surrounding. This explains why the WR% in controlled sample was the lowest compared to samples containing SAP and SAP-biochar coated CRWR Fertilizer granules.

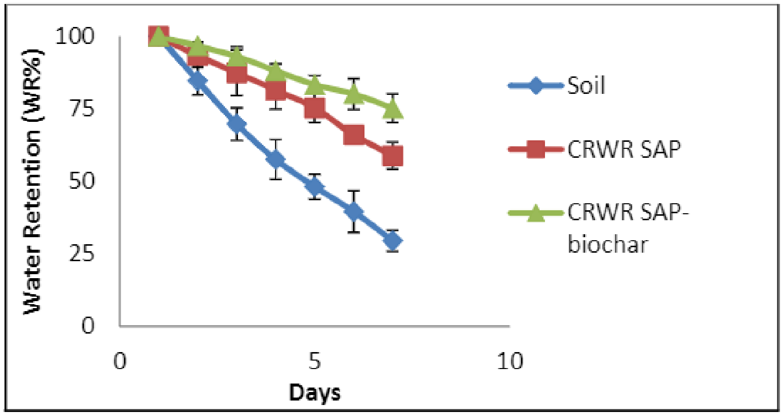

Fig. 2. Water retention (WR%) percentage loss.

Incorporation of biochar particles helps extending the polymeric chain of SAPs, increasing amount of crosslinking which results in higher absorption and stronger bonding to hold water molecules. This is why WR% in CRWR SAPs-biochar sample were higher compared to CRWR SAP sample. Biochar surface particles are naturally porous as well which can absorb water hence, enhancing water absorbing capacity so that more water can be retain inside the soil [19].

3.2. Nutrient release behavior of CRWR

In this study, the release behaviour of CRWR fertilizer in soil, were represented by the amount of potassium (K) in the soil at a certain period of time. Having a lower continuous release rate, a CRWR fertilizer is considered as more efficient to supply for a crop at a longer period of time. Using 8-8-8 NPK fertilizer granules in the CRWR production, the release rate of nutrients from the CRWR fertilizer was estimated and compared for all three components.

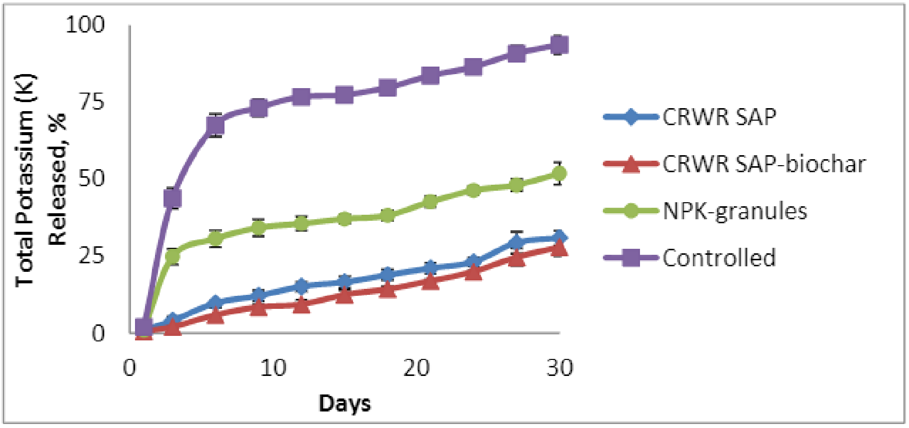

Fig. 3. Water retention (WR%) percentage loss.

As explained earlier in the methodology, element K were determined using Atomic Absorption Spectrometry (AAS). The trend release of K for CRWR SAP coated, CRWR SAP-biochar coated, NPK-granules and Control samples were observed in Figure 3. Control sample were observed to release a total amount of 94.5% of element K at the end of day 30. In comparison, in NPK-granules sample, the amount of K release is 55.99%, while CRWR SAP coated and CRWR SAP-biochar coated recorded an amount of 33.67% and 26.73% respectively at the end of 30 days period.

Observing Figure 3, total percentage release behavior of nutrient without the uptake of plants (plants were absent) in control sample, almost 50% of the total nutrients were released in the first 3 days. In comparison, NPK-granules sample were done to compare the nutrient intake of plants where the NPK-granules were used, without any coatings, and average results shows that at the end of the period, 44.01%, of K, were used up, while the rest were leached out. About 40-70% of nitrogen, 80-90% of phosphorus, and 50-70% of potassium of the applied normal fertilizer is lost to the environment during watering, which causes large economic resource losses and environmental pollution [20].

However, studying the effect of SAP coatings in CRWR fertilizers, the total release pattern for CRWR SAP coatings and CRWR SAP-biochar, shows improvement results of controlling the nutrient release in the 30 days period. There are no 'burst effect' and shows a slow, continual release manner. The term 'burst effect' means that the nutrients were released uncontrollably in a large amount as can be observe in NPK-granules sample, where nearly half amount of the nutrient total percentage were released at day 3 [21]. The presence of SAP coatings successfully acts as a barrier and inhibits nutrient release rate directly to the soil, avoiding leaching to occur.

The effect of SAP-biochar incorporation can be observed by comparing between CRWR SAP coatings and CRWR SAP-biochar coatings. The release trends for both of these two samples were quite similar to each other, showing slow, continuous release of nutrients. However, it can be seen from the total release trend, CRWR SAP coatings shows a slightly higher recorded data compared to CRWR SAP-biochar coatings. This shows that the total release of K is lower in SAP-biochar incorporation when applied as coatings. The application of biochar as filler in SAPs increases the nutrient holding ability. This is because biochars have a strong surface charge which helps it to hold nutrient and release nutrients in parallel to the plant's uptake. Hence, incorporation of SAP with biochars will help in controlling nutrient release, thereby preventing eco-system damage [22].

3.3. Effect of coating layer towards plant growth

Comparative study on the effect of coating layer of CRWR fertilizer towards SAPs-biochar incorporation as coatings were recorded in Figure 4. From the recorded data, the growth of okras in controlled sample on 12 days of planting was faster compared to the other samples. However the height recorded changed dramatically after 16 days of planting. The samples CRWR SAPs coated CRWR SAPs-biochar coated, showed continuous increase of growth during the period of 30 days although the growth rates were slow in the first 12 days of planting.

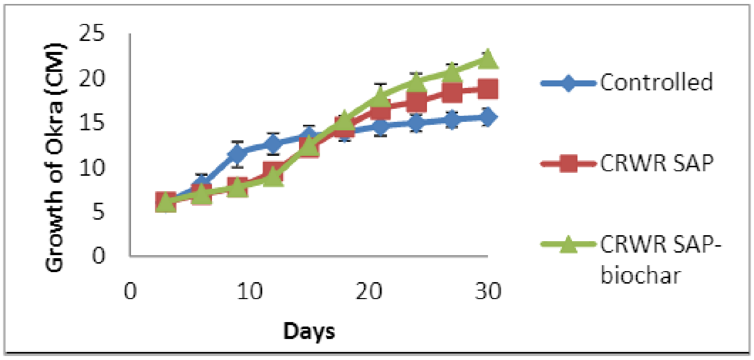

Fig. 4. Water retention (WR%) percentage loss.

The growth trend of okra in the controlled sample were faster compared to the coated SAPs was due to the direct exposure of nutrient from the fertilizer granules in the soil. This enables the plant to receive direct nutrient uptake in an abundance amount at the early stages of growth. This explains the slow rates of growth of okras in the coated CRWR fertilizer samples (CRWR SAP and CRWR SAP-biochar) as the nutrients were released slowly during osmotic build up. The application of coatings on the fertilizer granules slows down the release of nutrients into the soil in a continual manner.

Moreover, the advantages of incorporating biochar into the SAPs chain is that biochar has high surface charge which helps it to bind and hold nutrients in the soil while still making them available for plants, [23]. This explains the continuous increase growth of okras in both samples CRWR SAPs-biochar coating. Apart from that, the okra decreasing growth trends in controlled sample could be explain due to dehydration. The SAPs coatings helps retaining moisture content in soil. Apart from that, the absence of coatings that act as barrier in controlled sample was also the cause of the lacking increase of okra's growth. This is because commercial fertilizer are naturally soluble in water, most of the nutrients were leached out during watering [24].

4. Conclusion

Through this research, the incorporation of SAP-biochar as coatings for CRWR fertilizer has significant effect towards plants. From the morphological structure in the SEM imaging, biochar, acting as a filler enhances the properties of SAP itself by giving porous structure which increases the water intake of the hydrogel. The strong surface charge of the biochar contributes to an increase of water holding capacity as well. As a result, water retention can be maintained in the soil for a longer period of time. The nutrient release pattern were also improved as the presence of biochar, which were known to have a strong surface charge, are able to hold the nutrient, as well as making it available for the plant's uptake. The influence of biochar in the SAP-biochar incorporation also effects the growth of Okras as well. This is because biochar can act as a fertilizer itself by supplying carbon directly to plants.

Acknowledgements

The authors would like to thank University Malaysia Pahang Research Grant PGRS1703110 for material, financial and facilities support.

References

[1] U. N. Uka, K. S. Chukwuka, M. Iwuagwu, Journal of Agricultural Science. 58 (3) (2013) 159-166.
[2] R. Khetran, M. A. Kasi, S. Abdul, H. Agha, S. Fahmid, J. Ali, International Journal of Advanced Research in Biological Science, 3 (10) (2016) 213-218.
[3] K. Olamide, A. Christiana, Agronomski Glasnik. 15 (2012) 123-136.
[4] B. Azeem, K. Khushaari, Z. B. Man, A. Basit, T. H. Thanh, Journal of Controlled Release. 181 (1) (2014) 11-21.
[5] M. Liu, T. Guo, Journal of Applied Polymer Science, 82 (6) (2001) 1515-1520.
[6] F. Nnadi, C. Brave, Journal of Soil Science and Environmental Management. 2 (7) (2011) 206-211.
[7] B. Glaser, J. Lehmann, W. Zech, Biology and Fertility of Soils, 35 (4) (2002) 219-230.
[8] M. Tanaka, T. Hayashi, S. Morita, Polymer Journal, 45 (7) (2013) 701-710.
[9] A. Sannino, C. Demitri, M. Madaghiele, Design and Applications, (2009) 353-373.
[10] N. Shah, K. R. Patel, JPSBR. 4 (1) (2014) 114-120.
[11] D. Swantomo, K.T. Basuki, R. Sudiyo, Indo. J. Chem. 14 (2) (2014) 116-121.
[12] D. Özçimen, A. Ersoy-Meriçboyu, Renewable Energy. 35 (6) (2010) 1319-1324.
[13] S. S. Jamari, S. Ghazali, W. Siti, N. Wan, Journal of Advance Agricultural Technology. 2 (2) (2015) 156-159.
[14] L. Xia, R. Xie, X. Ju, W. Wang, Q. Chen, L. Chu, Nature Communications, 4 (2013) 1-11.
[15] N. Kamaly, B. Yameen, J. Wu, O. C. Farokhzad, Chemical Reviews. (2016).
[16] E. H. Simonne, C. M. Hutchinson, Hort Technology. 15 (1) (2005) 36-46.
[17] R. Nigmatullin, M. Bencsik, F. Gao, Royal Society of Chemistry. 10 (2014) 2035-2046.
[18] S.J. Sutanto, J. Wenninger, S. Uhlenbrook, W.R. Section, Hydrology and Earth System Sciences 16 (2012) 2605-2616.
[19] M. Gray, M.G. Johnson, M.G. Dragila, M.I Dragila, M. Kleber, Biomass and Bioenergy. 61 (2014).
[20] M.N.A. Hasaneen, A.M. Omer, African Journal Biotechnology. 13 (31) 3158-3164.
[21] P. Kumar, M. Bidhan, C. Krishi, S. Mondal, B. Chandra, K. Viswavidyalaya. Agri-nanotechniques for Plants Availability of Nutrients, SYSTEM View Project Agri-nanotechniques for Plant Availability. (2016)
[22] T. Xie, B.Y. Sadasivam, S.M. Asce, K.R. Reddy, F. Asce, C. Wang, K. Spokas, Journal of Hazardous, Toxic and Radioactive Waste, 20 (1) (1016)
[23] J. Lehman, M.C. Rillig, J. Thies, C.A. Masiello, W.C. Hockaday, D. Crowley, Soil Biology and Biochemistry, 43 (9) (2011) 1812-1836.
[24] S.I. Sempeho, H.T. Kim, E. Mubofu, A. Hilonga, Advances in Chemistry. (2014) 1-16.