



CHARACTERIZATION OF PHOSPHORIC ACID BIOCHAR DERIVED FROM RUBBER WOOD SAWDUST FOR ENHANCEMENT OF UREA FERTILIZER IMPREGNATION

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ABSTRACT

This paper examines the physiochemical properties of phosphoric acid treated biochar for improvement of urea fertilizer impregnation process. The biochar was heated with phosphoric acid (H_3PO_4) of 1.5 M (TB1) and 1 M (TB2) concentrations at 80 and 90°C temperature respectively. The treated biochar then were impregnated with 2 wt. % of dissolved urea fertilizer while continuously stirred until the mixture recrystallize to form solid urea impregnated biochar fertilizer (TB1-U and TB2-U). TB1 revealed highest composition of C (66.36%), H (6.53%) and N (1.65%) compared to TB2 composition of C (61.84%), H (4.60%) and N (1.06%). FT-IR results indicated the presence of C-O stretch functional group at 1200 cm^{-1} to 900 cm^{-1} wavelength and the presence of aromatic ring (C=O) stretching vibration at 1590 cm^{-1} - 1550 cm^{-1} wavelength revealed chemical reaction occurred due to phosphoric acid treatment. The microporosity results display more micropores formation on the sample surfaces, thus provide higher surface area possible for urea molecule to be impregnated. SEM-EDX exposed qualitatively and quantitatively the presence of 43% N on TB1-U surfaces compared with slightly lower at 42wt% of N on TB2-U surface evidenced the effectiveness of phosphoric acid treatment on enhancement of the biochar specific surface area to be impregnated with urea for nutrient retained.

Keywords: biochar; urea; slow release; fertilizer.

INTRODUCTION

One of the major concerns of the farmers is the efficiency of urea fertilizer being applied to the rice crop. Soil fertility need for improvement as the fertilizer applied especially for nitrogen (N) sources faces losses of 60% of the N (urea fertilizer) to the environment via ammonia (NH_3) volatilization, nitrate (NO_3) leaching and nitrous oxide (N_2O) emission which give high economic and environmental impact[1]. Thus, it is important to search an alternative as a substrate that can regulate the release of N from urea fertilizers. The use of organic substance such as biochar can be used as a substrate to regulate the adsorption and desorption pattern of N in different formed that can serve as a based to develop biochar based slow release fertilizer.

Biochar is the carbon-rich product of agricultural wastes such as wood, manure and leaves heated in a closed container with or without availability of oxygen[2,3]. It is well-known as a value-added product, which can be used for several purposes such as a support material for delivering plant nutrients [4]. Biochar is likely to be used as a soil amendment medium in agricultural application since it has the ability as a soil conditioner to improve soil fertility and nutrient-use efficiency using locally available and renewable material in a sustainable way. The diverse range of biochar applications depends on its physicochemical properties, which are governed by the pyrolysis conditions and their surface treatment [5].

Chemical treatment of biochar with phosphoric acid are widely used for researchers due to improvement of the biochar properties such as formation of surface active functional groups, enhance adsorption capacity [6]

and improve specific surface area through generation of micropores [7]. Phosphoric acid has attracted more attention than other strong acid/ activating agent such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) which is commonly used to modify and enhance the porous structure of biochar due to its more effective performance and environmental friendly property [8-10]. The use of phosphoric acid (H_3PO_4) treatment is also reported elsewhere to alter the properties of biochar surface and reduce environmental effect when it is being applied to the surface of soils[11].

Hence this research is mainly focusing on modification of biochar derived from rubber wood sawdust via phosphoric acid chemical treatment to improve their physical and chemical properties. Further examination on the physical and chemical characterization occurred on the acid treated biochar and biochar impregnated urea will be investigated, thus correlate them to biochar efficiency as slow release support materials for urea fertilizer.

MATERIALS AND METHODS

Preparation of acid treatment biochar

10g of biochar were blended with 400mL of phosphoric acid (H_3PO_4) at 1 M and 1.5 M concentrations and was heated at 80 and 90°C temperature respectively (Table-1) while stirred continuously. It was left cooled to room temperature before being vacuum-filtered and dried in the oven for 24 hours.



Biochar impregnated urea production

The urea fertilizer was impregnated into the porosity acid treated biochar. The urea (AR-Grade) granules (40g) were dissolved with deionized water at 4:1 ratio for recrystallization of urea after the impregnation process. The mixture then was heated at 70°C and stirred in 1 hour until the urea became completely dissolved, followed by adding 2 wt. % of acid treated biochar while continuously stirring for 1 hour until the mixture recrystallize to form solid urea impregnated biochar fertilizer. Next, the transferred compound into the petri dish were labelled and dried in an oven at 60°C for 24h. The samples were labelled as TB1 and TB2 as display on Table-1. Next, the urea impregnated biochar is label as TB1-U, TB2-U, and CB-U and characterized to determine their physiochemical properties.

Table-1. Designation of samples.

Label	Description
TB1	Treated biochar using 1.5M, 90°C and 1hour
TB2	Treated biochar using 1M, 80°C and 0.5 hour
CB	Control biochar
TB1-U	Treated Biochar 1-Urea
TB2-U	Treated Biochar 2- Urea
CB-U	Control biochar-urea

Elemental and surface analysis on treated biochar and biochar impregnated urea

The elemental analyzer (Elementar's Vario MICRO Cube) was used to determine quantitatively the presence of carbon (C), hydrogen (H) and oxygen (O) on the treated biochar surfaces. The surface functional group

analysis of treated biochar was analyzed via Fourier Transform Infrared Radiation (FT-IR) spectrophotometer (Jasco FT-IR-6100). The sample was prepared with KBr powders and compressed into a thin pellet before scanned for FT-IR spectra recorded at the range of 400 to 4000 cm^{-1} . The surface microstructural analysis of treated biochar and biochar impregnated urea was determined using SEM magnified 1000 X with the voltage set to 3.0kV. Carbon and oxygen content on the surface of the biochar sample were examined by using SEM-EDX spectroscopy with the voltage 1.0kV. Both samples were platinum coated using auto fine sputter coating technique set to 30A.

RESULTS AND DISCUSSIONS

C, H, N elemental analysis

Elements analysis of H /C ratios is useful indicators of the character of biochars (Nguyen and Lehmann, 2009). Figure-1 demonstrates the elemental composition of treated biochar labelled as TB1 and TB2 compared to biochar (CB) as control. The result demonstrates that the % of C in biochar (CB) is lowest compared to treated biochar (TB1 and TB2). The same trend observed for % of H and % of N. TB1 that treated with higher concentration of H_3PO_4 shows higher composition of C (66.36%), H (6.532%) and N (1.65%) than TB2 with composition of C (61.84%), H (6.532%) and N (1.65%). An increase in H_3PO_4 molarity results in a larger capture of C, H and N. Means that TB1 contained a higher biochar yield and enriched volatile-matter composition. An increased in the composition of H and N elements suggested of the strong H and N reaction on the treated biochar surface which is supported by the FT-IR results later.

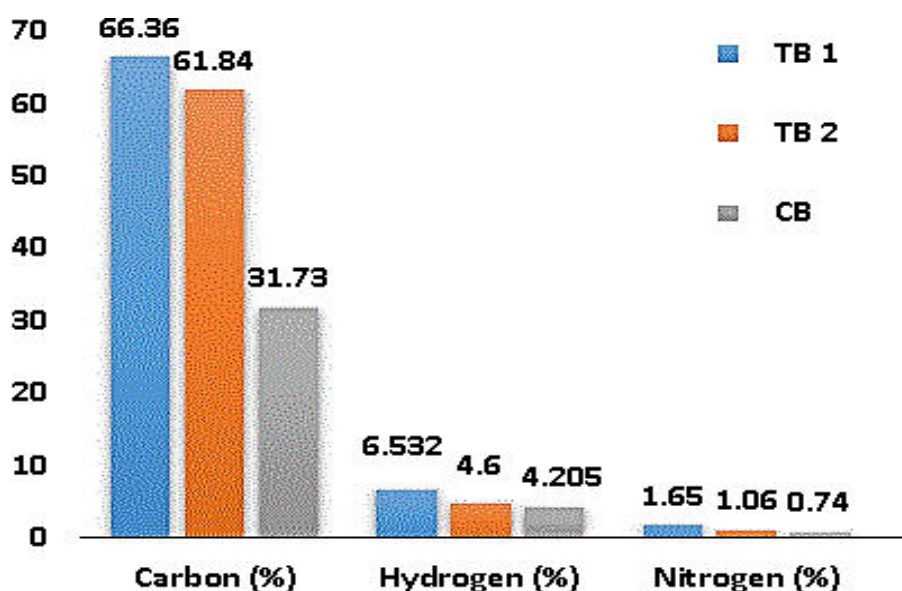


Figure-1. Histogram graph of elemental composition of the treated biochar control (CB).



H_3PO_4 reacted with biochar dispersed quickly out of the surface of particles during the acid treatment process (Patnukao & Pavasant, 2008). Analytical elements and both H/C and O/C ratios are one of the indicator to characterize chemical composition, degree of aromaticity, maturation and bonding arrangement of the biochar samples (Lehmann & Joseph, 2009). According to Glaser *et al.* [13], the high presence of H/C functional groups can serve as nutrient exchange sites after oxidation. This will lead to strong and success nutrient bonding with biochar. Thus, in slow release mechanism, it is important to prepare biochar with higher H:C ratio to facilitate retainment of nutrients from fertilizer in soil and results on the higher cation exchange capacity (CEC) [14]. This will lead to efficient plant nutrition because CEC is an inherent soil characteristic which indicates the total capacity of a soil to

hold exchangeable cations. It influences the soil's ability to hold onto essential nutrients and prevent their losses.

Fourier Transform Infrared (FTIR) spectroscopy analysis

Figure-2 displays the FT-IR spectra of control biochar (CB) and biochar treated with phosphoric acid labelled as TB1 and TB2. Broad band appeared at 3600cm^{-1} to 3200cm^{-1} which indicated stretching vibration of hydrogen-bonded (H-O) hydroxyl group. Peaks at 1155cm^{-1} and 1040cm^{-1} which were assigned as carbon-bonded C-O vibration were also observed at all samples [15]. Other significant peak observed for TB1 and TB2 were broad peak at 1200cm^{-1} to 900cm^{-1} indicating presence of C-O stretch in alcohol, phenols acid and esters and strong band appeared at 1590cm^{-1} - 1550cm^{-1} indicating presence of aromatic ring (C=O) stretching vibration [16, 17].

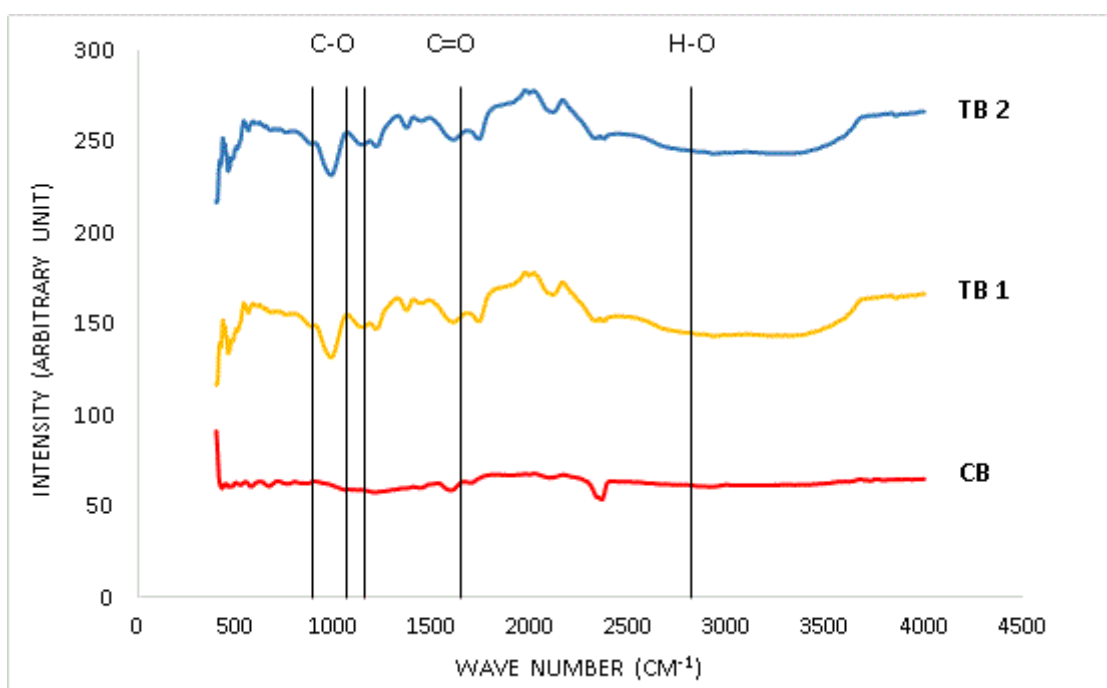


Figure-2. FT-IR spectra of biochar and treated biochar (CB, TB1 and TB2).

Figure-3 shows the FT-IR spectra of urea and urea impregnated samples with biochar (CB-U) and urea impregnated treated biochar (TB1-U and TB2-U). Similarly, broad band appears at 3600cm^{-1} to 3200cm^{-1} which indicated stretching vibration of hydrogen-bonded (H-O) hydroxyl group and the peaks

appear at 1155cm^{-1} and 1040cm^{-1} for TB1-U and TB2-U which were assigned as carbon-bonded C-O vibration. Broad peak at 1200cm^{-1} to 900cm^{-1} indicated presence of C-O stretch in alcohol, phenols acid and esters for TB1-U and TB2-U might due to the reaction of samples against the phosphoric acid [18, 19].

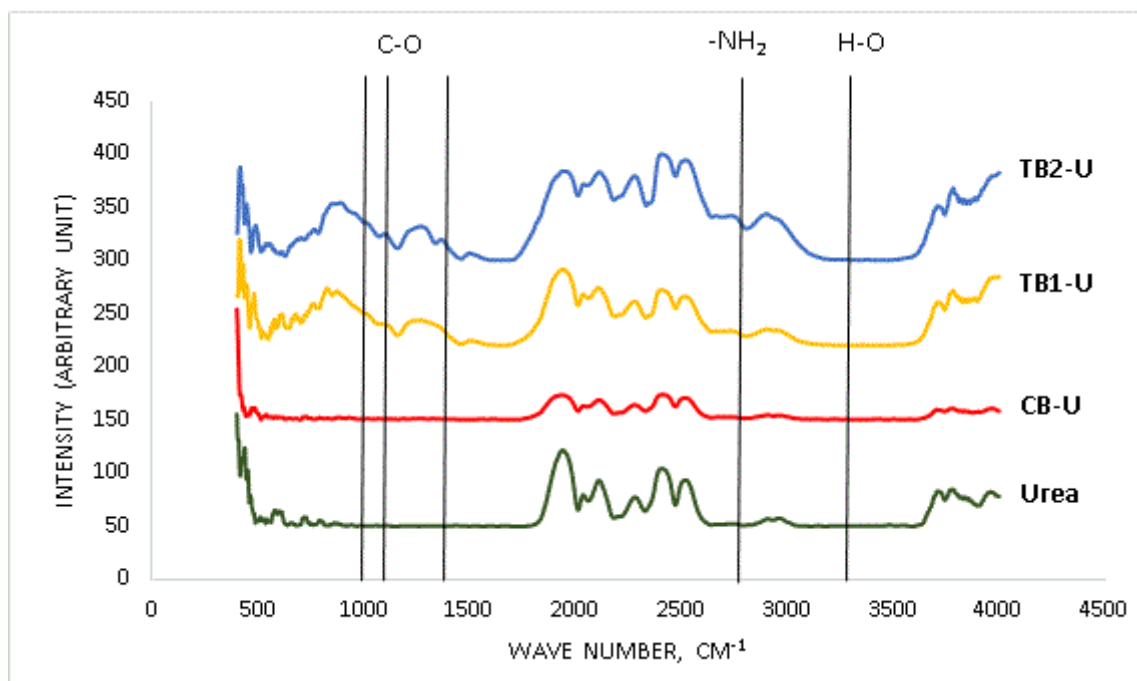


Figure-3. FT-IR spectra of urea and biochar impregnated urea sample (Urea, CB-U, TB1-U and TB2-U).

These proved chemical interaction occurred due to phosphoric acid treatment on the treated samples. There were also weak bands appeared at 2921 cm^{-1} - 2855 cm^{-1} FOR TB1-U and TB2-U samples, which showed the aliphatic of C/H and a sharp band at 1373 cm^{-1} . This is because there were stretching vibrations of CH_3 present in the samples [20-23]. However, carbonyl (C-O) stretching at urea spectra diminished at approximately 1500 cm^{-1} after interacted with biochar represent chemical interaction occurred result in the acid functional group available on the treated biochar surfaces are chemically adsorb with the urea.

Microporosity analysis of CB, TB1 and TB2

The porosity of the biochar before and after acid treatment was determined via mercury porosimetry. Table-2 shows the microporosity analysis of CB, TB1 and TB2. It is shown that the total pore area of acid treated biochar is lower compared to control. The average pore diameter of TB1, TB2 and CB are 22645.3 nm , 35772.24 nm and 13019.71 nm respectively. From the Table-2, the TB 1 percentage of porosity is highest (89.63%) compared to TB2 (78.77%) and CB (83.43%) which indicates that TB1 has more pores compared to TB2 after treatment.

Table-2. Microporosity analysis using mercury porosimetry.

Sample	Unit	TB1	TB2	CB
Total Intrusion volume	mL/g	5.08	4.62	5.3
Total pore area	m^2/g	1.2	0.52	1.63
Median pore diameter (volume)	mL/g	110297	121142.8	138919.4
Median pore diameter (area)	m^2/g	1830.23	10210.86	1975.24
Average pore diameter	nm	22645.3	35772.24	13019.71
Bulk density	(g/mL)	0.18	0.17	0.16
Apparent density (g/mL)	(g/mL)	1.69	0.8	0.95
Porosity	%	89.63	78.77	83.43

Decrement of micropore surface area might be due to the oxygen functional groups located at the entrance of the pore, hindering the nitrogen molecules from going inside the pore [24]. The treated biochar holds higher content of macropore (pore diameter $>50\text{ nm}$),

allowing the impregnation process of urea onto biochar's pores. The increase in average pore diameter of treated biochar with treatment indicating the destruction of micropore forming mesopore [25]. Higher microporosity and higher specific surface area of biochar has the ability



in the inhibition of soil organic microorganism mineralization after the application of biochar to the soil at which the mechanism involves diffusion and adsorption of organic matter into the micropore [26]. The pores on the biochar surface are covered by recrystallized urea molecule during impregnation. This demonstrated that the additional and bigger pores of biochar might be suitable for filling the urea molecules.

Surface morphology of treated biochar, biochar impregnated urea and treated biochar impregnated urea using SEM and SEM-EDX

Figure-4 shows morphological analysis of treated biochar compared to control. CB shows a porous structure and smooth wall surfaces while, TB1 and TB2 shows rough and edgy at the wall surface. This pointed out to the reaction of phosphoric acid against the adsorbent surface of biochar [27]. Additionally, both TB1 and TB2 samples has macro pores at the pre-existing structure but the

former showed higher presence of macro pore. H_3PO_4 treatment leads to increase in porosity of biochar surface was also reported elsewhere [12, 28-30]. Furthermore, the EDX analysis is conducted to determine the composition of biochar based on SEM micrograph. The results indicated that there was higher P in treated biochar (TB1 and TB2) as compared to control biochar (CB) and P that appeared to be localized at some pore at the treated biochar. Hence, this implies that localized reactions occurred during H_3PO_4 treatment. This is possibly associated with the formation of organic phosphate on the treated biochars, which may could serve as nutrient source when apply in the soils. TB1 showed to be the better treated biochar because the SEM micrograph showed smoother surface pores appeared and present of higher P compare to TB2. This might be due to the using different pH of acid with the biochar.

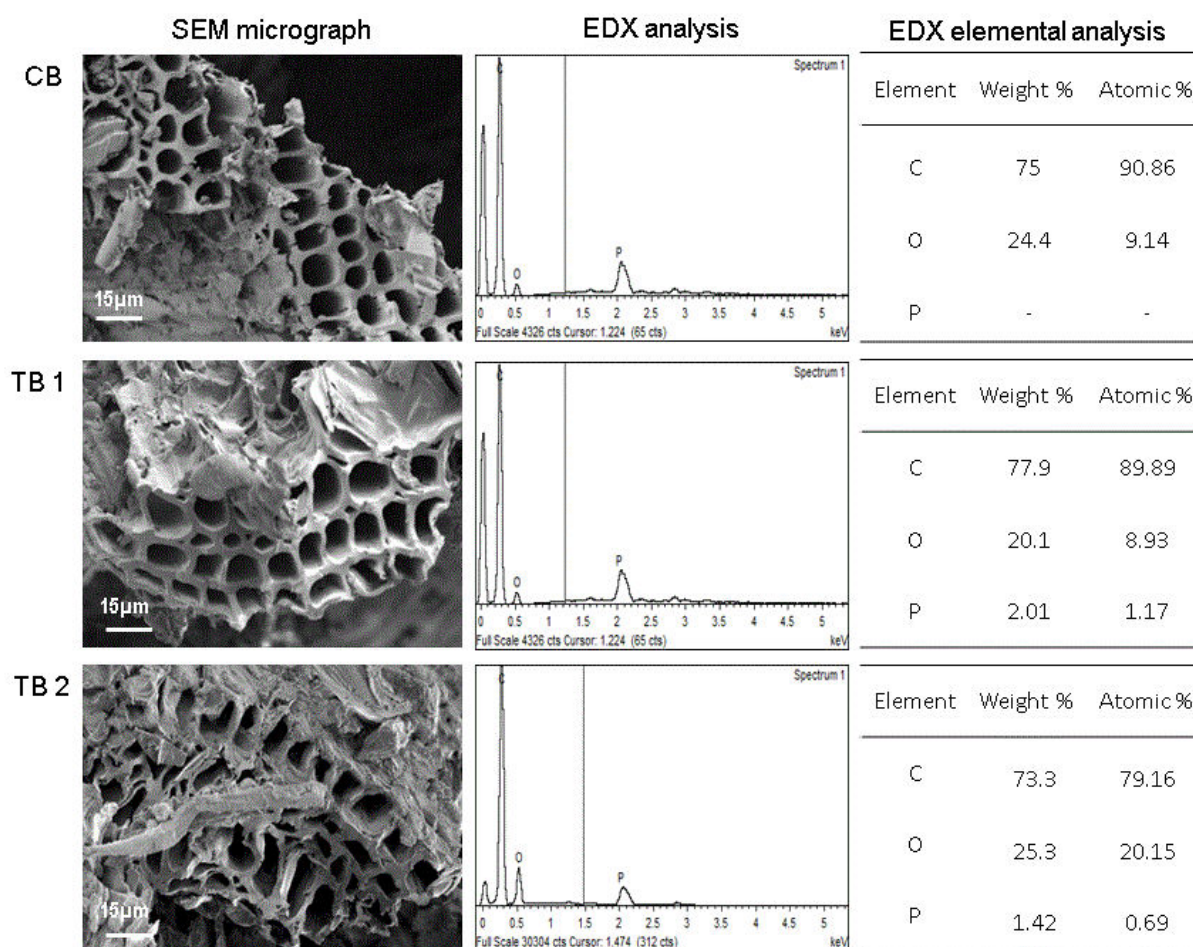


Figure-4. SEM-EDX analysis of treated biochar compared to control.

Figure-5 illustrates the SEM micrographs of urea impregnated with biochar sample labelled as CB-U, TB1-U and TB2-U. It can be clearly seen from the images, where the biochar are covered with urea and the presence of urea is proven by the SEM-EDX analysis. About 40%-45% of N is present from the analysis on the internal and

external surface of biochar. The urea molecule is diffused into the pores during impregnation process which makes the porosity of biochar becomes important to retain moisture and nutrient in the soil. After water molecules are being removed during heating, the concentration of urea become recrystallized into solid and initiates the



impregnation process. The impregnation of urea into biochar can help to slow down the mineralization process and the conversion of urea into ammonium and nitrate. Thus, the micro site of biochar will be closed and adsorbed the nutrient, enable it to hold the nutrient longer and prevented further nitrogen loss to the environment. The

higher amount of N seen at the treated samples shows there are chemical reaction happen after biochar treatment with acid, proved the effectiveness of phosphoric acid to enhance specific surface area for urea fertilizer impregnation process.

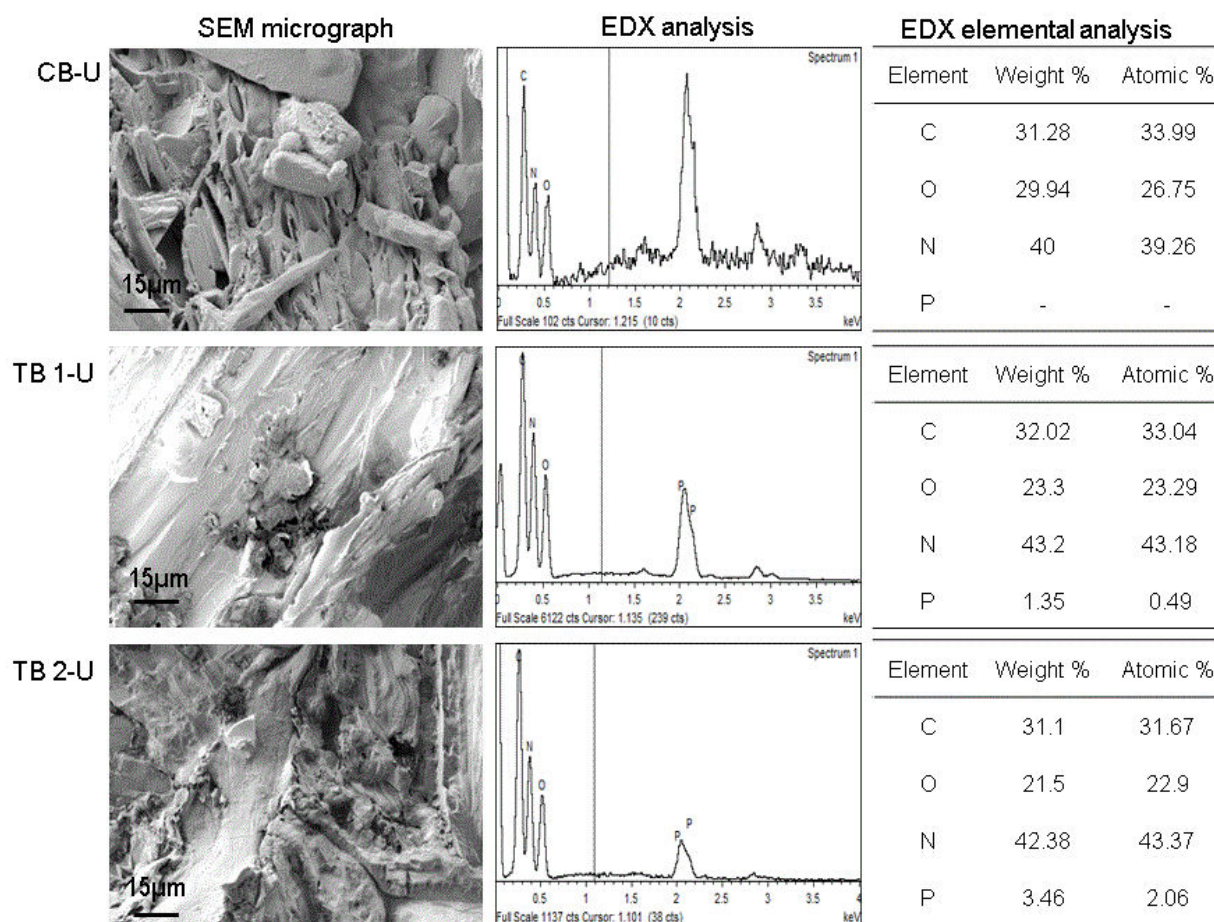


Figure-5. SEM-EDX analysis of untreated and treated biochar impregnated urea.

CONCLUSIONS

The physiochemical properties of phosphoric acid treated biochar-urea shows significant improvement when impregnated with urea fertilizer. Treated biochar (TB1 and TB2) contained a higher biochar yield and enriched with volatile-matter composition of H and N element as a result of the phosphoric acid treatment. This finding is supported with the FTIR results, indicated the presence of important acidic functional groups on the treated samples surfaces, thus proved the chemical reaction happened during the biochar treatment to improve the possibility for urea fertilizer to be impregnated and retained. The microporosity results display the treated sample has more micropores on the biochar surface, thus making urea molecule easily to be impregnated into the treated biochar. SEM-EDX analysis supported the effective impregnation process. Phosphoric acid treatment was proved to enhance the capability biochar derived from rubber wood sawdust to adsorb urea fertilizer and hold the nutrients. Further

analysis on leaching and mineralization test were needed to determine N_2O release and NH_3 loss for better understanding on the material roles and performances as a slow release enhancer.

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REFERENCES

- [1] Ramírez F, González V, Crespo M, Meier D, Faix O and Zúñiga V. 1997. Ammoxidized kraft lignin as a slow-release fertilizer tested on *Sorghum vulgare* Bioresour. Technol. 61: 43-6.
- [2] Lehmann J and Joseph S. 2009. Biochar for Environmental Management: An Introduction Sci. Technol. 1: 1-12.
- [3] Lee Y, Park J, Ryu C, Gang K S, Yang W, Park Y K, Jung J and Hyun S. 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C Bioresour. Technol. 148: 196-201.
- [4] M.E. G, M. C, J. M, A. G, M.C. D, P. C, C. M and R. N. 2015. Evaluation of biodegradable polymers as encapsulating agents for the development of a urea controlled-release fertilizer using biochar as support material Sci. Total Environ. 505: 446-53.
- [5] Enders A, Hanley K, Whitman T, Joseph S and Lehmann J. 2012. Characterization of biochars to evaluate recalcitrance and agronomic performance Bioresour. Technol. 114: 644-53.
- [6] Bhatnagar A, Hogland W, Marques M and Sillanpää M. 2013. An overview of the modification methods of activated carbon for its water treatment applications Chem. Eng. J. 219: 499-511.
- [7] G C, J Z, Y H, D Z, Y L, M W, H P, Q Z, B P and CEW S 2018 Phosphoric acid pretreatment enhances the specific surface areas of biochars by generation of micropores Environ. Pollut. 240 1-9
- [8] Guo Y and Rockstraw D A 2007 Activated carbons prepared from rice hull by one-step phosphoric acid activation Microporous Mesoporous Mater. 100: 12-9.
- [9] Kang S, Jian-chun J and Dan-dan C. 2011. Preparation of activated carbon with highly developed mesoporous structure from *Camellia oleifera* shell through water vapor gasification and phosphoric acid modification Biomass and Bioenergy. 35: 3643-7.
- [10] Lin Y, Munroe P, Joseph S, Henderson R and Ziolkowski A. 2012. Water extractable organic carbon in untreated and chemical treated biochars Chemosphere. 87: 151-7.
- [11] Doydora S A, Cabrera M L, Das K C, Gaskin J W, Sonon L S and Miller W P. 2011. Release of Nitrogen and Phosphorus from Poultry Litter Amended with Acidified Biochar Int. J. Environ. Res. Public Heal. Int. J. Environ. Res. Public Heal. 8: 1491-502.
- [12] Patnukao P and Pavasant P. 2008. Activated carbon from *Eucalyptus camaldulensis* Dehn bark using phosphoric acid activation.
- [13] Glaser B, Lehmann J and Zech W. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - A review Biol. Fertil. Soils. 35: 219-30.
- [14] M. Amutio, G. Lopez, M. Artetxe, G. Elordi, M. Olazar and J. Bilbao. 2012. No Title Influence of temperature on biomass pyrolysis in a conical spouted bed reactor Resour. Conserv. Recycl. 59: 23-31.
- [15] Guo Y and Bustin R M. 1998. FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: implications for studies of inertinite in coals Int. J. Coal Geol. 37: 29-53.
- [16] Puziy A M, Poddubnaya O I, Martínez-Alonso A, Suárez-García F and Tascón J M D. 2005. Surface chemistry of phosphorus-containing carbons of lignocellulosic origin Carbon N. Y. 43: 2857-68.
- [17] Fuente E, Menéndez J A, Díez M A, Suárez D and Montes-Morán M A. 2003. Infrared Spectroscopy of Carbon Materials: A Quantum Chemical Study of Model Compounds J. Phys. Chem. B. 107: 6350-9
- [18] Puziy A., Poddubnaya O., Martínez-Alonso A, Suárez-García F and Tascón J M. 2002. Synthetic carbons activated with phosphoric acid: I. Surface chemistry and ion binding properties Carbon N. Y. 40: 1493-505.
- [19] Solum M S, Pugmire R J, Jagtoyen M and Derbyshire F. 1995. Evolution of carbon structure in chemically activated wood Carbon N. Y. 33: 1247-54.
- [20] Boonamnuyvitaya V, Sae-Ung S and Tanthapanichakoon W. 2005. Preparation of activated carbons from coffee residue for the adsorption of formaldehyde Sep. Purif. Technol. 42: 159-68.
- [21] Sych N V., Trofymenko S I, Poddubnaya O I, Tsyba M M, Sapsay V I, Klymchuk D O and Puziy A M 2012 Porous structure and surface chemistry of phosphoric acid activated carbon from corncob Appl. Surf. Sci. 261: 75-82.
- [22] Lammers K, Arbuckle-Keil G and Dighton J. 2009. FT-IR study of the changes in carbohydrate chemistry



of three New Jersey pine barrens leaf litters during simulated control burning *Soil Biol. Biochem.* 41: 340-7.

- [23] Hadoun H, Sadaoui Z, Souami N, Sahel D and Toumert I. 2013. Characterization of mesoporous carbon prepared from date stems by H₃PO₄ chemical activation *Appl. Surf. Sci.* 280: 1-7.
- [24] Pradhan B K and Sandle N K. 1999. Effect of different oxidizing agent treatments on the surface properties of activated carbons *Carbon N. Y.* 37: 1323-32.
- [25] Yakout S M, El A, Daifullah H M and El-Reefy S A. 2015. Pore structure characterization of chemically modified biochar derived from rice straw *Environ. Eng. Manag. J.* 14: 473-80.
- [26] Ameloot N, Graber E R, Verheijen F G A and De Neve S. 2013. Interactions between biochar stability and soil organisms: Review and research needs *Eur. J. Soil Sci.* 64: 379-90.
- [27] Taha S M, Amer M E, Elmarsafy A E and Elkady M Y. 2014. Adsorption of 15 different pesticides on untreated and phosphoric acid treated biochar and charcoal from water *J. Environ. Chem. Eng.* 2: 2013-25.
- [28] Jagtoyen M and Derbyshire F. 1993. Some considerations of the origins of porosity in carbons from chemically activated wood *Carbon N. Y.* 31: 1185-92.
- [29] Ahmed Hared I, Dirion J L, Salvador S, Lacroix M and Rio S. 2007. Pyrolysis of wood impregnated with phosphoric acid for the production of activated carbon: Kinetics and porosity development studies *J. Anal. Appl. Pyrolysis.* 79: 101-5.
- [30] Yang R, Liu G, Xu X, Li M, Zhang J and Hao X. 2011. Surface texture, chemistry and adsorption properties of acid blue 9 of hemp (*Cannabis sativa* L.) bast-based activated carbon fibers prepared by phosphoric acid activation *Biomass and Bioenergy.* 35: 437-45.