ENGINEERING JOURNAL

Article

Production of Silicon Carbide Liquid Fertilizer by Hydrothermal Carbonization Processes from Silicon Containing Agricultural Waste Biomass

Mei-Yun Chang, and Wu-Jang Huang*

Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 912, Taiwan
E-mail: *wjhuang@mail.npust.edu.tw (Corresponding author)

Abstract. Wastes from agriculture or sewage systems have several properties, such as huge volume, high humidity, and high organic composition. According to past studies, sugarcane extract, peanut shells and rice husks have high silicon content. Chemical conversion of biomass feedstock will enhance usage and provide value to agricultural waste. In this research, we applied hydrothermal carbonization to convert silicon-rich waste biomass to produce silicon-doped liquid fertilizer. The experimental trial comprised five different treatments: the application of rice husks, peanut shells and sugarcane extract, silicon carbide fertilizer, water and soil without any additives. Concentrations used were 6% rice husk, peanut shells and sugarcane extract carbide liquid fertilizer, 30% water and 50% dried soil. The concentration effect of synthesized liquid on plant growth was compared. The statistical comparison showed that peanut shell application had a significant effect on cabbage seed germination and improved the plant's growth rate when silicon carbide content was increased. When the content of silicon carbide in the liquid fertilizer was higher than 12%, crop growth was inhibited.

Keywords: Agriculture wastes, silicon carbide fertilizer, rice husk, peanut shells.

ENGINEERING JOURNAL Volume 20 Issue 4
Received 3 March 2016
Accepted 13 June 2016
Published 1 August 2016
Online at http://www.engj.org/
DOI:10.4186/ej.2016.20.4.11

DOI:10.4186/ej.2016.20.4.11

1. Introduction

Fertilizers used in agricultural activities are commonly chemical fertilizers mainly due to the low cost, but if overused, this can lead to soil salinization, acidification, and other environmental problems, including calcification. Heavy levels of pesticide spraying on fruits and vegetables and the overuse of fertilizers lead to environmental pollution, as well as heavy metal residues of fruits and vegetables, thereby impacting food quality and safety. Some studies indicate that biomass charcoal regulates pH soil quality, aids in soil improvement and carbon sequestration, and enhances crop growth, among other characteristics; and small amounts of silicon can contribute to the development of plant roots, reducing pesticide usage and helping promote crop growth. This study aims to enhance the efficiency of biomass containing silicon carbide and assess the methods used in soil tillage and crop cultivation. The study assessed crops fertilized with liquid manure. The application of rice husks, peanut shells and sugarcane extract silicon carbide fertilizer, water and soil without the use of any additives was also looked into. The concentration effect of synthesized liquid on the plant growth was compared using 6% rice husks, peanut shells and sugarcane extract carbide liquid fertilizer. We attempted to grow Chinese cabbage leafy vegetables. Our expectations include future business operations using mass-produced models.

Agriculture waste has properties such as huge volume, high humidity, and high organic composition. Its sources are the residues of crops produced from agricultural activities. It can be used as an adsorbent [1], biomass fuel [2] and compost. The authors used plant waste and applied it to make high strength eco-materials, soil improvers and graphene sheet content carbon materials [3, 4].

According to previous studies, several cropping plants, such as rice husks, corn stalks and abases contain high amounts of silicon. These biomass materials can be carbonized above $700^{o}C$ for making β-SiC material, with a surface area of β-SiC at 150 m^2/g [5, 6]. In other studies, researchers used the hydrothermal carbonization method preparation of carbon materials from Elae at temperatures of 150, 250 and 350□ , respectively, and produced a carbon content of 68.52% [7].

Fertilizers provide plant nutrients necessary to improve soil fertility substances. Chemical fertilizers containing nitrogen, phosphorus and potassium have abundant N_2O that may cause destruction of the ozone layer in the atmosphere, which creates a myriad of problems for several ecosystems and agricultural activities. Biochar produced by agricultural waste is a clean anti-polluting method that can be used as a soil amendment reagent while aiding in the uptake of plant nutrients.

The analysis found that cane bark, rice-husk biochar has high silica (SiO_2) content. Silicon (Si) is a beneficial element for plant growth; it helps plants overcome multiple stresses, including biotic and abiotic stresses. The benefits of silicon in crop production are, therefore, healthier plants and higher yield with fewer applications of pesticides and other chemical products [8]. The analysis found that silicon-containing ingredients such as the raw material of cane bark, peanut shells and rice husks were beneficial in growing vegetables and, along with basal soil conditioner use, obtained high quality agricultural produce. [9] The use of Si in rice showed that its addition increased the gross number and overall grain content, while also improving the structure of stems and enhancing its wellbeing. Silicon (Si) is an essential nutrient for rice production. Continuous cropping can reduce soil silicon. The addition of silicon fertilizer aids in enhancing rice growth [10].

In global agricultural ecosystems, the largest biospheric sources of atmospheric carbon dioxide (CO_2), carbon sequestration is coupled with the Si cycle; the aim is to enhance C sequestration. This study attempts to produce a silicon carbide fertilizer by environmentally-friendly processes from silicon-containing biomasses. The use of carbon-containing silicon skin material from sugarcane extract, peanut shells and rice husk biomass was used as a starting material in the preparation of silicon carbide. The properties were analyzed in order to provide an alternative process of low energy consumption for the re-use of agricultural waste.

However, agronomists and farmers are not always aware that they can improve crop production and increase stress and disease resistance by adding a source of available silicon to the soil. Still, reports on the Si effect of rice husk biochar on plant seed germination are scant. Therefore, in global agricultural ecosystems, the largest biospheric sources of atmospheric carbon dioxide (CO_2), carbon sequestration is coupled with the Si cycle with the aim of enhancing C sequestration. This study aims to produce silicon carbide fertilizer by environmentally-friendly processes from silicon-containing biomasses. This study also assesses the concentration effect of synthesized liquid on plant growth.

2. Materials and Methods

2.1. Silicon Carbide Liquid Fertilizer *Preparation and Characterization*

In this study, (1) Sugarcane extract, peanut shells and rice husk biomass was obtained from farms in Ping-Tung County. It was dried and cut into smaller pieces with dimensions of 500 um. (2) Biochar was produced at the National Pingtung University of Science and Technology in a laboratory scale reactor with a process period of 1 hour at ~ 200 ^{o}C, 15 atm to convert it into Silicon Carbide Liquid Fertilizer.

2.2. Property Analysis of Samples

Energy Dispersive Spectrometers (EDX) were used to analyze the structural exterior of different samples (S-3000N, HITACHI, Japan). And used the Fourier transform infrared spectrometry (FT-IR) was used to analyze the functional groups of the samples (Vector22, Bruker, Germany). The parameters of this instrument were a scanning time of 128 times, with a wave number of 4000 to 400 cm^{-1}. Soil-phase and heavy metal analysis (ICP) were used to characterize the hydrothermal carbonization liquid properties.

2.3. Soil Characteristics

A clayey Ultisol soil from NPUST campus field was used in this investigation. Soil samples were dried in a precision oven at 35 ºC, mixed into a homogeneous sample, ground and passed through a 2 mm sieve (10 mesh). The experimental trial was composed of five different treatments: an application of rice husk, peanut shells and sugarcane extract silicon carbide fertilizer, water and soil without any additives. The concentrations used were 6%, 9% and 12% rice husk, peanut shells and sugarcane extract carbide liquid fertilizer, 30% water and 50% dried soil. The concentration effects of synthesized liquid on the plant growth were compared. To determine the pH of the different treatments, Fisher Scientific Accruement was used. The Silicon Carbide Liquid Fertilized soil (Soil-phase) and electrical conductivity (EC) were measured with a portable Conductivity/Resistivity Meter S-110 (Suntex®). To measure the water holding capacity of Silicon Carbide Liquid Fertilizer and soil mixtures, samples were tested before oven drying (after drying at 35 ºC but before drying for 24 h at 105 ºC). For this test we followed the procedure of a soil analysis manual [11].

2.4. Experimental Design

An in-house experiment was set up to study the effect of silicon carbide fertilizer. The experimental trial comprised five different treatments: application of rice husk, peanut shells and sugarcane extract silicon carbide fertilizer, water and soil, without any additive silicon carbide fertilizer on Chinese cabbage growth. In the study, we used concentrations of 100 ml, 150 ml and 200 ml water added to silicon carbide fertilizer to determine pH. The plastic pots used had the following dimensions: length 50 cm × width 30 cm × height 5 cm. Five kg of soil were applied in 5 pots at 3 concentrations - 100ml, 150ml and 200 ml water, added to silicon carbide fertilizer. After preparation, the pots were placed indoors for two days and over 10 days, water was added along with silicon carbide fertilizer.The growth of the cabbage plants was conducted and recorded in the following periods: 10 days, 20 days, 30 days and 40 days. The plants were then harvested and kept refrigerated for further analysis.

3. Results and Discussion

3.1. Soil and Silicon Carbide Analysis

In the elemental composition analysis of samples, the average carbon content of raw material from commercial biochar was 52.64 wt% at 200□, 1 h for 57.00 wt%, respectively. Average silicon content for sample raw materials of 0.8 wt% and 2.00 wt%, respectively. The average was found to be 1.20 wt% of silicon**.** In the elemental composition analysis of samples, the average carbon content of raw material from commercial biochar was 43.78 wt% and 62.04 wt%, respectively. Average silicon content for sample raw materials was 1.91 wt% and 2.17 wt%, respectively. The average was found to be 0.26 wt% of silicon**.** The rice husks raw materials form significant spherical crystals on the biochar's surface. In the elemental composition analysis of samples, the average carbon and oxygen content of raw material from commercial biochar was 32.41 wt% and 50.79 wt%, respectively. Average silicon content for sample raw materials was 19.71 wt% and 1.48 wt%, respectively. The silicon content of synthesized carbon materials changed with the carbonization temperature (Table 1).

Table 1. Energy dispersive spectrometer (EDX) analyse rice sugarcane peanut shells rice husks raw Material and hydrothermal carbonization.

Element / item	C	O	Si	N	K	Ca	Al	Ni	Cl	Mg
Sugarcane exocarp RawMaterial	52.64	46.56	0.80	NA	NA	NA	NA	NA	NA	NA
peanut shells Raw Material	43.78	44.69	1.91	0.92	2.75	1.82	0.56	NA	1.66	1.91
rice husks Raw Material	32.41	46.84	19.71	0.06	0.66	0.66	NA	NA	NA	0.06
Sugarcane Hydrothermal carbonization	57.00	41.70	2.00	0.25	NA	0.05	NA	NA	NA	NA
peanutshells Hydrothermal carbonization	62.04	33.58	2.17	0.23	0.18	0.57	1.02	NA	NA	0.21
rice husks Hydrothermal carbonization	50.79	43.51	4.09	NA	NA	0.03	NA	1.58	NA	NA

Unit: wt%

From an Energy Dispersive Spectrometer (EDX) analysis, sugarcane extract, peanut shells and rice husk raw materials contained the following elements: C, Si, Na, K, Ca, Mg, Al, Ni (Table 2), while in the hydrothermal carbonization processes, Inductively Couple Plasma (ICP) element analysis showed the materials dissolved into the reaction water bath and might have bonded to the surface of carbide, but we did not find the element silicon, and therefore speculate that the silicon element should not dissolve in water, and would therefore be solid silicon.

Table 2. Inductively couple plasma (ICP) element analysis sugarcane, peanut, rice husk.

Element	Ag	Al	B	Ca	Fe	k	Mg	Mn	Na	Sr	Zn
sugarcane	0.074	0.119	NA	9.847	1.304	15.37	13.6	NA	2.556	NA	0.071
peanut	NA	0.502	0.017	41.97	3.923	97.14	36.74	0266	17.98	0.405	0.042
rice husk	NA	0.090	NA	8.885	0.848	53.28	5.523	1.479	10.65	NA	0.037

Unit: wt%

Plant growth relies on carbon dioxide, oxygen and water, and the absorbance of essential elements from the soil such as: nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, zinc, copper, boron, molybdenum and chlorine to maintain the basic energy for the plants. Using the Energy dispersive spectrometer (EDX) and Inductively Couple Plasma (ICP), we were able to analyze the solution of liquid or solid carbon, which contains the elements required for plant growth through absorption.

From our results (Figs. 1 and 2), silicon carbide fertilizer made from organic matter, and the proportion of different materials, will affect silicon carbide fertilizer component content. Preferred growth mediums were the peanut shells Silicon Carbide Liquid Fertilizer, producing the best plant height, leaf number, fresh and dry matter weight, and so on. Test results can be understood from the above: as the disc seedlings were confined to a small space, the supply of water and nutrients to the seedlings was essential for growth. Other essential growth factors included buffering capacity, pH and EC. The concentration effect of synthesized liquid on the plant growth was compared.

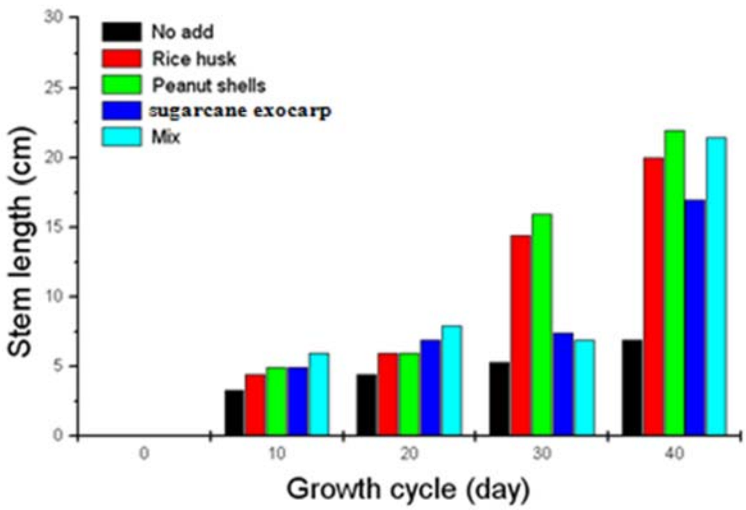

Fig. 1. Add Silicon carbonized liquid fertilizer of the cabbage growth influence effect.

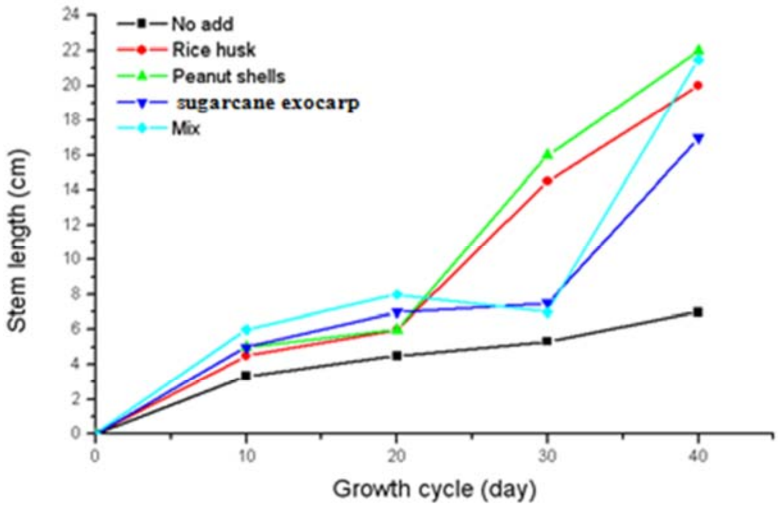

Fig. 2. Add Silicon carbonized liquid fertilizer of the cabbage growth influence effect trend.

The statistical comparison showed that peanut shell application significantly affected cabbage seed germination and improved the plants' growth rate, particularly when increasing silicon carbide content. This will not only improve fertilizer required to be applied to silicon carbide growth of crops, but also help to improve fertilizer efficiency.

Ultisols are acidic in nature and quite productive under good management [12]. However, high acidity and soils that are low in calcium, magnesium and potassium are not suitable for continuous agricultural production. The analysis of the soil used for the experiments showed that when using 70% clay, 20% sand and 10% culture soil, the soil had an acidic pH of 3.5 ~ 4.5; microbes cannot survive in this soil, which also affects the growth of plants. Therefore, the addition of 6%, 9% and 12% concentrations of silicon carbide fertilizer changed the soil pH to 7.0 ~ 7.5, which confirmed silicon carbide fertilizer will change soil pH value.

The statistics show that different concentrations of cabbage SiC fertilizer showed different reactions, and that the concentration which had 6% peanut shells silicon achieved good plant height and leaf number. When the content of silicon carbide liquid material is higher than 12%, it inhibits the growth of cabbage (because silicon carbide plant fertilizer contains minerals and trace elements needed, resulting in weak plants). Therefore, in this study, the physical properties of Silicon Carbide Liquid Fertilizer soil (Soil-phase) were: Solid Soil Liquid Average at 35.7, soil Solid phase Average at 32.2, Soil Gas phase Average at 28.1 (moisture, fertilizer, air permeability and good drainage), chemical (Table 3), (PH value of 7.0 ~ 7.5, conductivity EC value 211.40 μs/cm ~ 239.4 μs/cm.). They are within a reasonable range, contain trace elements and remain ecologically sound, as insects, microorganisms and earthworms are controlled within the balance of nature. The above results indicate that with disc seedlings in a small space, you need the supply of water and nutrients to assist the seedlings to grow, and the soil must have buffering capacity as pH value and the EC value also affect the growth of plants. Employing this environmentally-friendly method of using agricultural waste recycling preparation of silicon carbonized liquid fertilizer increases the added value of agriculture and creates sustainable land; this is the trend of the future. We look forward to developing production of silicon carbide within a liquid fertilizer business operations mode.

Table 3. The analysis of different rice husk, peanut, sugarcane and soil samples with and without added fertilizer.

SiC fertilizer item Pyrolysis Temerature	Original SiC fertilizer pH (200□ /1hr)	70％Clay+20％ Sand+10％ soil cultivation+ SiC 6 ％	9 ％	12％	Original SiC fertilizer EC (μs/cm; °C)	Original SiC fertilizer＋ soil EC (μs/cm;°C)	Solid Soil Liquid	soil Solid phase	soil Gas phase
Original Soil	3.5	4.5	6.8	7.4	- ; 26	231 ; 26	36.1	33.5	30.4
sugarcane	5.0	5.5	6.5	7.0	257 ; 26	211.8 ; 26	44.8	30.3	24.9
peanut shells	6.0	6.5	7.0	7.5	1,093 ; 26	218.2 ; 26	39.8	30.3	24.9
rice husk	5.5	6.0	7.0	7.5	291 ; 26	231.8 ; 26	37.3	33.1	29.6
MIX	6.74	6.5	7.0	7.3	584 ; 26	239.4 ; 26	35.8	33.7	30.5

4. Conclusions

This study showed that the use of 6% peanut shells silicon carbonized liquid fertilizer gave the best plant growth. When the content of silicon carbonized liquid fertilizer was higher than 12% growth was inhibited.

References

[1] O. H. Tunç, Tanacı, and Z. Aksu , "Potential use of cotton plant wastes for the removal of Remazolblack B reactive dye," *J. Hazard. Mater*, vol. 163, pp. 1871-1898, 2009.

[2] M. Y. Chang, and W. J. Huang, "Preparation of hydro-char materials and its assessment of adsorption efficiency from agriculture wastes," *The Chinese Institute Environmental Engineering, Waste Treatment Technology Seminar*, Chung Yuan Christian University, 2012.

[3] H. J. Huang, S. Ramaswamy, W. Al-Dajani, U. Tschirner, and R. A.Cairncross, "Effect of biomass species and plant size on cellulosic ethanol: A comparative process and economic analysis," *Biomass and Bioenergy*, vol. 33, pp. 234-246, 2009.

[4] C. C. Chien, Y. S. Lu, Y. J. Liou, and W. J. Huang, "Application of Waste Bamboo Materials on Produced Eco-brick," *J. Shanghai Jiaotong Univ.*, vol. 17, pp. 380-384, 2012.

[5] Y. J. Liou, and W. J. Huang, "Quantitative analysis of graphene sheet content in wood char powders during secondary graphitization," *J. Mat. Sci & Tech*, vol. 29, pp. 406-410, 2013.

[6] M. Y. Chang, W. J. Huang, and Y. J. Liou, "Production of Silicon-doped Graphene Contented Carbon Materials from Agriculture Wastes," *7th IWA International Young Water Professionals Conference*, pp. 370-373, 2014.

[7] J. Lai, H. Guo, Z. Wang, X. Li, X. Zhang, F. Wu, and P. Yue, "Preparation and characterization of flake graphite/silicon/carbon spherical composite as anode materials for lithium-ion batteries," *Journal of Alloys and Compounds*, vol. 530, pp. 30-35, 2012.

[8] J. R. Heckman, *The soil profile. Rutgers Cooperative Extension.* Plant Biology and Pathology Department. University of New Jersey. vol. 20, 2012.

[9] J. Mumme, L. Eckervogt, J. Pielert, M. Diakité, F. Rupp, and J. Kern, "Hydrothermalcarbonization of anaerobically digested maize silage," *Bioresour. Technol.*, vol. 102 , pp. 9255-9260, 2011.

[10] Y. X. Wang, S. L. Chou, J. H. Kim, H. K. Liu, S. X. Dou, "Nanocom posites of silicon and carbon derived from coal tar pitch: Cheap anode materials for lithium-ion batteries with long cycle life and enhanced capacity Electrochimica Acta," vol. 93, pp. 213-221, 2013.

[11] F. Y. Lee, *Laboratory manual for soil analysis* (in Chinese), New Wun Ching development publishing co., Ltd., pp. 70-75, 2007.

[12] N. C. Brady, R. R. Weil, *The nature and properties of soils: 12th ed.* Upper Saddle River, NJ: Prentice Hall, 1999.