Characterization of Solid Silicone Fertilizer Produced by Hydrothermal Processes from Silicon-containing Biomasses

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Abstract**—** *Wastes from agriculture or sewage systems have several properties, such as huge volume, high humidity, and high organic compositions. According to the past studied, sugarcane exocarp, peanut shells and rice husk contain 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 rice husk waste biomass to produce silicon-doped biochar carbon material. From SEM/SEX, FT-IR and XRD results, The silicon content of the synthesized carbon materials changed with increase in carbonization temperature. In addition, the averaged silicon content in carbon material was found : sugarcane exocarp to be 3.27wt %, peanut shells to be 3.01wt %, rice husks to be 7.26wt %. The silicon content of synthesized carbon materials changed with the carbonization temperature. It was speculated that due to silicon content of rice husk, peanut shells and sugarcane exocarp, Raw materials dissolve into reaction water bath and might have bonded to the surface of carbide whilst in hydrothermal carbonization processes. Silicon content of agriculture wastes through hydrothermal carbonization was found to be feasible for the production of silicon-doped Biochars carbon materials. It is suggested that this method be used for recycling of high carbon content waste material for the production of carbon materials. Recycled silicon doped biochars can be used as a base fertilizer for growing vegetables, organic soil conditioner, and also improve the added value of agriculture. Silicon containing biomasses are feasible methods for the recovery and recycling and processing of agricultural waste. Therefore, this study using agricultural waste sugarcane exocarp, peanut shells and rice husk raw carbon silicon fertilizer raw materials production, cultivation hypokalemia, hyponatremia high silicon vegetables Accord research of patients with hyperkalemia (kidney disease).*

Keywords**— agriculture wastes, fertilizer, kidney disease, high silicon vegetables, hyperkalemia**.

I. INTRODUCTION

Taiwan's annual agricultural waste outputs are summed up to over more than 200 million tonnes. 2.9 million tonnes of peanut shells, rice straw, and rice husk account for 1.5 million tonnes; sugarcane waste accounts for 35 million tonnes, and wood chips account for 22 million tonnes [1]. Agricultural waste material can be effectively utilized to achieve pollution reduction and also to add value to agricultural waste.

In recent years, domestic and foreign research has focused on organic agricultural waste raw material (peanut shells, bagasse, rice husk, rice straw, stone, seeds, wheat straw, corn stalks, softwood and hardwood, etc.).To make the most efficient use of the composition of these wastes are lignocelluloses, where in peanut shells, 25-30% Cellulose, 25-30% Hemicellulose, and 30-40% Lignin [2] (Table 1).

TABLE 1
VARIOUS COMPOSITION RATIO OF LIGNOCELLULOSE

item	Cellulose	Hemicellulose	Lignin
sugarcane exocarp	40%	24%	25%
peanut shells	25-30%	25-30%	30-40%
rice husks	35.16%	21.05%	25.41%
Straw	35%	25%	12%
Hardwood	40%	24%	18%
corkwood	45%	25%	25%
Wheat straw	40%	25%	23%
Corn stalks	41%	24%	17%

http://agbio.coa.gov.tw/image_doc/08.%e8%be%b2%e6%a5%ad%e5%bb%a2%e6%a3%84%e8%be%b2%e7%89%a9%e7%94%9f%e7%94%a2%e6%9c%a8%e8%b3%aa%e5%88%86%e8%a7%a3%e9%85%b5%e7%b4%a0%e4%b9%8b%e7%a0%94%e7%a9%b6.pdf (2015).

In the past, hydrothermal application has been used to convert cellulose of plant into coal-like structures. Because cellulose and lignin is present in sugarcane exocarps, peanut shells and rice husk, the biomass can be converted into activated carbon, thus creating a high value-added product by the recycling of agricultural waste.

Agricultural wastes have several properties (such as huge volume, high humidity, and high organic compositions). Residual crop sources are produced can be useful for agricultural activities. It can be used as an adsorbent [3, 4], biomass fuel [5] and compost. Researchers have applied plant wastes to make high strength eco-materials, soil improvers and graphene sheet contented carbon materials [6, 7, 8].

Silicon carbides anon-oxideceramic is characterized by covalent bonding, inert microbonding power, high hardness, and excellent electrical properties. The impedance of this material can be used as a key equipment component for mobile phones, digital cameras, laptops and electric vehicles bl[9,10].The material is characterized by high heat conductivity and special optical properties. Therefore, it's potential as a new material can be used for semiconductor, transparent conductive oxide thin film process and solar cells[11].With Si/C composite materials, manufacturing lithium-ion battery is practical[12,13]. According to 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 ^oC for making β-SiC material, with surface area of β-SiC at 150 m^2/g [14,15]. In other studied, researchers used the hydrothermal carbonization method preparation of carbon materials from Elae is at 150, 250 and 350 ^oC, respectively, and produced a carbon content of 68.52 % [16].

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. Biochars produced by agricultural waste is a clean anti- pollution method that can be used as a soil amendment reagent and aids in the uptake of plant nutrients. The analysis found that cane bark, peanut shells, and rice husk raw material of silicon-containing ingredients, can contribute to environmental protection in the country and the be advocates to various health diets today. Perhaps silicon components of agricultural wastes from rice husks, peanut shells and sugarcane exocarp can be obtained to develop hypokalemia, high silicon in silicon-doped Biochars, for growing vegetables and basal soil conditioner use, to achieve high quality agricultural produce.

[17] used Si in rice and showed that its addition to gross flower increased number and grain, improving structure of stems and enhanced its wellbeing. Silicon (Si) is an essential nutrient for rice production. Continuous cropping can cause soil silicon to reduce. Addition of silicon fertilizer aids in increase of rice growth[18] .

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 to enhance C sequestration. This study attempts to produce silicon carbide fertilizer by environmentally-friendly processes from silicon containing biomasses. The use of carbon-containing silicon skin material from sugarcane exocarp, peanut shells and rice husk biomass was used as a starting material prepared to contain silicon carbide. The properties were analyzed in order to provide an alternative process of low energy consumption for re-use of agricultural waste.

II. MATERIALS AND METHODS

Sugarcane exocarp, peanut shells and Rice husk biomass was collected from farms in Pingtung County. The material was dried and cut into smaller pieces of brick dimension and heated at 150^oC, 4.5 Atm for 1hr, 3hr and 5hr, at 200^oC, 15 Atm for 1hr, 3hr and 5hr, to be converted into silicon-doped biochar carbon material.

A Scanning Electron Microscope was used, Equipped with Energy Dispersive Spectrometers (SEM/EDX) to analyze the structural exterior of different samples (S-3000N, HITACHI, Japan). 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 set as scanning time of 128 times, with a wave number of 4000 to 400 cm^{-1}. The X-ray diffraction (XRD) was used to analyze the lattice structure (D8 Advance, Bruker, Germany). The scan angles were 10° to 80° (2θ degree).

III. RESULTS AND DISCUSSION

The surface structure of sugarcane exocarp, peanut shells, rice husk raw materials and silicon-doped biochars carbon materials (Fig. 1A). From results, the surface of sugarcane exocarp raw materials is lumpy and smooth. Through hydrothermal carbonization, the sugarcane exocarp raw materials form significant spherical crystals on the biochar's surface. In the elemental composition analysis of samples, the average carbon content of raw material from commercial biochar of

52.64wt , is 150℃ 1hr for 55.54wt %, and 200℃ 5hr for 79.32wt %, respectively. Average silicon content for sample raw materials of 0.8wt % is 150℃ 1hr for 1.06wt % and 200℃ 5hr for 1.38wt % respectively. The average was found to be 3.27wt% of silicon**.**

That the surface of peanut shells raw materials is lumpy and smooth. Through hydrothermal carbonization, the peanut shells raw materials form significant sp herical crystals on the biochar's surface(Fig. 1B).In the elemental composition analysis of samples, the average carbon content of raw material from commercial biochar of 43.78 wt %, is 150℃ 1hr for 54.43wt %, and 200℃ 5hr for 67.55wt %, respectively. Average silicon content for sample raw materials of 1.91wt % is 150℃ 1hr for 3.02wt % and 200℃ 5hr for 6.35wt % respectively. The average was found to be 3.01 wt% of silicon**.**

That the surface of rice husks raw materials is lumpy and smooth. Through hydrothermal carbonization, the rice husks raw materials form significant sp herical crystals on the biochar's surface (Fig. 1C). In the elemental composition analysis of samples, the average carbon and oxygen content of raw material from commercial biochar of 32.41 wt %, is 150℃ 1hr for 51.04wt %, and 200℃ 5hr for 52.42wt %, respectively. Average silicon content for sample raw materials of 19.71wt , is 150℃ 1hr for 3.65wt % and 200℃ 5hr for 13.31wt % respectively. The average was found to be 7.26 wt% of silicon**.** The silicon content of synthesized carbon materials changed with the carbonization temperature. It was speculated that due to silicon content of sugarcane exocarp, peanut shells and rice husk, raw materials with increasing carbonization temperature and time, the content of silicon was gradually increased(Table 2).

TABLE 2
ENERGY DISPERSIVE SPECTROMETER(EDX) ANALYZERICE

Element Temperature/ time)		C	O	Si	Na	K	Ca	Al	Au	Ni	Cl	Mg
sugarcane exocarp RawMaterial		52.64	46.56	0.80	NA	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	NA	1.66	1.91
rice husks Raw Material		32.41	46.84	19.71	0.06	0.66	0.66	NA	NA	NA	NA	0.06
sugarcane exocarp	150°C 1**hr**	55.54	40.16	1.06	0.93	1.65	0.04	NA	NA	NA	NA	0.62
peanut shells	150°C 1**hr**	54.43	38.61	3.02	0.13	0.75	0.73	NA	NA	NA	NA	0.33
rice husks	150°C 1**hr**	51.04	44.94	3.65	0.15	NA	0.13	NA	NA	NA	NA	0.09
sugarcane exocarp	150°C 3**hr**	62.97	18.82	17.32	0.33	0.44	NA	NA	NA	NA	NA	0.12
peanut shells	150°C 3**hr**	60.75	36.10	1.75	NA	0.06	0.36	NA	NA	NA	NA	0.11
rice husks	150°C 3**hr**	47.54	45.99	6.17	0.06	0.03	0.10	NA	NA	NA	NA	0.11
sugarcane exocarp	150°C 3**hr**	60.53	34.56	0.22	1.86	2.03	NA	NA	NA	NA	NA	0.81
peanut shells	150°C 3**hr**	51.62	46.61	1.21	NA	0.19	0.28	NA	NA	NA	NA	0.09
rice husks	150°C 3**hr**	63.49	23.03	1.48	NA	0.01	NA	NA	10.26	1.41	NA	0.39
sugarcane exocarp	200°C 1**hr**	57.00	41.70	2.00	0.25	NA	0.05	NA	NA	NA	NA	NA
peanut shells	200°C 1**hr**	62.04	33.58	2.17	0.23	0.18	0.57	1.02	NA	NA	NA	0.21
rice husks	200°C 1**hr**	50.79	43.51	4.09	NA	NA	0.03	NA	NA	1.58	NA	NA
sugarcane exocarp	200°C 3**hr**	69.35	30.00	0.14	NA	NA	0.31	NA	NA	NA	NA	NA
peanut shells	200°C 3**hr**	50.46	33.60	4.63	NA	0.74	0.15	3.43	NA	6.49	NA	0.49
rice husks	200°C 3**hr**	64.22	28.39	2.43	0.07	NA	NA	NA	NA	4.89	NA	NA
sugarcane exocarp	200°C 5**hr**	79.32	18.85	1.38	NA	0.02	0.13	NA	NA	NA	NA	0.31
peanut shells	200°C 5**hr**	67.55	23.74	6.35	0.51	1.25	0.36	NA	NA	NA	NA	0.24
rice husks	200°C 5**hr**	52.42	34.15	13.31	NA	0.02	NA	NA	NA	NA	NA	0.10

Unit: wt %

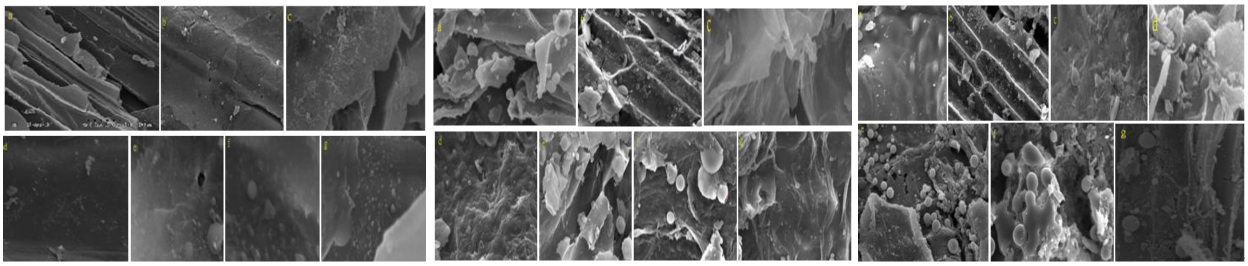

FIG.1 (A,B,C) THE SEM IMAGE
(A)SUGARCANE EXOCARP RAW MATERIAL (B) PEANUT SHELLS RAW MATERIAL (C) RICE HUSKS RAW MATERIAL
A(RAW MATERIAL) AND SILICON-DOPED BIOCHARS CONTENTED CARBON MATERIALS AT B(150 ^{o}C 1HR) C(150 ^{o}C 3HR) D(150 ^{o}C 5HR) E(200 ^{o}C 1HR) F(200 ^{o}C 3HR) G(200 ^{o}C 5HR)

In this study, with 1kg sugarcane exocarp , peanut shells and rice husks raw materials at 150^{o}C 1hr hydrothermal carbonization produced 95% Carbon yield; at 200^{o}C 5hr hydrothermal carbonization produced 65% Carbon yield, showing the high temperature and long time will affect the of carbon yields (Table 3).

TABLE 3
HYDROTHERMAL CARBONIZATION YIELD PRODUCED DIFFERENT RAW MATERIALS DATA OF SAMPLES

Raw Material	150 ^{o}C 1 hr	150 ^{o}C 3hr	150 5hr	200^{o}C 1 hr	200^{o}C 3hr	200^{o}C 5hr
sugarcane exocarp	0.95062	0.92035	0.85006	0.79946	0.69075	0.65088
peanut shells	0.95011	0.91075	0.84037	0.79775	0.69076	0.64018
rice husks	0.95070	0.93551	0.84021	0.79038	0.69009	0.64077

Unit: kg

In Table 2 Energy Dispersive Spectrometer(EDX) analyze learn of, sugarcane exocarp, peanut shells and rice husk raw materials Contain elements: C, Si, Na, K, Ca, Mg, Al, Ni, whilst in hydrothermal carbonization processes Inductively Couple Plasma (ICP) element analysis, dissolve into reaction water bath and might have bonded to the surface of carbide, but did not find the element silicon, speculate, silicon element should not dissolve in water, Should be within the solid silicon(Table 4).

Plant growth, it is necessary to get through the air of carbon dioxide, oxygen and water, and absorb essential elements from the soil, such as: nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, zinc, copper, boron, molybdenum, chlorine so as to maintain the basic energy plants. By Energy dispersive spectrometer (EDX) and Inductively Couple Plasma(ICP)analyze the solution of liquid or solid carbon-carbon, contain the elements required for plant growth, can provide plants absorb. Therefore, this study using agricultural waste sugarcane exocarp, peanut shells and rice huskraw carbon silicon fertilizer raw materials production, cultivation hypokalemia, hyponatremia high silicon vegetables Accord research of patients with hyperkalemia (kidney disease).

The FT-IR spectra of the sugarcane exocarp, peanut shells and rice husk synthesized samples(Fig. 2,A,B,C), All of them possess amide group (~3850 and 3745 cm^{-1}), aromatic group (~ 1400 cm^{-1}), -OH (~3500 cm^{-1}), -CH_2- (~2950 cm^{-1}), C=O (1700~1650 cm^{-1}), C=C (1640~1600 cm^{-1}), -CH_3 (~1390 cm^{-1}) and C-O (~1100 cm^{-1}), those peaks are contributed to the cellulose and lignin structure of plants. The peak of aromatic group (~ 1540 cm^{-1}) changes with the carbonization temperature. This phenomenon is attributed to deoxidation and cyclization of the carbon structures. And the peak of Si-Phenyl bonding at 1470 cm^{-1} might formed from the fusion of benzenes rings with silicon oxides. And the peak of C-O changes with changing the carbonization temperature.

The XRD spectra of samples (Fig. 3,A,B,C) All of them have characteristic peak of cellulose at 2θ degree =22^{o}, and the peak of cellulose not decomposition by hydrothermal carbonization. The crystals of C_{60} (30~31^{o} 2θ degree) and Si-C (34^{o} 2θ degree) are formed in the carbon materials, and the peak of Si-C changes with the carbonization temperature.

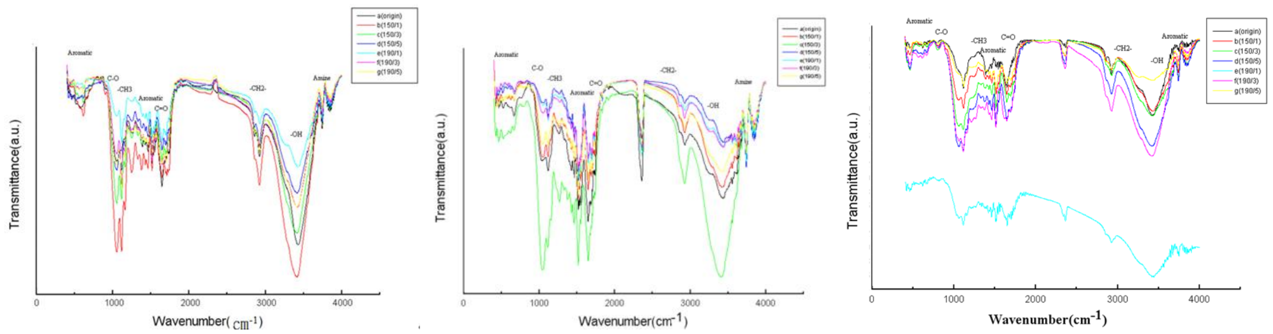

FIG.2 (A,B,C) THE FT-IR SPECTRUMS OF SAMPLES

(A)SUGARCANE EXOCARP (B)PEANUT SHELLS (C) RICE HUSKS

A(raw material) at B(150 °C 1hr) C(150 °C 3hr) D(150 °C 5hr) E(200 °C 1hr) F(200 °C 3hr) G(200 °C 5hr)

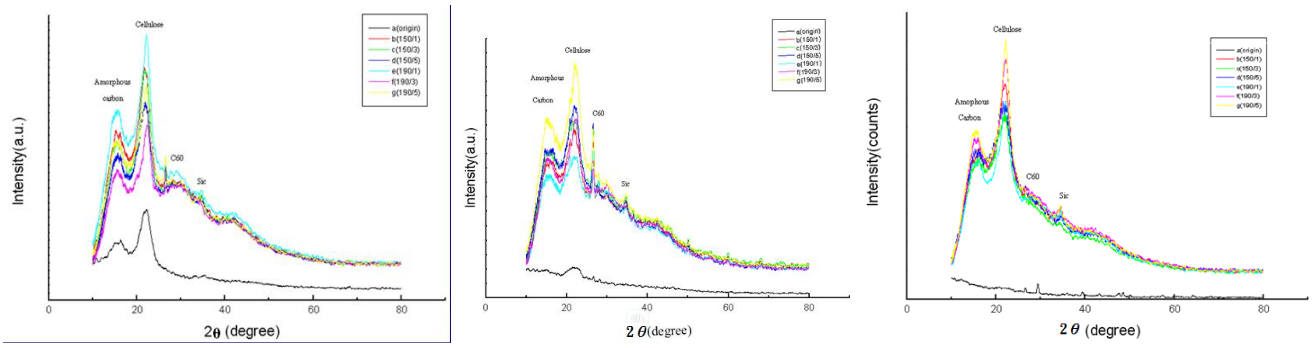

FIG.3 (A,B,C) THE XRD SPECTRUMS OF SAMPLES

(A) SUGARCANE (B) PEANUT SHELLS (C) RICE HUSKS

A(raw material) at B(150 °C 1hr) C(150 °C 3hr) D(150 °C 5hr) E(200 °C1hr) F(200 °C 3hr) G(200 °C 5hr)

TABLE 4

INDUCTIVELY COUPLE PLASMA (ICP) ELEMENT ANALYSIS SUGARCANE EXOCARP, PEANUT SHELLS , RICE HUSK OF SAMPLES

Element	Time (°C/hr)	Ag	Al	B	Ba	Ca	Cu	Fe	k	Mg	Mn	Na	Ni	Sr	Pb	Zn
S	150/1	NA	0.129	NA	NA	10.63	NA	0.321	13.49	12.29	NA	2.784	NA	NA	0.004	0.004
N	150/1	NA	0.013	NA	NA	21.46	NA	0.235	76.10	21.09	0.08	15.07	NA	0.153	NA	NA
R	150/1	NA	NA	NA	NA	6.455	NA	0.061	58.91	3.880	1.087	3.109	NA	NA	NA	NA
S	150/3	NA	0.227	NA	NA	10.61	NA	0.767	14.65	12.95	NA	2.836	NA	NA	NA	NA
N	150/3	NA	0.044	NA	NA	28.66	NA	0.504	76.52	24.74	0.11	16.17	NA	0.22	NA	NA
R	150/3	NA	NA	NA	0.005	12.72	0.012	NA	99.25	8.272	2.411	4.147	NA	NA	NA	0.064
S	150/5	NA	0.225	NA	NA	12.60	NA	0.620	31.41	11.88	0.024	2.639	NA	NA	NA	NA
N	150/5	NA	0.087	NA	0.009	32.63	NA	0.780	82.31	27.18	0163	16.58	NA	0.298	NA	NA
R	150/5	NA	NA	NA	NA	9.135	NA	0.208	55.42	5.943	1.522	9.083	NA	NA	NA	0.073
S	200/1	0.074	0.119	NA	NA	9.847	NA	1.304	15.37	13.6	NA	2.556	NA	NA	NA	0.071
N	200/1	NA	0.502	0.01 7	NA	41.97	NA	3.923	97.14	36.74	0266	17.98	NA	0.405	NA	0.042
R	200/1	NA	0.090	NA	NA	8.885	NA	0.848	53.28	5.523	1.479	10.65	NA	NA	NA	0.037
S	200/3	NA	0.033	NA	NA	9.110	NA	2.176	32.85	12.09	0.017	2.355	NA	NA	NA	0.214
N	200/3	NA	0.214	NA	0.098	37.86	NA	0.313	87.23	30.15	0.243	18.30	NA	0.335	NA	0.028
R	200/3	NA	NA	NA	0.015	13.03	NA	1.028	69.80	8.339	2.083	5.336	0.017	NA	NA	0.264
S	200/5	NA	0.004	NA	0.075	14.15	NA	2.193	40.36	17.35	0.149	2.606	0.198	NA	NA	0.275
N	200/5	NA	0.127	0. 0.53	0.136	42.47	NA	1.767	112.5	37.35	0.358	22.31	0.006	0.421	NA	0.052
R	200/5	NA	NA	NA	0.066	12.84	NA	2.195	83.21	9.617	2.409	10.18	0.031	NA	NA	0.184

nit: wt %

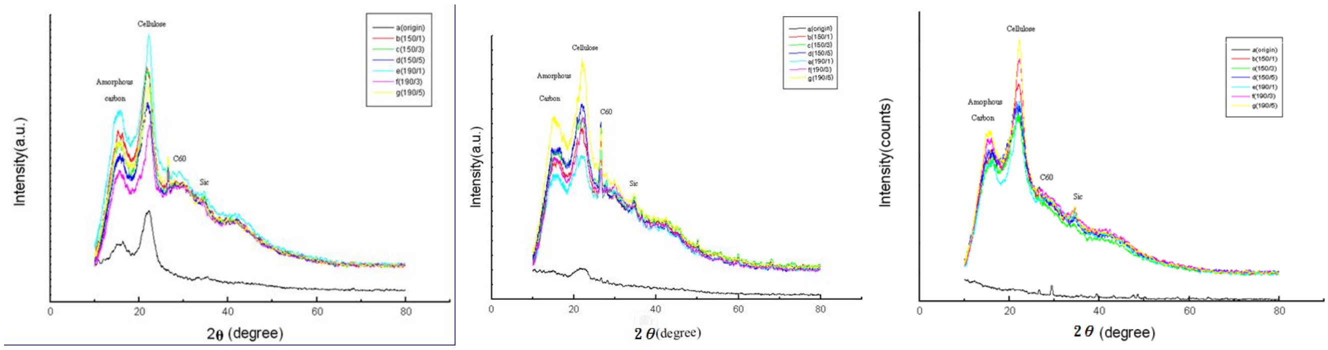

FIG.4 (A,B,C) THE XRD SPECTRUMS OF SAMPLES
(A) SUGARCANE EXOCARP (B) PEANUT SHELLS (C) RICE HUSKS
A(raw material) at B(150 ^{o}C 1hr) C(150 ^{o}C 3hr) D(150 ^{o}C 5hr) E(200 ^{o}C1hr) F(200 ^{o}C 3hr) G(200 ^{o}C 5hr)

IV. CONCLUSION

From our results, the silicon content of sugarcane exocarp, peanut shells and rice husk agriculture wastes through hydrothermal carbonization efficiently produces silicon carbide fertilizer, sugarcane exocarp to be 3.27wt% of silicon, Peanut shells to be 3.01 wt% of silicon, rice husk to be 7.26 wt % of silicon. The phenomenon is confirmed by XRD, FTIR and SEM analyzer, initially speculating that the structure of the carbon material produced by the hydrothermal process is C60-Si. The world today is faces energy shortage, thus cheaper and efficient materials must be produced for energy conservation. The use of sugarcane exocarp, peanut shells and rice husks pose a feasible option for the preparation of silicon carbide-containing fertilizers, produced at low costs and simple processes from an economic standpoint. Environmental and social development can be obtained by recycling of agricultural waste material.

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