engineering proceedings

MDPI

Proceeding Paper

The Influence of Impregnation of Sodium Carbonate Catalyst on Physicochemical Properties of Biochar †

Norbert Onen Rubangakene [1,*], Ahmed Elwardany [2,3], Manabu Fujii [4], H Sekiguchi [5] and Hassan Shokry [1,6]

[1] Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), New Borg El-Arab City 21934, Alexandria, Egypt; email1@email.com
[2] Energy Resources Engineering Department, Egypt-Japan University of Science and Technology (E-JUST), New Borg El-Arab 21934, Egypt; email2@email.com
[3] Mechanical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria 21544, Egypt
[4] Department of Civil and Environmental Engineering, Tokyo Institute of Technology, Meguro-Ku, Tokyo 152-8552, Japan; email3@email.com
[5] Chemical Science and Engineering Department, Tokyo Institute of Technology, S-4, 2-12-1 Ookayama, Meguro-Ku, Tokyo 152-8552, Japan; email4@email.com
[6] Electronics Materials Researches Department, Advanced Technology and New Materials Research Institute, City of Scientific Research and Technological Applications (SRTA-City)
* Correspondence: norbert.rubangakene@ejust.edu.eg

† Presented at the 2nd International Electronic Conference on Processes: Process Engineering—Current State and Future Trends (ECP 2023), 17–31 May 2023; Available online: https://ecp2023.sciforum.net/.

Abstract: Biochar (BC) has been a viable resource in producing functionalized carbonaceous materials beneficial in soil fertility, environmental remediation, and energy recovery. In this study, the influence of Na_2CO_3 in the pyrolytic conversion of green pea peels to BC was performed to assess BC's yield and physicochemical characteristics. Experimentations were conducted in batch processes at a constant temperature of 500 °C by wet impregnation using 0%, 10%, 20% and 30% (*w*/*w*) ratio of Na_2CO_3 Catalyst to biomass weight. Characterizations of produced BC materials have been conducted by bomb calorimetry, SEM, BET, FTIR, and XRD. Accordingly, catalyst incorporation by pre-treatment resulted in a decrease in yield while increasing the porous development. The specific surface area at constant temperature increased from 1.006 to 17.7 $m^2\,g^{-1}$, and the pore diameter decreased from 173.1 to 9.283 nm. The oxygenated functional groups negatively correlated with the increase in the amount of catalyst whereas the calorific values of the synthesized materials increased from 20.313 kJ g^{-1} to 25.479 k Jg^{-1} when catalyst impregnation ratio was enhanced from 0% to 30%**,** indicating that BC produced from catalyzed processes demonstrate better energy recovery potential.

Keywords: biochar yield; functional groups; impregnation; pore properties; pyrolysis

Citation: Rubangakene, N.O.; Elwardany, A.; Fujii, M.; Sekiguchi, H.; Shokry, H. The Influence of Impregnation of Sodium Carbonate Catalyst on Physicochemical Properties of Biochar. *Eng. Proc.* **2023**, *37*, x. https://doi.org/10.3390/xxxxx

Published: 17 May 2023

1. Introduction

Industrialisation and urbanisation have widened gaps in energy demands among the populace [1]. These have caused the utilisation of fossil fuels with draconian environmental consequences such as pollution, global warming, and acid rain [2]. Alternative renewable options such as biomass, wind, hydro and solar have been sought. The former exhibits high potential ranging from abundance to multiple energy products [3]. Categorically biomasses are either virgin biomass (lignocellulosic crops and vegetables) or waste biomass (municipal solid waste and sludge).

Thermochemical and biochemical methods can produce multiple energy forms. Biological techniques face resistance from natural cell walls to microbial and enzymatic breakdown [4]. On the other hand, thermochemical is the most attractive technique. Methods such as pyrolysis, gasification and liquefaction are utilised to produce desired products dependent on operating conditions [5]. Pyrolysis is the most reliable method to obtain pyrolysis products such as bio-oil, syngas, and biochar [6]. This process involves heating biomass from ambient to peak temperature and holding it at that temperature for the required residence time in anoxic conditions [7].

Pyrolysis is a complex process influenced by many factors such as feedstock composition, water content, inherent materials, temperature, heating rate, residence time and catalytic additives [8]. Numerous studies have focused on the roles of temperature, heating rate and residence time as significant influencers of biochar's morphological and physicochemical properties [9]. However, additives are more flexible in catalytic pyrolysis to obtain desired product yield and selectivity. According to research by W. Jun et al. investigated the catalytic roles of six inorganic compounds, i.e., NaCl, Na_2CO_3, NaOH, TiO_2, Na_2SiO_3 and zeolite, and the findings revealed sodium compounds promoted charring of solid fraction [8]. To the best authors knowledge, this is the first study that performs catalytic pyrolysis of green pea waste at different basic sodium carbonate catalyst ratios. Accordingly, the derived BC material from waste biomass shall demonstrate excellent structural properties enhancement such as pore properties, functional groups henceforth improving its application efficacy.

This study highlighted the synthesis of BC from green pea peels using pyrolysis technique at 500 °C in anaerobic environment. The influence of incorporating additive, i.e., sodium carbonate catalyst, on physicochemical characteristics of biochar was evaluated.

2. Materials and Methods

2.1. Materials

Green peas peels (GPP) procured from the local market at Alexandria, nitric acid (37% Darmstadt, Germany), sodium carbonate, potassium hydroxide, nitric acid (Fine chem, Mumbai, India). All chemicals were of high analytical grades.

2.2. Methods

2.2.1. Production of BC over Na_2CO_3 Catalyst

The peels were crushed to particles of sizes less than 212 um using an electric blender (Jumbo Nouval, China). BC was produced by the procedures below. The quantity of Na_2CO_3 in the weight of catalyst to green peas waste at 0%, 10%, 20% and 30% was dissolved in 50 mL of deionised water. 10 g of GPP was soaked in the basic sodium solution and oven-dried until no weight change was realised. The dried biomass and the Na_2CO_3 catalyst were placed in a tightly enclosed ceramic crucible. The crucible was heated at a temperature of 500 °C, ramping rate of 27 °C min^{-1} for 1 h in an anaerobic atmosphere created by purged nitrogen gas.

A brown solid was neutralised using 0.1 M HNO_3 and then washed with distilled water until it obtained a neutral pH and designated as R0%, R10%, R20% and R30%. The yield of BC produced is calculated from Equation (1).

$$\text{BC yield (\%)} = \frac{\text{Mass of BC}}{\text{Mass of GPP}} * 100 \quad (1)$$

2.2.2. Characterizations of Biochar

BC was characterised by Scanning Electron Microscope (JEOL JSM-6360LA, Japan), BET surface area analyser (Microtrac MRB Belsorp, Japan), Fourier Transform Infrared Spectroscopy (Shimadzu 8400s, Japan), X-ray Diffraction (Bruker D2 Phasor). For fuel properties, oxygen bomb calorimeter (Labtron, UK) was used to determine the Higher Heating Value (HHV).

3. Results and Discussions

3.1. Physicochemical Properties of BC

3.1.1. Influence of Catalyst on Biomass Conversion, Yield, and HHV of Char

The pre-treatment with Na_2CO_3 catalyst promoted simultaneous thermal degradation of green peas pods and deduction of char yield as in Figure 1 [10]. The reduction of char yield from 33.22% at R0% to 23.77% at R30% can be credited to the swelling effect during impregnation and the catalytic role of Na_2CO_3 during pyrolysis [8]. The addition of basic Na_2CO_3 catalyst facilitates the sodium ions penetrating the peels biomass structure and breaking intermolecular hydrogen bridges. This induces a mixture of green pea peels and a catalyst to gain higher reactivity under the pyrolysis process to undergo low-temperature catalytic conversion [10]. Furthermore, the reduction of char yield can be attributed to the promotion of liquid and gaseous products brought about by additional cracking and interaction with volatile hydrocarbons [11]. For the case of oxygen bomb calorimetry tests, the calorific value of the BC material increased with sodium carbonate impregnation indicating the potential of the resultant catalyst to acquire more potential energy.

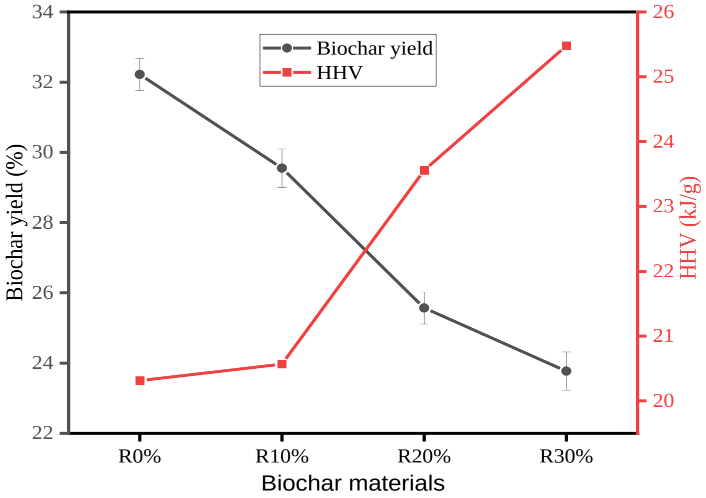

Figure 1. Changes in yield and HHV of produced BC materials.

3.1.2. Surface Morphology of the BC

The visual disparity in the remnant structure of BC produced at varying sodium carbonate catalyst ratios was identified from micrographs prepared from SEM. The untreated BC (R0%) possessed a melted wall with hardly any recognisable pores, as in Figure 2a [12]. The BC produced after sodium carbonate pre-treatment in Figure 2b–d has a bulky shape degraded with the production of pores. The creation of pores is attributed to the formation of volatiles and tar during pyrolysis. It's noteworthy that the visibility and clarity of the pores increase with the increased amount of sodium carbonate catalyst used during impregnation. Furthermore, the surface of BC at increasing sodium carbonate appears more degraded, indicating the activation of the produced biochar.

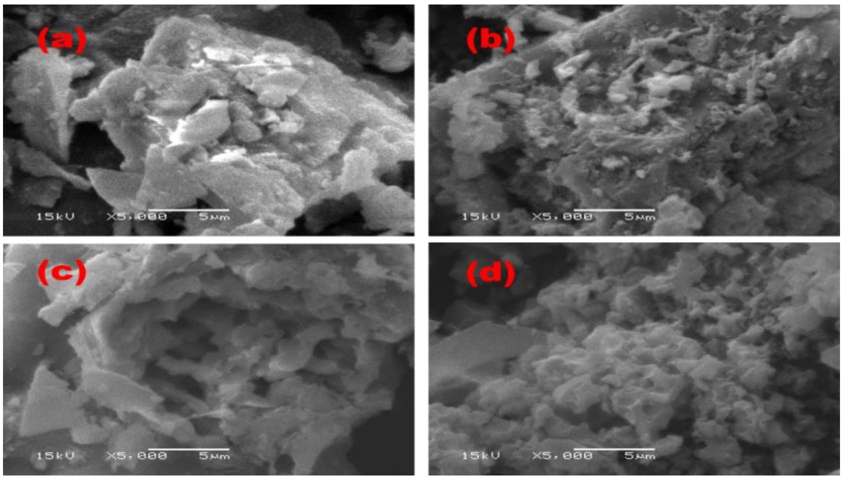

Figure 2. SEM image of BC produced using Na_2CO_3 catalyst impregnated at (**a**) 0%, (**b**) 10%, (**c**) 20%, and (**d**) 30%.

3.1.3. BC's Surface Area and Pore Properties

The pore outcomes of BC produced under impregnation of biomass with Na_2CO_3 catalyst at different ratios are in Table 1. The increase in carbonate ratio enhanced the improvement of BET surface area while the mean pore diameter experienced a negative correlation. Furthermore, the total pore volume exhibited an inconsistent trend with the addition of catalyst. The phenomenon can be ascribed to transforming the organic chemical structures of green pea peels by impregnation with Na_2CO_3 and pyrolysis processes [13,14]. Moreover, the basic catalyst initiates volatile compounds' catalytic cracking, further enhancing the production of volatiles at low temperatures creating pores.

Table 1. BET surface area, pore volume and mean pore diameter of the produced BC.

Parameter	**BET Surface Area [m^2 g^{-1}]**	**Average Pore Diameter [nm]**	**Total Pore Volume [cm^3 g^{-1}]**
R0%	1.007	174.090	0.044
R10%	3.005	16.002	0.012
R20%	11.510	15.643	0.045
R30%	17.700	9.283	0.041

The N_2 adsorption and desorption studies of the BC are revealed in Figure 3. The BC isotherm was convex towards the relative pressure axis (p/p°) over most of its entire length. This is synonymous with an uncommon Type III isotherm, according to IUPAC nomenclature, that exhibits strong lateral interaction between adsorbate and adsorbent [15]. The BC pore size distribution in Figure 3, ranged from mesoporous to macroporous. The suited BCs applications are in the mode; mesoporous for pollutant decontamination and catalyst supports, microporous for nutrient retention in the soil and macroporous for aeration of the soil [6].

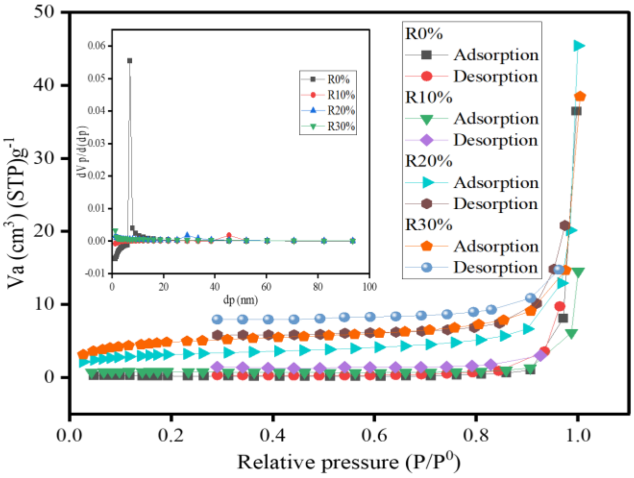

Figure 3. Nitrogen sorption- desorption isotherm and pore properties of the produced BC.

3.1.4. Functional Properties of the Produced Char Materials

The FTIR spectrum of the produced BC is represented in Figure 4. The infrared spectra revealed a strong, broad band in the range of 3400- 3600 cm$^{-1,}$ ascribing to the O-H stretching of water and phenol. Other significant peaks are observed at 1624 cm^{-1} in the range of 1600–1630 cm^{-1} attributed to aromatic C=C and C=O skeletal vibration. A peak at 1249 cm^{-1} is due to aromatic methoxy from the hemicellulose. The Peaks at 879 cm^{-1} and 616 cm^{-1} ascribe to O-H vibration stretching and aliphatic and aromatic C-H stretching, respectively [16]. The BC produced in the presence of sodium carbonate and at higher ratios encountered a reduction in the intensity and shape of prominent functional groups. The band assigned to hydroxyl weakened and became less intense. This is attributed to the role of impregnation by sodium ions to weaken hydrogen bridges and make them susceptible to thermal degradation [10]. On the other hand, the peak encountered at 1249 cm^{-1} is not exist in other BC samples because the methoxy of the aromatic ring undergoes hydrolysis and the side chain fraction dissolves, causing disappearance at higher ratios [17]. This observation can be further confirmed by the ability of basic alkali solution to split off the acetyl groups attached to hemicellulose [14].

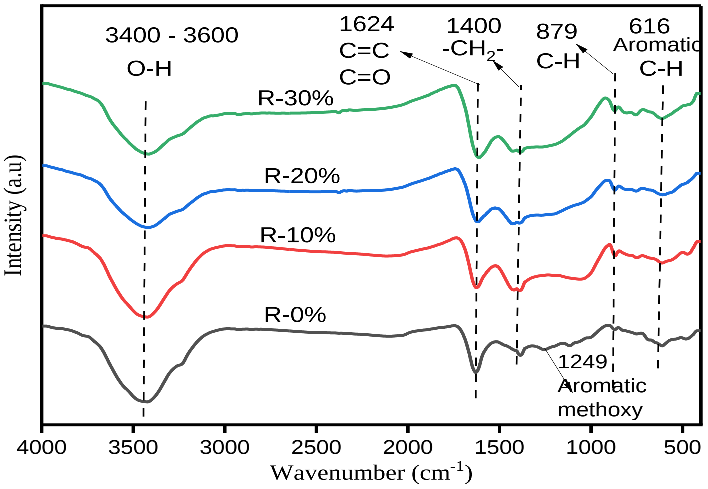

Figure 4. Changes in functional groups of BC materials with varying Na_2CO_3 ratios.

3.1.5. XRD Diffraction Pattern of the Produced BC materials

The spectral analysis of BC produced from green pea peels under the different ratios of sodium carbonate catalyst impregnation is shown in Figure 5. The disparity in strength and position of the peaks indicate diversity in the formation and emergence of different crystals [18]. The BC at R0% revealed two peaks at 28.1° and 40.4° at the plane of (111) and (520) (JCPDS 049-1720), suggesting the emergence of carbon oxide and C60 fullerite crystals at 500 °C, respectively. The same crystals emerge in the BC at R10% with decreasing intensities. With increasing the quantity of Na_2CO_3 catalyst at R20%, graphite peak appeared at 26.4° at miler plane of (002) (JCPDS 008-0415), whereas the BC at R30% indicated synthesis of C8 carbon (JCPDS 082-0619). The BC with fullerite crystal can be well suited for biomedication application whereas those that have experienced immense impact of activation can be suited for wastewater treatment technologies.

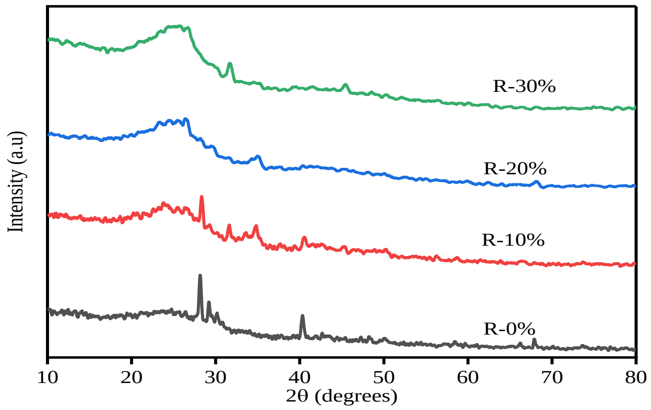

Figure 5. Changes in crystallographic structures of the BC materials**.**

4. Conclusions

In this work, the authors successfully studied the effect of the impregnation of Na_2CO_3 additive on BC's chemical and physical properties. An increase in the amount of additives reduced the BC yield whereas the calorifc properties increased. The pore properties of the specific surface area increased, whereas the mean pore diameter decreased. Furthermore, the oxygen-enriched functional groups were reduced, and they were changes in crystallographic carbon structure with changes in impregnation of sodium carbonate. The microporous BCs are suitable for nutrient retention and adsorption, while macoporous chars are appropriate for aeration. Pollutant remediation could be proper via mesoporous BC.

Author Contributions: Writing—original draft, Validation, Investigation, Formal analysis. N.O and H.S. (H Sekiguchi); Methodology, Writing, Editing, Formal analysis. N.O.R. and A.E; Writing—review & editing, Supervision. M.F and H.S. (Hassan Shokry); Supervision, review & editing. H.S. (H Sekiguchi) and A.E. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: This work was supported by EJUST-TICAD7 Scholarship. Authors thank Egypt- Japan University of Science and Technology and staff under Environmental Engineering department for their utmost diligent support during this study.

References

1. Zhang, X.; Zhao, B.; Liu, H.; Zhao, Y.; Li, L. Effects of Pyrolysis Temperature on Biochar's Characteristics and Speciation and Environmental Risks of Heavy Metals in Sewage Sludge Biochars. *Environ. Technol. Innov.* **2022**, *26*, 102288.
2. Smets, K.; Schreurs, S.; Carleer, R.; Yperman, J. Journal of Analytical and Applied Pyrolysis Valorization of Raspberry Seed Cake by Flash and Slow Pyrolysis: Product Yield and Characterization of the Liquid and Solid Fraction. *J. Anal. Appl. Pyrolysis* **2014**, *107*, 289–297.

3. Smets, K.; Roukaerts, A.; Czech, J.; Reggers, G.; Schreurs, S. Slow Catalytic Pyrolysis of Rapeseed Cake: Product Yield and Characterization of the Pyrolysis Liquid. *Biomass Bioenergy* **2013**, *57*, 180–190.
4. Elsayed, A.; Fodah, M.; Kumar, M.; Behera, D. Bio-Oil and Biochar from Microwave-Assisted Catalytic Pyrolysis of Corn Stover Using Sodium Carbonate Catalyst. *J. Energy Inst.* **2021**, *94*, 242–251.
5. Huang, Y.; Kuan, W.; Chang, C.; Tzou, Y. Catalytic and Atmospheric Effects on Microwave Pyrolysis of Corn Stover. *Bioresour. Technol.* **2013**, *131*, 274–280.
6. Rubangakene, N.O.; Elkady, M.; Elwardany, A.; H, S.; Fujii, M.; Shokry, H. Novel Nano—Biosorbent Materials from Thermal Catalytic Degradation of Green Pea Waste for Cationic and Anionic Dye Decolorization. *Biomass Convers. Biorefinery* **2022**. https://doi.org/10.1007/s13399-022-03299-y.
7. Mohd Hasan, M.H.; Bachmann, R.T.; Loh, S.K.; Manroshan, S.; Ong, S.K. Effect of Pyrolysis Temperature and Time on Properties of Palm Kernel Shell-Based Biochar. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *548*, 012020.
8. Jun, W.; Mingxu, Z.; Mingqiang, C.; Fanfei, M.; Suping, Z.; Zhengwei, R.; Yongjie, Y. Catalytic Effects of Six Inorganic Compounds on Pyrolysis of Three Kinds of Biomass. *Thermochim. Acta* **2006**, *444*, 110–114.
9. Angin, D. Effect of Pyrolysis Temperature and Heating Rate on Biochar Obtained from Pyrolysis of Safflower Seed Press Cake. *Bioresour. Technol.* **2013**, *128*, 593–597.
10. Babich, I.V.; Van Der Hulst, M.; Lefferts, L.; Moulijn, J.A.; Connor, P.O.; Seshan, K. Catalytic Pyrolysis of Microalgae to High-Quality Liquid. *Biomass Bioenergy* **2011**, *35*, 3199–3207.
11. Dandik, L.; Ays, H. Pyrolysis of Used Sunflower Oil in the Presence of Sodium Carbonate by Using Fractionating Pyrolysis Reactor. *Fuel Process. Technol.* **1998**, *57*, 81–92.
12. Jalalabadi, T.; Drewery, M.; Tremain, P.; Wilkinson, J.; Moghtaderi, B.; Allen, J. The Impact of Carbonate Salts on Char Formation and Gas Evolution during the Slow Pyrolysis of Biomass, Cellulose, and Lignin. *Sustain. Energy Fuels* **2020**, *4*, 5987–6003.
13. Rubangakene, N.O.; Elkady, M.; Elwardany, A.; Fujii, M.; Sekiguchi, H.; Shokry, H. Effective Decontamination of Methylene Blue from Aqueous Solutions Using Novel Nano-Magnetic Biochar from Green Pea Peels. *Environ. Res.* **2023**, *220*, 115272.
14. Wei, Y.; Shen, C.; Xie, J.; Bu, Q. Study on Reaction Mechanism of Superior Bamboo Biochar Catalyst Production by Molten Alkali Carbonates Pyrolysis and Its Application for Cellulose Hydrolysis. *Sci. Total Environ.* **2020**, *712*, 136435.
15. Ehiomogue, P.; Ahuchaogu, I.; Ahaneku, I.E. Review of Adsorption Isotherms Models. *Hunedoara* **2022**, *14*, 87–96.
16. Rubangakene, N.O.; Elwardany, A.; Fujii, M.; H, S.; Elkady, M.; Shokry, H. Biosorption of Congo Red Dye from Aqueous Solutions Using Pristine Biochar and ZnO Biochar from Green Pea Peels. *Chem. Eng. Res. Des.* **2023**, *189*, 636–651.
17. Zhao, C.; Lv, P.; Yang, L.; Xing, S.; Luo, W. Biodiesel Synthesis over Biochar-Based Catalyst from Biomass Waste Pomelo Peel. *Energy Convers. Manag.* **2018**, *160*, 477–485.
18. Usman, A.R.A.; Abduljabbar, A.; Vithanage, M.; Ok, Y.S.; Ahmad, M.; Ahmad, M.; Elfaki, J.; Abdulazeem, S.S.; Al-Wabel, M.I. Biochar Production from Date Palm Waste: Charring Temperature Induced Changes in Composition and Surface Chemistry. *J. Anal. Appl. Pyrolysis* **2015**, *115*, 392–400.