

## ORANGE PEEL AS SUBSTRATE TO SYNTHESIZE CONDUCTIVE CARBON NANOSTRUCTURES BY A GREEN THERMAL PROCESS

Cáscara de naranja como sustrato para sintetizar nanoestructuras de carbón conductivas por un proceso térmico verde

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### ABSTRACT

Orange (*Citrus sinensis* L.) peel (OP) has been considered a waste due to its high processing costs and complicated management, resulting in environmental pollution issues. Alternatives have been proposed to generate economic benefits by developing efficient technologies to produce and store electrical energy. Moreover, valorization of OP will bring municipal and agro-industrial waste management reduction. This work aimed to develop a cost-effective and environmentally friendly thermal process to synthesize a conductive carbon from OP using a new methodology herein described. First, the OP was washed using an ultrasonic bath and dried by sun and dehydrated in muffle. Then, dehydrated pieces of OP were covered with fine-grained sea sand to limit air interaction and was carbonized at 1000 °C for one hour. The resulting bio-carbon was analyzed by cyclic voltammetry. The electrical double layer capacitance was estimated to assess the electrochemical behavior of the carbon in the electrolyte. Interestingly, with the newly proposed heat treatment, the carbon material showed a specific capacitance of 272 F/g at 20 mV/s. Therefore, the new proposed thermal process allows the synthesis of graphitized carbon with good electrochemical properties at a low cost. The results show the potential for the development of new conductive carbon materials from residual biomass by a simple, economical, and environmentally friendly air-limited heat treatment.

Palabras clave: nanotecnología, supercapacitores, voltametría cíclica

## RESUMEN

La cáscara de naranja (*Citrus sinensis* L.) se ha considerado como un residuo debido al elevado costo y la compleja gestión de su procesamiento, convirtiéndose en un problema de contaminación ambiental. Por esta razón, se ha prestado gran atención a la valorización de este residuo agroindustrial para obtener beneficios monetarios con una reducción del volumen de residuos orgánicos y la posibilidad del desarrollo de tecnologías eficientes para generar y almacenar energía eléctrica. Este trabajo presenta un proceso térmico ambientalmente amigable para producir un carbón conductivo. Primero las cáscaras de naranja se lavaron por baño ultrasónico y se secaron al sol y en mufla. Posteriormente pedazos de cáscara de naranja deshidratada se cubrieron completamente con arena de mar de grano fino y se carbonizaron a 1000 °C durante 1 hora. Después, el biocarbón fue estudiado por voltametría cíclica. La capacitancia eléctrica de doble capa de la muestra fue estimada para conocer el comportamiento electroquímico del carbono en el electrolito. El material de carbón sintetizado mostró una capacitancia específica de 272 F/g a 20 mV/s. Los resultados observados demostraron que el nuevo proceso térmico propuesto produce carbono grafitizado con buenas propiedades electroquímicas a bajo costo. Además, esta propuesta contribuye con el desarrollo de nuevos materiales conductores de carbón usando un tratamiento térmico simple, económico y respetuoso con el medio ambiente a partir de biomasa residual de bajo valor.

## INTRODUCTION

There has been recent interest to valorize orange peel (OP) considering that it represents 50 % wt of the fruit, at 20 % of total solids content (Siles et al. 2016, Mackenzie et al. 2019); besides, it is an economic burden to juices industries that pay for its disposal (Raciti et al. 2019). Indeed, it is reported that industries pay € 25-30 per ton for the disposal of orange peel, which is generally used for animal feeding, composting, or dumped to parcels proximate to the juice industries or to municipal landfills (Raciti et al. 2019). This represents an important source of pollution due to the acidic pH and the large amounts of decomposing biomass that also contains phenolic compounds (Fernandez et al. 2014). For instance, in Tamaulipas, Mexico, approximately 570 000 tons of oranges were produced in 2018 (Barrón-Bravo et al. 2020), which meant a generation of 285 000 tons of practically unused wastes.

Therefore, attempts have been carried out to valorize OP: it has been used as feedstock to produce activated carbon, bioethanol, biomethanol (Foo and Hameed 2012, Zhang et al. 2019), and even for animal feeding (Ruiz- et al. 2019).

The depletion of fossil fuels and the increase in electrical energy demand have motivated the research on sustainable and feasible functional materials to

generate and store electrical energy (Wan et al. 2020). As a result, electrochemical energy storage systems such as supercapacitors and lithium-ion batteries have increased in interest to address intermittent energy generation sources.

Supercapacitors are a hotspot technology from the electrochemical devices due to their formidable advantages, such as moderate energy density and long theoretical cycle life (Yao et al. 2015, Ghosh and Yue 2018). The main drawback of supercapacitors is the elevated costs of the production of the activated carbon and the highly porous nanostructured materials, which are the material of choice for electrode fabrication (Yao et al. 2015). Porous carbon nanostructures have remarkable advantages such as good chemical stability, high surface area, easy availability, and low cost (Ramalingam et al. 2018). In this sense, organic wastes can be used to fabricate carbonaceous nanostructures with good electrochemical properties and, at the same time, to reduce their negative environmental impact.

Carbonaceous nanomaterials are prepared by carbonizing organic compounds where the precursors are converted to stacks of aggregations. In this regard, many synthesis processes of carbonaceous materials have been reported. For example, the hydrothermal carbonization between 200-300 °C, at pressures from 20 bars (Libra et al. 2011, Tekin et al. 2014) up to 150 bars (Pawlak-Kruczek et al. 2020). Pyrolysis is

performed between 700 to 1000 °C under an inert atmosphere (Yun et al. 2001, Arie et al. 2016, Chen et al. 2019, Volperts et al. 2019, Arias-Niquepa et al. 2019). Microwave heating processes are carried out between 600 to 1200 °C (Li et al. 2015, Lam et al. 2016, Liew et al. 2019). Other authors have reported the construction of special reactors (Brito et al. 2019, Yu et al. 2020). Hydrothermal carbonization variants (Hu et al. 2010) as flash carbonization (Antal et al. 2003) allow carbon synthesis to be achieved at low temperatures and high pressures.

Meanwhile, pyrolysis is the process by which the carbon is synthesized at high temperatures and inert atmospheres (Chen et al. 2014, Sankari and Vivekanandhan 2020). However, intending to reduce the energy consumption during thermal treatments, a microwave heating process has been incorporated as it allows rapid and homogeneous heating of the sample under a nitrogen atmosphere (Li et al. 2015, Lam et al. 2016, Liew et al. 2019).

Carbonaceous structures have been achieved under special synthesis conditions such as high temperatures or high pressures, in a time-consuming and very expensive process. Alternatively, biomass has been extensively used as feedstock for carbon structure production (Chen et al. 2020). It is an economical and environmentally friendly alternative to utilize plants and fruit wastes to obtain value-added products such as carbon-based electrodes. For that, pyrolysis, or chemical activation, must be applied to obtain efficient carbon nanostructures (Raymundo-Piñero et al. 2006). For instance, Sayed et al. (2020) created an amorphous carbon fiber using palm loofah fibers as a carbon source. As the first step, chemical activation was achieved in a KOH for 2 hours and dried at 100 °C overnight. Then, a carbonization process was performed at 1000 °C under an inert atmosphere, requiring 0.1 M HCl. On the other hand, Saha et al. (2014) synthesized mesoporous carbon by a pre-chemical activation of hardwood Kraft lignin and carbonization of the samples at 1000 °C under an N<sub>2</sub> environment. Also, this group proposed a post-chemical treatment under CO<sub>2</sub> or KOH.

Another research reported a high specific capacitance of 182 F/g from a self-template synthesis of banana peel (Liu et al. 2009). For this, the biomass was treated with zinc nitrate, and then it was thermally treated at 1000 °C for eight hours under a nitrogen atmosphere. According to these studies, the carbonization of wastes requires the use of high temperatures, high pressure, inert atmospheres, chemical activators, and expensive reactors to produce conductive materials. All of this elevates their cost and impacts to the

environment. Thus, other methods must be sought to use agro-industrial wastes in economical and environmentally friendly carbonization processes.

The first attempt to synthesize carbon from biomass pyrolysis without an inert atmosphere was published by Sebag-Bernd et al. (2017). They designed a tubular reactor at 750 °C that held a KOH filter and a bed compartment that was the place for the mixture of sawdust (biomass), calcite, and catalysts. Although this procedure was easy and promising, a relevant problem was observed. The physical and chemical characterization was observed in carbon-based materials containing impurities such as magnetite, lime, calcite, zincite, and others. Thus, it was expected to have a negative effect on the electrochemical properties of the materials, such as specific capacitance, electronic conductivity, and mass diffusion of the reactive species. Other conventional techniques have been explored to build a pilot reactor and obtain carbon. For instance, one-step drum rotary carbonizer (Girgis et al. 2009, Brito et al. 2019, Yu et al. 2020) produces carbons in more considerable quantities at low temperatures. However, their research did not explore electrochemical characteristics (Antal et al. 2003). Nonetheless, all the processes mentioned above are expensive, energy- and time-consuming. Moreover, the proposed methodology to obtain active carbons is not environmentally safe because of chemicals such as ZnCl<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, KCl, HCl, and KOH (Chen et al. 2014, Wei et al. 2019, Sankari and Vivekanandhan 2020). For instance, KOH is considered a toxic strong base, classified in group 3 risk according to health hazards. Laboratory workers manipulating this organic substance risk skin irritation and severe eye damage (Hui and Zaini 2015). Meanwhile, hydrochloric acid used to wash the carbon is cataloged as a strong acid with a high risk for the health and potentially dangerous to the environment when dumped into water bodies (Moya-Salazar and Rojas-Zumaran 2016). Therefore, it is highly desirable that new synthesis methods should be explored to eliminate the use of chemical activators and reduce the negative environmental impact.

This work aims to develop a cost-effective process to synthesize carbon-based nanostructures from OP valorization without using any chemical agents. The combustion of the OP is proposed to be avoided by using fine-grain sea sand to limit the oxygen in the vicinity of the biomass.

## MATERIALS AND METHODS

### Materials

Small alumina crucibles of 15 mL and 30 mL, fine grain sea sand composed mainly of silicon dioxide

(SiO<sub>2</sub>) with particle sizes from 0.075 to 4.75 mm, and a muffle furnace (Thermolyne, FD1540M) were used to synthesize conductive biocarbon. The OP was obtained from local producers (Ciudad Victoria, Tamaulipas, Mexico).

### Preparation of orange peel biocarbon

First, the OP was washed with soap and abundant water and then cut into small pieces of approximately 1 cm<sup>2</sup>. Afterward, three cleaning cycles were carried out with deionized water and ethyl alcohol, following the procedure described by Raghu et al. (2020). Next, the OP pieces were sun-dried for three hours, and then they were further dehydrated for two hours in a muffle at 150 °C. Finally, the dried OP pieces were stored in hermetic bags for their future use.

The newly designed thermal process for carbonization is illustrated in **figure 1**. First, the smaller alumina crucible was filled with the pieces of dehydrated OP and placed face down into the large alumina crucible. Then, the space between the smaller and bigger crucible was filled with sea sand to limit the oxygen availability near the OP biomass. Finally, the crucibles arrangement was placed in the muffle furnace with a heating ramp of 10 °C/min up to 1000 °C at atmospheric pressure.

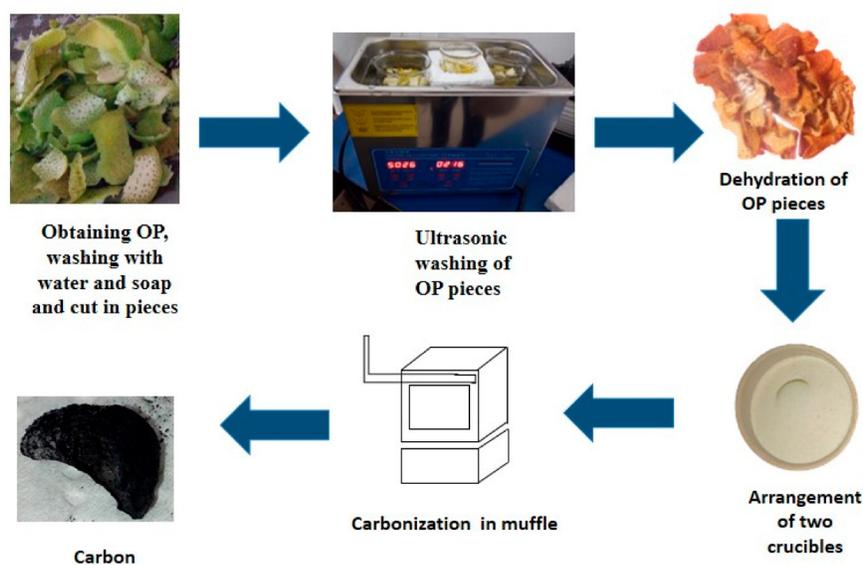
### Characterization of orange peel biocarbon

The OP biocarbon morphology was analyzed by Field Emission Scanning Electron Microscopy

(FESEM) at 25 kV (Jeol JSM-7800F). In contrast, elemental analysis was conducted using copper holders in a SEM/EDS with a 20 kV working voltage (Philips XL30 series).

The phase and crystal structures of the obtained carbon were analyzed with X-Ray Diffraction (XRD) using Philips-X'Pert with a working voltage of 40 kV and Cu K  $\alpha$  radiation. In addition, the chemical bonds and functional groups at the surface of the synthesized OP biocarbon were studied by Fourier Transform Infrared spectroscopy (FTIR) in a WQF-510A Rayleigh instrument.

The electrochemical behavior of the conductive OP biocarbon was analyzed by cyclic voltammetry at different scan rates (10, 15, 20, 25, and 30 mV/s) in a three-electrode cell configuration using a Gill-AC-ACM instruments Ltd brand potentiostat. The counter and reference electrodes were a graphite bar and Ag/AgCl electrode. The working electrode was obtained by transferring 10 mL of carbon ink onto the glassy carbon electrode surface. The carbon ink was prepared by mixing 5 mg of the synthesized biocarbon with 0.5 mL of 2-propanol and 10  $\mu$ L of Nafion<sup>®</sup>. As a supporting electrolyte, one mol/L of H<sub>2</sub>SO<sub>4</sub> was used. The voltage sweep for the cyclic voltammetry (Dujearic-Stephane et al. 2020) was selected considering the corrosion voltage of carbon-based materials at 1.4 V vs. RHE in acid media (Oh et al. 2009).



**Fig. 1.** Novel carbonization process using fine sea sand as an oxygen barrier.

The specific capacitance of the synthesized sample was calculated by using the equation (1) that governs the process in a three-electrode cell setup (Ghosh and Yue 2018):

$$C = \frac{\int_{V_0}^{V_1} I dV}{\nu * (V_0 - V_1)} \quad (1)$$

where  $C$  is the specific capacitance (F/g),  $I$ , is the current density (A/g),  $\nu$  is the scan rate (V/s),  $V_0$  and  $V_1$  are the potential limits in of the selected scan range.

## RESULTS AND DISCUSSION

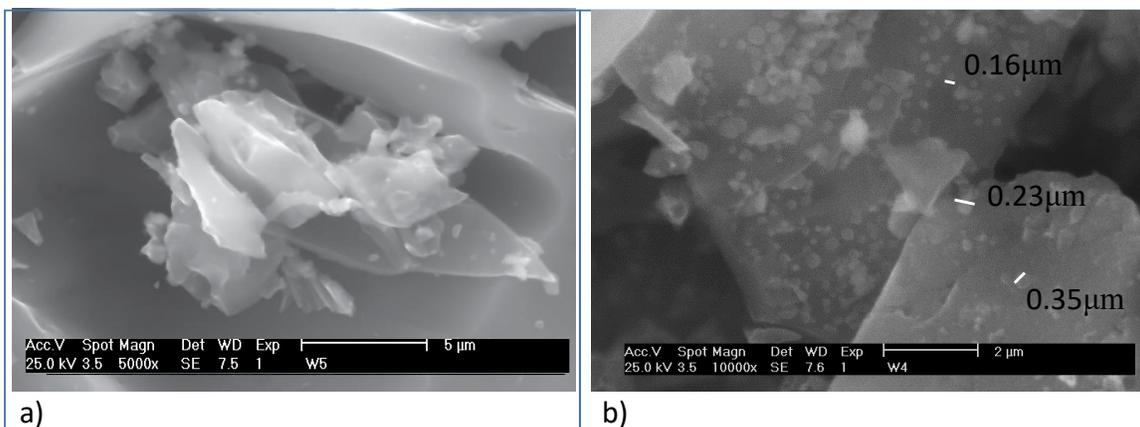
### Morphology and composition of orange peel biocarbon

The structural morphology of the obtained OP biocarbon is shown at different magnifications in **figure 2**. As can be seen, it is composed of three-dimensional large and small rough flakes with high porosity (Liu et al. 2014). This characteristic is significant because ion diffusion can occur at a high rate, therefore, good electrochemical properties could be obtained. **Figure 2a** displays a porous structure with large open channels with an average diameter of 20  $\mu\text{m}$  that result from the rapid release of gases during the thermal treatment. Meanwhile, **figure 2b** reveals the presence of small particles with diameters less than 160 nm on the surface of the rough flakes that might result from broken frameworks. The images supply evidence for the

successful conversion of the OP waste to a material that can be employed for energy storage (Ranaweera et al. 2017). Furthermore, since the proposed green thermal process does not use inert gases, nor sophisticated expensive furnaces, nor chemical agents, it may be considered a cost-effective way to obtain carbonaceous structures.

The chemical content of the obtained conductive material studied by EDS analysis showed the following composition: C (67.96 %), Ca (19.23 %), K (4.87 %), Mg (0.95 %), P (1.82 %), S (0.87 %), and O (4.3 %). These results confirmed the effectiveness of the oxygen limitation with fine-grain sea sand. It is worth mentioning that when sea sand was not used, complete combustion of the OP was observed, and only ash as residue was obtained, which was may be mainly constituted of  $\text{SiO}_2$  and  $\text{CaO}$  compounds (Olumide et al. 2019).

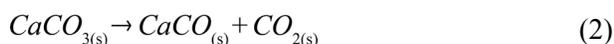
The XRD profile for the OP biocarbon is shown in **figure 3**. The diffraction peaks of graphite structure are located between  $15\text{-}30^\circ 2\theta$  and  $40\text{-}50^\circ 2\theta$ , ascribed to (002) and (101) plane (Liu et al. 2010, Rajan et al. 2014, Cholake et al. 2015). These peaks are broad, suggesting that the obtained carbon is in the nanostructure range or with some degree of the amorphous phase. From the diffractogram, it is observed that carbon reflections are overlapped with other signals. Further indexation was achieved, and phases of  $\text{CaCO}_3$  with high crystalline quality were observed (JCPDS data file 00-005-0586). These are the signals that overlap with the reflections of the graphite structure (Ramalingam et al. 2018). Also, the characteristic peaks of  $\text{CaO}$  at  $33^\circ$ ,  $37.5^\circ$ , and  $54^\circ$  at  $2\theta$ , were observed according to the JCPDS



**Fig. 2.** FESEM of orange peel biocarbon obtained at 1000 °C without an inert atmosphere a) at 5000x b) at 10000x showing possible incrustations of Ca.

card (data file 004-0777) and  $\text{Ca}(\text{OH})_2$  at  $62^\circ 2\theta$  (Ramacharyulu and Abbas 2020). These results are in good agreement with the SEM-EDS measurements, where C and Ca were the significant elements in the sample.

The present results show well-crystallized  $\text{CaCO}_3$ , CaO, and  $\text{Ca}(\text{OH})_2$  phases at  $1000^\circ\text{C}$ , as revealed by XRD in **figure 3**. Besides, previous reports on  $\text{CaCO}_3$  pyrolytic decomposition have demonstrated that this compound is further transformed to CaO up to  $800^\circ\text{C}$  (Karunadasa et al. 2019) by the reaction:



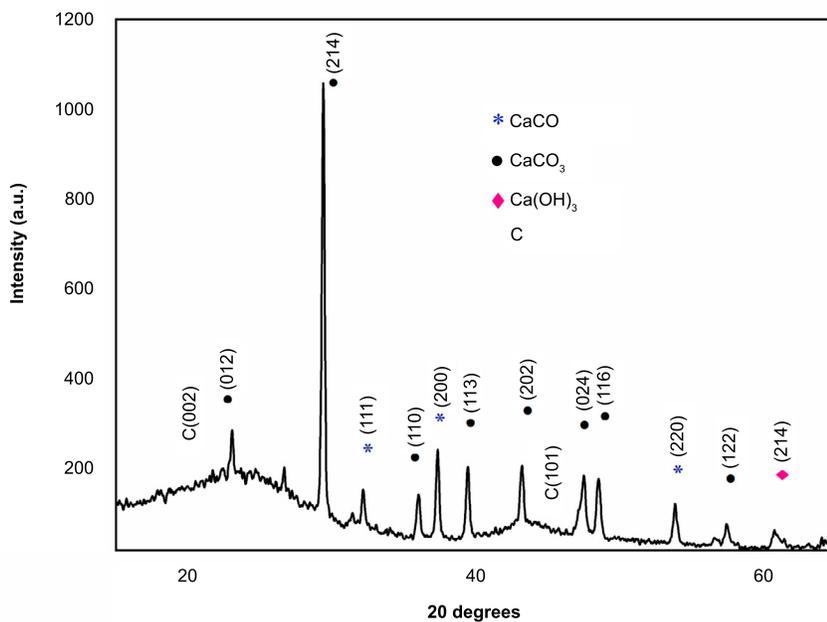
The prevalence of  $\text{CaCO}_3$  at  $1000^\circ\text{C}$  can be explained by the sea sand air-limited pyrolytic process that delays the decomposition of  $\text{CaCO}_3$  at  $800^\circ\text{C}$ . Such accounted for degasification of byproducts without air replacement; therefore, the absence of free oxygen led to a limited decomposition process. Also, silica sand avoids the rapid liberation of the produced  $\text{CO}_2$  gases, and this reacts with the sample, forming in this way  $\text{CaCO}_3$  at elevated temperatures.

This phenomenon was also observed by Zhang et al. (2014), who reported the pyrolysis reactivity of peanut shells and pine sawdust in the presence of

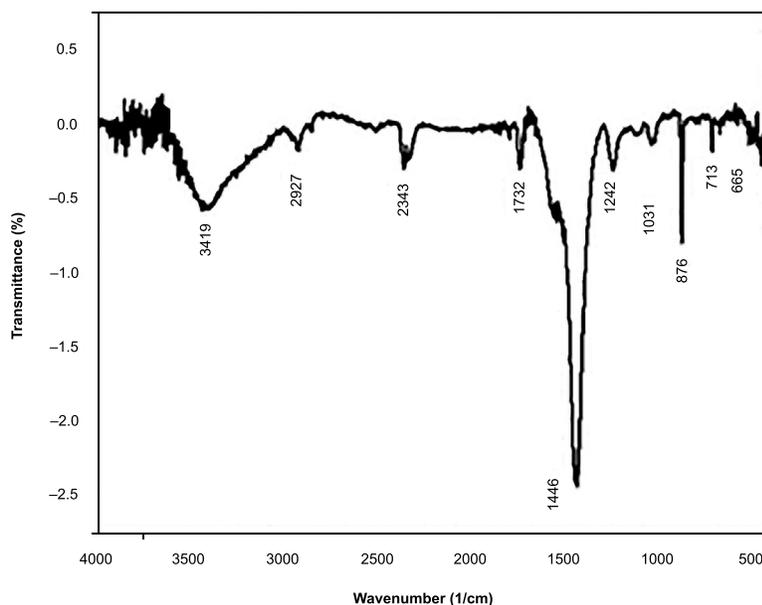
different Ca-based additives. They stated that at temperatures in the range of  $400$  to  $620^\circ\text{C}$ , CaO reacts with the generated  $\text{CO}_2$  to form  $\text{CaCO}_3$  directly. It is worth noting that OP has a conveniently natural Ca content, which according to Tran et al. (2015) is around 2.2 % weight basis.

The FTIR measurement of the OP biocarbon is shown in **figure 4**. At high wavenumber, a peak is observed within the range of  $3300$  to  $3500\text{ cm}^{-1}$  due to the stretching modes of the OH groups (Velázquez-González et al. 2019). Meanwhile, the C-H stretching vibration of alkene species was observed close to  $2927\text{ cm}^{-1}$  (Lu et al. 2012). The band at  $2343\text{ cm}^{-1}$  was ascribed to the asymmetric stretching mode and bending mode of  $\text{CO}_2$  (Pech-Rodríguez et al. 2017). Another band was observed at  $1441\text{ cm}^{-1}$  due to carbonate C—O bonds (Galván-Ruiz et al. 2009). The peak localized at  $876\text{ cm}^{-1}$  was attributed to carbonate ions related to the presence of  $\text{CaCO}_3$  in the sample (Rau et al. 2004). The peak at  $1031\text{ cm}^{-1}$  is ascribed to C-O stretching vibration (Shamsuddin et al. 2016).

It is essential to mention that the  $\text{CO}_2$  signals of the OP biocarbon are powerful, suggesting that  $\text{CO}_2$  molecules are present at the surface of the carbon structure. Sea sand may not have only limited the oxygen transfer, but also the  $\text{CO}_2$  molecules diffusion in the carbon side. Thus,  $\text{CO}_2$  might have improved the structural properties of the OP biocarbon structure. In research,  $\text{CO}_2$  gas has been



**Fig. 3.** XRD analysis of orange peel biocarbon.



**Fig. 4.** FTIR spectrum of orange peel biocarbon at 1000°C without inert atmosphere obtained by the green thermal process.

used as a physical treatment for carbonaceous structures, and their porosity was comparable with the materials that were chemically activated (Guo et al. 2005, Saha et al. 2014). Although the synthesized OP biocarbon has an added value per se due to its calorific energy or its adsorptive properties, it is believed that the profits from OP waste are boosted if presenting electrochemical characteristics. Hence, it is proposed that the thermal process induces a self-activated carbon-based nanostructure with good porosity and excellent electrical conductivity.

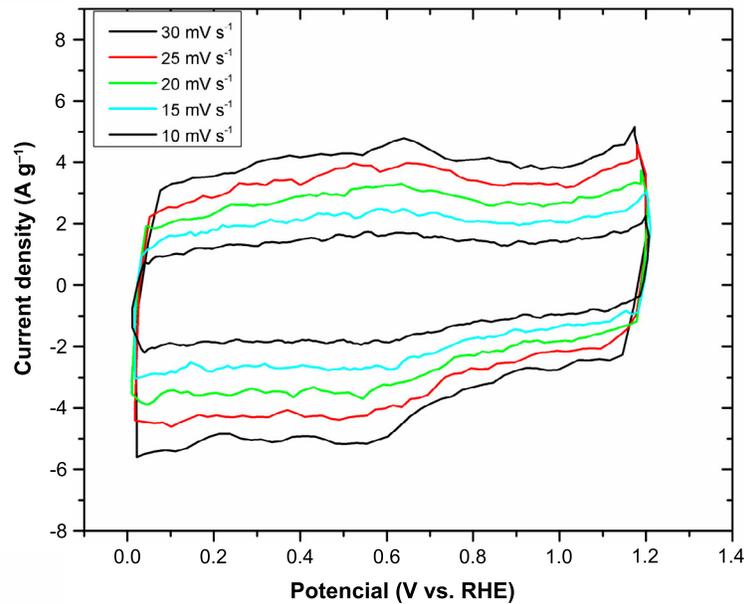
#### **Electrochemical performance of orange peel biocarbon in acid medium**

The cyclic voltammetry (**figure 5**) shows that the OP biocarbon delivers significant current densities under the potential working windows. All the conducted cyclic voltammetry measurements present a quasi-rectangular shape, an inherent characteristic of electrical double-layer capacitors. The deviation to the rectangular form is attributed to the polarization resistance or pseudo-capacitance (Sahu et al. 2013).

**Table I** resumes the obtained specific capacitance and current density or sweep velocity of the relevant research works reported in the literature. Accordingly, it can be observed that the OP biocarbon had a similar specific capacitance compared to other materials obtained in inert atmospheres.

According to common knowledge, the capacitive behavior is related to high porous structures that facilitate ion transport (Chai et al. 2020), and this can be corroborated by the FESEM images observed in this work. The specific capacitance of the sample is calculated according to equation (1) and plotted vs. the scan rate (**Fig. 6**). As can be seen, the OP biocarbon presents high specific capacitance values that can be applied in all areas of supercapacitors; for example, at 20 mV/s has a specific capacitance of 272 F/g. From **figure 6** is inferred that capacitance decrease as the scan rate increase, this may be since at low scan rate the electrolyte has enough time to diffuse through the porous biocarbon. The high specific capacitance could be related to the tall porous structure (Fu et al. 2012) of the OP biocarbon synthesized at oxygen limitation.

The contribution of the pseudo-capacitance of the charge storage process at the electrode was estimated by the Trasatti and Lee method (Shao et al. 2015). First, the capacitance vs. the inverse of the scan rate is plotted (**Fig. 7a**) to obtain the electrical double layer capacitance ( $C_{EDL}$ ) contribution. Second, the Total Capacitance (TC) was determined by plotting the scan rate vs. the inverse of the capacitance (**Fig. 7b**), assuming a linear diffusion and considering a linear extrapolation, the value of  $C/T$  was obtained.



**Fig. 5.** Cyclic voltammetry of the three electrodes measurement in 1 mol/L  $\text{H}_2\text{SO}_4$  at different scan rates.

**TABLE I.** SPECIFIC CAPACITANCE OF BIOCARBONS OBTAINED BY DIFFERENT METHODS.

Carbon source	Electrolyte	Specific Capacitance (F/g)	Sweep velocity (mV/s)	Reference
<i>Datura metel</i> peels in inert atmosphere at 800°C	1 mol/L $\text{H}_2\text{SO}_4$	76.4	20	Dujearic-Stephane et al. (2020)
<i>Fagus sylvatica</i> in inert atmosphere at 800°C	1 mol/L $\text{H}_2\text{SO}_4$	185	2	Orlova et al. (2018)
Orange peel in inert atmosphere	0.1 mol/L $\text{H}_2\text{SO}_4$	275	10	Dhelipan et al. (2017)
Sorghum pith	0.1 mol/L $\text{H}_2\text{SO}_4$	224	10	Senthilkumar et al. (2011)
Orange peel without inert atmosphere	1 mol/L $\text{H}_2\text{SO}_4$	288	10	This work
		272	20	

Under the experimental conditions, the OP biocarbon experimented 32.7 % of pseudo-capacitance and 67.3 % due to the double-layer charge process; this is well correlated with the work of Fu et al. (2012), where the pseudo-capacitance was 37.8 % of the TC.

The Impedance Nyquist plot for OP biocarbon is shown in **figure 8**. A resistive-capacitive behavior is observed as a semicircle at high frequencies,

while a linear tendency to the imaginary axis is attributed to the diffusion process (Saha and Kuila 2020). From **figure 8** it can be appreciated that the OP biocarbon material has good electron transfer properties because no semicircle is observed at high frequencies. That means the electron is easily moved along the porous structure of the OP biocarbon. Also, the extended curve to the imaginary axis reveals that OP biocarbon has good ionic diffusion (Du et al. 2017).

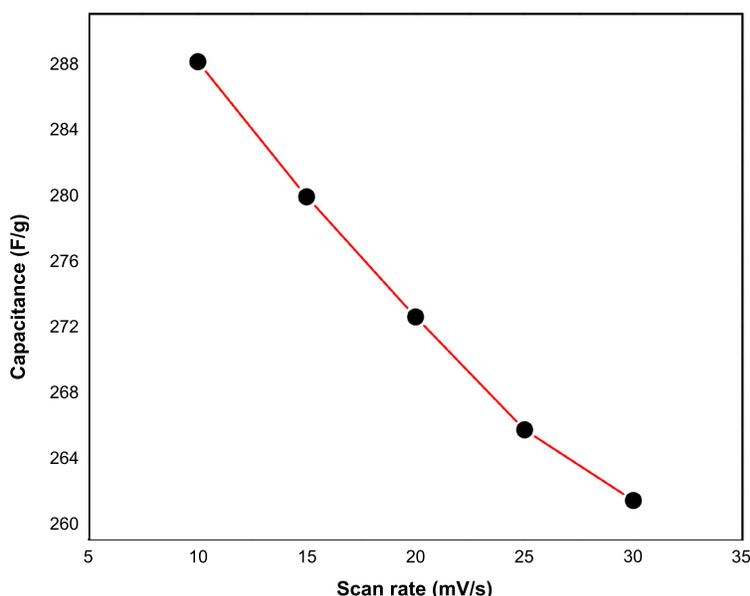


Fig. 6. Change in the specific capacitance of the orange peel biocarbon with the potential scan rate.

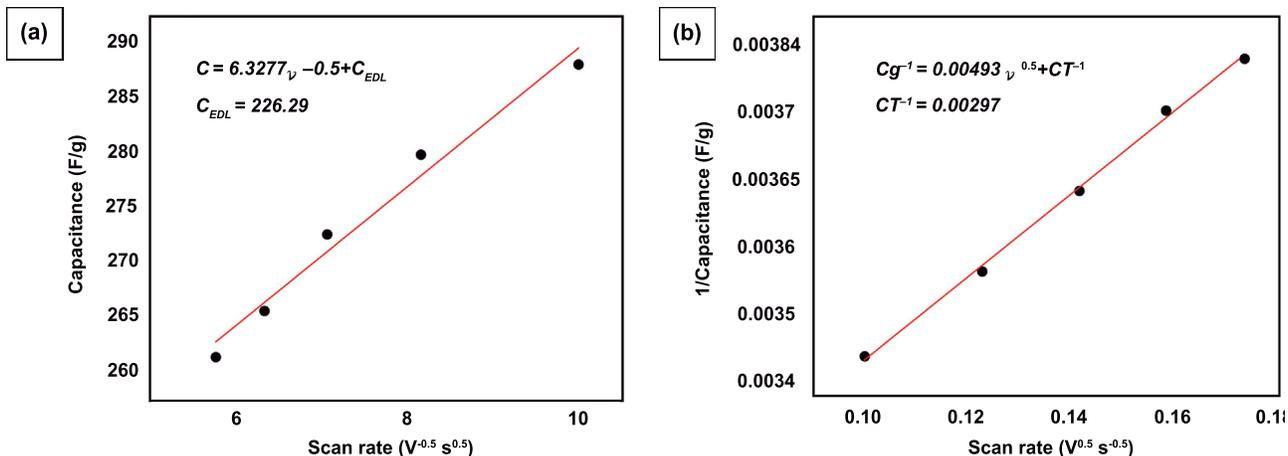
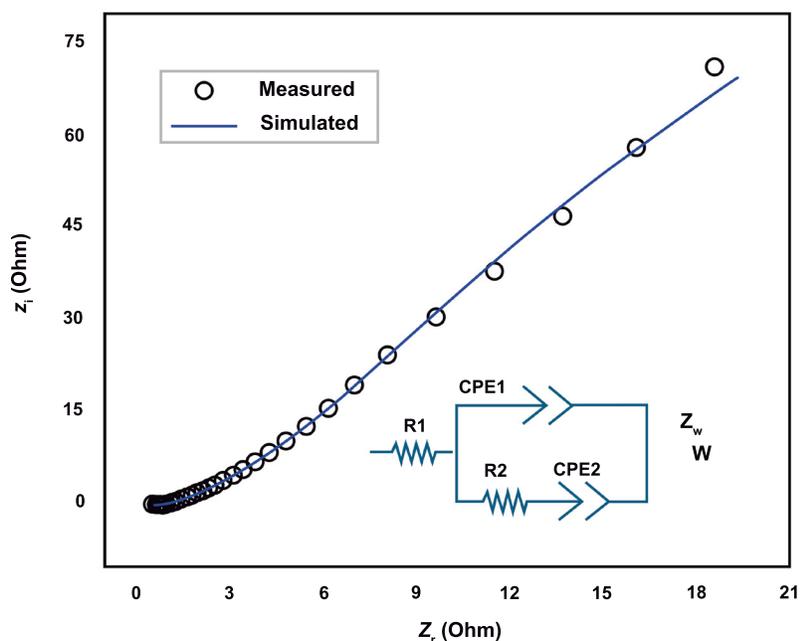


Fig. 7. Trasatti and Lee analysis to obtain the a) the Electrical Double Layer capacitance (EDLC) and b) pseudocapacitance.

Therefore, good charge storage behavior is presented in the carbon structure, and this suggests its use as electrode materials in supercapacitor applications (Maharjan et al. 2017).

As a result, the proposed thermal treatment can be classified as a green process because it does not use any harmful or toxic chemical reagent in considerable amounts. The carbonaceous material obtained was porous and presented good electrical

conductivity and high specific capacitance. The fact that no inert gas is required, eliminates the cost of acquiring argon, nitrogen, or a mix of them. In addition, no sophisticated equipment is needed. This method could promote large-scale production of orange peel biocarbon in an eco-friendly and economical manner since the OP is a waste not commercialized in most parts of the world notwithstanding an inherent cost for juice companies.



**Fig. 8.** Nyquist plot for the as prepared orange peel biocarbon in the frequency range of 100 kHz to 0.6 Hz.

## CONCLUSIONS

A successful synthesis of orange peel biocarbon was obtained via a novelty method that does not use a gas-induced inert atmosphere or any chemical reagent. The proposed green thermal process is based on the suppression or limitation of air close to the surroundings of the OP. FESEM studies revealed large and small rough 3D flakes 3D with high porosity relevant to energy storage applications. Besides, XRD and EDS analysis indicated that the synthesized material contains mainly carbon and calcium carbonate. The electrochemical measurements suggest that the developed carbon exhibited excellent specific capacitance, 272 F/g, which is in the same range that the chemical-treated samples reported in the literature.

Therefore, the results suggest that the proposed cost-effective and straightforward thermal treatment based on oxygen limitation using fine sea sand is a versatile process to get conductive carbonaceous electrodes with high capacitance. Other advantages of the process are the low cost of the OP. Also, sophisticated equipment is not required as either strong acids or bases. Finally, this green thermal process may have a broad spectrum for future applications

where time, energy consumption, and environmental impacts are the primary concerns.

## ACKNOWLEDGMENTS

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## DECLARATION OF COMPETING INTEREST OR DISCLOSURE STATEMENT

The authors state that there are not conflicts of interest.

## REFERENCES

- Antal M. J., Mochidzuki K. and Paredes L. S. (2003). Flash carbonization of biomass. *Ind. Eng. Chem. Res.* 42 (16), 3690–3699. <https://doi.org/10.1021/ie0301839>
- Arias-Niquepa R. A., Prías-Barragán J. J., Ariza-Calderón H. and Rodríguez-García M. E. (2019). Activated carbon obtained from bamboo: synthesis, morphological, vibrational, and electrical properties and possible temperature

- sensor. *Phys. Status Solidi A*. 216 (4), 1–11. <https://doi.org/10.1002/pssa.201800422>
- Arie A. A., Kristianto H., Halim M. and Lee J. K. (2016). Synthesis and modification of activated carbon originated from Indonesian local orange peel for lithium ion capacitor's cathode. *J. Solid. State. Electrochem.* 21 (5), 1331-1342. <https://doi.org/10.1007/s10008-016-3445-7>
- Barrón-Bravo O. G., Alcalá-Rico J., Mireles-Rodríguez E., Felipe-Victoriano M. (2020). Caracterización y problemáticas de las unidades de producción familiar de cítricos en Llera, Tamaulipas. *Ciencia e Innovación* 3 (1), 243-250 .
- Brito G. M., Fernandes-Cipriano D., Schettino M. A., Gonçalves-Cunha A., Cabral-Coelho E.R. and Checon-Freitas J. C. (2019). One-step methodology for preparing physically activated biocarbons from agricultural biomass waste. *J. Environ. Chem. Eng.* 7 (3), 103113. <https://doi.org/10.1016/j.jece.2019.103113>
- Chai Y., Hu Z., Jia W. and Ji H. (2020). Ion transport in porous carbon electrode for supercapacitors probed by electrochemical quartz crystal microbalance. *Electrochim. Acta*. 356, 136780. <https://doi.org/10.1016/j.electacta.2020.136780>
- Chen D. Y., Yu Q. L. and Hu Y.Q. (2014). Study on the pyrolysis characteristics and mechanism of KCl-pre-treated sunflower stalk. *Appl. Mech. Mater.* 448-453, 1665–1674. <https://doi.org/10.4028/www.scientific.net/AMM.448-453.1665>
- Chen S., Chen G., Chen H., Sun Y., Yu X., Su Y. and Tang S. (2019). Preparation of porous carbon-based material from corn straw via mixed alkali and its application for removal of dye. *Colloids Surf., A*. 568, 173–183. <https://doi.org/10.1016/j.colsurfa.2019.02.008>
- Chen Q., Tan X., Liu Y., Liu S., Li M., Gu Y., Zhang P., Ye S., Yang Z. and Yang Y. (2020). Biomass-derived porous graphitic carbon materials for energy and environmental applications. *J. Mater. Chem. A*. 8 (12), 5773–5811. <https://doi.org/10.1039/c9ta11618d>
- Cholake S. T., Moran G., Bai Y., Singh-Raman R. K., Zhao X. L., Rizkalla S. and Bandyopadhyay S. (2015). Physico-chemical characterization of novel epoxy matrix system reinforced with recycled short milled carbon fibre. *J. Miner. Charact. Eng.* 03 (05), 373–389. <https://doi.org/10.4236/jmmce.2015.35040>
- Dhelipan, M., A. Arunchander, A. K. Sahu and D. Kalpana. (2017). Activated carbon from orange peels as supercapacitor electrode and catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *J. Saudi Chem. Soc.* 21 (4), 487–494. <https://doi.org/10.1016/j.jscs.2016.12.003>
- Dujearic-Stephane K., Panta P., Shulga Y. M., Kumar A., Gupta M. and Kumar Y. (2020). Physico-chemical characterization of activated carbon synthesized from *Datura metel's peels* and comparative capacitive performance analysis in acidic electrolytes and ionic liquids. *Bioresour. Technol. Rep.* 11, 100516. <https://doi.org/10.1016/j.biteb.2020.100516>
- Fernandez M. E., Nulle G. V., Bonelli P. R. and Cukierman A. L. (2014). Activated carbon developed from orange peels: batch and dynamic competitive adsorption of basic dyes. *Ind. Crops. Prod.* 62, 437–445. <https://doi.org/10.1016/j.indcrop.2014.09.015>
- Foo, K. Y. and Hameed B. H. (2012). Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbon via microwave induced  $K_2CO_3$  activation. *Bioresour. Technol.* 104, 679–686. <https://doi.org/10.1016/j.biortech.2011.10.005>
- Fu Y., Cai X., Wu H., Lv Z., Hou S, Peng M., Yu X. and Zou D. (2012). Fiber supercapacitors utilizing pen ink for flexible/wearable energy storage. *Adv. Mater.* 24 (42), 5713–5718. <https://doi.org/10.1002/adma.201202930>
- Galván-Ruiz M., Hernández J., Baños L., Noriega-Montes J. and Rodríguez-García M.E. (2009). Characterization of calcium carbonate, calcium oxide, and calcium hydroxide as starting point to the Improvement of lime for their use in construction. *J. Mater. Civ. Eng.* 21 (11), 694-698. [https://doi.org/10.1061/\(ASCE\)0899-1561\(2009\)21:11\(694\)](https://doi.org/10.1061/(ASCE)0899-1561(2009)21:11(694))
- Ghosh K. and Yue C.Y. (2018). Development of 3D  $MoO_3$ /graphene aerogel and sandwich-type polyaniline decorated porous  $MnO_2$ -graphene Hybrid film based high performance all-solid-state asymmetric supercapacitors. *Electrochim. Acta* 276, 47–63. <https://doi.org/10.1016/j.electacta.2018.04.162>
- Girgis B. S., Smith E., Louis M. M. and El-Hendawy A.N.A. (2009). Pilot production of activated carbon from cotton stalks using  $H_3PO_4$ . *J. Anal. Appl. Pyrolysis* 86 (1), 180–184. <https://doi.org/10.1016/j.jaap.2009.06.002>
- Guo J., Xu W. S., Chen Y. L. and Lua A. C. (2005). Adsorption of  $NH_3$  onto activated carbon prepared from palm shells impregnated with  $H_2SO_4$ . *J. Colloid Interface Sci.* 281 (2), 285–290. <https://doi.org/10.1016/j.jcis.2004.08.101>
- Hu B., Wang K., Wu L., Yu S. H., Antonietti M. and Titirici M. M. (2010). Engineering carbon materials from the hydrothermal carbonization process of biomass. *Adv. Mater.* 22 (7), 813-828. <https://doi.org/10.1002/adma.200902812>
- Hui T. S. and Zaini M. A. A. (2015). Potassium hydroxide activation of activated carbon: a commentary. *Carbon Lett.* 16 (4), 275–280. <https://doi.org/10.5714/CL.2015.16.4.275>

- Karunadasa K. S. P., Manoratne C. H., Pitawala H. M.T.G.A. and Rajapakse R. M. G. (2019). Thermal decomposition of calcium carbonate (calcite polymorph) as examined by in-situ high-temperature X-ray powder diffraction. *J. Phys. Chem. Solids* 134, 21–28. <https://doi.org/10.1016/j.jpcs.2019.05.023>
- Lam S. S., Liew R. K., Wong Y. M., Azwar E., Jusoh A. and Wahi R. (2016). Activated carbon for catalyst support from microwave pyrolysis of orange peel. *Waste and Biomass Valorization* 285 (1), 121356. <https://doi.org/10.1007/s12649-016-9804-x>
- Li P., Xia J., Shan Y., Nie Z. and Wang F. (2015). Effects of surfactants and microwave-assisted pretreatment of orange peel on extracellular enzymes production by *Aspergillus japonicus* PJ01. *Appl. Biochem. Biotechnol.* 176 (3), 758–771. <https://doi.org/10.1007/s12010-015-1609-z>
- Libra J. A., Ro K. S., Kammann C., Funke A., Berge N. D., Neubauer Y., Titirici M. M., Fühner C., Bens O., Kern J. and Emmerich K.H. (2011). Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* 2 (1), 89–124 <https://doi.org/10.4155/bfs.10.81>
- Liew R. K., Chai C., Yuh Yek P. N., Phang Y. X., Chong M. Y., Nam W. L., Su M. H., Lam W. H., Ma N. L. and Lam S. S. (2019). Innovative production of highly porous carbon for industrial effluent remediation via microwave vacuum pyrolysis plus sodium-potassium hydroxide mixture activation. *J. Cleaner Prod.* 208, 1436–1445. <https://doi.org/10.1016/j.jclepro.2018.10.214>
- Liu B., Shioyama H., Jianga H., Zhang X. and Xu Q. (2009). Metal–Organic Framework (MOF) as a template for syntheses of nanoporous carbons as electrode materials for supercapacitor. *Carbon* 48 (2), 456–463. <https://doi.org/10.1016/j.carbon.2009.09.061>
- Liu X. Y., Huang M., Ma H. L., Zhang Z. Q., Gao J. M., Zhu Y. L., Han X. J. and Guo X. Y. (2010). Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules* 15 (10), 7188–7196. <https://doi.org/10.3390/molecules15107188>
- Liu L., Shen Z., Yi M., Zhang X. and Ma S. (2014). A green, rapid and size-controlled production of high-quality graphene sheets by hydrodynamic forces. *RSC Adv.* 4 (69), 36464–36470. <https://doi.org/10.1039/c4ra05635c>
- Lu Y., Gan L., Liu M., Xiong W., Xu Z., Zhu D. and Wright D. S. (2012). A self-template synthesis of hierarchical porous carbon foams based on banana peel for supercapacitor electrodes. *J. Power Sources* 209, 152–157. <https://doi.org/10.1016/j.jpowsour.2012.02.089>
- Mackenzie L. S., Tyrrell H., Thomas R., Matharu A. S., Clark J. H. and Hurst G. A. (2019). Valorization of waste orange peel to produce shear-thinning gels. *J. Chem. Educ.* 96 (12), 3025–3029. <https://doi.org/10.1021/acs.jchemed.8b01009>
- Maharjan M., Ulaganathan M., Aravindan V., Sreejith S., Yua Q., Madhavi S., Wang J. Y. and Lim T. M. (2017). Fabrication of high energy Li-ion capacitors from orange peel derived porous carbon. *Chemistry-Select* 2 (18), 5051–5058. <https://doi.org/10.1002/slct.201700574>
- Moya-Salazar J. J. and Rojas-Zumaran V. A. (2016). Environmental performance of xylene, hydrochloric acid and ammonia solution during pap stain for diagnosing cervical cancer. *J. Health Pollut.* 6 (11), 58–65. <https://doi.org/10.5696/2156-9614-6-11-58>
- Oh H. S., Lim K. H., Roh B., Hwang I. and Kim H. (2009). Corrosion resistance and sintering effect of carbon supports in polymer electrolyte membrane fuel cells. *Electrochim. Acta* 54 (26), 6515–6521. <https://doi.org/10.1016/j.electacta.2009.06.028>
- Olumide O. O., Ade-Odey O. and Abdullahi B. (2019). Potential of orange peel ash as a cement replacement material. *Traek. Nau. Path. Sci.* 5 (7), 2009–2019. <https://doi.org/10.22178/pos.48-3>
- Orlova T. S., Shpeizman V. V., Glebova N. V., Nechitailov A. A., Spitsyn A. A., Ponomarev D. A., Gutierrez-Pardo A. and Ramirez-Rico J. (2018). Environmentally friendly monolithic highly-porous biocarbons as binder-free supercapacitor electrodes. *Rev. Adv. Mater. Sci.* 55 (1–2), 50–60. <https://doi.org/10.1515/rams-2018-0027>
- Pawlak-Kruczek H., Niedzwiecki L., Sieradzka M., Mlonka-Mędrala A., Baranowski M., Serafin-Tkaczuk M. and Magdziarz A. (2020). Hydrothermal carbonization of agricultural and municipal solid waste digestates – structure and energetic properties of the solid products. *Fuel* (275), 117837. <https://doi.org/10.1016/j.fuel.2020.117837>
- Pech-Rodríguez W. J., González-Quijano D., Vargas-Gutiérrez G., Morais C., Napporn T.W. and Rodríguez-Varela F. J. (2017). Electrochemical and in situ FTIR study of the ethanol oxidation reaction on PtMo/C nanomaterials in alkaline media. *Appl. Catal., B* (203), 654–662. <https://doi.org/10.1016/j.apcatb.2016.10.058>
- Raciti A., Dugo G., Piccione P., Zappalà S. and Martelli C. (2019). A new sustainable product in the green building sector: the use of sicilian orange peel waste as high performance insulation. *Procedia Environ. Sci. Eng. and Manag.* 6 (2), 229–235.
- Raghu M. S., Parashuram L., Kumar K. Y., Prasanna B. P., Rao S., Krishnaiah P., Prashanth K. N., Pradeep-Kumar C. B. and Alrobei H. (2020). Facile green synthesis of

- boroncarbonitride using orange peel; its application in high performance supercapacitors and detection of levodopa in real samples. *Mater. Today Commun.* 24 (1), 1–8. <https://doi.org/10.1016/j.mtcomm.2020.101033>
- Rajan A. S., Sampath S. and Shukla A.K. (2014). An in situ carbon-grafted alkaline iron electrode for iron-based accumulators. *Energy Environ. Sci.* 7 (3), 1110–1116. <https://doi.org/10.1039/c3ee42783h>
- Ramacharyulu P. V. R. K., Jahir-Abbas S. and Shyue-Chu K. (2020). Enhanced charge separation and photoactivity in heterostructured g-C<sub>3</sub>N<sub>4</sub>: a synergistic interaction in environmental friendly CaO/g-C<sub>3</sub>N<sub>4</sub>. *Catal. Sci. Technol.* 4 (1), 1–10. <https://doi.org/10.1039/c7cy01623a>
- Ramalingam R. S., Robinson C., John A. and Baskaran S. (2018). Novel method to prepare activated carbon nanomaterials from defunct leaves. *Am. J. Chem. Mater. Sci.* 6 (1), 1–6
- Ranaweera C. K., Kahol P. K., Ghimire M., Mishra S. R. and Gupta R.K. (2017). Orange-peel-derived carbon: designing sustainable and high-performance supercapacitor electrodes. *J. Carbon Res.* 3 (4), 1-17. <https://doi.org/10.3390/c3030025>
- Rau J. V., Cesaro S. N., Ferro D., Barinov S. M. and Fadeeva I. V. (2004). FTIR study of carbonate loss from carbonated apatites in the wide temperature range. *J. Biomed. Mater. Res., Part B* 71 (2), 441–447. <https://doi.org/10.1002/jbm.b.30111>
- Raymundo-Piñero E., Leroux F. and Béguin F. (2006). A high-performance carbon for supercapacitors obtained by carbonization of a seaweed biopolymer. *Adv. Mater.* 18 (1), 1877–1882. <https://doi.org/10.1002/adma.200501905>
- Ruiz-Hernández O., Ibarra-Hinojosa M., Hernández-Meléndez J., Lucero-Magaña F., Cienfuegos-Rivas E. and Martínez-González J. (2019). Comportamiento de corderos de ovejas alimentadas con cáscara fresca de naranja y niveles de suplementación. *Abanico Vet.* 1 (9), 1-9. <http://dx.doi.org/10.21929/abavet2019.98>
- Saha D., Li Y., Bi Z., Chen J., Jong K. K., Hensley D. K., Grappe H. A., Meyer H. M., Dai S., Paranthaman M. P. and Naskar A. K. (2014). Studies on supercapacitor electrode material from activated lignin-derived mesoporous carbon. *Langmuir* 30 (3), 900–910. <https://doi.org/10.1021/la404112m>
- Saha S. and Kuila T. (2020). Part 3 Supercapacitor: nanostructured carbon-based electrodes for supercapacitor applications in nanomaterials for electrochemical energy storage devices. (Roy P., Srivastava S.K.) Wiley Online Library, 467-520. <https://doi.org/10.1002/9781119510000>
- Sahu V., Shekhar S., Ahuja P., Gupta G., Singh S. K., Sharma R. K. and Singh G. (2013). Synthesis of hydrophilic carbon black; role of hydrophilicity in maintaining the hydration level and protonic conduction. *RSC Adv.* 3 (12), 3917–3924. <https://doi.org/10.1039/c3ra23136d>
- Sankari M. S. and Vivekanandhan S. (2020). Jatropha oil cake based activated carbon for symmetric supercapacitor application: a comparative study on conventional and hydrothermal carbonization processes. *Chemistry Select* 5 (4), 1375–1384. <https://doi.org/10.1002/slct.201903492>
- Sayed D. M., El-Deab M. S., Elshakre M. E. and Allam N. K. (2020). Nanocrystalline cellulose confined in amorphous carbon fibers as capacitor material for efficient energy storage. *Phys. Chem. C* 124 (13), 7007–7015. <https://doi.org/10.1021/acs.jpcc.9b12045>
- Sebag-Bernd M. G., Bragança S. R., Heck N. and Da Silva-Filho L. C. P. (2017). Synthesis of carbon nanostructures by the pyrolysis of wood sawdust in a tubular reactor. *J. Mater. Res. Technol.* 6 (2), 171–177. <https://doi.org/10.1016/j.jmrt.2016.11.003>
- Senthilkumar S. T., Senthilkumar B., Balaji S., Sanjeeviraja C. and Kalai Selvan R. (2011). Preparation of activated carbon from sorghum pith and its structural and electrochemical properties. *Mater. Res. Bull.* 46 (3), 413–419. <https://doi.org/10.1016/j.materresbull.2010.12.002>
- Shamsuddin M. S., Yusoff N. R. N. and Sulaiman M. A. (2016). Synthesis and characterization of activated carbon produced from kenaf core fiber using H<sub>3</sub>PO<sub>4</sub> activation. *Procedia Chem.* 19, 558–565. <https://doi.org/https://doi.org/10.1016/j.proche.2016.03.053>
- Shao J., Zhou X., Liu Q., Zou R., Li W., Yang J. and Hu J. (2015). Mechanism analysis of the capacitance contributions and ultralong cycling-stability of the isomorphous MnO<sub>2</sub>@MnO<sub>2</sub> core/shell nanostructures for supercapacitors. *J. Mater. Chem. A* 3 (11), 6168–6176. <https://doi.org/10.1039/c4ta06793b>
- Siles J. A., Vargas F., Gutiérrez M. C., Chica A. F. and Martín M. A. (2016). Integral valorisation of waste orange peel using combustion, biomethanisation and co-composting technologies. *Bioresour. Technol.* 1 (211), 173-182. <https://doi.org/10.1016/j.biortech.2016.03.056>
- Tekin K., Karagöz S. and Bektaş S. (2014). A review of hydrothermal biomass processing. *Renewable Sustainable Energy Rev.* 40 (1), 673–687. <https://doi.org/10.1016/j.rser.2014.07.216>
- Tran H. N., You S.-J. and Chao H.-P. (2015). Effect of pyrolysis temperatures and times on the adsorption of cadmium onto orange peel derived biochar. *Waste Manage. Res.* 34 (2), 129-138. <https://doi.org/10.1177/2F0734242X15615698>
- Velázquez-González C. E., Armendáriz-Mireles E. N., Pech-Rodríguez W. J., González-Quijano D. and Rocha-Rangel E. (2019). Improvement of dye sensitized solar

- cell photovoltaic performance by using a ZnO-semiconductor processed by reaction bonded. *Microsyst. Technol.* 25 (12), 4567–4575. <https://doi.org/10.1007/s00542-019-04476-2>
- Volperts A., Plavniece A., Dobele G., Zhurinsh A., Kruusenberg I., Kaare K., Locs J., Tamasauskaite-Tamasiunaite L. and Norkus E. (2019). Biomass based activated carbons for fuel cells. *Renewable Energy*. 1 (141), 40–45. <https://doi.org/10.1016/j.renene.2019.04.002>
- Wan L., Chen D., Liu J., Zhang Y., Chen J., Du C. and Xie M. (2020). Facile preparation of porous carbons derived from orange peel via basic copper carbonate activation for supercapacitors. *J. Alloys Compd.* 1 (823), 153747. <https://doi.org/10.1016/j.jallcom.2020.153747>
- Wei Q., Chen Z., Cheng Y., Wang X., Yang X. and Wang Z. (2019). Preparation and electrochemical performance of orange peel based-activated carbons activated by different activators. *Colloid Surface A*. 1 (574), 221–227. <https://doi.org/10.1016/j.col-surfa.2019.04.065>
- Yao F., Pham D.T. and Lee Y.H. (2015). Carbon-based materials for lithium-ion batteries, electrochemical capacitors, and their hybrid devices. *ChemSusChem* 8 (14), 2284–2311. <https://doi.org/10.1002/cssc.201403490>
- Yu J., Wu J., Yang Z., Cai J. and Zhang Z. (2020). A cheese-shaped bio-carbon for high performance supercapacitors prepared from *Juncus effusus*. *L. J. Energy Storage* 1 (30), 101531. <https://doi.org/10.1016/j.est.2020.101531>
- Yun C. H., Park Y. H. and Park C. R. (2001). Effects of pre-carbonization on porosity development of activated carbons from rice straw. *Carbon*. 4 (39), 559–567. [https://doi.org/10.1016/S0008-6223\(00\)00163-9](https://doi.org/10.1016/S0008-6223(00)00163-9)
- Zhang L., Zhang B., Yang Z. and Yan Y. (2014). Pyrolysis behavior of biomass with different Ca-based additives. *RSC Adv.* 4 (74), 39145–39155. <https://doi.org/10.1039/c4ra04865b>
- Zhang Y., Song X., Xu Y., Shen H., Kong X. and Xu H. (2019). Utilization of wheat bran for producing activated carbon with high specific surface area via NaOH activation using industrial furnace. *J. Cleaner Prod.* (210), 366–375. <https://doi.org/10.1016/j.jclepro.2018.11.041>