Orange Peel biowaste used as a nanoscopic hydrogen reservoir

Juliana M. Juárez, Brenda C. Ledesma, Oscar A. Anunziata, Marcos B. Gómez Costa, Andrea R. Beltramone.
Centro de Investigación en Nanociencia y Nanotecnología (NANOTEC). Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro López y Cruz Roja Argentina, 5016, Córdoba, Argentina.
jjuarez@frc.utn.edu.ar

Abstract
This work addresses the bio-waste vaporization approach for the development of a novel carbonaceous nanomaterial to be used in the adsorption of hydrogen as an alternative in the use of green hydrogen. In this research, activated carbons were synthesized from orange peel using different synthesis conditions. With the activated carbons obtained with the best structure and texture, the adsorption of hydrogen and the effects on their meso / microporosity were studied. The activation of the carbon was carried out by means of a chemical process with phosphoric acid as activating agent, varying the acid concentration, the substrate / activating agent ratio, and the contact time between them.
The best support was obtained using a carbonization time of 1 h, a carbonization temperature of 470oC, a phosphoric acid concentration of 50% by weight and a BET area of 1402 m^2 / g. Said material significantly improved H_2 storage behaviour compared to CMK-3 type nanostructured carbon (3.1% by weight at -196,15 ºC and 10 bar). The synthesized material shows promise in absorbing hydrogen by weak binding forces (physisorption).

Introduction
Economic systems are established where goods are produced, used and discarded, this is a linear economy where the flow has a clear beginning and end. A circular economy works very differently. Products and services in a circular economy are designed in a way that allows their reuse, whether in biological or technical cycles.
Orange peels are one of these valuable waste materials that are discarded from the juice industry The disposal of residual orange peel has become a major problem for many food industries. By producing activated carbons from agro-industrial waste such as orange peel (which is a renewable source), there are several advantages; It allows the elimination of polluting waste by carrying out effective management, increasing its added value, increases the possibility of obtaining activated carbon at a lower cost and reduces imports in a producing country [1]. Activated carbon can be produced by physical, chemical, physicochemical and microwave-assisted activation using biochar and biomass as the source. The objective of this research is the evaluation of the operative conditions in the preparation of activated carbon from orange peel residues, preeminent in the manufacturing process of local industrial juices. These activated carbons can be used as a reservoir for hydrogen storage. One of the main problems for the use of hydrogen as a fuel is its storage so that it can be safe and transportable with all the risks that this entails [2]. In this sense, considering the available alternatives, their advantages and disadvantages, nanomaterials and nanostructured materials have diverse physicochemical characteristics, which vary depending on their size and shape due to the physical-quantum effect and the large surface area they possess. Based on these facts, nanocomposites, or hybrid nanomaterials, can be successfully used for hydrogen storage.

Experimental
The oranges were purchased from a local fruit market, washed to remove dust and other residue, and peeled. Orange peels were cut into small pieces and dried at 100°C overnight. The dried samples were then crushed, ground and further rinsed with warm water, dried again and sieved. The obtained precursor material is hereinafter abbreviated as CN. The particle diameter fraction between 500 and 1000 µm was selected for the preparation of activated carbon. A sample of CN was mixed with a solution of H_3PO_4 with a concentration of 50 wt%, in different acid/precursor weight ratio of 3: 1 or 6: 1 and left to soak for 24 h at room temperature or it is fed directly into the next stage without dwell time. Subsequently, the impregnated sample was heated in an electric oven. The temperature was raised from room temperature to 470 °C at a heating rate of 3 °C/min and held for 1 h. The choice of temperature agrees with that used in the literature, [3-5]. The highest surface area values were found at activation temperatures around 450 ºC when H_3PO_4 was used as activating agent. After cooling to room temperature, deionized water was used to remove excess acid from the impregnated activated carbon until the pH of the filtrate became neutral. The sample was then dried in an oven to constant weight and the yield was evaluated. Developed activated carbon is hereinafter abbreviated as CA. The summary of the samples is shown in Table 1.

Table 1. Sample Description

Sample	Acid/Precursor Ratio	Rest Time (hs)
CA1	3:1	0
CA2	3:1	24
CA3	6:1	24

Results and Discussion

Table 2 shows the textural properties determined from nitrogen physisorption analysis. The surface area, mesopore volume and mean mesopore size of the samples are investigated using the BET and BJH method. The micropore volume is drawn using the t-plot.

Table 2. Textural Properties

Sample	BET Area (m^2/g)	Total Pore Volme (cm^3/g)	Mesoporous Volume (cm^3/g)	Microporous Volume (cm^3/g)	Pore Diameter (nm)
CA1	1003	0.48	0.18	0.3	4.2
CA2	1185	0.63	0.32	0.31	4
CA3	1402	1.06	0.7	0.36	5.5

Figure 1 is an example of the morphology of sample CA3, the typical morphology of an activated carbon is observed, the surface presents irregular cavities and fine open pores, which implies the success of the material synthesis method.
Figure 2 shows the hydrogen adsorption capacity of the synthesized activated carbons and the adsorption of a highly studied CMK-3 mesoporous carbon in energy storage is added as a reference. As can be seen in the graph, all activated carbons have a good hydrogen adsorption greater than a CMK-3, with CA3 being the best.

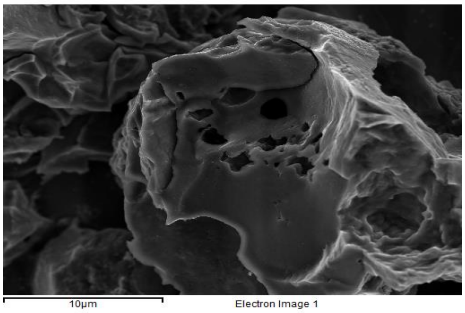

Figure 1 – SEM Image of CA3

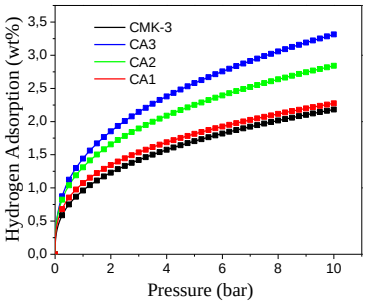

Figure 2 – Hydrogen Adsorption/Desorption Isotherms at -196,15 °C

Hydrogen penetrates through the porosity of said carbons, remaining occluded in the porous network of said carbons, probably on the surface of the porous wall, producing a kind of weak adsorption that is completely reversible as if it were a “sponge” effect when adsorb/desorb hydrogen from the carbon matrix.

Conclusion

The achievement of this research lies in the use of agro-industrial waste, which can be transformed in a very simple and economical way into a nanomaterial with a high surface area, with textural properties that make it a promising material in the adsorption of hydrogen by weak bond forces (physisorption) fully reversible. Different synthesis conditions were used, obtaining the best hydrogen adsorption using carbonization time of 1 h, carbonization temperature of 470°C, phosphoric acid concentration of 50% by weight and BET area of 1402 m^2/g. This material significantly improved the H_2 storage behaviour compared to the CMK-3 type nanostructured carbon (3.1% by weight at -196.15 °C and 10 bar).

References

[1] M. Danish and T. Ahmad, *Renewable Sustainable Energy Rev*. **87**,1-21 (2018).
[2] M. Jurczyk, A. Kumar, S. Srinivasan and E. Stefanakos, *Int. J. of Hydrogen Energy*, **32**, 1010 (2007)
[3] I.I. Misnon, N.K.M. Zain, R.A. Aziz, B. Vidyadharan and R. Jose, *Elect. Acta*. **174**, 78-86 (2015).
[4] Q. Wei, Z. Chen, Y. Cheng, X. Wanga, X. Yanga and Z. Wanga, *Colloids Surf., A*, **574**, 221–227 (2019).
[5] P. González-García; *Renewable Sustainable Energy Rev*. **82,** 1393–1414 (2018).

Aknowledgment

JMJ, BCL, OAA, MGC, ARB, CONICET researchers, UTN-FRC. Los autores agradecen a FONCyT. PICT 2017-2021 1740 y PICT 2016-1135.