CHEMICAL ENGINEERING TRANSACTIONS
VOL. 97, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-96-9; **ISSN** 2283-9216
DOI: 10.3303/CET2297031

Carbon Aerogel from Jackfruit Waste as New Material for Electrodes Capacitive Deionization

Van Cuong Tran[a,*], Nghiep Quoc Pham[b], Anh Kien Le[a], Anh Khoi Tran[c], Cong Minh Pham[a]

[a]VITTEP, 57a Truong Quoc Dung street, ward 10, Phu Nhuan district, Ho Chi Minh city Vietnam
[b]Institude for Tropicalization and Evironment, 57a Truong Quoc Dung street, ward 10, Phu Nhuan district, Ho Chi Minh city Vietnam
[c]Ho Chi Minh city University of Technology, 268 Ly Thuong Kiet street, district 10, Ho Chi Minh City, Vietnam
kh.cntn.vittep@gmail.com

In Vietnam, every year hundreds of thousands of tons of jackfruit were harvested. A large part of the jackfruit, such as pulp, peel and seeds is unused and discarded, polluting the environment. This study aims to reuse this potential biomass to produce new advanced materials-carbon aerogel. Carbon aerogel from jackfruit waste was synthesized via hydrothermal method combined with the freeze-drying technique and followed by carbonization in nitrogen. Specific surface area, pore size, thermal properties of carbon aerogel were determined by Brunauer-Emmett-Teller (BET), TGA/DSC analysis, while the functional groups and were considered by FTIR. Synthesized carbon aerogel with low density (0.035 - 0.048 g/cm^3), high porosity (95 - 98 %), specific surface area of 495.8 - 712.3 m^2.g^{-1} and pore size 2.8 - 4.2 nm was then utilized as a component to prepare CDI electrodes. The results of desalination experiment confirmed that carbon aerogel electrodes have a good NaCl-removal capacity in low initial concentration.

1. Introduction

Every year a large amount of biomass is discharged into the surrounding environment. Industrial waste and animal waste, plant waste is a problem to be solved in recent years. There are many studies to reduce the effects of various types of plant waste, mainly recycling and reuse.
Peels, pods, pulps, seeds, etc. are common biomass waste of fruit and vegetable harvesting and processing. In addition to chemical extraction and adsorption in wastewater treatment, biomass from fruit and vegetable have been used to synthesize aerogel and carbon aerogel (Do et al., 2022). These materials have excellent properties, such as low density, porous structure with high porosity, adjustable pore size and high specific surface area.
Currently, exist two main directions to synthesize biomass aerogel and carbon aerogel. The traditional method involves separation of cellulose from biomass waste, combined with synthesis cellulose aerogel and carbonization. Each sample of cellulose aerogel usually takes 1-2 weeks to fabricate and require chemicals for pre-treatment. Synthesized aerogels by this method can obtain from pineapple leaves (Do et al., 2020), coir (Kien et al., 2020), jackfruit, and sugarcane bagasse. Antony et al. (2018) successful synthesized cellulose aerogel from de-pectinated jackfruit peel using chemical process treatment. Cellulose aerogel from jackfruit has low density, pore size 0.73 nm and zeta potential value 15.7 mV.
In the second direction, biomass is directly used. Carbon aerogel is synthesized through 3 steps process, including hydrothermal treatment, freeze-drying, followed by carbonization. Li et al. (2014) prepared carbon aerogel from winter melon peels by this method, with hydrolysis temperature of 180 °C for 10 h. Sam et al. (2020) also used the same hydrothermal condition to synthesize carbon aerogel from cabbage. All fabricated carbon aerogels possessed low density (0,048 - 0.058 g/cm^3) and high adsorption capacity for organic solvents and oil (Yang et al., 2019). Lee et al. (2020) used jack fruit and durian core as input material to synthesize carbon aerogels. Jackfruit carbon aerogel (JCA) obtained lower specific surface area (511.42 m^2.g^{-1}) and total

Paper Received: 1 June 2022; Revised: 6 July 2022; Accepted: 8 July 2022
Please cite this article as: Tran V.C., Pham N.Q., Le A.K., Tran A.K., Pham C.M., 2022, Carbon Aerogel from Jackfruit Waste as New Material for Electrodes Capacitive Deionization, Chemical Engineering Transactions, 97, 181-186 DOI:10.3303/CET2297031

pore volume 0.275 cm^3. g^{-1}. Two materials show high specific capacitance, (298 F. g^{-1} and 591 F. g^{-1}). Based on this, JCA and DCA can be used to manufacture capacitors and electrodes.
In recent years, capacitance deionization (CDI) technology, with its advantages such as low-pressure operation and energy saving, is increasingly being used for water treatment (Weinstein and Dash, 2013). The electrode material is the most important part for CDI. Carbon-based materials, such as activated carbon, carbon nano tubes and carbon aerogel are widely used in CDI-electrodes fabrication (Zhao et al., 2020).
According to research, despite having suitable properties such as good hydrophobicity, high conductivity, large specific surface area and total pore volume, biomass carbon aerogels is rarely used to fabricate CDI- electrodes. It can be explained by the fact that, these materials have only recently studied. In this work, the carbon aerogels from jackfruit (JCAs) were used as component of CDI electrodes for the first time. Capacitive deionization experiments were also set up to examine NaCl-removal capacity.

2. Materials and Experiments

2.1 Materials

In present work, jackfruit biomass is collected from a fruit store in Ho Chi Minh City. All chemical reagents (ethanol, Potassium hydroxide KOH, glutamic hydroxide) were purchased from China. In all experimental solutions, distilled water was used.

2.2 Preparation of carbon aerogel from jackfruit

Firstly, the raw jackfruit coir was cut into small pieces with dimension about 3*3*2 cm^3 and washed with water several times for removal dirty particles. After that, jackfruit's pieces were placed into Teflon-lined stainless-steel autoclave, which was heated to different temperature for 1 h and held for 10 h in oven. Hydrogels were then washed with distilled water and exchanged with ethanol 96 % for 72 h, during which ethanol solution was renewed every 24 h. Afterward, the gel was frozen with nitrogen liquid and freeze-dried in TVF-50 vacuum oven (China). Prepared JAs were carbonized at high temperatures (600 - 800 °C) for 30 min in nitrogen atmosphere, flowing rate 150 mL/min and heating rate 5 °C /min.
To produce activated carbon aerogel, JCA samples were immersed into potassium hydroxide solution (KOH, 1 mol/L, rate JCAs to KOH 1:10) for 12 h, ambiently dried in oven at 105 °C to removal residual water and solvent. The JCAs were then heated in a tube furnace to 800 °C with heating rate of 5 °C /min and kept at 800 °C for 1 h under nitrogen (flow rate 0,2 L/min). Lastly, JCAs were thoroughly neutralized to pH = 7, dried in oven at 105 °C.
All using samples in this study were obtained in Table 1.

Table 1: Different synthesized samples

Symbol	Sample properties
JA-150 JA-180 JA-210	Jackfruit aerogel (JA) with different hydrothermal temperatures (150, 180 and 210 °C)
JCA-600 JCA-700 JCA-800	Jackfruit carbon aerogel (JCA) with different pyrolysis temperatures
a-JCA	Activated jackfruit carbon aerogel

2.3 Fabrication of carbon aerogel electrodes

Activated JCAs was grinded into powder and mixed with carbon black (mass ratio of CBs to JCAs was controlled 10 %w). The mixture was then stirred with 1,200 rpm at 80 ˚C for 2 h in colloidal polyvinyl alcohol solution (PVA), using glutamic hydroxide as a curing agent. The ratio of solid components to binder system was fixed 9:1. Homogenous mixture was coated on titanium-grade plates with dimension 10*10 cm^2 (collectors), followed by drying under ambient pressure at 30°C for 12 h and 80°C for 36 h. Coating area was about 90 cm^2 and thickness about 1.5 - 1.7 mm. Total JCA used for one pair electrode was fixed 4.0 g.

2.4 Characterizations

Specific surface area, pore size and total pore volume of aerogels and carbon aerogels were determined by Brunauer-Emmett-Teller (BET), Barrer-Joyner-Halenda (BJH) methods. Thermal behaviour was evaluated on TGA/DSC instrument METLER TOLEDO, and the functional groups were considered by FTIR. The density of all samples also analysed.

2.5 Capacitive deionization experiments

In this study, an experimental model like that of Le et al. (2016) was used. Water with fixed salinity was fed from storage to experiment cell, where electrodes were placed face to face and connected with DC power supply. The distance between the two electrodes was about 2 mm and the applied voltage 1.2 /0 V was used (Kang et al., 2014).

The experiments were carried out with different inlet salt concentrations in a constant flow rate (40 mL/min) and the change of the output concentration over time periods. The removal capacity was calculated as the maximum amount of adsorption divided by the total carbon weight of two electrodes.

3. Results and discussion

3.1 Thermal properties

The thermal properties of aerogels and carbon aerogels were evaluated in several conditions, using thermogravimetric analyzer TGA/DSC METLER TOLEDO in laboratory.

For three samples of aerogel JA-150, JA-180 and JA-210, there are three stages in pyrolysis process in nitrogen. It is obvious on the graph that, at range between 50 - 120°C the mass of all 3 samples has been slowly decreased, corresponding to the first stage. The weight loss in this stage can be attributed to the evaporation of water. The breakdown of hemicellulose, cellulose and lignin could explain the weight loss in the second stage of pyrolysis (Vaidya et al., 2016). As seen on the graph, about 50 - 60 % weight has been removed between the range of temperature 200 - 370 °C.

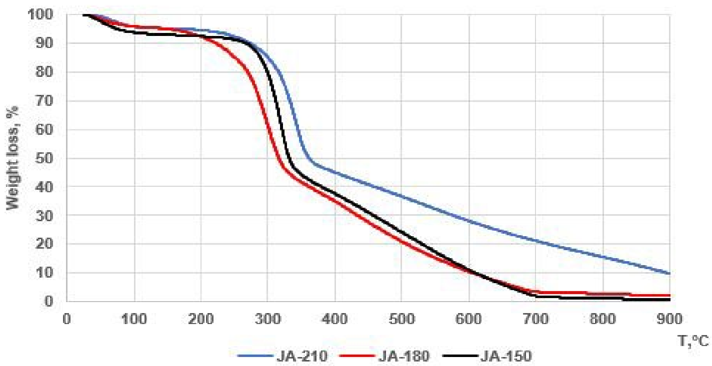

Figure 1: Thermogravimetric analysis (TGA) curves of different JA samples

In the next stage occurred lignin degradation and carbonization of aerogel between 350 - 700 °C. Similar results were reported for jackfruit cellulose (Sundarraj et al., 2018), jackfruit peels (Elisadiki et al., 2019). It could be also observed that, JA-210 shown higher thermal stability and higher residual char compared with other samples.

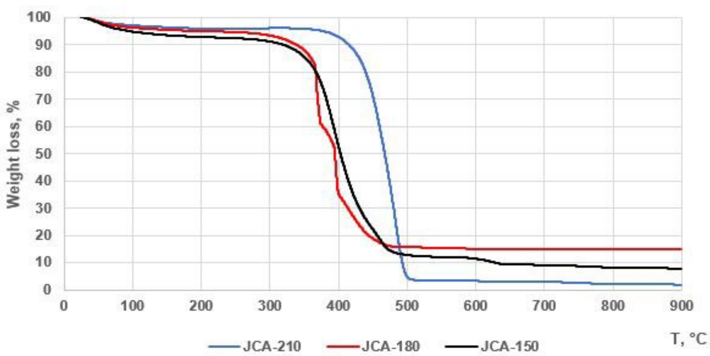

Figure 2: Thermogravimetric analysis (TGA) curves of different JCA samples

In this study, the thermal stability in air of JCAs with different hydrothermal temperature were investigated, that could be observed on the Figure 2. High decomposition temperature (400 - 500 °C) allows JCA materials to work under extreme conditions. Continuous increasing temperature facilitates reaction between oxygen and element of carbon framework, leading destruction of material structure.

From the thermal curves, the carbonization temperature of aerogel and activation temperature of carbon aerogel were also determined.

3.2 Density and porous properties of JCAs

To calculate the density of a material, cylinders or cubes with fixed dimensions were prepared. Samples were then dried at 105 °C for 6 h in oven to remove moisture. Density was determined as the weight after drying divided by the volume of the samples. Specific surface area, of aerogels and carbon aerogels was determined by Brunauer-Emmett-Teller (BET), while pore size and total pore volume were evaluated by Barrer-Joyner-Halenda (BJH) methods.

It can be obvious in Table 2 that, aerogel and carbon aerogels from jackfruit have extremely low densities (0.035 - 0.064 g/cm^3) and high porosity (95 - 98 %). During pyrolysis, some components such as cellulose, lignin and carbon framework are decomposed, creating pores, and increasing the specific surface area of the material. Specifically, surface area of aerogel is only 60.54 m^2/g, while the values of carbon aerogel samples were distributed in range of 495 to 580 m^2/g.

The difference in specific surface area, pore size of carbon aerogel samples at different pyrolysis temperatures can be explained by the decomposition of cellulose and lignin, which occurs at temperature range of 500 - 700 °C (Kien et al., 2021).

Activation with KOH at 800 °C markedly increased the specific surface area and surface activity of the material. In addition, the average pore size of a-JCA is higher than that of the un-activated material. This is possible because the second carbonization process at high temperature leads to the breaking of some bonds in the carbon framework, that can increase the size or form large pores.

Table 2: Density and porous properties of JA and JCA samples

Properties	JA-180	JCA-600	JCA-700	JCA 800	a-JCA
Density (g/cm^3)	0.064	0.048	0.039	0.037	0.035
Specific surface area (m^2/g)	60.54	495.8	525.3	580.4	712.3
Total pore volume (cm^3/g)	-	0.174	0.263	0.285	0.412
Average pore diameter (nm)	-	2.8	3.2	3.8	4.2
Porosity (%)	-	95.6	96.8	97.2	97.9

"-": No data

3.3 FTIR -spectra of aerogel and carbon aerogel

The FTIR spectra of the different aerogel samples are presented in Figure 3a. For all aerogel samples, a broad band at 3,500 - 3,000 cm^{-1} can be attributed to the OH-group stretching vibration (Ramli et al., 2014).

The displayed peak at 2,916 cm^{-1} was originated from the C-H stretching of methyl and methylene groups of cellulose compounds (Sanchez et al., 2014).

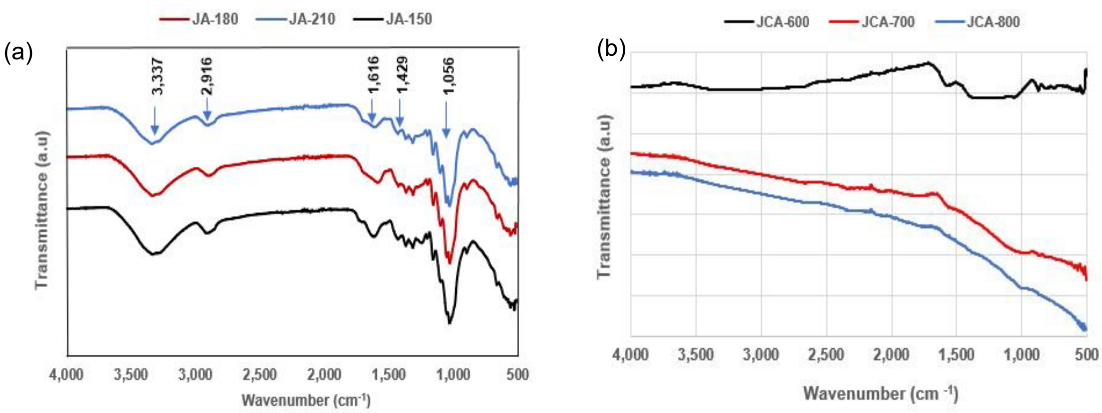

Figure 3: FTIR spectra of (a) jackfruit aerogel, and (b) jackfruit carbon aerogel samples

Two bands at 1,616 tcm^{-1} and 1,429 cm^{-1} could be corresponded the aliphatic compound deformations with reference to C-H and CH_2 or indicated the present of lignin group in materials. The peak located at 1,056 cm^{-1} confirmed the C-O-C or C-C framework vibrations (Zhu et al., 2017).
Comparing the two samples, it could be observed that increasing the hydrothermal temperature leads to a decrease in the intensity of the adsorption peaks. This confirms that some substances such as hemicellulose, lignin and cellulose were dissolved in the hydrothermal process.
The FTIR -spectra of JCAs was also studied. As seen as in Figure 3b, JCA-700 and JCA-800 show the same spectra of carbonized material, representing the absence of peaks. This is because from a temperature of 700 °C, only occurred carbonization process, as explained when considering thermogravimetric curves. It was observed that JCA-600 obtained typical peaks of cellulose and lignin fragments, causing the continuous degradation at range between 350 - 700 °C.

3.4 Removal capacity of carbon aerogel electrodes.

Figure 4 shows the schematic diagram of the laboratory-scale CDI model. Inlet water was pumped from the storage cell into the system with a controlled flow. At CDI-cell with a pair of electrodes dissolved salt was partially removed. Measure the input and output concentrations to determine the specific removal capacity of the electrodes.

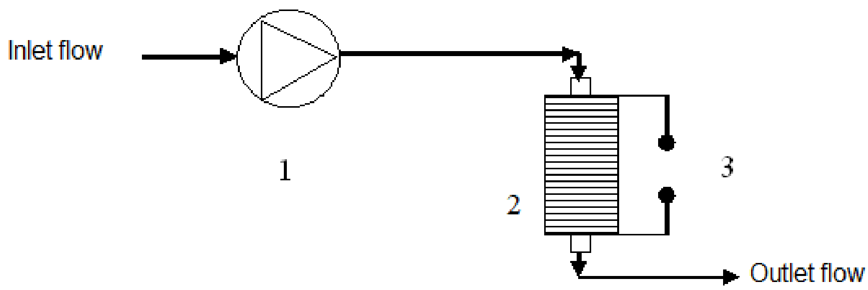

Figure 4: Schematic diagram of the laboratory CDI model

In the experiments, different input concentrations (500, 1,000, 2,000, 3,000 ppm) and carbon aerogel electrodes (JCA-800 and a-JCA) were used. The results were presented in Table 3.

Table 3: Removal capacity of carbon aerogel electrodes

Initial NaCl concentration (ppm)	Removal capacity	
	JCA-800	a-JCA
500	5.10	8.95
1,000	4.41	5.92
2,000	3.68	4.32
3,000	2.68	2.75

The maximum removal capacity of JCA-800 and activated carbon aerogel a-JCA was 5.10 mg/g and 8.95 mg/g, achieved at the lowest concentration. Activated carbon aerogel has a larger pore size and better surface activity than JCA, and the adsorption capacity at different concentrations is also higher.
In addition, a-JCA electrodes showed higher removal capacity than those reported for jackfruit peel activated carbon (Elisadiki et al., 2019), activated carbon cloth (Maddah et al., 2018). The maximum adsorption capacities were 5.74 mg/g and 1.18 mg/g for jackfruit carbon and carbon cloth electrodes, respectively. Under the same experimental conditions, the resorcinol-formaldehyde carbon aerogel electrodes gave capacity up to 21.6 mg/g, much higher than the mentioned materials (Le et al., 2016).
At high NaCl concentration, high hydrated ions Na^+ and Cl^- in the solution with radius of 0.358 and 0.333 nm, lead to the filling of pores, which have been used to adsorb ion. Removal capacity then decreased, increasing initial concentration on all two carbon aerogel electrodes.

4. Conclusions

In present work, carbon aerogel from jackfruit was synthesized, using hydrothermal treatment combined with freeze-drying and carbonization. JCAs indicated high specific surface area (495.8 to 712.3 m^2/g), low density (0,035 - 0,048 g/cm^3), high porosity (95 - 98 %) and pore size 2.8 - 4.2 nm. The specific salt adsorption capacity of the electrode at low input concentrations (500 – 1,000 ppm) ranges from 4.41 to 8.95 mg/g, which is higher compared to activated carbon electrodes. It can be concluded that carbon aerogel is a promising material in CDI application. In nearly research, the effect of experimental conditions such as inlet flow rate, weight of electrode material, distance between the two electrodes, the applied voltage on the salt removal capacity and the electrical conductivity of the carbon material should be investigated.

Acknowledgments

This research is funded by Academy of Military Science and Technology, Vietnam.

References

Do N. H. N., Nguyen P. T. T., Xue Y. G., Chong G. J., Ren O. H., Le P. K., Phan T. N., Duong H. M., 2022, Recent Progresses in Eco-Friendly Fabrication and Applications of Sustainable Aerogels from Various Waste Materials. Waste and Biomass Valorization, 13, 1825 –- 1847.

Do N. H. N., Thao P. L., Duyen K. L., Le K. P., Duong H. M., 2020, Morphology control and advanced properties of bio-aerogels from pineapple leaf waste. Chemical Engineering Transactions, 78, 433 –- 438.

Elisadiki J., Jande Y. A. C., Machunda R. L., Kibona T. E., 2019, Porous carbon derived from Artocarpus heterophyllus peels for capacitive deionization electrodes. Carbon, 147, 582 - 593.

Kang J., Kim T., Jo K., Yoon, J., 2014, Comparison of salt adsorption capacity and energy consumption between constant current and constant voltage operation in capacitive deionization. Desalination, 352, 52 –- 57.

Le, D. K., Pham N. Q., Le K. A., 2016, Capacitive deionization (CDI) for desalisation using carbon aerogel electrodes. Science and Technology Development Journal, 19(3), 155 –- 164.

Lee K., Shabnam L., Faisal S. N., Hoang V. C., 2020, Aerogel from fruit biowaste produces ultracapacitors with high energy density and stability. Journal of Energy Storage, 27,101152.

Li Y. Q., Samad Y. A., Polychronopoulou K., Alhassan S. M., 2014, Carbon aerogel from winter melon for highly efficient and recyclable oils and organic solvents absorption. ACS Sustain Chem. Eng., 2, 1492 –- 1497.

Maddah H. A., Shihon, M. A., 2018, Activated Carbon Cloth for Desalination of Brackish Water Using Capacitive Deionization. Desalination and Water Treatment.

Ramli R., Khan M. M. R., Yunus R. M., Ong H. R., Halim R. H., Aziz A. A., Ibrahim Z., Zainul N. H., 2014, In-situ impregnation of copper nanoparticles on palm empty fruit bunch powder. Advances in Nanoparticles, 3, 65 - 71.

Sam D. K., Sam E. K., Durairaj A., Lee X., 2020, Synthesis of biomass-based carbon aerogels in energy and sustainability. Carbohydrate Research, 491, 107986.

Sanchez O. R., Hernandez P. B., Morales G. R., Nunez F. U., Villafuerte J. O., Lugo V. L., Ramirez N. F., Diaz Vazquez P. C., 2014, Characterization of Lignocellulosic Fruit Waste as an Alternative Feedstock for Bioethanol Production. Bio Resources, 9, 1873 - 1885.

Sundarraj A. A., Ranganathan T. V., 2018, Extraction and Characterization of Cellulose from Jackfruit (*Artocarpus Integer*) Peel. Journal of Experimental Biology and Agricultural Sciences, 6(2320), 414 –- 424.

Vaidya A. A, Gaugler M., Smith D. A., 2016, The Green route to modification of wood waste, cellulose and hemicellulose using reactive extrusion. Carbohydrate Polymers, 136, 1238 - 1250.

Weinstein L., Dash R., 2013, Capacitive Deionization: Challenges and Opportunities. Desalination & Water Reuse, December, 34–37.

Yang W. J., Yuen A. C. Y., Li A., 2019, Recent progress in bio-based aerogel absorbents for oil/water separation. Cellulose, 26(11), 6449 –- 6476.

Zhao X., Wei H., Zhao H., Wang Y., Tang N., 2020, Electrode materials for capacitive deionization: A review. Journal of Electroanalytical Chemistry, 873, 114416.

Zhu L., Wang Y., Wang Y., You L., Shen X., Li S., 2017, An environmentally friendly carbon aerogels derived from waste pomelo peels for the removal of organic pollutants/oils. Microporous and Mesoporous Materials, 241, 285–292.