Preparation of N-Functionalized Graphitic Carbon by Catalyst-Free Pyrolysis of the Biomass Wastes Chitosan and Chitin

Author: Thatiana Crispim da Silva[1], José Carlos Netto-Ferreira[2], Eric Cardona Romani[3], Suzana Bottega Peripolli [4], Rachel Novaes Gomes[5,6], Paula Dias Barboza[5,6], Sergio Noboru Kuriyama[5,6], Cecília Vilani[7], Juan Lucas Naches[8], José Brant de Campos[1], Antonio Augusto Fidalgo Neto[5,6#]

[1] Programa de Pós-Graduação em Engenharia Mecânica – PPG-EM, Universidade do Estado do Rio de Janeiro, Brazil; [2]Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Brazil; [3] Instituto SENAI de Inovação em Sistemas Virtuais de Produção, Sistema Firjan, RJ, Brazil ; [4] Instituto SENAI de Tecnologia Solda, Sistema Firjan, RJ, Brazil; [5] **Centro de Inovação SESI em Higiene Ocupacional, Sistema Firjan, RJ, Brazil**; [6] Instituto SENAI de Inovação Química Verde, Sistema Firjan, RJ, Brazil. ; [7]Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro, RJ, Brazil; [8] Centro de Pesquisas Gerais, Universidade Federal Fluminense, Brazil.

PPG-EM Seminars: season **2017**
www.ppg-em.uerj.br

July 18, 2016

Keywords: Chitin, Chitosan, Adsorption, Formaldehyde.

1 Introduction

Formaldehyde (FA) is a volatile organic compound considered one of the largest pollutants in indoor environment. Of predominant anthropogenic origin, it is a major irritant to the eyes and pharynx. However, the major concern of FA exposure is related to IARC classification on group 1 – carcinogenic to humans - which raised great public awareness. In this context, developing a new material for FA adsorption has a global interest due to the large industrial use in several segments. Therefore, here we propose the use of a new carbonaceous material containing Nitrogen derived from the biomass wastes Chitosan and Chitin for the detection and adsorption of formaldehyde. Favorable carbonyl–adsorbent interaction in the case of formaldehyde can be expected due to the presence of the N-functionalized graphitic carbon. Following green chemistry principles, avoiding any unfriendly metal catalyst and using a single carbon and nitrogen source from inexpensive biomass wastes, graphitic carbons were produced upon pyrolysis of chitosan and chitin at 700 °C.

2 Methodology

The synthesis of the graphitic carbons was carried out at 700 ºC using either chitosan or chitin as a carbon source. In a typical synthesis, 1.00 g of chitosan or chitin was heat-treated in a furnace, under air, at 700 ºC with a ramp time of 5 ºC / min. Microelemental analysis was performed with a Vario Micro cube elemental analyzer. Raman spectroscopy was performed with WITec and using a 532 nm laser excitation source. X-Ray Diffraction was performed with a PANalytical X'Pert diffractometer using a angular detector.

Formaldehyde was detected and quantified as described by the NIOSH FORMALDEHYDE: METHOD 2016, Issue 2, 2003.

3 Results

Elemental analysis (tab. 1) shows that with the pyrolyzed material there is an increase in the amount of nitrogen present. Raman spectroscopy results with peaks at 1400 and 1600 show that the material is carbonaceous (Fig. 1). Finally, the results of X-ray diffraction reveal the phase change that occurs after pyrolysis. Chitosan that had an amorphous and nanocrystalline phases, after pyrolysis has amorphous, crystalline phases. However, the chitin that before the pyrolysis had basically crystalline phases, after the pyrolysis process shows amorphous, nanocrystalline and crystalline phases (fig.2).

Sample	Weight (mg)	N [%]	C [%]	H [%]	O [%]
Chitosan	1.937	7.67	40.92	7.44	43.96
Chitosan T700	2.059	11.22	76.03	3.04	9.71
Chitin	1.896	7.21	42.73	7.66	57.60
Chitin T700	2.028	10.49	76.11	2.97	10.42

Table 1 – Elemental analysis: Chitosan, chitin and pyrolyzed samples at 700 ° C.

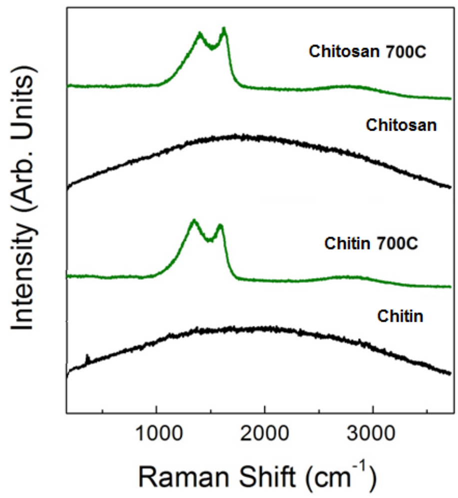

Fig.1 – Raman spectra of commercial chitin and chitosan and pyrolysed at 700°C. Spectra were obtained using a Raman spectrometer with a 532 nm laser excitation source.

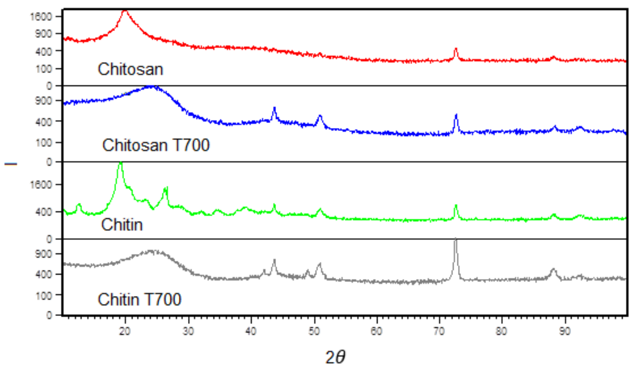

Fig. 2 – X-ray diffraction results of commercial chitin and chitosan and pyrolyzed at 700°C.

For the adsorption test, a formaldehyde concentration of 25ppm was generated in the adsorption system (chamber of 5,35 L). Forty milligram of pyrolyzed (700°C) chitosan or chitin were submitted to a flow of 500 cc/min during 1h (fig.3). After that, the remaining gaseous FA was evaluated and expressed as % of FA removed (tab. 2).

Sample	Amount of adsorbed formaldehyde (%)
Chitin T700	28,8
Chitosan T700	41,6

Table 2 – Adsorption data for formaldehyde

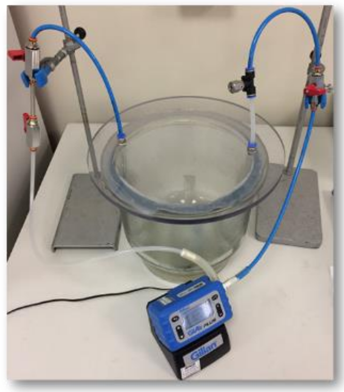

Fig. 3 – Adsorption test system

4 Conclusions

In conclusion, pyrolysis of the biomass wastes chitin and chitosan at 700 °C led to the formation of carbon materials which were characterized by Elemental Analysis, FTIR and Raman Spectroscopy and X-ray diffraction. From the later, the carbon material structures clearly show crystalline, nanocrystalline and amorphous phases. The preliminary results of the adsorption experiments confirm that formaldehyde can be efficiently adsorbed on these materials and could be used as a possible alternative for adsorption of formaldehyde in the occupational environment.

References

[1] Primo, A., Forneli, A., Corma, A., Garcia, H. ChemSusChem, 2012, 5, 2207.

[2] Primo, A., Atienzar, P., Sanchez, E., Delgado, J. M., Garcia, H. Chem. Comm., 2012, 48, 9254.

[3] Olejniczak, A., Lezanska, M., Wloch, J., Kucinska, J., Lukaszewicz, P., J. Mater. Chem. A, 2013, 1, 8961.

[4] Lezánskaa, M., Olejniczaka, A. Pacułac, A., Szymánskia, G., Włoch, J., Cat. Today 2014, 227, 223.

[5]Xia, Y., Yang, Z., Mokaya, R., Nanoscale, 2010, 2, 639.