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

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.

aaneto@firjan.com.br

Summary

1- Abstract

2- Precursor substance

3- Elemental analysis

4- Scanning Electron Microscopy

5- Fourier Transform Infrared Spectroscopy

6- Espectroscopia Raman

7- X-ray diffraction

8- Adsorption Test system

9- Conclusion

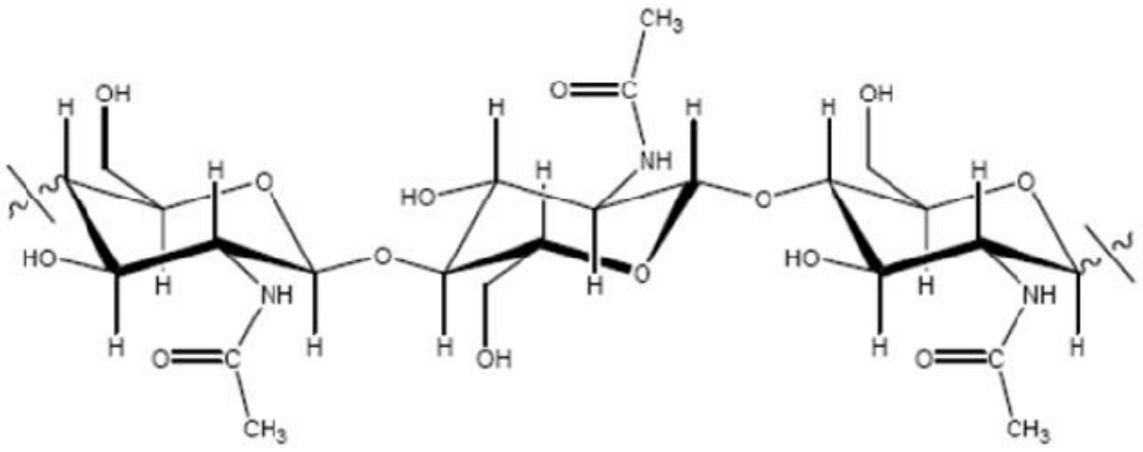
10 – References

11 - Acknowledgments

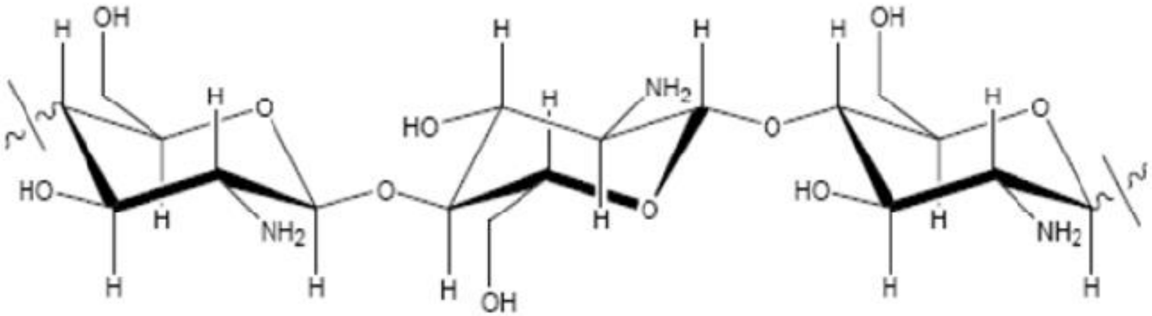
Abstract

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 International Agency for Research on Cancer - 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.

Precursor substance



Chitin

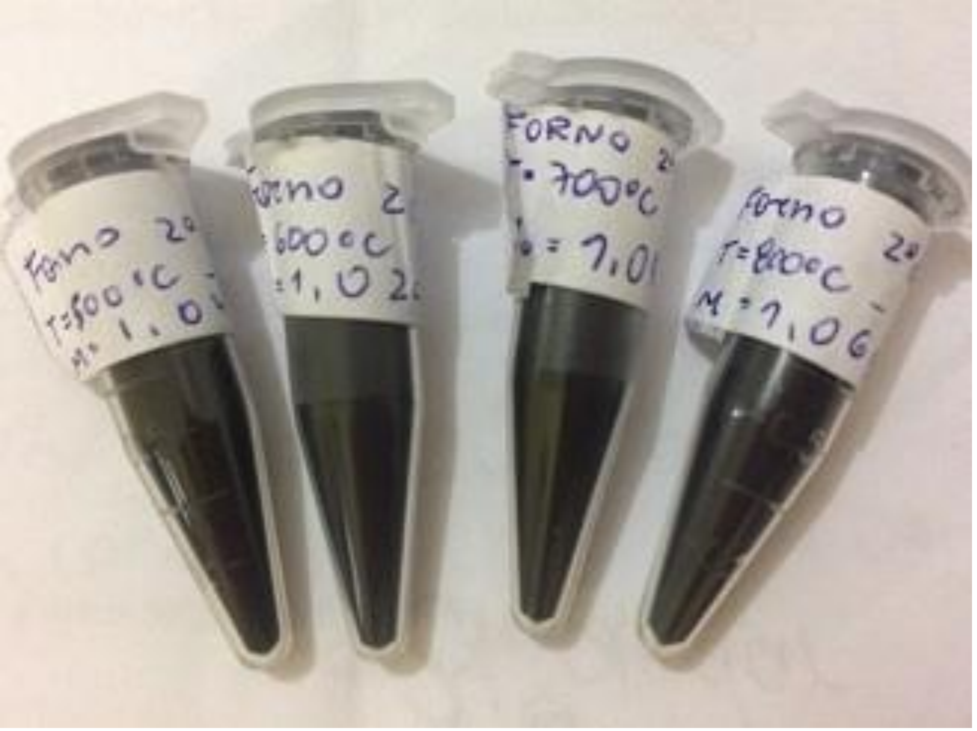


Chitosan

Chemical structure of chitin and chitosan

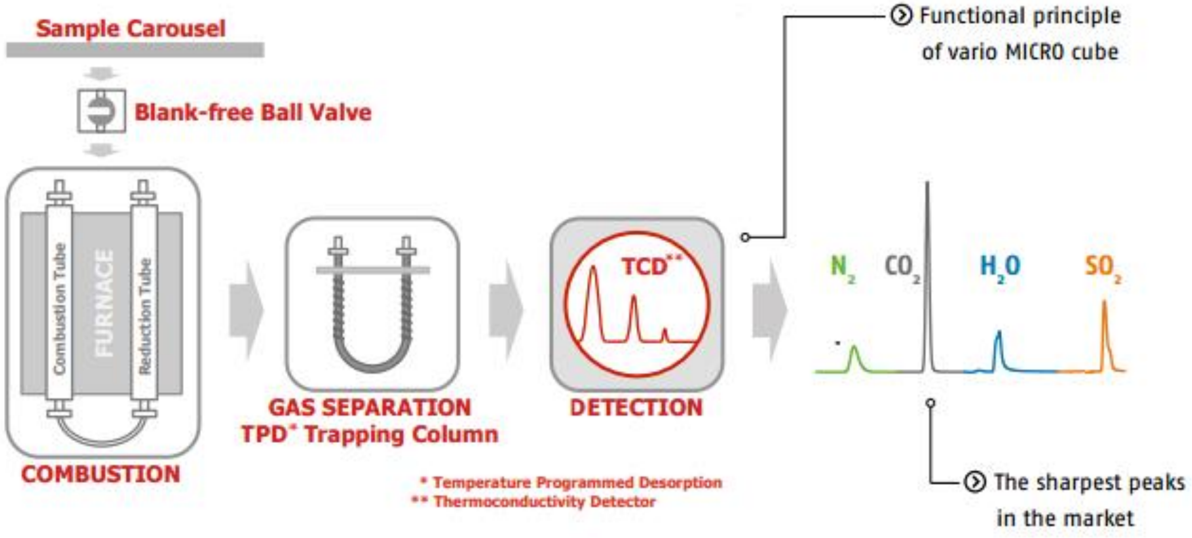
Chitin and chitosan pyrolyzed

Chitin



Chitosan

Elemental analysis: N,C,H.



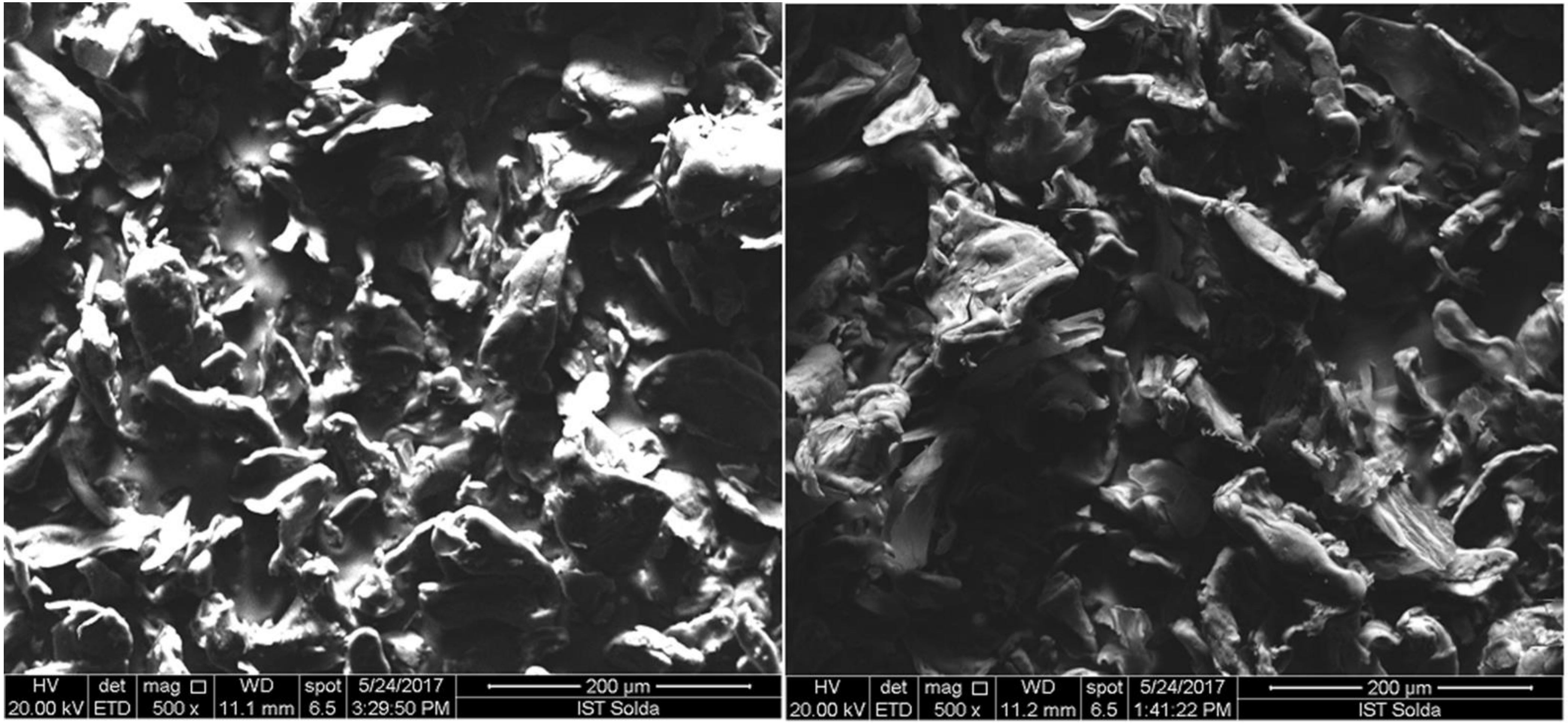
Substance	Weight (mg)	N [%]	C [%]	H [%]	O [%]
Chitin	1.8960	7.21	42.73	7.66	42.4
Chitin500	2.0870	10.31	68.43	3.22	18.04
Chitin600	1.9800	10.02	70.08	3.87	16.03
Chitin700	**2.0280**	**10.49**	**76.11**	**2.97**	**10.43**
Chitin800	1.9480	7.48	78.89	2.64	10.99

Results of the chitin elemental analysis

Substance	Weight (mg)	N [%]	C [%]	H [%]	O [%]
Chitosan	1,937	7.67	40.92	7.44	43.97
Chitosan 500	1,959	13.13	72.76	4.12	9.99
Chitosan 600	1,988	12.03	72.86	3.28	11.83
Chitosan 700	**2,059**	**11.22**	**76.03**	**3.04**	**9.71**
Chitosan 800	1,953	9.48	76.64	2.62	11.26

Results of the chitosan elemental analysis

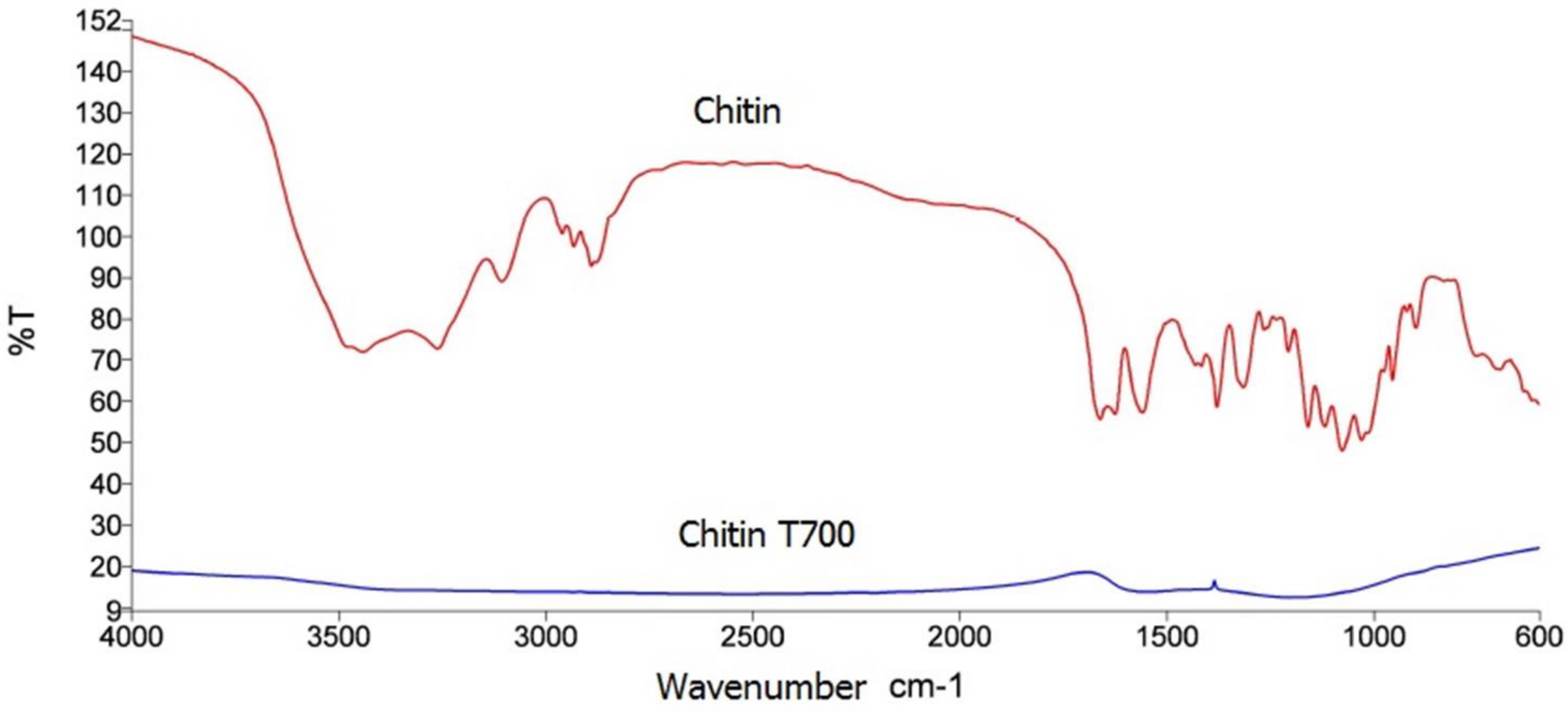
Scanning Electron Microscopy - SEM



a) b)

SEM image (a) chitosan, b) Chitin pyrolyzed ate 700° C

Fourier Transform Infrared Spectroscopy - FTiR

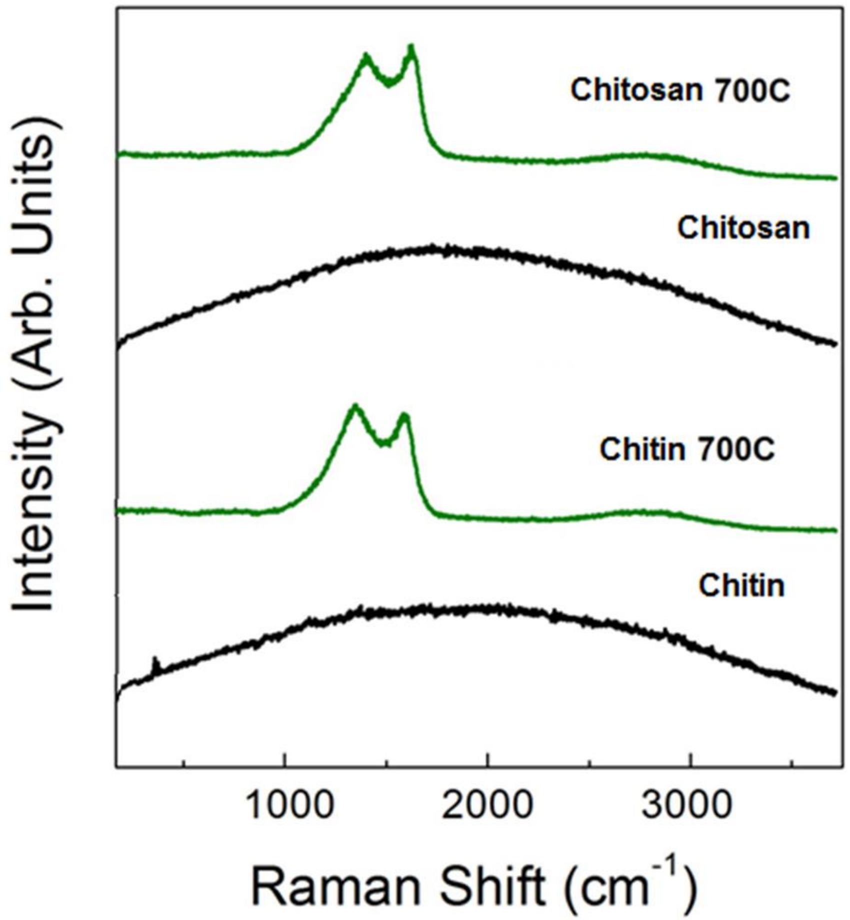


FTIR spectra of commercial chitin and pyrolysed at 700°C.

Fourier Transform Infrared Spectroscopy - FTiR

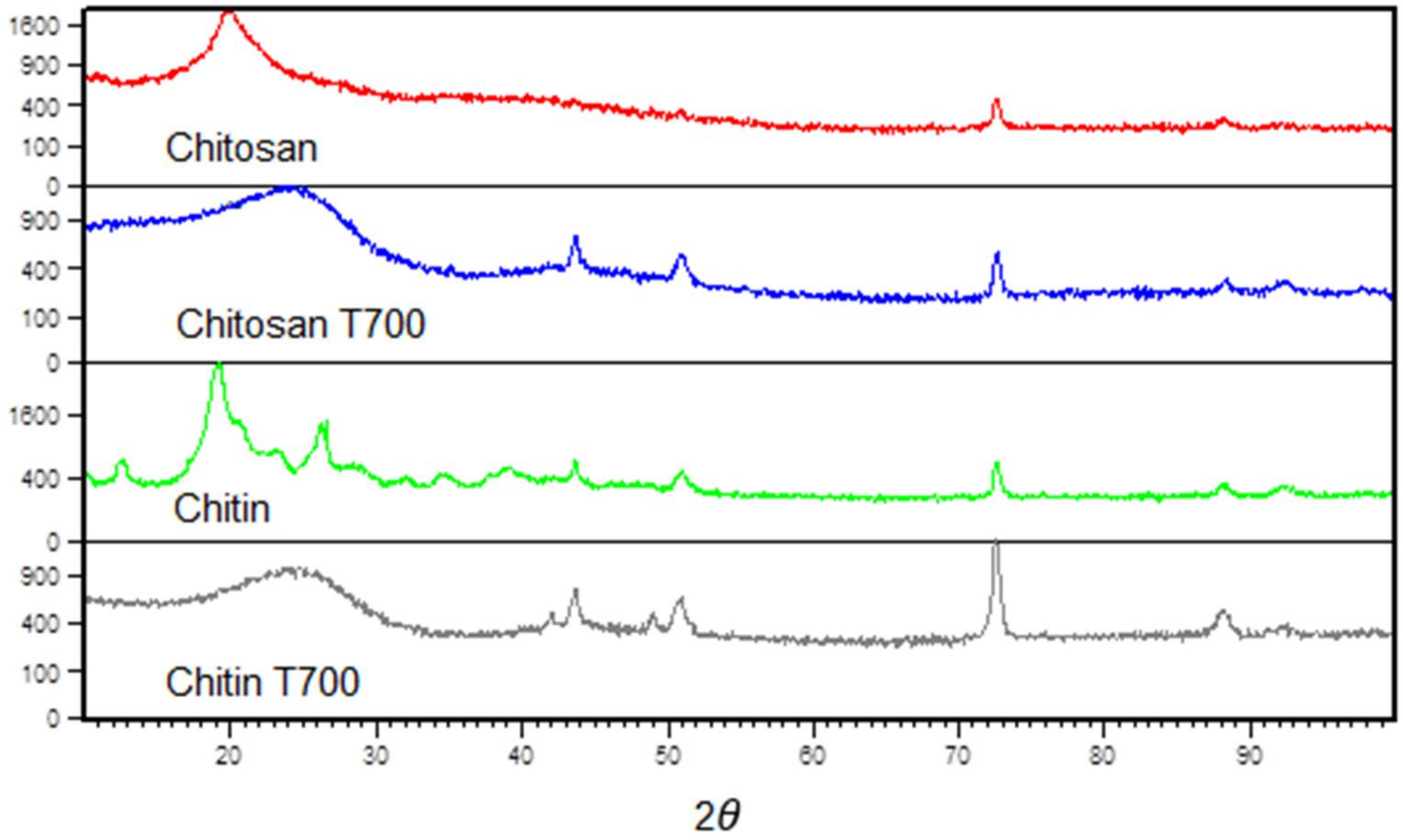
FTIR spectra of commercial chitosan and pyrolyzed at 700°C

Espectroscopia Raman



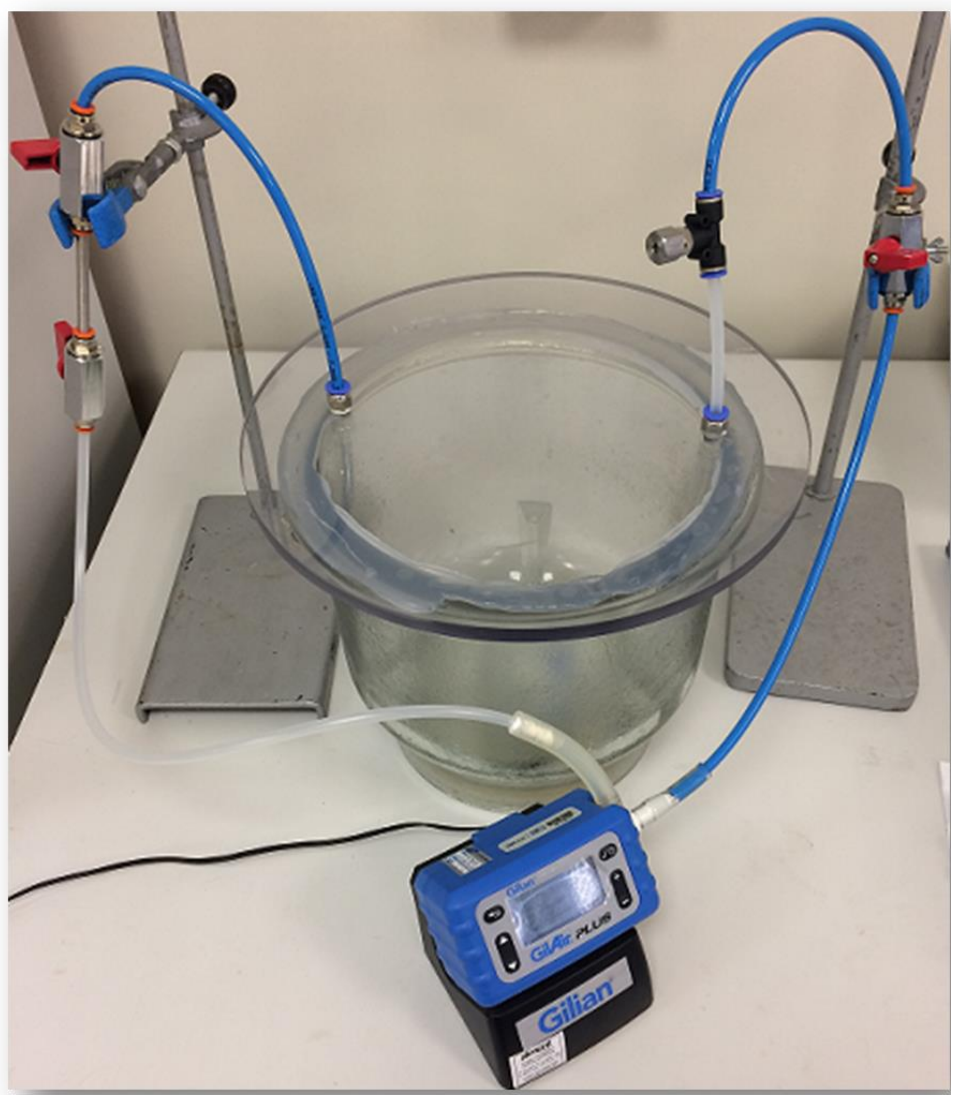
Raman spectra of commercial chitin and chitosan and pyrolysed chitin and chitosan at 700°C. Spectra were obtained using a Raman microscope with a 532 nm laser excitation source

X-ray diffraction



X – ray diffraction of commercial chitin and chitosan and pyrolysed chitin and chitosan at 700°C.

Adsorption Test system

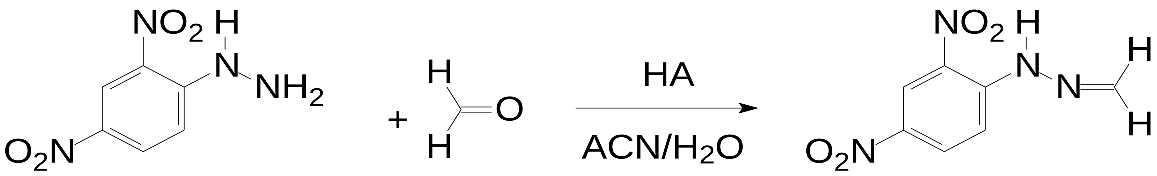


A formaldehyde concentration of 25ppm was generated in the adsorption system (chamber of 5,35 L). Forty milligram of pyrolyzed (700°C) chitosan or chitin were submitted to a flow of 500 cc/min during 1h. After that, the remaining gaseous FA was evaluated and expressed as % of FA removed.

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

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

Adsorption data for formaldehyde



Conclusion

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

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

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

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

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

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

Acknowledgments

INSTITUTO SENAI DE TECNOLOGIA SOLDA

INSTITUTO SENAI DE INOVAÇÃO SISTEMAS VIRTUAIS DE PRODUÇÃO

UERJ UNIVERSIDADE DO ESTADO DO RIO DE JANEIRO

PPG-EM PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA MECÂNICA

PUC RIO

uff 1960 DISCERE DOCERE SEMINARE

UNIVERSIDADE FEDERAL RURAL DO RIO DE JANEIRO UFRRJ

CBPF Centro Brasileiro de Pesquisas Físicas