Microwave-assisted activated carbon as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents

Liziê D. T. Prola[1] (PG), Éder C. Lima[1] (PQ)*, Caroline Saucier[1] (PG), Pascal S. Thue[1] (PG), Mayerly J. P. Rosero[1] (PG), Cibele S. Umpierres[1] (IC).

[1]-Institute of Chemistry, Federal University of Rio Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, P.O. Box 15003, 91501-970, Porto Alegre, RS, Brazil, eder.lima@ufrgs.br.

Keywords*: activated carbon, anti-inflammatory, microwave assisted activation*

Introduction

Pharmaceuticals compounds are polar substances with high solubility in water[1] that could not completely removed by conventional wastewater treatment plants.[2] Adsorption is the simpler and efficient process used for the removal these organic compounds from wastewater.[3] In this sense, activated carbon is one of the most employed adsorbents owing its excellent adsorption properties.[4] However, the extensive use of activated carbon is expensive due to its high initial and regeneration costs.[4] Therefore there is a growing interest in finding alternative low cost adsorbents for this compounds from aqueous solution. Some chemical modifications and inorganic activating agent(s) on the biomass have been proposed to improve the maximum sorption capacity of the biosorbent.[5] A way for chemical modifications in activated carbons is microwave irradiation, that also offers some advantages than over conventional heating methods, such as rapid temperature rise that leads to shorter pyrolysis time[6] and a remarkable decrease of energy consumption.[7] In this work the microwave-induced chemically activation process was used to prepare an activated carbon from cocoa shell with inorganic components for efficient removal of two anti-inflammatories, sodium diclofenac (DFC) and nimesulide (NM), from aqueous solutions.

Results and Discussions

The activated carbon adsorbent was prepared using 100.0 g of inorganic components (20% lime + 40% $ZnCl_2$ + 40% $FeCl_3$), with inorganic:organic ratio of 0:1, 1:1, 1:1.5, 1:2 and 40.0 mL of water. To the microwave-induced pyrolysis, the heating programs were: 360 W (80 s); 480 W (80 s); 600 W (80 s); 960 W (160 s); and 1200 w (160 s). The inorganic compounds were leached from the carbonized adsorbents using a 6 mol L^{-1} HCl. From preliminary experiments, the carbon cocoa-shell induced by microwave acidified (MWCS-1.0) was the best adsorbent, and was used for all next experiments. The table 1 shows the characterization of MWCS-1.0 (acidified) and its precursor CSC-1.0 (non-acidified) of the effects of chemical activation on the cocoa shell activated carbon. Evaluation the solid-liquid system is usually based on two types of research: study kinetics and equilibrium.

Table 1. Comparison the textural properties of the adsorbents.

Textural Properties	CSC-1.0	MWCS-1.0
S_{BET} (m^2 g^{-1})	66.5	618.5
BJH (nm)	7.6	4.8
Total pore volume (cm^3 g^{-1})	0.030	0.315
Pores diameter (nm)	3.41	3.31

The optimum pH for adsorption of DCF and NM onto MWCS-1.0 was pH 7 and 8, respectively. The minimum contact time pharmaceuticals to achieve balance was approximately 6 hours for DFC and 1 hour for NM. The Liu isotherm was the best fit to the experimental data. The general order kinetic model showed that the order of adsorption process is similar to a chemical reaction. $Q_{máx}$ is the maximum adsorption capacity of the material. The better conditions and the parameters of DCF and NM pharmaceuticals adsorption onto MWCS-1.0 are in the table 2.

Table 2. Conditions: 25°C; 150.0 mg L^{-1} of pharmaceutical, mass of adsorbent 50.0 mg.

	DFC	NM
pH	7	8
Equilibrium time (h)	6	1
% Removal	89	95
Kinetic model	General order	General order
Isotherm model	Liu	Liu
$Q_{máx}$ (mg g^{-1})	63.47	74.81

Conclusion

MWCS-1.0 showed highest adsorption capacity for the removal of DCF and NM pharmaceuticals from aqueous solutions, at optimum pH 7.0 (DCF) and 8.0 (NM). The general order kinetic model best described the adsorption process and isothermal data were best described by Liu isotherm model.

Acknowledgment

CNPq, CAPES, TWAS, UFRGS

[1]Dutta K.; Lee, M.Y.; Lai, W.W.P.; Lee, C.H.; Lin, A.Y.C.; Lin ,C.F.; Lin, J.G. *Bioresou. Technol.* **2014**, *165,* 42.
[2]Alidina, M.; Li, D.; Ouf, M.; Drewes, J.E. *J. Environ. Manage* **2014**, *144*, 58.
[3]Dotto, G.L.; Lima, E.C.; Pinto, L.A.A. *Bioresour. Technol.* **2012**, *103*, 123.
[4]Cardoso, F.; Lima, E.C.; Royer, B.; Bach, M.V.; Dotto, G.L.; Pinto, L.A.A.; Calvete, T. , *J. Hazard. Mater.*, 2012, *241-242*, 146.
[5]Marsh, H.; Reinoso, F.R. Activated Carbon, *Amsterdam: Elsevier*, **2006**.
[6]Alencar, W.S.; Lima, E.C.; Royer, B.; dos Santos, B.D.; Calvete, T.; da Silva, E.A.; Alves, C.N. *Sep. Sci. Technol.* **2012**, *47,* 513.
[7]Hesas, R.H.; Daud, W.M.A.W.; Sahu, J.N.; Niya, A.A. J. *Anal. Appl. Pyrol*. **2013**, *100*, 1.