CARBON 2019
LEXINGTON, KY

CAFFEINE AND DICLOFENAC ADSORPTION ON FIQUE BAGASSE BIOCHAR

Yaned Milena Correa-Navarro[1,2]*, Juan Carlos Moreno-Piraján[2], Liliana Giraldo[3]
[1] *Departamento de Química, Universidad de Caldas, Manizales, Colombia*
[2] *Departamento de Química, Universidad de los Andes, Bogotá, Colombia*
[3] *Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia*
* Presenting author's e-mail: ym.correa@uniandes.edu.co

Introduction

In recent decades a group of compounds called emerging contaminants (EC) have been detected in different aquatic environments. Caffeine (CFN) and diclofenac (DCF) are considered as EC, and have been found in various studies on surface water and wastewater around the word[1]. For environmental decontamination biochar is a carbonous solids with potential use in the remotion of pollutants[2]. Fique bagasse is a waste of process of fique fiber (*Furcraea* spp.)[3]. This material has few use. However, their physicochemical composition, indicates that bagasse is a prospective substrate for biochar production. This study evaluated the potential of fique bagasse biochar for the removal of CFN and DCF in aqueous solutions.

Materials and Methods

The fique bagassse (FB) was dried at 100 °C for 48 h in a furnace oven. After that six types of biochars were produced by combining three temperature: 650, 750, 850 °C, and two residence time: 120 and 180 min; in the presence of nitrogen (to generate an oxygen free atmosphere)[4]. For each run, heating rate was fixed at 1 °C min^{-1}. These samples were coded as FB650-2, FB750-2, FB850-2, FB650-3, FB750-3 and FB850-3.

Surface area was obtained by N_2 adsorption at -77 K[4]. Thermogravimetric analyses (TGA) were conducted between 25-900 °C with nitrogen as inert purge gas[5]. The surface functional groups were determined by Fourier transform infrared spectroscopy[4]. Surface morphology was obtained by SEM[5]. The point of zero charge (PZC) were determined by reverse mass titration[6]. Surface acidity and basicity were determined by Boehm's titration method[7].

For all experiments 50 mg of biochars were placed in a flask containing 5 mL solution of known CFN or DCF concentration and shaken at 200 rpm at room temperature. After that, concentration of CFN or DCF were obtained carefully by a calibration curve, using UV-Vis spectrometry. The effect of different variables, including pH (2−10), contact time (0–48h), initial concentration CFN (25–200 mg L^{-1}) or DCF (12,5–100 mg L^{-1}) were evaluated. The adsorption capacity of the adsorbent at any time (Qt, mg g^{-1}) and at equilibrium (Qe, mg g^{-1}), were obtained from the Eq. (1). All studies were carried out in triplicate.

$$Q_e = \frac{V(Co - Ce)}{W} \quad (1)$$

Where Co is the initial concentration of CFN or DCF (mg L^{-1}), Ce is the concentration of CFN or DCF at equilibrium, V (L) is the volume of CFN or DCF solution and W (g) is the dry mass of Bchs used[8].

Results and Discussion

Fique bagasse biochars (FBB) studied in this work have an alkaline character, whose value increases when the temperature raise. Furthermore, Calcium was detected as the most abundant chemical element in this materials by using SEM-EDS technique, which correlate also well with the basic character found in the biochars evaluated. On the other hand, FT-IR spectra of FBB studied have the typical bands at 3600, 2900 and 1600 cm^{-1}, characteristic of the O-H, C-H and C=O groups. Besides, the Brunauer Emmett Teller (BET) specific surface area increases with raise of pyrolysis temperature, being FB850-3 the one of greater specific surface area (211,788 m^2 g^{-1}).

Fique bagasse biochar pH effects were minimal, but time and initial adsorbate concentration was an influential parameter in adsorption capacity. Besides, of all adsorbents evaluated, the one with the highest removal of CFN and DCF was FB850-3. In addition, in relation to kinetic models used, pseudo-second order was the one that best fitted model for DCF and CFN adsorption on FB850-3 (Fig. 1). Furthermore, while sorption data were evaluated employing three isotherm models as shown in Fig. 1. Of the isotherm models assessed, the adsorption of CFN and DCF onto fique bagasse biochars the Redlich-Peterson isotherm was the one that best fitted with the experimental data. Redlich-Peterson isotherm takes into consideration both the Langmuir and Freundlich isotherm in one model. This suggest that the heterogeneity of the surface of the evaluated FBB plays an important role on the remotion of CFN and DCF.

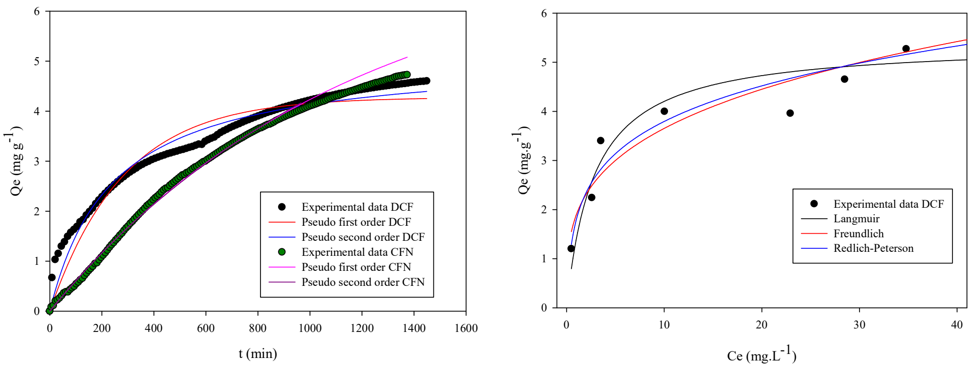

Figure 1. Kinetic data and isotherms of diclofenac (DCF) and caffeine (CFN) adsorption on FB850-3

Maximum adsorption capacity (*Qe*) of CFN onto fique bagasse biochars evaluated was 19.55 mg g^{-1}, this value was higher than the result found for normal and modified grape stem, and was similar to remotion capacity with activated carbon from grape stem[9]. However, the *Qe* of FB850-3 was lower than others carbonous materials[10,11,12,13,14]. On the other hand, maximum adsorption capacity (*Qe*) of DCF onto fique bagasse biochars was 5.4023 mg g^{-1}, this value was superior than obtained with biochar from pinewood but was inferior than remotion capacity determined with biochar from pig manure[15], commercial activated carbon[13,14], activated carbon derived from pine tree[16] and carbon xerogel[17].

It is expected that chemical or physical treatments onto carbonous materials improve different characteristics on the adsorbent used, which increase remotion of molecules evaluated. Furthermore, commercial activated carbons have better adsorption capacities than alternative adsorbents[11]. But, it is important to search other biomass to obtain carbonous materials and evaluated properties of these adsorbents.

Conclusions

The surface properties and porous structure of fique bagasse biochar influence the capacity adsorption of CFN and DCF. The results indicate that π– π interactions were the predominant mechanism for remotion of this pollutants onto biochars. In addition, pore diffusion promotes remotion of CFN and DCF. The results showed the potential of fique bagasse biochar to be employed for environmental remediation and for other pollutants from aqueous environments.

Acknowledgments

Authors thank the Faculty of Ciencias of Universidad de los Andes for the partial funding through the project INV-2018-33-1283 and Universidad de Caldas for the support to doctoral studies.

References

1. Yang, Y., Ok, Y. S., Kim, K.-H., Kwon, E. E. & Tsang, Y. F. Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. *Sci. Total Environ.* **596–597**, 303–320 (2017).
2. Mohan, D., Sarswat, A., Ok, Y. S. & Pittman, C. U. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - A critical review. *Bioresour. Technol.* (2014). doi:10.1016/j.biortech.2014.01.120
3. Escalante, H., Guzmán, C. & Castro, L. Anaerobic digestion of fique bagasse: An energy alternative. *Dyna* **81**, 74–85 (2014).
4. Creamer, A. E., Gao, B. & Zhang, M. Carbon dioxide capture using biochar produced from sugarcane bagasse and hickory wood. *Chem. Eng. J.* **249**, 174–179 (2014).
5. Suliman, W. *et al.* Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. *Biomass and Bioenergy* **84**, 37–48 (2016).
6. Kodama, S. & Sekiguchi, H. Estimation of point of zero charge for activated carbon treated with atmospheric pressure non-thermal oxygen plasmas. *Thin Solid Films* **506–507**, 327–330 (2006).
7. Boehm, H. P. Surface oxides on carbon and their analysis: a critical assessment. *Univ. Munchen* **40**, 145–149 (2001).
8. Awad, Y. M. *et al.* Biochar, a potential hydroponic growth substrate, enhances the nutritional status and growth of leafy vegetables. *J. Clean. Prod.* **156**, 581–588 (2017).
9. Portinho, R., Zanella, O. & Féris, L. A. Grape stalk application for caffeine removal through adsorption. *J. Environ. Manage.* **202**, 178–187 (2017).
10. Beltrame, K. K. *et al.* Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves. *Ecotoxicol. Environ. Saf.* **147**, 64–71 (2018).
11. Couto, O. M. *et al.* Effect of solution pH and influence of water hardness on caffeine adsorption onto activated carbons. *Can. J. Chem. Eng.* **93**, 68–77 (2015).
12. Álvarez-Torrellas, S., Rodríguez, A., Ovejero, G., Gómez, J. M. & García, J. Removal of caffeine from pharmaceutical wastewater by adsorption: Influence of NOM, textural and chemical properties of the adsorbent. *Environ. Technol. (United Kingdom)* **37**, 1618–1630 (2016).
13. Sotelo, J. L. *et al.* Competitive adsorption studies of caffeine and diclofenac aqueous solutions by activated carbon. *Chem. Eng. J.* **240**, 443–453 (2014).
14. Sotelo, J. L., Rodríguez, A., Álvarez, S. & García, J. Removal of caffeine and diclofenac on activated carbon in fixed bed column. *Chem. Eng. Res. Des.* **90**, 967–974 (2012).
15. Lonappan, L., Rouissi, T., Kaur Brar, S., Verma, M. & Surampalli, R. Y. An insight into the adsorption of diclofenac on different biochars: Mechanisms, surface chemistry, and thermodynamics. *Bioresour. Technol.* **249**, 386–394 (2018).
16. Singh, R. *et al.* Multifaceted application of crop residue biochar as a tool for sustainable agriculture: An ecological perspective. *Ecol. Eng.* **77**, 324–347 (2015).
17. Álvarez, S., Ribeiro, R. S., Gomes, H. T., Sotelo, J. L. & García, J. Chemical Engineering Research and Design Synthesis of carbon xerogels and their application in adsorption studies of caffeine and diclofenac as emerging contaminants. **5**, 229–238 (2014).