CARBON 2019
LEXINGTON, KY

CALORIMETRIC STUDY OF ADSORBATE-ADSORBENT INTERACTIONS IN THE METHYLPARABEN ADSORPTION PROCESS ON ACTIVATED CARBONS

Astrid R. Moreno-Marenco[1*], Liliana Giraldo[1], Juan C. Moreno-Piraján[2]

[1]*Department of Chemistry. Universidad Nacional de Colombia, Bogotá, Colombia*
[2]*Department of Chemistry. Universidad de los Andes, Bogotá, Colombia*

*Presenting author's e-mail: armorenom@unal.edu.co

Introduction

Methylparaben (MePB) is a type of emerging contaminant, commonly present in wastewater and surface water, widely used as preservatives in cosmetics, pharmaceuticals, food and industrial. The risk associated with the presence of this pollutant in the environment is due to their classification as an endocrine disruptor[1]. The activated carbon is an adsorbent widely used for the removal of various pollutants, due to the ability of this material to modify its chemical properties by pre and post-preparation treatments, as well as its textural characteristics depending on the activating agent used[2] and its activation temperature, generating solids with different porosity. The immersion calorimetry of activated carbons allow study and to know the intensity of the energetic interactions between the MePB and the activated carbons.

Materials and Methods

Preparation of activated carbons and characterization

Activated carbons obtained from African palm shell (Elaeis Guineensis) were modified chemically by impregnation with $CaCl_2$ at 1-2% wt/v (GC1 and GC2, respectively) and carbonized in CO_2 atmosphere at 973 K and 1173 K. BET surface area and micropore volumes of the adsorbents were determined from N_2 adsorption isotherms at 77 K.

Methylparaben adsorption

Methylparaben adsorption studies were done in batch conditions in the range from 20 to 200 $mg.L^{-1}$ for 3 weeks at 18 ^oC. The residual concentration of MePB was measured by UV-Vis Spectroscopy at 254 nm.

Immersion enthalpy determination

Immersion calorimetry took place in a calorimeter type Calvet (local construction)[3] with a cell in stainless steel in which 10 mL of the MePB aqueous solution of 200 $mg.L^{-1}$ was placed. The capture of the output electric potential started and the stabilization of the calorimeter until base line was achieved. Around 100 mg of each activated carbon was weighed into a glass ampoule with a fragile peak and the immersion of the sample into the liquid was performed. Finally, an electric calibration was performed.

Results and Discussion

Table 1. Activated carbons textural parameters from N_2 isotherms at 77 K

GAC	BET	DR			
	S_{BET} ($m^2.g^{-1}$)	V_T ($cm^3.g^{-1}$)	V_o ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)	E ($KJ.mol^{-1}$)
GC1-973	150	0.082	0.056	0.026	36.67
GC2-973	375	0.21	0.14	0.073	33.27
GC1-1173	1320	0.57	0.54	0.030	19.48
GC2-1173	723	0.36	0.30	0.069	21.45

Table 1 reports the textural characteristics obtained from the N_2 adsorption isotherms at 77 K, obtaining solids with areas between 150 and 1320 $m^2.g^{-1}$ and micropore volumes between 0.056 and 0.54 $cm^3.g^{-1}$. It can be observed that the increase in the activation

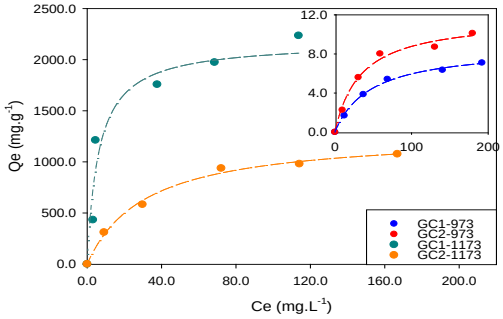

Figure 1. Adsorption isotherms of activated carbons into MePB solutions

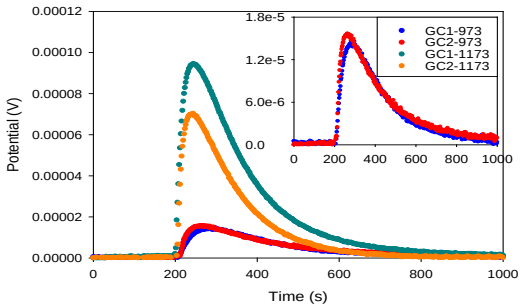

Figure 2. Termograms of the immersion of activated carbons into MePB solution.

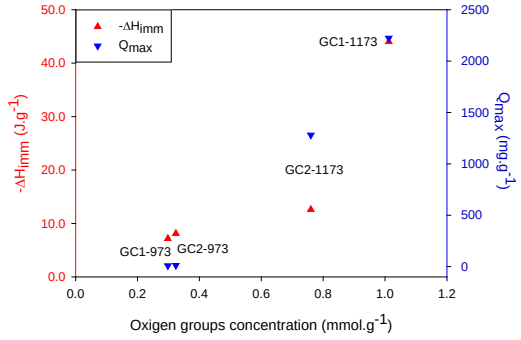

Figure 3. Adsorption isotherms of activated carbons into MePB solutions.

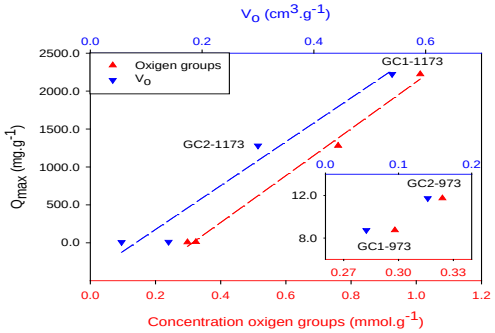

Figure 4. Adsorption isotherms of activated carbons into MePB solutions

temperature brings an increase in the microporosity, because gasification process is favored[4], while the mesoporosity is conserved.

Figure 1 compares the methylparaben adsorption isotherms for the activated carbons, where it is evident that the thermal treatment produces changes in the adsorption properties of all the carbons, since their textural characteristics are modified which is also evidenced in **Figure 2** where they are presented the immersion enthalpies thermograms finding values between -7.36 and -45.77 Jg-1 for the activated carbons immersed in the 200 mg.L^{-1} MePB solution. The observed behavior is related to the interaction that is established between the oxygenated functional groups present in the activated carbon with the MePB molecules, which manifests itself in greater adsorption as shown in **Figure 3**. Although it is noteworthy that this greater interaction and therefore greater adsorption is given by the contribution of surface chemistry and microporosity developed in the coals during thermal treatments as presented in **Figure 4**.

Conclusions

An increase in temperature is required to develop a highly porous structure. However, too high activation and major concentration of activating agent results in the widening of micropores to meso- and macropores. The results obtained show that immersion enthalpy varies with the content of functional groups due to changes in the interactions betweeen activated carbon-MePB, which favors the process of adsorption of this emerging contaminant.

Acknowledgment

The authors thank the Framework Agreement between the Universidad Nacional de Colombia and the Universidad de los Andes.

References

1. Forte, M.; Mita, L.; Perrone, R.; Rossi, S.; Argirò, M.; Mita, D. G.; Guida, M.; Portaccio, M.; Godievargova, T.; Ivanov, Y.; et al. (2017). Removal of Methylparaben from Synthetic Aqueous Solutions Using Polyacrylonitrile Beads: Kinetic and Equilibrium Studies. *Environ. Sci. Pollut. Res. 24*, 1270–1282.
2. Molina-Sabio, M.; Rodríguez-Reinoso, F. (2004). Role of Chemical Activation in the Development of Carbon Porosity. *Colloids Surfaces A Physicochem. Eng. Asp. 241*, 15–25.
3. Giraldo, L.; Moreno, J. C.; Huertas, J. I.(2002). Heat Conduction Micro-Calorimeter With Metallic Reaction Cell and

Improved Heat Flux Sensing System. *Instrum. Sci. Technol. 30* (2), 177–186.
4. Lua, A. C.; Yang, T. (2004). Effect of Activation Temperature on the Textural and Chemical Properties of Potassium Hydroxide Activated Carbon Prepared from Pistachio-Nut Shell. *J. Colloid Interface Sci. 274*, 594–601.