# Synthesis and textural characterization of a templated nanoporous carbon from MCM-22 zeolite and its use as adsorbent of amoxicillin and ethinylestradiol

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**Abstract** A templated nanoporous carbon was obtained from a zeolite MCM-22 type. The study about their textural properties was carried out by means of adsorption isotherms of nitrogen and carbon dioxide at 77 and 273 K, respectively. Due to the importance of the microporosity of these materials to be used as adsorbents, the micropore volume was analyzed by different methods/models (Dubinin–Radushkevich,  $\alpha_s$ -plot and Density Functional Density). The templated carbon obtained was evaluated in the adsorption of amoxicillin and ethinylestradiol from aqueous solutions. A relationship between the textural properties and the adsorption capacities of amoxicillin and ethinylestradiol on the templated carbon was analyzed. Results were compared with the adsorption capacities of other carbon materials as a commercial activated carbon and a templated carbon CMK-3 type.

**Keywords** Templated nanoporous carbon · MCM-22 zeolite · Textural characterization · Amoxicillin and ethinylestradiol adsorption

#### 1 Introduction

Porous materials are of great scientific and technological interest due primarily to its ability to interact with atoms,

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J. C. Tara · E. I. Basaldella Centro de Investigación y Desarrollo en Ciencias Aplicadas, Universidad Nacional de La Plata, 47 N° 257, CP: 1900 La Plata, Argentina in the internal surface of the material (Davis 2002). Different methods of synthesis and a wide range of precursors have been studied to obtain different porous materials with interesting textural properties. Among these, carbons materials have acquired great interest because of their hydrophobic nature and high chemical inertness (Rodríguez-Reinoso 1998). The more well-known microporous carbon material is the activated carbon, which frequently present narrow pore size distributions (with pore sizes less than 2 nm) and high surface areas making of them suitable materials for applications in adsorption. However, the small pore sizes of these materials limits their future use in other applications such as capture or separation of large molecules, so the development of micro-mesoporous carbons gained attention in the last years. Among them are the templated carbons, obtained by using the nanocasting technique (Sakintuna and Yürüm 2005; Xia et al. 2010). Through this technique is possible to improve the level of structural ordering using an inorganic matrix (template) to guide the formation of pores and producing novel materials with a broad control of the porosity. Thus, an inorganic porous material is selected as template and it is impregnated with a carbon precursor such as sucrose, furfuryl alcohol or acetylene, among others. After polymerization and pyrolysis steps, the template is removed by using HF or NaOH. Different templates may be used to obtain templated carbons including porous silica, zeolites, pillared clays and others (Jun et al. 2000; Barata-Rodrigues et al. 2003; Sandí et al. 2008). Thus, due to the variety of different templates and inorganic carbon sources it is possible to design materials with several carbonaceous structures and desired pore sizes. Therefore, the templated nanoporous carbons are a negative replica of the porous structure of the templates. Depending on synthesis

ions and molecules not only in the external surface but also



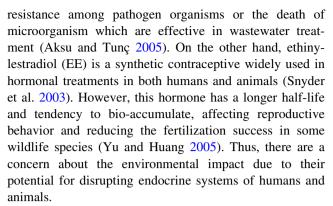
conditions, inorganic templates and the selected organic precursors, different micro-mesoporous (nanoporous) carbons should be obtained with different geometries, sizes and pore wall thicknesses as well as different connectivities (Dai et al. 2010). These materials present interesting textural properties, including specific surfaces areas with values up to 3,000 m $^2$ /g and pore sizes ranging from a few angstroms to hundreds of nanometers (Lu et al. 2005). Their textural properties are generally determined by N<sub>2</sub> adsorption–desorption isotherms at 77 K, while CO<sub>2</sub> adsorption isotherms at 273 K is used in order to have a complementary narrow microporosity information of such materials.

Different zeolite materials have been studied by several authors as templates for the development of nanoporous carbons. Among them, the Zeolite-β (Barata-Rodrigues et al. 2003), the Y zeolite using propylene vapor deposition (Ma et al. 2002) and a natural zeolite using furfuryl alcohol as carbon source (Sakintuna and Yürüm 2005). Thus, zeolites represent an interesting template sample in the replication process, because of their "boxes" sizes and channels are very similar to the size of the organic molecules constituting the replica. It has been found that zeolites with three-dimensional porous structure are the suitable for use as templates (Kyotani et al. 1997; Sakintuna and Yürüm 2005) and different nanoporous carbons have been obtained from them and retaining the original shape (Ma et al. 2002; Barata-Rodrigues et al. 2003; Garsuch and Klepel 2005). However, zeolites with one-dimensional pore structure were not effective (Johnson et al. 1997).

The MCM-22 zeolite has a bi- and tridimensional microporous structure with two sets of independent pores, one of them one-dimensional formed by large cylindrical cavities interconnected by straight and oblique channels, and other two-dimensional, formed by sinusoidal channels around six membered rings connecting the cavities. Due to their structural and chemical features, this material is interesting to be used as a template in developing of templated nanoporous carbons. A few reports were published using this zeolite as template (Srinivasu et al. 2007; 2008), therefore additional studies of their textural and structural properties could be enrich the use of this type of material.

A relevant topic in environmental remediation is the use of adsorbents to remove pollutants from aqueous systems. In the last years, among the studied organic compounds, the antibiotics and hormones have been considered emerging pollutants of the aquatic ecosystem even at low concentrations.

Amoxicillin is a broad-spectrum  $\beta$ -lactam antibiotic belonging to penicillin organism class and used in human and veterinary medicine for the treatment of bacterial and systemic infections (De Baere and De Backer 2007). The presence of this antibiotic in water may cause microbial



In this work, a MCM-22 zeolite was synthesized to be used as template to obtain a templated nanoporous carbon (TNC). Both, the zeolite and TNC were structurally characterized by X-ray diffraction. The textural properties were studied by  $N_2$  adsorption–desorption at 77 K and  $CO_2$  adsorption at 273 K, and due to the importance of their microporosity to be used as adsorbents, the micropore volume was analyzed by different methods/models (DR,  $\alpha_s$ -plot and DFT). The synthesized nanoporous carbon was evaluated in the adsorption of amoxicillin and ethinylest-radiol pollutants and, its performance was compared with those obtained with a commercial activated carbon and a nanoporous carbon CMK-3 type. A relationship between textural properties of TNC and its adsorption capacities was studied.

#### 2 Materials and methods

#### 2.1 MCM-22

MCM-22 was synthesized according to the procedure described by Corma et al. (1995) and adapted by Basaldella et al. (2008). The synthesis mixture was prepared using hexamethylenimine (Aldrich), silica (Aerosil 200, Degussa), sodium aluminate (Carlo Erba), sodium hydroxide (Carlo Erba), and deionized water. 0.92 g of aluminate and 0.6 g of NaOH were dissolved in 124 g of H<sub>2</sub>O. Then, 7.6 g of hexamethyleneimine, and 9.2 g of SiO<sub>2</sub> were slowly added to this solution under vigorous stirring. The Si/Al ratio obtained was 30. The resulting gel was maintained under stirring for 0.5 h and placed in a stainless steel stirred autoclave at 60 rpm, at 150 °C for 7 days. After this time, the sample was centrifuged (at 10,000 rpm), washed and dried at 80 °C overnight. Finally, the precursor of MCM-22 was calcined in air at 580 °C for 6 h.

#### 2.2 Templated nanoporous carbon (TNC)

The synthesis of the templated carbons used in this work was performed based on different reported conditions



(Barrera et al. 2013; Srinivasu et al. 2008; Jun et al. 2000). The nanocasting process to obtain the TNC involves five main steps: (i) inorganic template synthesis; (ii) template impregnation with the carbon source; (iii) polymerization; (iv) pyrolysis of the organic material and (v) template removal. The inorganic template was impregnated with an aqueous solution of sucrose dissolved in sulfuric acid and water in a mass ratio of 1:1.3:0.14:5 (template: sucrose: H<sub>2</sub>SO<sub>4</sub>: H<sub>2</sub>O). The mixture was stirred at room temperature for 1 h and then the polymerization step was carried out drying at 100 °C for 6 h and subsequently the temperature was raised to 160 °C for 6 h. The pyrolysis step was carried out by heating the composite from room temperature up to 700 °C in a N<sub>2</sub> flow of 180 ml/min with a heating rate of 3 °C/min. Template was removed by leaching the framework in a 5 wt.% hydrofluoric solution at room temperature under stirring for 24 h. Subsequently, the templated carbons were filtered and washed several times with deionized water and ethanol (50/50 % v/v), until the conductivity values were smaller than 10 µS/cm. Finally, TNC was overnight dried at 80 °C.

## 2.3 Adsorption experiments of amoxicillin and ethinylestradiol

Removal capacity of amoxicillin and ethinylestradiol was carried out using the TNC material and the results were compared with those obtained with a commercial activated carbon provided by Alpha Carbo Industrial S.A. and a synthesized templated carbon CMK-3 type (Barrera et al., 2013). In the case of the amoxicillin, 20 ml of a solution with an initial concentration of 200 mg/l was used with 10 mg of adsorbent. The initial concentration of ethinylestradiol solution was 25 mg/l, using a volume of 40 ml and 10 mg of adsorbent. In both cases, in base of experience with other solids and the same organic compounds, the adsorbents were maintained in contact with the respective solutions during 24 h at room temperature, ensuring that the equilibrium time was reached. Then, the solutions were filtered and the supernatant were analyzed by UV-VIS (Shimadzu UV 2550) in a wavelength of 272 nm (amoxicillin) and 280 nm (ethinylestradiol). Adsorption isotherms of the adsorbents were carried out in a concentrations range from 30 up to 400 mg/l and from 2 up to 15 mg/l for amoxicillin and ethinylestradiol, respectively.

#### 3 Characterization and calculations

The MCM-22 zeolite and TNC were characterized by X-ray diffraction (XRD) and energy dispersive spectroscopy X-ray (EDS). Textural properties of these materials

were studied by  $N_2$  adsorption—desorption at 77 K and  $CO_2$  adsorption at 273 K in manometric adsorption equipment (Quantachrome–Autosorb iQ and Micromeritics ASAP-2050). The samples were previously degassed at 200 °C for 10 h.

The specific surface area  $(S_{BET})$  was estimated by the Brunauer, Emmett and Teller method (Brunauer et al. 1938) using N<sub>2</sub> adsorption data at 77 K for relative pressures between 0.03 and 0.1 for MCM-22 and between 0.01 and 0.03 for the TNC. For evaluation of the micropore volume  $(V_{uP})$  the Dubinin-Radushkevich (DR) (Dubinin 1960),  $\alpha_S$ -plot (Gregg and Sing 1982) and the Density Functional Theory (DFT) (Gor et al. 2012) methods were used. For the \alpha\_S-plot method, carbon black graphitized GCB-1 (Nakai et al. 2010) and the nonporous hydroxylated silica Fransil-I (Bhambhani et al. 1972) were used as reference materials for TNC and MCM-22, respectively. The total pore volume  $(V_{TP})$  was obtained by Gurvich rule (Rouguerol et al. 1999) at a relative pressure of 0.98. The pore volumes were calculated using a density of liquid N<sub>2</sub> value of 0.808 g/cm<sup>3</sup> (Gregg and Sing 1982). The pore size distributions of the studied materials were obtained by the DFT method included in ASiQwin software, v. 2.0 (Quantachrome Instruments) where the Kernels used were: (i) "N<sub>2</sub> at 77 K on carbon (slit/cylindr. pore, QSDFT adsorption branch)" and "CO2 at 273 K on carbon" for TNC; and (ii) "N<sub>2</sub> at 77 K on silica (cylindr. pore, NLDFT adsorption branch)" for MCM-22.

Infrared spectroscopies were obtained in an ALPHA FT-IR Spectrometer (Bruker corporation), in a region from 4,000 to 1,000 cm<sup>-1</sup>.

The experimental adsorption isotherms from aqueous solution of amoxicillin and ethinylestradiol using TNC as adsorbents were adjusted using the Langmuir (L) and Freundlich (F) isotherm models. These isotherm models were fitted to experimental data using nonlinear regression, in order to determine the characteristic parameters of each model (Ho 2006; Salarirad and Behnamfard 2011).

## 4 Results and discussion

4.1 X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS)

In Fig. 1 the TNC and MCM-22 diffractograms are shown. The TNC sample exhibits a broad peak between 22 and 25°  $(d_{002})$  as well as one with less intensity near 43° in 2 $\theta$ , corresponding to the basal spacing  $d_{100}$  of graphite-like carbon. Moreover, the disappearance of the characteristic peaks of zeolite MCM-22 indicates that the template removal process was effective and the synthesis conditions were suitable to obtain the TNC. These results agree with



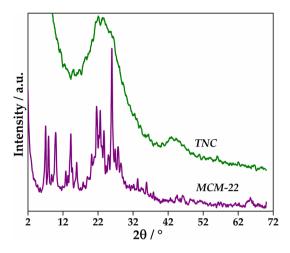


Fig. 1 X-ray diffraction patterns of TNC and MCM-22 samples

Table 1 EDS analysis of TNC and MCM-22 samples

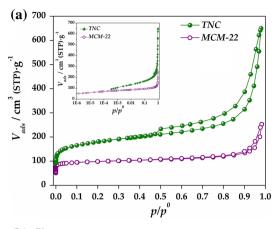
Material	C [%]	O [%]	Al [%]	Si [%]
TNC	93	7	-	_
MCM-22	9	23	5	63

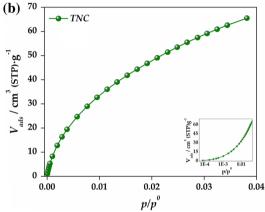
analysis of EDS shown in Table 1, where a high content of carbon in the TNC and low content of impurities (oxygen) were found.

# 4.2 Textural characterization of TNC and MCM-22 samples

Figure 2a, b shows N<sub>2</sub> adsorption–desorption isotherms at 77 K of TNC and MCM-22, and the CO<sub>2</sub> adsorption isotherm at 273 K of TNC, respectively. It can be seen that the N<sub>2</sub> adsorption-desorption isotherm of the TNC sample is type IIb with a hysteresis loop type H3 according to the IUPAC classification (Sing et al. 1985). In contrast, the isotherm of the MCM-22 is a type I at lower relative pressures with a small hysteresis loop type H3 at higher relative pressures. In both isotherms can be seen the rapid growth of the adsorbed volume at low relative pressures indicating that these materials are microporous. TNC presents the highest micropores volume, as may be seen in Table 2. The most developed hysteresis loop in TNC sample is related with its mesopores amount. Additionally, the abrupt increment observed at relative pressures close to 1 indicates that these materials, besides having micro and mesopores, have large mesopores and/or macropores, mainly in the case of the TNC.

In Fig. 2b it is observed that the CO<sub>2</sub> adsorption isotherm at 273 K of TNC sample has a significant adsorbed amount. In the zoom in on Fig. 2b is presented the same





**Fig. 2 a** N<sub>2</sub> adsorption–desorption isotherms at 77 K of TNC and MCM-22 samples and **b** CO<sub>2</sub> adsorption isotherm at 273 K of TNC sample

Table 2 Textural properties obtained by adsorption data of  $N_2$  at 77 K and  $CO_2$  at 273 K for TNC and MCM-22 samples

Textural property	TNC	MCM-22	
$S_{BET}$ (m <sup>2</sup> /g)	660	380	
$V\mu_P (N_2 \text{ at } 77 \text{ K}) \text{ (cm}^3/\text{g)}$	0.20	0.13	
$V\mu_P$ (CO <sub>2</sub> at 273 K) (cm <sup>3</sup> /g)	0.20	_	
$V_{TP}$ (cm <sup>3</sup> /g)	1.00	0.35	

curve but in logarithm scale, showing the quality of the experiment.

The study of the micropore volume is presented in Figs. 3 and 4 where the DR and  $\alpha_S$ -plot curves of TNC and MCM-22 are shown. Micropore volumes obtained by these methods are compared with those obtained by the DFT method.

From the results of the Fig. 3a, the  $V_{\mu P}$  of TNC obtained with the DR (N<sub>2</sub> at 77 K) is larger than those obtained by the DFT method (N<sub>2</sub> at 77 K) and DR (CO<sub>2</sub> at 273 K). This overestimation is observed in materials with a significant amount of mesopores such as the TNC, as it was previously



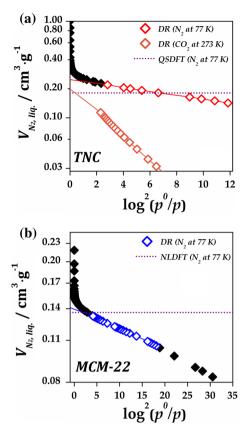


Fig. 3 Micropore volume calculation from DR and DFT methods for a TNC and b MCM-22 samples

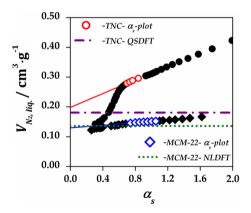


Fig. 4 Micropore volume calculation from  $\alpha_S$ -plot and DFT methods for TNC and MCM-22 samples

reported (Villarroel-Rocha and Barrera 2013). In Fig. 3b, it can be seen that the  $V_{\mu P}$  of MCM-22 is more in agreement with the value obtained by the DFT method (N<sub>2</sub> at 77 K), because this material is essentially microporous. Furthermore, analyzing the results obtained with the  $\alpha_{S}$ -plot method (Fig. 4), it can be seen that the  $V_{\mu P}$  values, for both materials, are agree with that obtained by the DFT method, showing the effectiveness of this method.

Table 2 shows the textural properties of TNC and MCM-22 materials, where the  $V_{\mu P}$  is the obtained by  $\alpha_{S}$ -

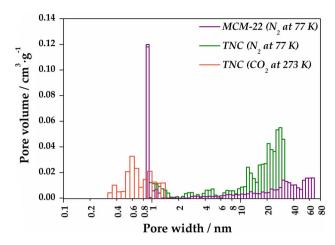


Fig. 5 Pore size distributions by the NLDFT (MCM-22) and QSDFT (TNC) methods

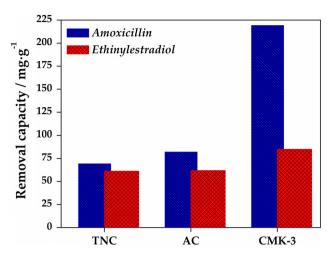
plot method. This results show that the TNC has higher surface area, micropore volume and total pore volume respect to MCM-22 material. It is important to highlight that  $V_{\mu P}$  of TNC obtained from CO<sub>2</sub> adsorption data using the DR equation is similar to the obtained by  $\alpha_{S}$ -plot method using N<sub>2</sub> adsorption data at 77 K. In addition, it can be seen that the 80 % of the total pore volume of the TNC is given by the mesopores volume.

Figure 5 shows the pore size distributions of the MCM-22 and TNC materials obtained by N2 adsorption at 77 K and CO<sub>2</sub> adsorption at 273 K (CO<sub>2</sub> adsorption only in the case of the TNC). In this figure it is possible appreciate that the MCM-22 material exhibits a large number of pores in the microporous zone (about 0.86 nm) with a slight amount of larger pores (30-70 nm). In the case of TNC, the presence of a large number of micropores in the same zone of the MCM-22 is observed. Additionally, it can be seen a significant contribution of pores in the mesoporous region (between 10 and 30 nm). From CO<sub>2</sub> adsorption data it is possible to appreciate the presence of micropores between 0.3 and 1.2 nm. As it was mentioned above, the  $V_{uP}$  values of TNC obtained with CO<sub>2</sub> and N<sub>2</sub> adsorption were the same but in this figure is possible to appreciate that the ranges of them are different. These results indicate that the nitrogen (for this material specifically) identifies all micropores in a fixed region (supermicropores > 0.7 nm) while the CO<sub>2</sub> let us see with a great definition the ultramicropore size distribution (pores < 0.7 nm).

### 4.3 Amoxicillin and ethinylestradiol adsorption

In Fig. 6a, removal capacities of amoxicillin and ethiny-lestradiol of TNC are compared with other carbonaceous materials as reference, such as templated carbon CMK-3 and a commercial powder activated carbon. In this figure it





**Fig. 6** Removal capacity of amoxicillin and ethinylestradiol for TNC, AC and CMK-3 samples in mg/g

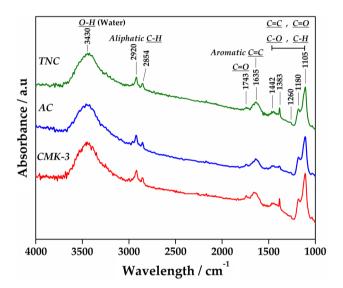
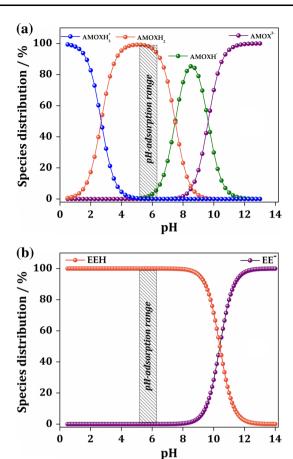


Fig. 7 DRIFT spectra for TNC, AC and CMK-3 samples

can be seen that the TNC (69  $mg_{AMOX}/g$  and 61  $mg_{EE}/g$ ) has removal capacities similar to those obtained by the AC (82  $mg_{AMOX}/g$  and 62  $mg_{EE}/g$ ). However, these removal capacities are lower than those obtained by CMK-3 (219  $mg_{AMOX}/g$  and 85  $mg_{EE}/g$ ). These removal capacities values could be related to: (i) surface functional groups and/or (ii) textural properties of the carbon porous materials under study.

Respect to surface functional groups, DRIFT spectra (Fig. 7) showed that there are not differences among the three analyzed materials, indicating that the surface groups effect for amoxicillin and ethinylestradiol adsorption is the same in all the evaluated carbon materials. The assignments of the observed bands are shown in Fig. 7.

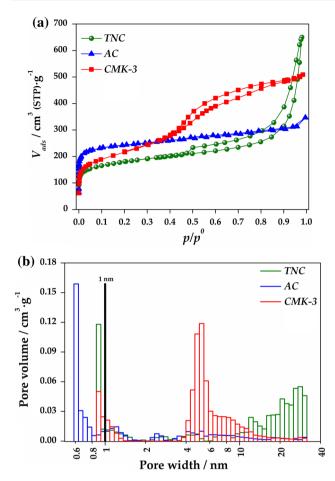


**Fig. 8** Speciation diagrams of  ${\bf a}$  amoxicillin ( $C_0 = 200$  mg/l) and  ${\bf b}$  ethinylestradiol ( $C_0 = 25$  mg/l) molecules in aqueous solution

Furthermore, in the experiments conditions, pH range 5.1–6.3, the amoxicillin and ethinylestradiol molecules are mostly neutral (AMOXH<sub>2</sub> and EEH) as is shown in speciation distributions (Fig. 8a and b), then the electrostatic effects are not relevant.

Regarding the textural properties, in Fig. 9a, b N<sub>2</sub> adsorption-desorption isotherms at 77 K and pore size distributions, respectively, of all the carbon materials are shown. The isotherms shape of these materials shows that the commercial AC is mostly a microporous material and the templated carbons, TNC and CMK-3, are micro-mesoporous materials. This fact is clearly seen in the pore size distributions where all the materials present micropore sizes above of 1.6 nm. Respect to the mesopores, the AC only has a few mesopores amount in comparison with the other analyzed materials. CMK-3 and TNC materials exhibit mesopores sizes from 4 to 15 nm and 10 to 30 nm, respectively. The textural properties obtained from adsorption data are shown in Table 3, where external surface area  $(S_{EXT})$  and  $V_{\mu P}$  where obtained by the  $\alpha_{S}$ -plot method. The carbon black non-graphitized Cabot BP 280 (Kruk et al. 1997) and the carbon black graphitized GCB-1





**Fig. 9** a N<sub>2</sub> adsorption–desorption isotherms at 77 K and **b** pore size distributions by QSDFT method for TNC, AC and CMK-3 samples

**Table 3** Textural properties obtained by N<sub>2</sub> adsorption data at 77 K for TNC, AC and CMK-3 samples

Textural property	TNC	AC	CMK-3
$S_{BET}$ (m <sup>2</sup> /g)	660	935	770
$S_{EXT}$ (m <sup>2</sup> /g)	180	185	460
$V\mu_P \text{ (cm}^3/\text{g)}$	0.20	0.30	0.13
$V_{TP}$ (cm <sup>3</sup> /g)	1.00	0.52	0.78

(Nakai et al. 2010) were selected as reference materials for AC and CMK-3 samples, respectively, taking into account selection criteria reported elsewhere (Villarroel-Rocha and Barrera 2013).

Figures 10a, b show removal capacities normalized with their total and external surface areas, respectively. In Fig. 10a it can be seen that the removal of ethinylestradiol normalized (in  $mg/m_{total}^2$ ) of the three materials have very similar values ( $\sim 0.1~mg/m^2$ ), indicating a direct relationship between the adsorption capacity with the total surface

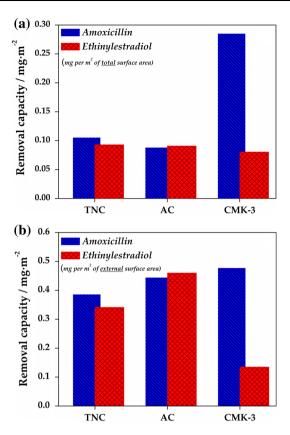


Fig. 10 Removal capacity of amoxicillin and ethinylestradiol for TNC, AC and CMK-3 in  $a \text{ mg/m}_{\text{total}}^2$ , and  $b \text{ mg/m}_{\text{external}}^2$ 

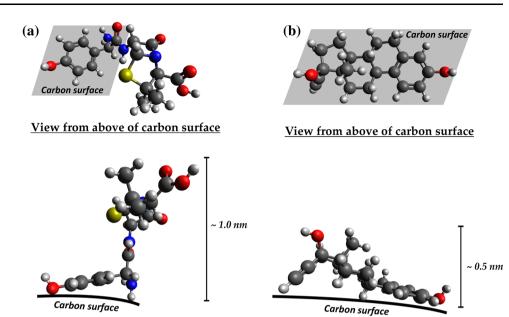
area of the material using the all micro- and mesoporosity. By contrast, the removal of amoxicillin normalized (in  $mg/m_{total}^2$ ) of CMK-3 (0.28  $mg/m^2$ ) was higher than carbons under study ( $\sim 0.09-0.11~mg/m^2$ ), suggesting that this molecule is being adsorbed in some specific pore sizes (i.e. mesopores). In Fig. 10b it is possible observe this behavior where the removal of amoxicillin normalized (in  $mg/m_{external}^2$ ) of the three materials have similar values ( $\sim 0.45~mg/m^2$ ), finding a direct relationship between the amoxicillin removal capacities and the external surface area (related to the area of those pores that are not micropores).

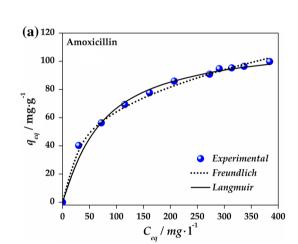
These results could be related to the amoxicillin and ethinylestradiol molecular sizes and the preferential adsorption geometry in which these molecules are being adsorbed on the carbon surface. The *Avogadro* v. 1.1.1 (software for drawing molecules) was employed to obtain the sizes and possible geometries of the molecules under study. In Fig. 11a, b a possible adsorption geometry are proposed. Comparing both molecules, ethinylestradiol is a *more attractive* molecule for adsorption process in micropores due to its stearic effect is less than that of the amoxicillin which is more branched.

In Fig. 11a it is possible to observe that the amoxicillin has adsorption limitations in pore sizes below of 1 nm. Similar adsorbed geometry was previously reported elsewhere in other kind of surface (Bebu et al. 2011). For this

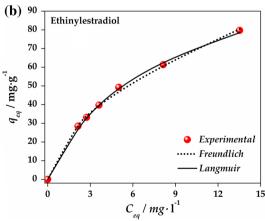


Fig. 11 Adsorption geometry of a amoxicillin and b ethinylestradiol on carbon surface





View from side of carbon surface



**Fig. 12** Equilibrium adsorption isotherms of **a** amoxicillin and **b** ethinylestradiol for TNC sample. The *solid line* represents the Langmuir model fit to the experimental isotherm and the *dashed line* the Freundlich model

reason, this molecule cannot be adsorbed into the microporous region (see Fig. 9b) as it was previously explained. Respect to ethinylestradiol, this molecule can been adsorbed in all the micropores of the carbon materials under study due to its adsorption geometry on carbon surface needs pore sizes higher than 0.5 nm to be adsorbed (Fig. 11b).

View from side of carbon surface

In Fig. 12a, b equilibrium adsorption isotherms in aqueous solution of amoxicillin and ethinylestradiol, respectively, for TNC material are shown. It can be observed that the adsorption isotherms for both pollutants exhibit L-type isotherms according to the Giles classification (Giles et al. 1960), indicating that as the adsorbent becomes saturated increases the difficulty for the adsorptivés molecules to find adsorption sites. In addition, in these type of isotherms is not usually the competition between the adsorptive and the solvent by the adsorption sites of the adsorbent. Additionally, in Fig. 12a, b, the fitting curves of Langmuir (solid line) and Freundlich (dashed line) models are shown. Adjustment parameters are detailed in Table 4, where it can be seen that both models present a good fit to the experimental data  $(R^2 > 0.99)$ .

Comparing the  $q_{max}$  (adsorption capacity) parameter of Langmuir shown in Table 4, can be seen that TNC exhibits similar removal capacity values ( $\sim 120$  mg/g) of amoxicillin and ethinylestradiol.

#### 5 Conclusions

A templated micro-mesoporous carbon was obtained from the zeolite MCM-22 by nanocasting technique.



**Table 4** Adjustment parameters of isotherms model for adsorption data of amoxicillin and ethinylestradiol on TNC sample

Compound	$q_{eq} = rac{q_{ ext{max}} \cdot K \cdot C_{eq}}{1 + K \cdot C_{eq}}$			Freundlich		
				$q_{eq} = k \cdot C_{eq}^n$		
	$q_{max}$ (mg/g)	K (l/mg)	$R^2$	$k (mg^{(1-n)} \cdot l^n/g)$	n	$R^2$
Ethinylestradiol	121.2	0.136	0.998	19.8	0.538	0.998
Amoxicillin	116.1	0.014	0.994	13.4	0.342	0.996

Textural properties exhibited by the TNC were higher than those obtained in the inorganic template.

Micropore volume values of the MCM-22 evaluated by DR and  $\alpha_s$ -plot methods agreed between them. However, in the case of the TNC, the DR method overestimates the  $V_{\mu P}$  value respect to  $\alpha_s$ -plot and DFT whereas the last methods agreed.

A complete microporosity evaluation of materials as TNC could be obtained by using nitrogen and carbon dioxide adsorption at 77 and 273 K, respectively.

TNC material could be used as a potential adsorbent of different pollutants. In the case of the ethinylestradiol adsorption the total specific surface area is a relevant property. On the other hand, in the amoxicillin adsorption pore sizes in the range of the mesopores are necessary.

Finally, this type of templated carbonaceous materials presented interesting properties to keep been studied and used in different environmental applications.

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