

SYNTHESIS AND CHARACTERIZATION OF GLYCEROL-BASED CARBON MATERIALS AND THEIR EVALUATION IN THE ADSORPTION OF ANTIBIOTIC COMPOUNDS

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ABSTRACT

This study is focused on the synthesis and application of glycerol-based carbon materials (GBCM₂₀₀, GBCM₃₀₀ and GBCM₃₅₀) as adsorbents for the removal of the antibiotic compounds flumequine and tetracycline from aqueous solution. The synthesis enrolled the partial carbonization of a glycerol-sulphuric acid mixture, followed by thermal treatments under inert conditions and further thermal activation under oxidative atmosphere. The textural properties were investigated through N₂ adsorption-desorption isotherms, and the presence of oxygenated groups was discussed based on zeta potential and Fourier transform infrared (FTIR) data. The adsorption kinetic data revealed that the equilibrium time for flumequine adsorption was achieved within 96 h, while for tetracycline, it was reached after 120 h. It was found that the pseudo-second order model was the most suitable model for the fitting of the experimental kinetic data. The maximum adsorption capacities for flumequine and tetracycline were of 41.5 and 58.2 mg.g⁻¹ by GBCM₃₅₀ activated carbon. As it is based on SSE values, Sips model well-fitted the experimental FLQ and TCN adsorption isotherm data, followed by Freundlich equation.

Keywords: Adsorption, Antibiotics, Carbon materials, Emerging contaminants.

1. INTRODUCTION.

In the past few decades, the presence of emerging compounds has been detected at trace concentrations (ng.L⁻¹ to µg.L⁻¹) in many water sources. An important characteristic of these compounds is that they are continuously introduced into the environment, compensating the transformation/biodegradability rates. In general, these pollutants are persistent, bioaccumulative and potentially toxic at medium to long term [1].

Among this group of substances, antibiotics have raised a significant interest from the scientific community. It has been reported that most of the antibiotics are not adequately digested by organisms, leading to the excretion of these substances and their metabolites through the excrements and urine. In addition, the antibiotic residues –metabolites- in the environment are of great concern due to can induce antibiotic resistance genes at relatively low concentrations [2].

Flumequine is an antibiotic widely used in veterinary medicine to control bacterial infections, being present in farms effluents, but it has also been detected in hospital effluents [3].

On its turn, tetracycline belongs to a broad spectrum antimicrobial activity family of antibiotics, which has been specifically identified as one of the most developers of resistance in ecosystems. Tetracycline concentrations up to 10.0 µg.L⁻¹ have been detected in sediments near to poultry slaughterhouses and higher

concentrations of tetracycline metabolites have been measured, up to 25.0 µg.L⁻¹ [4].

Adsorption, since it is a non-destructive tertiary process, has been revealed as one of the most advantageous physicochemical technique in wastewater treatment processes. Crude glycerol, obtained from the biodiesel production, is actually an abundant feedstock. Thus, the preparation of carbonaceous materials by partial carbonization and sulfonation of this by-product consists of an interesting research focus. Bearing this in mind, the aim of this study is to explore several types of glycerol-based carbon materials synthesized by partial carbonization of glycerol in concentrated sulphuric acid solution for the removal of flumequine and tetracycline from aqueous solutions.

2. MATERIALS AND METHODS.

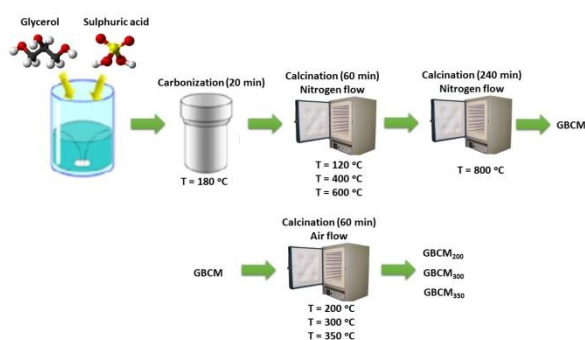
2.1. Materials.

Sulphuric acid (95-97 wt.%) was obtained from Panreac and glycerol (99 wt.%) was purchased from Alfa Aesar. Antibiotics, flumequine (FLQ) and tetracycline (TCN) were purchased from Sigma-Aldrich, showing a purity higher than 98%. All the chemicals were used as received, without further purification. Ultrapure water was used in all the experiments.

2.2. Synthesis procedure of glycerol-carbon materials.

Glycerol-based carbon materials were prepared adapting the procedure described in the work of Ribeiro et al. [5]. A mixture of glycerol (10 g) and concentrated (95-97 wt.%) sulphuric acid (40 g) was gently heated to 180 °C

and left at that temperature for 20 min to allow in situ partial carbonization. The resulting material was ground in a ceramic mortar to obtain particle sizes in the range 0.425-0.600 mm and further calcined in a tube furnace under a nitrogen flow ($100 \text{ cm}^3 \cdot \text{min}^{-1}$) at $120 \text{ }^\circ\text{C}$, $400 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$ during 60 min at each temperature, and finally at $800 \text{ }^\circ\text{C}$ for 240 min, defining a heating rate of $2 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The as-calcined material was named GBCM and showed a basic character, due to the decomposition of the sulphonic groups during the calcination process. Then, the GBCM material was thermally activated in a tube furnace under oxidative atmosphere (air flow of $100 \text{ cm}^3 \cdot \text{min}^{-1}$) during 60 min at different temperatures, $200 \text{ }^\circ\text{C}$, $300 \text{ }^\circ\text{C}$ and $350 \text{ }^\circ\text{C}$, resulting in materials with different textural and chemical properties. The carbon materials were labelled as GBCM followed by a subscript number corresponding to the activation



temperature; e.g., GBCM₂₀₀, GBCM₃₀₀ and GBCM₃₅₀. Figure 1 show the synthesis of GBCM.

Figure 1. Synthesis of GBCM materials.

2.3. Characterization of the carbon materials.

Textural characterization of the activated carbons was obtained from N_2 adsorption isotherms at $-196 \text{ }^\circ\text{C}$, using a Micromeritics ASAP 2020 apparatus. Specific surface area (S_{BET}) of the materials was determined using BET equation. Total micropore volume (V_{Mic}) was calculated by Dubinin-Radushkevich equation and the total pore volume (V_{Total}) was determined at $P/P^0 = 0.95$. The pore size distribution was estimated using the Density Functional Theory (DFT) method.

Chemical surface characterization was performed by using Fourier transformed infrared spectrum (FTIR), recorded in the range $400\text{-}4600 \text{ cm}^{-1}$ and using a Thermo Nicolet FTIR spectrophotometer. The isoelectric point (pH_{IEP}) was measured in a Zeta sizer Nano ZS equipment, using 0.05 g of sample suspended in 20 mL of deionized water. The zero potential point of the sample was calculated by interpolation method. Finally, the composition of the carbon materials was determined by elemental analysis, in a LECO CHNS-932 elemental micro-analyzer.

2.4. Kinetic and equilibrium adsorption experiments.

Both adsorption kinetic and equilibrium studies were carried out in an orbital shaker, by contacting different weights of adsorbent with 1.5 mL of FLQ or TCN solutions ($C_0 = 100 \text{ mg} \cdot \text{L}^{-1}$). Temperature and shaking were controlled at $30 \pm 1 \text{ }^\circ\text{C}$ and 300 rpm , respectively.

Samples were filtered before analysis in $0.45 \text{ } \mu\text{m}$ nylon filters. FLQ concentration was measured in a Varian Prostar high performance liquid chromatograph equipped with a UV-vis diode array detector. The measurements were performed in a Mediterranea C18 column $250 \text{ mm} \times 4.6 \text{ mm} \times 5 \text{ } \mu\text{m}$ (Teknokroma), using a mobile phase of acetonitrile:water ($0.1 \text{ \%v H}_3\text{PO}_4$) ($60:40 \text{ v/v}$) at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ and using a loop volume of $20 \text{ } \mu\text{L}$. TCN concentration measurements were accomplished in a Perkin Elmer Lambda 35 UV-vis spectrophotometer. The maximum wavelength used in the detection was 356 nm .

3. RESULTS AND DISCUSSION.

3.1. Characterization of the carbon materials.

Textural properties, e.g., specific surface area (S_{BET} , $\text{m}^2 \cdot \text{g}^{-1}$), total pore volume (V_{Total} , $\text{cm}^3 \cdot \text{g}^{-1}$), and micropore volume (V_{Mic} , $\text{cm}^3 \cdot \text{g}^{-1}$) of the carbonaceous materials are shown in Table 1. The N_2 adsorption-desorption isotherms of the tested carbonaceous

Material	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{Mic} ($\text{cm}^3 \cdot \text{g}^{-1}$)	V_{Total} ($\text{cm}^3 \cdot \text{g}^{-1}$)	$V_{\text{Mic}}/V_{\text{Total}}$
GBCM	10	-	0.02	-
GBCM ₂₀₀	352	0.170	0.1704	0.997
GBCM ₃₀₀	391	0.192	0.1933	0.994
GBCM ₃₅₀	436	0.217	0.2354	0.921

materials are shown in Figure 2.

Table 1. Textural properties of the tested materials.

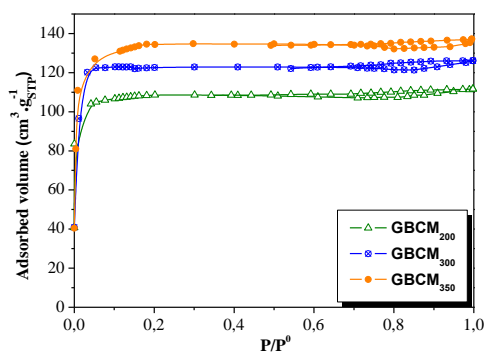


Figure 2. N_2 adsorption-desorption isotherms at $-196 \text{ }^\circ\text{C}$ of the tested glycerol-based carbon materials.

GBCM is a non-porous material ($S_{\text{BET}} = 10 \text{ m}^2 \cdot \text{g}^{-1}$ and $V_{\text{Total}} = 0.02 \text{ cm}^3 \cdot \text{g}^{-1}$). The thermal activation allowed the development of porosity in the carbon materials, GBCM₂₀₀, GBCM₃₀₀ and GBCM₃₅₀. From textural properties (Table 1), it can also be observed the effect of the different thermal treatments on the specific surface area of the glycerol-based carbon materials. These results are in agreement to those previously reported for similar materials, but with smaller particle sizes [5], since higher activation temperatures led to an increase in the specific surface area. Although all the glycerol-activated carbons possess a strong microporous nature, with low non-microporous surface areas, the increase in

the thermal activation temperature affects the micropore volume, with the largest micropore volume being obtained in the sample activated at the highest temperature ($0.217 \text{ cm}^3 \cdot \text{g}^{-1}$ for GBCM_{350} carbon).

Pore size distribution, evaluated by Density Functional Theory method, confirmed that the thermal treatment temperature had an effect on the pore size of the glycerol-based carbon materials, showing values from 0.86 to 1.21 nm, as the treatment temperature increased from $200 \text{ }^\circ\text{C}$ to $350 \text{ }^\circ\text{C}$.

SEM micrographs of GBCM_{300} and GBCM_{350} (Figures 3a-b) show quite similar surface morphology and the presence of pores dispersed on their surface.

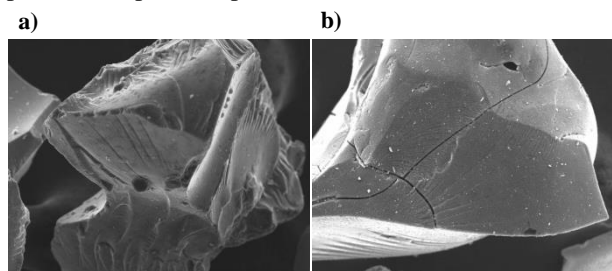


Figure 3. SEM micrographs of (a) GBCM_{300} and (b) GBCM_{350} .

FT-IR spectra of the tested activated carbons in the wavelength range from 400 to 4000 cm^{-1} are shown in Figure 4. The results correspond to the characteristic bands found in FT-IR analyses of carbonaceous materials.

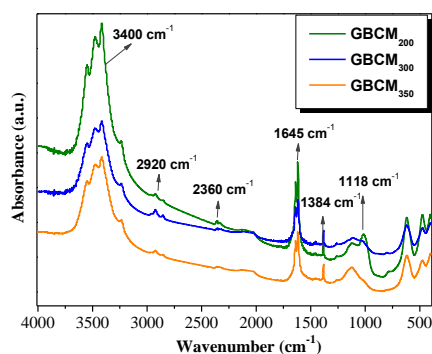


Figure 4. FT-IR spectra of the tested glycerol-based carbon materials.

The isoelectric point (pH_{IEP}) results are shown in Table 2. GBCM_{200} material possesses a pH_{IEP} value of 5.6, and as the activation temperature increased, the oxygenated functionalities of the materials also increased, as suggested by the isoelectric points of GBCM_{300} and GBCM_{350} carbons ($\text{pH}_{\text{IEP}} = 3.8$ and 2.6 , respectively).

Elemental analysis results (Table 2) are in accordance to the acidic/basic character of the samples as inferred by the isoelectric point measurements. As expected, findings suggest that the acidic character of the carbonaceous materials is mainly due to the incorporation of oxygen-containing surface groups during the thermal activation in air [6]; so, carbon treated at the highest temperature, GBCM_{350} , is more hydrophilic than GBCM_{200} and GBCM_{300} .

3.2. Adsorption kinetic studies.

The evolution of FLQ and TCN adsorption versus time onto GBCM_{300} carbon material is illustrated in Figures 5a-b. FLQ equilibrium time was achieved within 96 hours, while for TCN it was reached after 120 hours. Generally, an initial faster increasing in the adsorption capacity was observed during first 6-10 hours, approximately. In this behaviour, it is involved the external surface area of the carbons, supporting the access of the molecules to the inner porous structure. So, the faster kinetic range is directly related to the contribution of the external area of the material.

Material	Elemental analysis					pH_{IEP}
	N (%)	C (%)	H (%)	O (%)	S (%)	
GBCM_{200}	0.78	84.23	1.05	12.54	1.40	5.6
GBCM_{300}	0.50	79.97	0.90	17.52	1.11	3.8
GBCM_{350}	0.33	78.75	0.70	19.32	0.90	2.6

Table 2. Elemental analysis and pH_{IEP} data of the tested materials.

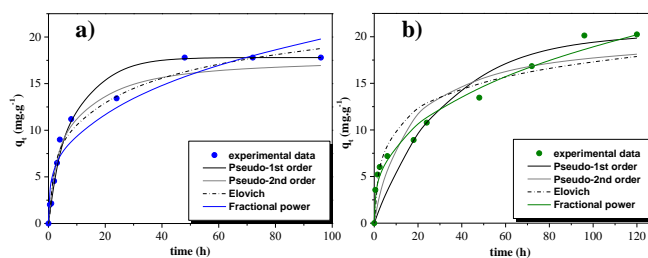


Figure 5. Kinetic experimental and theoretical adsorption data for the removal of (a) FLQ and (b) TCN onto GBCM_{300} carbon (Conditions: $C_0 = 100 \text{ mg} \cdot \text{L}^{-1}$; $\text{pH} = 6.3$; particle size = $425\text{-}600 \text{ }\mu\text{m}$; adsorbent dosage = $2.4 \text{ g} \cdot \text{L}^{-1}$; temperature = $30 \text{ }^\circ\text{C}$; stirring rate = 300 rpm).

With the purpose of studying the kinetic adsorption behavior of both contaminants onto GBCM_{300} , several kinetic models, i.e., fractional power function, pseudo-first order, pseudo-second order and Elovich model have been used for the fitting of the experimental data.

The goodness of the fitting to the experimental data was studied through the non-linearized forms of the kinetic models equations, minimizing the sum of the squares of the residuals (SSE):

$$SSE = \sum (q_{\text{exp}} - q_{\text{cal}})^2 \quad (1)$$

The non-linearized fitting to the experimental data revealed good results for pseudo-second order model, since better fitting was obtained by applying fractional power model to TCN adsorption data and both pseudo-second order and Elovich models to FLQ experimental adsorption data.

3.5. Adsorption isotherms. Equilibrium modelling.

Both FLQ and TCN experimental adsorption isotherms (Figures 6 a-b) showed two-step or three-step adsorption profiles, and could be classified as S-3 type,

according to Giles classification [7]. Accordingly, important information about the adsorbate-adsorbent interactions could be withdrawn from the multistep-shaped isotherms. Maybe this sigmoid trend could be attributed to a synergistic effect, which is favouring the adsorption of FLQ or TCN molecules by adsorbate-adsorbent interactions to the adsorbed molecules. The sudden increasing in the adsorption capacity at higher aqueous concentration could be related to a more favourable reorientation of the adsorbate molecules, generating more availability for adsorption in the active sites.

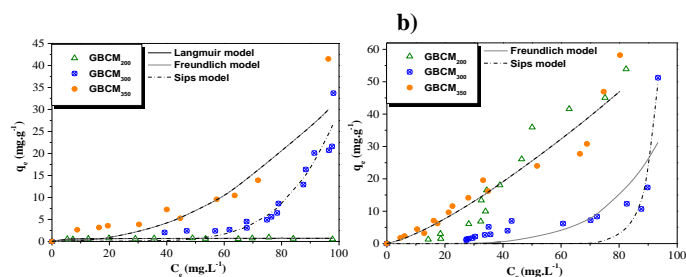


Figure 6. Experimental and theoretical adsorption isotherms of (a) FLQ and (b) TCN onto the glycerol-based carbon materials (Conditions: $C_0 = 100 \text{ mg.L}^{-1}$; pH = 6.3; particle size = 425-600 μm ; temperature = 30 $^\circ\text{C}$; stirring rate = 300 rpm).

From Fig. 6 a-b can be stated that FLQ removal was highly influenced by the textural properties of the carbonaceous materials, since GBCM₃₅₀ carbon, which offered the highest specific surface area among the tested adsorbents, led to the maximum FLQ adsorption capacity, i.e., 41.5 mg.g^{-1} . In the opposite, TCN adsorption isotherms did not reveal a trending related to the textural properties of the materials; this is, GBCM₂₀₀, GBCM₃₀₀ and GBCM₃₅₀ carbons showed similar adsorption capacity values: 53.9, 51.2 and 58.2 mg.g^{-1} , respectively.

In this work, the fitting of the experimental data to Langmuir, Freundlich and Sips adsorption models, widely applied to describe experimental adsorption isotherms, was carried out. Generally, Sips model, with the lowest values of sum of square of residuals (SSE), showed the best fitting to both FLQ and TCN adsorption data, as compared to the other models. It could be found that Langmuir model was not a suitable equation for the prediction of flumequine and tetracycline removal onto the glycerol-based activated carbons. The good fitting of Sips isotherm model to the experimental data suggested that adsorption is taking place both on homogeneous and heterogeneous surface of activated carbons.

4. CONCLUSIONS.

In this work, several glycerol-based carbon materials for the removal of flumequine and tetracycline from aqueous solution have been developed. The obtained activated carbons exhibited high surface area, microporous structure and acidic character. It was found that the increasing in the thermal activation temperature increased both the porosity and the acidity of the

materials, due to the incorporation of new oxygenated functionalities on the carbon surface.

The experimental kinetic data were well-fitted to the pseudo-second order kinetic model, suggesting that chemisorption, e.g., binding interactions, could be occurring.

The adsorption of FLQ was found to be dependent on the textural properties of the carbon materials, with a maximum adsorption capacity of 41.5 mg.g^{-1} onto GBCM₃₅₀ activated carbon. Therefore, TCN adsorption capacities were found to be of 53.9, 51.3 and 58.1 mg.g^{-1} for GBCM₂₀₀, GBCM₃₀₀ and GBCM₃₅₀ materials, respectively. The adsorption of both antibiotics could be well described by Sips isotherm model, confirming that the adsorption process was mainly multilayer. Then the synthesized materials are promising materials for environmental remediation, since they could be used for the removal of other antibiotic and/or organic compounds from water.

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