

HYDROPHOBIC ORGANOSILICA ADSORBENTS FOR REMOVAL OF SODIUM DICLOFENAC FROM AQUEOUS SOLUTIONS*

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Abstract

Micropore organosilicas (MOs) were synthesized using methyl-phenyl-polysiloxane as precursor. The MOs were characterized using several analytical and functional techniques. The materials were assigned as micropores materials, with specific surface area up to 642 m² g⁻¹ and yield up to 72.55%. The adsorbents have hydrophobic surfaces and were used for removal of diclofenac from aqueous solutions. The adsorption kinetic and isothermal data were well described by the general order and Sips models, respectively. Diclofenac exhibited a better affinity than NM and the mechanism of adsorption suggested that hydrophobic groups play a key role in the adsorption process.

Keywords: Methyl-phenyl-polysiloxane; Organosilica adsorbents; Hydrophobic surfaces; Kinetic and isotherm models; Pharmaceuticals adsorption.

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1 INTRODUÇÃO

In the last years, pharmaceutical effluents have caused increasing environmental concerns [1]. The contamination of aquatic systems by drugs may come from domestic sewage and hospitals, where drugs are excreted or discarded, in addition to, pharmaceutical-industry effluents and compounding pharmacies [1]. Therefore, the removal of emerging contaminants is now very important in the production of safe drinking-water and the environmentally responsible release of wastewater [1].

However, it is well known that conventional wastewater treatment and drinking-water treatment processes are not so efficient in the removal of micropollutants, which include pharmaceuticals [1]. Therefore, development of effective methods of removing pharmaceuticals from water becomes very urgent. Membrane filtration, coagulation, advanced oxidation processes (ozonation and oxidation) and adsorption have been proposed for removal the pharmaceuticals from the aqueous media [11]. Although advanced oxidation can be effective for the removal of emerging contaminants, this treatment is frightening due to high costs and the formation of unknown oxidation intermediates compounds [2].

In this context, in last years, many studies have reported the use of the adsorption method for the removal of pharmaceuticals from wastewaters [2]. Adsorption technique is a common one, and represents a cost-effective approach for solving many problems pertaining to treatment of wastewaters [2].

Adsorption is a surface process, where pollutants are transferred from the effluent to a solid phase. One advantage of adsorption technology is that the adsorbents can be regenerated and reutilized. This merit makes this process cheaper [3].

A myriad of adsorbents are in existence, and among the available adsorbents, the activated carbons are prevailing because of their excellent adsorptive characteristics. The adsorptive characteristics of activated carbons could be linked to their enhanced pore structures and higher specific surface area. However, these adsorbents are expensive, must be regenerated on a regular basis, and have poor mechanical strength [3].

In recent times, organosilica-based adsorbents have emerged [4]. Organosilica supports have several advantages with respect to activated carbon—organosilicas have better mechanical stability, they do not swell, they can sustain high temperatures and posses higher concentration of chelating groups on the surface [4]. It is advantageous to use organosilica materials because they are easy to modify, and function in many ways due to the existence of free hydroxyl groups (O–H) on their surfaces, which can be utilized as points of attachment with functional agents [4].

Recently, a few papers using organosilicas as the effective adsorbents for scavenging micropollutants, such as pesticides, heavy metals and dyes [4], have been reported. In this work, we report the synthesis of organosilica-micropores adsorbents under acid conditions using methyl-phenyl-polysiloxane (H44) as precursor. The adsorbents were tested for the removal of sodium diclofenac (DCF) from aqueous solutions.

2 MATERIAIS E MÉTODOS

2.1 Preparation of adsorbents

The raw material used for preparing the adsorbents was the methyl-phenyl-polysiloxane (Silres® H44, Wacker Chemie AG). This precursor was used to prepare four samples. The organosilica-based adsorbents were prepared using this procedure: powdered H44 (15.0 g) was mixed with 100 mL of HCl (2 or 5 mol L⁻¹) in a 250 mL boiling flask, the mixture was magnetically stirred under reflux at 75 °C for 1 hour. The slurry was cooled down and placed in a crucible and dried at room temperature for 2 h. After that, the sample was placed in the pyrolysis furnace at inert atmosphere (N₂ at 100 mL min⁻¹) to produce an adsorbent. Subsequently, the sample was pyrolyzed at 500 or 600 °C for 1 h.

The adsorbent was later cooled down to room temperature under inert atmosphere, milled, sieved to a particle size ≤ 90 mesh and kept properly prior use.

The organosilica-based adsorbents were named on the basis of the conditions of preparation, for instance, H44-500-2M was made using pyrolysis temperature of 500°C and a treatment of 2 mol L⁻¹ HCl. Other adsorbents, H44-500-5M, H44-600-2M and H44-600-5M, were also prepared using the procedure described above.

2.2 Characterization of adsorbents

The adsorbents were analyzed using scanning electron microscopy (SEM) – microscope, model JEOL JSM 6060.

Nitrogen adsorption isotherms were recorded with a commercial system (Belsorp-Mini, Bel Japan Inc.) at -196 °C after drying for 3 h at 120 °C under reduced pressure (< 2 mbar). The specific surface areas were determined with using the Brunauer, Emmett and Teller (BET) method.

The CHN elemental analyses of the adsorbent materials were performed using a CHN Perkin Elmer M CHN Analyzer, model 2400.

The functional groups of the adsorbents were determined using Fourier Transform Infra-Red Spectroscopy with the ATR (Attenuated Total Reflectance) accessory.

Thermogravimetric (TGA) analysis of four micropore organosilicas (MOs) were obtained on a TA Instruments model SDT Q600 with a heating rate of 20 °C min⁻¹ at 100 mL min⁻¹ of synthetic air flow. Temperature was varied from 20 to 1000 °C (acquisition time of 1 point per 5 s) using 10.00–15.00 mg of solid.

For vapor adsorption experiments, the powdered samples were dried in 5 ml glasses at 70 °C for 24 h. The samples were cooled at room temperature in a desiccator before determining the accurate weight (ca. 0.5 g). Storage in an atmosphere of saturated solvent vapor was performed in Erlenmeyer flasks plugged with a ground glass joint, using 60 ml of solvent (water and n-heptane). The powdered samples, inside glasses, were placed in such a way that they were not in contact with the wall of the Erlenmeyer. The samples were removed from the Erlenmeyer flask after 24 h. The weight gain during storage was used to determine the maximal adsorption of the vapor.

2.3 Batch adsorption studies

All solutions were prepared using deionized water. The diclofenac (DCF) was supplied by Sigma-Aldrich and used without purification.

Aliquots of 20.00 mL of 5.00 – 500.00 mg L⁻¹ of DCF were added to 50.0 mL Falcon flat tubes containing 80 mg of adsorbents. The flasks were capped, and placed horizontally in a shaker model TE-240, and the system was agitated between 5–360 min. Afterwards, to separate the adsorbents from the aqueous solutions, the flasks were centrifuged using Fanem centrifuge. The residual solutions of DCF after adsorption were quantified using UV-Visible spectrophotometer at a maximum wavelength of 275 nm.

The amount of DCF adsorbed by the MOs and the percentage of removal were calculated using Eqs. (1) and (2), respectively:

$$q = \frac{(C_o - C_f)}{m} \cdot V \quad (1)$$

$$\% \text{Removal} = 100 \cdot \frac{(C_o - C_f)}{C_o} \quad (2)$$

Where q is the amount of DCF uptake by the adsorbent (mg g⁻¹); C_o is the initial DCF concentration put in contact with the adsorbent (mg L⁻¹), C_f is the DCF concentration (mg L⁻¹) after the batch adsorption experiment, V is the volume of DCF solutions (L) put in contact with the adsorbent, and m is the mass (g) of MO.

2.4 Quality assurance and statistical evaluation of models

All the experiments were carried out in triplicate to ensure reproducibility, reliability and accuracy of data. Blanks were run in parallel and corrected when necessary [1,5]. The solutions of DCF were stored in glass bottles, which were cleaned by immersing in 1.4 mol L⁻¹ HNO₃ for 24 h [1,5], rinsing with deionized water, drying and keeping them in cabinets.

Standard DCF solutions (5.00–50.00 mg L⁻¹), which is in parallel with a blank, were used for linear analytical calibration. The calibration curve was performed on the UV-Win software of the T90+ PG spectrophotometer. All the analytical measurements were repeated thrice, and the precisions of the standards were better than 3 % ($n=3$). Nonlinear methods with successive interactions calculated by the Levenberg–Marquardt method were used to fit the kinetic and equilibrium data. A determination coefficient (R^2), an adjusted determination coefficient (R^2_{adj}) and the F_{error} were employed to analyze the suitability of the models [1,5]. The R^2 , R^2_{adj} and F_{error} are given in Eqs (3), (4) and (5), respectively.

$$R^2 = \left(\frac{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2 - \sum_i^n (q_{i,exp} - q_{i,model})^2}{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2} \right) \quad (3)$$

$$R^2_{adj} = 1 - (1 - R^2) \cdot \left(\frac{n - 1}{n - p - 1} \right) \quad (4)$$

$$SD = \sqrt{\left(\frac{1}{n-p} \right) \cdot \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (5)$$

In these equations, $q_{i,model}$ represents individual theoretical q value predicted by the model; $q_{i,exp}$ represents individual experimental q value; \bar{q}_{exp} is the average of experimental q values; n represents the number of experiments; p represents the number of parameters in the model [1,5].

2.5 Kinetic models

Pseudo-first order, pseudo second-order, general order kinetic and intra-particle diffusion models were used to analyze the kinetic data. The mathematical representations of respective models are shown in Eqs (6), (7), (8) and (9).

$$q_t = q_e \cdot [1 - \exp(-k_1 \cdot t)] \quad (6)$$

$$q_t = q_e \cdot \frac{q_e}{[k_2(q_e) \cdot t + I]} \quad (7)$$

$$q_t = q_e \cdot \frac{q_e}{[k_N(q_e)^{n-1} \cdot t \cdot (n-1) + I]^{1/(1-n)}} \quad (8)$$

$$q_t = k_{id} \sqrt{t} + C \quad (9)$$

More details of the models are described in the references [1,5].

2.6 Equilibrium models

Eqs (10), (11) and (12) represent respective Langmuir, Freundlich and Sips models. These models were used for analysis of equilibrium data.

$$q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (10)$$

$$q_e = K_F \cdot C_e^{1/n_F} \quad (11)$$

$$q_e = \frac{Q_{\max} \cdot K_s \cdot C_e^{1/n_s}}{1 + K_s \cdot C_e^{1/n_s}} \quad (12)$$

More details of the models are described in the references [1,5].

3 RESULTADOS E DISCUSSÃO

3.1 Characterization of the adsorbents

For determination of the surface morphology of the synthesized materials, the adsorbents were comparatively examined using scanning electron microscopy (SEM), and the results are illustrated in Figure 1, SEM images were taken from the surfaces obtained at different temperatures using different acid concentrations. As depicted in Figure 1, all the materials show similar trend—plain and homogeneous surfaces, irregular particles powders, and sizes on the micrometer scale. It seems that the temperature values and acid concentrations have no influence on the textural surface characteristics.

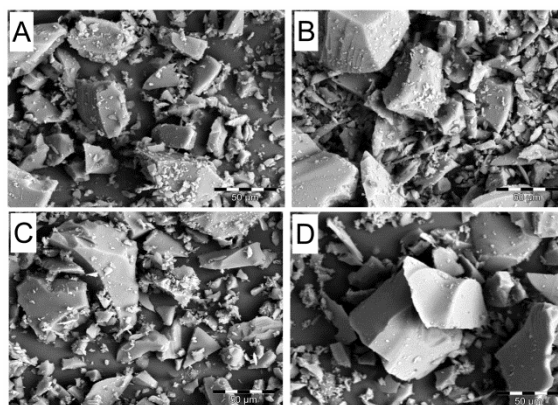


Figura 1. SEM images.

For N_2 isotherms, all samples are assigned to be a type I isotherm according to IUPAC classification. Type I is typical of many microporous adsorbents (pore widths below 2 nm) [6]. However, it should be noted that the adsorbed N_2 volumes are different (see Figure 2), depending on the conditions of preparation of the adsorbents.

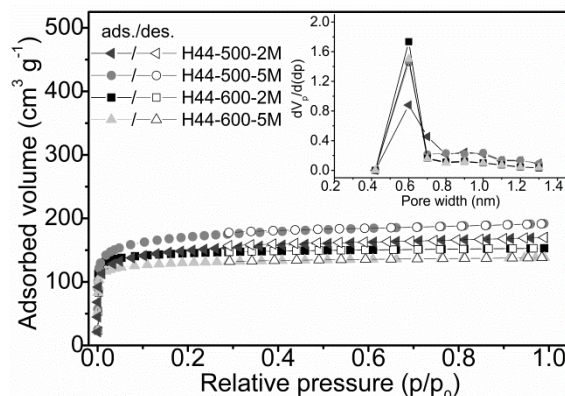


Figura 2. N_2 isotherms of the MOs.

It is also shown in Figure 2 that the volume of N_2 adsorbed increased gradually from H44-600-5M ($138 \text{ cm}^3 \text{ g}^{-1}$), H44-500-2M ($152 \text{ cm}^3 \text{ g}^{-1}$), H44-600-2M ($169 \text{ cm}^3 \text{ g}^{-1}$) to H44-500-5M ($191 \text{ cm}^3 \text{ g}^{-1}$). When the relative pressure P/P_0 was about 0.10, the adsorption of N_2 was saturated, and when $P/P_0 > 0.10$, N_2 began to be adsorbed onto the large pores or on the external surface, but the amount was very small.

All samples possess micropores (diameters $< 2 \text{ nm}$) [6] as illustrated in the MP plots (see Figure 2), which are agreement with the values shown in the Table 1. Perusing through the Table 1, the highest specific surface area (S_{BET}) is exhibited by the sample H44-500-5M ($642 \text{ m}^2 \text{ g}^{-1}$), and thus has the highest pore volume ($0.2857 \text{ cm}^3 \text{ g}^{-1}$). The lowest values is obtained for the sample H44-600-5M (see Table 1) which is an evidence that the pyrolysis temperature has influence on surface characteristics.

Table 1. Textural characteristics of the adsorbents obtained by BET method, and their yields

Samples	H44-500-2M	H44-500-5M	H44-600-2M	H44-600-5M
Parameters				
S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	545	642	565	505
V ($\text{cm}^3 \text{ g}^{-1}$)	0.252	0.285	0.233	0.210
Pore size (nm)	1.84	1.78	1.64	1.66
Yield (%)	72.55	64.00	60.30	57.10

The structural heterogeneity and solid internal structure can be represented by characterization of the pore size distribution [6]. The pore size distribution, through of MP plots of the samples are also shown in Figure 2, it appears that pyrolysis conditions do not have effect on the pore structure of the adsorbents and all samples show sharp peak in the range of wide homogeneous micropores. The average size of the pores ranged from 1.64 to 1.84 nm.

In terms of the yield of adsorbents, the yield increased gradually from H44-600-5M (57.1%), H44-600-2M (60.3%), H44-500-5M (64.0%) to H44-500-2M (71.8%) (See Table 1). It is seen that samples pyrolyzed at same temperature but different acid concentrations; the yield decreased, slightly with the increasing of the acid concentration, from 71.8 to 64.0% for H44-500-2M and H44-500-5M, respectively. The same trend was observed for the samples pyrolyzed at 600 °C; the yield also decreased from 60.3 to 57.1% for H44-600-2M and H44-600-5M, respectively. Regarding the influence of temperature, it is seen that samples pyrolyzed at 600 °C gave yields, which are somewhat lower than those pyrolyzed at 500 °C.

The surface characteristics of adsorbents are underlying factors for understanding the interactions between adsorbents and adsorbates. Solvent vapors of different polarities and sterical extents were used to characterize the surface of the adsorbents [50] prepared in this work—as shown in Figure 3 for selected materials. Figure 3 shows the adsorption values of water and *n*-heptane ratio. For the four samples, the uptakes of *n*-heptane were higher than the uptakes of water; it infers that the organosilica-adsorbents possessed more hydrophobic surfaces.

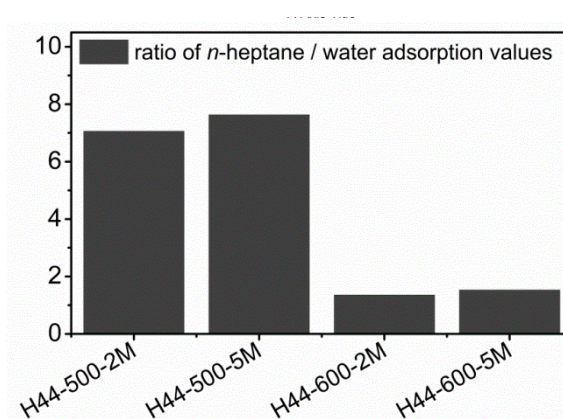


Figure 3. Maximal adsorption of water and *n*-heptane vapors at 25 °C for materials prepared from H44 and HCl, and pyrolyzed at 500°C and 600°C.

The samples pyrolyzed at 500 °C (H44-500-2M and H44-500-5M) presented much higher uptake of *n*-heptane than water uptake compared with samples pyrolyzed at 600 °C, thus it can be inferred that the samples pyrolyzed at 500 °C are more hydrophobic. Higher temperature can influence the surface characteristics with regards to hydrophobicity, a possible explanation for this could be linked to the fact that at 500 °C the organic content of the samples are higher than those samples pyrolyzed at 600 °C; this can be easily seen in the CHN analysis (see Table 3). In contrast, the concentration of the acid did not significantly affect the hydrophobicity of the surfaces, as shown in the Figure 3 despite temperature variation. For instance, H44-600-2M and H44-600-5M gave similar ratio of *n*-heptane/water adsorption. The same behavior was observed for samples pyrolyzed at 500 °C. However, samples pyrolyzed at different temperatures and same acid concentration, such as H44-500-2M and H44-600-2M, showed different values of uptake ratio.

The FTIR spectra of H44-500-2M, H44-500-5M, H44-600-2M and H44-600-5M are presented in Figure 4. Considering that the FTIR spectra of the MOs were obtained by ATR-FTIR technique, which gives the possibility the comparing the intensities of vibrational bands among the FTIR spectra, it is clear that the adsorbents prepared at 500 °C present higher contents of organic pendant groups (CH₃ and C₆H₅) compared to the adsorbents prepared at 600 °C. This observation is consistent with the data in Figure 3, where the materials prepared at 500 °C present higher hydrophobicities than those prepared at 600 °C. The FTIR band assignments are made inside the graphs of Figure 4 [1,5].

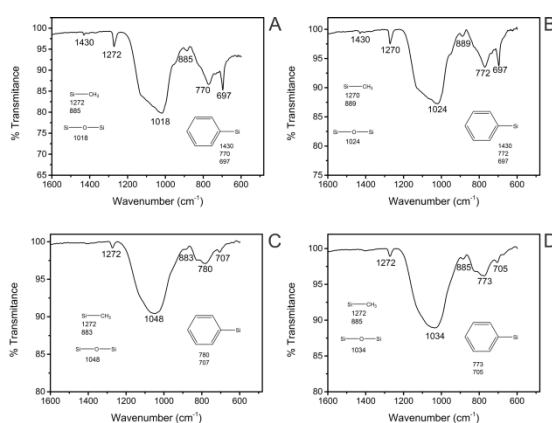


Figure 4. FTIR vibrational spectra of **A:** H44-500-2M; **B:** H44-500-5M; **C:** H44-600-2M; **D:** H44-600-5M. Numbers are vibrational FTIR bands in cm⁻¹.

The data of CHN analysis of the adsorbents are presented on Table 2. The hybrid materials prepared at 500 °C present higher carbon contents than those prepared at 600 °C. These results reinforce the FTIR data previously discussed, and the n-heptane/water vapor adsorption data. The H44-500-2M and H44-500-5M possessed higher organic contents that result in higher hydrophobicities of the adsorbents. On the other hand, the H44-600-2M and H44-600-5M have higher silicate contents, which explain lower n-heptane/water ratio.

Table 2. Elemental composition of adsorbents

Sample	%C	%H	%N
H44-500-2M	37.98	3.54	0.0
H44-500-5M	31.62	3.80	0.0
H44-600-2M	27.33	2.63	0.0
H44-600-5M	26.51	2.71	0.0

Figure 5 shows the thermogravimetric curves in air. One-stage weight loss can be observed in the curves. In general, all MOs exhibit similar thermogravimetric profiles. Below 500 °C, there is no significant mass loss. The mass loss of the MOs was observed within the range of 490 to 680 °C. Between 490 and 680 °C, the weight loss was ascribed to the abscission of methyl and phenyl groups.

Compare the thermogravimetric data with that of CHN analysis (Table 2), it is observed that the final weight loss is in line with theoretical calculation value based on the CHN analysis. Going by the Table 2, the samples with higher carbon contents have higher weight loss, for instance H44-500-2M with highest carbon content gives highest weight loss follow by H44-500-5M, H44-600-2M and H44-600-5M.

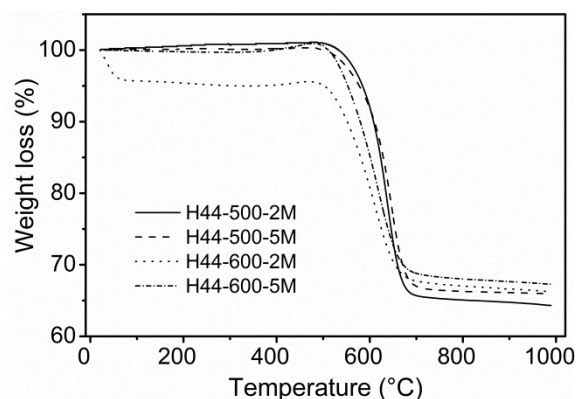


Figure 5. TGA curves of the organosilica adsorbents.

3.2 Kinetic studies

Table 4 shows the results of kinetic experiments performed to determine the equilibrium time required for the uptake of DCF by H44-500-5M adsorbent. The curves at 25 °C were obtained by plotting the DCF uptake capacity versus time at 50 mg L⁻¹ of initial DCF. Nonlinear pseudo-first order, pseudo-second order and general order kinetic models were used. An error function, F_{error} , was used to validate the fit of the experimental data since our experimental data were subjected to nonlinear kinetic models.

Table 3. Kinetic parameters of DCF adsorption onto H44-500-5M. Conditions: temperature, 25 °C; pH, 8.0; mass of adsorbent, 80.0 mg

H44-500-5M	
	DCF
Pseudo-first order	
k_f (min ⁻¹)	2.419×10^{-2}
q_e (mg g ⁻¹)	14.51
h_0 (mg g ⁻¹ min ⁻¹)	0.3514
R^2_{adj}	0.9309
F_{error} (mg g ⁻¹)	1.248
Pseudo-second order	
k_s (g mg ⁻¹ min ⁻¹)	2.20×10^{-3}
q_e (mg g ⁻¹)	16.05
h_0 (mg g ⁻¹ min ⁻¹)	0.5231
R^2_{adj}	0.9661
F_{error} (mg g ⁻¹)	0.9232
General order	
k_N [h ⁻¹ (g mg ⁻¹) ⁿ⁻¹]	4.39×10^{-2}
q_e (mg g ⁻¹)	15.821
N	1.122
h_0 (mg g ⁻¹ min ⁻¹)	0.9724
R^2_{adj}	0.9789
F_{error} (mg g ⁻¹)	0.7024

The general order kinetic model gave lowest F_{error} values. The pseudo-first order kinetic model present F_{error} values of 1.25 and 0.21 for DCF. For the pseudo-second

order model, the respective F_{error} values are 0.92 and 0.38. The lower the error function, the lower the difference between the q calculated by the model and the q measured experimentally [1,5]. In this context, it is noted that the q_e values of the general order kinetic model are closer to the experimental q_e values compared to other kinetic models. These results indicate that the general order kinetic model best explains the adsorption process of DCF using H44-500-5M adsorbent.

Taking into account that the general order kinetic equation requires different values for n (order of adsorption) when the concentration of the adsorbate is changed, it is difficult to compare the kinetic parameters of the model.

In order to continue this work, the contact time between the MOs and DCF was fixed at 240 min to guarantee that the equilibrium would be attained.

3.3 Equilibrium studies

The adsorption isotherms express the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Three isotherm models, Langmuir, Freundlich and Sips models, were used to fit to the experimental data and evaluate the isotherm performance for DCF and NM adsorption.

The isotherms of adsorption of DCF on H44-500-2M, H44-500-5M, H44-600-2M and H44-600-5M adsorbents were performed using the following experimental conditions: pH 7.0, contact time of 240 min, mass adsorbent dosage of 4.0 g/L, and temperature was fixed at 25 °C. The isotherms fitting parameters are in Table 5. On the basis of F_{error} values, the Sips model is the best isotherm model for adsorption of DCF onto the four adsorbents. The Sips model presents the lowest values for F_{error} , which means that the values of q calculated by the isotherm model was similar to the q measured experimentally.

Table 4. Isotherm parameters for DCF adsorption using H44-500-2M, H44-500-5M, H44-600-2M and H44-600-5M. Conditions: pH 8.0; adsorbent mass, 80.0 mg; contact time, 240 min

	H44-500-2M	H44-500-5M	H44-600-2M	H44-600-5M
DCF				
Langmuir				
Q_{max} (mg g ⁻¹)	33.87	45.83	41.42	31.89
K_L (L mg ⁻¹)	0.02732	0.04424	0.03872	0.02565
R^2_{adj}	0.9818	0.9853	0.9835	0.9771
F_{error} (mg g ⁻¹)	2.346	1.792	1.879	1.690
Freundlich				
K_F (mg g ⁻¹ (mg L ⁻¹) ^{-1/n_F})	4.881	8.744	7.284	4.447
n_F	3.077	3.454	3.335	3.056
R^2_{adj}	0.8853	0.8284	0.8467	0.8647
F_{error} (mg g ⁻¹)	3.854	6.133	5.737	3.986
Sips				
Q_{max} (mg g ⁻¹)	32.08	43.14	37.34	29.43
K_g (L mg ⁻¹)	0.03124	0.05138	0.04666	0.03064
n_L	0.8597	1.2301	0.6663	1.2735
R^2_{adj}	0.9870	0.9892	0.9972	0.9865
F_{error} (mg g ⁻¹)	1.193	1.532	0.7713	1.441

On the other hand, the Freundlich model presents the highest F_{error} , which indicates that the model is not suitable for the description of removal of DCF onto organosilicas in this work.

4 CONCLUSION

The microporous organosilica adsorbents were successfully synthesized using methyl-phenyl-polysiloxane (H44) as precursor. The H44 was pyrolyzed at 500 or 600 °C, and treated with 2 or 5 mol L⁻¹ HCl and refluxed for 4 h to obtain samples named H44-500-2M, H44-500-5M, H44-600-2M and H44-600-5M. The applicability of the adsorbents for the removal of diclofenac and nimesulide was investigated.

The samples were analyzed using vapors of different polarity for surface characteristics, BET surface area, SEM analytical technique, FTIR vibrational spectra, and CHN elemental analysis. All samples were assigned as microporous materials with observed S_{BET} values up to 642 m² g⁻¹. Water and *n*-heptane could be used to categorize the surface characteristics into either polar or dispersive interaction. The materials were proven to be hydrophobic according to the ratios of *n*-heptane and water adsorption values. These ratios were in agreement with the content of organic groups present on the organosilica materials as shown by CHN elemental analysis and the ATR-FTIR analysis.

The general order kinetic model and Sips isotherm model best described the adsorption of DCF onto the organosilica adsorbents. The Q_{max} values (maximum amounts) of DCF adsorbed was 45.83 mg g⁻¹ onto H44-500-5M.

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