

Prediction of Siloxane Adsorption in Activated Carbons by Molecular Simulation

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Abstract

Siloxanes are organosilicon compounds produced from the anaerobic digestion of materials found in domestic sewage and solid waste that contain silicon, such as cosmetics, soaps, and paints. These compounds are also present in biogas generated from landfills and sewage treatment plants. When biogas containing siloxanes is combusted, the siloxanes are converted into silica deposits, which can cause significant damage or failure of equipment. The most commonly used method to remove siloxanes from biogas is adsorption on activated carbon, which effectively retains the siloxane particles, thereby purifying the biogas. In our study, we employed molecular simulation to predict the adsorption capacity of siloxanes on three different activated carbons. Using a methodology based on representative pores, we successfully estimated the adsorption behavior of siloxanes on these carbons. Our predictions achieved an accuracy with an error margin of less than 8%.

Keywords: Activated Carbon; Siloxane; Molecular Simulation; Representative pores

1. Introduction

The use of biogas from sewage treatment is a sustainable and viable alternative for the production of renewable energy [1]. However, the presence of contaminants, such as siloxane, can cause problems in equipment and systems that generate energy from biogas.

Siloxane is a volatile organic compound that can be found in biogas in different physical states, and can cause problems such as the formation of solid deposits on the internal surfaces of equipment. Therefore, the removal or reduction of siloxanes is usually necessary to prevent damage and ensure the proper functioning of the systems. The siloxane concentration in biogas varies greatly and can go up to 140 mg·m⁻³. This concentration is far beyond the limits required by the engine manufacturers (5–28 mg·m⁻³ for internal combustion engines). The adsorption of siloxanes on activated carbon (AC) is the most widely used technique for removal of siloxanes from biogas. In standard conditions (room temperature, atmospheric pressure) ACs exhibit varying adsorption capacities depending on siloxane molecules, for example, 20 to 225 mg D4 (octametilclotetrasiloxano)·g⁻¹(sorbent) [2].

The prediction of siloxane adsorption in activated carbons can be performed from molecular simulation using the Monte Carlo method.

The main objective of this work is to study the adsorption of siloxane on commercial *Activated Carbons* (CAs) through molecular simulation. Using the characterization methodology with N₂ at 77K by representative pores[3] we were able to predict the maximum adsorption capacity of siloxanes in different activated carbons.

2. Molecular Simulation

The simulations of adsorption isotherms in microporous were performed using the Monte Carlo algorithm in Gran Canonic Ensemble (GCMC) [4]. This method allows a direct calculation of phase equilibrium. The interactions among the molecules were computed using the Lennard-Jones (LJ) potential:

$$U(r) = -4e \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right] \quad (1)$$

where ϵ and σ are the energetic and geometric parameters of LJ potential, and r is the distance between the particles.

The Siloxane molecule was used octametilclotetrasiloxano (D4) because it is the highest concentration of siloxane found in biogas from sewage treatment plants (ETE). The model of the molecule was obtained from the website PubChem[5].

The adsorption of Siloxane in slit-like micropores was investigated by GCMC simulations[6] because this method allows a direct calculation of the phase equilibrium between a gaseous phase and an adsorbate phase.

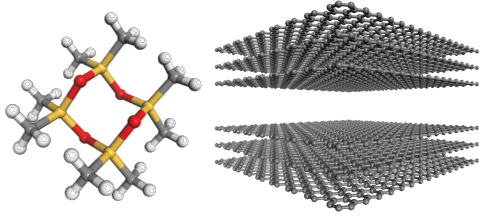


Figure 1 – a) Siloxane molecule D4, b) Pore of 8.9 Å.

The optimization of the D4 molecule was done using the DFT method, the B3LYP functional combined with double numerical base sets containing polarization functions (DNP).

The parameters of Lennard ones used in adsorption are shown in table 1.

Table 1 - Force field parameters [7]

Atom	D0/(kcal/mol)	R0/Å
Si	0.402	4.295
O	0.060	3.500
H	0.044	2.886
C	0.105	3.851
C	0.062	3.786

2. 1 Representative pore model

Representative pores are extracted from N₂ characterization at 77 K to take advantage of the broad base of experimental isotherms in the literature. In this study, we will use 4 pores (7, 8.9, 18.5 and 27.9 Å)

The Pore Size Distribution representative (PSDrep) were determined using an set of representative pores isotherms. The PSD_{rep} [8] was obtained solving Equation 2 by introducing regularization Method[9]. The integral equation of adsorption isotherm for PSD_{rep} can be write:

$$Q(P) = \int dH q(P_i, H) f_{RP}(H) \quad (2)$$

where Q(P) is the total adsorbed amount per gram of adsorbent at pressure P (experimental isotherm), q(P, H) is a function that represents the adsorption isotherm for an material characterized by

pores with size H, f_{RP}(H) is a PSDrep. The PSDrep is obtained through of deconvolution of Eq. 2 using the experimental isotherm and the kernel of simulated isotherms. Once our PSD_{rep} is determined it is possible to determine the theoretical isothermal capacity (Q_{theoretical}) of Siloxano isotherm for each carbon. Q_{theoretical} is estimated based on PSD_{rep} and the simulated adsorbed amount of each component (equation 4).

$$Q(P_i, T) = \sum_{Hmin}^{Hmax} \rho_{RP}(H, P_i, T) f_{RP}(H) \delta H \quad (3)$$

The ρ_j(H,P_i,T) is the simulated local isotherms database to the component j (Siloxane) and f_{RP}(H) represents the PSDrep [3].

3. Results

2. 1 Pore Size Distribution Representative

The activated carbon isotherms AP4, STiX and 207C, were obtained by Tran et al 2019 [2]. After calculating the representative PSD, the pore volume for each pore size is obtained, the PSDreps obtained for each of the three carbons studied (figure 2) and the volumes of each pore in the construction of the PSDrep are shown in the table 2.

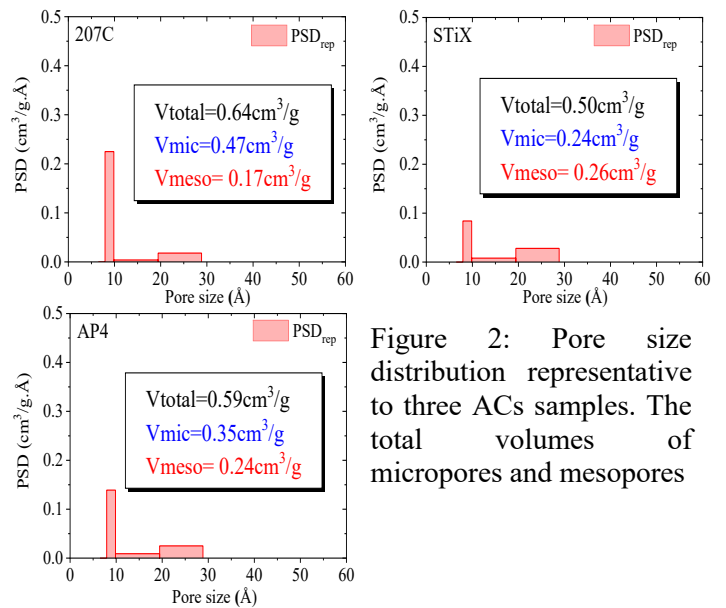


Figure 2: Pore size distribution representative to three ACs samples. The total volumes of micropores and mesopores

From these PSDrep data we can observe that the activated carbon 207C is the most microporous while the other two carbons have a more developed mesoporosity, it is expected that the adsorption capacity of the STiX and AP4 carbons is similar because they have similar representative pore volumes. From the analysis of N₂ at 77K it was not detected volumes in the pore region of 7.0Å, in future

works we will add analysis with CO₂ at 273K, for a better reading of the ultramicropore region, in this work we focus on the characterization with N₂ at 77K.

Tabela 2 - Activated Carbons PSDs.

Sample	PSD _{rep} (cm ³ /g)			
	7.0 Å	8.9 Å	18.5 Å	27.9 Å
207C	0	0.4275	0.0384	0.1692
STIX	0	0.1596	0.0768	0.2632
AP4	0	0.2641	0.0864	0.235

2. 2 - Siloxane isotherms

When we examine the number of siloxane molecules adsorbed (Figure 3) in the representative pores, an intriguing observation emerges, as noted by Hamelink et al. (1996)[10] and confirmed by our molecular simulation results. Due to the cross-sectional molecular size of the D4 molecule, which measures 1.08 × 1.03 nm, the D4 molecule is unable to be adsorbed by pores smaller than 10 Å. This means that pores with sizes of 7.0 and 8.9 Å cannot adsorb the D4 molecule, a finding clearly reflected in the adsorption isotherms we obtained.

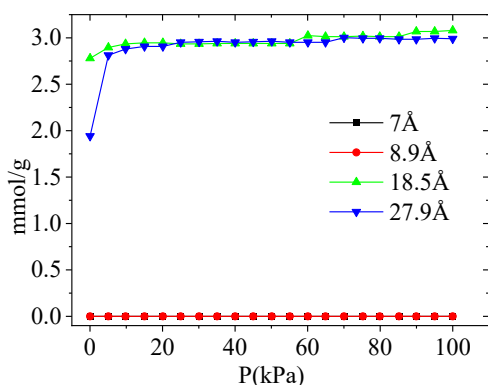


Figure 3 – a) Siloxane adsorption isotherms in representative pores

2. 3 Adsorption capacity of Siloxane

When analyzing the results of maximum adsorption capacity obtained (figure 4), the STIX and AP4 samples showed very similar adsorption capacities, this occurs because the PSDs of STIX and AP4 are very similar, as well as the total volume of pores and the proportion of mesopores present in the samples. The 207C sample showed a lower adsorption capacity, this is due to the fact that it is a more microporous sample compared to the other two

samples, and as previously mentioned the siloxano D4 it cannot be adsorbed by pores smaller than 1 nm, so a large portion of the micropore volume of 207C cannot adsorb the D4 molecule.

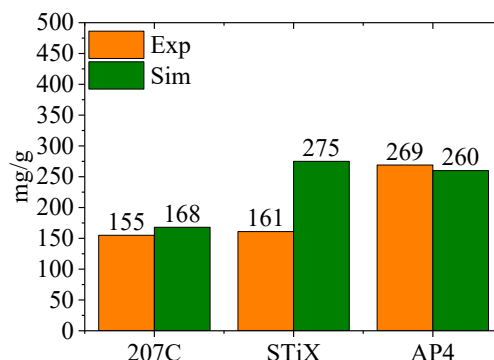


Figure 4 – Adsorption capacity of Siloxane, experimental and simulation: 207C, STiX and AP4

When comparing the simulated adsorption capacities with the experimental data, we find that the predictions for the 207C and AP4 samples are quite satisfactory, as the simulated values closely to experimental results. However, there was a discrepancy between the simulated result of the STiX sample and the experimental data, this was possibly due that the N₂ characterization isotherms at 77K, obtained from Tran et al 2019 [2], were presented in a linear manner (Figure 5), with lacking resolution at low pressures, which may have influenced the PSD of the STiX sample.

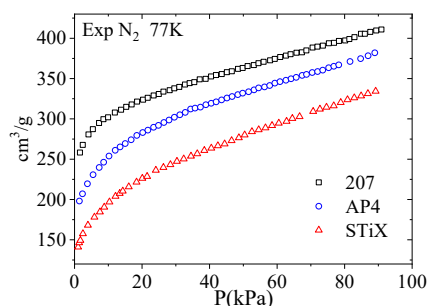


Figure 5 – a) Experimental adsorption isotherms of N₂ at 77K .

2. 3 Adsorption capacity of Siloxane on other activated carbons.

Following the methodology previously applied, the PSDs were obtained based on the representative pores for the two proposed activated carbons, the result of which can be seen in the table 3.

Tabela 3 – Activated Carbons PSDrep

Sample	PSDrep (cm ³ /g)			
	7.0 Å	8.9 Å	18.5 Å	27.9 Å
WV1050	0	0.124	0.312	0.645
Maxsorb	0	0.269	0.791	0.63

It can be observed (figure 6) that the two activated carbon samples have pore volumes much higher than the previously studied samples, so it is expected that the adsorption capacity will be high. Both WV1050 and Maxsorb indicate a high adsorption capacity of siloxanes.

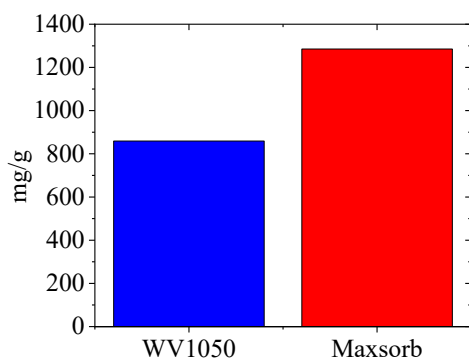


Figure 6 – Adsorption capacity of Siloxane, simulation: WV1050 and Maxsorb

4. Conclusions

In the present study, it was demonstrated that the use of representative pores in the characterization of activated carbons proved to be an efficient approach, providing cost reduction and preserving the reliability of the results, in addition to reducing the time required to obtain the desired data. The results obtained from the theoretical models were consistent and, although the STIX sample presented some divergence, a satisfactory approximation of the values of maximum adsorptive capacity for activated carbons was observed.

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