Prediction of Chlorophenols Adsorption on Activated Carbons By Representative Pores Method

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Abstract

The specification of a particular activated carbon adsorbents for removal of phenol and related derivatives, from dilute aqueous solutions, is still based on lengthy trial and error experimental tests. A predictive model of adsorption of these compounds would considerably reduce the carbon selection time and could also bring new information to support more efficient carbon synthesis. The use of molecular simulation and the methodology of representative pores, proved to be adequate for quantitative prediction of phenol adsorption. Here the methodology is being extended to chlorophenols, an important class of phenol-derived pollutants. A set of ortho and para-chlorophenol isotherms were simulated for different representative pores in order to predict carbon adsorption and determine the most significative pore size. At low concentrations (1x10^{-4} \text{ mol/L}), the pores of 8.9 and 18.5 Å are the most effective. For concentrations above 3 x10^{-4} \text{ mol/L} pores in the range of 27.9 Å must be present in the activated carbon. The adsorption isotherm difference between ortho and para-chlorophenol, identified experimentally, was reproduced in the simulation and its origin was investigated further. Finally, the adsorption isotherms of chlorophenols for other activated carbons were predicted with the help of the model.

Introduction

Chlorophenolic compounds are part of a group of pollutants often associated with unwanted scenarios of environmental contamination (Häggblom and Bossert 2003). The widespread use of chlorophenols in the production of fertilizers, biocides, medicines and paints, in addition to the generation of industrial and landfill waste, transfers part of these contaminants to water, soil and food chains. The majority of known environmental exposures are for surface water being classified as priority pollutants (ATSDR 2021).

Despite the usefulness and applications of these chemicals, the deleterious ecotoxicological effects to a variety of organisms are highlighted. Some of the outcomes in the health assessment parameters observed in laboratory animals exposed to chlorophenols after oral administration were effects on the liver, central nervous system, body weight, immune system and reproductive function. (ATSDR 2021). The need to reduce the entry of toxic compounds into the environment and to study methods for their removal from contaminated sites remains relevant (Olaniran and Igbinosa 2011). Adsorption is a method with many advantages over other methods due to its low investment and operating cost, ease of operation, simplicity and flexibility in design and efficacy and versatility in a variety of adsorption processes (Hadi et al. 2021). Adsorption on activated carbon, a nanoporous materials that has low production cost and abundance of raw materials (Gryglewicz et al. 2002; Marsh and Rodriguez-Reinoso 2006) is a first choice for the removal of organic pollutants in water (Wang et al. 2020).

The adsorption on activated carbons has been thoroughly studied by molecular simulation method (Vishnyakov et al. 1999; Ravikovitch et al. 2000; Blanco et al. 2010; Oliveira et al. 2011; Lucena et al. 2017; Soares Maia et al. 2018). The main reference kernels for a good characterization is obtained using N_2, Ar or CO_2 as probe molecules and they are all based in this technique (Frenkel et al. 1996). The molecular simulation of super diluted solutions of organic compounds, present huge obstacles because
we do not have consistent vapor pressure data to apply the Monte Carlo method in the grand canonical ensemble and the low concentration of the solute impair the use of molecular dynamics.

In a previous study (Galdino et al. 2021), our group applied molecular simulation associated with the representative pore methodology (de Oliveira et al. 2021) to analyze the adsorption of dilute aqueous phenol solutions. In that study, simulated isotherms quantitatively reproduced the experimental adsorption of phenol on activated carbon NCB-8h (styrene-divinylbenzene copolymer) (Kowalczyk et al. 2018). We also observed that other phenol related compounds could benefit from the same technique for predicting adsorption isotherms. Here, our study aims to extend the technique to two phenol derivatives: o-chlorophenol and p-chlorophenol. These phenolic species were chosen because their experimental isotherms present an interesting adsorption delay, with o-chlorophenol adsorbing more than p-chlorophenol in a large range of the low concentration values in the aqueous solution (Gryglewicz et al. 2002).

Thus, we present the predicted individual adsorption isotherms of o- and p-chlorophenol for selected representative pores (Lucena et al. 2013; Aguiar et al. 2016; Gonçalves et al. 2018), in the micropores and mesopores range sizes. We validated the results by comparing our simulation with experimental data, and identified the origin of the uptake difference between o- and p-chlorophenol. Finally, we estimated the adsorption capacity of the studied chlorophenols on a set of others activated carbons, carefully characterized for the pore size distribution.

Methods

Among the models proposed in the literature for activated carbon (Do and Do 2006; Lucena et al. 2008, 2017; Nguyen et al. 2008; Oliveira et al. 2011), we choose the most used model. The molecular representation of activated carbon is then defined as slits of graphene layers walls. The simulation box is built with graphene walls of 40 x 40 Å (Figure 1c). For the chlorophenols molecules, we implement the atom-atom model from Rai and Siepmann, 2013 (Figure 1a and 1b), for a better description of the interaction in both aromatic ring and hydroxy group.

The Monte Carlo algorithm in grand canonical ensemble (GCMC) (Allen and Tildesley, 1987; Frenkel, Smit, et al., 1996) was applied in the calculation of the adsorption isotherms of o-chlorophenol and p-chlorophenol in the selected pores. The GCMC method is one of the most used in the adsorption studies and allows a direct calculation of phase equilibrium (Nicholson and Parsonage 1982). The interactions among the molecules were computed using the Lennard-Jones (LJ) potential:

\[
U_{gg}(r) = -4\epsilon_{gg} \left[ \left( \frac{\sigma_{gg}}{r} \right)^6 - \left( \frac{\sigma_{gg}}{r} \right)^{12} \right]
\]
where $\varepsilon_{gg}$ and $\sigma_{gg}$ are the energetic and geometric parameters of LJ potential, respectively, and $r$ is the distance between the particles. The electrostatic interactions were also computed. The Table 1 shows all the parameters used in the simulation.

Table 1
The Lennard-Jones parameters and charges used in the simulations. For atom references, see figure 1 (Rai and Siepmann 2013).

|        | $\varepsilon$(kcal/mol) | $R_0$(Å) | Cargas OCP(e) | Cargas PCP(e) |
|--------|--------------------------|----------|---------------|---------------|
| C1     | 0,07                     | 3,9845   | +0,149        | 0,137         |
| C2     | 0,07                     | 3,9845   | -0,065        | -0,241        |
| C3     | 0,07                     | 3,9845   | -0,100        | -0,093        |
| C4     | 0,07                     | 3,9845   | -0,181        | -0,074        |
| C5     | 0,07                     | 3,9845   | -0,101        | -0,097        |
| C6     | 0,07                     | 3,9845   | -0,244        | -0,175        |
| H      | 0,000                    | 0,000    | +0,432        | 0,431         |
| H2     | 0,03                     | 2,7162   | 0,157         | 0,158         |
| H3     | 0,03                     | 2,7162   | 0,154         | 0,167         |
| H4     | 0,03                     | 2,7162   | +0,159        | 0,17          |
| H5     | 0,03                     | 2,7162   | +0,170        | 0,176         |
| O      | 0,17                     | 3,5      | -0,486        | -0,495        |
| OCP    | 0,03                     | 3,8116   | -0,043        | -             |
| PCP    | 0,03                     | 3,8116   | -             | -0,064        |
| C*     | 0,0497                   | 3,8162   | -             | -             |

C* - graphene carbon.

The kernel of chlorophenol isotherms were calculated at 298 K for three pore sizes (8.9, 18.5 and 27.9Å). The Pore Size Distribution (PSD) of the carbons, except for the AGL3 carbon, were determined using an entire set of N$_2$ isotherms. After, representative pore volumes are assigned. This methodology of representative pores was used and validated in previous study reported in literature (Aguiar et al. 2016; Gonçalves et al. 2018). The integral equation of adsorption isotherm for PSD can be written as:

$$Q(P) = \int q(P, H)f(H) dH$$
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 a material characterized by pores with size $H$, $f(H)$ is a PSD. The Monte Carlo steps used were $2 \cdot 10^6$ for equilibrium and $1 \cdot 10^6$ for production. The value of cutoff ($r_{\text{cutoff}}$) was 12.5 Å. For a cutoff above 12.5 Å the energy values no longer change and there is an increase in computational cost, thus we decided to keep the value of 12.5 Å, also used by other authors in similar systems (Yang and Zhong 2006; Bae et al. 2008; Lucena et al. 2013). The PSD is obtained through deconvolution of Eq. 2 using the experimental isotherm and the kernel of simulated isotherms (Lucena et al. 2010).

**Results And Discussion**

**Chlorophenol adsorption in individual pores**

In figure 2 we show the representative pore adsorption isotherms for both ortho-chlorophenol (OCP) and para-chlorophenol (PCP). We observed that the pore filling occurs abruptly and at low concentrations for the pores of 8.9 and 18.5 Å. In the larger pore of 27.9 Å the filling occurs more smoothly.

Adsorption discrepancies between the two species of chlorophenols already appear in the 18.5 Å pore with a small delay in pore filling for the PCP molecule. The difference in uptake is amplified considerably for the 27.9 Å pore. This same uptake difference in the adsorption of the two chlorophenols was experimentally observed (Gryglewicz et al. 2002). To investigate this discrepancy in the adsorption isotherms, we perform a calculation of the angular distribution of the dipole moment of the chlorophenol molecules in the 27.9 Å pore for similar loading (figure 3). The results show that OCP has a preference for angles close to 90° which means that the molecule is parallel to the carbon surface in the face-to-face conformation. This conformation has two consequences: it maximizes the fluid-fluid interaction allowing for faster filling from the pore to the same time that it optimizes the packaging of molecules. For the same loading, the PCP has a smaller number of molecules in the face-to-face position (less than the 90° angle), this distribution of configurations reduces both the molecule-molecule interaction and the packing. These two factors result in delayed pore filling and decrease in uptake for PCP.

**Predicting Chlorophenol Adsorption In Carbons**

As previously mentioned, the experimental isotherm of Gryglewicz et al., 2002 will be used to validate the simulation. In this study, the authors evaluated the adsorption of chlorophenols on AGL3 activated carbon, highlighting the differences in the adsorption regime for OCP and PCP molecules. In figure 4, we present the pore size distribution (PSD) for the AGL3 carbon, obtained in the experimental study. This distribution was used to allow the evaluation of the respective volumes corresponding to each of the representative pores of 8.9, 18.5 and 27.9 Å. We emphasize that the representative pore methodology, extract the pore sizes distribution from a detailed $N_2$ isotherm at 77 K of the material. As we do not have a detailed $N_2$ isotherm for carbon AGL3, the volumes were determined only from the PSD presented by Gryglewicz et al., 2020.
Knowing the volume corresponding to each pore, together with the pore isotherms presented in figure 2, and using equation 2, we can estimate the adsorption isotherms of chlorophenols for the entire activated carbon (figure 5).

In our previous study with phenol (Galdino et al. 2021), it was possible to correlate the pore pressure with the vapor pressure values estimated by Henry's Law constant.

\[ P_{i,G} = H_{pc} \times C_{i,L} \]

where \( C_{i,L} \) and \( P_{i,G} \) are the concentrations of the solute in the liquid and in the gas phases, respectively, and \( H_{pc} \) is the Henry's Law constant (HLC). Unfortunately, for chlorophenols, it was not possible to identify an estimate of \( H_{pc} \) obtained by the liquid-liquid chromatographic method, with underlying phenomenology similar to the adsorption on activated carbons. In addition, the literature presents ranges of values with variations of the order of magnitude of 10^2, as evidenced by Sander, 2015. From the reconstituted isotherms, we estimated the \( H_{pc} \) values to be 33 and 16 kPa L/mol for the OCP and PCP molecules, respectively.

We obtained a good agreement between the experimental and simulated isotherms. The maximum adsorption capacity obtained by simulation is compatible with that determined experimentally. The smaller uptake for the PCP molecule was qualitatively reproduced. The disagreement between the predicted and the experimental adsorption for low concentrations, which did not identify a delay in the adsorption of p-chlorophenol, may be related to the difficulty of the experimental finite bath method to adequately measure very low concentrations. This value is obtained from the difference between the concentration of the initial solution and the concentration after adsorption, which is extremely sensitive to the analytical method used.

To demonstrate the versatility of the methodology, we estimate the adsorption isotherm for chlorophenol at 298 K on the commercial carbons WV1050, Maxsorb, NORIT-RB4 (Figure 6) and the PC series of carbon (Figure 7) that are produced from PET polymer and are neutral and without heteroatom species (Ania et al. 2007). The volumes of representative pores of each carbon are presented in Table 2.
Table 2

Pore volume attributed to each representative pore for the activated carbons investigated

| Sample    | 8.9 Å (cm$^3$/g) | 18.5 Å (cm$^3$/g) | 27.9 Å (cm$^3$/g) | Total (cm$^3$/g) |
|-----------|------------------|-------------------|-------------------|------------------|
| Maxsorb   | 0.27             | 0.79              | 0.63              | 1.69             |
| WV1050    | 0.12             | 0.31              | 0.64              | 1.07             |
| Norit-RB4 | 0.18             | 0.27              | 0.08              | 0.53             |
| PC12      | 0.23             | 0.06              | 0.0               | 0.29             |
| PC35      | 0.34             | 0.27              | 0.0               | 0.61             |
| PC58      | 0.32             | 0.44              | 0.16              | 0.92             |
| PC76      | 0.25             | 0.55              | 0.50              | 1.30             |

Among the commercial carbons (figure 6), Maxsorb had a higher adsorption capacity, thanks to the volumes in the different regions of porosity, which are higher than the other carbons. Norit-RB4 carbon, despite having a greater volume of micropores than WV1050, adsorbs much less, highlighting the importance of pore volume in the range of 27.9 Å (Table 2).

The analysis of representative pores has the advantage of clarifying the contribution of each pore size to adsorption. This can be seen in the series of activated carbons shown in Figure 7. The development of mesoporosity favors adsorption for both molecules and widens the adsorption difference between them. The four carbons have very similar pore volumes in the 8.9 Å range, however the pore volumes of 18.5 Å and 27.9 Å for the samples PC35, PC58 and PC76 grow with the longer burn-off time (Table 2), therefore, presenting a more developed mesopores volume. The maximum adsorbed amount of OCP grows from only 200 mg/g in sample PC12 to 1200 mg/g in sample PC76.

The pore size influence in the differences of amount adsorbed between chlorophenol molecules can be also examined in the carbon series. The carbons PC12 and PC35, with low mesoporosity, did not present maximum uptake differences for o- and p-chlorophenol. This interesting adsorption-structure dependence can be used in separation process of the two species. These results represent an important step in obtaining predictive models for adsorption of phenol derivatives.

**Conclusions**

A predictive model of adsorption of phenol derivatives OCP and PCP, was developed based on molecular simulation and the methodology of representative pores. The prediction of the OCP and PCP isotherms quantitatively reproduced the maximum experimental adsorption capacity and described the difference in adsorption between the species. The analysis allowed both the study of individual pore performance and the reproduction of isotherms on real carbons, using the PSD obtained with N$_2$ at 77 K as input data. The
adsorption difference between the two chlorophenols is basically due to the configuration change of the molecules identified most intensely in the 27.9 Å pore. OCP molecules assume a face-to-face configuration more frequently than PCP molecules. Face-to-face configuration increases fluid-fluid interaction and optimizes molecular packing. Among the carbons tested, those that were more favorable to the adsorption of o-chlorophenol and p-chlorophenol were Maxsorb and PC76, as they have a more developed mesoporosity.

In addition to supporting carbon selection, we believe that methodology applied to phenols, can be extended to other families of organic pollutants that are preferentially adsorbed by activated carbon.

**Declarations**

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**Author Contributions**

JC and SM assisted in the development and writing of the paper. JC and PR were involved in molecular simulation. SM perform the review and editing of the manuscript.

**Ethical approval and consent** Ethical approval is not required

**Consent for publication** The authors give consent to publish.

**Availability of data and materials** All relevant data are included in the paper. Additional data are available from the corresponding author on reasonable request.

**Competing interests** The authors declare no competing interests.

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Figures
Figure 1

Molecular representation of a) o-chlorophenol, b) p-chlorophenol molecules and c) Carbon slit pore model with graphene walls of 40x40 Å.

Figure 2
Simulated adsorption isotherms at 298 K of o- (OCP) and p-chlorophenol (PCP) for the pore sizes of a) 8.9 Å b) 18.5 Å and c) 27.9 Å. d) Molecular positioning of OCP in the 27.9 Å pore at 0.015 kPa.

**Figure 3**

a) Angular distribution of the dipole moment of OCP and PCP molecules in relation to the z-axis. b) Face-to-face configuration. Light gray: small cluster of carbon surface. Dark gray, white, red and green: OCP molecule.

**Figure 4**
Pore size distribution of AC AGL3 at 77 K (Gryglewicz et al. 2002) and the representative's pores volumes of 8.9 Å, 18.5 Å and 27.9 Å, red color – total volume of the 8.9 Å pore. Green color – total volume of the 18.5 Å pore. Blue color – total volume of the 27.9 Å pore.

Figure 5

Simulated adsorption isotherms of o- and p-chlorophenol in AGL3 carbon at 298 K based in the representative pore methodology.

Figure 6
Adsorption of o-chlorophenol and p-chlorophenol in AGL3 carbon. Experimental data from Gryglewicz et al. 2020 (symbols). Simulation results (solid line) using the representative pores methodology.

**Figure 7**

Predicted o-chlorophenol and p-chlorophenol adsorption isotherms in a commercial activated carbon at 298K. a) Maxsorb, b) Norit-RB4 and c) WV1050
Figure 8

Predicted o-chlorophenol and p-chlorophenol adsorption isotherms in and PC series at 298K. a) PC12, b) PC35, c) PC58 and d) PC76