SIMULATION OF BENZENE ADSORPTION ONTO ACTIVATED CARBON

COSTA WA¹, LIMA CR², SILVA FILHO FGS³, SILVA CC¹, MARTELLI MC¹, BRASIL DSB¹

¹ Federal University of Pará, Institute of Technology, Faculty of Chemical Engineering
² Federal University of Pará, Institute of Technology, Faculty of Biotechnology
³ Federal University of Pará, Institute of Technology, Faculty of Electrical Engineering

E-mail: Wanessa.almeida712@yahoo.com.br

ABSTRACT – Monoaromatic hydrocarbons are large contaminants of soils and rivers. Its removal is generally done by adsorption on activated carbon. The objective of this work is to elucidate, through simulations of molecular dynamics, the interactions between the molecular structures of activated carbon and those of benzene. The simulation model was represented by an aqueous solution of benzene and two molecules of activated carbon spaced in 20 Å. The system was subjected to heating up to 298 K and molecular dynamics for 30 ns, with semi-empirical method. The oxygen groups present in the activated carbon structure give it acidic character and negative surface charge. Due to this, the adsorption became feasible once the pollutant assumes positive charge.

1. INTRODUCTION

Monoaromatic hydrocarbons are among the major contaminants of groundwater. These contaminants such as benzene, toluene and xylenes (ortho-, meta- and para-) are powerful depressants of the central nervous system, presenting chronic toxicity, even at small concentrations (μg.L⁻¹) (Silva et al., 2002).

Among the various methods of removal of these pollutants, activated carbon adsorption is the most widely used method, since it has perfect ability to adsorb organic components of low molecular weight, such as benzene (Schneider, 2008).

Computer and dynamical simulations of molecular systems have become an increasingly important way to investigate structures (Jorgensen et al., 1998). Figure 1a represents the model assumed for the molecular representation of activated carbon, that was proposed by Costa (2014). The pollutant used in the simulation was benzene, which is shown in Figure 1b.

In this work, molecular modeling is described as an interesting tool to study the structure-activity relationships of the activated carbon under analysis, especially regarding the analysis of the adsorption process of benzene on the surface of the activated carbon.
2. METHODOLOGY

2.1. Molecular Models

This model was designed using the Marvin Sketch software and optimized by DFT calculation, at BELYP theory level and 6-31G basis by the software Gaussian version 9. The files obtained from the optimization were used to generate the data of three-dimensional coordinates, loads, angles, bond dihedrals and topology, using the Antechamber code of the AMBER package and the FF99SB force field.

2.2. Molecular Dynamics

The data regarding the pore diameter, diameter of the molecule of each pollutant and the distance between the plates were obtained from literature data and molecular modeling tools (Lima et al., 2005; Ramos, 2012). The Ambertools version 13 package was used for the construction of the mesopore model and the adsorption system containing the carbon and pollutants (Amber, 2013). Then, the model was parameterized and solvated with the tleap tool and submitted to calculations of minimization, heating and molecular dynamics. The FF99SB force field was used. The heating step simulated the temperature rising from 0 to 25 °C and it was divided into five stages with increment of 5 °C and 500 ps of simulation in each step. The molecular dynamics stage simulated the state of the system in instants from 0 to 30 ns, divided in five steps with increment of 2 ns in each.

3. RESULTS AND DISCUSSION

The results, a three-dimensional representation of the imposed conditions, are images obtained and rendered by the VMD software, as shown in Figure 2a. Figure 2b represents the final state of the molecular dynamics omitting the water molecules, after 30 ns of calculations.
Figure 2 – Model with the benzene molecules inserted (a); Model after 30 ns of molecular dynamics (b).

Geometric optimization alters the molecular geometry to decrease the energy of the system and produces a more stable conformation (Hyperchem, 2002; Leach, 2001). The model was solvated to simulate an aqueous environment as it happens in real adsorption systems. The minimization of energy before the performance of the molecular dynamics, besides taking the structure to a minimum of energy, was also done with the intention to remove any "bad contact" created by the solvation (due to the ionic dissociation of the water molecules (Ramos, 2012). Functional groups and delocalized electrons are factors that determine the chemical (acidic or basic) character of the activated carbon surface, since oxygen may be present in various forms. In the case of the structure of the carbon under analysis, the ether, carbonyl and lactone groups make the structure more acidic, apolar and consequently, it ends up exhibiting a negative surface charge (Fernandes, 2005; Lopez-Ramon et al., 1999).

According to Wibowo et al. (2006), carbons with few surface oxygenated acid groups have a higher adsorption capacity. The non-polar character of the surface in activated carbon is a preponderant factor in the adsorption of non-polar molecules and can be enhanced by the appropriate modification of the chemical nature of the carbon surface (e.g.: acid treatment). Because of its non-polarity and its larger volume of micropores, carbons adsorb more strongly the apolar or weakly polar organic molecules, as is the case of benzene (Yang, 2003).

4. CONCLUSION

It was verified that the carbon structure used presented good adsorption capacity of benzene in aqueous solution, which is mainly due to the non-polar character of the structure, characterized by the functional groups identified therein.

4. NOMENCLATURE

°C – Celsius degrees
Å – Angstrom

AMBER – Assisted Model Building with Energy Refinement
DFT - Density Functional Theory

ns – nanosecond

ps – picosecond

VMD - Visual Molecular Dynamics

5. REFERENCES

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