Adsorption of Benzene and Toluene on Activated Charcoal and Gasified Biochar in Mono-compound Systems

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Abstract

The focus of this research was to evaluate the benzene and toluene adsorption potential onto activated charcoal (commercial material - named as C1) and gasified biochar (named as C2) at different temperatures. This research focused on an adsorption study of benzene and toluene (mono)compounds on gasified biochar (C2) and commercial activated charcoal (C1) through equilibrium studies, at different temperatures (15°C, 25°C, and 35°C). The equilibrium studies were performed in duplicate, with solutions of benzene from 35-350 mg/L and toluene from 20-200 mg/L, with a ratio of 0.05 g of adsorbent material and 0.1 L of solution volume, in each system. The main results indicated maximum adsorptive capacities for benzene of 5.64 mol/kg and 3.75 mol/kg (approximately 440 mg/g and 290 mg/g for C1 and C2 charcoals, respectively), and for toluene, 3.74 mol/kg and 3.52 mol/kg (approximately 340 mg/g and 320 mg/g for C1 and C2 charcoals, respectively). The Freundlich and Langmuir adsorption isotherms fit the experimental data satisfactorily, and in all adsorption processes studied, $\Delta°H_{ads} < 0$ and $\Delta°G_{ads} < 0$. The proximity of the results obtained between the gasified biochar (residual material), and the activated charcoal (commercial material) encourages further research for new systems.

Keywords: Adsorption; benzene; biochar; thermodynamic process, toluene.

1. Introduction

Water is a renewable mineral resource, essential for human development in various aspects and applications (Garcia et al, 2015). Depending on the type of use, water must have specific physical, chemical, and biological characteristics that ensure user safety and the quality of the final product.

The petroleum industry is one example of extensive water use in its operations, from extraction to fuel refining, generating effluents contaminated with various harmful compounds. Although the use of compounds such as petroleum-derived hydrocarbons is a crucial force for economic and social development, the generation of contaminated effluents can lead to a series of negative effects on human health [2]. Many of these aqueous effluents present in the petrochemical industry consist of mixtures of alkanes, aromatic hydrocarbons (monocyclic or polycyclic), resins, phenols, among others, which are often known for their carcinogenic, mutagenic, and teratogenic effects [3].

Due to the magnitude of the environmental impact and its potential health risks resulting from the carcinogenic effects of some components, soil and groundwater contamination by petroleum derivatives is a global concern [3]. Most occurrences of these contaminants in the environment primarily result from accidental oil spills, discharge of oily wastewater from oil production/refining, rupture of underground storage tanks, and damage to underground pipelines. Among these contaminants, the BTEX mixture, composed of benzene, toluene, ethylbenzene, and xylene isomers, stands out. These are classified as monoaromatic hydrocarbons and are frequently found in industrial compounds such as gasoline, in engine exhaust, and in the burning of wood and tobacco [4]. These compounds are toxic and exhibit some mobility in water, often due to a co-solubilization process, and can be persistent pollutants when incorporated into the soil.

Due to issues associated with the remediation of oil-contaminated areas and the recognition of the potential danger to human health and the environment, there is a need for the development of feasible, rapid remediation technologies applicable to the various conditions of a hydrocarbon-contaminated area.

Moreover, conventional effluent treatment plants often cannot remove BTEX compounds, making adsorption (among other methods) a viable and low-

cost option. Additionally, the use of industrial waste, such as biochars from pyrolysis (or gasification) processes, may provide a robust alternative for this purpose and for other matrices, such as the treatment of textile effluents, pharmaceuticals, BTEX, PAHs, agricultural effluents, among others [4].

Given the information presented, this research will aim to study the removal of BT compounds from water using biochar derived from a gasification process. The specific objectives include a detailed study of the adsorption process, which involves: comparison of results with commercial activated charcoal, equilibrium study, thermodynamic study, and a brief discussion on the characterization of the two materials (activated charcoal – referred to as C1; and biochar from a gasification processs – referred to as C2), through specific surface area analysis (BET), and X-ray diffraction (XRD).

2. Methodology

2.1 Biochar production

The first material was commercial activated charcoal from the brand Synth (referred to as C1), with limited information on its label, such as details of its activation process. However, some of the textural characteristics of this material were observed through the characterizations performed, such as BET isotherm and XRD.

The second material was biochar from a gasification process (referred to as C2). This material was obtained from the Activated Charcoal Laboratory at the Universidade Federal da Paraíba and was produced from wood industry waste in a natural gas gasifier, which produced synthesis gas in an oxygen-deficient combustion, generating the biochar as a residual material. The same characterization techniques mentioned, BET and XRD, were also employed for this biochar.

In all processes used in the laboratory, the charcoals were pulverized and sieved through a 100 mesh sieve. They were then washed with distilled water in a 1:5 mass ratio (charcoal/water), using beakers and glass rods. Subsequently, they were filtered using qualitative filters and dried in a desiccator with the use of an infrared lamp. Finally, they were sieved again through 100 mesh sieves and stored in an oven at 60°C

2.2 Characterization

The crystalline structure of the charcoals was obtained using the XRD D8 ADVANCE Bruker.

The specific surface area was determined by the BET isotherm (Brunauer-Emmett-Teller). The pore radius and volume were determined using the average experimental results, on a MICROMETRICS surface area analyzer (ASAP 2020).

2.3 Adsorption test

Analytical curves were constructed by High-Performance Liquid Chromatography (HPLC), correlating chromatographic areas with analyte concentration. For benzene and toluene, curves containing 9 points between 7 mg/L and 350 mg/L were constructed (dissolved in methanol). The equipment used was a Shimadzu 6A High-Performance Liquid Chromatograph, with a UV detector at a wavelength of 254 nm. The chromatographic column was a Phenomenex Luna C18 250 mm, 4.6 mm, and 5.0 μm. The mobile phase consisted of acetonitrile and water (60/40 v/v), with a flow rate of 1.5 mL/min.

In all adsorption experiments, the pH of the solutions was kept constant, varying slightly depending on the initial concentrations, but remaining between 6.0-7.0. The temperatures were 15°C, 25°C, and 35°C. All amber vials were sealed with double seals and agitated at 150 RPM on an orbital shaker with temperature control. For the equilibrium study, suspensions containing 100 mL of solution and 0.05 g of adsorbent material were used, with mass/volume suspensions of 0.5 g/L, agitated for 180 minutes. It's noteworthy that, in previous studies, the equilibrium time did not exceed 60 minutes. For this study, the initial concentrations (in each individual Erlenmeyer flask) were 35-350 mg/L for benzene, and 20-200 mg/L for toluene, individually. After quantifying the equilibrium concentrations in the liquid phase (C_{eq} = mol/m^3, by liquid chromatography) and calculating the concentrations in the solid phase (q_{eq} = mol/kg, using Equation 1), it was possible to model the Equilibrium study according to the Langmuir and Freundlich Isotherms (Equations 2 and 3).

With these preliminary characterization results of the activated charcoal (C1) and biochar (C2), and the equilibrium study results, it was possible to discuss the efficiency of the process with a brief comparison to the current technical literature. Furthermore, by calculating different equilibrium constants at different temperatures, it was possible to quantify some important thermodynamic

properties for the adsorption process using the Van't Hoff Equation (Equation 4).

$$q_i = (C_0 - C_i)\frac{V}{m} \qquad (1)$$

$$q_{i,eq} = \frac{q_i^{sat}K_L C_{i,eq}}{1+K_L C_{i,eq}} \qquad (2)$$

$$q_{i,eq} = K_F C_{i,eq}^{1/n} \qquad (3)$$

$$\frac{dlnK}{dT} = \frac{\Delta H^0}{RT^2} \qquad (4)$$

3. Results

Both charcoals were characterized using X-Ray Diffraction Analysis (XRD), and specific surface area determination by the BET isotherm (Brunauer-Emmett-Teller).

The crystalline structure of the charcoals was obtained using the XRD D8 ADVANCE Bruker, as shown in Figure 1. The X-ray diffractometry was similar between the charcoals (like an amorphous carbon), with a 'peak' observed in C2, likely due to the presence of some impurity.
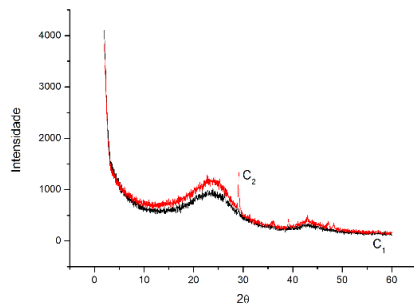

Fig 1 – XRD [C1 (black) e C2 (red)]

The specific surface area was determined by the BET isotherm (Brunauer-Emmett-Teller). For the determination of pore radius and volume, the average results were used, with a MICROMETRICS surface area analyzer (ASAP 2020). The results are described in Table 1 and Figure 2, and it can be identified that C1 has a larger surface area and pore volume than C2, but they have similar pore diameters. Both materials fall into the mesoporous category, as they are within the 2.0 to 50.0 nm diameter range, with a moderated hysteresis typically H2, possibly due to size poorly distributed pores [4].

Tab 1 – Results of Specific Surface Area Analysis

Sample	Surface Area $(m^2/g)^1$	Pore Volume $(cc/g)^2$	Pore Diameter $(nm)^3$
Activated charcoal (C1)	545.4	0.358	13.13
Biochar (C2)	350.4	0.219	12.55

[1]BET; [2]pores with radius less than 77 nm (C1) and less than 134 nm (C2); [3]average pore radius
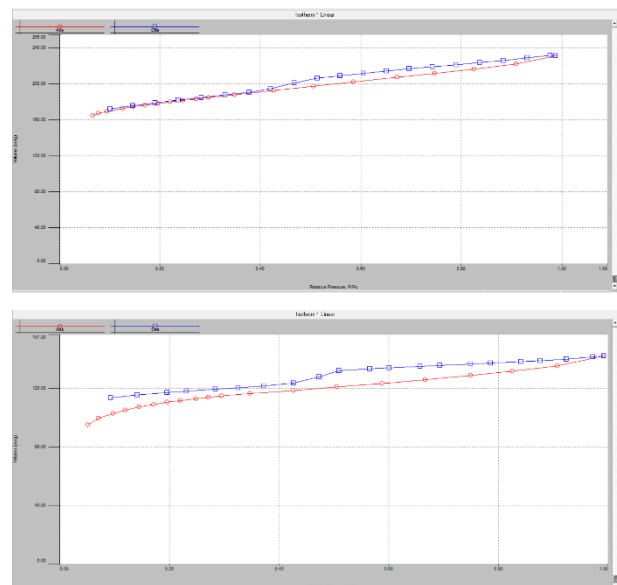

Fig 2 – N$_2$ adsorption-desorption isotherms - C1 and C2 respectively

Following the equilibrium studies, the results are presented in Figure 3 and Table 2.

Finally, Table 2 shows the results of the equilibrium parameters. It is noteworthy that other studies in the literature have obtained equivalent results, such as Pan et al., 2024 [5], with 470 mg/g of benzene in lignin-based pyrolyzed biochar (6.02 mol/kg), and Cheng et al., 2023 [6], with 223 mg/g of toluene in N2-doped biochar (2.43 mol/kg). The results indicate that increasing the temperature favors the shift of the equilibrium towards desorption, suggesting a physical adsorption process ($\Delta°H < 80$ kJ/mol), in exothermic/spontaneous systems.
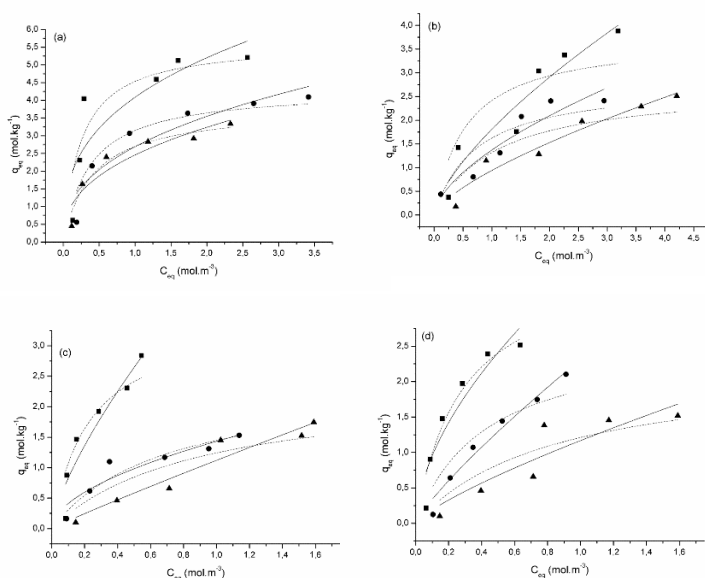
Fig 3 – Equilibrium Studies (15°C■, 25°C● e 35°C▲) – Benzene C1 and C2 ("a" and "b") and toluene C1 and C2 ("c" and "d") – Langmuir Isotherm as dash line and Freundlich Isotherm as solid line

Tab 2 – Equilibrium Parameters

Benzene	C1	C2
q^{sat} (mol/kg)	5.64 ± 0.46[1]	3.75 ± 0.40[1]
1/n	0.40[2]*	0.69[2]*
K (15°C)	4.09 ± 0.45	1.81 ± 0.24
K (25°C)	2.69 ± 0.25	1.37 ± 0.16
K (35°C)	2.46 ± 0.18	0.94 ± 0.12
Δ°H (kJ)	-18.89	-24.12
Δ°G (kJ)	-2.71	-0.69
Toluene	**C1**	**C2**
q^{sat} (mol/kg)	3.74 ± 0.20[1]	3.52 ± 0.31[1]
1/n	0.57[2]*	0.72[2]*
K (15°C)	4.39 ± 0.45[2]	3.60 ± 0.42[2]
K (25°C)	1.43 ± 0.12[2]	2.31 ± 0.14[2]
K (35°C)	1.12 ± 0.09[2]	1.17 ± 0.13[2]
Δ°H (kJ)	-50.55	-41.42
Δ°G (kJ)	-1.60	-1.87

[1]Langmuir isotherm (at 15°C), [2]Freundlich isotherm (* at 15°C)

4. Conclusion

The main results indicated the potential use of a residual material as an adsorbent for organic compounds derived from petroleum, in physical exothermic processes, with maximum adsorption capacities approximately 3.7 mol/kg and 3.5 mol/kg for benzene and toluene, respectively, concerning the residual biochar (the focus of this research). These results encourage further research with this material.

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