Carbon Nanotubes-phenol Materials: A Microcalorimetric Approach and Potential Energy Storage Applications

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Abstract: Phenols can play an important role in the functionalization of carbon nanotubes to enhance energy storage properties. The adsorption of this class of molecules is a facile process applied to reach functional carbon nanotubes. In this study, the thermodynamics of phenol, 2-methylphenol and 4-chlorophenol onto pristine multi-walled carbon nanotubes (MWCNTs) was evaluated by measuring standard adsorption free energy change ($\Delta_{ads}G^o$), standard adsorption enthalpy change ($\Delta_{ads}H^o$) and standard adsorption entropy change ($\Delta_{ads}S^o$). The adsorption of all phenolic compounds onto MWCNTs was a thermodynamically spontaneous process and the decrease in $\Delta_{ads}G^o$ follows the order phenol < 2-methylphenol < 4-chlorophenol. Isothermal Titration Calorimetry results show that the adsorption process is enthalpically driven and that MWCNT interfaces have sites with different interaction energies that allow specific interactions with phenolic compounds, not only by π-π dispersion interactions.

Keywords: Surface heterogeneity, carbonaceous adsorbents, immobilization mechanism, energy storage, allotropy of carbon, functionalized phenols.

1. INTRODUCTION

Among the more than 800 products based on nanoparticles or nanofibers, those formed by carbon materials, including fullerenes and carbon nanotubes, are the most numerous [1]. Carbon nanotubes (CNTs) possess unique physicochemical properties that have led to the research and the development of new products, advanced by the findings of Iijima in 1991, regarding the synthesis of the multi-walled carbon nanotubes (MWCNTs) [2]. Today, CNTs are employed in a wide range of applications, which include systems for energy conversion/power sources, sensors, supports for catalysts and biomedical materials [3,4, 26]. In 2001, Long and Yang reported for the first time that CNTs could act as more efficient adsorbents for dioxin than activated carbon (AC) [5]. Due to their enhanced rate capability, excellent specific capacitance and good cycle life, CNTs are applied to electrochemical energy storage assemblies, such as batteries and supercapacitors, as well in energy conversion structures, such as solar cells, fuel cells and microbial fuel cells [26].

Adsorption is an established technique for removing organic pollutants from water [6] particularly using strategic materials as adsorbents [7]. Since 2001, several papers have been published seeking to evaluate the adsorption of organic pollutants by CNTs [3,6,8-17] with special attention paid to phenolic compounds (PhCs), which possess high toxicity to human health and the environment even at low concentrations [12,13]. On the other hand, some studies revealed the potential application of phenol-CNT structures for electrochemical energy storage [27, 28].

In the adsorption experiments, porosity and surface area of the adsorbent (especially of the carbon materials) were considered the primary factors influencing the phenomena. However, a knowledge of the surface chemistry is important, as even a small number of surface groups can exert a significant influence on the physicochemical properties of the carbon materials [18] and, therefore, on their adsorptive characteristics, including the nature of their interactions with the adsorbate molecules [10]. In the case of CNTs, according to N_2 adsorption data, the largest numbers of available spaces for adsorption are on the cylindrical external surface, not in the inner cavities or inner wall spacing [12,19]. Some studies reveal that the adsorption of phenolic compounds (PhCs) onto MWCNTs does not follow exactly the same mechanism observed in activated carbon. Evidence of this can be found in the fact that the total amount adsorbed reaches equilibrium within 30–40 min with MWCNTs, in comparison to 7–150 h with activated carbon [6,12,13]. CNTs are recognized as hydrophobic structures, and several works indicated that the π–π dispersion forces are responsible for the adsorption of aromatic compounds onto CNTs [3].

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When functional groups are attached to CNT surfaces, the resulting materials become a subject of great interest in recent studies, due to its versatile properties for gas sensing systems [33], transistors [34], flexible thermoelectric devices [35] and thin films for high-performance flexible electronics applications [36].

It is well known that some oxygen groups such as carbonyl, carboxylic and hydroxyl groups exist on the surface of CNTs [13], and recent studies demonstrate their influence on the adsorption process [6,11-15]. However, there is no agreement concerning the main driving force for the adsorption of phenol and phenolic derivatives onto the CNTs. Therefore, this study aims to evaluate the adsorption behavior of model molecules, formed with different functional groups that modulate the electron density of the phenol ring, onto MWCNTs. The study also contributes to the understanding of the nature of the interaction between nanotubes and PhCs as assessed by the thermodynamic properties, primarily using isothermal titration calorimetry.

2. EXPERIMENTAL

All adsorption experiments, ITC microcalorimetry and UV-Vis characterizations were performed in the laboratories of the QUIVECOM group at the Chemistry Department of the Federal University of Viçosa (UFV). Thermogravimetric analysis and N_2 adsorption experiments were performed at the Chemistry Department, Federal University of Minas Gerais (UFMG). The SEM and TEM images were obtained at the UFMG Microscopy Center.

2.1. Materials

The phenolic compounds (PhCs), phenol (PH), 2-methylphenol (MP) and 4-chlorophenol (CP), were purchased from Sigma-Aldrich, all with purity above 99.9%. Multi-walled carbon nanotubes, C_{TUBE} 100 MWCNTs, were purchased from CNT CO., LTD., Korea. Technical specifications for the MWCNTs were supplied by the manufacturer (average diameter: 10–40 nm; length: 1–25 μm; purity: 93 wt% min.; contaminants: 7 wt% max.; bulk density: 0.03–0.06 g cm^{-3}; specific surface area: 150–250 $m^2 g^{-1}$).

2.2. Adsorption Experiments

Adsorption isotherms were carried out in duplicate by mixing solutions (20mL) containing various concentrations of adsorbates with 15 mg of MWCNT, except for the phenol solutions, in which 50 mg of MWCNT were used. All experiments were performed in 40-mL glass centrifuge tubes sealed with headspace screw caps. Initial concentrations were chosen to cover a complete spectrum of isotherm adsorption behavior. The tubes were shaken manually for 10 minutes in the dark to guarantee complete contact between the MWCNTs and the dissolved phenolic compound. After shaking, all tubes were placed vertically in a thermostatically controlled bath at 298.15 K in the absence of light. After reaching thermodynamic equilibrium, samples were taken from the adsorption tubes to determine the PhC concentration in the supernatants. Separation of the MWCNTs and the supernatants was achieved by centrifugation. The collected aliquots were then properly diluted to ensure that the absorbance readings in the UV/Vis spectrometer obeyed Beer's Law. PhC concentrations in the supernatants (equilibrium concentrations − C_e) were determined after 24 h, 120 h and 168 h of thermodynamic equilibrium. Blank experiments were carried out using the same experimental procedure without MWCNTs to examine the potential sorption of PhCs onto the glass tubes. The results indicated that such losses were negligible. Therefore, the amounts of PhCs adsorbed by the MWCNTs were directly calculated from difference between the initial and final equilibrium concentrations as follows:

$$\Gamma = \left(\frac{C_0 - C_e}{m}\right) V \qquad (1)$$

in which Γ is the amount of each PhC adsorbed by the MWCNTs (mg g^{-1}) after thermodynamic equilibrium; C_0 is the initial concentration (mg mL^{-1}); C_e is the equilibrium concentration (mg mL^{-1}); V is the solution volume (mL); and m is mass of the MWCNTs (g).

The adsorbates were dissolved in distilled water, and the final concentrations were limited to <50% of their water solubility to guarantee complete dissolution. According to the literature, there is no considerable difference in the adsorption of PhCs on CNTs at pH values lower than the pK_a for each compound [12,17]. Therefore, the adsorption experiments were accomplished at the pH of distillate water at which PhC is in its non-dissociated form.

2.3. Characterization

N_2 adsorption: The specific surface area of the MWCNT was determined from the N_2 adsorption/desorption isotherms obtained in an automated gas sorption system, AUTOSORB-1 ASIAG (QUANTACHROME INSTRUMENTS), using the Brunauer-Emmett-Teller (BET) method.

Thermogravimetric Analysis (TG): Thermogravimetric measurements were carried out using a TA INSTRUMENTS SDT 2960 simultaneous TG/DTG at 5 °C min^{-1} in a dry airflow of 100 mL min^{-1} between 25 and 1000 °C in an alumina crucible.

Scanning Electron Microscopy: Scanning electron microscopy (SEM) was performed with a Quanta 200 FEG (FEI) scanning microscope. The carbon nanotube sample was placed on conductive carbon tape and covered with a thin gold layer (10 nm) for better visualization, improving contrast.

Transmission Electron Microscopy: Transmission electron microscopy (TEM) was carried out with a Tecnai G-20 (FEI) microscope employing a LaB_6 filament with an acceleration voltage of 200 kV. The samples for TEM studies were dispersed in ethanol and dripped onto a carbon-coated copper grid.

UV/Vis Spectroscopy: After the proper equilibrium time (24 h, 120 h and 168 h), aliquots of each flask were collected and diluted by different factors. The samples were then measured in a Shimadzu UV-2550 UV/Vis spectrophotometer.

Isothermal Titration Calorimetry (ITC): Measurements of the enthalpy changes in the adsorption process of PhCs onto MWCNT were performed in triplicate using a CSC-4200 microcalorimeter (Calorimeter Science Corp.) controlled by ItcRun software with a 1.75 mL reaction cell (sample and reference). The entire calorimetry procedure was calibrated chemically and electrically to the heat of protonation for tris(hydroxymethyl) aminomethane and the joule effect, respectively [20]. The titrations were carried out via step-by-step injections (10 µL) of concentrated PhC titrant solutions using an instrument-controlled gas-tight Hamilton syringe (250 µL) at 60 min intervals between each injection. Aliquots of concentrated PhC solutions, dissolved in water, were added to a sample cell containing a suspension of 1 mg of MWCNT in aqueous solution. The solution was titrated in the sample cell stirred at 300 rpm by a helix stirrer, and measurements were carried out at a constant temperature of 25.000 ± 0.001 °C. Distilled water was used for preparing all solutions and carbon nanotube suspensions. The concentrations of the initial PhC solutions were chosen so that after each injection, the resulting concentrations in the sample cell would become identical to the concentrations used to obtain the adsorption isotherms.

3. RESULTS AND DISCUSSION

3.1. Carbon Nanotube Characterization

From the thermogravimetric analysis (Figure **1a**) and SEM and TEM images (examples can be found in Figure **1b** and Figure **1c**, respectively), the multi-walled carbon nanotube sample has a purity higher than 90%, with tube diameter of approximately 10–40 nm (with a predominance of tubes having an average diameter of approximately 13 nm). Its surface area, determined by nitrogen adsorption/desorption isotherms at 77 K using the BET equation, is in the order of 188 $m^2 g^{-1}$. These data are in agreement with the information provided by the supplier of the material, as previously presented.

By the SEM images, one can observe a great amount of entanglements, curves and bends, which probably present different energies of adsorption. This surface heterogeneity, also found in a previous work [29] may provide some alternatives for the immobilization of phenols, giving a good variety of energy storage purposes, according to the structure of the electron-donor functional sites. The density of energy can be increased by the functionalization of the carbon nanotube surface, as described by Telgerafchi *et al.* (2018).

3.2. Adsorption Isotherms

Generally, when activated carbon (the most common adsorbent) is employed in adsorption experiments, a long time is required to reach thermodynamic equilibrium [6,13]. Considering this information and the fact that the use of CNTs for adsorption of contaminants is a developing field, the influence of the equilibrium time (24 h, 120 h and 168 h) on the adsorption process was evaluated. We observed that the adsorption of the different phenolic compounds onto the MWCNTs reaches thermodynamic equilibrium in 24 h or less. No significant change was observed after 24 h (at 120 h or 168 h) in all cases. In fact, Peng and co-workers [13] observed that the process of the adsorption of 1,2-dichlorobenzene on as-grown and graphitized CNTs requires 40 min to reach equilibrium. Liao *et al.*, [12] evaluating the adsorption time of resorcinol on pristine and HNO_3-treated MWCNTs, observed that after only 1 min of shaking, the amount of adsorbed molecules reaches 60% of the total amount adsorbed at equilibrium. It was suggested that this short time could be related to the fact that CNTs do not have the same porous structure as activated carbon in which the adsorbent molecules must move from the exterior surface to the inner surface of the pores to achieve equilibrium [13].

The adsorption isotherms of the phenolic compounds on MWCNT are shown in Figure **2** in which the amount of each adsorbed PhC (mg g^{-1}) of MWCNT is plotted against the equilibrium concentration of the respective PhC (mg mL^{-1}). The curves were obtained after 24 h to achieve thermodynamic equilibrium.

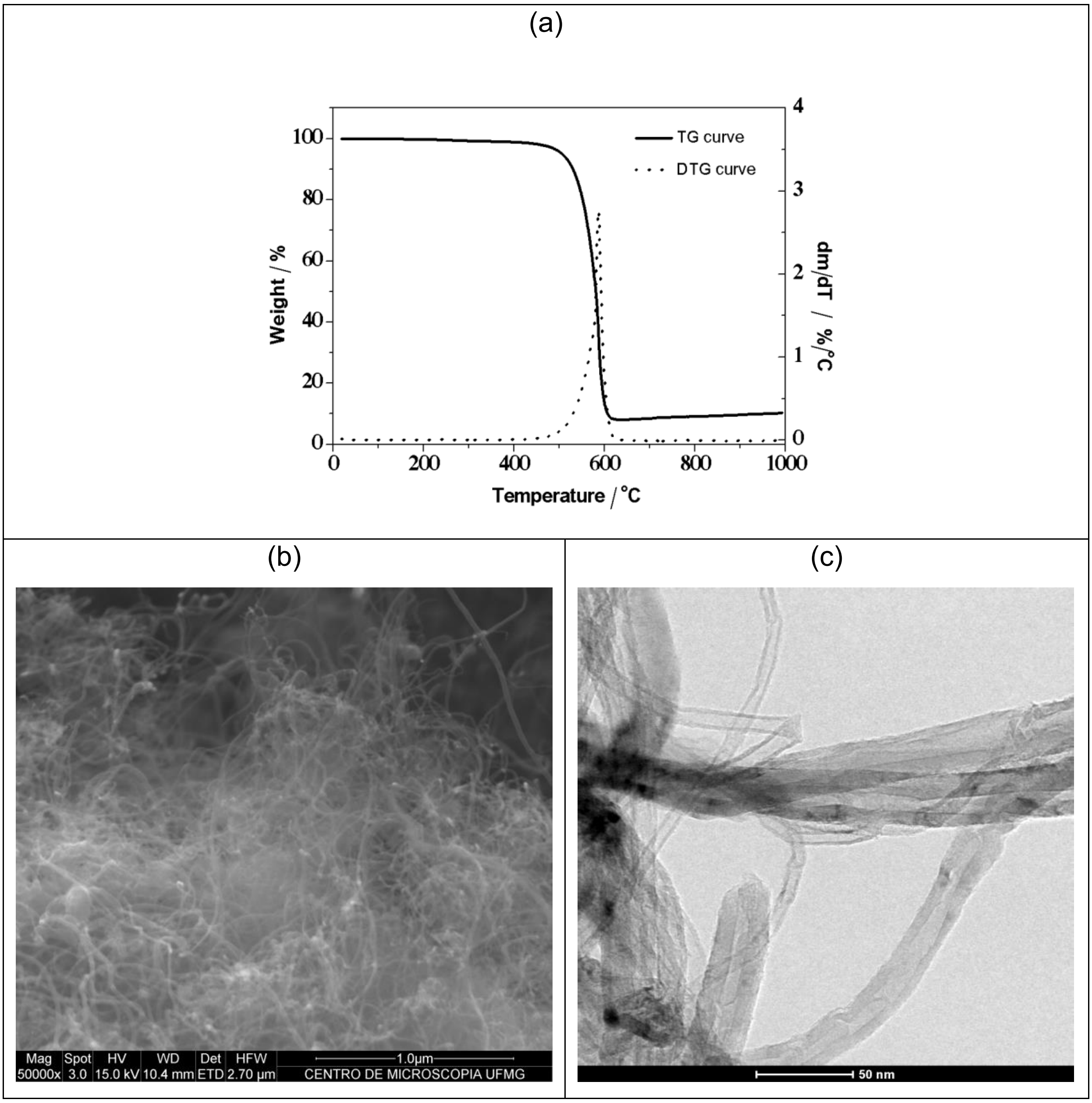

Figure 1. (a) TGA and DTG curves, (b) scanning electron micrograph and (c) transmission electron images of MWCNT samples.

The isotherms are non-linear and of the same type. They are characterized by an increase in the amount of PhC adsorbed with increasing equilibrium concentrations, followed by a tendency toward the formation of a plateau at higher concentrations, which represents the maximum adsorption capacity. All curves present a shape suggesting a process that can be described by the Langmuir model as clearly observed in the phenol curve that is reproduced in the inset of Figure **2**. This inset curve shows a maximum adsorption of approximately 43 mg·g^{-1}. The presence of chlorine and methyl groups enhances the adsorption onto the MWCNTs. The isotherms clearly indicate maximum adsorption following the order phenol < 4-chlorophenol < 2-methylphenol. The amount of adsorbed 2-methylphenol (in mg) per gram of MWCNT reaches values as high as 166 mg·g^{-1} at an equilibrium concentration of 1.0 mg mL^{-1} (Figure **2**). This amount is considerable and makes possible the use of MWCNTs as an adsorbent for wastewater treatment as well as for energy-related applications. Wang, Hua and Dai (2016) publish a review showing that functionalization of CNTs and graphene is preferable than the pristine materials for the assembly of electrode materials in high-performance super-capacitors and batteries. In 2024, Meskher *et al*. reviewed publications showing the role of carbon nanotubes in supercapacitor applications and mentioned that the functionalization of CNTs to improve their functionalities and super capacitance performance were widely used to prepare functionalized CNTs-based supercapacitors. They concluded that the morphology and performance of the CNT may be tuned or functionalized according to the desired electrical application, being an attractive and

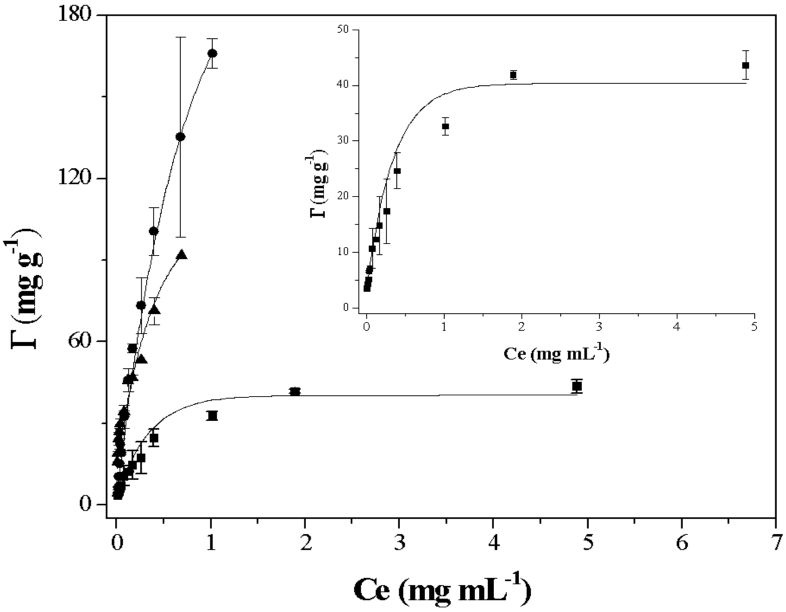

Figure 2. Adsorption isotherms of phenol (■), 2-methylphenol (▲) and 4-chlorophenol (●) on MWCNT. The isotherm of phenol is also presented in detail in the inset.

cost-effective alternative for a Li-ion battery and a supercapacitor.

The equations of Langmuir and Freundlich are the most commonly applied models for representing the nonlinear adsorption of organic chemicals, such as phenolic compounds, to activated carbon, charcoal, and carbon nanotubes [14,15]. Both models were employed to fit the experimental data presented in Figure **2**.

The Langmuir isotherm can be derived by assuming an ideal system in which the adsorbent molecules adsorb onto the adsorbate surface at well-defined sites forming a homogeneous monolayer. Each site can adsorb only one molecule, and the energy involved in the adsorption of one adsorbent molecule is the same for all sites on the adsorbate surface and is independent of the presence or absence of other molecules on the adjacent sites. There is no interaction between adjacent adsorbent molecules. Equation 2 represents the mathematical expression of the Langmuir model:

$$\Gamma = \frac{\Gamma_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

in which C_e is the equilibrium PhC concentration (mg mL^{-1}), Γ is the amount of PhC adsorbed (mg g^{-1}), K_L is a Langmuir constant related to the affinity of the binding sites (adsorption energy), and Γ_{max} (mg g^{-1}) is a Langmuir constant related to the maximum monolayer adsorption capacity, which describes a saturated monolayer of solute molecules on the adsorbent surface (the theoretical saturation capacity of the monolayer) and specifies that further adsorption will contribute to a prohibitive increase in the Gibbs free energy of the interface.

The Freundlich empirical isotherm assumes the existence of heterogeneous surfaces having different sites with diverse energies of adsorption and the possibility for the formation of multilayers:

$$\Gamma = K_F C_e^{\frac{1}{n}} \quad (3)$$

in which C_e and Γ were previously described. K_F (mg$^{(1-1/n)}$ mL$^{(1/n)}$ g^{-1}) is the Freundlich constant describing the adsorption capacity and the energy distribution of the adsorption sites. The Freundlich constant, *n,* describes the magnitude of the adsorption driving force.

The Langmuir and Freundlich equations can be fitted to the data by linear regressions using their linearized forms as follows:

$$\frac{C_e}{\Gamma} = \frac{1}{\Gamma_{max}} C_e + \frac{1}{K_L \Gamma_{max}} \quad (4)$$

$$ln\Gamma = lnK_F + \frac{1}{n} lnC_e \quad (5)$$

in which plots of $\frac{C_e}{\Gamma}$ versus C_e and lnΓ versus lnC_e allow for the calculation of the Langmuir and Freundlich constants, respectively. The values obtained following these data fittings are presented in Tables **1** and **2**.

Taking into account the quality of the fit given by the correlation coefficient (R^2) in Table **1**, both adsorption models adjust the data in a reasonable way. The constants Γ_{max} and K_F indicate the same tendency observed in the isotherms: 2-methylphenol exhibits

Table 1: Langmuir Constants Obtained by the Linear Forms of the Equations

PhC	LANGMUIR			
	Γ_{max} / (mg g^{-1})	K_L / g mg^{-1}	Linear Equation	R^2
phenol	46.08	3.34	Ce/Γ = 0,02174Ce + 0,00652	0.989
4-chlorophenol	95.97	9.22	Ce/Γ = 0,01042Ce + 0,00113	0.9280
2-methylphenol	242.72	1.93	Ce/Γ = 0,00412Ce + 0,00214	0.951

Table 2: Freundlich Constants obtained by the Linear Forms of the Equations

PhC	FREUNDLICH			
	K_F / mg$^{(1-1/n)}$ mL$^{(1/n)}$ g^{-1}	1/n	Linear Equation	R^2
phenol	29.76	0.45	lnΓ = 0,4531lnCe + 3,3931	0.968
4-chlorophenol	100.41	0.40	lnΓ = 0,39622lnCe + 4,60925	0.984
2-methylphenol	194.75	0.75	lnΓ = 0,74531lnCe + 5,27177	0.973

greater adsorption than 4-chlorophenol, which exhibits greater adsorption than phenol. However, the Langmuir Γ_{max} values seem to be a more reasonable fit in relation to the data (see Figure **2**). Therefore, apart from the mathematical quality of the fit, considering the Γ_{max} values the Langmuir model appears to be more applicable. For example, Γ_{max} observed in the isotherm is approximately 43 mg g^{-1}, and Γ_{max} obtained from the fit was 46.08 mg g^{-1} (Table **1**) for phenol.

In the Freundlich approach, the magnitude of 1/n quantifies the "favorability" of adsorption and the degree of heterogeneity of the CNT surface. If 1/n is less than unity, suggesting a favorable adsorption with a negative $\Delta_{ads}G^o$, the adsorption capacity increases, and new adsorption sites form [11,21]. Considering the data presented in Table **1**, the values of 1/n are less than unity for phenol, 2-methylphenol and 4-chlorophenol, reinforcing the assertion that the adsorption of PhCs on MWCNTs is favorable.

3.3. Microcalorimetry Experiments

The energy released or absorbed as heat in a thermodynamic process can be measured by equipment and calorimetric techniques that allow its detection. Among these, isothermal titration microcalorimetry has been widely used for the determination of many molecular processes due to its high sensitivity and its ability to detect energy flows occurring in a given process on the order of 10^{-9} J.

Curves of the adsorption enthalpy change ($\Delta_{ads}H$) versus the equilibrium concentrations of phenol, 2-methylphenol and 4-chlorophenol on MWCNT, obtained from ITC measurements at 298 K, are shown in Figure **3**.

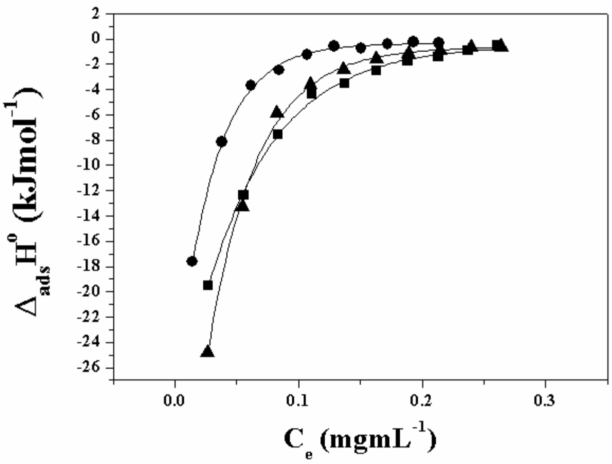

Figure 3. ΔH of adsorption (kJ mol^{-1}) versus equilibrium concentration (mg mL^{-1}) for the adsorption process of phenol (■), 2-methylphenol (▲) and 4-chlorophenol (●) on MWCNT.

The total value of $\Delta_{ads}H$ attributed to adsorption process may be expressed as follows:

$$\Delta_{ads}H = \Delta_{deh}H_{ChP-H_2O} + \Delta_{des}H_{MWCNT-H_2O} + \Delta_{int}H_{H_2O-H_2O} + \Delta_{int}H_{ChP-ChP(MWCNT)} + \Delta_{int}H_{MWCNT-ChP} \quad (6)$$

According to equation 6, the $\Delta_{ads}H$ values reflect the contributions of five processes: the $\Delta_{deh}H_{PhC-H_2O}$ and the $\Delta_{deh}H_{MWCNT-H_2O}$, which are the enthalpy changes of dehydration for the specific phenolic compound and MWCNT, respectively (both endothermic); the exothermic $\Delta_{int}H_{H_2O-H_2O}$ that is related to the interaction between water molecules released during the desolvation process; $\Delta_{int}H_{PhC-PhC(MWCNT)}$ (exothermic or endothermic), which describes the interaction energy between molecules of the phenolic compound adsorbed onto adjacent sites on the MWCNT surface; and the exothermic

$\Delta_{int}H_{MWCNT-PhC}$ that indicates the intensity of the enthalpic interaction between the PhC molecules and the carbon nanotube surface. As is well known, the $\Delta_{deh}H_{PhC-H_2O}$, $\Delta_{int}H_{ChP-ChP(MWCNT)}$ and $\Delta_{int}H_{MWCNT-PhC}$ values differ from one phenolic compound to another.

As observed in Figure **3**, the $\Delta_{ads}H$ is negative, which means that the adsorption process onto MWCNT is exothermic for all phenolic compounds and approaches zero for equilibrium concentrations of the order of 0.1-0.2 mg mL^{-1}. At the beginning of the adsorption process, the amount of energy released as heat ($\Delta_{ads}H$) in the adsorption of 2-methylphenol is greater than that liberated in the adsorption of phenol, which, in turn, is greater than the energy released in the adsorption of 4-chlorophenol. With increasing PhC concentration, the $\Delta_{ads}H$ values become less negative showing remarkable evidence for the existence of different sites at the MWCNT interface that accomplish specific interactions with the distinct phenolic compounds. These interactions are dependent on the electron density of the ring, which is modulated by its functional groups (CH_3, H and Cl). The interactions caused by dispersion forces (lower energy) occur only after saturation of these specific sites.

As previously indicated, although the adsorption isotherms have adjustable profiles within the Langmuir equation, microcalorimetry measurements show that CNT surfaces are not homogeneous regions. If an adsorption process follows the Langmuir model, constant values of $\Delta_{ads}H$ would be expected throughout the process. This finding suggests that models like those of Freundlich and others, which describe the adsorption on heterogeneous surfaces that have sites at which the adsorption occurs with different energies, seem to be more realistic for the systems studied in this work. In fact, considering the adjustments of the adsorption isotherms, the quality of the mathematical fit should not be a defining parameter to choose between models with such different physicochemical implications.

According to several researchers [19,22-24], there are seven possible adsorption sites on a bundle of carbon nanotubes: (i) inner (internal) nanotube cavity, (ii) inter-wall spaces (in the case of MWCNTs), (iii) interstitial channels between neighboring nanotubes in the bundle, (iv) external grooves on the periphery of a nanotube bundle, (v) external surface, (v) partial coating of the external surface by nanometer-thick layered carbon, and (vii) carbon-coated catalyst particles. The last two sites are present in the case of unpurified samples. Yang and Xing presented evidence that most spaces available for adsorption of N_2 molecules onto MWCNTs are on the cylindrical external surface. N_2 did not readily adsorb onto the inner cavities because of blocking impurities (i.e., amorphous carbons), nor did it adsorb in the inter-wall spacing because of the small interlayer spacing (0.335 nm) [19]. According to Sheng and co-workers [16], ionizable aromatic compounds were thought to preferentially occupy the external graphene surface of MWCNTs during the initial adsorption process, while the overall adsorption included contributions from both adsorptions on the graphene surface and pore filling. Liao and coworkers indicated that the adsorption of resorcinol onto MWCNT is not dependent on the porous structure, but that the chemical properties of the surface, rather than specific surface areas or pore volumes, are crucial factors to determine the final adsorption ability of MWCNTs [12]. This evidence validates the rapid adsorption of organic contaminants on CNTs discussed previously. Therefore, based on the data in Figure **3** and on the assumption that the external surface is the primary, or at least the preferential, adsorption site, we can indicate the existence of different functional groups chemisorbed onto the surface of the MWCNTs employed in the present work (i.e., carbonyl, carboxylic, hydroxyl). In fact, Sheng and coworkers show the presence of functional groups such as carboxylic, lactone and phenolic groups on pristine CNT surfaces synthesized by CVD [16]. As previously described, functional groups chemisorbed onto the surfaces of carbon materials have a remarkable influence on the adsorption process, even in small quantities [10].

Several studies indicate the π-π dispersion interactions (Figure **4**) as those primarily responsible for the adsorption of aromatic compounds on CNTs, by the closeness of respective aromatic rings [3,6,15,25]. According to Sheng *et al.*, hydrogen bonding, hydrophobic interactions, electrostatic interactions and Lewis acid-base interactions could also be present [16]. Electrostatic and Lewis acid-base interactions are not present in our case because at the solution pH used for the experiments, the PhCs are undissociated (uncharged). This result was also observed by Dias-Florez and colleagues studying the adsorption of phenol on N-doped carbon nanotubes [9]. As previously indicated by the values of $\Delta_{ads}H$ (Figure **3**), dispersion forces are not the only forces responsible for the adsorption process of PhCs onto MWCNTs. We can speculate that hydrogen bonding could be responsible for the large negative values of $\Delta_{ads}H$ observed for all phenolic compounds. In fact, the $\Delta_{ads}H$ values are on the order of those reported for hydrogen bonding interactions (10–40 kJ mol^{-1}). The inductive effect, caused by the functional groups (CH_3, H and Cl) present in 2-methylphenol, phenol and 4-chlorophenol, respectively, interacts with the oxygen functional groups on the MWCNT surface through phenolic OH and resonance effects can be the reason for the difference in the enthalpic energies observed in Figure **3**. In other words, $\Delta_{ads}H$ in the adsorption of 2-methylphenol has a larger negative value than that of phenol, which in turn has a larger negative value than that of 4-chlorophenol. The CH_3 groups are electron donating (Hammett σ is negative), and the Cl groups are electron withdrawing (Hammett σ is positive). Yang and colleagues [17], analyzing the relationship between solvatochromic and Dubinin-Astakhov model parameters, concluded that hydrogen-bonding interactions play an important role in the adsorption of anilines and phenols by carbon nanotubes in which the solutes may act as hydrogen-bond donors, and the carbon nanotubes act as hydrogen-bond acceptors. Franz and colleagues verified that the adsorption mechanisms of different aromatic compounds (including phenol) onto activated carbon are influenced by the properties of the oxygen-containing functional groups on the aromatic adsorbate, especially their ability to hydrogen bond and their activating/ deactivating influence on the aromatic ring (Figure **4**) [10].

The evaluation of the presence of different functional groups chemisorbed onto the CNT external walls is not a simple experimental task. Generally, combinations of different techniques, such as infrared, Raman and XPS spectroscopies, are employed. To our knowledge, this study is the first to use microcalorimetry to detect the existence of distinct functional groups on the external walls of carbon nanotubes.

3.4. Thermodynamic Properties

The change in the standard Gibbs free energy for the adsorption process ($\Delta_{ads}G^o$) is calculated from the thermodynamic relationship as follows:

$$\Delta_{ads}G^o = -RTlnK^o \tag{7}$$

in which K^o is the equilibrium constant for the adsorption process, R is the universal gas constant, and T is the temperature in Kelvin.

The equilibrium constant for the adsorption process, K^o, can be obtained if $\mu_i^{int} = \mu_i^{sol}$, and $\mu_{i^{sol,or,int}} = \mu_i^o + RTlna_{i^{sol,or,int}}$ in which μ_i^{int} is the chemical potential of *i* (in our case PhC) adsorbed at the MWCNT–solution interface; μ_i^{sol} is the chemical potential of *i* in solution (at equilibrium); μ_i^o is the chemical potential of *i* at a standard condition; and $a_{i^{sol,or,int}}$is the activity of *i* (in solution or at the MWCNT–solution interface). After some manipulation of the equations, we obtain the following relationship:

$$lnK^o = ln\left(\frac{a_i^{int}}{a_i^{sol}}\right) = ln\left(\frac{\gamma_i^{int}}{\gamma_i^{sol}}\cdot\frac{C_i^{int}}{C_i^{sol}}\right) \tag{8}$$

in which C_i^{int} is the concentration of the adsorbed PhC at the MWCNT–solution interface (mg g^{-1}), C_i^{sol} is the concentration of the PhC in solution at equilibrium (mg mL^{-1}), $\gamma_i^{int}$is the activity coefficient of the adsorbed PhC, and γ_i^{sol} is the activity coefficient of the PhC in solution at equilibrium conditions.

As the concentration of the solute in the solution approaches zero, the activity coefficient approaches unity, and Eq. (8) reduces to the following form:

$$lnK^o = ln\left(\frac{a_i^{int}}{a_i^{sol}}\right) = ln\left(\frac{C_i^{int}}{C_i^{sol}}\right), \text{ with } \frac{C_i^{int}}{C_i^{sol}} = \frac{\Gamma}{C_e} \tag{9}$$

The values of lnK^o can be obtained by plotting $ln(\Gamma/C_e)$ versus C_e and by extrapolating C_e to zero. The straight line obtained is fitted to the points based on a least-squares analysis. Its intercept with the vertical axis yields the values of lnK^o that are used in Eq. (7).

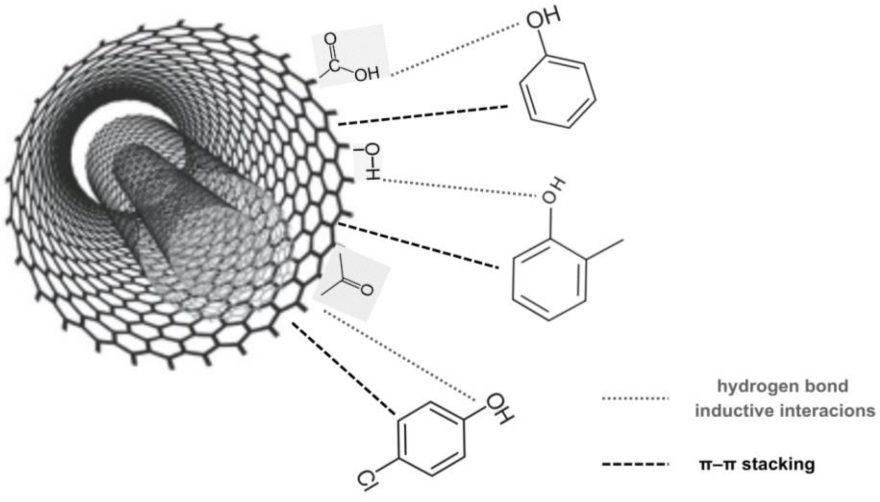

Figure 4: Schematic illustration summarizing the proposed interaction mechanisms between phenolic compounds and the functional groups present on the nanotube surface.

The change in the standard entropy of the adsorption process ($\Delta_{ads}S^o$) is calculated using the classic thermodynamic equation (T = 298 K):

$$\Delta_{ads}G^o = \Delta_{ads}H^o - T\Delta_{ads}S^o \tag{10}$$

The values of $\Delta_{ads}H^o$ for each PhC were obtained from the data presented in Figure **3** following the extrapolation of C_e to zero using an exponential fit (the solid lines in Figure **3**).

The values obtained for the thermodynamic properties are listed in Table **3**. The adsorption of PhC onto MWCNT is a spontaneous process ($\Delta_{ads}G^o < 0$). The $\Delta_{ads}G^o$ values follow the order: phenol < 2-methylphenol < 4-chlorophenol.

The value of $\Delta_{ads}S^o$ is negative, indicating an entropy decrease in the PhC molecules adsorbed onto the MWCNT–solution interface, caused primarily by a decrease in the configuration entropy of the PhC molecules. As the value of $\Delta_{ads}S^o$ is negative, the decrease in the Gibbs free energy of the system is caused by the negative $\Delta_{ads}H^o$, so the adsorption process is enthalpically driven. The specific interactions of the PhC molecules with the functional groups chemisorbed onto the surface of the MWCNTs (probably hydrogen bonds) are the driving force for the adsorption process. As observed in Figure **3** and table 3 the enthalpy of interaction is higher in the adsorption of the 2-methylphenol ($\Delta_{ads}H^o$ is more negative). Thus, the decrease in the configurational and conformational entropies is higher for this compound during its adsorption onto the MWCNT-interface (the $\Delta_{ads}S^o$ values are more negative than those of the other PhCs). Shen and colleagues [15] and Chen and colleagues [8] obtained the same behavior (enthalpic driven adsorption process) for the adsorption of nitroaromatic compounds (including 4-nitrophenol) and atrazine, respectively, on as-grown and oxidized MWCNTs. The thermodynamic description of the three phenols onto MWCNTs comes with some implications: the CNTs surface is not energetically homogeneous, presenting different chemical sites; the nature of interaction between the adsorbed molecule and adsorbent can vary according to the electronic density of the type of phenol; and the functional carbonaceous materials obtained by adsorption processes, as MWCNTs-phenols, can be customized for potential applications for electronic and energy storage devices.

The immobilization of all phenols onto MWCNT by exothermic interactions indicate that the modified adsorbent surface probably presents a higher chemical heterogeneity. The formation of intermolecular interactions, i.e. van der Waals, π-π or ion-inducted dipole, and the presence of phenol functional groups at MWCNTs surface, can provide a large and repeatable range of redox reactions. This may suggest an utilization of this material for electrode or film assembly for energy storage purposes [32].

4. CONCLUSIONS

This report describes, for the first time, the use of microcalorimetric techniques to evaluate the surface of an MWCNT sample and its interactions with phenolic compounds. The adsorption thermodynamics of phenol, 2-methylphenol and 4-chlorophenol on pristine multi-walled carbon nanotubes (MWCNTs) were evaluated using isothermal titration calorimetry (ITC) as the primary technique. The adsorption of any phenolic compound onto MWCNTs is a spontaneous process ($\Delta_{ads}G^o < 0$). Small variations in the chemical structures of phenolic compounds can considerably alter their energies of adsorption. The decrease in the Gibbs free energy of adsorption follows the order phenol < 2-methylphenol < 4-chlorophenol. The adsorption process is enthalpically driven, and the ITC data shows that the MWCNT interfaces have sites that allow specific interactions with phenolic compounds, not only hydrophobic and π-π dispersion interactions. Therefore, we can speculate that hydrogen bonding could be responsible for the large negative $\Delta_{ads}H^o$ values observed for all phenolic compounds.

The isotherms obtained at 298 K were fitted by the Langmuir and Freundlich models. Taking into account the quality of the fit given by the correlation coefficient (R^2), both adsorption models adjust the data in a reasonable way. However, according to the $\Delta_{ads}H^o$ values, models like that of Freundlich and others, which

Table 3: Thermodynamic Properties Obtained for the Adsorption of Phenolic Compounds on MWCNTs

PhC	Thermodynamic Properties				
	$\Delta_{ads}G^o$ / kJ mol^{-1}		$\Delta_{ads}H^o$ / kJ mol^{-1}	$T\Delta_{ads}S^o$ / kJ mol^{-1}	
	Langmuir	Thermodynamic		Langmuir	Thermodynamic
phenol	-12.48	−13.18	−31.08	-18.60	−17.90
2-methylphenol	-15.22	−15.07	−47.57	-32.34	−32.50
4-chlorophenol	-16.81	−18.01	−28.12	-11.31	−10.11

describe the adsorption on heterogeneous surfaces that have sites where adsorption occurs with different energies, seem to be more realistic models for the systems studied in this work. Finally, MWCNTs present a good alternative for the removal of pollutants from the environment, as well as the functional material obtained by adsorption process can be potentially used as a relevant component for electronic devices and energy storage.

CONFLICT OF INTEREST

The authors declare no competing financial or non-financial interests.

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