

# Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption

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## Abstract

The influence of surface chemistry and solution pH on the adsorption of benzene and toluene on activated carbon and its acid and heat treated forms were studied. A commercial coal-based activated carbon F-400 was chosen as carbon parent. The carbon samples were obtained by modification of F-400 by means of chemical treatment with HNO<sub>3</sub> and thermal treatment under nitrogen flow. The treatment with nitric acid caused the introduction of a significant number of oxygenated acidic surface groups onto the carbon surface, while the heat treatment increases the basicity of carbon. The pore characteristics were not significantly changed after these modifications. The dispersive interactions are the most important factor in this adsorption process. Activated carbon with low oxygenated acidic surface groups (F-400Tox) has the best adsorption capacity.

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## 1. Introduction

Aromatic organic compounds such as benzene and toluene are important materials in the chemical process industries. These materials are usually used as raw materials in numerous chemical productions and also often as solvent in a wide variety of manufacturing processes [1]. Since these organic compounds are classified as flammable, toxic, carcinogenic, and/or mutagenic agents, their presence in water stream even at low concentrations is of major environmental concern [2,3]. Hence, the removal of these organic pollutants from the water stream is critical to ensure the safety of water supplies.

A considerable effort has been dedicated in the past years concerning the removal of these compounds from wastewater, several methods have been proposed and developed, and the most extensively used is adsorption process [4–8]. For this purpose, various types of adsorbent have been used for removal of these organic compounds and adsorption onto activated carbons is a proven, reliable technology for removal of

small quantities of soluble organic compounds from water or wastewater.

To the present, activated carbon remains to be one of the most important microporous adsorbent from an industrial view of point. This adsorbent has very complex surface characteristics (porosity and surface chemistry), with pore size ranging from micropores (less than 2 nm) to macropores (more than 50 nm), and has a variety of surface groups, impurities and irregularities. The surface characteristics of activated carbon depend on the raw material used and the method of activation [9,10].

The surface chemistry of activated carbons determines their moisture content, catalytic properties, acid-base character, and adsorption capacity [11]. The surface chemistry of activated carbon is related to the presence of heteroatoms (oxygen, hydrogen, and nitrogen) other than carbon atom within the carbon matrix [10,11]. For adsorption of organic compounds in aqueous phase, the surface chemistry and the pH of the solution are the most important factors in controlling the adsorption process. The nature of surface groups in activated carbon can be modified through physical, chemical, and electrochemical treatments, and the most common is liquid phase treatment (chemical) using nitric acid and hydrogen peroxide. The treatment using oxidiz-

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ing chemicals will selectively remove some of the functional groups [12].

In present study, the commercial coal-based activated carbon F-400 was chosen as an adsorbent for the adsorption of benzene and toluene in aqueous solutions. The carbon was modified using acid and thermal treatments in order to change its surface chemistry. The adsorption performances of activated carbon before and after chemical treatment (oxidation) were examined. Surface groups of activated carbons were determined using Boehm titration. This titration technique was selected due its ability to provide qualitative and quantitative information of the carbon surface [10,11,13,14]. Here, the nature of interaction between the activated carbon surface chemistry and adsorptive molecules will be obtained, and this will allow the development of specified carbon adsorbent for benzene and toluene removal. The Langmuir adsorption isotherm model was then used to correlate the adsorption experimental data.

## 2. Experimental

### 2.1. Materials

Commercial coal-based granular activated carbon Filtrasorb-400 (F-400) was used in this study. Prior to use, the carbon was repeatedly washed with distilled water in order to remove fine particles and subsequently dried using vacuum drying oven at 110 °C for at least 24 h. The dried activated carbon was then kept in a desiccator for later use.

The adsorbates used in this study were benzene and toluene. These chemicals were analytical grade with greater than 99% purity and purchased from Merck. These chemicals were used without any further purification.

### 2.2. Preparation of modified activated carbon

To prepare modified activated carbon, chemical treatment using nitric acid and thermal treatment were carried out on F-400 activated carbon sample in order to obtain carbons with different surface chemistry.

#### 2.2.1. Chemical treatment using nitric acid

The chemical treatment of F-400 was carried out using nitric acid at a concentration of 12 M for 6 h. After oxidation completed, the resulting samples were repeatedly washed to neutral pH using distilled water in order to remove any excess oxidizing agent, and water soluble compounds. Subsequently the samples were dried in a vacuum drying oven at 110 °C for 24 h and stored in a desiccator for later use. Here the oxidized samples are referred as F-400Cox.

#### 2.2.2. Thermal treatment

Thermal treatment was carried out in a tubular reactor (Tube furnace Thermolyne 21100). Twenty grams of F-400 were placed in a tubular reactor and heated at a temperature of 800 °C. The thermal treatment was performed under nitrogen flow of 150 cm<sup>3</sup>/min. The thermal process was initiated by heating

the sample at heating rate of 10 °C/min from room temperature (around 30 °C) until the desired temperature (800 °C) was reached. Samples were held at 800 °C for 3 h before cooling under nitrogen flow. After the samples reached the room temperature, air with a flow rate of 150 cm<sup>3</sup>/min was introduced into the tubular reactor and kept for 1 h. With introducing the air into the heat treated samples, the fixation of oxygen in the active sites generated by the decomposition of carboxylic acid, lactone, and phenol groups occurred. These new oxygen-containing surface groups were basic pyrone-type groups, which resulted from the combination of the remaining carbonyl groups and the ether-type oxygen groups that have been previously formed [12,15]. Here the thermal treatment samples are referred as F-400Tox.

### 2.3. Pore structure characterization

The pore structure characteristics of the resulting char and activated carbons were determined by nitrogen adsorption at 77.35 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. Prior to gas adsorption measurements, the carbon was degassed at 300 °C in vacuum condition for a period of at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure ( $P/P_0$ ) range from approximately 10<sup>-5</sup> to 0.995. The BET surface area ( $S_{BET}$ ), micropore volume ( $V_{micro}$ ) and micropore surface area ( $S_{micro}$ ) of the activated carbons were determined by application of the Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) analysis software available with the instrument, respectively. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3 [16]. The mesopore surface areas ( $S_{meso}$ ) were determined by the application of  $t$ -method on adsorption isotherms. The pore size distributions of carbons were determined from adsorption isotherm data using the Micromeritics density functional theory (DFT) software, with medium regularization.

### 2.4. Surface chemistry determination

The surface oxides or surface chemistry on a carbon can have acidic as well as basic properties and can be conveniently determined by titration method [13]. The amount of acidic surface oxygen groups (carboxylic, lactonic, and phenolic groups) was determined using Boehm titration method [10,11,13]. The Boehm method is described as follows: 0.5 g of carbon sample was added to a series of flasks containing 50 cm<sup>3</sup> of 0.05 M: NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, and HCl solutions. The flasks were then sealed and shaken for 24 h at room temperature. The suspension was then decanted and 10 cm<sup>3</sup> of the remaining solution was titrated with 0.05 M HCl or NaOH, depending on the original solution used. The number of acidic groups was calculated based on the assumptions that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na<sub>2</sub>CO<sub>3</sub> neutralizes carboxylic and lactonic groups; and NaHCO<sub>3</sub> neutralizes only carboxylic groups. The number of basic sites was determined from the amount of HCl that reacted with the carbon.

## 2.5. $pH_{PZC}$ determination

The  $pH_{PZC}$  is the pH on zero point charge, which is the point at which the net charge of the adsorbent is zero. The  $pH_{PZC}$  of carbons was determined from acid–base titration. The procedure of  $pH_{PZC}$  determination is described as follows [17]: aliquots with 50 cm<sup>3</sup> of 0.01 M NaCl solution were prepared in different flasks. Their pH values were adjusted to the value between 2 and 12 with the addition of 0.01 M solutions of HCl or NaOH. When the pH value was constant, 0.15 g of activated carbon sample was added to each flask and it was shaken for 48 h. The final pH was measured using pH meter Schott CG 825 after 48 h. The  $pH_{PZC}$  value is the point where the curve  $pH_{final}$  versus  $pH_{initial}$  crosses the line  $pH_{initial} = pH_{final}$ .

## 2.6. Adsorption procedure

Adsorption experiments were carried out by adding a known mass of activated carbon to glass flasks filled with 100 ml of benzene or toluene aqueous solutions. No headspace was left in the flasks in order to avoid any possible losses of the aromatic compounds due to volatilization during the course of the experiments. The glass flasks containing the solution and carbons were tightly covered with Teflon caps and then placed in thermostatic shake water bath (Thermolyne) at a controlled temperature of  $30 \pm 0.1$  °C and at a maximum shaking speed for 10 h. Preliminary experiments indicated that the adsorption equilibrium was reached in about 8 h for both benzene and toluene with no appreciable decrease in adsorbate bulk concentration for time period up to 1 week. The pH was measured at the beginning and at the end of each experiment using a pH meter (Schott CG 825). The results indicated that no significant variation in the pH was detected in all of experiments. Adsorption experiments were carried out at pH of 3, 7, and 11. In order to adjust the solution pH, NaOH and HCl solutions of different concentrations were added to the systems. Since the added amounts of these solutions were insignificant compared to the total volume of the systems (suspensions), it was assumed that the concentration of solutes was not affected by these additions.

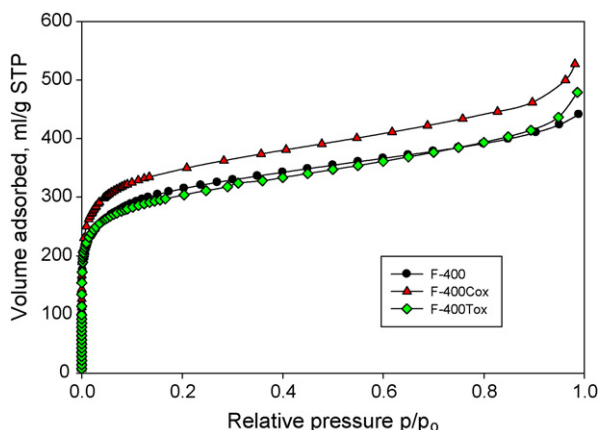


Fig. 1. Nitrogen adsorption on activated carbon F-400 and its modified carbons.

The initial and equilibrium concentrations of adsorbate solutions were determined by means of Shimadzu visible spectrophotometer (UV-1201) at 206 and 254 nm wavelength for toluene and benzene, respectively. The amount of benzene and toluene adsorbed on the activated carbon ( $q_e$ ) was determined from the initial liquid phase concentration and equilibrium concentration:

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations, respectively,  $V$  the volume of solution, and  $m$  is the mass of adsorbent.

## 3. Results and discussion

### 3.1. Activated carbon pore structure characterization

Low temperature nitrogen adsorption isotherms were used to characterize the pore structure of the activated carbons. The adsorption isotherms of nitrogen on F-400, F400Cox, and F-400Tox are shown in Fig. 1. These isotherms clearly show the largely microporous nature of the carbons, with some mesopores leading to a gradual increase in adsorption after the initial filling of the micropores, followed by a more rapid increase near saturation.

The pore characteristics of the three carbon samples used in this study obtained from the interpretation of nitrogen isotherm are given in Table 1. From this table, it can be seen that the pore characteristic of activated carbon samples are approximately the same for all samples. By comparing the pore characteristics of the samples, it is clear that the chemical as well as the thermal treatments used in this study caused insignificant effect on the textural properties. Therefore the adsorption properties of these carbons will depend mainly on their surface chemistry.

In order to give more evidence about the effect of the chemical and thermal treatment on the pore structure of the samples, we also present the DFT pore size distribution of carbons as depicted in Fig. 2. Here, the pore size distribution represents a model of solid internal structure, which indicates that an equivalent set of non-interacting and regularly shaped model pores can represent the complex void spaces within the real solid. The pore size distribution is closely related to both kinetic and equilibrium properties of porous material, and perhaps is the most important aspect for characterizing the structural heterogeneity of porous materials used in industrial application. From Fig. 2, it can be seen that regularization-based pore size of carbon has essentially the same type of distribution (bimodal distribution) with peaks around 0.40–0.60 and 1.40–1.70 nm.

Table 1  
Pore structure characteristic of activated carbon samples

Sample	Pore structure characteristic			
	$S_{BET}$ (m <sup>2</sup> /g)	$S_{micro}$ (m <sup>2</sup> /g)	$S_{meso}$ (m <sup>2</sup> /g)	$V_{micro}$ (cm <sup>3</sup> /g)
F-400	877.82	761.81	83.74	0.342
F-400Cox	938.36	807.19	107.56	0.351
F-400Tox	863.66	734.32	114.65	0.339

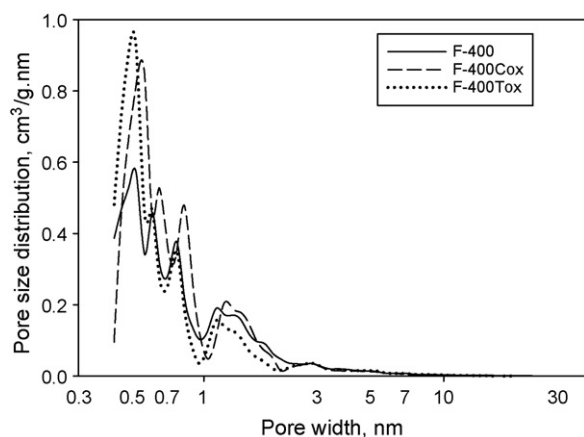


Fig. 2. Pore size distributions of the carbons.

### 3.2. Effect of treatments on the surface chemistry

The carbon matrix does not consist of carbon atoms alone, but is also formed by other heteroatom like hydrogen, oxygen, nitrogen, halogen, sulfur, phosphorus, etc. [18]. These heteroatoms bonded to the edges of the carbon layers, which govern the surface chemistry of activated carbon [10,19]. The surface chemistry of carbon materials is basically determined by the acidity and basicity of their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, etc., has been postulated as constituting the source of surface acidity [18,20,21]. Whereas the basic properties of activated carbon is associated with two types of structures: (i) the presence of oxygen containing groups, i.e. pyrone, chromene, and carbonyl structures, at the edge of carbon crystallite and (ii) oxygen free Lewis basic site on the graphene layers. The Lewis basicity of delocalized  $\pi$  electrons is influenced by the aromatic system on the carbon surface [20,22,23].

The surface chemistry of carbons has been indicated to have a significant effect on the uptake of small molecules of organic compounds. Hence, the surface chemistry of commercially coal-based activated carbon F-400 was modified using chemical ( $\text{HNO}_3$ ) and thermal treatments in order to study this effect. The content of surface chemistry of  $\text{HNO}_3$  and thermal treated of F-400 samples obtained from Boehm titration, along with the  $\text{pH}_{\text{PZC}}$  values of the carbon surface are shown in Table 2. It is clear that the number of oxygenated acidic surface groups increases upon oxidation or treatment with nitric acid, and decrease upon thermal treatment. It also can be seen that  $\text{HNO}_3$  is a strong oxidizing acid so it would oxidize carbon atoms and cause the carbon surfaces to lose its electrons and become positively charges. Simultaneously, oxygen anions

exist in the solution would be adsorbed to form surface oxides. In the thermal treatment, the surface oxide decompose to carbon monoxide and carbon dioxide, highly reactive sites remain on the carbon surface which have free-radical character to some relatively small extent. After cooling to room temperature and insertion of air to the system, they can react with oxygen present in air, giving new surface oxide, which can be assigned to some carbonyls, pyrone, and chromene-type structures [12,13]. These groups have a basic character, conferring basic properties to sample F-400Tox. As expected, for  $\text{HNO}_3$  treatment, the  $\text{pH}_{\text{PZC}}$  and basicity values decrease with the increase in the amount of oxygenated acidic surface groups, while the opposite is observed for the thermal treatment.

### 3.3. Adsorption studies

The analysis and design of adsorption separation processes require relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process. Adsorption in the liquid phase is, in general, a more complex phenomenon than gas phase adsorption. In the liquid phase adsorption, the adsorbed molecules are not necessarily tightly packed with identical orientation. The presence of solvent molecules and the formation of micelles from adsorbed molecules also increase the complexity of liquid phase adsorption. Adsorption from the liquid phase is influenced by numerous factors such as pH, solubility of adsorbate in the solvent, temperature, and surface chemistry of the adsorbent [24].

In the adsorption mechanism of aromatic compounds in liquid phase on activated carbons there are two main types of interactions: electrostatic and dispersive [12]. The functional group linked to the adsorptive aromatic ring can activate or deactivate it, delocalizing its electronic charge. Electron-withdrawing groups on an aromatic ring create a partial positive charge in the ring, while deactivating groups produce the opposite effect, creating a partial negative charge [12].

The adsorption equilibrium data of benzene and toluene on activated carbon samples were fitted by several well-known isotherm models to assess their efficacies. These include Langmuir and Freundlich models. Langmuir model is the most widely used isotherm equation, which has the form as follow:

$$q_e = q_0 \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_0$  and  $K_L$  are Langmuir isotherm parameters, representing the maximum adsorption capacity for the solid phase loading and the Langmuir equilibrium constant related to the heat of adsorption, respectively. Figs. 3 and 4 depict the adsorption

Table 2  
Surface chemistry of activated carbon samples

Sample	$\text{pH}_{\text{PZC}}$	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Acidity (meq/g)	Basicity (meq/g)
F-400	8.72	0	0.031	0.169	0.200	0.531
F-400Cox	3.51	0.432	0.217	0.322	0.971	0.174
F-400Tox	11.9	0	0.013	0.039	0.052	0.827

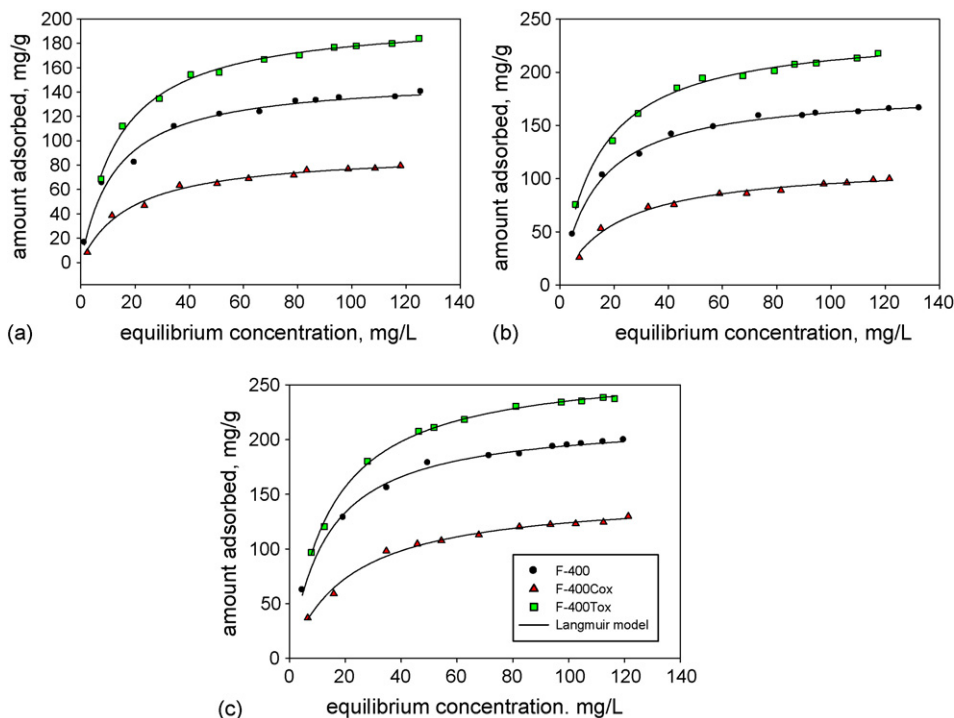


Fig. 3. Adsorption isotherms of benzene and Langmuir model prediction: (a) pH 3, (b) pH 7, and (c) pH 11.

isotherm of benzene and toluene on activated carbon samples at various solutions pH. In these figures, the experimental data are represented as symbols and the Langmuir model as solid lines. These figures clearly show that the Langmuir equation can describe the experimental data fairly well. The equation parameters were calculated using nonlinear regression fitting using Sigmaplot software version 9. The optimal parameters from the

fitting of Langmuir equation with the experimental data are given in Tables 3 and 4 for benzene and toluene, respectively.

Here, benzene and toluene are in the molecular form in the whole ranges of pH, in this case, dispersive interactions are predominant, mainly because of the attraction between the  $\pi$  orbital on the carbon basal planes and the electronic density in the benzene and toluene aromatic rings ( $\pi$ - $\pi$  interactions) [12].

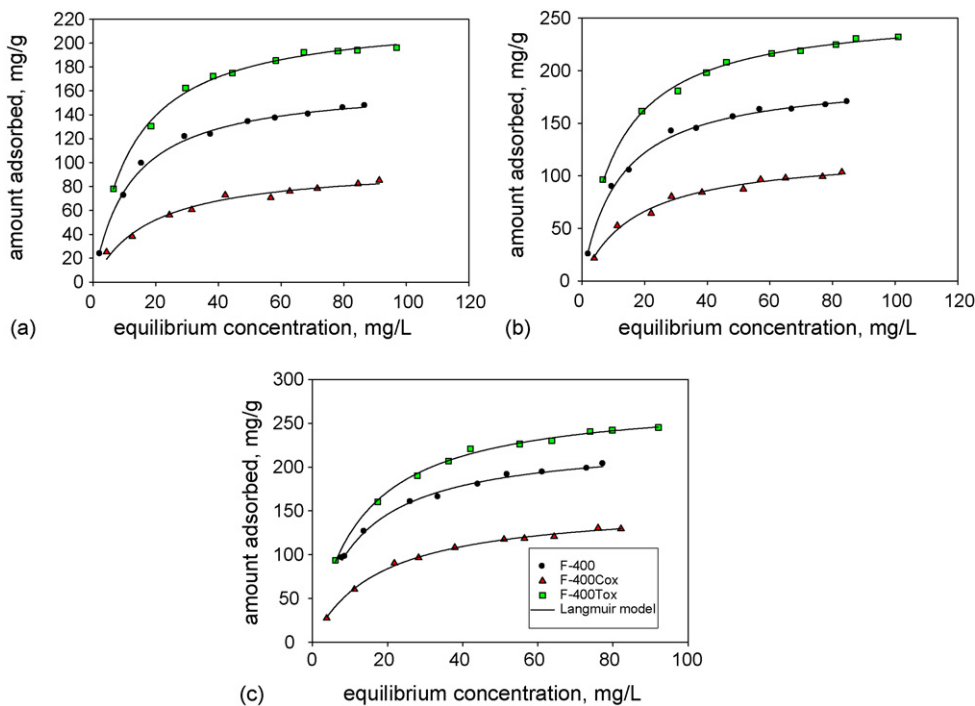


Fig. 4. Adsorption isotherms of toluene and Langmuir model prediction: (a) pH 3, (b) pH 7, and (c) pH 11.



Table 3  
Parameters of the Langmuir equation for the adsorption of benzene

Sample	$q_0$ (mg/g)			$K_L$ (l/mg)		
	pH 3	pH 7	pH 11	pH 3	pH 7	pH 11
F-400	151.82	183.29	219.42	0.0777	0.0765	0.0775
F-400Cox	90.82	114.41	150.13	0.0540	0.0498	0.0473
F-400Tox	201.52	240.07	268.97	0.0737	0.0729	0.0699

Table 4  
Parameters of the Langmuir equation for the adsorption of toluene

Sample	$q_0$ (mg/g)			$K_L$ (l/mg)		
	pH 3	pH 7	pH 11	pH 3	pH 7	pH 11
F-400	166.27	194.11	230.53	0.0849	0.0841	0.0862
F-400Cox	98.34	122.33	157.07	0.0563	0.0586	0.0572
F-400Tox	223.64	257.74	279.16	0.0828	0.0856	0.0797

From Figs. 3 and 4 as well as Tables 3 and 4, it is evident that the adsorption capacity increase from F-400Cox < F-400 < F-400Tox which indicates the same trend as the carbon basicity (see Table 2), and this supports the statement that the dispersive interactions increase with the carbon basicity. Removal of the oxygenated acidic surface groups by thermal treatment (F-400Tox) favors the specific interactions between  $\pi$  orbital on the carbon basal plane and the aromatic rings of benzene and toluene, thus enhancing the adsorption.

#### 4. Conclusions

The results obtained in this study show that the aqueous phase adsorption of benzene and toluene on activated carbons F-400, F-400Cox, and F-400Tox is governed by dispersive interaction. Furthermore the surface chemistry and solution pH play important roles on the adsorption of these aromatic compounds on activated carbons used in this study. From a practical point of view, in order to improve the adsorption capacity of organic compounds in the molecular state for a broad range of pH, the thermal treatment is desired. The sample with highest basicity gave the best adsorption capacity.

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