# Adsorption of aromatic organic acids onto high area activated carbon cloth in relation to wastewater purification

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## Abstract

Adsorption of aromatic organic acids: benzoic acid (BA), salicylic acid (SA), $p$-aminobenzoic acid ($p$ABA) and nicotinic acid (NA), onto high area activated carbon cloth from solutions in 0.4 M $H_2SO_4$, in water at natural pH, in 0.1 M NaOH and also from solutions having pH 7.0 were studied by in situ UV-spectroscopic technique. The first-order rate law was found to be applicable for the kinetic data of adsorption. The rates and extents of adsorption of the organic acids were the highest from water or 0.4 M $H_2SO_4$ solutions and the lowest from 0.1 M NaOH solution. The order of rates and extents of adsorption of the four organic acids in each of the four solutions (0.4 M $H_2SO_4$, water, solution of pH 7.0 and 0.1 M NaOH) was determined as SA > BA > NA ∼ $p$ABA. These observed orders were explained in terms of electrostatic, dispersion and hydrogen bonding interactions between the surface and the adsorbate species, taking the charge of the carbon surface and the adsorbate in each solution into account. Adsorption of BA in molecular form or in benzoate form was analyzed by treating the solution as a mixture of two components and applying Lambert–Beer law to two-component system. The adsorption isotherm data of the systems studied were derived at 30 °C and fitted to Langmuir and Freundlich equations.
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## 1. Introduction

Benzoic acid and its derivatives are commonly used as a preservative or reaction intermediate, as well as antiseptic agents in various industrial branches such as food, pharmaceutics, textile and cosmetic. Therefore they are often found in domestic and industrial wastewaters [1–3]. Salicylic acid is used today in wart-removing medicines, to externally treat fungus infections, as an acne topic treatment and to increase the cell turnover as a component of skin creams. Other applications of salicylic acid are related to the plant protection against insects and pathogens. Salicylic acid may enter the environment through a variety of sources including homes, hospitals, animal feeding operations and pharmaceutical manufactures [4]. Salicylic acid is also used as an intermediate in the manufacture of dyes [5].

Because of their harmful effects, wastewaters containing aromatic acids must be treated before discharging to receiver water bodies. Popular treatment processes are destruction of these compounds by biological degradation or chemical oxidation and removal of them by adsorption [1]. For the treatment by adsorption, some of the main adsorbents in commercial and laboratory use include activated carbon, alumina, silica, bentonite, peat, chitosan and ion-exchange resins [6].

Activated carbon is one of the oldest and the most widely used adsorbents for the adsorption of organic compounds. It has been utilized in powder or granular form. These forms have been the primary adsorbent material for many adsorption studies on organics [7–11]. In recent years, activated carbon cloth or fiber has received considerable attention as a potential adsorbent for water treatment applications. These materials in the form of felt or cloth have the advantages of having high specific surface area (as high as 2500 $m^2\,g^{-1}$), mechanical integrity, easy handling and minimal diffusion limitation to adsorption [12].

Activated carbon cloth has been used for successful adsorptive removal of various inorganic anions. Adsorption of related sulfur containing anions onto carbon cloth was reported by Ayranci and Conway [13]. Sulfide and thiocyanate anions were

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found to be adsorbed to greater extents than others. A reduction of 68% in $SCN^-$ concentration was achieved on open circuit with 0.5 g activated carbon cloth from 20 mL $5 \times 10^{-4}$ M solution. This degree of removal was increased to 95% upon polarization of carbon cloth. Adsorbability of such impurity ions was related to their hydration properties in water. Afkhami [14] reported adsorptive and electrosoprtive removal of some other oxyanions by activated carbon cloth. It was concluded that carbon cloth was an effective sorbent for Cr(VI), Mo(VI), W(VI) and V(V) ions and acidification of the solution significantly increased adsorption of investigated ions except V(IV). Therefore it was suggested that the method provides an interesting mean for separation of V(IV) and V(V) species in solution. Afkhami and Conway [15] achieved lowering of initial $1 \times 10^{-4}$ M concentration of $NO_3{}^-$ and $NO_2{}^-$ by 22 and 10%, respectively, using the method of adsorption onto carbon cloth. Adsorption and electrosorption of another noxious sulfur containing anion, ethyl xanthate, onto carbon cloth was studied by Ayranci and Conway [16] and the results were compared with those of $SCN^-$. The possibility of using carbon cloth for effective and selective separation of anions was demonstrated. Increase in adsorbability upon pre-wetting of carbon cloth was first noted in this work. Successful use of activated carbon cloth for adsorptive removal of various groups of organic compounds has also been demonstrated. A series of phenolic and anilinic compounds were studied for their removal from aqueous solutions by adsorption onto activated carbon cloth [17–21]. Kinetic and equilibrium aspects of adsorption were given in these works. A similar adsorption work onto activated carbon cloth was also carried out by Conway et al. [22] for a series of aromatic heterocyclic compounds. Thiophene was found to exhibit the highest adsorption rate among seven compounds studied. This was attributed to the presence of electron donative S heteroatom in the structure of thiophene. The influences of dipole moment, the orientation at the carbon cloth surface and the size of the compound as well as the type of heteroatom in the ring and the adsorbates' hydration parameters, on the extent of adsorption of these compounds at the carbon cloth were investigated. Niu and Conway [23] have taken pyridine alone and investigated an extensive study on its adsorption and electrosorption on carbon cloth. The present work takes another important group of compounds, aromatic organic acids, to investigate their adsorption behavior on activated carbon cloth.

The adsorption behavior of activated carbon from adsorbate solutions is affected by both the surface and the solution properties [10]. The presence of surface functional groups such as carboxyl, lactone, phenol, carbonyl, ether, pyrone and chromene, gives activated carbon an acid–base character [24]. Surface charge density is also an important factor in determining the adsorption characteristics of activated carbon. It is determined by the solution pH and by the parameter $pH_{PZC}$ which is the pH of a solution when the net surface charge is zero. The net charge on carbon surface is positive at a solution pH lower than $pH_{PZC}$ and is negative at a solution pH higher than $pH_{PZC}$ [25]. Not only the net surface charge but also the amount of ionic species arising from ionizable adsorbates is determined by the pH of the solution. The $pK_a$ or $pK_b$ values of the ionizable molecule are

also important together with the solution pH for determining the extent of ionization.

The purpose of the present work was to investigate the adsorption behaviors of benzoic acid (BA), salicylic acid (SA), $p$-aminobenzoic acid ($p$ABA) and nicotinic acid (NA) from aqueous solutions having a range of pH onto high area activated carbon cloth by means of in situ UV spectroscopy. The examination of the effect of ionization of these aromatic acids on their adsorption was also aimed.

## 2. Materials and methods

### 2.1. Materials

The activated carbon cloth (ACC) used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225. Benzoic acid and nicotinic acid (pyridine-3-carboxylic acid) were obtained from Merck, salicylic acid ($o$-hydroxy benzoic acid) from BDH and $p$-amino benzoic acid from Riedel-de Häen. NaOH, $H_2SO_4$, HCl, $NaHCO_3$, $Na_2CO_3$, $HNO_3$ and $NaNO_3$ were reagent grade. Deionized water was used in adsorption experiments.

### 2.2. Treatment and properties of the carbon cloth

The activated carbon fibers are known to provide spontaneously a small but significant quantity of ions into the conductivity water probably due to their complex structures originating from their somewhat unknown proprietary preparation procedure [13,26]. Therefore a deionization cleaning procedure was applied to avoid desorption of these ions during adsorption studies, as described previously [13,20,22]. In this procedure, a carbon cloth sample was placed in a flow-through washing cup and eluted with 5 L of warm (60 °C) conductivity water in a kind of a series of batch operations for 2 days with $N_2$ bubbling in order to avoid possible adsorption of $CO_2$ that might have been dissolved in water. The out-flow water from each batch was tested conductometrically for completeness of the washing procedure. The washed carbon cloth modules were then dried under vacuum at 120 °C and kept in a vacuum desiccator for further use.

The specific surface areas of the treated and untreated carbon cloth pieces were measured as 1870 and 2200 $m^2\,g^{-1}$, respectively, by $N_2$ adsorption isotherm method. (These measurements were done by central laboratory of Middle East Technical University, Ankara, Turkey, according to multipoint BET method.) There is an obvious decrease in specific surface area upon the washing treatment. A similar decrease was observed in surface area of granular activated carbon upon aqueous treatment by László et al. [27]. Pore size distribution measurements were also carried out in the same laboratory for the treated ACC. The pore volume distribution curve obtained according to density functional theory (DFT) is given in Fig. 1. Calculations have shown that the total pore volume is 0.827 $cm^3\,g^{-1}$. The portions of micro- and meso-pores in this total volume were found to be 0.709 and 0.082 $cm^3\,g^{-1}$, respectively. SEM pictures of treated (washed) carbon cloth were previously given [16]. The average
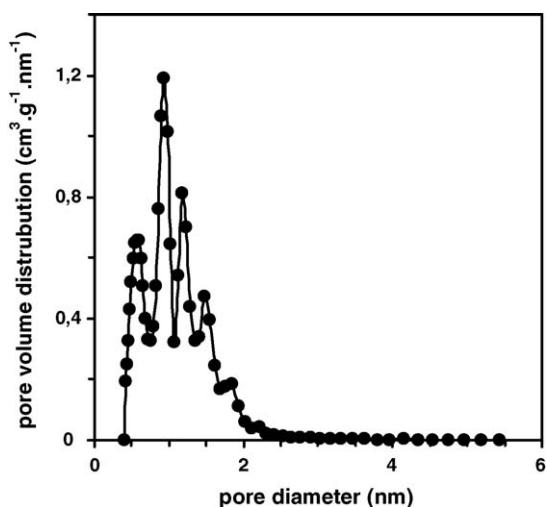
Fig. 1. Pore size distribution of treated ACC according to DFT theory.



Fig. 2. Plot of $pH_f$ vs. $pH_i$ for the determination of $pH_{PZC}$ of the carbon cloth in 0.01 M NaNO$_3$ (○), in 0.05 M NaNO$_3$ (▲) and in 0.1 M NaNO$_3$ (●).

fiber diameter was measured as 17 μm from these SEM pictures [21].

The electrochemical characterization of the carbon cloth was reported previously [13,16]. Another property of the carbon cloth in relation to adsorption studies is the $pH_{PZC}$ which was defined above. The $pH_{PZC}$ of the activated carbon cloth used in the present study was previously measured in 0.1 M NaNO$_3$ by batch equilibrium method described by Babić et al. [28] and determined to be 7.4 [20]. This value was also determined at different ionic strength values. For this purpose, the carbon-cloth samples of $100 \pm 0.1$ mg were dipped into 40 mL solutions of 0.1 M NaNO$_3$, 0.05 M NaNO$_3$ or 0.01 M NaNO$_3$ at different initial pH values which were adjusted by adding NaOH or HNO$_3$ solutions. These solutions were shaken in erlenmeyer flasks for 24 h. At the end of 24 h contact period, the amount of H$^+$ or OH$^-$ ions adsorbed by the carbon cloth was calculated from the difference between the initial and the final concentrations of H$^+$ or OH$^-$ ions, determined from the initial and the final pH values ($pH_i$ and $pH_f$, respectively) measured with a Jenway 3040 ion analyzer using glass electrode. $pH_f$ readings for the determination of $pH_{PZC}$ were plotted as a function of $pH_i$ in Fig. 2. It is seen that data points obtained at different concentrations of NaNO$_3$ fit into one common curve. This shows that $pH_{PZC}$ is independent of ionic strength. Similar conclusion was arrived by Babić et al. [28] after making measurements at 0.1 M NaNO$_3$ and 0.01 M NaNO$_3$ solutions for their carbon cloth. The $pH_f$ value of the plateau observed in Fig. 2 corresponds to the pH at which there is no net OH$^-$ or H$^+$ adsorption [28]. At this pH, the difference between the initial and the final [H$^+$] or [OH$^-$] is zero. This pH was determined to be 7.4 and taken as the $pH_{PZC}$ of the carbon cloth used [20,21].

The contents of acidic and basic surface groups on the activated carbon cloth were determined according to the Boehm method [29]. Activated carbon cloth samples of $100.0 \pm 0.1$ mg were placed in 75 mL 0.01 M solutions of NaHCO$_3$, Na$_2$CO$_3$, NaOH and HCl separately. The erlenmeyer flasks containing the samples were shaken in Nüve ST 402 shaking waterbath at a constant shaking speed of 150 rpm for 48 h. Then, 20 mL
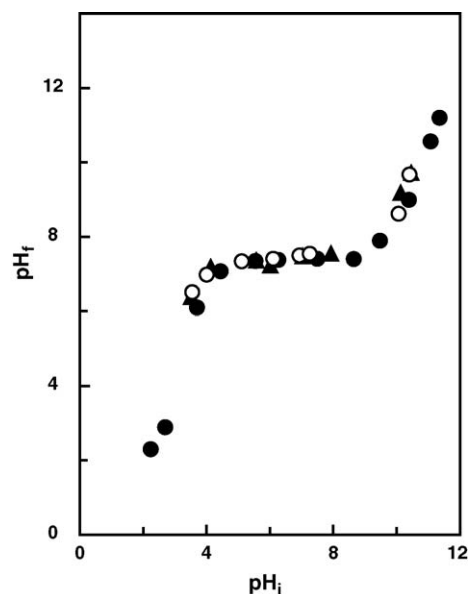
aliquots from each solution were back titrated with standard HCl or NaOH for the excess base or acid. Titrations were carried out with Metrohm E 274 burette. A blank titration was also carried out for correction. The amount of acidic sites of various types were calculated based on the assumption that NaOH neutralizes carboxylic, lactonic and phenolic groups; Na$_2$CO$_3$ titrates carboxylic and lactonic groups and NaHCO$_3$ neutralizes only carboxylic groups on the activated carbon cloth [29]. The amount of surface basic sites was calculated from the amount of HCl reacted with the carbon cloth. It was found from the above treatment that the activated carbon cloth used in this study has 0.093 mmol/(g carbon cloth) carboxylic groups, 0.020 mmol/(g carbon cloth) lactonic groups and 0.14 mmol/(g carbon cloth) phenolic groups, giving a total of 0.25 mmol/(g carbon cloth) acidic groups, and 0.28 mmol/(g carbon cloth) basic groups.

## 2.3. The design of the adsorption cell and optical absorbance measurements

A specially designed cell was used to carry out the adsorption and simultaneously to perform in situ concentration measurements by means of UV absorption spectrophotometry. This cell was described in detail, including a diagram, in our previous works [20,22]. With the use of this special adsorption cell, it was possible to follow the changes in concentration of the adsorbate solution during the course of adsorption by in situ UV spectroscopy. Solutions of organic acids were prepared in water at natural pH, in water at pH 7.0 adjusted by dilute NaOH, in 0.4 M H$_2$SO$_4$ or in 0.1 M NaOH to examine the effects of both the surface charge of the carbon cloth and the ionization of organic acids on adsorption. The initial concentrations of organic acids and the amount of carbon cloth were kept as constant as possible for kinetic studies of adsorption in order to make an easy comparison (concentration: $1.70–1.75 \times 10^{-4}$ M, mass of carbon cloth: $15.0 \pm 0.1$ mg). The carbon-cloth pieces were pre-wetted

by leaving in water for 24 h before use. During this long contact period with water, the pores of the carbon cloth may expand and become more accessible for the adsorbates in the actual adsorption process. The idea of using pre-wetted carbon cloth originated from our previous findings that pre-wetting enhances the adsorption process [13,16].

The carbon cloth piece was dipped into the adsorption cell initially containing only water and vacuum was applied to remove all air in the pores of the carbon cloth. Then wetted and degassed carbon cloth was removed from the cell for a short time and water in the cell was replaced with a known volume of sample solution (20 mL). The sliding door of the sample compartment of the spectrophotometer was left half-open and quartz cuvette fixed at the bottom of the adsorption cell (which now contained the sample solution) was inserted into the front sample compartment. A teflon tube connected to the tip of a thin $N_2$-bubling glass tube was lowered from one arm of the adsorption cell down the UV cell to a level just above the light path to provide effective mixing. Finally, the carbon cloth, which was removed temporarily after wetting and degassing, was re-inserted from the other arm of the adsorption cell into the solution. Then, quickly, an opaque curtain was spread above the sample compartment of the spectrophotometer, over the cell, to prevent interference from external light. A Shimadzu 160A UV/vis spectrophotometer was used for the optical absorbance measurements.

The program for monitoring the absorbance at the specific wavelength of maximum absorbance pre-determined by taking the whole spectrum of each organic acid was then run on the built-in microcomputer of the spectrophotometer. Absorbance data was recorded in programmed time intervals of 1 min over a period of 90 min.

Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each organic acid species in neutral, cationic or anionic form.

### 2.4. Determination of adsorption isotherms

The adsorption isotherms of organic acids were determined on the basis of batch analysis. The carbon cloth pieces of varying masses were allowed to equilibrate with solutions of organic acids in 0.4 M $H_2SO_4$, in water at natural pH, in water at pH 7.0 or in 0.1 M NaOH with known initial concentrations at 30 °C for 48 h. Preliminary tests showed that the concentration of organic acids remained unchanged after 20–24 h contact with the carbon cloth. So, the allowed contact time of 48 h ensures the equilibration. Similar equilibrium times were obtained after preliminary tests in our previous works [20,21]. The equilibration was allowed in 100 mL erlenmeyer flasks kept in Nüve ST 402 shaking waterbath at a constant shaking speed of 150 rpm. The concentrations after the equilibration period were measured spectrophotometrically. The amount of organic acid adsorbed per unit mass of the carbon cloth, $q_e$, was calculated by the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where $V$ is the volume of the solution of organic acid in L, $C_0$ and $C_e$ are the initial and equilibrium concentrations, respectively, in mmol L$^{-1}$ and $m$ is the mass of carbon cloth in g. Then Eq. (1) gives $q_e$ in mmol adsorbate adsorbed/g carbon cloth.

## 3. Results and discussion

### 3.1. Chemical nature, optical absorption characteristics and calibration data of the organic acids

Chemical, spectral and calibration data for the organic acids studied are given in Table 1. Separate calibration experiments were run to determine the molar absorptivities ($\varepsilon$) required for calibration using aqueous solutions of the pure compounds. Absorbance versus concentration data for each single compound were treated according to the Lambert–Beer law by linear regression analysis to determine $\varepsilon$ and the regression coefficient, $r$.

### 3.2. Adsorption behaviors of the organic acids over 90 min

Adsorption of organic acids studied were followed by in situ UV spectroscopy in one min intervals over 90 min period, starting with the same initial concentration for each of the organic acids and using the same mass of carbon cloth. Adsorption behaviors from solutions of organic acids in 0.4 M $H_2SO_4$, in water at natural pH, in solution at pH 7.0 or in 0.1 M NaOH onto activated carbon cloth are shown in Fig. 3 for BA, in Fig. 4 for SA, in Fig. 5 for NA and in Fig. 6 for $p$ABA. The adsorption could not be followed for $p$ABA in water because the continuous shift in the wavelengths of absorption in this solvent did not allow obtaining a reliable calibration curve.
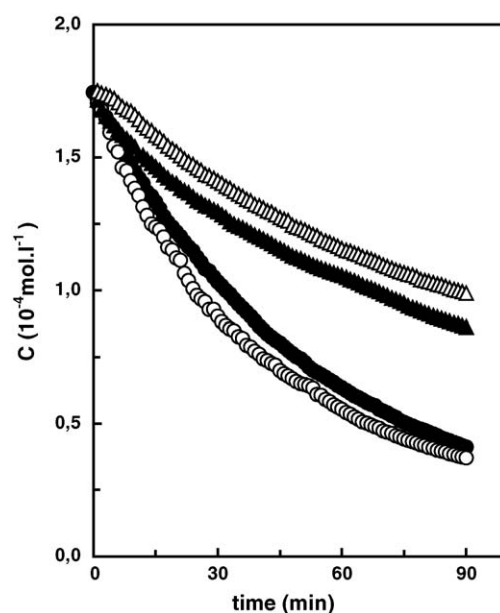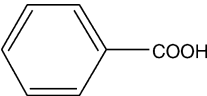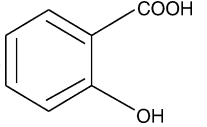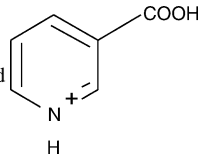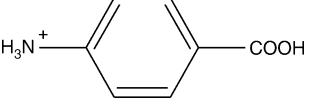


Fig. 3. Adsorption behavior of BA: in 0.4 M $H_2SO_4$ (●), in natural pH (○), in solution at pH 7.0 (▲) and in 0.1 M NaOH (△).

Table 1
Spectral and calibration data for the organic acids

| Organic acids and their molecular structure | $pK_{a1}$ | $pK_{a2}$ | Solvent | $\lambda_{max}$ (nm) | $\varepsilon$ (L mol$^{-1}$ cm$^{-1}$) | $r$ |
|---|---|---|---|---|---|---|
| Benzoic acid | 4.20[a] | – | 0.4 M H$_2$SO$_4$ | 231 | 10500 | 0.9998 |
| | | | Solution at pH 7.0 | 224 | 8000 | 0.9999 |
| | | | 0.1 M NaOH | 224 | 7900 | 0.9998 |
| Salicylic acid | 2.97[a] | 13.74[a] | 0.4 M H$_2$SO$_4$ | 303 | 3400 | 0.9998 |
| | | | Water | 297 | 3400 | 0.9996 |
| | | | Solution at pH 7.0 | 297 | 3500 | 0.9999 |
| | | | 0.1 M NaOH | 297 | 3300 | 0.9997 |
| Nicotinic acid | 2.05[a] | 4.81[a] | 0.4 M H$_2$SO$_4$ | 261 | 4500 | 0.9999 |
| | | | Water | 262 | 4200 | 0.9997 |
| | | | Solution at pH 7.0 | 263 | 3100 | 0.9999 |
| | | | 0.1 M NaOH | 263 | 2800 | 0.9996 |
| 4-Aminobenzoic acid | 2.50[b] | 4.87[b] | 0.4 M H$_2$SO$_4$ | 227 | 11200 | 0.9994 |
| | | | Solution at pH 7.0 | 266 | 12600 | 0.9999 |
| | | | 0.1 M NaOH | 266 | 13900 | 0.9997 |

[a] From Ref. [30].
[b] From Ref. [31].

### 3.2.1. The effect of medium on adsorption of organic acids

It is seen from Figs. 3–6 that in general the rate and extent of adsorption is the highest from solutions in water or in 0.4 M H$_2$SO$_4$, the lowest from solutions in 0.1 M NaOH and intermediate from solutions at pH 7.0 for all the organic acids studied. In order to explain these behaviors, primarily on the basis of electrostatic interactions between the surface and the adsorbate species, one has to look at the charges possessed by the surface and the adsorbates in these solutions.

Adsorbates under study are found as mixtures of two forms in water due to partial ionization. Simple analytical calculations using the p$K_a$ values given in Table 1 at the initial concentrations of acidic adsorbates applied in adsorption experiments show that BA is 55% in neutral molecular form and 45% in anionic form, SA is 13% in neutral molecular form and 87% in anionic form and NA is in 74% in zwitterionic form (negative charge is on carboxylate and positive charge is on N center) and 26% in anionic form.
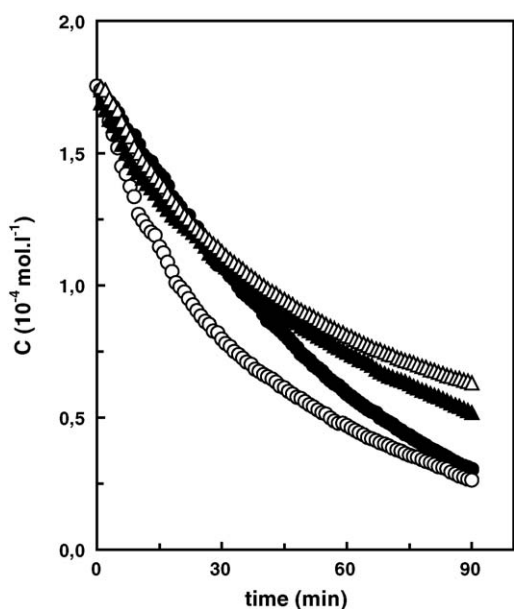


Fig. 4. Adsorption behavior of SA: in 0.4 M H$_2$SO$_4$ (●), in natural pH (○), in solution at pH 7.0 (▲) and in 0.1 M NaOH (△).
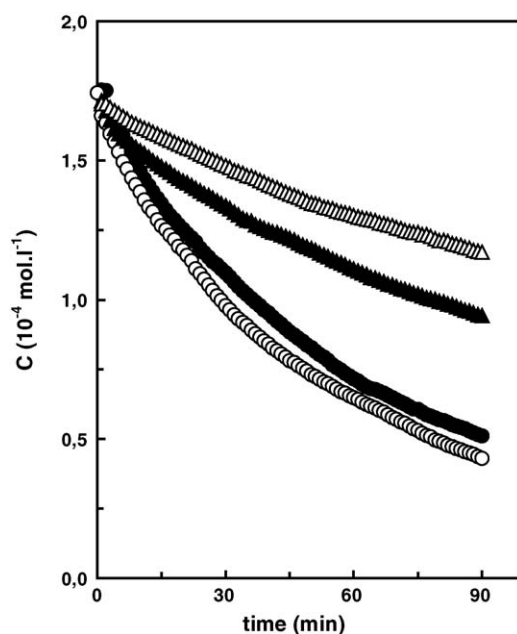


Fig. 5. Adsorption behavior of NA: in 0.4 M H$_2$SO$_4$ (●), in natural pH (○), in solution at pH 7.0 (▲) and in 0.1 M NaOH (△).
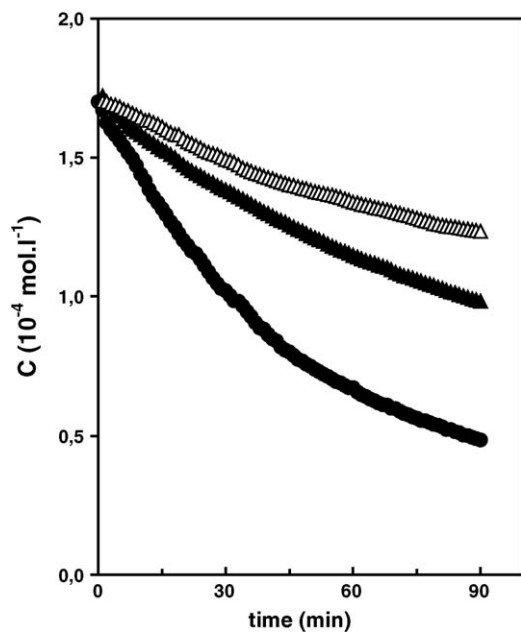
Fig. 6. Adsorption behavior of *p*ABA: in 0.4 M $H_2SO_4$ (●), in solution at pH 7.0 (▲) and in 0.1 M NaOH (△).

Adsorbate solutions in water are slightly acidic due to partial ionization of organic acids. In other words, the pH values of water solutions of organic acids studied are smaller than $pH_{PZC}$ (=7.4). Thus the carbon surface in water solutions of organic acids is positively charged. So, the relatively high rate and extent of adsorption observed in water solutions is expected to result both from the electrostatic attractions of positively charged surface and anionic adsorbate species and also from the dispersion interactions between the carbon surface and neutral adsorbate molecules.

In 0.4 M $H_2SO_4$ solutions, the carbon surface is definitely positively charged since the pH values of these solutions are much less than $pH_{PZC}$, the two of the four adsorbates (BA and SA) are almost 100% in neutral molecular form and the other two (*p*ABA and NA) are in cationic state, positive charge being on N center. Here, the dispersion interactions and to a certain extent the electrostatic interactions between positively charged surface and either the π electrons of the aromatic ring or the dipole of the adsorbate are expected to be effective in the resulting high rate and extent of adsorption observed in 0.4 M $H_2SO_4$.

In 0.1 M NaOH solutions, the carbon surface possesses some net negative charge since the pH values of these solutions are greater than $pH_{PZC}$ and the adsorbates are also negatively charged. BA, *p*ABA and NA are in single negatively charged form, SA is 85% in single negatively charged form and 15% in double negatively charged form, the second negative charge being on phenolic O atom. Considering all these charges and electrostatic interactions, it is understandable to observe the least adsorption in basic solutions, because in all cases both the surface and the adsorbates posses charges of the same sign. The small amounts of adsorptions observed in 0.1 M NaOH solutions are expected to result from dispersion interactions.

In solutions at pH 7.0, the carbon surface is almost neutral since the pH $\sim$ $pH_{PZC}$. Analytical calculations show that all four organic acids are in >99% singly charged anionic form, negative charge being on the acidic carboxylate center. So in this case the main adsorption force is expected to be of dispersion type between π electrons of the aromatic ring and of the carbon basal plane with little contribution from electrostatic or hydrogen bonding interactions. This may explain the intermediate rate and extent of adsorption observed in solutions at pH 7.0.

Adsorption data over 90 min period were treated according to the first-order kinetics by plotting $\ln[C_0/C_t]$ as a function of time, *t*, and applying linear regression analysis to obtain the rate constant, *k*, according to the following equation:

$$\ln\left[\frac{C_0}{C_t}\right] = kt \tag{2}$$

where $C_0$ and $C_t$ are the initial concentration and the concentration at any time of the organic acid, respectively. The slopes of the lines provided the first-order rate constants for the adsorption process. The regression coefficient of each analysis was used as a criterion for the validity of the assumption of the first-order rate law for the adsorption. The rate constants and the regression coefficients obtained by this treatment for the adsorption of organic acids in 0.4 M $H_2SO_4$, in water at natural pH, in a solution at pH 7.0 and in 0.1 M NaOH are given in Table 2. The closeness of regression coefficients to 1 (>0.98) supports the assumption of the first-order rate law for the adsorption process.

It should be noted that the possibility of intraparticle diffusion model to control the kinetics of adsorption was also tested using the equation: $q_t = k_i t^{1/2}$ where $q_t$ is the amount of adsorbate adsorbed per gram of ACC at time *t* and $k_i$ is the intraparticle diffusion constant. The regression coefficients of linear $q_t$ versus $t^{1/2}$ plots for the present kinetic data were smaller than those listed in Table 2 for first-order treatment. Therefore, treatment according to the intraparticle diffusion model was eliminated.

Another quantitative comparison for the adsorption of organic acids onto the carbon cloth can be made on the basis of the amount of adsorbate adsorbed per unit mass of carbon cloth, *M*, at the end of 90 min adsorption calculated by the following equation:

$$M = \frac{(C_0 - C_t)V}{m} \tag{3}$$

where $C_0$ and $C_t$ are the concentrations of the solutions at the beginning and at 90 min of adsorption, respectively. *V* is the volume of the solution and *m* the weight of carbon cloth module. The calculated *M* values are given in the last column of Table 2.

The numerical values of *k* and *M* for the adsorption of all four organic acids in four solutions follow the order 0.4 M $H_2SO_4 \sim$ water > pH 7.0 > 0.1 M NaOH. This order, which was also predicted from visual analysis of Figs. 3–6, results from electrostatic, dispersion and hydrogen bonding interactions as discussed above in detail.

Analysis of the adsorption data also reveals some interesting conclusions about the order of rate and extent of adsorption of the four adsorbate species in each solution. According to *k* and *M* values in Table 2 the adsorption rates and extents of

Table 2
First-order rate constants, regression coefficients and $M$ values at 90 min for the adsorption of organic acids

| Organic acid | Solvent | $C_0$ (mol l$^{-1}$) | $k$ ($\times 10^{-3}$ min$^{-1}$) | $r$ | $M$ ($\times 10^{-4}$ mol (g C-cloth)$^{-1}$) |
|---|---|---|---|---|---|
| BA | 0.4 M H$_2$SO$_4$ | $1.74 \times 10^{-4}$ | $16.60 \pm 0.01$ | 0.9984 | 1.77 |
| | Water (pH 4.15) | $1.72 \times 10^{-4}$ | $18.51 \pm 0.12$ | 0.9905 | 1.79 |
| | Solution at pH 7.0 | $1.74 \times 10^{-4}$ | $8.358 \pm 0.071$ | 0.9826 | 1.17 |
| | 0.1 M NaOH | $1.75 \times 10^{-4}$ | $6.699 \pm 0.028$ | 0.9966 | 1.02 |
| SA | 0.4 M H$_2$SO$_4$ | $1.74 \times 10^{-4}$ | $18.22 \pm 0.11$ | 0.9941 | 1.91 |
| | Water (pH 3.62) | $1.75 \times 10^{-4}$ | $21.94 \pm 0.16$ | 0.9873 | 1.98 |
| | Solution at pH 7.0 | $1.74 \times 10^{-4}$ | $14.02 \pm 0.09$ | 0.9914 | 1.63 |
| | 0.1 M NaOH | $1.75 \times 10^{-4}$ | $12.44 \pm 0.10$ | 0.9848 | 1.49 |
| NA | 0.4 M H$_2$SO$_4$ | $1.75 \times 10^{-4}$ | $14.48 \pm 0.07$ | 0.9950 | 1.66 |
| | Water (pH 4.39) | $1.74 \times 10^{-4}$ | $16.40 \pm 0.12$ | 0.9888 | 1.75 |
| | Solution at pH 7.0 | $1.75 \times 10^{-4}$ | $7.001 \pm 0.05$ | 0.9880 | 1.08 |
| | 0.1 M NaOH | $1.70 \times 10^{-4}$ | $4.331 \pm 0.02$ | 0.9963 | 0.708 |
| $p$ABA | 0.4 M H$_2$SO$_4$ | $1.70 \times 10^{-4}$ | $15.15 \pm 0.10$ | 0.9899 | 1.62 |
| | Solution at pH 7.0 | $1.73 \times 10^{-4}$ | $6.690 \pm 0.40$ | 0.9924 | 0.998 |
| | 0.1 M NaOH | $1.70 \times 10^{-4}$ | $3.867 \pm 0.03$ | 0.9918 | 0.623 |

organic acids studied follow the order SA > BA > NA ~ $p$ABA (NA being slightly greater than $p$ABA in most cases) in all four solutions. This order may be explained in each solution in terms of structural effects of the adsorbates.

### 3.2.2. The effect of structure of organic acids on adsorption

In 0.4 M H$_2$SO$_4$, the surface is positively charged. SA being neutral and having two functional groups (−OH and −COOH), has the highest rate and extent of adsorption through charge-dipole and dispersion interactions. BA comes next having one less functional group (only −COOH) than SA. NA and $p$ABA show the least rate and extent of adsorption since they both have a positive charge on their N centers and the carbon surface has also a net positive charge.

In water solutions carbon surface is again positively charged. In this solution SA is mainly in singly charged anionic state (87%) and thus shows the highest rate and extent of adsorption due to electrostatic attraction by the surface. Some dispersion and charge dipole interactions are also expected to be effective in its adsorption. BA experiences less electrostatic attraction than SA because it is only 45% in anionic form in this solution. Furthermore it has one less functional group than SA. Thus it shows smaller rate and extent of adsorption than SA. $p$ABA being 74% in zwitterionic form (no net charge) experiences the least electrostatic attraction resulting in the least rate and extent of adsorption in this solution.

In solutions at pH 7.0 the carbon surface is almost neutral. All four adsorbates in this solution are in singly charged anionic state (>99%), the charge being on the carboxylate group. So, the order is determined mainly by the remaining structure (other than −COO$^-$ group) of the molecule. SA, having an −OH substituent (in *ortho* position to carboxylate) that possesses two lone pairs of electrons on O atom, shows the highest rate and extent of adsorption via dispersion and hydrogen bonding interactions. An intramolecular hydrogen bonding is also expected in SA. Although the $k$ and $M$ values of BA, NA and $p$ABA indicate an order of BA > NA > $p$ABA in solutions at pH 7.0, the numbers are very close to each other. It would be speculative to attribute these small differences into structural factors.

In 0.1 M NaOH solutions the carbon surface is definitely negatively charged since pH values of these solutions are much greater than pH$_{PZC}$. SA in this solution is 85% in singly charged anionic and 15% in doubly charged anionic state. The effect of single negative charge in 85% of SA is slightly reduced by the intramolecular hydrogen bonding between the negatively charged O atom of carboxylate group and partial positively charged H atom of −OH group in *ortho* position to carboxylate group. So, SA experiences the least electrostatic repulsion from the carbon surface among the four adsorbates and thus shows the highest rate and extent of adsorption in this solution. BA is almost 100% in anionic state with a full negative charge on it in this solution and thus experiences more electrostatic repulsion than SA. So it shows smaller rate and extent of adsorption than SA. NA and $p$ABA have a functional group having a lone pair of electrons in *para* and *meta* positions to the carboxylate group, respectively, in addition to a full negative charge on carboxylate group. So these two adsorbates experience the most electrostatic repulsion from the surface resulting in the least rate and extent of adsorption in this solution.

### 3.3. Adsorption behavior of benzoic acid in water

BA in water is in neutral BA and benzoate forms almost in equal amounts as discussed above. The two forms absorb UV light at slightly different $\lambda_{max}$ values (Table 1): benzoate at 224 nm and BA at 231 nm. This allows monitoring the two species simultaneously by analyzing the adsorbate solution as a mixture of two components according to Lambert–Beer law. So it would be interesting to see how the concentrations of benzoate and BA decrease during the course of 90 min adsorption. Similar situation exists for SA and NA in water but such binary analysis was not possible for them due to closeness of $\lambda_{max}$ values of the neutral and ionic species for NA and due to initial much higher percentage of anionic species (87%) than neutral species for SA.

The simultaneous analysis of binary mixture was achieved spectroscopically by recording the total absorbances at two wavelengths, 224 and 231 nm, the former being the absorption maximum of benzoate and the latter being the absorption max-
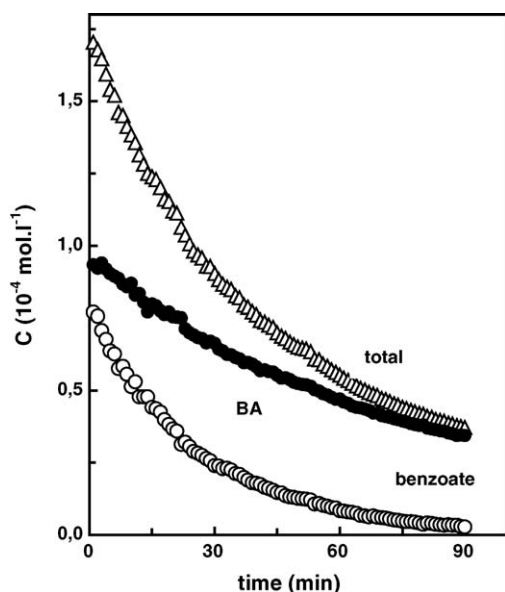
Fig. 7. Adsorption behavior of BA species in water at natural pH: benzoate ($\bigcirc$), BA ($\bullet$) and the sum of benzoate and BA ($\triangle$).

imum of BA. The total absorbance at 224 nm, $A^{224}_{(total)}$, can be given by

$$A^{224}_{(total)} = \varepsilon^{224}_{(benzoate)}C_{(benzoate)} + \varepsilon^{224}_{(BA)}C_{(BA)} \tag{4}$$

and that at 231 nm, $A^{231}_{(total)}$, can be given by

$$A^{231}_{(total)} = \varepsilon^{231}_{(benzoate)}C_{(benzoate)} + \varepsilon^{231}_{(BA)}C_{(BA)} \tag{5}$$

where $\varepsilon$ is the molar absorptivity of the species indicated in parenthesis at the wavelength indicated as a superscript and $C$ is concentration of the species indicated in parenthesis. Since 1 cm cuvette was used in all measurements, the light path does not appear in the above equations. $\varepsilon$ values were determined in separate calibration experiments in 0.1 M NaOH for benzoate and 0.4 M $H_2SO_4$ for BA and are given in Table 1. Simultaneous solutions of Eqs. (4) and (5) give concentrations of benzoate and BA in the adsorbate solution.

Concentration of benzoate anion, BA in molecular form and the sum of the two are plotted separately as a function of time in Fig. 7. It is seen that the concentration of benzoate anion in adsorbate solution is rapidly decreased almost to zero level over 90 min adsorption period. This is mainly due to the electrostatic attraction of benzoate anion by the positively charged carbon surface. The decrease in neutral benzoic acid concentration is not so rapid and not to zero level. The lowering of concentration of neutral BA molecule is expected to be due to its ionization to benzoate anion as the already existing benzoate anions are decreased by adsorption. Of course, a small amount of BA may also have been adsorbed in neutral molecular form. However, it is clear from Fig. 7 that the unadsorbed BA remaining in the solution is mainly in neutral molecular form. This figure clearly demonstrates the importance of electrostatic interactions between adsorbate and adsorbent in adsorption process.
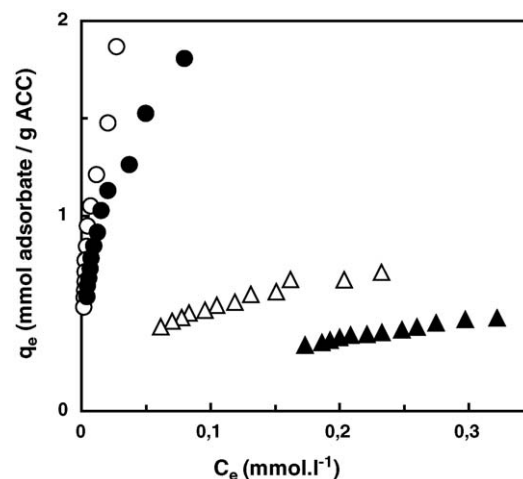


Fig. 8. Adsorption isotherms at 30 °C for the organic acids in 0.4 M $H_2SO_4$: BA ($\bullet$), SA ($\bigcirc$), NA ($\blacktriangle$) and $p$ABA ($\triangle$).

### 3.4. Adsorption isotherms

Adsorption isotherm data of organic acids obtained at 30 °C in 0.4 M $H_2SO_4$, in water, in a solution of pH 7.0 and in 0.1 M NaOH are given in Figs. 8–11, respectively. The isotherm data were treated according to two well-known isotherm equations: Langmuir and Freundlich. The linearized forms of Langmuir and Freundlich isotherm equations can be given in Eqs. (6) and (7), respectively [32,33]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \tag{6}$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \tag{7}$$

where $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mmol $g^{-1}$, $C_e$ the final concentration at equilibrium in mmol $L^{-1}$, $q_{max}$ the maximum adsorption at monolayer coverage in mmol $g^{-1}$, $b$ the adsorption equilibrium constant related to the energy of adsorption in L mmol$^{-1}$, $K_F$ the Freundlich constant representing the adsorption capacity in
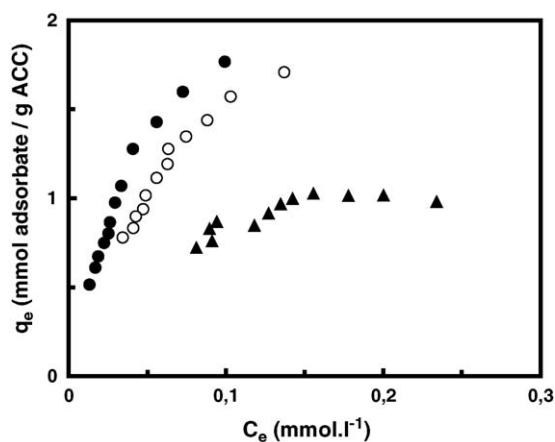


Fig. 9. Adsorption isotherms at 30 °C for the organic acids in water at natural pH: BA ($\bullet$), SA ($\bigcirc$) and NA ($\blacktriangle$).
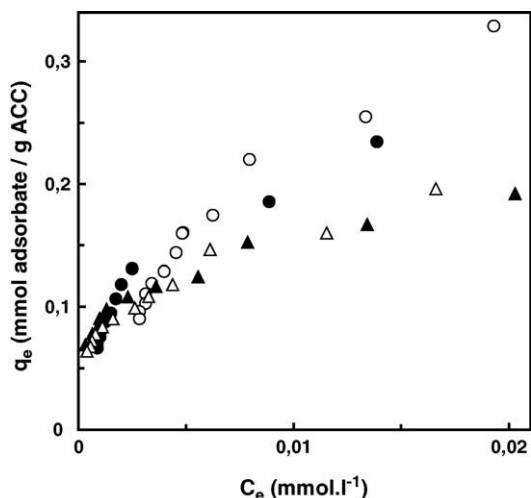
Fig. 10. Adsorption isotherms at 30 °C for the organic acids in solution at pH 7.0: BA (●), SA (○), NA (▲) and *p*ABA (△).
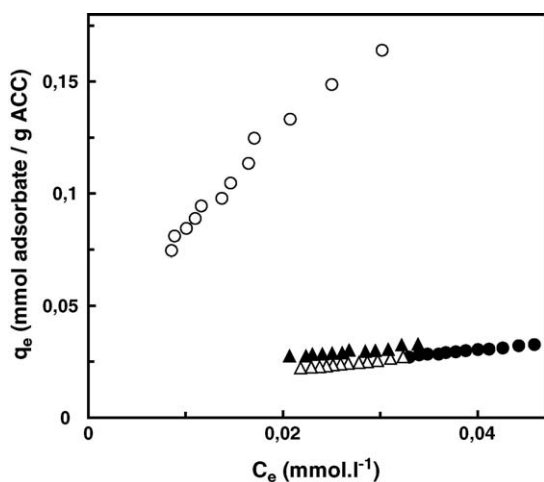


Fig. 11. Adsorption isotherms at 30 °C for the organic acids in 0.1 M NaOH: BA (●), SA (○), NA (▲) and *p*ABA (△).

$(\text{mmol g}^{-1})(\text{L mmol}^{-1})^{1/n}$ and $n$ is a constant related to surface heterogeneity. The parameters of these equations obtained from linear regression analysis for the adsorption systems studied are given in Table 3 together with regression coefficients.

One way of assessing the fit of experimental isotherm data to Langmuir and Freundlich equations can be on the basis of regression coefficients, $r$. The regression coefficients are all close to each other and are mostly >0.95. Thus it is very difficult to decide which model represents the experimental data better on the basis of values of regression coefficients. This result is not surprising on the basis of just regression coefficients. For example the regression coefficients for fitting adsorption data of aqueous aromatic pollutants on various granular activated carbon samples to both Langmuir and Freundlich equations were also found to be mostly >0.98 by Yenkie and Natarajan [34]. A similar result can be seen in the work of Leboda et al. [35]. A better criterion for the assessment of experimental isotherm data is a parameter known as normalized percent deviation [36] or in some literature as percent relative deviation modulus, $P$ [37,38] given by the following equation:

$$P = \left(\frac{100}{N}\right) \sum \left(\frac{|q_{e(\text{expt})} - q_{e(\text{pred})}|}{q_{e(\text{expt})}}\right) \qquad (8)$$

where $q_{e(\text{expt})}$ is the experimental $q_e$ at any $C_e$, $q_{e(\text{pred})}$ is the corresponding predicted $q_e$ according to the equation under study with the best fitted parameters and $N$ is the number of observations. It is clear that the lower the $P$ value, the better is the fit. The $P$ values calculated for the fit of isotherm data of the organic acids to the two isotherm equations are given in Table 3. It is generally accepted that when the $P$ value is less than 5, the fit is considered to be excellent [37]. Most of the $P$ values for both Langmuir and Freundlich models are lower than 5 with a few exceptions (Table 3). It should be recognized that the goodness of fit of isotherm data to Langmuir and Freundlich equations depends on the range of equilibrium concentration studied. When the $P$ values for the two models are compared with each other, it is very

Table 3

Parameters of Langmuir and Freundlich isotherm equations, regression coefficients ($r$) and normalized percent deviation ($P$) for the organic acids at 30 °C

| Organic acids | Solvent | Langmuir parameters | | | | Freundlich parameters | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $q_{max}$ (mmol g$^{-1}$) | $b$ (L mmol$^{-1}$) | $r$ | $P$ | $K_F$ (mmol g$^{-1}$)(L mmol$^{-1}$)$^{1/n}$ | $1/n$ | $r$ | $P$ |
| BA | 0.4 M H$_2$SO$_4$ | 1.96 ± 0.09 | 80.1 ± 10.2 | 0.9886 | 9.21 | 4.48 ± 0.22 | 0.361 ± 0.011 | 0.9955 | 2.29 |
| | Water | 2.97 ± 0.15 | 15.8 ± 0.97 | 0.9764 | 3.11 | 8.83 ± 1.10 | 0.644 ± 0.036 | 0.9850 | 5.38 |
| | Solution at pH 7.0 | 0.264 ± 0.010 | 388 ± 32.4 | 0.9930 | 4.10 | 1.51 ± 0.23 | 0.427 ± 0.024 | 0.9841 | 5.74 |
| | 0.1 M NaOH | 0.064 ± 0.025 | 22.7 ± 1.17 | 0.9927 | 0.506 | 0.168 ± 0.01 | 0.531 ± 0.019 | 0.9937 | 0.511 |
| SA | 0.4 M H$_2$SO$_4$ | 2.07 ± 0.11 | 172 ± 20.1 | 0.9851 | 6.45 | 8.29 ± 0.93 | 0.422 ± 0.021 | 0.9881 | 5.03 |
| | Water | 3.03 ± 0.19 | 10.1 ± 0.79 | 0.9809 | 2.76 | 6.26 ± 0.69 | 0.610 ± 0.039 | 0.9800 | 3.97 |
| | Solution at pH 7.0 | 0.525 ± 0.032 | 81.8 ± 5.90 | 0.9822 | 4.11 | 4.33 ± 0.84 | 0.639 ± 0.037 | 0.9839 | 6.12 |
| | 0.1 M NaOH | 0.305 ± 0.019 | 37.8 ± 2.75 | 0.9817 | 2.34 | 1.43 ± 0.14 | 0.615 ± 0.023 | 0.9933 | 2.14 |
| NA | 0.4 M H$_2$SO$_4$ | 0.948 ± 0.044 | 3.23 ± 0.187 | 0.9896 | 1.01 | 0.929 ± 0.03 | 0.570 ± 0.022 | 0.9927 | 1.11 |
| | Water | 1.25 ± 0.083 | 21.0 ± 4.47 | 0.9807 | 4.78 | 1.69 ± 0.20 | 0.306 ± 0.056 | 0.8636 | 5.15 |
| | Solution at pH 7.0 | 0.195 ± 0.008 | 649 ± 138 | 0.9914 | 16.3 | 0.497 ± 0.03 | 0.252 ± 0.011 | 0.9910 | 3.66 |
| | 0.1 M NaOH | 0.047 ± 0.003 | 65.1 ± 8.69 | 0.9791 | 1.67 | 0.106 ± 0.01 | 0.352 ± 0.037 | 0.9495 | 1.53 |
| *p*ABA | 0.4 M H$_2$SO$_4$ | 0.931 ± 0.027 | 13.7 ± 0.83 | 0.9958 | 1.73 | 1.26 ± 0.05 | 0.378 ± 0.018 | 0.9887 | 1.72 |
| | Solution at pH 7.0 | 0.200 ± 0.011 | 552 ± 113 | 0.9847 | 18.0 | 0.601 ± 0.05 | 0.290 ± 0.012 | 0.9916 | 3.78 |
| | 0.1 M NaOH | 0.050 ± 0.003 | 35.8 ± 2.73 | 0.9852 | 0.878 | 0.151 ± 0.01 | 0.504 ± 0.023 | 0.9896 | 0.755 |

Table 4
Literature values of $q_{max}$ for the adsorption of BA or SA under different conditions

| Adsorbent | Organic acid | $T$ (°C) | pH | $q_{max}$ (mmol g$^{-1}$) | Reference |
|---|---|---|---|---|---|
| Granular activated carbon | BA | 25 | Natural pH | 3.22 | [1] |
| | BA | 35 | Natural pH | 3.22 | [1] |
| | BA | 45 | Natural pH | 2.99 | [1] |
| | BA | 55 | Natural pH | 2.67 | [1] |
| Commercial granular activated carbon | | | | | |
| RRL | BA | 35 | Natural pH | 2.22 | [34] |
| CAL | BA | 35 | Natural pH | 1.95 | [34] |
| KUKARE | BA | 35 | Natural pH | 2.72 | [34] |
| LCK | BA | 35 | Natural pH | 2.98 | [34] |
| FILTRSORB200 | BA | 35 | Natural pH | 2.01 | [34] |
| FILTRASORB400 | BA | 35 | Natural pH | 3.27 | [34] |
| Commercial activated carbon | BA | 28 | 2 | 1.53 | [10] |
| | BA | 28 | 4 | 1.48 | [10] |
| | BA | 28 | 8 | 0.32 | [10] |
| | BA | 28 | 10 | 0.18 | [10] |
| | BA | 28 | 12 | 0.16 | [10] |
| | SA | 28 | 2 | 1.44 | [10] |
| | SA | 28 | 3 | 1.43 | [10] |
| | SA | 28 | 8 | 0.34 | [10] |
| | SA | 28 | 10 | 0.37 | [10] |
| | SA | 28 | 12 | 0.32 | [10] |
| Activated charcoal (FILTRASORB F400) | SA | 20 | Natural pH | 2.54 | [4] |
| Polymeric adsorbent (SEPHABEADS SP-206) | SA | 20 | Natural pH | 0.59 | [4] |
| Polymeric adsorbent (SEPHABEADS SP-207) | SA | 20 | Natural pH | 0.59 | [4] |

difficult to generalize which model represents the experimental isotherm data better. Thus, one can say that Freundlich and Langmuir isotherm models represent the adsorption isotherm data of the organic acids studied in 0.4 M H$_2$SO$_4$, in water, in solution at pH 7.0 and in 0.1 M NaOH almost equally well. This seems to be rather unexpected since Langmuir model considers only monolayer coverage while Freundlich model takes also the multilayer coverage into account. However a simple calculation based on the close packed arrangement of the adsorbed molecules, the specific surface area of the carbon cloth used and using 6 Å as the approximate average size of the adsorbate molecule shows that the maximum amount of adsorbate adsorbed are not sufficient even for the monolayer coverage. So, the well fit of data to both models below the monolayer coverage is not surprising.

A final comment can be added about the $q_{max}$ values of Langmuir and $K_F$ values of Freundlich models since both parameters are related to the adsorption capacity of the carbon cloth. The orders of the values of these parameters for each adsorbate in four solutions (0.4 M H$_2$SO$_4$, water, pH 7.0 and 0.1 M NaOH) and in each solution for four adsorbates (Table 3) are in agreement with the corresponding orders observed according to $k$ and $M$ values (Table 2) discussed in Section 3.2.

The parameters of the isotherm equations given in Table 3 are difficult to compare with the literature values because the isotherm data are collected under different conditions: pH, temperature, type of adsorbent and the form of adsorbate species. The most important parameter to compare is probably the Langmuir $q_{max}$ value since it is a measure of adsorption capacity of the adsorbent. Some of the literature $q_{max}$ values and the conditions under which they were obtained are listed in Table 4. The

comparison of these literature values with our values reported in Table 3 shows that the carbon cloth used in our work has adsorption capacities either higher than or comparable to those carbon materials used in other works.

## 4. Conclusions

Adsorption of aromatic organic acids, BA, SA, NA and *p*ABA onto high area activated carbon cloth from solutions in 0.4 M H$_2$SO$_4$, in water, in 0.1 M NaOH and also from solutions at pH 7.0 was found to follow the first-order kinetics. The rate and extent of adsorption of all four compounds were the highest in water or in 0.4 M H$_2$SO$_4$ solutions and the lowest in 0.1 M NaOH solution. The order of rate and extent of adsorption of the four organic acids in each of the four solutions was SA > BA > NA ~ *p*ABA. Electrostatic, dispersion and hydrogen bonding interactions depending on the charges possessed by the carbon surface and by the adsorbate in four solutions played important roles in determining these orders. BA in water was found to be adsorbed mainly in benzoate form leaving some neutral benzoic acid molecules in solution. Adsorption isotherm data for the systems studied fitted to both Langmuir and Freundlich models almost equally well.

## Acknowledgements

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