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Structural and ionization effects on the adsorption behaviors of some anilinic compounds from aqueous solution onto high-area carbon-cloth

Osman Duman, Erol Ayranci *

Department of Chemistry, Akdeniz University, Antalya, Turkey

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Abstract

The adsorption of anilinic compounds; aniline, *p*-toluidine, 1-napthylamine and sodium salt of diphenylamine-4-sulfonic acid from solutions in H_2O, in 1 M H_2SO_4 or in 0.1 M NaOH onto activated carbon-cloth was studied by in situ UV spectroscopy. A specially designed adsorption cell was used for this purpose. The adsorption processes were found to follow first-order kinetics and the rate constants were determined. The pH at the point of zero charge of the carbon-cloth surface was measured as 7.4. The highest rates and extents of adsorption were observed from H_2O solutions for aniline, *p*-toluidine and 1-napthylamine and from solution in 1 M H_2SO_4 for the sodium salt of diphenylamine-4-sulfonic acid. The adsorption behaviors of these four anilinic compounds in the three solutions (in H_2O, in 0.1 M NaOH and in 1 M H_2SO_4) were explained in terms of electrostatic and dispersion interactions between carbon-cloth surface and the anilinic species. The adsorption isotherm data for the anilinic compounds were derived at 30 °C and treated according to Langmuir and Freundlich models. The Freundlich model was found to represent the experimental isotherm data better than Langmuir model.
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Keywords: Adsorption; Anilinic compounds; Activated carbon-cloth; Ionization; UV spectroscopy

1. Introduction

Aromatic compounds constitute a major class of pollutants in waste-waters from many industries. These compounds must be removed from waste-waters before they are discharged into the environment because of their high toxicological, carcinogenic, mutagenic and ecotoxicological potential [1]. Aniline and its derivatives are among such compounds.

The major uses of aniline are in the manufacture of polymers, rubber, agricultural chemicals, dyes and pigments, pharmaceuticals and photographic chemicals. Aniline is highly toxic and may be fatal if swallowed, inhaled or absorbed through the skin [2]. Conventional methods for the removal or destruction of aniline from waste-waters include photodecomposition, electrolysis, oxidation by ozone and adsorption [3].

There are many studies reported in the literature on the adsorption of aniline on various adsorbents such as organo clay [4,5], silica-gel [6], organic soil [7], montmorillonite [8], silica [9], α-Al_2O_3, iron powders [10], zeolites [11] and Ca-bentonite [12]. Beside these adsorbents, activated carbon which can be in granular, powder or fiber (cloth or felt) form has been widely used for the removal of many pollutants including some anilinic compounds from waste-waters via adsorption by many authors [13–17]. Terzyk [18], in his extensive report on the effect of carbon surface chemical composition on the adsorption of organics including aniline, discussed possible mechanisms of adsorption taking various interactions such as electrostatic, π–π dispersion, hydrogen bonding, possibility of chemisorption and of polymerization (of aniline) into account. His results suggested that, generally, the mechanism of adsorption of organics from dilute aqueous solutions in carbon micropores is micropore filling, combined with adsorption on the "active" sites.

Carbon-cloth has the advantage of higher specific surface area, practical applicability, mechanical strength and

* Corresponding author. Tel.: +90 242 310 23 15; fax: +90 242 227 89 11.
E-mail address: eayranci@akdeniz.edu.tr (E. Ayranci).

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possibility of regeneration over the most other adsorbent materials [19]. Thus the use of activated carbon-cloth or fiber on removal of organic and inorganic compounds by adsorption and/or electrosorption has gained an increasing interest in recent years. Adsorption of some organic compounds including aniline on activated carbon-cloth or fiber has been studied by Niu and Conway [20]. We have studied the adsorption and electrosorption of some sulfur containing oxyanions [21], thiocyanate and ethyl xanthate [22] onto high specific area carbon-cloth.

The purpose of the present study was to investigate the adsorption behavior of aniline and its derivatives *p*-toluidine, 1-naphtylamine and sodium salt of diphenylamine-4-sulfonic acid at the high area activated carbon-cloth (ACC) in relation to waste-water purification.

2. Materials and methods

2.1. Materials

The carbon-cloth used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225, having an apparent BET surface area of 2500 $m^2\,g^{-1}$. Aniline and *p*-toluidine were obtained from Merck, 1-napthylamine from Fisher and sodium salt of diphenylamine-4-sulfonic acid from Serva. NaOH, H_2SO_4, HNO_3 and $NaNO_3$ were reagent grade. Deionized water was used in adsorption experiments.

2.2. Treatment of carbon-cloth

Activated carbon fibers are known to provide spontaneously a small but significant quantity of ions forming conductivity water, probably due to their complex structure originating from its somewhat unknown proprietary preparation procedure [21,23]. Therefore a deionization cleaning procedure was applied to avoid desorption of ions during adsorption studies. 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 desiccator for further use.

2.3. Procedure for the determination of pH_{PZC} of carbon-cloth

The carbon surface charge is mainly determined by the pH of the adsorbate solution. It is known that [24] the net charge on carbon surface is positive at a solution pH lower than that corresponding to the point of zero charge (pH_{PZC}) of the surface and is negative at a solution pH higher than pH_{PZC}. Therefore it is very important to determine the pH_{PZC} for the carbon material.

Batch equilibrium method described by Babić et al. [25] was applied for the determination of pH_{PZC} of the activated carbon-cloth used in the present study. 0.1000 g carbon-cloth samples were shaken in Erlenmeyer flasks for 24 h with 40 mL 0.1 M $NaNO_3$ at different initial pH values which were adjusted by adding NaOH or HNO_3 solutions. Since it was found by Babić et al. [25] that there is no effect of ionic strength on pH_{PZC} after measurements in 0.1 M $NaNO_3$ and 0.01 M $NaNO_3$, the pH_{PZC} of carbon-cloth used in this study was measured only at the ionic strength of 0.1 M provided by $NaNO_3$. 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 analyser using glass electrode. The pH_{PZC} is determined either from such calculations or from the plots of pH_f versus pH_i as will be discussed in Section 3.

2.4. 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. The cell (Fig. 1) was V-shaped with one arm containing the carbon-cloth attached to a short Pt wire sealed to a glass rod and the other arm containing a thin glass tube through which N_2 gas was passed for the dual purposes of mixing and eliminating any dissolved CO_2. The two arms were connected to a glass joint leading to a vacuum pump at the upper part of the V-shaped cell in order to provide the opportunity for initial outgassing of the carbon adsorbent and the cell and solution. A quartz spectrophotometer cuvette was sealed to the bottom of the adsorption cell.

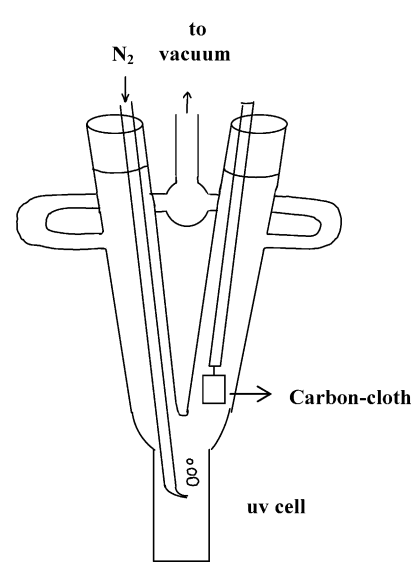


Fig. 1. Diagram of the adsorption cell.

With the use of the adsorption cell described above 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 anilinic compounds were prepared in water, in 1 M H_2SO_4 or in 0.1 M NaOH to examine the effects of both the surface charge of carbon-cloth and the ionization of anilinic compounds on adsorption. The initial concentrations of anilinic compounds 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: 1×10^{-4} M, mass of carbon-cloth: 15 mg). However actual weights of carbon-cloth samples were recorded for the calculation of fractional coverage, θ, by the adsorbates or the extent of adsorption per unit area of the carbon-cloth, M. The carbon-cloth pieces were pre-wetted by leaving in water for 24 h before use. In this way pores may expand and surfaces may become more accessible or active toward adsorption during long contact with water. The idea of using pre-wetted carbon-cloth originates from our previous findings that pre-wetting enhances the adsorption process [21,22].

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 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 anilinic compound 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 anilinic species; neutral, cationic or anionic.

2.5. Determination of adsorption isotherms

The adsorption isotherms of anilinic compounds on the carbon-cloth were determined on the basis of batch analysis. Carbon-cloth pieces of varying masses were allowed to equilibrate with solutions of anilinic compounds at acidic, basic or natural pH conditions with known initial concentrations at 30 °C for 48 h. Preliminary tests showed that the concentration of anilinic compounds remained unchanged after 13–14 h contact with the carbon-cloth. So, the allowed contact time of 48 h ensures the equilibration. The equilibration was allowed in 100 mL Erlenmeyer flasks kept in a Nüve ST 402 shaking water bath at a constant shaking speed of 150 rpm. The concentrations after the equilibration period were measured spectrophotometrically. The amount of anilinic compound adsorbed per unit mass of carbon-cloth, q_e, was calculated by the following equation:

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

where V is the volume of the solution of anilinic compound 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 per g carbon-cloth.

3. Results and discussion

3.1. pH_{PZC} of carbon-cloth

Final pH readings (pH_f) for the determination of pH_{PZC} (Section 2.3) were plotted as a function of initial pH (pH_i) in Fig. 2. The pH_f value of the plateau observed in this plot corresponds to the pH at which there is no net OH^- or H^+ adsorption [25]. 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.

3.2. Chemical nature, absorption characteristics and calibration data of the anilinic compounds

Chemical, spectral and calibration data for the anilinic compounds studied are given in Table 1. The ultraviolet

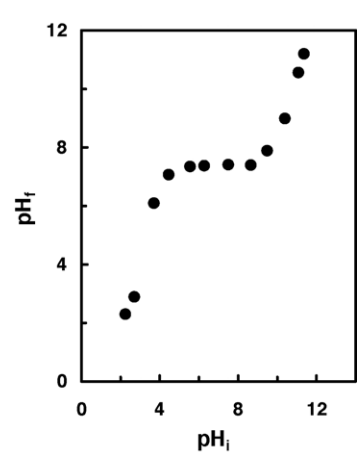
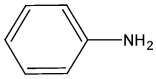
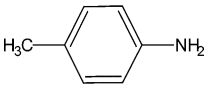
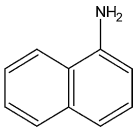
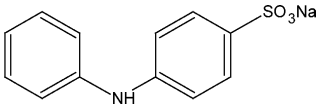


Fig. 2. Plot of pH_f vs. pH_i for the determination of pH_{PZC} of the carbon-cloth.

Table 1
Spectral and calibration data for anilinic compounds

Anilinic compound and its molecular structure	K_a[a] of NH_3^+ form	Solvent	λ_{max}/(nm)	ε/(M^{-1} cm^{-1})	r
Aniline	2.5×10^{-5}	H_2O	230	8300	0.9997
		H_2O	280	1400	0.9999
		0.1 M NaOH	231	8200	0.9997
		0.1 M NaOH	280	1400	0.9999
		1 M H_2SO_4	203	7500	0.9964
		1 M H_2SO_4	254	150	0.9991
p-Toluidine	8.2×10^{-6}	H_2O	233	7600	0.9987
		H_2O	287	1400	0.9999
		0.1 M NaOH	234	8000	0.9996
		0.1 M NaOH	287	1400	0.9999
		1 M H_2SO_4	207	6800	0.9986
		1 M H_2SO_4	260	240	0.9945
1-Napthylamine	1.2×10^{-4}	H_2O	237	21000	0.9996
		H_2O	305	4700	0.9998
		0.1 M NaOH	217	27000	0.9968
		0.1 M NaOH	237	22000	0.9999
		0.1 M NaOH	305	4800	0.9999
		1 M H_2SO_4	220	85000	1.000
		1 M H_2SO_4	278	5300	0.9995
Sodium salt of diphenylamine-4-sulfonic acid	[b]	H_2O	293	20000	0.9999
		0.1 M NaOH	293	20000	0.9998
		1 M H_2SO_4	294	16000	0.9996

[a] From Martell and Smith [28] and Weast [29].
[b] Not available.

spectra of aromatic hydrocarbons are characterized by three sets of bands originating from $\pi \rightarrow \pi^*$ transitions. These bands for benzene appear at about 179, 200 and 230–260 nm. $-NH_2$ substituent has an auxochromic effect on the benzene chromophore. The nonbonding electrons in aniline are lost by the formation of anilinium cation and as a consequence, the auxochromic effect disappears [26,27]. Thus in anilinium ion both the band intensities and the absorption wavelengths decrease compared to those in aniline (Table 1).

The analytical calculations using the K_a values given in Table 1 show that the major species of aniline, *p*-toluidine and 1-napthylamine is the neutral molecule and of sodium salt of diphenylamine-4-sulfonic acid is the anionic form in water and in 0.1 M NaOH. Although K_a value of diphenylamine-4-sulfonic acid is not available, it is well known that sulfonic acids are very strong acids, for example the K_a value of benzenesulfonic acid is 0.7 [28]. On the other hand in 1 M H_2SO_4 all the anilinic compounds except sodium salt of diphenylamine-4-sulfonic acid gain a proton and acquire a positive charge. Due to the strong acidic character of diphenylamine-4-sulfonic acid, diphenylamine-4-sulfonate remains in anionic form even in 1 M H_2SO_4.

Measured absorbances as a function of concentration for each single compound were treated according to the Lambert–Beer law by linear regression analysis in order to determine the calibration parameters. The results are given in Table 1 together with regression coefficients of analysis. Although the calibration data were derived at the two λ_{max} values given in Table 1 for each compound, only one of them was utilized in the actual adsorption experiment depending on the intensities of absorption bands. When the intensity at one λ_{max} value is too strong (>1.5 absorbance unit) deviation from Lambert–Beer law occurs or when it is too weak the sensitivity of absorbance measurement becomes too low. In such cases absorbance measurements were made at the other λ_{max} value and the corresponding calibration data in Table 1 were utilized.

3.3. Adsorption behaviors of anilinic compounds over 90 min

Adsorption behaviors of anilinic compounds were followed by in situ UV spectroscopy in 1 min intervals over 90 min period starting with the same initial concentration and using the same mass of carbon-cloth. Concentration versus

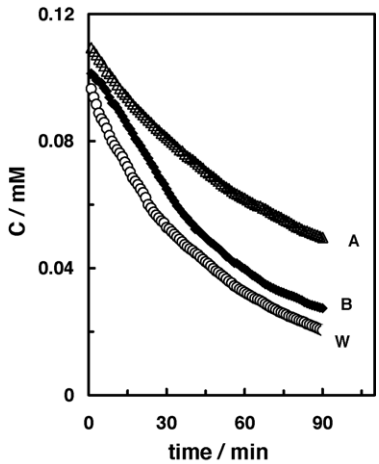


Fig. 3. Concentration vs. time plots for the adsorption of aniline from solutions in water (W), in 0.1 M NaOH (B) and in 1 M H_2SO_4 (A).

time plots for the adsorption from solutions in H_2O, in 1 M H_2SO_4 and in 0.1 M NaOH are given in Fig. 3 for aniline, in Fig. 4 for 1-napthylamine, in Fig. 5 for *p*-toluidine and in Fig. 6 for the sodium salt of diphenylamine-4-sulfonic acid. These adsorption data over a 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 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 anilinic compound and *k* is the rate constant. The slopes of the lines provided the first-order rate constants for the adsorption processes. The regression coefficient of each analysis was used as a criterion for the validity of the assumption of first-order rate law for the adsorption. The rate constants and the regression coefficients obtained by this treatment for the anilinic compounds in

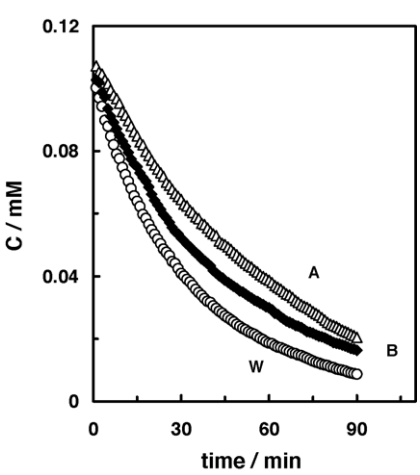


Fig. 4. Concentration vs. time plots for the adsorption of 1-napthylamine from solutions in water (W), in 0.1 M NaOH (B) and in 1 M H_2SO_4 (A).

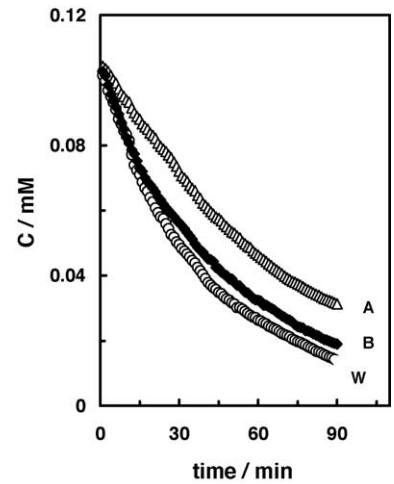


Fig. 5. Concentration vs. time plots for the adsorption of *p*-toluidine from solutions in water (W), in 0.1 M NaOH (B) and in 1 M H_2SO_4 (A).

H_2O, in 1 M H_2SO_4 and in 0.1 M NaOH are given in Table 2. Regression coefficients, being very close to 1 (>0.99) indicate that the adsorption processes follow a first-order rate law.

Two other quantitative measures of the adsorption of anilinic compounds onto carbon-cloth are the amount of adsorbate adsorbed per unit area of the carbon-cloth, *M*, and the percent coverage of the carbon-cloth surface by the adsorbate, θ, at the end of 90 min adsorption. These two parameters are closely related to each other and calculated by the following equations:

$$M = \frac{(C_0 - C_t)V}{2500m} \tag{3}$$

$$\theta = \frac{[(C_0 - C_t)VN_A \times 100]}{4 \times 10^{19} \times 2500m} \tag{4}$$

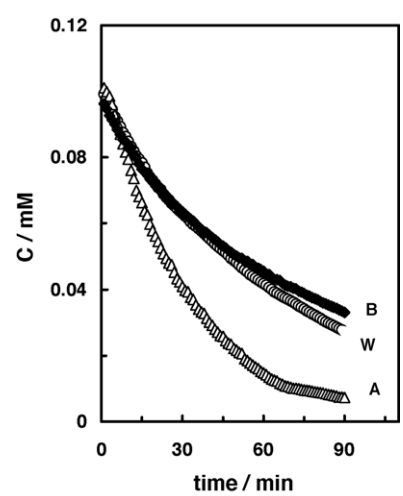


Fig. 6. Concentration vs. time plots for the adsorption of sodium salt of diphenylamine-4-sulfonic acid from solutions in water (W), in 0.1 M NaOH (B) and in 1 M H_2SO_4 (A).

Table 2
First-order rate constants, regression coefficients, M and θ values at 90 min for the adsorption of anilinic compounds

Anilinic compound	Solvent	pH or pH range during the course of adsorption	k/(min^{-1})	r	M/[10^{-8} mol (m^2 C-cloth)$^{-1}$]	θ
Aniline	H_2O	5.9–6.1	0.0185	0.9932	4.26	0.064
	1 M H_2SO_4	0.0	0.0093	0.9958	3.22	0.048
	0.1 M NaOH	13	0.0153	0.9968	3.96	0.060
p-Toluidine	H_2O	6.1–6.3	0.0226	0.9972	4.75	0.072
	1 M H_2SO_4	0.0	0.0134	0.9981	3.90	0.059
	0.1 M NaOH	13	0.0193	0.9982	4.48	0.068
1-Napthylamine	H_2O	5.8–5.9	0.0280	0.9978	4.98	0.075
	1 M H_2SO_4	0.0	0.0176	0.9983	4.62	0.070
	0.1 M NaOH	13	0.0209	0.9986	4.66	0.070
Sodium salt of diphenylamine-4-sulfonic acid	H_2O	6.2–6.4	0.0146	0.9985	3.89	0.059
	1 M H_2SO_4	0.0	0.0308	0.9970	5.01	0.075
	0.1 M NaOH	13	0.0124	0.9936	3.37	0.051

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, m the weight of carbon-cloth module and N_A Avogadro's number. The calculations are based on the known specific surface area of 2500 m^2 g^{-1} for the carbon-cloth as determined by the manufacturer by means of Kr-desorption BET procedure, corresponding to an approximate value of 4×10^{19} carbon sites per square meter of the surface determined by the atomic radius of carbon but dependent on the actually unknown geometry of surface carbon atom packing. The calculated M and θ values are given in the last two columns of Table 2.

The effect of pH on adsorption of anilinic compounds was examined by carrying out the adsorption experiments in H_2O, in 0.1 M NaOH and in 1 M H_2SO_4. The rates and extents of adsorption as determined from k, M and θ values were found to decrease in these solutions in the following orders: H_2O > 0.1 M NaOH > 1 M H_2SO_4 for aniline, *p*-toluidine and 1-napthylamine; 1 M H_2SO_4 > H_2O > 0.1 M NaOH for sodium salt of diphenylamine-4-sulfonic acid. These observed orders can be explained in terms of electrostatic interactions between anilinic species and the surface of carbon-cloth. In water solutions, aniline, *p*-toluidine and 1-napthylamine are neutral i.e. they do not dissociate significantly. The net charge on the surface of carbon-cloth in these solutions is close to zero since the pH_{PZC} value was measured as 7.4 (see Section 3.1). Therefore these three compounds in H_2O solution are attracted by the carbon-cloth surface mainly via dispersion forces with very small contribution from electrostatic forces. In 0.1 M NaOH solutions the three anilinic compounds maintain their neutral character while the carbon surface attain some net negative charge. The decrease in the rates and extents of adsorption from 0.1 M NaOH solutions compared to that from H_2O solution may result from two reasons. The carbon surface may be occupied by OH^- ions and adsorption of anilinic compounds require desorption of OH^- ions first. Secondly, there might be a slight repulsion between surface negative charge and lone electron pairs of anilinic compounds. On the other hand in 1 M H_2SO_4 solution anilinic compounds take a proton and become anilinium cations while the carbon surface gains some net positive charge. So the lowest rate and extent of adsorption observed for the three compounds in 1 M H_2SO_4 among the three solutions may be attributed to the electrostatic repulsion between the positively charged adsorbate and the adsorbent.

Diphenylamine-4-sulfonate maintains its negative charge even in 1 M H_2SO_4 due to the strength of diphenylamine-4-sulfonic acid. Since the carbon surface in 1 M H_2SO_4 solution has some net positive charge, an electrostatic attraction is expected between carbon surface and diphenylamine-4-sulfonate in 1 M H_2SO_4. The highest rate and extent of adsorption observed for diphenylamine-4-sulfonate in 1 M H_2SO_4 may result from this electrostatic attraction.

The effect of structures of adsorbates on the adsorption of anilinic compounds from any of the three solutions (in H_2O, in 0.1 M NaOH or in 1 M H_2SO_4) can also be examined on the basis of k, M and θ values given in Table 2. The decreasing order of rate and extent of adsorption from water and from 0.1 M NaOH is 1-napthylamine > *p*-toluidine > aniline > sodium salt of diphenylamine-4-sulfonic acid while that from 1 M H_2SO_4 is sodium salt of diphenylamine-4-sulfonic acid > 1-napthylamine > *p*-toluidine > aniline.

In water solutions, the net charge on carbon surface is expected to be zero (pH_{PZC} = 7.4) and 1-naptyhlamine, *p*-toluidine and aniline are neutral molecules. So, the main interaction forces between carbon surface and these three compounds are expected to be dispersion forces between the π electrons of aromatic rings in the adsorbate and π electrons in the carbon surface. 1-Napthylamine has the strongest of such interactions due to possession of two aromatic rings, resulting in the highest rate and extent of adsorption. *p*-Toluidine has lower rate and extent of adsorption than 1-napthylamine due to possession of one less aromatic ring but higher rate and extent of adsorption than aniline due to the presence of an

hydrophobic methyl substituent in the ring and the fact that the carbon surface is also known to be hydrophobic. This does not necessarily mean that *p*-toluidine is being adsorbed by its methyl group but hydrophobic interaction between methyl group and carbon surface is believed to facilitate the adsorption. Diphenylamine-4-sulfonate anion is attracted least strongly by uncharged hydrophobic carbon surface in water.

In 0.1 M NaOH, carbon surface is negatively charged, but the same structural factors of adsorbates discussed above are expected to be effective. Thus, the same order of rate and extent of adsorption as in H_2O is observed in 0.1 M NaOH.

In 1 M H_2SO_4 the carbon surface is positively charged while diphenylamine-4-sulfonate maintains its negative charge. Thus an electrostatic attraction exists between the carbon surface and diphenylamine-4-sulfonate in 1 M H_2SO_4 resulting in the highest rate and extent of adsorption. On the other hand, the other three anilinic compounds are in cationic forms in 1 M H_2SO_4. Therefore, their rates and extents of adsorption are smaller than those for diphenylamine-4-sulfonate in 1 M H_2SO_4.

The θ values in Table 2 indicate that only a very small fraction of carbon-cloth surface is covered by the adsorption of anilinic species. This is reasonable when the huge specific surface area of carbon-cloth is considered. It should be noted that what fraction of this large surface area is accessible for the adsorbate species is not exactly known, although the pore size distribution indicated an average pore radius of approximately 2.3 ± 0.3 nm and an overall pore volume of 1.2 mL g^{-1} [30].

3.4. Adsorption isotherms

Adsorption isotherm data of anilinic compounds derived at 30 °C in water, in 1 M H_2SO_4 and in 0.1 M NaOH are shown in Figs. 7–9, 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. (5) and (6), respectively [31]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (5)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (6)$$

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, K_F the Freundlich constant representing the adsorption capacity in (mmol g^{-1})(L $mmol^{-1})^{1/n}$ and n is a constant depicting the adsorption intensity. The main difference between these two isotherm models is in the variation of heat of adsorption with the surface coverage. The Langmuir model assumes unifor-

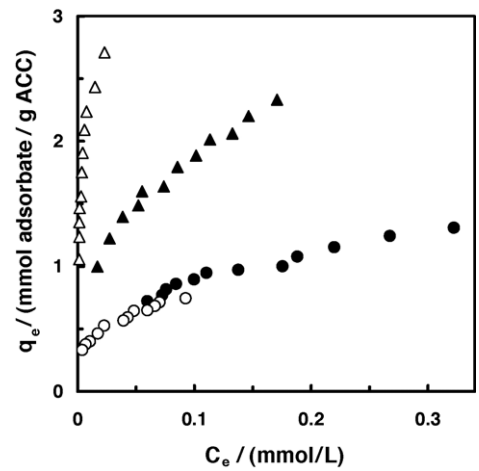


Fig. 7. Adsorption isotherm data of 1-napthylamine (△), *p*-toluidine (▲), sodium salt of diphenylamine-4-sulfonic acid (◯) and aniline (●) in water.

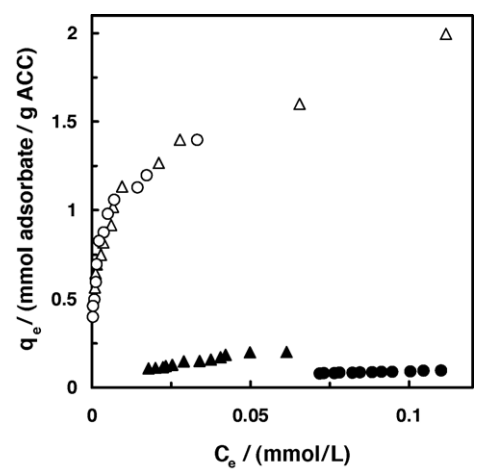


Fig. 8. Adsorption isotherm data of 1-napthylamine (△), *p*-toluidine (▲), sodium salt of diphenylamine-4-sulfonic acid (◯) and aniline (●) in 1 M H_2SO_4.

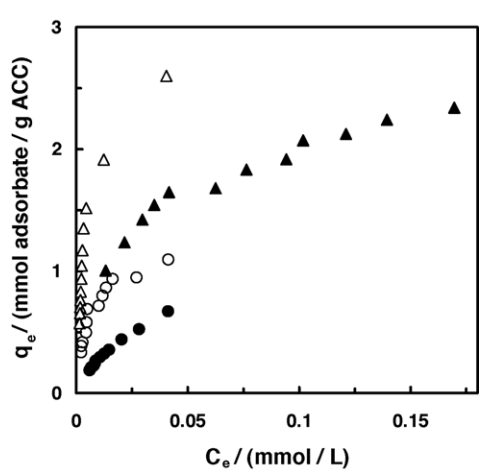


Fig. 9. Adsorption isotherm data of 1-napthylamine (△), *p*-toluidine (▲), sodium salt of diphenylamine-4-sulfonic acid (◯) and aniline (●) in 0.1 M NaOH.

Table 3
Parameters of Langmuir and Freundlich isotherm equations, regression coefficients (r) and normalized percent deviation (P) for anilinic compounds at 30 °C

Anilinic compound	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
Aniline	H_2O	1.58	12.7	0.9928	3.56	1.89	0.333	0.9884	2.20
	1 M H_2SO_4	0.154	15.0	0.9836	1.21	0.245	0.424	0.9729	1.13
	0.1 M NaOH	1.12	33.6	0.9908	2.59	5.36	0.645	0.9969	2.49
p-Toluidine	H_2O	2.72	25.8	0.9916	5.08	4.28	0.352	0.9959	1.91
	1 M H_2SO_4	0.358	22.6	0.9742	3.17	1.08	0.578	0.9838	3.18
	0.1 M NaOH	2.62	37.5	0.9952	17.9	4.14	0.313	0.9879	3.02
1-Napthylamine	H_2O	2.89	480	0.9984	5.25	10.3	0.324	0.9573	8.54
	1 M H_2SO_4	1.97	158	0.9906	20.6	3.35	0.248	0.9936	3.82
	0.1 M NaOH	2.91	202	0.9970	8.84	12.7	0.436	0.9248	14.5
Sodium salt of diphenylamine-4-sulfonic acid	H_2O	0.793	95.5	0.9935	7.89	1.38	0.262	0.9943	2.47
	1 M H_2SO_4	1.40	570	0.9953	13.9	3.70	0.266	0.9838	6.50
	0.1 M NaOH	1.21	186	0.9960	5.57	4.17	0.383	0.9580	8.79

mity and the Freundlich model assumes logarithmic decrease in heat of adsorption with surface coverage.

The parameters of Eqs. (5) and (6) obtained by the linear regression analysis of the isotherm data for the adsorption of four anilinic compounds from water, from 1 M H_2SO_4 and from 0.1 M NaOH solutions are given in Table 3. Monolayer adsorption capacity, q_{max}, for aniline, *p*-toluidine and 1-napthylamine are higher in H_2O than in both 1 M H_2SO_4 and 0.1 M NaOH. On the other hand the highest q_{max} value for sodium salt of diphenylamine-4-sulfonic acid was found in 1 M H_2SO_4. Similar pH effects (in H_2O, in 1 M H_2SO_4 or in 0.1 M NaOH) were observed on k, M and θ values of the anilinic compounds studied (Table 2).

q_{max} values for the anilinic compounds follow the order 1-napthylamine > *p*-toluidine > aniline > sodium salt of diphenylamine-4-sulfonic acid in water, 1-napthylamine > *p*-toluidine > sodium salt of diphenylamine-4-sulfonic acid > aniline in 0.1 M NaOH and 1-napthylamine > sodium salt of diphenylamine-4-sulfonic acid > *p*-toluidine > aniline in 1 M H_2SO_4. This order, that represent the effect of structures of anilinic compounds on adsorption, shows some disagreements in 1 M H_2SO_4 and in 0.1 M NaOH with the orders observed according to k, M and θ values. This is not surprising because the extent of adsorption of a slowly adsorbing species may exceed that of a rapidly adsorbing species over a long run of adsorption process until the attainment of equilibrium. Rapidly adsorbing species may reach to equilibria much earlier than the slowly adsorbing species.

One way of assessing the fit of experimental isotherm data to Langmuir and Freundlich equations can be on the basis of linear regression coefficients. Regression coefficients, r, obtained from the analysis of isotherm data according to both Langmuir and Freundlich models (Table 3) are close to each other and are mostly >0.92. Thus it is very difficult to decide which model represents the experimental data better on the basis of linear regression coefficients. A better criterion for the assessment of experimental isotherm data is a parameter known as normalized percent deviation [32] or in some literature percent relative deviation modulus, P, [33] given by the following equation:

$$P = \frac{100}{N} \sum \left(\frac{|q_{e(expt)} - q_{e(pred)}|}{q_{e(expt)}} \right) \quad (7)$$

where $q_{e(expt)}$ is the experimental q_e at any C_e, $q_{e(pred)}$ the corresponding predicted q_e according to the equation under study with the best fitted parameters and N 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 anilinic species 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 [33]. Most of the P values for Freundlich model are lower than 5 and are also lower than those for Langmuir model. So, it can be concluded that the Freundlich isotherm model represents the experimental isotherm data of the systems studied better than the Langmuir model.

4. Conclusions

It was demonstrated that the adsorption of anilinic compounds; aniline, *p*-toluidine, 1-napthylamine and sodium salt of diphenylamine-4-sulfonic acid from aqueous solutions onto activated carbon-cloth can be followed by in situ UV spectroscopy. The adsorption processes were found to follow first-order kinetics. The pH of the solution of anilinic compound determines both the charge on the carbon-cloth surface and the charge of the anilinic species. Electrostatic interactions between carbon-cloth and anilinic species resulting from these charges determine the extent of adsorption in an important way. In the absence of such electrostatic interactions, dispersion forces become effective in determining the

rate and extent of adsorption. The adsorption isotherm data of anilinic species studied in H_2O, in 1 M H_2SO_4 and in 0.1 M NaOH were found to be better represented by Freundlich model than Langmuir model.

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