

Adsorption of phthalic acid and its esters onto high-area activated carbon-cloth studied by in situ UV-spectroscopy

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Abstract

The adsorption behavior of phthalic acid and its three esters dimethyl phthalate, diethyl phthalate and diallyl phthalate onto high-area activated carbon-cloth was studied by in situ UV-spectroscopic technique. The effect of ionization of phthalic acid on its adsorption was examined by carrying out the adsorption process in three media; water, 1 M H₂SO₄ and 0.005 M NaOH. Maximum adsorption was observed in 1 M H₂SO₄ and almost no adsorption in 0.005 M NaOH. These results were discussed in terms of electrostatic and dispersion interactions between the adsorbate species and the carbon-cloth surface taking the point of zero charge (pH_{pzc}) of the carbon-cloth into account. The adsorption process for the phthalate species studied was found to follow the first-order rate law, and the rate constants were determined. The isotherm data for the adsorption of phthalic acid and its esters were derived experimentally and fitted to Langmuir and Freundlich isotherm equations. Both equations were found to represent the experimental isotherm data almost equally well.

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Keywords: Adsorption; Activated carbon-cloth; Ionization; Phthalic acid; Phthalate esters; UV-spectroscopy

1. Introduction

Phthalates are mainly used as plasticizers for cellulosic and some vinyl ester resins. Other uses of phthalates are in ceramic, paper, cosmetic, ink and paint industries. These industries discharge phthalates in their waste waters. Phthalates are known to be chemicals which are hazardous to human health and fertility as they can be readily adsorbed through the skin. They have been linked to birth defects, organ damage, infertility and cancer. They are also known to be among the endocrine-disrupting compounds [1,2]. Therefore, the waste water from phthalate processes must be treated before discharging to a municipal system or a water body. This treatment may involve destruction and/or removal of phthalates from waste waters. The destruction of phthalates may be achieved by biological treatments [3] or photocatalytic techniques [4].

Removal of many organic and inorganic compounds from waste waters is achieved by adsorption onto various adsorbents. Activated carbon materials in the form of granules, powder or fiber (felt or cloth) are among the most widely used adsorbents. The carbon-cloth adsorbents have the advantage of higher specific surface area, mechanical strength and possibility of regeneration over the others [5]. These advantages lead to an extensive use of carbon-cloth as adsorbent in adsorption studies in recent years [6–8]. Brasquet et al. [9] examined the quantitative structure–property relationship for the adsorption of 55 organic compounds onto activated carbon-cloth. Brasquet and Le Cloirec [10] studied the effects of activated carbon-cloth surface on organic adsorption in aqueous solutions. We have studied the adsorption of various organic materials such as heterocyclic compounds [11], some pesticides [12,13], benzoic acid [14] and the adsorption/electrosorption of some organic and inorganic species such as sulfur containing anions [15], thiocyanate and ethyl xanthate [16] onto high specific area carbon-cloth in relation to waste-water purification.

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Phthalic acid and its esters can be removed from solutions by adsorption onto various adsorbents including activated carbon materials. Herbert and Zeng [17] studied the adsorption of phthalates by activated sludge and its biopolymers. Bodzek et al. [18] studied the removal of phthalates as an application of membrane techniques to water purification. Adhoum and Monser [19] reported the removal of phthalate on modified activated carbon in powder form.

The type of adsorbing species is important in understanding the adsorption of ionizable compounds such as phthalic acid and is mainly dependent on the pH of the solution containing the adsorbate [20]. The pH of the solution determines not only the predominant species in the solution but also the net charge on the carbon-cloth. This aspect has been studied by Haghseresht et al. [21] on adsorption of some aromatic acids and phenolic compounds onto activated carbon and by Ayrançi and Conway [22] on adsorption and electrosorption of phenol and phenoxide at the high-area carbon-cloth.

In the present work, we report the adsorption behavior of phthalic acid and its three esters onto high-area carbon-cloth studied by in situ UV-spectroscopy. The esters were chosen in an order of increasing hydrophobicity as dimethyl phthalate, diethyl phthalate and diallyl phthalate. Phthalic acid can be found in single or double negatively charged anions or in neutral molecular form in solutions depending on the pH determined by the two step acid dissociation constants. On the other hand it is known that phthalate esters can be hydrolyzed into alcohols and phthalic acid in strongly acidic medium.

2. Materials and method

2.1. Materials

The carbon-cloth used in the present work was obtained from Spectra Corp. (MA, USA) coded as Spectracarb 2225, having a specific surface area of $2500 \text{ m}^2 \text{ g}^{-1}$. Phthalic acid and its esters dimethyl phthalate, diethyl phthalate and diallyl phthalate were obtained from Aldrich. NaOH and H_2SO_4 were reagent grade. Deionized water was used in adsorption experiments.

2.2. Properties and treatment of carbon-cloth

The carbon-cloth has a specific surface area of $2500 \text{ m}^2 \text{ g}^{-1}$ as determined by the manufacturer by means of Kr-desorption BET procedure. The pore size distribution of it indicated an average pore radius of approximately $2.3 \pm 0.3 \text{ nm}$ and an overall pore volume of 1.2 mL g^{-1} [6]. The SEM pictures and electrochemical characterization of carbon-cloth were given in our earlier reports [15,16].

The carbon surface charge is mainly determined by the pH of the adsorbate solution. It is known that [20,23] the net charge on the 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} .

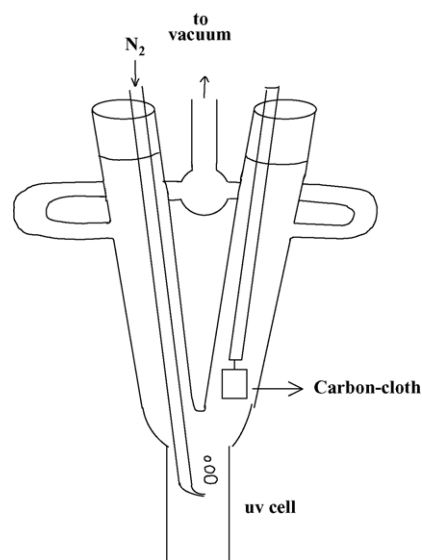


Fig. 1. Diagram of the adsorption cell.

The pH_{pzc} of the carbon-cloth used in the present work was measured by batch equilibrium method described by Babić et al. [8] and determined to be 7.4 in our earlier work [14].

The activated carbon fibers are known to provide spontaneously a small but significant quantity of ions into conductivity water probably due to its complex structure originating from its somewhat unknown proprietary preparation procedure [15,24]. Therefore, a deionization cleaning procedure was applied to avoid desorption of ions during adsorption studies. In this procedure, the details of which are given in our earlier report [15], the carbon-cloth samples were washed with warm conductivity water in a kind of a series of batch operations until no more ions are desorbed as tested conductometrically. The washed carbon-cloth modules were then dried under vacuum at 120°C and kept in a desiccator for use in actual adsorption experiments.

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 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 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.

With the use of adsorption cell described above it was possible to follow the changes in concentration of the ad-

sorbate solution during the course of adsorption by in situ UV-spectroscopy. Solutions of phthalic acid were prepared in water, in 1 M H₂SO₄ and in 0.005 M NaOH to examine the ionization effect on adsorption while the solutions of phthalates were prepared only in H₂O as they cannot dissociate into ions. The initial concentrations of phthalic acid or phthalate esters in all these solutions and the amount of carbon-cloth dipped into these solutions were taken to be almost the same for kinetic studies of adsorption in order to make an easy comparison between the observed adsorption behavior of different adsorbents in water, acid or base solutions. The concentration was about 2.4×10^{-4} M and the carbon-cloth piece was about 18 ± 0.1 mg. However, the actual weights of carbon-cloth pieces and the initial concentrations were recorded for the calculation of the amount 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. The idea of using the pre-wetted carbon-cloth originates from our previous findings that pre-wetting enhances the adsorption process [15,16].

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 N₂-bubbling 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 had been removed temporarily after wetting and degassing, was reinserted 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.

The program for monitoring the absorbance at the specific wavelength of maximum absorbance predetermined by taking the whole spectra of phthalic acid, phthalate ions or phthalate esters was run on the built-in microcomputer of the spectrophotometer. Absorbance data was recorded in programmed time intervals of 1 min over a period of 125 min.

Absorbance data were converted into concentration data using calibration relations pre-determined at the wavelength of maximum absorbance for each phthalic species: neutral acid, anion or ester.

2.4. Determination of adsorption isotherms

The adsorption isotherms were determined on the basis of batch analysis. Carbon-cloth pieces of varying masses were allowed to equilibrate with solutions of phthalic species at 30 °C for 48 h. Preliminary tests showed that the concentra-

tion of phthalic species remained unchanged after 12–14 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 Nüve ST 402 shaking water bath at a constant shaking speed of 150 rpm. The concentration after the equilibration period was measured spectrophotometrically. The amount of adsorbate adsorbed at equilibrium per unit mass of carbon-cloth, q_e , was calculated by Eq. (1),

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

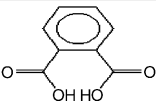
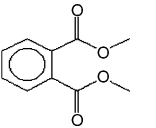
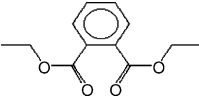
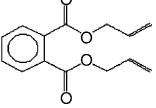
where V is the volume of the adsorbate solution in L; C_0 and C_e the initial and equilibrium concentrations in mol L⁻¹, respectively and m is the mass of carbon-cloth in grams. Then Eq. (1) gives q_e in mol adsorbate adsorbed per gram carbon-cloth.

3. Results and discussion

3.1. Absorption characteristics and calibration data of phthalic acid and its esters

All the spectral and calibration data for the phthalic acid species and its esters studied are given in Table 1 together with regression coefficients. The data for phthalate esters were obtained using pure water as the solvent as there is no possibility of these esters to hydrolyze. Phthalic acid being a divalent weak organic acid may hydrolyze into hydrogen phthalate and phthalate anions. The stepwise acid dissociation constants of phthalic acid are $K_{a1} = 1.2 \times 10^{-3}$ and $K_{a2} = 3.9 \times 10^{-6}$. Analytical calculations show that phthalic acid at an analytical concentration of 1×10^{-4} M is found about 90% in hydrogen phthalate form in water. So, phthalic acid in water is a mixture of neutral phthalic acid and hydrogen phthalate anion, the ratio of the two being dependent on the initial analytical concentration. When the hydrolysis is suppressed in strongly acidic medium such as 1 M H₂SO₄ the predominant species will be the neutral phthalic acid. Calculations show that in an alkaline solution, such as 0.005 M NaOH, phthalic acid is almost completely hydrolyzed into divalent phthalate anion. Therefore, the absorption data for phthalic acid were derived in three solvents; water, 0.005 M NaOH and 1 M H₂SO₄ (Table 1). Concentrations were followed at 230 nm in water and in 1 M H₂SO₄ solutions, since the predominant species hydrogen phthalate and/or neutral phthalic acid in these solvents, give a strong characteristic UV absorption band maximum at this wavelength. In 0.005 M NaOH, the conversion of all the phthalic acid into phthalate anion causes the band maximum at 230 nm to disappear. Therefore, the concentrations of phthalic acid in 0.005 M NaOH solution were followed at 272 nm where the phthalate anion shows relatively weak UV absorption band maximum.

Table 1
Spectral and calibration data for phthalic acid and its esters

Molecule	Solvent	Structure	$\lambda_{(\max)}$ (nm)	ϵ (au cm ⁻¹ M ⁻¹)	Regression coefficient (<i>r</i>)
Phthalic acid	H ₂ O		230	7196.4	0.9997
Phthalic acid	1 M H ₂ SO ₄		230	8020.9	0.9993
Phthalic acid	0.005 M NaOH		272	732.32	0.9991
Dimethyl phthalate	H ₂ O		230	8068.5	0.9996
Diethyl phthalate	H ₂ O		230	8306.2	0.9997
Diallyl phthalate	H ₂ O		230	9066.9	0.9996

3.2. Adsorption behavior of phthalic acid

Adsorption behavior of phthalic acid over 125 min period from solutions in water, in 1 M H₂SO₄ and in 0.005 M NaOH onto activated carbon-cloth is shown in Fig. 2. Phthalic acid presents almost the same adsorption behavior in H₂O and in 1 M H₂SO₄. The pH of the adsorbate solution in H₂O was found to vary from 3.78 to 4.12 during the course of adsorption. It was mentioned above that about 90% of phthalic acid is in monovalent hydrogen phthalate ion form in water. Carbon surface at this pH range, which is much lower than p*H*_{pzc} of 7.4, is positively charged [20]. So, phthalic acid in water is adsorbed onto carbon surface by electrostatic attraction forces between oppositely charged adsorbate and carbon surface. Of course some dispersion forces between π electrons of benzene ring in phthalic acid molecules or in

hydrogen phthalate anion and π electrons of carbon surface are also expected to be operative in the adsorption process. In 1 M H₂SO₄ solution, calculations showed that phthalic acid is more than 99% in neutral form. So, the main adsorption force between carbon surface and phthalic acid molecules in this solvent is expected to be of dispersion type. Carbon surface is expected to be more positively charged in this strongly acidic solution than in H₂O. Therefore, some electrostatic forces between the carbon surface and π electrons of phthalic acid are also expected to be effective. These forces make the extent of adsorption of phthalic acid in 1 M H₂SO₄ to be almost the same as or slightly higher than that in water.

Phthalic acid in 0.005 M NaOH is completely in divalent phthalate ion form. Carbon surface in this alkaline solution is also expected to have a net negative charge since the pH of this solution is much higher than p*H*_{pzc} of 7.4. Strong electrostatic repulsions between the carbon surface and the phthalate anions prevent the adsorption of phthalate anion onto the carbon-cloth. This behavior is seen in curve (c) of Fig. 2.

Adsorption data of phthalic acid in water and in 1 M H₂SO₄ over a 125 min period were treated according to the first-order kinetics by plotting $\ln [C_0/C_t]$ where C_0 and C_t are initial concentration and concentration at any time, respectively, as a function of time and applying linear regression analysis. This treatment was not applied for data in 0.005 M NaOH since there is only a very small (almost negligible) adsorption in this solution. The slopes of the lines provided the first-order rate constants, *k*, for the adsorption process. Initial concentrations, concentrations at 125 min and the rate constants together with regression coefficients are given in Table 2. It is seen that there is about six- or seven-fold decrease in concentration over 125 min adsorption. Closeness of regression coefficients to 1 (>0.99) support the assumption of first-order kinetics for the adsorption process. Closeness

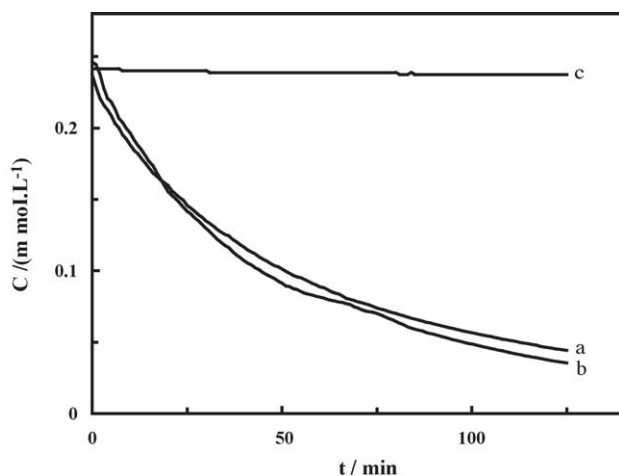


Fig. 2. Adsorption behavior of phthalic acid from solutions in (a) water, (b) 1 M H₂SO₄ and (c) 0.005 M NaOH onto activated carbon-cloth.

Table 2

Initial concentrations (C_0), concentrations at 125 min (C_{125}), M values at 125 min, first-order rate constants (k) and regression coefficients for the adsorption of phthalic acid and its esters from solutions onto carbon-cloth

Molecule	Solvent	C_0 ($\times 10^4$ mol L $^{-1}$)	C_{125} ($\times 10^5$ mol L $^{-1}$)	M ($\times 10^8$ mol m 2 C-cloth) $^{-1}$	k (min $^{-1}$)	Regression coefficient (r)
Phthalic acid	H $_2$ O	2.39	4.42	8.57	0.0130	0.9948
Phthalic acid	1 M H $_2$ SO $_4$	2.41	3.54	9.36	0.0148	0.9944
Phthalic acid	0.005 M NaOH	2.40	23.6	0.11	0.0001	0.9234
Dimethyl phthalate	H $_2$ O	2.39	2.78	9.39	0.0181	0.9988
Diethylphthalate	H $_2$ O	2.39	1.55	9.93	0.0202	0.9978
Diallyl phthalate	H $_2$ O	2.39	0.63	10.31	0.0317	0.9996

of the rate constant for the adsorption in H $_2$ O to that in 1 M H $_2$ SO $_4$ shows that phthalic acid and hydrogen phthalate have similar adsorption behavior.

The extent of adsorption may also be quantified by calculating the amount of adsorbate adsorbed per unit area of carbon-cloth, M , at the end of 125 min adsorption using the following equation:

$$M = \frac{(C_0 - C_t)V}{2500m} \quad (2)$$

where C_0 and C_t are the concentrations at the beginning and at 125 min of adsorption, respectively. V is the volume of the solution and m is the weight of carbon-cloth module. The calculations are based on the known specific surface area of 2500 m 2 g $^{-1}$ for the carbon-cloth. These M values are included in Table 2. The extent of adsorption of phthalic acid seems to be slightly higher in 1 M H $_2$ SO $_4$ than in H $_2$ O.

3.3. Adsorption behavior of phthalate esters

Adsorption behavior of dimethyl phthalate, diethyl phthalate and diallyl phthalate from aqueous solutions onto activated carbon-cloth over 125 min is shown in Fig. 3

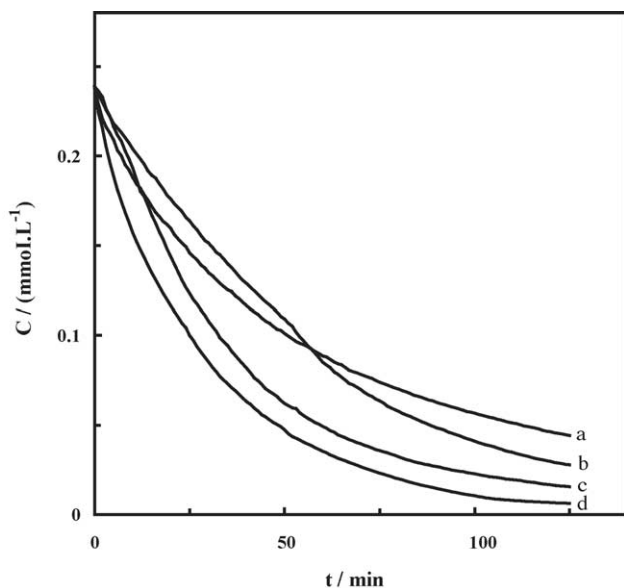


Fig. 3. Adsorption behavior of (a) phthalic acid, (b) dimethyl phthalate, (c) diethyl phthalate and (d) diallyl phthalate from aqueous solution onto activated carbon-cloth.

where the curve for phthalic acid in H $_2$ O is also included for comparison purposes. The first-order rate constants and the corresponding regression coefficients determined as described above, M values at 125 min of adsorption calculated from Eq. (2), initial concentrations (C_0) and the concentrations at 125 min (C_{125}) for the adsorption of phthalate esters are given in Table 2. The regression coefficients show that the assumption of first-order rate law for the adsorption of phthalate esters seems to be valid. The rate of adsorption of phthalic acid and its esters as determined by the first-order rate constants, k (Table 2) increases in the order phthalic acid < dimethyl phthalate < diethyl phthalate < diallyl phthalate. The extent of adsorption at 125 min as determined by M values also follows the same order. This observed order of adsorption can be explained on the basis of hydrophobic and dispersion effects. The hydrophobicity of groups attached to phthalic acid for the formation of esters increases in the order dimethyl phthalate < diethyl phthalate < diallyl phthalate. So, hydrophobic interactions which are characterized as unusually strong attraction by Moreno-Castilla [20], between hydrophobic sites of carbon surface and apolar alkyl or allyl groups of phthalates determine the observed order of rate and extent of adsorption. In the case of diallyl phthalate there are additional π electrons from diallyl group resulting in increasing dispersion interactions. Thus, the highest rate and extent of adsorption are observed with diallyl phthalate.

3.4. Adsorption isotherms of phthalic acid and its esters

Adsorption isotherm data of phthalic acid and its esters from aqueous solutions onto activated carbon-cloth were derived at 30 °C. They are given in Fig. 4. The isotherm data were treated according to Langmuir and Freundlich equations. The linearized forms of Langmuir and Freundlich equations are given in Eqs. (3) and (4), respectively, [25]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \quad (3)$$

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \quad (4)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mol g $^{-1}$, C_e the final concentration at equilibrium in mol L $^{-1}$, q_{\max} the maximum adsorption at monolayer coverage in mol g $^{-1}$, b the adsorp-

Table 3

Parameters of Langmuir and Freundlich adsorption isotherm equations, regression coefficients and percent deviations for phthalic acid and its esters

Molecule	Langmuir				Freundlich				
	q_{\max} ($\times 10^4$ mol g $^{-1}$)	b (L mol $^{-1}$)	r	P	K_f (mol g $^{-1}$) (L mol $^{-1}$) $^{1/n}$	$1/n$	r	P	
Phthalic acid	8.96	47292	0.9968	3.581	0.02063	0.3576	0.9949	2.084	
Dimethyl phthalate	11.62	100030	0.9958	5.101	0.11563	0.4666	0.9661	8.458	
Diethyl phthalate	25.98	61106	0.9869	6.387	0.12407	0.4173	0.9819	4.893	
Diallyl phthalate	36.77	63231	0.9779	3.484	0.13584	0.3981	0.9737	4.367	

tion equilibrium constant related to the energy of adsorption, K_f the Freundlich constant representing the adsorption capacity in (mol g $^{-1}$) (L mol $^{-1}$) $^{1/n}$ and n is a constant depicting the adsorption intensity. Langmuir model assumes uniformity in the heat of adsorption while Freundlich model assumes a logarithmic decrease in the heat of adsorption with the surface coverage.

The experimental isotherm data presented in Fig. 4 for phthalic acid and its esters were fitted to Eqs. (3) and (4) by applying linear regression analysis. The parameters of Langmuir and Freundlich equations obtained from regression analysis are given in Table 3 together with regression coefficients, r . The order of adsorption capacity of carbon-cloth for phthalic acid and its esters as determined by Langmuir q_{\max} parameter and Freundlich's K_f parameter appears to be the same as the order of rate and extents of adsorption at 125 min of adsorption discussed above.

The fit of adsorption isotherm data to Langmuir and Freundlich equations seems to be equally well as all regression coefficients are greater than 0.96. In order to make differentia-

tion between the two models for representing the experimental isotherm data of phthalic acid and its esters, the parameter known as normalized percent deviation [26] or in some literature percent relative deviation modulus [27] shown by the symbol P was utilized. P is given by the following equation:

$$P = \left(\frac{100}{N} \right) \sum \left(\frac{|q_{e(\text{expt})} - q_{e(\text{pred})}|}{q_{e(\text{expt})}} \right) \quad (5)$$

where $q_{e(\text{expt})}$ and $q_{e(\text{pred})}$ are the amount of adsorbate adsorbed per unit mass of adsorbent determined experimentally and predicted from the isotherm equation, respectively, and N is the number of data pairs. The P values for the isotherm data of phthalic acid and its esters are included in Table 3. It is generally accepted that when the P -value is less than 5 the fit of experimental data to the model is considered to be excellent [27]. The P -values obtained for the isotherm data of phthalic acid and its esters are mostly less than 5 or not very much higher than 5 for both models. So, it can be concluded that both models represent the experimental data almost equally well. This implies that in the concentration range of isotherm data, adsorption takes place up to the monolayer coverage, because it is known that Langmuir equation does not take multilayer coverage into account [28].

4. Conclusions

Phthalic acid and its esters as pollutants can be removed to a great extent from aqueous solutions by adsorption onto high-area activated carbon-cloth. This work constitutes a model study for purification of actual waste-waters which may contain other species (pollutants or not) than phthalic acid and its esters. Actual systems may be approached by studying the adsorption of individual pollutants from multi-component solutions. Further study is required in this matter. The carbon-cloth as an adsorbent may be more expensive than granular activated carbon but it has the advantage of possibility of regeneration which can make it more economical.

The rate of removal of phthalic acid and its esters from aqueous solutions by adsorption is of first order. The pH of adsorbate solution was found to be important in the adsorption of phthalic acid due to its ionizability. At pH values higher than the pH_{pzc} of carbon-cloth, phthalic acid was not adsorbed at all onto the carbon-cloth due to possession of the same negative charge with the carbon surface. Adsorp-

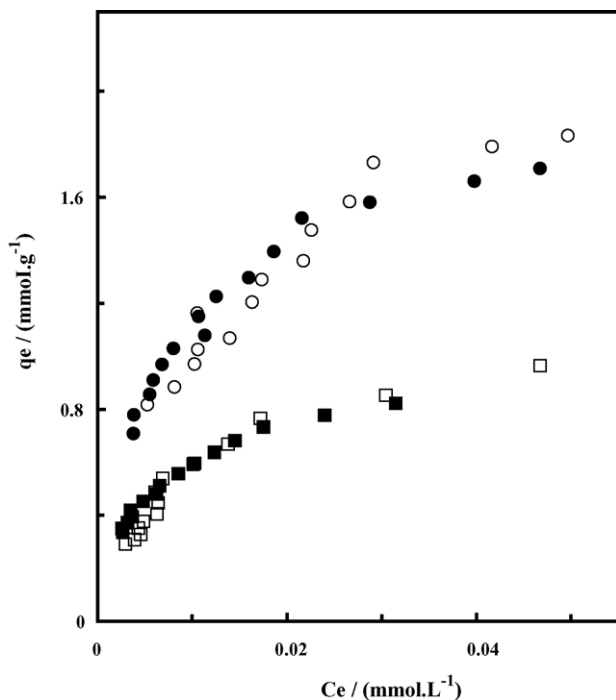


Fig. 4. Adsorption isotherms for phthalic acid (■), dimethyl phthalate(□), diethyl phthalate (○) and diallyl phthalate (●) at 30 °C.

tion isotherm data obtained for phthalic acid and its esters can successfully be represented by both Langmuir and Freundlich equations.

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