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Estimation of Adsorption Capacity for Dissociating and Non Dissociating Aromatic Compounds on Activated Carbon with Different Models

SIROUS NOURI
Chemistry Department, College of Science, Urmia University, Urmia 57135-165, Iran
s.nouri@mail.urmia.ac.ir

F. HAGHSERESHT
Chemical Engineering Department, University of Queensland, Brisbane, QLD 4072, Australia

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Abstract. The process of adsorption of two dissociating and two non-dissociating aromatic compounds from dilute aqueous solutions on an untreated commercially available activated carbon (B.D.H.) was investigated systematically. All adsorption experiments were carried out in pH controlled aqueous solutions. The experimental isotherms were fitted into four different models (Langmuir homogenous Models, Langmuir binary Model, Langmuir-Freundlich single model and Langmuir-Freundlich double model). Variation of the model parameters with the solution pH was studied and used to gain further insight into the adsorption process. The relationship between the model parameters and the solution pH and pK_a was used to predict the adsorption capacity in molecular and ionic form of solutes in other solution.

A relationship was sought to predict the effect of pH on the adsorption systems and for estimating the maximum adsorption capacity of carbon at any pH where the solute is ionized reasonably well.

N_2 and CO_2 adsorption were used to characterize the carbon. X-ray Photoelectron Spectroscopy (XPS) measurement was used for surface elemental analysis of the activated carbon.

Keywords: activated carbon, adsorption, Langmuir homogenous models, Langmuir binary models, spectrophotometer

Introduction

Because of widespread use of aromatic compounds as ingredients and solvents in various manufacturing industries, these compounds are common water contaminants. This has led to an upsurge of interest in developing and implementing methods for removing them.

It is well known that the uptakes of gaseous, vapor, or liquid adsorbates by different carbon adsorbents can vary over a remarkably wide range. Many of these variations are due to differences in the physical surface properties, i.e., to surface area effects, as well as to different degrees of molecular sieving because of their widely varying pore size distributions. Examination of the literature shows an abundance of experimental adsorption studies for aqueous organic solute systems involving activated carbon (Hsieh and Teng, 2000; Leng and Pinto, 1997; Radovic et al., 1997, 1996; Haghseresht et al., 2002a; Nouri et al., 2001).

In water treatment by activated carbon, both the molecular and the ionic species of aromatic compounds are present. The adsorption of dissociating aromatic compounds onto the surface of activated carbons is affected by the properties of adsorbate and the adsorbent. The adsorbate chemical nature, the type of functional groups, molecular size, and its solubility affect the adsorbate behaviour significantly. The chemical heterogeneity of the carbon surface together with its porous structure characterizes the adsorption properties of the carbon surface (Halhouli et al., 1995; Banasal et al., 1988; Nouri et al., 2002a, 2002b).

A number of authors have shown ample evidence for the effect of solution pH and carbon surface chemistry on the adsorption of organic compounds from aqueous solutions (Coughlin and Ezra, 1968; Ward and Getzen, 1970; Muller et al., 1980, 1985). In our previous work (Nouri, 2002; Nouri and Haghseresht, 2002) we used the binary Langmuir isotherm to explain the effect of pH on the adsorption of electrolytes.

In this work, adsorption characteristics of four aromatic compounds (two dissociating and two non-dissociating aromatic compounds) in various solution conditions are investigated systematically. All isotherms were obtained in pH controlled solutions. The experimental isotherms are fitted into four different models (Langmuir homogenous Models, Langmuir binary Model, Langmuir-Freundlich single model and Langmuir-Freundlich binary model). Variation of the model parameters with the solution pH are studied and used to gain further insight into the adsorption process. The relationship between the model parameters and the solution pH is used to predict them in other solution.

Theoretical Section

In our previous works (Nouri et al., 2002a; Nouri and Haghseresht, 2004a, 2004b), all adsorption experiments were carried out in a solution condition, where the molecular species of the solutes were dominant (pH = 2) or in different pH. Therefore in our analysis single solute Langmuir (Eq. (1)) and Langmuir-Freundlich (Eq. (2)) models were selected and used to obtain the fitted parameters ($Q_{\max}$, K_1 and n).

$$\theta = \frac{K_1 C_{\mathrm{eq}}}{1 + K_1 C_{\mathrm{eq}}} \tag{1}$$

$$\theta = \frac{K_1 C_{\mathrm{eq}}^{1/\mathrm{n}}}{1 + K_1 C_{\mathrm{eq}}^{1/\mathrm{n}}} \tag{2}$$

where

$$\theta = \frac{q}{Q_{\max}}$$

In the adsorption process of dissociating aromatic compounds, both the molecular and the ionic species of aromatic compounds are present. When the solution pH is changed, the ratio of the molecular to ionic species changes, depending on the $\mathrm{pK_a}$ of the solute. As described in our previous works (Nouri, 2002; Nouri and Haghseresht, 2002), the binary Langmuir model (Eq. (3)) can fit the isotherm data.

$$\theta = \frac{C_m K_m + C_i K_i}{1 + C_m K_m + C_i K_i} \tag{3}$$

where $K_m = K_{0m} \exp(-E_m/RT)$ and $K_i = K_{0i} \exp(-E_i/RT)$.

In Eq. (3), subscripts i and m represent the ionic and the molecular species. The other symbols C, K and E represent the bulk concentration, the equilibrium constant and the adsorption energy of the species.

At any pH the dissociating species would be in equilibrium and their equilibrium constant, K_a can be calculated.

We can then use the solution concentration of the individual species in terms of the total measured equilibrium concentration:

$$C_m = \left(\frac{C_{\mathrm{eq}}}{1+\alpha}\right) \quad \text{and} \quad C_i = \left(\frac{C_{eq}\alpha}{1+\alpha}\right)$$

where $\alpha = \frac{C_i}{C_m}$, $\log(\alpha) = \mathrm{pH} - \mathrm{pK_a}$ and $C_{eq} = C_i + C_m$.

Using the above relationships, Langmuir binary and Langmuir-Freundlich binary models can be shown as Eqs. (4) and (5).

$$\frac{C_{eq}}{q} = \frac{(1+\alpha)}{(K_m + K_i\alpha)Q_{\max}} + \frac{1}{Q_{\max}} C_{eq} \tag{4}$$

$$q = \frac{Q_{\max} C_{eq}^{1/n} [K_m + K_i \alpha^{1/n}]}{(1+\alpha)^{1/n} + C_{eq}^{1/n} [K_m + K_i \alpha^{1/n}]} \tag{5}$$

When adsorption is carried out in solution pH where both the molecular and ionic species are present, the fitted equilibrium constant K_l, defined below, would be a lumped parameter containing K_m, K_i and α. Their relationship can be extracted from Eq. (3) (Eq. (6)) and its linear form can be used to investigate the relationship between the lumped affinity coefficient and those of the molecular and ionic species.

$$K_1 = \frac{K_m + K_i\alpha}{1+\alpha} \tag{6}$$

Equation (6) allows determination of K_1 in the following situations:

1. In low pH, where the molecular species are dominant, $\alpha \approx 0$. Therefore $K_1 \approx K_m$.

2. When pH = pK_a of the solute $\alpha = 1$. The value of K_1 then becomes the average of the K_m and K_i.
3. In highly alkaline solution when the solute is highly ionized $K_1 \approx K_i$.

Experimental Section

The granular activated carbon (GAC) was BDH from Merck. Prior to the experiments, a sample of GAC was ground and sieved. The particle size of 400–800 μm, was used in this work. Chemicals used were as follows Benzene (BZ), Toluene (Tol) (99.9% purity) and p-Cresol (PC) (99.7% purity)-from Merck, Benzoic acid (BA) (99.9% purity)—from BDH, HCl and NaOH (A. R. Grade)—from Ajax Chemicals.

Table 1 shows some properties of the solutes.

The adsorption experiments were carried out by placing 45 mg of the activated carbon into 50 ml of the solution containing different concentrations of the adsorbates. Solution pH conditions were adjusted using dilute NaOH or HCl. All solutions were then left in Thermostat shaking bath for 4 days at 301 K to reach equilibrium. After reaching equilibrium conditions, the residue concentrations of the solutes, after filtration, were measured spectrophotometrically using Jasco-V550 spectrophotometer.

Experimental isotherms of the solutes, Benzoic acid, p-Cresol, Toluene and Benzene were obtained in various solution conditions, covering pH = 2 to 12.

The $pH_{(PZC)}$ of the carbon was determined as described in our previous works (Nouri and Haghseresht, 2002; Haghseresht et al., 2003; Nouri et al., 2002a). This was done by adding various amounts of the carbon in to 10 ml solutions of 0.1 M NaCl (prepared in pre-boiled water). The sealed bottles were then placed in a constant temperature shaker overnight. The equilibrium pH values of the mixtures were then measured. The limiting pH was taken as the $pH_{(PZC)}$ (i.e. $pH_{(PZC)} = 10.2$) Fig. 1.

Table 1. Selected properties of the solutes.

			Dipole moment (debye)	
Solutes	Molecular (Wt.)	pK_a	Molecular	Ionic
Benzene	78	–	–	–
Toluene	92	–	–	–
p-Cresol	108	10.2	1.32	6.83
Benzoic acid	122	4.2	2.18	8.89

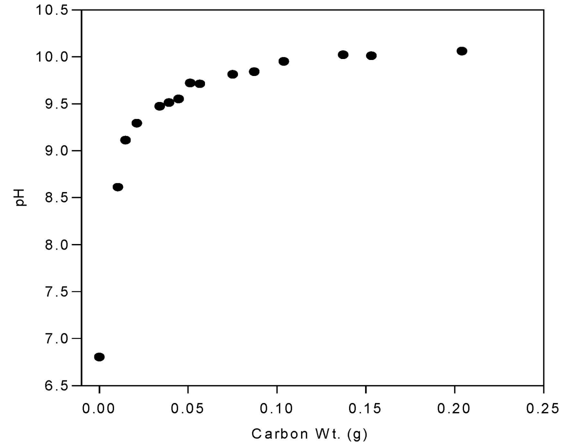


Figure 1. P. Z.C. of activated carbon.

It is suggested that in the pH = $pH_{(PZC)}$ the surface of carbon is neutral. At values higher than $pH_{(PZC)}$, it's surface is negatively charged and at values lower than $pH_{(PZC)}$ the carbon surface is positive.

For characterization of the carbon, as described in our previous works (Haghseresht et al., 2002b; Nouri, 2003a, 2003b) N_2 and CO_2 adsorption were used. The nitrogen adsorption data were used to determine the BET surface areas (S_{BET}), the total pore volumes (V_{tot}), and the micropore volumes (V_{mic}) of the activated carbon. The BET surface area was obtained by applying the BET equation to the adsorption data in the P/P_0 range of 0.01 to 0.1, V_{tot} was obtained from the adsorption at $P/P_0 = 0.96$, and micropore volume, V_{mic}, was obtained using the *t*-plot method (Gregg and Sing, 1982). The ultramicropore volumes (V_{ulimc}) of the carbon were obtained by applying the Dubinin-Radushkevich equation (DR) to CO_2 adsorption isotherms obtained at 273 K (Marsh, 1987).

Toluene and water adsorption experiments were carried out gravimetrically using an in-house adsorption apparatus equipped with quartz springs, a MKS transducer, measuring absolute pressure with the precision of ±1 mTorr and a temperature-controlled oven capable of heating to 200°C. Prior to the adsorption experiments, all samples were degassed overnight at 150°C. A lower degassing temperature was used than that of the gas adsorption experiments. This was for maintaining the integrity of the surface oxides, as these functional groups affect the observed water adsorption behavior significantly.

In these experiments, the samples were subjected to a step change in the sorbate pressure from the initial zero

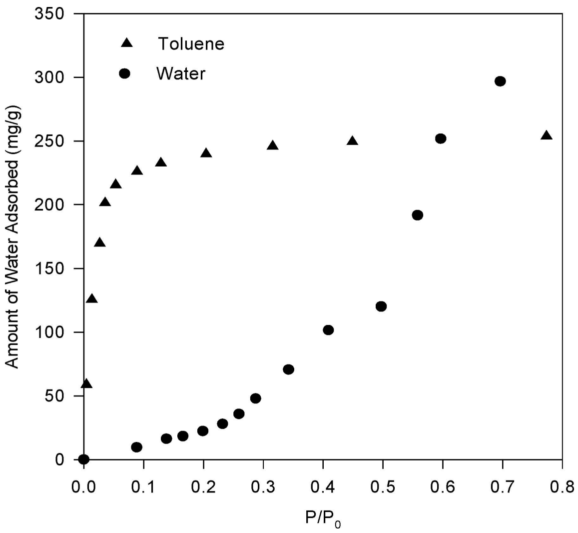


Figure 2. Water and Toluene adsorption Isotherms of carbon.

to its saturation pressure. Figure 2 shows the toluene and water adsorption isotherms of activated carbon.

Toluene pore volumes of the activated carbon,(V_{Tol}), is determined by using the monolayer adsorption capacity of the activated carbon for toluene and using 0.866 g cm^{-3} as the toluene density.

The water adsorption data were analyzed by fitting the water adsorption isotherm to Eq. (7), the DS-2 equation (Barton et al., 1991).

$$c(Q_0 - q)(1 - kq) = q/(P/P_0) \tag{7}$$

where q is the measured adsorption amount per gram of the carbon, P/P_0 is the relative pressure, c is the kinetic parameter, k is the constant involved in decreasing active site concentration, and Q_0 is the concentration of the primary sites.

Gas Adsorption Experiments

Nitrogen adsorption/ desorption experiments were carried out volumetrically at 77 K using an Autosorb (Quantachrome Corp., 1996). Carbon dioxide adsorption experiments were also carried out volumetrically, at 273 K, using a NOVA 1200 (Quantachrome Corp.). Samples of 20–30 mg for the N_2 and 90–100 mg for the CO_2 adsorption experiments were degassed overnight at 200°C, prior to the adsorption experiments.

Using the N_2 and CO_2 adsorption data, the S_{BET}, V_{tot}, V_{mic}, and V_{ulmic} of the activated carbon were determined (Table 2).

Table 2. Pore structure characteristics of the BDH activated carbon.

S_{BET} ($\mathrm{m}^2\mathrm{g}^{-1}$)	V_{tot} ($\mathrm{cm}^3\mathrm{g}^{-1}$)	V_{mic} ($\mathrm{cm}^3\mathrm{g}^{-1}$)	V_{ulmic} ($\mathrm{cm}^3\mathrm{g}^{-1}$)	V_{Tol} ($\mathrm{cm}^3\mathrm{g}^{-1}$)
1118	0.618	0.416	0.282	0.28

Further insights into the pore structures of the activated carbons can be obtained by using the toluene adsorption data (Fig. 2). Similar to the N_2 adsorption isotherms, the toluene isotherms of the activated carbons exhibit a rapid rise in the adsorption amount followed by a plateau. The toluene pore volumes of the carbon (Table 2) were determined by using the plateaus of the toluene isotherms. Table 2 shows that the toluene pore volumes, V_{Tol}, of the carbon is significantly smaller than their corresponding V_{tot}.

This is because the N_2 molecule is much smaller than toluene and can penetrate micropores that are inaccessible to the toluene molecules.

Two of the most important surface properties of activated carbons affecting their solution adsorption behavior are their acidity/alkalinity and hydrophilicity. The former affects the extent of the electrostatic and the latter affects the extent of the dispersive interactions, respectively. Generally, hydrophobic activated carbons are basic, and exhibit high $\mathrm{pH}_{\mathrm{PZC}}$. The converse is not true: whereas most hydrophilic activated carbons are acidic, and exhibit low $\mathrm{pH}_{\mathrm{PZC}}$, some surface treatments, such as nitriding, can make the carbon both hydrophilic and basic.

The water adsorption isotherms can be used to compare the hydrophilicities of activated carbons. The water adsorption isotherm in Fig. 2 shows low adsorbate-adsorbent interactions at low relative pressures, followed by a rapid rise in the adsorption amount at higher pressures, typical of water adsorption on activated carbon (Gregg and Sing, 1982).

X-ray Photoelectron Spectroscopy (XPS) Studies

XPS measurements were conducted with a PHI-Model 560ESCA system (Perkin Elmer) which employed a Model 25–270 AR cylindrical mirror analyzer. All spectra were acquired at a basic pressure of 2×10^{-7} Torr with Mg KR excitation and at 400 W.

Survey (wide) scans were recorded with a pass energy of 100 eV and multiplex (narrow) scans, over

Table 3. Surface chemical characteristics of the activated carbon.

pH_{PZC}	C (atom %)	O (atom %)	Q_0 (mg g^{-1})
10.2	94.7	5.3	72.5

selected elemental regions, were recorded at 50 eV pass energy. Because of sample charging, the binding energies were referenced to carbon(1s) at 285 eV (Perry and Grint, 1983). Elemental concentrations were calculated after correction of the peak areas for atomic sensitivity factors (Ward and Wood, 1992).

The concentrations of the primary adsorption sites, Q_0, of the carbon were calculated by using Eq. (7). Those values, together with their surface elemental analysis determined by XPS, are shown in Table 3.

Results and Discussion

The experiment and fitted isotherms of non-dissociating aromatic compounds (Benzene and Toluene) at different pH values are shown in Fig. 3.

The isotherms are plotted using a mass based solid concentration, q_e (in mg of the solute adsorbed per gram of the carbon) versus the liquid concentration, C_e (in ppm) at equilibrium conditions. As shown in this figure the uptake of these solutes is not significantly affected by the solution pH. Since their molecular species are dominant in the entire pH range.

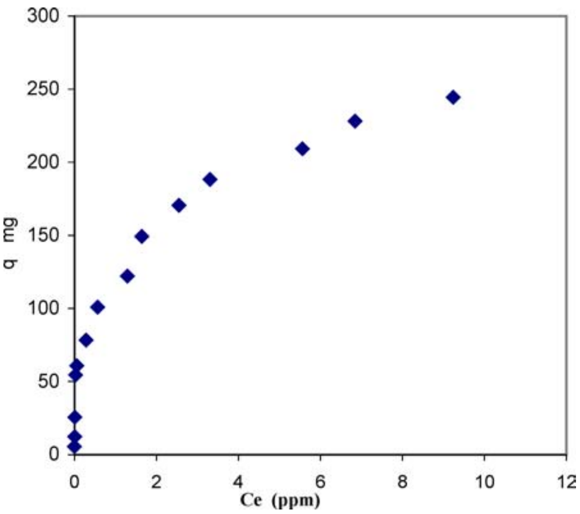


Figure 4. Adsorption isotherm of Benzoic acid at pH = 2.

Figure 4 shows experiment isotherm of Benzoic acid at pH = 2 and Fig. 5 shows the experimental data and fitted isotherms of dissociating aromatic compounds (Benzoic acid and p-Cresol) at different pH values.

When adsorption is carried out at a pH well below the p*K*a of the solutes, the main adsorption forces are the dispersive and dipolar interactions, with the latter being dominant when basic surface oxides are present. Furthermore, the −OH group in p-Cresol is more basic ($pK_a = 10.2$) and the lone pair of electron of the −OH group is more available for hydrogen bonding. In other

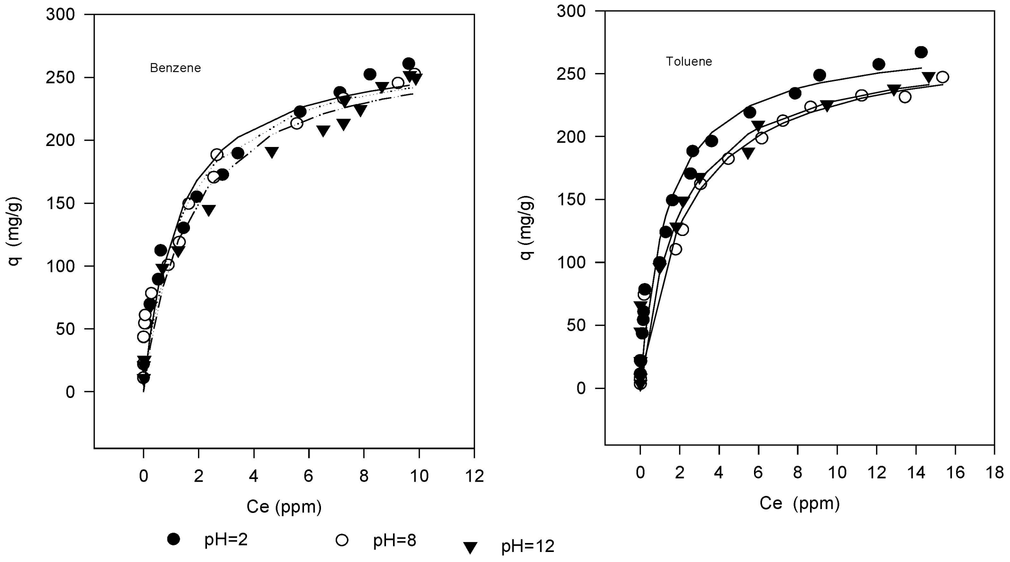


Figure 3. Experimental and fitted isotherms of Benzene and Toluene at different pH.

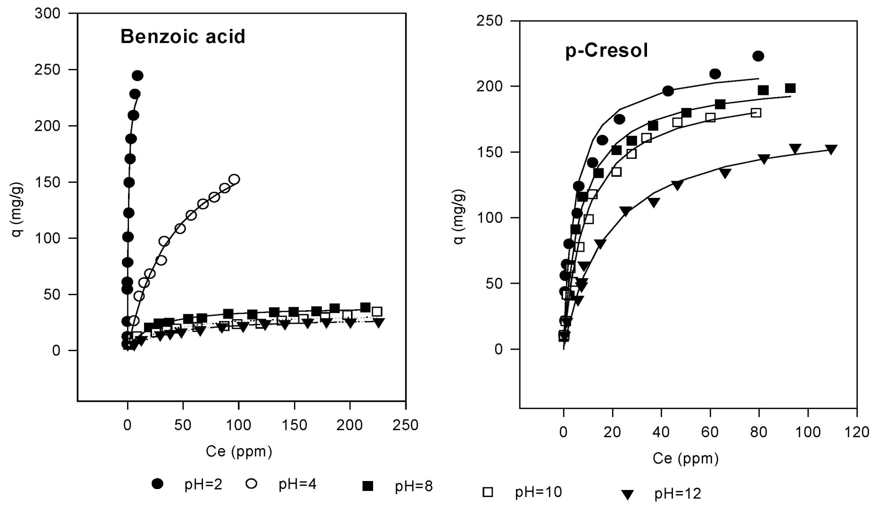
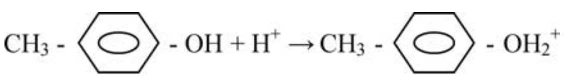


Figure 5. Experimental and fitted isotherms of BA and PC at different pH.

words, since p-Cresol is a stronger base, under acidic conditions (pH = 2) more of p-Cresol molecules would tend to be positively charged. This would lead to a lower uptake of p-Cresol at pH = 2 (Fig. 5).



However, when adsorption experiments are carried out at a high pH, the presence of the ionic species can alter the adsorption mechanism significantly.

It was observed that increasing the solution pH lowered the uptake of the dissociating solutes. This is related to the degree of ionization of the solutes, as shown by the adsorption isotherms of Benzoic acid and p-Cresol. The extent of decrease for dissociating solutes, however, was observed to be dependent on its pK$_a$, as illustrated in Fig. 5. It shows that, the lower the pK$_a$ of a solute, the more drastically its uptake decreased. Table 4 shows the (A$^-$/HA) ratio of p-Cresol and Benzoic acid at each pH.

Table 4. The ratio of (A$^-$ / HA) for p-Cresol and Benzoic acid in different pH.

pH	p-Cresol A$^-$/HA	Benzoic acid A$^-$/HA
2	6.31E-09	0.00631
4		0.631
8	0.0063	6309.57
10	0.631	630957.34
12	63.1	63095734.45

Detailed discussion of these studies can be found in our earlier works (Nouri and Haghseresht, 2002; Haghseresht et al., 2002).

Considering that the pH$_{(pzc)}$ of the carbon is 10.2, when the solution pH = 12, the carbon surface is negatively charged. Therefore, when the extent of dissociation of a solute is greater (lower pK$_a$), the extent of electrostatic repulsive forces is also expected to be greater as well. Consequently, lower adsorption capacities are observed for BA than PC. Figure 6 shows the adsorption isotherms of al solutes in pH = 2 and pH = 12.

The experimental results described here show that the solution pH affects the adsorption process significantly for dissociating compounds. The extent of this influence appears to be influenced by the pK$_a$ of the solute.

Using different models, fitted isotherm parameters were obtained and compared for all solutes. Tables 5 and 6 shows the fitted parameters ($Q_{\max}$, K, K_m and K_i) obtained from Langmuir models for Benzoic acid and p-Cresol in different pHs.

One observation is that for dissociating compounds, values of $Q_{\max}$ obtained from both models are the same, and using binary model in molecular form $K_1 = K_m$ and in ionic form $K_1 = K_i$.

Fitted parameters obtained from Langmuir-Freundlich models for Benzoic acid and p-Cresol in different pHs are shown in Tables 7 and 8.

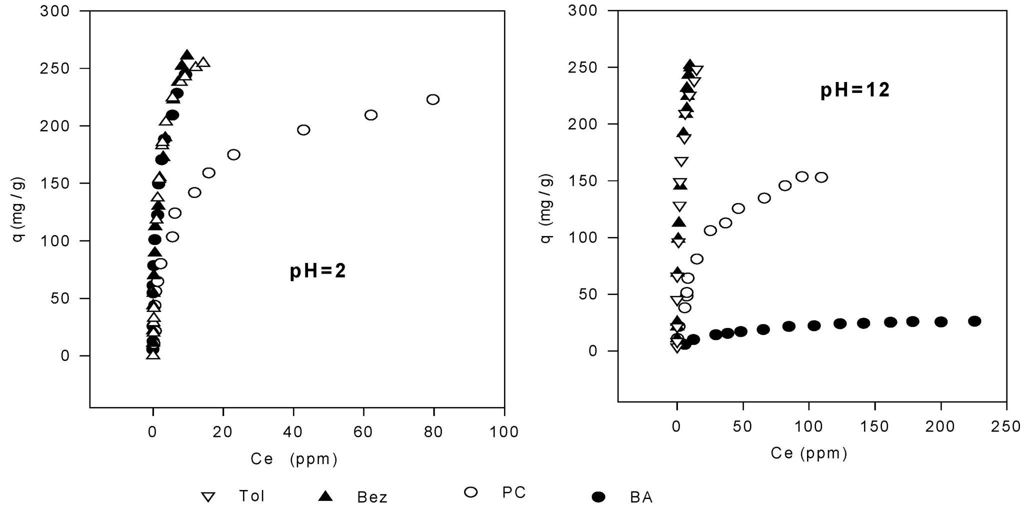


Figure 6. Adsorption of all solutes in pH = 2 and pH = 12.

As shown in these tables, when adsorption is higher at low values of pH (e.g., 2) the value of $Q_{\max}$ obtained from the Langmuir-Freundlich model is not close to the value of this factor obtained via the Langmuir equation alone, and also the values obtained from single and binary model are not the same.

Table 5. Comparison of fitted parameters obtained from the Langmuir models for Benzoic acid.

PH	2	4	8	10	12
Single model					
$Q_{\max}$ (mg/g)	247.6	214.6	39.5	33.5	29.5
K (mg/l)$^{-1}$	1.1	0.023	0.05	0.076	0.03
Binary model					
$Q_{\max}$ (mg/g)	247.9	214.6	39.5	33.5	29.5
Km	1.1	0.023	3.9E-9	7.7E-7	4.7E-6
Ki	2E-9	0.01	0.051	0.076	0.03
a	0.006	0.63	6300	6.3E5	63E6

Table 6. Comparison of fitted parameters obtained from the Langmuir models for p-Cresol.

PH	2	8	10	12
Single model				
$Q_{\max}$ (mg/g)	216.7	206.6	200.5	176.5
K (mg/l)$^{-1}$	0.22	0.145	0.11	0.056
Binary model				
$Q_{\max}$ (mg/g)	217	206.6	200.5	176.5
Km	0.23	0.145	0.13	3E-10
Ki	7.3E-9	1.9E-9	0.09	0.057
a	6.31E-09	0.006	0.63	63

Tables 9 and 10 show the fitted parameters obtained from Langmuir model and Langmuir-Freundlich model for Benzene and Toluene in different pH.

As one can see, values of $Q_{\max}$ obtained from the Langmuir-Freundlich model for both solutes are higher, indicating that the Langmuir-Freundlich model for all compounds used in this work, is not satisfactory.

Consequently we used the Langmuir models to predict the adsorption capacity in other solutions.

Figure 7 shows the variation of $Q_{\max}$ (obtained from single isotherms of each solute) with pH for all solutes. It shows that the maximum uptake of the solutes

Table 7. Comparison of fitted parameters obtained from the Langmuir-Freundlich model for Benzoic acid.

PH	2	4	8	10	12
Single model					
$Q_{\max}$ (mg/g)	1548	242	49.5	46.9	35.8
K (mg/l)$^{-1}$	0.088	0.025	0.10	0.13	0.05
N	0.34	0.91	0.61	0.42	0.74
Binary model					
$Q_{\max}$ (mg/g)	1761	242	49.5	46.9	35.8
Km	0.076	0.036	3.5E-10	1.3E-10	1.8E-8
Ki	1.5E-3	6.5E-3	0.1	0.13	0.053
N	0.35	0.91	0.63	0.41	0.74
a	0.006	0.63	6300	6.3E5	63E6

Table 8. Comparison of fitted parameters obtained from the Langmuir-Freundlich model for p-Cresol.

PH	2	8	10	12
Single model				
$Q_{\max}$ (mg/g)	277.6	216.6	230.9	203
K (mg/l)$^{-1}$	0.23	0.16	0.13	0.07
N	0.64	0.89	0.78	0.81
Binary model				
$Q_{\max}$ (mg/g)	220	206.6	200.5	176.5
Km	0.3	0.15	0.21	3E-10
Ki	9E-7	3E-9	0.01	0.057
N	1	1	1	1
a	6.31E-09	0.006	0.63	63

Table 9. Comparison of fitted parameters obtained from the Langmuir and Langmuir-Freundlich single model for Benzene.

PH	2	8	12
Langmuir model			
$Q_{\max}$ (mg/g)	274.7	274.5	276.1
K (mg/l)$^{-1}$	0.82	0.76	0.61
Langmuir-Freundlich model			
$Q_{\max}$ (mg/g)	1539	2736	2206
Km	0.086	0.048	0.052
n	0.38	0.32	0.39

Table 10. Comparison of fitted parameters obtained from the Langmuir and Langmuir-Freundlich single model for Toluene.

PH	2	8	12
Langmuir model			
$Q_{\max}$ (mg/g)	278	277	274
K (mg/l)$^{-1}$	0.75	0.42	0.52
Langmuir-Freundlich model			
$Q_{\max}$ (mg/g)	429	690	3495
Km	0.40	0.18	0.036
n	0.54	0.43	0.28

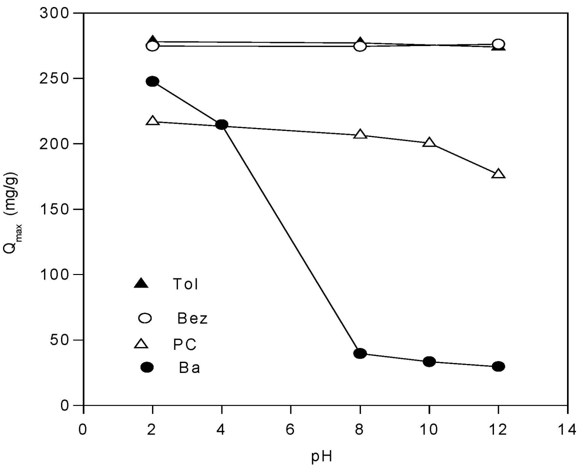


Figure 7. Variation of $Q_{\max}$ with pH for all solutes.

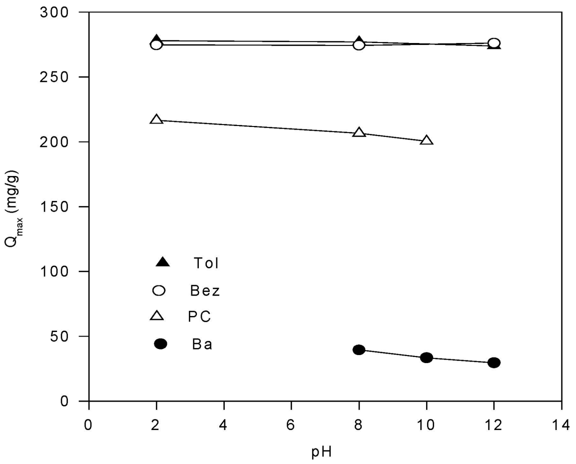


Figure 8. Variation of $Q_{\max}$ with pH before and after pK$_a$.

occurs in low pH (pH = 2), where they mainly exist in molecular form (except for p-Cresol). The maximum adsorption capacities of the activated carbon, $Q_{\max}$, for dissociating solutes are observed to decrease with pH. However, the extent of this decrease is dependent on the pK$_a$ of the solutes. The higher the degree of ionization (lower pK$_a$), the more drastically $Q_{\max}$ is lowered with pH.

To understanding the relationships between $Q_{\max}$ and pH, for molecular (pH $<$ pK$_a$) and ionic (pH $>$ pK$_a$) form of dissociating solutes, Fig. 7 is separated in two parts for dissociating solutes, before pK$_a$ and after pK$_a$, (Fig. 8). We can assume that the values of $Q_{\max}$ at different pH values must be some fraction of the $Q_{\max}$ at pH = 2 (solute with higher pK$_a$) or at pH $>$ pK$_a$ (solute with lower pK$_a$) for dissociating solute (where molecular or ionic form dominate). The following function (Eq. (11)) was then found to be the best line of fit for Figs. 8.

$$Q = A^{*} Q_{\max}/\mathrm{pH} + B \tag{11}$$

Table 11. Comparison of estimated $Q_{\max}$ and Langmuir $Q_{\max}$ for all solutes after Eq. (11).

pH	2	8	10	12	A & B
Benozic acid					
Langmuir $Q_{\max}$(mg/g)	247	39.5	33.5	29.5	A = 8.1 B = 9.5
Estimated $Q_{\max}$(mg/g)	–	39.5	33.5	29.5	
p-Cresol					
Langmuir $Q_{\max}$(mg/g)	217	206.6	200.5	176	A = 0.16 B = 199.5
Estimated $Q_{\max}$ (mg/g)	217	204	206	-	

Table 11 shows the estimated $Q_{\max}$ together with the A and B coefficient obtained from Eq. (11) for dissociating solutes.

The above-mentioned relationship was then used to see if it is possible to predict the effect of pH on the adsorption systems of dissociating aromatic compounds discussed in this work.

It was shown earlier that the value of $Q_{\max}$ decreases more significantly beyond the pK$_a$ for dissociating solutes and it was dependent on degree of ionisation of these solutes (α).

Considering this point we propose the following model (Eq. (12)) for estimating the maximum adsorption capacity of carbon at any pH where the solute is ionized reasonably well.

$$Q_{\max}(I) = Q_{\max}(M)\,[F/\ln(\mathrm{pH}-\mathrm{pK}_a) + G/(\mathrm{pH}-\mathrm{pH}_{\mathrm{PZC}})] \quad (12)$$

Where $Q_{\max}(I)$ and $Q_{\max}(M)$ are maximum adsorption capacity of carbon for adsorbate in ionic and molecular forms. F and G are correction coefficients.

The estimated $Q_{\max}$ values, $Q_{\max}$(Est), using Eq. (12) together with those that were determined from the homogenous Langmuir equation are shown in Table 12.

As it can be seen, the estimated $Q_{\max}$ values are very close to the $Q_{\max}$ values determined from the homogenous Langmuir equation.

Conclusions

In this work, four adsorption models were used for two dissociating (Benzoic acid and p-Cresol) and two non-dissociating (Benzene and Toluene) aromatic compounds in different solution pHs.

Variations of the fitted model parameters with pH were observed; and those obtained for the Langmuir models are very close to the apparent real values.

It was found that when the solution pH > pK$_a$ of the dissociating solutes, an increase in the solution pH will lead to the lowering of the solute uptake. The extent of this decrease is found to depend on the pK$_a$ of the solutes. For solutes having higher pK$_a$ values (basic solutes, for example: p-Cresol) there is lower uptake under acidic conditions because of the positive charge of the solute. For the non-dissociating solutes, the uptake solutes is not significantly affected by the solution pH.

Finally, it was shown that the two significant parameters, i.e., the maximum adsorption capacity ($Q_{\max}$) and affinity coefficient (K_1) of the carbon, are dependent on the value of $\log\alpha$, pH$_{(\mathrm{pzc})}$ and pH of the solution.

Table 12. Comparison of estimated $Q_{\max}$ and Langmuir $Q_{\max}$ for ionic form of dissociating solutes after Eq. (12).

pH	8	10	12	F, G and $Q_{\max}$ (M)
Benzoic acid				
Lang. $Q_{\max}$ (mg/g)	39.5	33.5	29.4	$F = 0.22$ $G = -0.001$ $Q_{\max}$ (M) = 247
Estimated $Q_{\max}$ (mg/g)	41.5	33	27	
p-Cresol				
Lang. $Q_{\max}$ (mg/g)	–	–	176	$F = 0.45$ $G = 0.09$ $Q_{\max}$ (M) = 217
Estimated $Q_{\max}$ (mg/g)	–	–	176	

For dissociating solutes in molecular form $K_1 = K_m$ and in ionic form $K_1 = K_i$.

The suggested relationships were used to predict the $(Q_{\max})$ of the dissociating solutes at other solution conditions where the solute is ionized reasonably well.

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