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Adsorption of *p*-Nitrophenol in Untreated and Treated Activated Carbon

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Abstract. The adsorption of *p*-nitrophenol in one untreated activated carbon (F100) and three treated activated carbons (H_2, H_2SO_4 and Urea treated F100) was carried out at undissociated and dissociated conditions.

To characterize the carbon, N_2 and CO_2 adsorption were used. X-ray Photoelectron Spectroscopy (XPS) was used to analyze the surface of the activated carbon.

The experimental isotherms are fitted via the Langmuir homogenous model and Langmuir binary model. Variation of the model parameters with the solution pH is studied. Both Q_{max} and the adsorption affinity coefficient (K_1) were dependent on the PZC of the carbons and solution pH. The Effect of pH must be considered due to its combined effects on the carbon surface and on the solute molecules. Adsorption of *p*-nitrophenol at higher pH was found to be dependent on the concentration of the anionic form of the solute.

Keywords: adsorption, *p*-nitrophenol, treated activated carbon, langmuir equation, characterization of activated carbon

Introduction

As a result of the extensive use of organic compounds in various industries, the level of organic pollutants in water systems has been increasing. With increasing concern for public health and environmental quality, more stringent regulations have come into effect regarding the acceptable levels of these compounds. This has led to an upsurge of interest in developing and implementing methods for removing them.

Due to their widespread use as ingredients and solvents in various manufacturing industries, aromatic compounds are common water contaminants. Increasing environmental awareness in the recent times has lead to more stringent limits on the quality of water and wastewater. Examination of the literature shows an abundance of experimental adsorption studies for aqueous organic solute systems involving activated carbon. In liquid-phase adsorption, it has been established that the adsorption capacity of an activated carbon depends on a number of factors: first, the physical nature of the adsorbent-pore structure, ash content, and functional groups (Hsieh and Teng, 2000; Leng and Pinto, 1997; Moreno-Castilla et al., 1995) second, the nature of the adsorbate, its pK$_a$, functional groups present, finally, the solution conditions such as pH, ionic strength, and the adsorbate concentration (Radovic et al., 1996, 1997). Activated carbons are carbonaceous materials of highly developed porous structure and high specific surface area. Properties of activated carbon such as their surface area, microporous structure and surface chemistry can be tailored, making them versatile materials for a range of separation applications (Banasal et al., 1988; Jankowska et al., 1991). These applications include the removal of contaminants from water and gas streams, and as catalyst supports (Banasal et al., 1988).

Activated carbon is prepared in two steps: carbonisation and activation. Carbonisition is a thermal decomposition process of the starting material in an inert atmosphere, where the non-carbon species are eliminated and a fixed carbon mass with a rudimentary pore structure is produced (Banasal et al., 1988). The objective of activation, on the other hand, is to enhance the surface area, to enlarge the diameters of the micropores formed during carbonisation and to create new pores accessible to the adsorbate molecules.

Since the 1960s 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; Tamon and Okazaki, 1996; Ward and Getzen, 1970; Getzen and Ward, 1969; Muller et al., 1980, 1985). However, theoretical approaches that could explain the effects of the solution pH and the carbon surface chemistry on the adsorption process quantitatively have been developed only to a small degree.

In most applications of activated carbons in water treatment, both the molecular and the ionic species of aromatic compounds are present. As the adsorption behavior is affected by both the surface properties of the activated carbon and the solution conditions, theoretical descriptions of such systems are more complicated than the adsorption of the molecular species.

The process of adsorption of dissociating aromatic compounds onto the surface of carbonaceous materials is affected by the properties of adsorbate and the adsorbent. The adsorbate chemical nature, its solubility, molecular size and shape and the type of functional groups affect the adsorbate behaviour significantly (Halhouli et al., 1995; Nouri et al., 2001, 2002a, 2002b). The chemical heterogeneity of the carbon surface together with its porous structure characterizes the adsorption properties of the carbon surface. Other factors such as the effects of the solution conditions, i.e. its pH and ionic strength and the presence of competing solutes can alter the adsorption properties of a given carbon-solute system drastically (Derylo-Marczewska and Jaroniec, 1987; Radovic, 1999; Nouri, 2002). It can therefore be seen that developing appropriate theoretical descriptions has been very challenging (Derylo-Marczewska, 1993). The early attempts to quantitatively explain the effects of pH can be dated as far back as the 1960s. Getzen and Ward (1969), used the binary Langmuir isotherm to explain the effect of pH on the adsorption of electrolytes. At the same time, others such as Rosene and Manes applied the Polanyi potential to explain the same phenomenon (Rosene and Manes, 1977).

In this work, adsorption of p-Nitrophenol on a commercially available activated carbon (F100) in untreated and treated form, are investigated systematically.

Isotherms of this compound at pH = 2 and pH = 12 were obtained and the results are discussed in terms of the two major forces that are involved in the adsorption process.

The experimental isotherms are fitted into Langmuir model (homogenous model & binary Langmuir model). Variation of the model parameters with the solution pH and PZC are studied and used to gain further insight into the adsorption process.

Theoretical Section

In our previous work (Nouri et al., 2002a), all adsorption experiments were carried out in a solution condition, where the molecular species of the solutes were dominant (pH = 2). Therefore in our analysis single solute Langmuir Equation was selected as the local isotherm equation (Eq. (1)). The linear form of the (Eq. (2)) was then used to obtain the parameters of the homogenous model.

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

where

$$\begin{aligned} \theta &= \frac{q}{Q_{\max}} \\ \frac{C_{\mathrm{eq}}}{q} &= \frac{1}{K_1 Q_{\max}} + \frac{1}{Q_{\max}} C_{\mathrm{eq}} \end{aligned} \tag{2}$$

However, for dissociating compound, when 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 work (Nouri, 2003; Nouri and Haghseresht, 2002; Haghseresht et al., 2002), the binary Langmuir model (Eq. (3)) can then represent the isotherm Equation.

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

where

$$\begin{aligned} K_m &= K_{0m} \exp(-E_m) \\ K_i &= K_{0i} \exp(-E_i) \end{aligned}$$

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 as shown in Eq. (4), where HA refers to the neutral species and the A^- refers to the ionized species and their equilibrium constant, K_a, is given in Eq. (5).

$$HA \leftrightarrow H^+ + A^- \tag{4}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{5}$$

We can then use the relationship shown in Eq. (5) to express the solution concentration of the individual species in terms of the total measured equilibrium concentration (Eqs. (6) and (7)).

$$C_m = \left(\frac{C_{eq}}{1+\alpha}\right) \tag{6}$$

$$C_i = \left(\frac{C_{eq}\alpha}{1+\alpha}\right) \tag{7}$$

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

Using the relationships shown in Eqs. (6) and (7), Eq. (3) can then be rearranged into its linear form as shown in Eq. (8).

$$\frac{C_{eq}}{q} = \frac{(1+\alpha)}{(K_m + K_i\alpha)Q_{\max}} + \frac{1}{Q_{\max}}C_{eq} \tag{8}$$

Comparison of Eqs. (2) and (8) shows that the plot of C_{eq}/q versus C_{eq} for an adsorption system, where the molecular species are dominant would lead to the determination of $Q_{\max}$ from the slope and K_l which is the equilibrium constant for the molecular species. However, when adsorption is carried out in solution pH where both the molecular an ionic species are present, the fitted equilibrium constant K_l would be a lumped parameter containing K_m, K_i and α. Their relationship can be extracted from Eqs. (8) and (9). Furthermore, Eq. (9) can be rewritten in its linear form (Eq. (10)), which can be used to investigate the relationship between the lumped affinity coefficient and those of the molecular and ionic species.

$$K_l = \frac{K_m + K_i\alpha}{1+\alpha} \tag{9}$$

$$(K_l + K_l\alpha) = K_m + K_i\alpha \tag{10}$$

Equation (10) allows determination of K_l in the following situations:

1. In low pH, where the molecular species are dominant, $\alpha \approx 0$. Therefore $K_l \approx K_m$.
2. When pH = pK$_a$ of the solute $\alpha = 1$. The value of K_l then becomes the average of the K_m and K_i.
3. In highly alkaline solution Eq. (9) can be rewritten as follows:

$$K_l = \frac{\frac{K_m}{\alpha} + K_i}{\frac{1}{\alpha} + 1} \tag{11}$$

Equation (11) indicated that in alkaline conditions, when the solute is highly ionized $K_l \approx K_i$.

Characterization of the Activated Carbon

For characterization of the carbon, as decribed in our previous works (Nouri, 2003; Haghseresht et al., 2002) the 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 0.01–0.1, 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, 1983). The ultramicropore volumes (V_{ulimc}) of the carbon was obtained by applying the Dubinin-Radushkevich equation (DR) to CO_2 adsorption isotherms obtained at 273 K (Marsh, 1987).

The water adsorption data were analyzed by fitting the water adsorption isotherms to Eq. (10), the DS-2 equation (Barton et al., 1991).

$$c(Q_0 - q)(1 - kq))q/(P/P_0) \tag{12}$$

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.

Methods and Materials

The granular activated carbon (GAC) used in this work was F100 from Calgon. Prior to the experiments, a sample was ground and sieved. The fraction between 400–800 μm, was used in this work. Chemicals used were as follows: p-Nitrophenol (PNP) (99.9% purity, pK$_a$ = 7.2)—Merck Chemicals, HCl and NaOH (A. R. Grade)– Ajax Chemicals.

The adsorption experiments were carried out by placing 45 mg of the activated carbon with 50 ml of the solution containing different concentrations of the adsorbates. Solution pH was adjusted by using dilute solution of NaOH or HCl. All solutions were then left in a temperature controlled shaking bath for 4 days at 301 K to reach equilibrium. After reaching equilibrium conditions, the residue concentrations of the solutes were then measured spectrophotometrically, (for PNP between 260 & 275 nm) using Jasco-V550 spectrophotometer.

The $pH_{(PZC)}$ of the carbons was determined as described in our previous works (Nouri and Haghseresht, 2002; Haghseresht et al., 2002; Nouri et al., 2002a). This was done by placing various amounts of the carbon in 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 $pH_{(PZC)}$. Noh and Schwarz (Noh and Schwarz, 1989) suggest that at pH = $pH_{(PZC)}$ the surface of carbon is neutral. At pH higher than $pH_{(PZC)}$ its surface is negatively charged and at pH lower than $pH_{(PZC)}$, carbon surface is positive. So in this case carbon has a high affinity for anions.

Figure 1 shows the variation of pH by the amount of activated carbon used to find the PZC of each carbon (untreated F100 = 7.8, H2 treated F100 = 11, urea treated = 9.9 and acid treated = 3.3).

Vapor Adsorption. 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 ad-

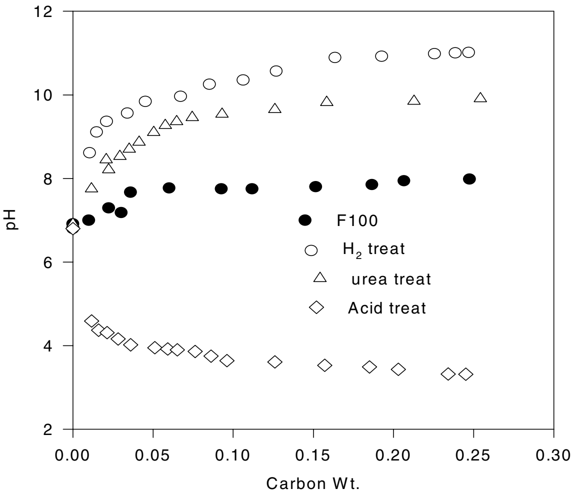
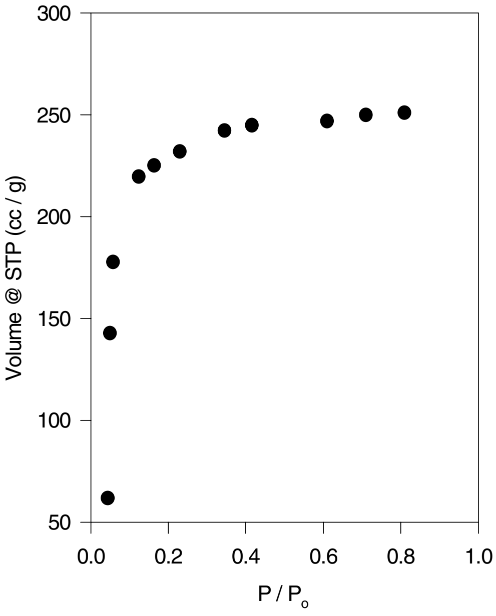
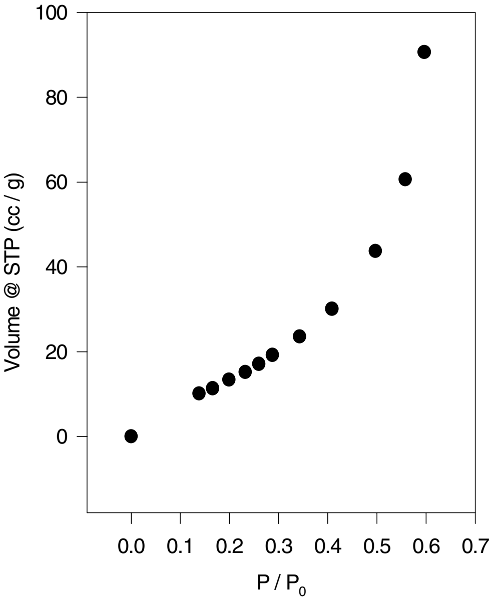


Figure 1. P.Z.C. of the carbons.



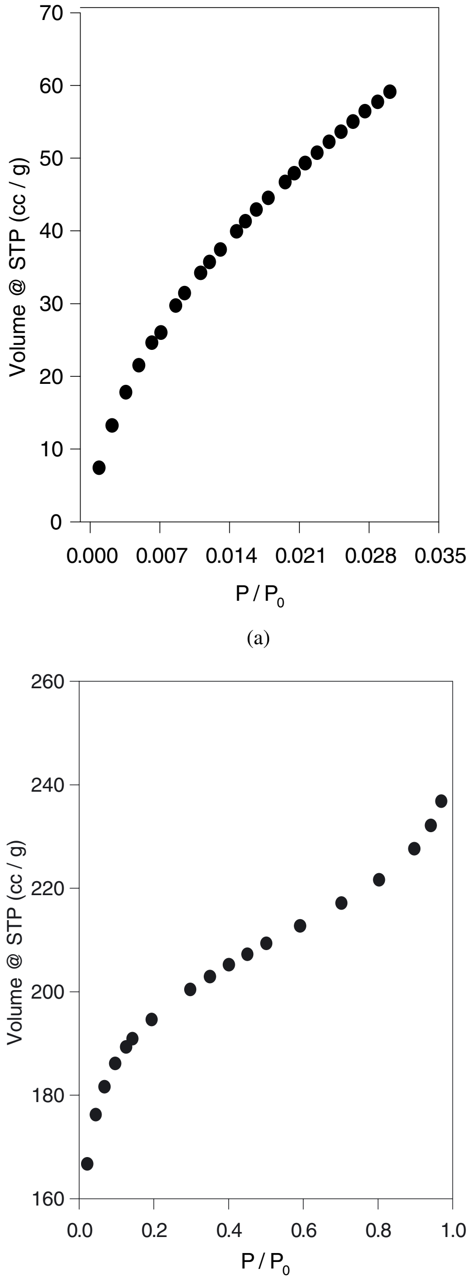
(a)



(b)

Figure 2. (a) Toluene adsorption isotherm. (b) Water adsorption isotherm.

sorption behavior significantly. In these experiments, the samples were subjected to a step change in the sorbate pressure from the initial zero to its saturation pressure, Fig. 2 shows the toluene and water adsorption isotherms of untreated activated carbon.



(a)

(b)

Figure 3. (a) CO_2 adsorption isotherm. (b) N_2 adsorption isotherm.

Gas Adsorption Experiments. Nitrogen adsorption/desorption experiments were carried out volumetrically at 77 K using an Autosorb (Quantachrome Corp.). 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. The N_2 and CO_2 adsorption isotherms for untreated F100 are shown in Fig. 3.

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 400 W.

Survey (wide) scans were recorded with pass energy of 100 eV and multiplex (narrow) scans, over selected elemental regions, 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).

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 1).

Table 1 shows that Toluene pore volumes (V_{Tol}) value is significantly smaller than V_{tot} value. This is because the N_2 molecule is much smaller than toluene and can penetrate micropores inaccessible to the toluene molecules.

The concentrations of the primary adsorption sites, Q_0, of the carbon calculated by using Eq. (10), together with their surface elemental analysis determined by XPS, are shown in Table 2.

Table 1. Pore structure characteristics of the F100 activated carbon.

S_{BET} (m^2g^{-1})	V_{tot} (cm^3g^{-1})	V_{mic} (cm^3g^{-1})	V_{ulmic} (cm^3g^{-1})	V_{ulmic}/V_{tot}	V_{Tol} (cm^3g^{-1})
957	0.5260	0.3811	0.207	0.393	0.21

Table 2. Surface chemical characteristics of the activated carbons used.

pH_{PZC}	C (atom %)	O (atom %)	Si (atom %)	S^{-2} (atom %)	Q_0 ($mg\ g^{-1}$)
7.8	94.3	4.9	0.57	0.20	23.8

Results and Discussion

By treating with urea, nitrogen atoms enter in the aromatic rings and increase the electron density on the carbon surface. H_2 treatment reduces carboxylic and hydroxide groups and effect on the electron density by increasing it. By dehydration and oxidation with H_2SO_4, carbonyl and carboxyl groups increase on the surface of the carbon so there is a decrease on electron density.

The experiment and fitted isotherms are shown in Figs. 4 and 5 respectively at $pH = 2$ and $pH = 12$. As expected, in comparison with untreated F100, the adsorption of H_2 treated carbon increases and for acid treated carbon, it decreases. There is less effect for urea treated carbon.

The isotherms are plotted using a mass based solid concentration, q_e (in mmol of the solute adsorbed per gram of the carbon) versus the liquid concentration, C_e (in mmol/l) at equilibrium conditions. Considering the pK_a of the *p*-Nitrophenol ($pK_a = 7.2$), the adsorption capacity of the carbons for the solute in molecular form was dependent on the electron density of the solute and carbon surface. This is because the dispersive interaction between the aromatic ring of the solute and those of the carbon surface are the main forces involved in the adsorption process. However, when the solute is ionized, a different situation arises, and as the solutions pH is increased, the concentration of the anionic form of P.N.P. is increased, it would mean a greater degree of electrostatic repulsive forces, the adsorption capacity of the carbons are expected to be lower.

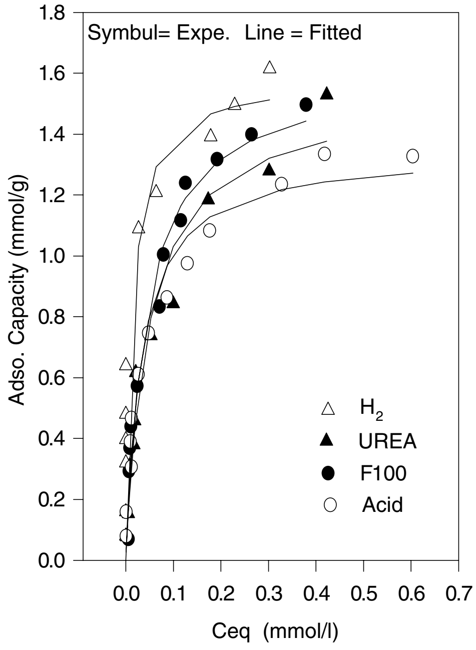


Figure 4. Adsorption isotherm of PNP ($pH = 2$).

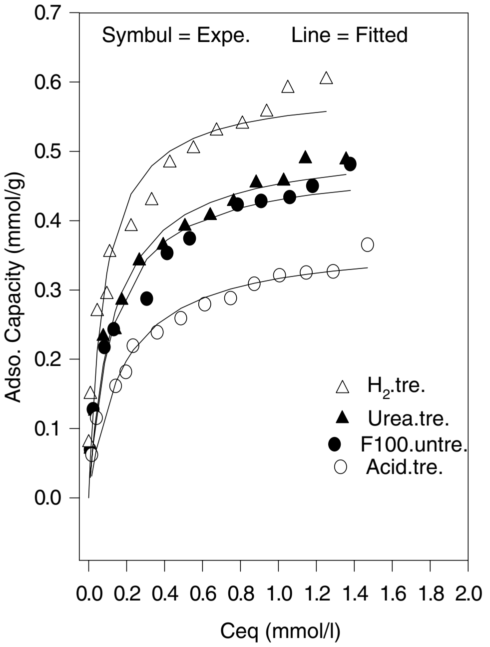


Figure 5. Adsorption isotherm of PNP ($pH = 12$).

The Effect of pH must be considered from its combined effects on the carbon surface and on the solute molecules. In pH higher than $pH_{(pzc)}$ of the carbons, carbon surface is negatively charged.

The data fit better in low concentration and high pH. As shown in Figs. 4 and 5, the adsorption capacity of the carbons for PNP are as follows: H_2 treated > urea treated ≥ untreated >acid treated.

The fitted parameters obtained from homogenous model, Eq. (2), are shown in Tables 3 and 4 at $pH = 2$ and $pH = 12$ respectively.

Adsorption of the PNP in higher pH was found to be dependent on the concentration of anionic form of

Table 3. Fitted parameters from Eq. (2) (Langmuir homogenous model) at $pH = 2$.

Carbon	Untreated F100	H_2 treated F100	Urea treated F100	Acid treated F100
Q_{max} (mmol/g)	1.6	1.62	1.54	1.34
K_1 (mmol/l)	22	69	21	29

Table 4. Fitted parameters from Eq. (2) (Langmuir homogenous model) at pH = 12.

Carbon	Untreated F100	H_2 treated F100	Urea treated F100	Acid treated F100
$Q_{\max}$ (mmol/g)	0.48	0.59	0.51	0.37
K_1 (mmol/l)	8.1	12.7	8	5.7

Table 5. Fitted parameters from Eq. (8) (Langmuir binary model) at pH = 12.

Carbon	Untreated F100	H_2 treated F100	Urea treated F100	Acid treated F100
$Q_{\max}$	0.48	0.59	0.51	0.37
K_m (mmol/l)	2500	7e-4	3.9e-6	6e-6
K_i (mol/l)	8	11.4	8	5.74

the solute. A lower uptake level was observed for electrolyte. This is because when the anion concentration is higher the electrostatic repulsive forces between the solute molecules and between the solute and carbon surface would be higher. The fitted parameters obtained from Eq. (2) show that $Q_{\max}$ and adsorption affinity of carbon (K_1) decrease more significantly with pH. Figure 6 shows the variation of $Q_{\max}$ with PZC at pH 2 & 12.

The relationship shown in Eq. (9) indicates that if the binary Langmuir isotherm (Eq. (8)) is applied, the molecular and the ionic equilibrium constants, K_m and K_i can not be optimized simultaneously. Furthermore, for K_m to be constant for a given system, Eq. (10), must hold true for a set of isotherms that were obtain in different solution conditions. Analysis of our results showed that the plot ($K_l + K_l\alpha$) versus α did not hold for any of the experimental data. If we consider that charge is smeared on the carbon surface as suggested by previous authors (Muller et al., 1985), then the composition of the types of sites on the carbon surface would be very different depending on the solution pH. Table 5 shows the fitted parameters from binary (Eq. (8)) for PNP. It shows that $Q_{\max}$ values are very close to the $Q_{\max}$ obtained from Eq. (2).

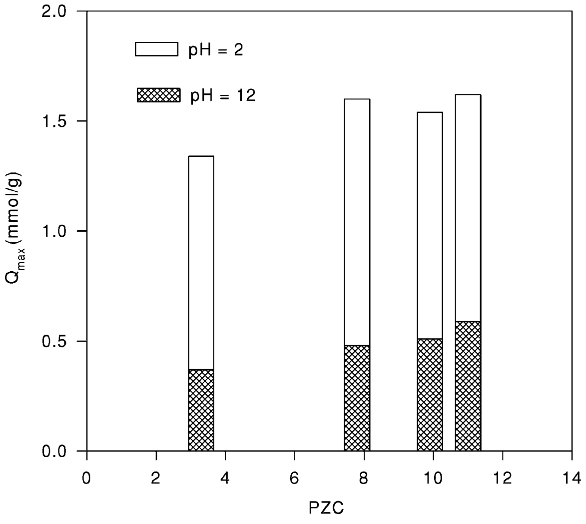


Figure 6. Variation of $Q_{\max}$ with PZC.

In low pH, where the molecular species are dominant, ($\alpha \approx 0$) $K_l \approx K_m$.

In highly alkaline solution, when the solute is highly ionized $K_l \approx K_i$.

Conclusion

The adsorption capacity of a commercially available activated carbon in untreated and treated form for an aromatic compound, in different solution pH conditions, was investigated. The different pore volumes were determined by using the N_2 and CO_2 adsorption and X-ray Photoelectron Spectroscopy (XPS) measurement was used to surface elemental analysis of activated carbon. It was found that the uptake of the molecular forms of the aromatic solute was dependent on the PZC of the carbons. Adsorption of the solutes in higher pH values was found to be dependent on the concentration of anionic form of the solute. This is because when the anion concentration is higher the electrostatic repulsive forces between the solute molecules and between the solute and carbon surface would be higher.

The fitted parameters obtained from Langmuir Equation (homogenous model & binary Langmuir model) show that $Q_{\max}$ and adsorption affinity of carbon (K_1) depends to the electron density of the solute and carbon. Different treatment changes the adsorption capacity of the carbon.

In low pH, where the molecular species are dominant, $K_l \approx K_m$ and when the solute is highly ionized $K_l \approx K_i$.

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