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Comparison of Adsorption Capacity of p-Cresol & p-Nitrophenol by Activated Carbon in Single and Double Solute

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Abstract. Adsorption of p-Cresol and p-Nitrophenol by untreated activated carbon in single and multisolute solutions was carried out at 301 K and at controlled pH conditions. In acidic conditions, well below the pK_a of both solutes, it was observed that the adsorbate solubility and the electron density of aromatic rings influenced the extent of adsorption by affecting the extent of London dispersion forces. The fitted parameters obtained from single-solute Langmuir equation show that Q_{max} and the adsorption affinity of carbon for the compound with low pK_a decrease more significantly. In higher solution pH conditions, on the other hand, it was found that electrostatic forces played a significant role on the extent of adsorption. The presence of another compound decreases Q_{max} and the adsorption affinity of carbon for the principal compound. The effect of pH, on the carbon surface and on the solute molecules, must be considered. Adsorption of the solute at higher pH values was found to be dependent on the concentration of anionic form of the solute. The isotherm data were fitted to the Langmuir isotherm equation for both single and double solute solutions.

Keywords: effects of pH, point of zero charge (PZC), adsorption capacity, activated carbon, Langmuir, spectrophotometer

1. Introduction

Organic compounds constitute a very large group of pollutants. Many of them are recognized carcinogens and are known to be toxic to the environment. Among the available methods for removing these pollutants, adsorption is still one of the most preferred methods, especially for effluents with moderate to low pollutant concentrations (Juang et al., 1996). The use of activated carbon in municipal and industrial wastewater has been known for generations. With ever-increasing concern for public health and environmental quality, however, there is now a much greater demand for the production of more efficient carbon adsorbents. Increasing environmental awareness in the recent times has lead to more stringent limits on the quality of water and wastewater.

Carbon adsorbents are very versatile due to their high surface area, well-developed pore structure, and surface properties. In spite of their huge application in water and wastewater treatment for the removal of organic pollutants, however, the mechanism of the adsorption process is yet not fully understood and much confusion exists in the literature regarding these mechanisms (Arafat et al., 1999).

Activated carbons are known to have a heterogeneous physical and chemical structure. The former arises from the existence of micro-, meso-, and macropores of different sizes (Derylo-Marczewska and Marczewska, 1999). The latter arises from the variety of functional groups (mainly in the form of carbon-oxygen) that exist on the surface. The variety of the

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oxides produced during the manufacture of activated carbons is a result of oxygen present in precursors of activated carbons (Rodriguez-Reinoso et al., 1997). Research on the surface chemistry of activated carbons can be found as far back as the 1950s and 1960s (Boehm, 1966). A thorough discussion of this subject can be found in more recent reviews (Leon y Leon and Radovic, 1994).

The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler (1951). A decade later, other authors (Coughlin and Ezra, 1968; Ward and Getzen, 1970) shed significant light into the effects of surface carbon-oxygen groups and the sorbate-sorbent π-π interactions on the adsorption mechanism of organic compounds. Since then, theoretical and experimental approaches have come a long way, as demonstrated by various reviews in the last twenty years (Derylo-Marczewska and Jaroniec, 1987; Radovic, 1999). However, it appears that there is no general consensus on the significance of this issue in the literature, as demonstrated by the recently published work of Hsieh and Teng (2000). In their work, Hsieh and Teng attribute the differences in the phenol adsorption capacities of a number of carbons with different degrees of burn-off to the differences in the physical properties of the activated carbons, ignoring any differences in their chemical properties.

In liquid-phase adsorption, it is established that the adsorption capacity of an activated carbon depends on the following factors: Firstly, the nature of the adsorbent such as its pore structure, ash content, and functional groups; Secondly, the nature of the adsorbate (e.g. its pK_a, functionality, polarity, molecular weight, and size; and Finally, the solution conditions, referring to its pH, ionic strength, and the adsorbate concentration (Radovic et al., 1997). It is well understood that cost-effective removal of organic pollutants cannot be achieved by relying on the physical properties of activated carbons alone (Radovic, 1999; Cookson, 1978).

Most organic pollutants are weak electrolytes, for which the adsorption equilibria depend on the solution pH. The main challenge for researchers has been taking to account the effects of the carbon surface chemistry, as well as the solution pH, simultaneously. In other words, it is important to discern the relative importance of the effects of electrostatic and dispersion forces in a given sorbate-sorbent system (Radovic et al., 1997). Even though there has been extensive experimental studies in this area, the contribution of theoretical studies has been limited. This situation is due to the great variety of adsorption systems. The wide variety of behaviours exhibited by liquid-solid adsorption systems has led to recognition of eighteen types of isotherms, versus six for gas-solid isotherms (Jaroniec and Madey, 1988).

In the last few decades a number of authors have investigated the effects of pH on the adsorption of aromatic compounds. In the 1960s and 70s, Ward and Getzen (1970) and Getzen and Ward (1969) used the binary Langmuir isotherm to explain the effect of pH on the adsorption of electrolytes. Whereas others such as Rosene and Manes applied the Polyani potential to explain the same phenomenon (Rosene and Manes, 1977). Derylo-Marczewska and Jaroniec (1987) report a detailed analysis of the various theoretical approaches applied to adsorption of organic solutes onto activated carbon. Muller et al. in a series of papers (Muller et al., 1980, 1985a, 1985b) give the most advanced contribution that takes into account both the effects of pH and carbon surface chemistry. Based on the Langmuirian approach, the authors take into account the effects of adsorbent surface charge as determined by pH and ionic strength. They also take into account solid heterogeneity by assuming a truncated Gaussian adsorption energy distribution. Even though they had excellent fit of their model into the corresponding experimental data, in their second paper of the series (Muller et al., 1985a), they were unable to use the fitted parameters of their model to explain any aspects of the adsorption mechanism. They stated that "similar values for s, U_0 and K_0" (referring to the heterogeneity of the system, adsorption potential and equilibrium constant, respectively) "suggest that carbonisation, activation and acidisation have proceeded so far that the surface structures relevant for adsorption equilibrium have become similar."

Derylo-Marczewska and Marczewski (1999) also examined the adsorption behaviour of model aromatic compounds using a Langmuirian approach. They assumed a Gaussian adsorption energy distribution and determined relevant parameters by fitting. Even though, their model fitted the experimental data well, the parameters could not shed new light on the adsorption process.

In this work the adsorption behaviour on activated carbon of p-Nitrophenol, with constant concentration of p-Cresol and in their molecular and ionic form, was investigated. All experimental data were then fitted to the single and double solute Langmuir isotherm equation to obtain the corresponding parameters.

2. Theoretical Section

In aqueous solutions, the pH determines the concentrations of the neutral and ionic species based on the following equilibrium:

$$HA \leftrightarrow H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]} \tag{1}$$

where HA refers to the neutral species and the A^- refers to the ionized species. Taking the negative log of the equilibrium would yield the pK_a of the solute and hence calculating the other species would become a matter of simple mathematical manipulation.

Using the single-solute Langmuir equation (Eq. (2)), we assume that both the ionic and the neutral species compete for the same site. However, only one solute molecule can be adsorbed per site.

$$\theta = \frac{K_1 C_{eq}}{1 + K_1 C_{eq}} \tag{2}$$

In Eq. (2), θ is the fractional coverage, which is determined from the equilibrium solid concentrations (q_{eq}) and Q_{max}, the amount of solute adsorbed per gram of carbon, corresponding to complete coverage (Eq. (3)) and C_{eq} is the equilibrium solution concentration. The equilibrium constant is related to the adsorption energy as expressed in Eq. (4).

$$\theta = \frac{q_{eq}}{Q_{max}} \tag{3}$$

$$K_1 = K_{10} \exp(-E) \tag{4}$$

where K_{10} is the pre-exponential factor and $E = \varepsilon/RT$ is the reduced adsorption energy.

The Langmuir isotherm equation (Eq. (6)) for a two-solute system ("1" and "2") are:

$$q_1 = k_1 Q_{m1} C_{e1}/(1 + k_1 C_{e1} + k_2 C_{e2}) \tag{6}$$

3. Methods and Materials

3.1. Materials

The granular activated carbon (GAC) used in this work is F100 from Calgon. Prior to the experiments, a sample was ground and sieved. The fraction between 400–800 μm, of each carbon was used in this work. Chemicals used were as follows: p-Cresol (PC) and p-Nitrophenol (PNP) from Merck Chemicals HCl and NaOH (A. R. Grade)—Ajax Chemicals.

3.2. Equilibrium Studies

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 stock solutions of NaOH or HCl. The solutions were not buffered. 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 (the concentration of both molecular and ionic form), after filtration, were then measured spectrophotometrically, using Jasco-V550 spectrophotometer. For single solutes we used one wavelength according to pH (for PNP between 249 and 255 nm, for PC between 285 and 310 nm). For double solutes there was not a separation step prior to detection, but we used two different wavelengths that in one of them there is adsorption only for one adsorbate and in other wavelength, the adsorption acquire for both adsorbates. For example in pH 2; 371 nm that there is adsorption only for PNP and 269 nm that there is adsorption for both PNP and PC, or in pH 12; 460 nm (for PNP) and 296 nm (for both PNP and PC). The first wavelength gives the adsorption of PNP and the second gives the sum adsorption of PNP & PC (both adsorbates). After a few mathematical manipulations, the amount of solute adsorbed per gram of carbon for each adsorbate is obtained.

3.3. Determination of PZC (Point of Zero Charge)

The $pH_{(PZC)}$ of the carbon was determined as suggested by Noh and Schwarz (1989). 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. 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

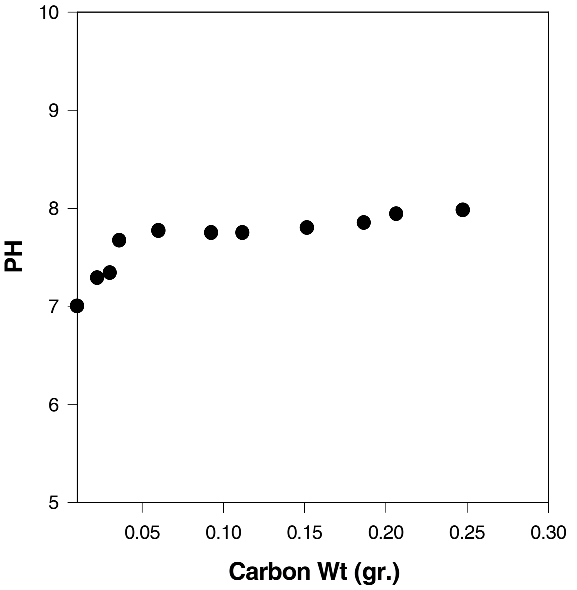

Figure 1. P.Z.C. of the carbon (F100).

pH lower than $pH_{(PZC)}$, the 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.

4. Results and Discussion

4.1. Difference Between the Aromatic Compounds in Single-Solute

The isotherms for both solutes at pH 2 and pH 8 are shown in Fig. 2. 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/liter) at equilibrium conditions. Considering the pK_a values of the electrolytes, at pH 2 both solutes are in their molecular form. Furthermore, the —OH group in PC is more basic ($pK_a = 10.2$) and the lone pair of electrons of the —OH group is more available for hydrogen bonding. In other words, since PC is a stronger base, in acidic conditions, more PC molecules would tend to be positively charged. This would lead to a lower uptake of PC. As shown in Fig. 2, the adsorption capacity of the carbon for the sorbates in pH 2 is as follows: PNP > PC.

The effect of pH on the carbon surface and on the solute molecules must be considered. The effects of the pH on the carbon surface are well documented in various reviews, such as the recently published one by Radovic (1999).

Figure 3 shows the adsorption isotherms of both solutes at pH 10 and pH 12. The adsorption data for

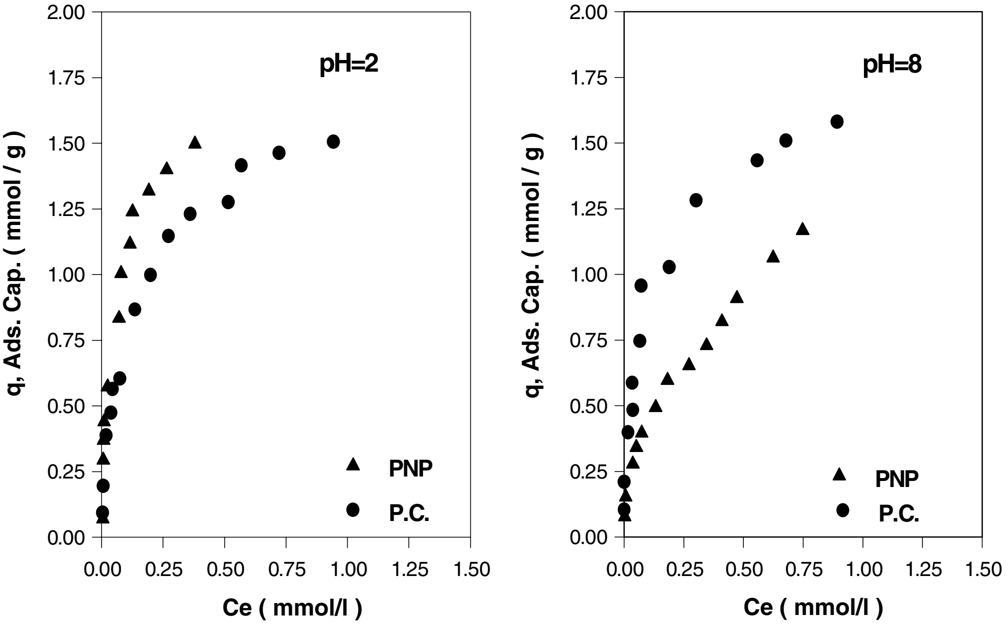

Figure 2. PC & PNP isotherms different pH (single solute).

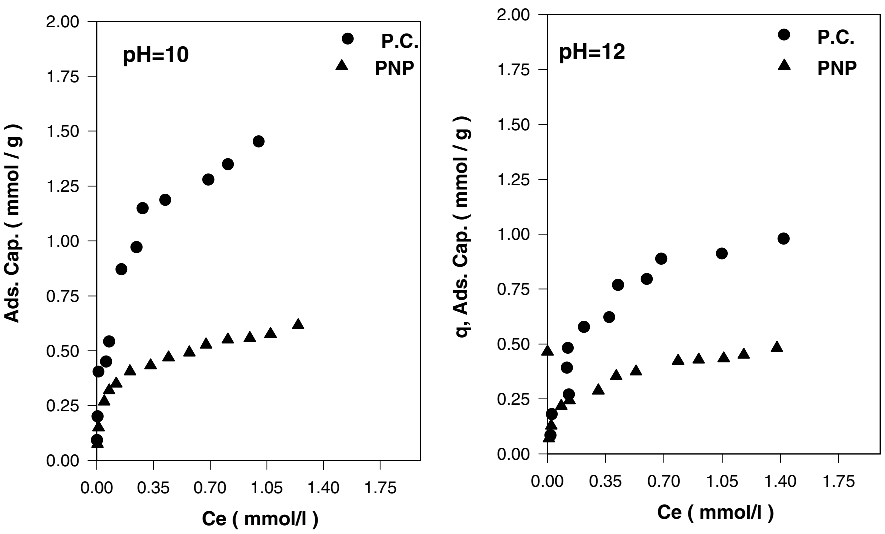

Figure 3. PC & PNP isotherms in single solute.

pH higher than 2, show that the adsorption capacity of the adsorbates is as follows: PC > PNP. Comparing the functional groups of the solutes can reveal insight into the observed adsorption pattern. Methyl and the hydroxyl are both electron-donating groups, whereas the —NO_2 group is an electron withdrawing group. This indicates that the electron densities of the aromatic ring of the solutes is as follows: PC > PNP, which is the same as the observed adsorption pattern. In other words, when the electron density of the aromatic ring of a solute is higher, its affinity for the carbon surface is also higher. Furuya et al. (1997) also found that increase in the electron density of the adsorbate led to an increase in its uptake by activated carbon.

In the previous section, it was observed that the order in the adsorption capacity of the carbon for the solutes in their molecular form was dependent on the electron density of the solutes. This is because the dispersive interactions between the aromatic rings of the solutes and those of the carbon surface are the main forces involved in the adsorption process. However, when the solutes are ionized, a different situation arises, as discussed below.

At high pH, e.g., 12, the carbon surface is negatively charged, since the solution pH is much higher than the $pH_{(pzc)}$ of the carbon ($pH_{(pzc)}$ of $F100 = 7.8$). This pH is also well above the pK_a of the solutes (Table 1), which means that all solutes are mainly in their ionic form. This means that at pH 12 there is much less molecular form of PC and PNP. In other words, due to the high electrostatic repulsive forces of the adsorbent-adsorbate and adsorbate-adsorbate, the adsorption capacities of both solutes are lower than when the solutes are in their molecular forms.

Adsorption experiments were also carried out in solutions with different initial pH values (pH_{ini}). Table 2 shows the initial and equilibrium pH values (pH_{eq}). It shows that the initial and equilibrium pH values for both solutes in two extremes of the pH range did not change significantly. However, the solution pH

Table 1. Properties of the solutes.

Solute	Molecular weight	pK_a	Solubility (g/l)
P-Cresol	108.14	10.2	18
P-Nitrophenol	139.11	7.2	16

Table 2. Equilibrium pH of the adsorption experiments.

	Equilibrium pH	
Initial pH	p-Cresol	p-Nitrophenol
2	2 ± 0.1	2 ± 0.1
8	7.9 ± 0.2	8.4–9.4
10	9.8–10.4	9.8–10.6
12	12 ± 0.2	12 ± 0.2

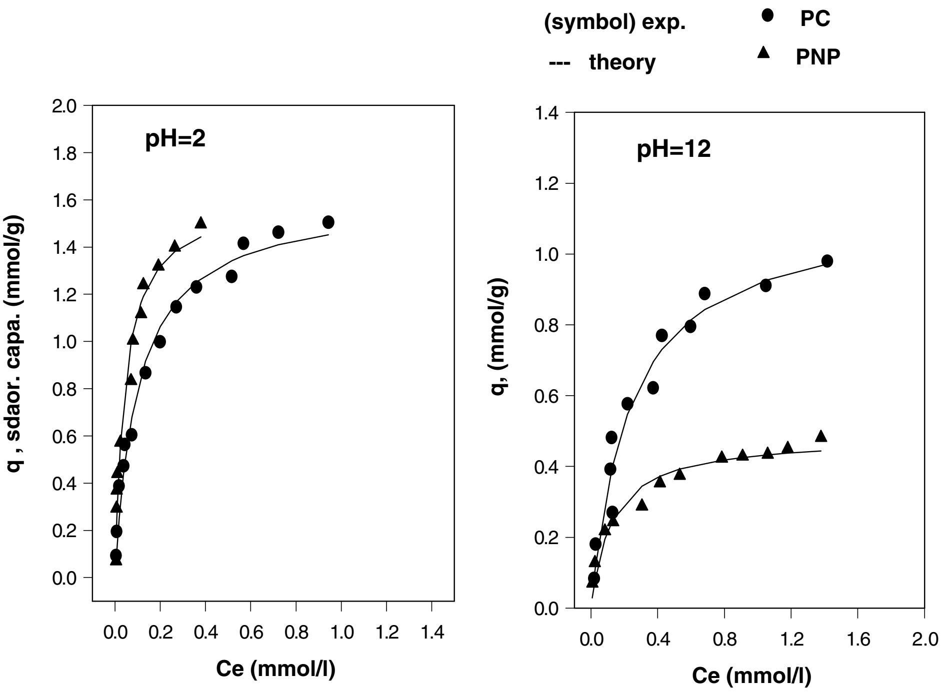

Figure 4. Langmuir fit single solute.

values after equilibrium increased significantly, when pH_{ini} 7.8 and 10. The increase in pH_{eq} is explained by Snoeyink et al. (1969) in terms of the change in the structure of the double layer. They explain that the adsorption of the anions by the carbon surface leads to an increase in the surface negative charge. There must then be an increase in the positive charge in the diffuse double layer to neutralise this negative charge. This is achieved by removing hydrogen ions from the bulk solution, which in turn would lead to an increase in the solution pH.

Another plausible explanation is that as more molecules are adsorbed, the equilibrium shown in Eq. (7), would tend to be directed more to the left, converting more ions into the molecular form, producing more OH^- ions in the process. During our pH measurements for the isotherms, it was observed that the higher the q_e, the higher was the measured pH value.

$$HA + OH^- \leftrightarrow H_2O + A^- \qquad (7)$$

Figure 4 shows the experimental data and fitted isotherms in pH 2 and pH 12 for single solute. Figure 5 and Table 3 shows the change in the maximum adsorption capacity of the carbon, Q_{max} as determined from the Langmuir Equation (Eq. (2)), with pH for two solutes. It shows that the decrease in the value of Q_{max} with pH for PNP appears to be much more significant than for PC. As a result of the difference between the pK_a values of the solutes (Table 1), it is expected that PNP dissociates more

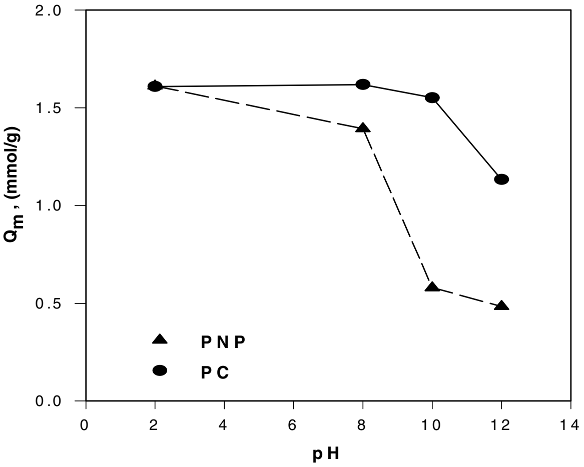

Figure 5. Variation Q_m with pH.

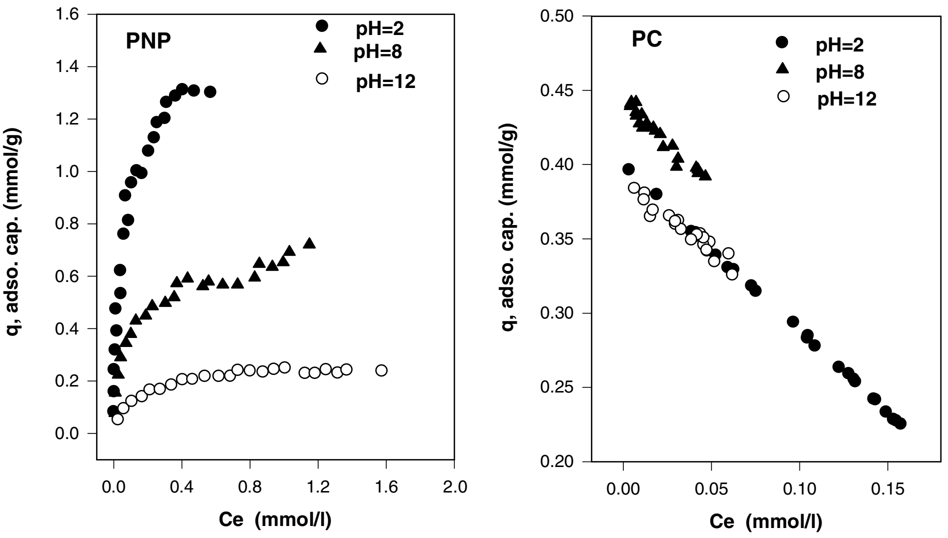

Figure 6. PNP & PC adsorption at different pH, double solute.

extensively than PC. Hence, more PNP ions are in solution at any pH than the corresponding anions of PC. Since higher anion concentration would mean a greater degree of electrostatic repulsive forces, the adsorption capacity of the carbon for PNP in solutions with higher pH values is expected to be lower than for PC.

4.2. Adsorption in Double Solute

To compare the adsorption capacity for PNP of the carbon, $Q_{\max}$, in single and double solute solutions, we used a constant concentration of PC (40 ppm) with different concentrations of PNP.

Figure 6 shows the adsorption isotherms of both solutes at different pHs. The difference observed for adsorption of PC at pH 2, should be because of its chemical structure as detailed above (the —OH group in PC is more basic ($pK_a = 10.2$), since PC is a stronger base, in acidic conditions more PC molecules would tend to be positively charged. This would lead to a lower uptake of PC).

The experimental data and fitted isotherms for PNP are shown in Fig. 7 and the comparison of adsorption isotherms between single and double solute are shown in Fig. 8.

Table 3. Variations of fitted parameters ($Q_{\max}$, and k_1) obtained from Eq. 2.

	Initial pH	2	8	10	12
PC	$Q_{\max}$ (mmol/g)	1.61	1.62	1.55	1.13
	K_1	0.1	0.13	0.07	0.04
PNP	$Q_{\max}$ (mmol/g)	1.61	1.39	0.58	0.48
	K_1	0.16	0.03	0.11	0.06

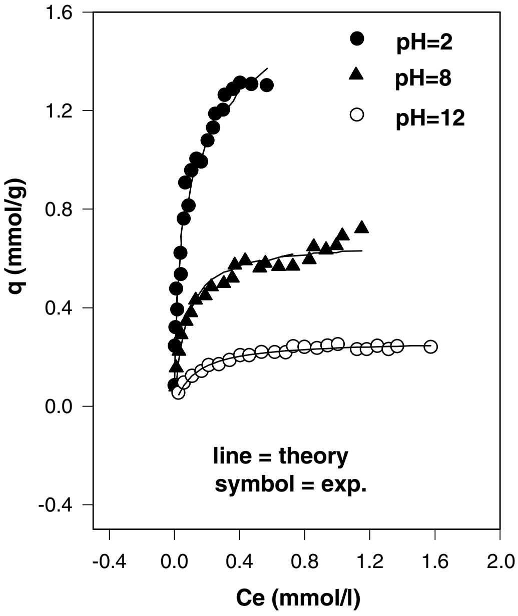

Figure 7. PNP Langmuir fit double solute.

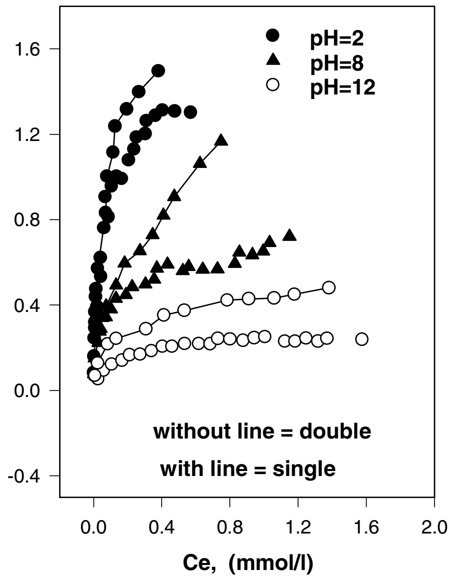

Figure 8. Comparison of adso. capa. for PNP in single & double solute.

The variations of different parameters (Q_m, k_1 and k_2) obtained from Eq. (6) with pH are shown in Fig. 9 and Table 4. It shows that, as the solutions' pH increased, the concentration of the anionic form of p-Nitrophenol and the negative charge of the carbon

Table 4. Variations of fitted parameters ($Q_{\max}$, k_1 and k_2) obtained from Eq. (6).

Initial pH	2	8	12
$Q_{\max}$ (mmol/g)	1.68	0.68	0.27
K_1	0.88	0.11	0.16
K_2	0.88	0.05	0

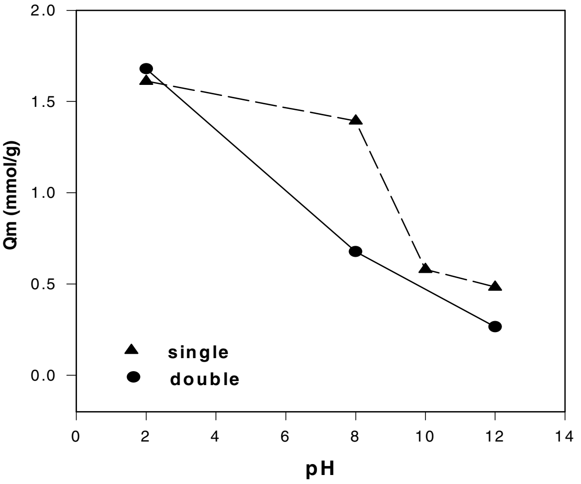

Figure 10. Variation of Q_m for PNP in single & double solute.

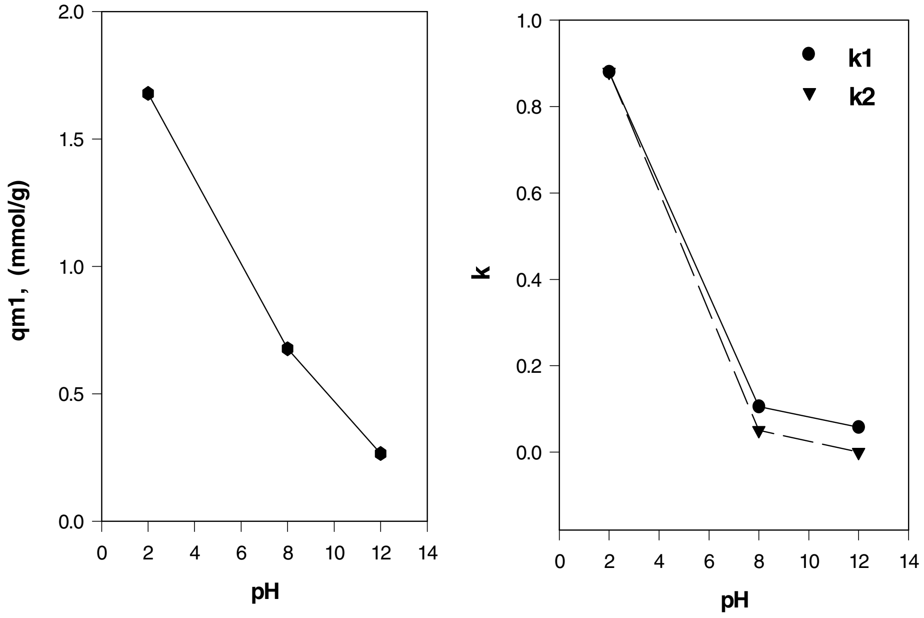

Figure 9. Variation of Q_m for PNP, k_1 & k_2 with pH (two-solute system).

increased. Hence, the solute adsorptivity decreased. Figure 10 shows the comparison of maximum adsorption between single and double solute mixtures of PNP. One observes that the presence of PC reduces the Q_{m} of PNP.

5. Conclusion

The adsorption capacity of a commercially available activated carbon for two aromatic compounds, in different solution pH conditions, was investigated. It was found that the uptake of the molecular forms of the aromatic solutes was dependent on the substituents of the aromatic ring. Electron-donating groups on the ring led to a higher uptake and electron-withdrawing groups led to lower uptake by the carbon. Adsorption of the solutes in higher pH values was found to be dependent on the concentration of anionic form of the solutes. A lower uptake level was observed for the compound with the lower $\mathrm{p}K_{\mathrm{a}}$. 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 single-solute Langmuir equation show that $Q_{\max}$ and the adsorption affinity of carbon for the compound with low $\mathrm{p}K_{\mathrm{a}}$ decrease more significantly. The presence of another compound decreases $Q_{\max}$ and the adsorption affinity of carbon for the principal compound.

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