

Figure (8) 1/n with pH. PC. Lang-fred.

Figure (9) n with pH. Lang-Fred.

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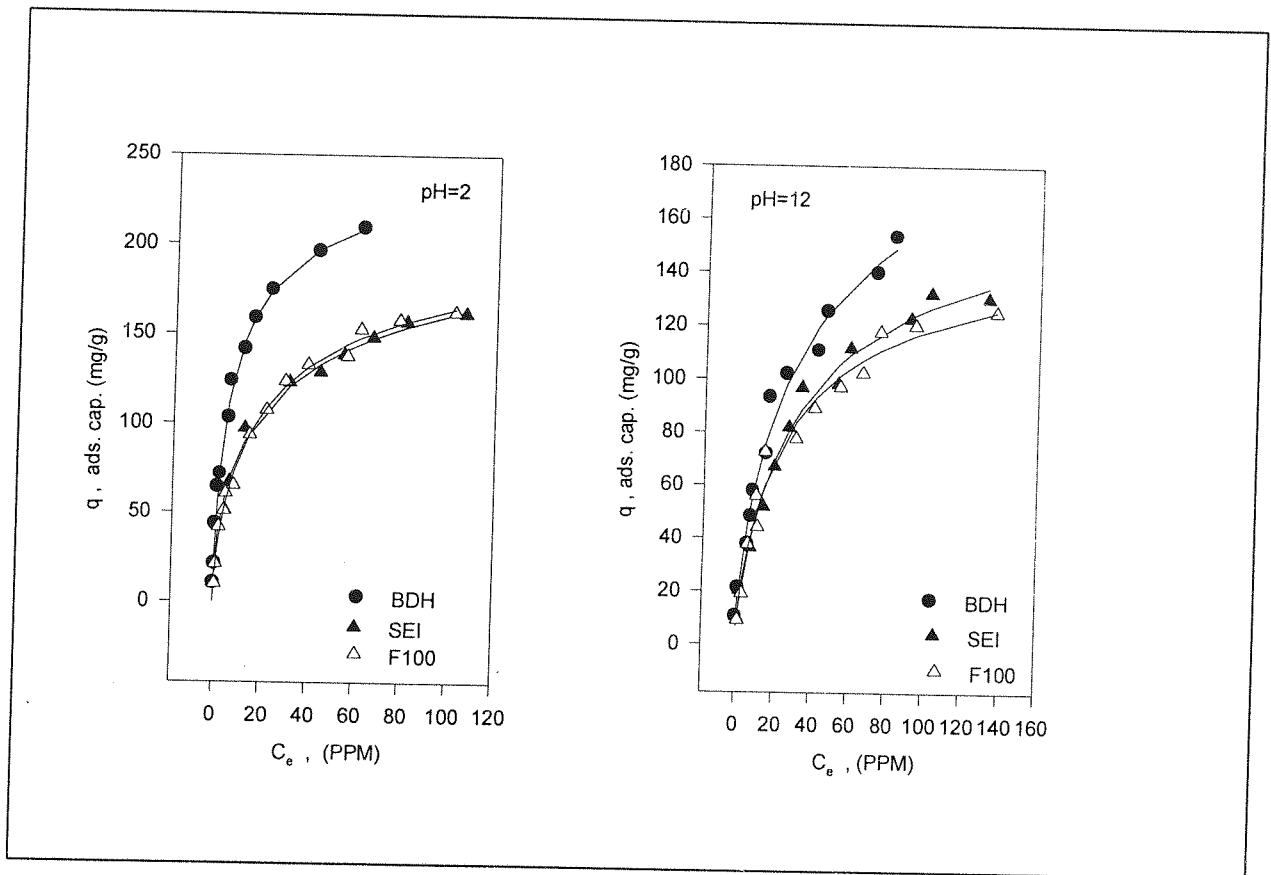


Figure (5) p-Cresol Langmuir-Freundlich fit.

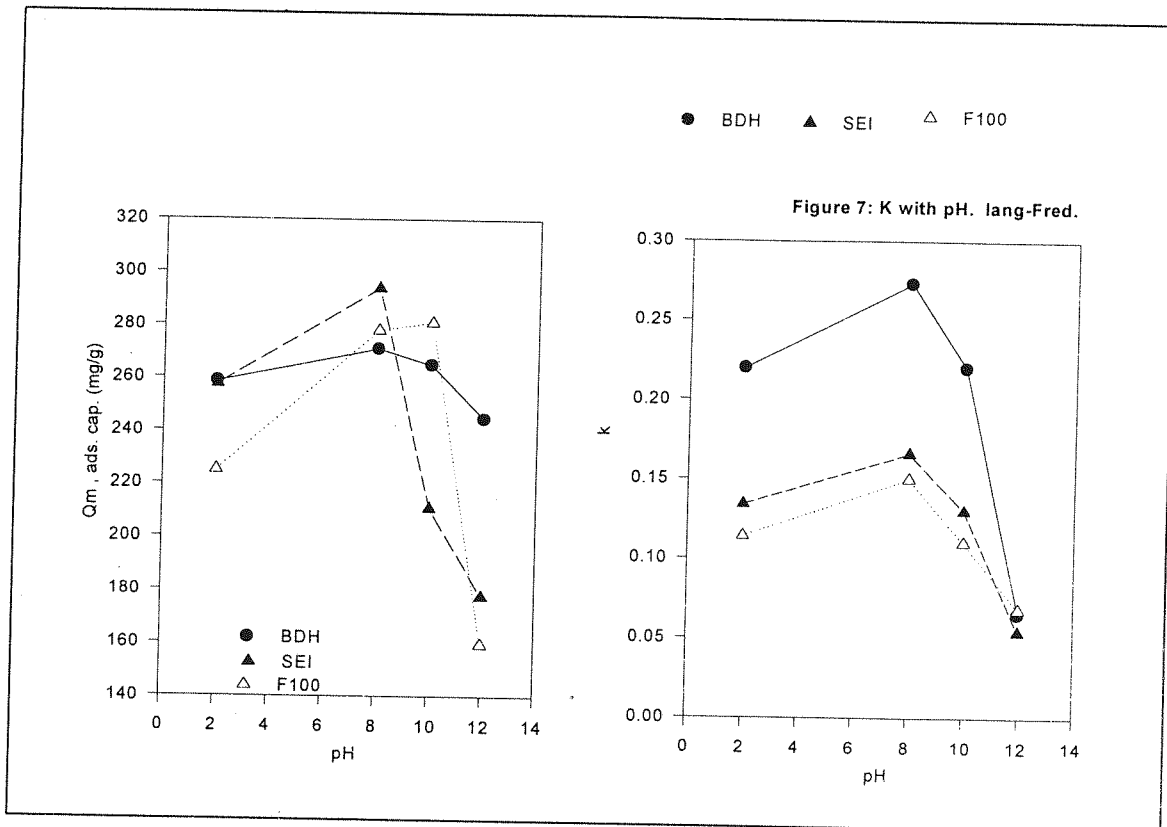


Figure (6) Q_m with pH. PC. Lang-Fred.

Figure (7) k with pH. Lang-Fred.

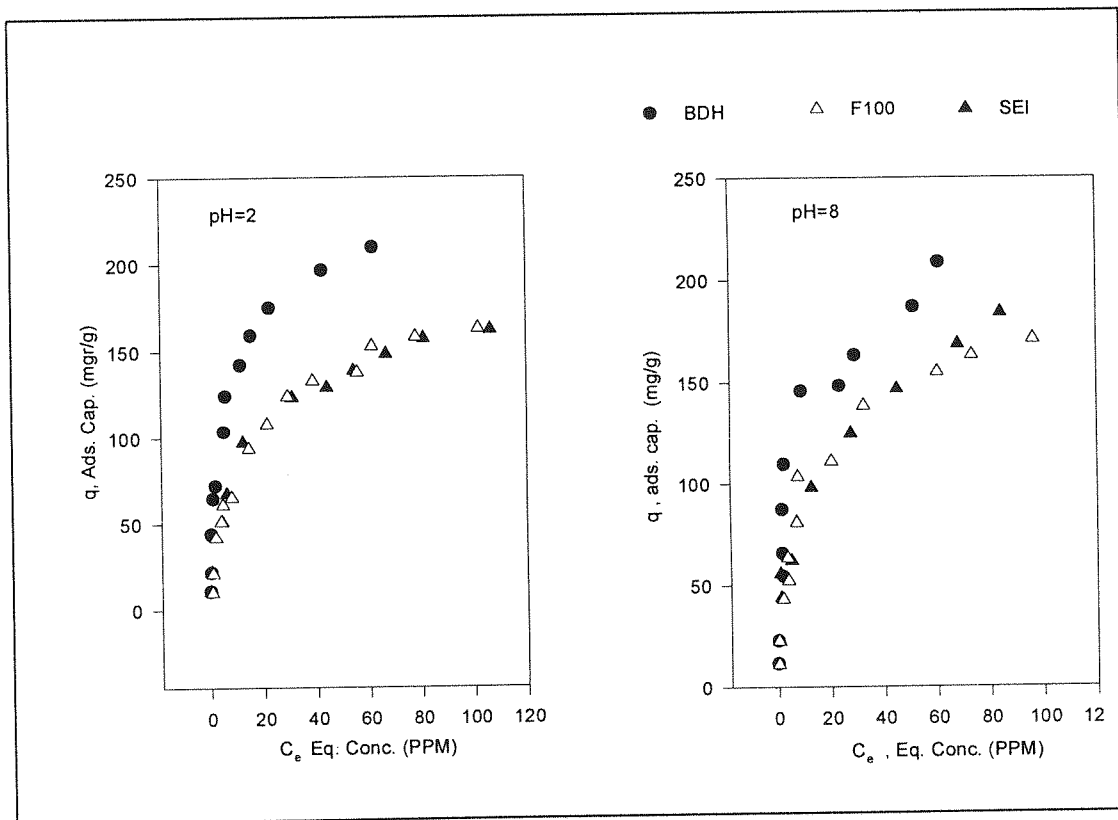


Figure (3) p-Cresol in different Carbon

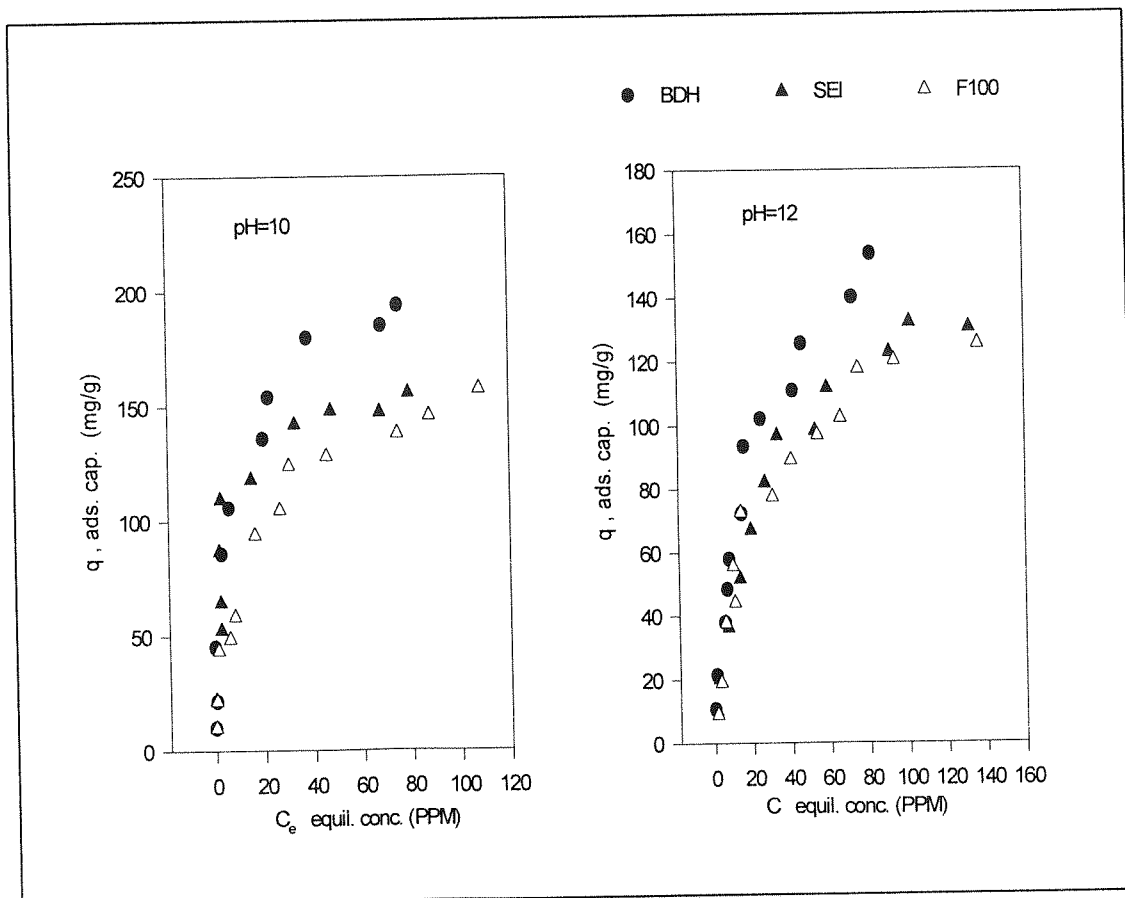


Figure (4) p-Cresol in different Carbon.

4-Conclusion

The adsorption capacity of three commercially available activated carbons for an aromatic compound in different solution pH conditions was investigated. It was found that the uptake of the molecular forms of the aromatic solute was dependent on the surface area and 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-Freundlich equation) showed that the affinity and the Q_{max} depend to the homogeneity of the adsorption systems and pH of solute.

Table(1) Properties of the solute.

Solute	Molecular Weight	pK _a	Solubility (g/l)
p-Cresol	108	10.2	18

Table(2) Properties of the Carbons.

Carbon	PZC	Surface area m ² /gr
F100	7.8	749
S.E.I.	9.2	851
B.D.H.	10.1	1128

Table(3) Equilibrium pH of the adsorption experiments.

Initial pH	Equilibrium Ph
2	2±0.1
8	8.2-9.1
10	9.7-10.4
12	12±0.2

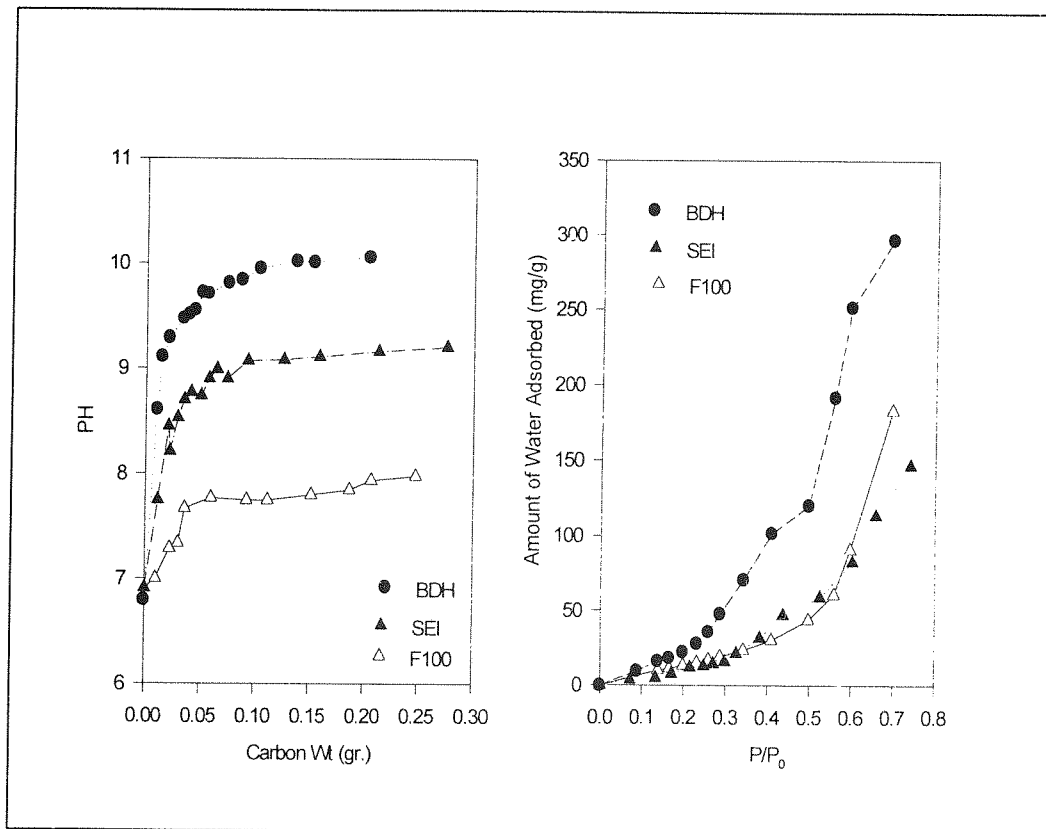


Figure (1) P.Z.C. of the Carbons.

Figure (2) Water Adsorption Isotherms.

repulsive forces, the adsorption capacity of the carbons are expected to be lower.

The effect of pH must be considered from its combined effects on the carbon surface and on the solute molecules. The effects of the pH on the carbon surface are well documented in various reviews, such as the recently published by Radovic [8]. 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 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, as discussed below.

In pH higher than $pH_{(pzc)}$ of the carbons, the carbon surface is negatively charged. This pH is also well above the pK_a of the PC (Table 1), which means that this solute is mainly in their ionic form. In other words, due to the high electrostatic repulsive forces in adsorbent-adsorbate and adsorbate-adsorbate, the observed adsorption isotherm is mainly due to the molecular forms of the solute.

Table 3 shows the initial and equilibrium pH values (pH_{eq}). It shows that the initial and equilibrium pH values in two extremes of the pH range did not change significantly. However the solution pH values after equilibrium increased significantly, when $pH_{ini}=7.8$ and 10. The increase in pH_{eq} is explained by Snoeyink et al. [19] 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 Equation 4, 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 measurement for the isotherms, it was observed that the higher was the q_e , the higher the measured pH value.



3-2-Langmuir -Freundlich equations

All isotherms were then fitted into the **Langmuir -Freundlich** isotherm Equations (Eq 2). Figure 5 shows fitted isotherms and experimental data in $pH=2$ and $pH=12$ for this equation.

Variation of maximum adsorption capacity (Q_m) with pH for three carbons is shown in figure 6 and the fitted affinity coefficients (k) for three carbons versus the pH are shown in figure 7. These plots show both factors follow a similar trend in three carbons. One observe that the trend for Q_m and k is similar. Both factors increase and attain maximum about $pH=8$ before decreasing by increase of pH.

Figures 8 and 9 show the variation of $1/n$ (heterogeneity parameter) and n with pH respectively. Decrease of heterogeneity is equal to increase of homogeneity. Figure 9 shows that homogeneity of system is maximum when pH is about 8. In this condition the adsorption affinity (k) and Q_m are maximum. This is because PC is adsorbed more in its molecular form and homogeneous sites. Decrease in the value of Q_{max} and solute adsorptivity with pH is expected. It is because as the solutions pH increased, the concentration of the anionic form of solute and negative charge of the carbon increased, and higher anion concentration would mean a greater degree of electrostatic repulsive forces between the solute molecules and between the solute and carbon surface would be higher. The adsorption capacity of the carbon for PC in solutions with higher pH values is expected to be lower.

corresponding to complete coverage (Equation 3) and C_{eq} is the equilibrium solution concentration. The equilibrium constant is related to the adsorption energy as expressed in Equation 4.

$$\theta = \frac{q_{eq}}{Q_{max}} \quad (3)$$

$$k = k_{10} \exp(-E) \quad (4)$$

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

2 - Methods and Materials

2-1-materials

The granular activated carbons (GAC) used in this work are S.E.I. and F100 from Calgon and B.D.H. from BDH. 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) (99.9% purity) from Merck Chemicals HCl and NaOH (A. R. Grade)-Ajax Chemicals.

2-2-Equilibrium Studies

The adsorption experiments were carried out by placing 45mg 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, after filtration were then measured spectrophotometrically, using Jasco-V550 spectrophotometer.

2-3-Determination of PZC (Point of zero charge).

The $\text{pH}_{(PZC)}$ of the carbons was determined as suggested by Noh et al. [18]. 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 $\text{pH}_{(PZC)}$. Noh et al suggest that in the $\text{pH}=\text{pH}_{(PZC)}$ the surface of carbon is neuter. In pH higher than $\text{pH}_{(PZC)}$ it's surface is negatively charged and in pH lower than $\text{pH}_{(PZC)}$ carbon surface is positive. So in this case carbon has high affinity for anions.

Figure 1 shows the variation of pH by amount of activated carbon to find the PZC. It shows that the adsorption affinity of carbon for H^+ ions is as follow: $\text{BDH} > \text{SEI} > \text{F100}$, it mean that the electron density of the basal layer of the carbon is as: $\text{BDH} > \text{SEI} > \text{F100}$. In figure 2, water adsorption isotherms of three activated carbons (in vapor phase) are shown.

3-Results and Discussion

3-1-Difference of adsorption between the activated carbons

The isotherms of p-Cresol at $\text{pH}=2$ and $\text{pH}=8$ are shown in Figure 3 and at $\text{pH}=10$ & 12 in figure 4. 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. Considering the surface area values of the carbons (table 1), the adsorption capacity of BDH is higher than SEI and F100 in each pH. The adsorption capacity for SEI and F100 in low pH is the same. As the solutions pH was increased, the concentration of the anionic form of p-cresol also increased, it would mean a greater degree of electrostatic

relying on the physical properties of activated carbons alone [8].

Most organic pollutants are weak electrolytes, for which the adsorption equilibria depend on the solution pH. The main challenge for researchers has been taking into account the effects of the carbon surface chemistry as well as the solution pH simultaneously. In other words, the relative importance of the effects of electrostatic and dispersion forces in a given sorbate-sorbent system [12]. 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 the adsorption systems. 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, Getzen and Ward [6, 13] 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 Polanyi potential to explain the same phenomenon [14]. Derylo-Marczewska and Jaronic [7] report a detailed analysis of the various theoretical approaches applied to adsorption of organic solutes onto activated carbon.

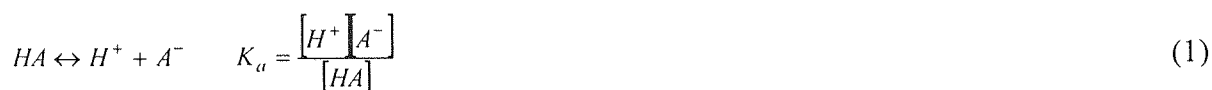
Muller et al in a series of papers [15-17] gives the most advance contribution that takes into account both the effects of pH and the carbon surface chemistry. Based on the Langmuirian approach the authors take into account the effects of the adsorbent surface charge determined by pH and ionic strength. They also take into account the 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 [16], they were unable to use the fitted parameters of their model to discuss 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 [7] also examined the adsorption behaviour of model aromatic compounds using a Langmuirian approach. They assumed 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 into the adsorption process.

In this work the adsorption behaviour of p-Cresol on the three different activated carbons and in their molecular and ionic form was investigated. All experimental data were then fitted into the Langmuir-Freundlich isotherm equation to obtain the corresponding factors.

1-Theoretical Section

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



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 Langmuir-Freundlich Equation (Eq.2)

$$q = \frac{[kQ_m(C_e)^{1/n}]}{[1+k(C_e)^{1/n}]} \quad (2)$$

where k is constant (adsorption affinity), $1/n$ is a heterogeneity parameter which is usually between 0 and 1 and Q_m is maximum amount of solute adsorbed per gram of carbon. Q_{max}

Adsorption of p-Cresol by different Carbon at different pH (Freundlich–Langmuir isotherm)

Sirous Nouri

Chemistry Department,
College of Science, Urmia University Urmia

Abstract

Adsorption of p-Cresol by three different activated carbons was carried out at 301 K and at controlled pH conditions. Langmuir-Freundlich isotherm equations were studied and relative parameters were found. In acidic conditions that pH of solution is well below the pK_a of p-cresol (in molecular form), it was observed that the adsorbate solubility and the electron density of aromatic ring were the influencing factors on the extent of the adsorption by affecting the extent of London dispersion forces. It was found that the uptake of the molecular form of the aromatic solute was dependent on the PZC and surface area of the carbon. In higher solution pH conditions (in ionic form), the electrostatic forces played a significant role on the extent of adsorption. The effect of pH must be considered from its combined effects on the carbon surface and on the solute molecules. Adsorption capacity (Q_{max}) and affinity (K) decrease with pH. Adsorption of the solute in higher pH values was found to be dependent on the concentration of anionic form of the solute. All isotherms were fitted into Langmuir-Freundlich isotherm equations to find the relative factors.

Keywords

Effects of pH, Point of Zero Charge (PZC), Adsorption Capacity, Activated Carbon, Langmuir-Freundlich, p-Cresol, Spectrophotometer.

Introduction

Examination of the literature shows an abundance of experimental adsorption studies for aqueous organic solute systems involving activated carbon. 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 [1-3]. The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler [4] in the 1950s. A decade later, other authors [5, 6] 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, our theoretical and experimental approaches have come a long way, as demonstrated by various reviews in the last twenty years [7, 8]. 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 [9]. 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, it is 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 , functional group present, polarity, molecular weight and size). Finally, the solution conditions, referring to its pH, ionic strength and the adsorbate concentration [10, 11, 12]. It is well understood that cost-effective removal of organic pollutants can not be achieved by