

References

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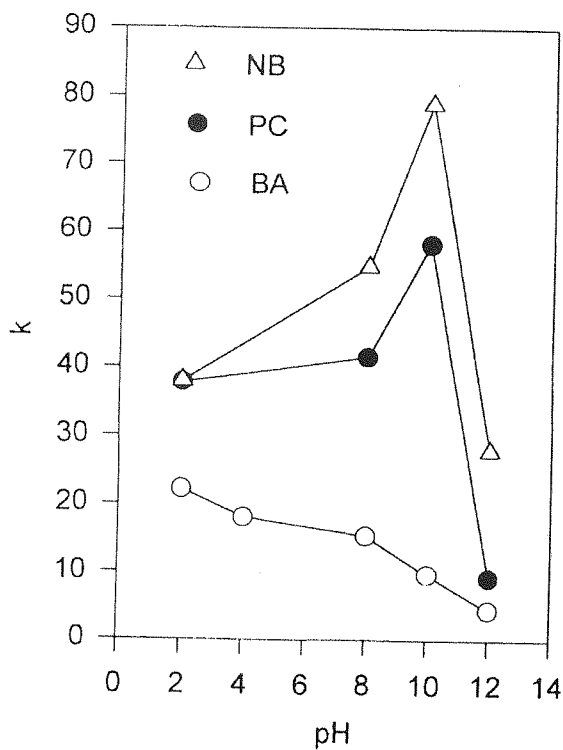


Figure (8) Variation of k(Freundlich)with pH.

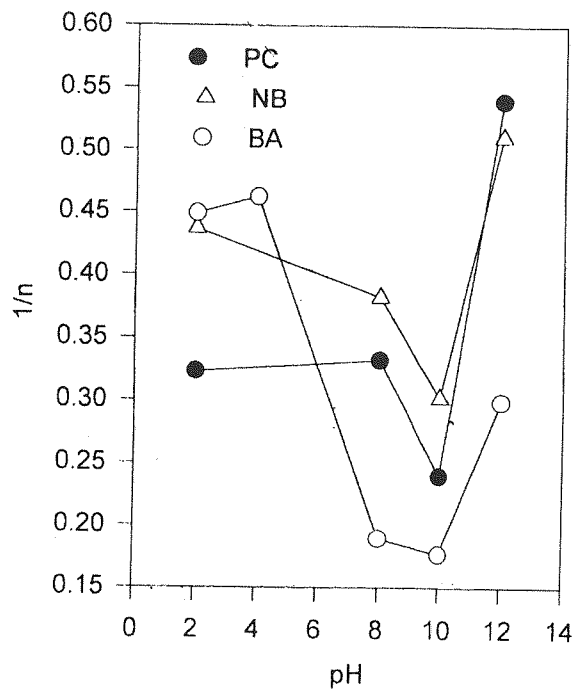


Figure (9) Variation of 1/n with pH.

Table (1) Properties of the solutes.

Solute	Molecular Weight	pK _a	Solubility (g/l)
P-Cresol	108	10.2	18
Nitro Benzene	123	-	1.9
Benzoic acid	122	4.2	2

Initial pH	Equilibrium pH		
	P-Cresol	Nitro Benzene	Benzoic acid
2.2±0.1	2±0.1	2±0.1	2±0.1
4.2±0.1	-	-	4.8-5.7
7.8±0.1	7.8±0.2	7.8±0.2	7.5-8.1
10.1±0.1	9.8-10.3	9.8±0.2	9.8-10.2
12±0.1	12±0.1	12±0.1	12±0.1

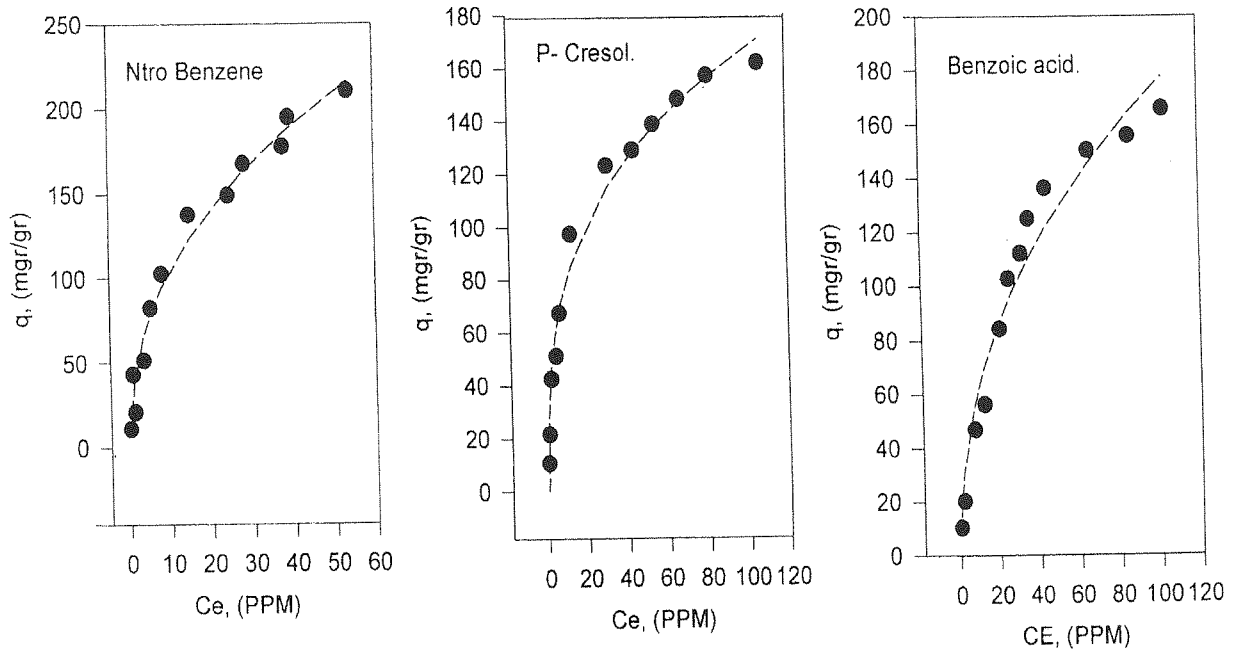


Figure (6) Freundlich fit in pH = 2.

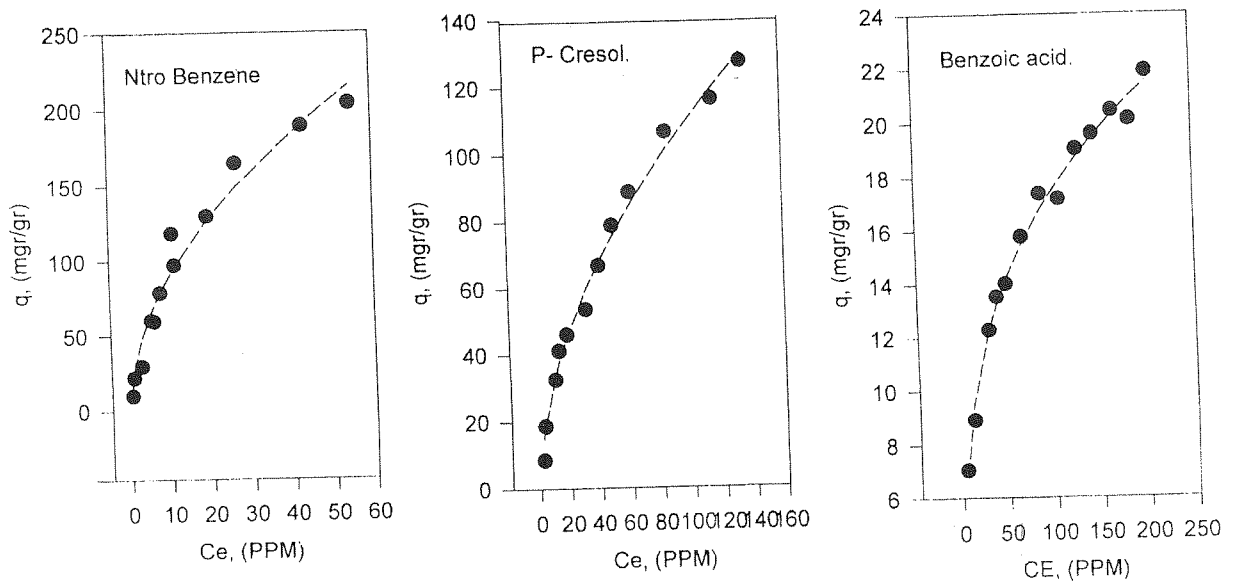


Figure (7) Freundlich fit in pH = 12.

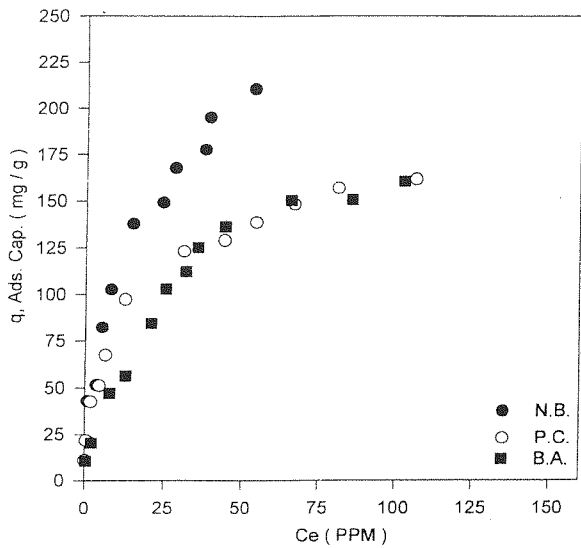


Figure (1) SEI isotherms, PH = 2.

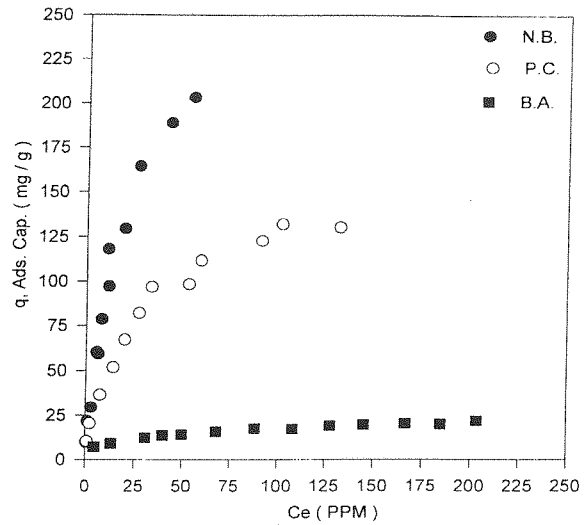


Figure (3) SEI isotherms, PH = 12.

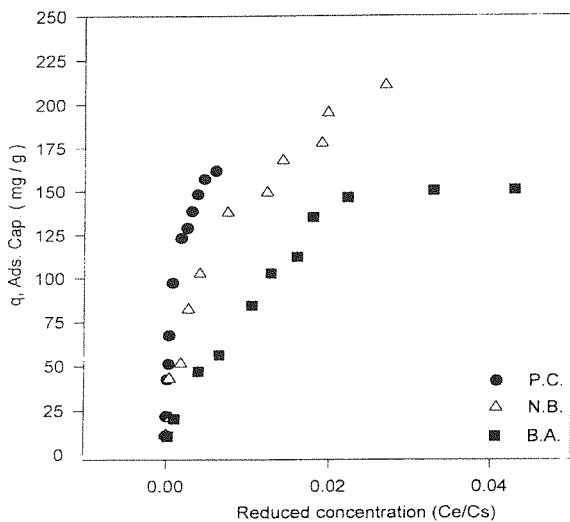


Figure (2) Reduced concentration (Ce/Cs).

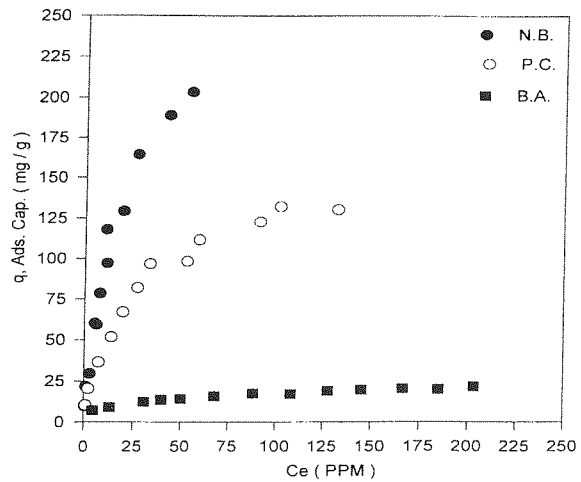


Figure (4) PC, NB and BA isotherms, PH = 10.

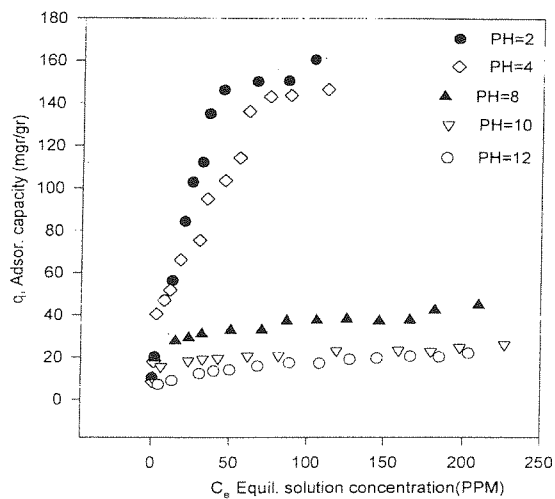


Figure (5) B. A. isotherms in S. E. I. (different PH).

the adsorption isotherms of BA in different pH. As the solutions pH is increased, the concentration of the anionic form is increased, it would mean a greater degree of electrostatic repulsive forces, the adsorption capacity of the carbon is expected to be lower.

All isotherms were then fitted into the Freundlich isotherm Equations (Eq 2). Figure 6 and 7 show fitted isotherms in pH=2 and pH=12 respectively.

Variation of Freundlich constant (k) with pH for all solutes is shown in figure 8. One observation is that the increase in the value of k with pH to a maximum in pH=10 (pH=pH_(PZC)) and then decrease of k value for PC and NB appears to be much more significant than for BA that decrease with pH. This could be due to reason that when pH increased it is then expected that the electron density of the basal layers of the carbon also increase. As a result London dispersion forces between the aromatic ring of the solute and the basal planes will increase. Therefore, the adsorptivity of the solutes is highest when carbon surface is neutral (pH \cong pH_(PZC)).

As the solutions pH increased, the concentration of the anionic form of solutes and negative charge of the carbon also increased, hence the solute adsorptivity decreased.

As a result of the difference between the pK_a values of the solutes (Table 1), it is expected that BA (weak electrolyte) and PC (very weak electrolyte) would dissociate more extensively than NB (no electrolyte). Hence more BA and PC ions in solution at any pH than the corresponding anions of NB. Since higher anion concentration would mean a greater degree of electrostatic repulsive forces, the adsorption affinity of the carbon for BA and PC in solutions with higher pH values is expected to be lower. Influence of

the pH on the adsorption affinity of the carbon (k) is more significant for no or very weak electrolyte than electrolyte compound. This plot shows that the adsorption affinity of the carbon for solutes with high pK_a values is highest.

Figure 9 shows the variation of $1/n$ with pH for all solutes. It shows that $1/n$ values decrease to a minimum value at pH=10 (pH=pH_(PZC)) before increasing at higher pH values. $1/n$ correspond to the heterogeneity of the system and in pH = pH_(PZC) that there is no charge on the carbon surface (only site that are high in dispersion energy become available for adsorption process), it is minimum. In low and high pH a greater variety of sites become available for adsorption, hence a larger heterogeneity factor is obtained.

5-Conclusion

The adsorption capacity of a commercially available activated carbon for three aromatic compounds, two of which were electrolytes in different solution pH conditions, were 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 stronger acids (lower pK_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 showed that the affinity and the heterogeneity of the adsorption systems could be explained by the extent of dissociation of these compounds.

withdrawing group. This indicates that the electron densities of the aromatic ring of the solutes is as follows: $PC > NB \leq BA$, 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. [22] also found that increase in the electron density of the adsorbate led to an increase in its uptake by activated carbon.

4-2-Difference Between the pH of the Solutions

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 one by Radovic [11]. 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 interaction between the aromatic ring 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.

Figure 3 shows the adsorption isotherms of the solutes in pH=12. In such a high pH the carbon surface is negatively charged, since the solution pH is much higher than the $pH_{(PZC)}$ of the carbon ($pH_{(PZC)}$ of S.E.I.=9.5). This pH is also well above the pK_a of the PC and BA (Table 1), which means that those solutes are mainly in their ionic form except for NB that is in molecular form. Figure 3 shows that the adsorption capacity of the carbon for Nitrobenzene is still high, followed by PC and BA ($NB > PC > BA$). This is expected, since BA is stronger acid than PC, according to their pK_a values. Therefore the amount of the

molecular form of PC in pH=12 is still high. This means that in pH=12 there is much less molecular form of BA than the p-cresol. In other words, due to the high electrostatic repulsive forces in adsorbent-adsorbate and adsorbate-adsorbate, the observed absorption isotherm is mainly due to the molecular form of the solutes.

The 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 all solutes 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. [23] 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.



Figure 4 shows the adsorption isotherms of all solutes in pH=10 and figure 5 shows

p-Cresol (PC) (99.9% purity)-Merck Chemicals, benzoic acid (BA) (99.9% purity)-BDH Chemicals, HCl and NaOH (A.R. Grade)-Ajax Chemicals.

3-2 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 concentration of the solutes were then measured spectrophotometrically, using Jasco-V550 spectrophotometer.

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

The $pH_{(PZC)}$ of the carbon was determined as suggested by Noh et al. [21]. 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 measured. The limiting pH was taken as the $pH_{(PZC)}$. Noh et al suggest that in the $pH = pH_{(PZC)}$ the surface of carbon is neutral. In pH higher than $pH_{(PZC)}$ its surface is negatively charged and in pH lower than $pH_{(PZC)}$ carbon surface is positive. So in this case carbon has high affinity for anions.

4-Results and Discussion

4-1-Difference Between the Aromatic Compounds

The isotherms for all solutes at $pH = 2$ are shown in Figure 1. 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 pK_a values of the electrolytes, in $pH = 2$ all solutes are in their molecular form. Furthermore, the -OH group in PC 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 words, since PC is a stronger base, in acidic conditions more of PC molecules would tend to be positively charged. This would lead to a lower uptake of PC. As shown in Figure 1, the adsorption capacity of the carbon for the sorbates is as follows: N.B. > P.C. > B.A.

However, this observation is in contrary to what one would expect from the solubility data (Table 1) of these solutes. If the affinity of the solutes for the solvent is to be considered, BA and NB should be adsorbed the most, since their solubility in water are the least. This suggests that the observed pattern of adsorption is not governed only by the affinity of the solute for the solvent. In order to take into account the effect of the affinity of the solutes for the solvent, the equilibrium solution concentration of the solutes, C_e , are normalized with respect to their solubility. The basis of this normalization is the Traube's rule, used by various workers for a number of decades. The use of reduced concentration normalizes that amount of energy required to bring a molecule of solute from bulk to the surface of a solution. The adsorption data are re-plotted using these normalized values (Figure 2).

The adsorption data given in Figure 2, show that the adsorption capacity of the carbon for the adsorbates is as follows: PC > NB > BA. 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-COOH and NO_2 are an electron

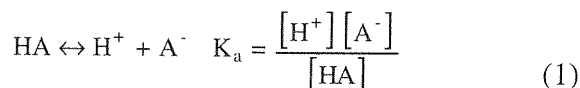
heterogeneity by assuming a truncated Gaussian adsorption energy distribution. Even though, they had excellent fit of their model into the corresponding experimental data, in their second paper of the series [19], they were unable to use the fitted parameters of their model to discuss any aspects of 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 and Marczewski [3] 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 with, the parameters could not shed new light into the adsorption process.

In part I of this work the adsorption behaviour of three model aromatic compounds in their molecular and ionic form was investigated. All experimental data were then fitted into the Freundlich isotherm equation to obtain the corresponding factors. The adsorption behaviour of the solutes was investigated. In Part II of this work, using heterogeneous models, the heterogeneity and the topography of the adsorption systems in different solution conditions will be investigated.

2-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 Freundlich Equation (Eq. 2), we assume that both the ionic and the neutral species compete for the same site. However, only one solute particle can be adsorbed per site.

$$q = K.(C_e)^{1/n} \quad (2)$$

where n is a constant which is usually greater than 1. In the civil engineering literature, the Freundlich equation is commonly written as $x/M=K (C_e)^{1/n}$ (x is the amount of solute adsorbed (e. g., mg), M is the weight of carbon (e. g., g)). $1/n$ correspond to the heterogeneity of the system. If one takes the logarithm of each side of the Freundlich equation, one obtains

$$\log q = \log K + (1/n) \log C_e \quad (3)$$

Thus, a plot of $\log q$ vs. $\log C_e$ will yield a straight line with a slope of $1/n$ and an intercept of $\log K$.

3-Methods and Materials

3-1 materials

The granular activated carbon (GAC) used in this work was S. E. I. from Calgon. Prior to the experiments, a sample was ground and sieved. The fraction between 400-800 $\mu\mu$, was used in this work. Chemicals used were as follows: Nitro Benzen (NB) (99.7% purity),

carbon-oxygen) that exist on the surface. The variety of the oxides produced during the manufacture of activated carbons, is a result of the presence of high concentration of oxygen present in precursors of activated carbons [4]. The research on the surface chemistry of activated carbons can be found as far back as early 1960s [5]. A thorough discussion of this subject can be found in more recent reviews [6].

The significance of the carbon surface chemistry in the adsorption process was first raised by Hassler [7] in the 1950s. A decade later, other authors [8, 9] 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 the theoretical and experimental approaches has come a long way, as demonstrated by various reviews in the last twenty years [10, 11]. 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 [12]. 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 [13]. It is well understood that

cost-effective removal of organic pollutants can not be achieved by relying on the physical properties of activated carbons alone [11, 14].

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, the relative importance of the effects of electrostatic and dispersion forces in a given sorbate-sorbent system [13]. 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. 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 [15].

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 [9, 16], 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 [17]. Derylo-Marczewska and Jaronic [10] 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 [18-20] gives the most advance contribution that takes to account both the effects of pH and the carbon surface chemistry. Based on the Langmuirian approach the authors take to account the effects of the adsorbent surface charge determined by pH and ionic strength. They also take to account the solid

Effects of Solution pH on the Adsorption of Aromatic Compounds from Aqueous Solutions by Activated Carbon

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Abstract

Adsorption of p-Cresol, Benzoic acid and Nitro Benzen by activated carbon from dilute aqueous solutions was carried out under controlled pH conditions at 310k. In acidic conditions, well below the pK_a of all solutes, it was observed that the adsorbate solubility and the electron density of its aromatic ring were the influencing factors on the extent of the adsorption by affecting the extent of London dispersion forces. In higher solution pH conditions, on the other hand, it was found that 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. It was found that the uptake of the molecular forms of the aromatic solutes was dependent on the substituents of the aromatic ring. Adsorption of the solutes in higher pH Values was found to be dependent on the concentration of anionic form of the solutes. All isotherms were fitted into Freundlich isotherm Equations.

Keywords

Effects of pH, Point of Zero Charge (PZC), p-Cresol, Benzoic Acid, Nitro Benzen, Adsorption Capacity, Activated Carpacity, Activted Carbon (S. E. I), Freundlich Equation, Spectrophotometer, Adsorption of Aromatic.

1-Introduction

Increase of environmental awareness in the recent times has lead more stringent limits on the quality of water and wastewater. Organic compounds constitute a very large group of the known pollutants. Most of them are recognized carcinogens and 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 and low pollutant concentration [1].

The traditional use of activated carbon in both water and wastewater treatment is very well known. These materials are very vesratile

adsorbents due to their high surface area, a well-developed pore structure and surface properties. In spite of their huge application in water treatment for the removal of organic pollutants, however, the mechanism of the adsorption process is yet not fully understood and much confusion exist in the literature regarding their mechanisms [2].

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 [3] and the latter arises from the variety of functional groups (mainly in the form of