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Effect of Different Treatment on the Adsorption of *p*-Cresol by Activated Carbon (Langmuir Isotherm)

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Adsorption of *p*-cresol by four activated carbons (one untreated and three treated) was carried out at 301 K and at controlled pH conditions. In acidic conditions such that pH of solution is well below the pK_a of *p*-cresol (molecular form), it was observed that the adsorbate solubility and the electron density of aromatic ring and also those of the carbon surface, are the main forces involved in the adsorption process, by affecting the extent of London dispersion forces. In higher solution pH conditions (in ionic form), 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 form of the aromatic solute was dependent on the substituents of the aromatic ring. 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 isotherm equations to find the relative factors.

Key Words: Effects of pH, Adsorption capacity, Activated carbon, *p*-Cresol, Langmuir isotherm, Spectrophotometer.

INTRODUCTION

Increasing environmental awareness in recent times has led to 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 recognised 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 versatile 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 exists in the literature regarding these 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 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 the 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 on 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[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). Finaliy, the solution conditions, referrinng to its pH, ionic strength and the adsorbate concentration[13–15]. It is well understood that cost-effective removal of organic pollutants cannot be achieved by relying on the physical properties of activated carbons alone[11] .

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 electrostate and dispersion forces in a given sorbate-sorbent system[15]. Even though there have 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 between 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 Polyani 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 on to activated carbon.

Muller *et al.*[18–20] in a series of papers give the most advanced 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 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, the parameters could not shed new light on the adsorption process.

In this work the adsorption behaviour of *p*-cresol on the untreated and treated activated carbons and on their molecular and ionic forms was investigated. All experimental data were then fitted into the Langmuir isotherm equation to obtain the corresponding factors.

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

Using the Langmuir equation (Eq. (2)),

$$\frac{C_{eq}}{q_{eq}} = \left(\frac{1}{K_1 Q_{max}}\right) + \left(\frac{1}{Q_{max}}\right) C_{eq} \tag{2}$$

where K_1 is constant (adsorption affinity) and Q_{max} is maximum amount of solute adsorbed per gram of carbon. Q_{max} corresponds to complete coverage (Eq. 3) and C_{eq} the equilibrium solution concentration. The equilibrium constant is related to the adsorption energy as expressed in Eq. (4).

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

$$K_i = k_{10} \exp(-E) \tag{4}$$

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

EXPERIMENTAL

The granular activated carbons (GAC) used in this work are untreated F100 and F100 treated with urea, H_2 and acid (H_2SO_4) from Calgon. Prior to the experiments, a sample was ground and sieved. The fraction between 400–800 μm of carbon was used in this work. Chemicals used were as follows: *p*-cresol (PC) (99.9% purity), H_2SO_4 from Merck Chemicals, HCl and NaOH (AR grade) from Ajax Chemicals.

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. The pH of the solution 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.

Determination of point of zero charge (PZC): The $pH_{(PZC)}$ of the carbons 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 then measured. The limiting pH was taken as the $pH_{(PZC)}$ (Fig. 1). Noh *et al.*[21] 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. Thus in this case carbon has high affinity for anions. Table-1 shows PZC of the carbons.

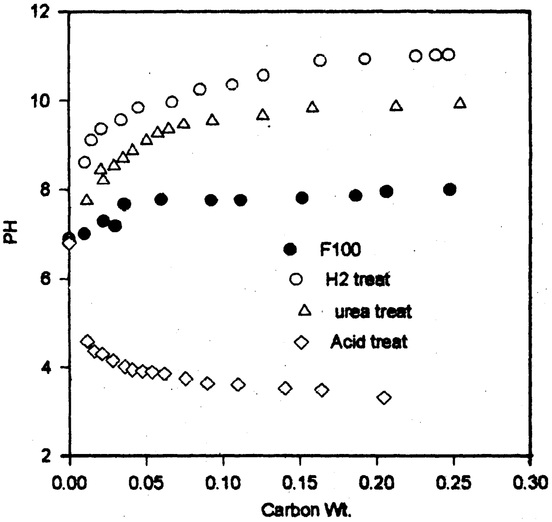

Fig. 1. P.Z.C. of the carbons

TABLE-1
PZC OF THE CARBONS

Carbon	F100	H_2 treated	Urea treated	Acid treated
PZC	7.8	11	9.9	3.3

RESULTS AND DISCUSSION

Difference of adsorption in different pH: First the adsorption of *p*-cresol on the untreated F100 is investigated. The isotherms of *p*-cresol at different pH are shown in Fig. 2. The isotherms are plotted using a mass based solid concentration, q_e (in mg of the solute adsorbed per gram of the carbon) *vs.* the liquid concentration, C_e (in ppm) at equilibrium conditions. One observes that as the solutions pH is increased, the concentration of the anionic form of *p*-cresol is increased; it would mean with a greater degree of electrostatic repulsive forces, the adsorption capacities of the carbons are expected to be lower.

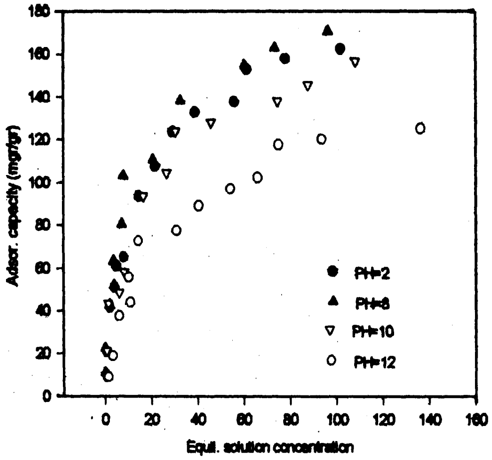

Fig. 2. P.C. in untreated P100 (different pH)

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]. 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 higher pH than $pH_{(PZC)}$ of the carbons, ($pH_{(PZC)}$ of the F100 = 7.8), carbon surface is negatively charged. This pH is also well above the pK of the *p*-cresol (Table- 2), which means that this solute is mainly in its 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 and ionic forms of the solute.

TABLE-2
PROPERTIES OF THE SOLUTE

Solute	m.w.	pK_a	Solubility (g/L)
p-Cresol	108	10.2	18

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 pH values of the solution after equilibrium increased signifi- cantly, when $pH_{ini} = 7.8$ and 10. The increase in pH_{eq} is explained by Snoeyink *et al.*[22] 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 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 pH of the solution.

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

Another plausible explanation is that as more molecules are adsorbed, the equilibrium shown in Eq. (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.

$$HA + OH^- \leftrightarrow H_2O + A^- \qquad (4)$$

Langmuir equations: All isotherms were then fitted into the Langmuir isotherm equations (Eq. 2) to calculate Q_{max}. Variation of maximum adsorption capacity (Q_{max}) with pH for untreated F100 is shown in Fig. 3. One observes that Q_{max} decreases with pH because of electrostatic repulsive forces.

Decrease in the value of Q_{max} and solute adsorptivity with pH is expected. It is because as the solution 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. The adsorption capacity of the carbon for p^--cresol in solutions with higher pH values is expected to be lower.

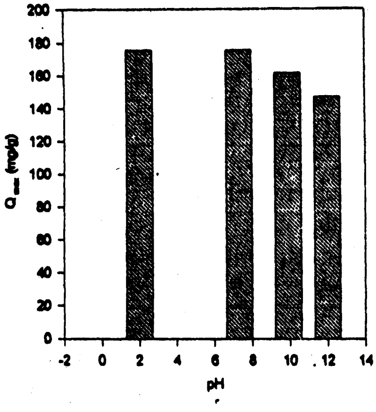

Fig. 3. Variation of Q_{max} with pH in untreated 100

To observe the effect of different treatment on the adsorption of activated carbon, untreated F100 is treated with urea, H_2 and H_2SO_4.

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

The adsorption of treated carbons is observed at pH = 2 and pH = 12. Fig. 4 shows the adsorption of different carbons in acidic and basic condition. As

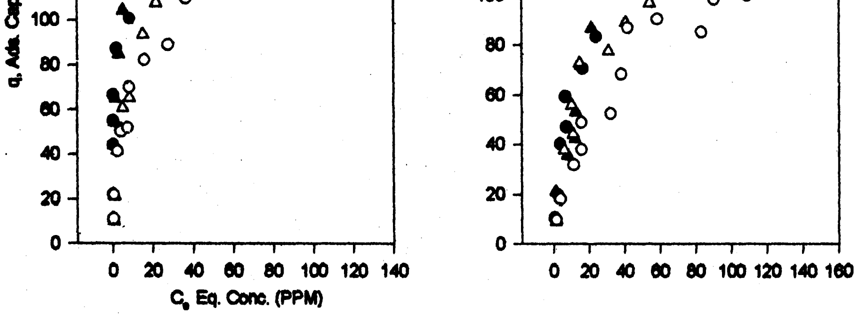

Fig. 4. p-Cresol in different carbon

expected, in comparison with untreated F100, the adsorption of urea and hydrogen treated carbon increases and for acid treated carbon, it decreases. Fig. 5 shows Langmuir fit for different carbons at pH = 2 and pH = 12. One observes that the experiment fit better in low concentration and high pH.

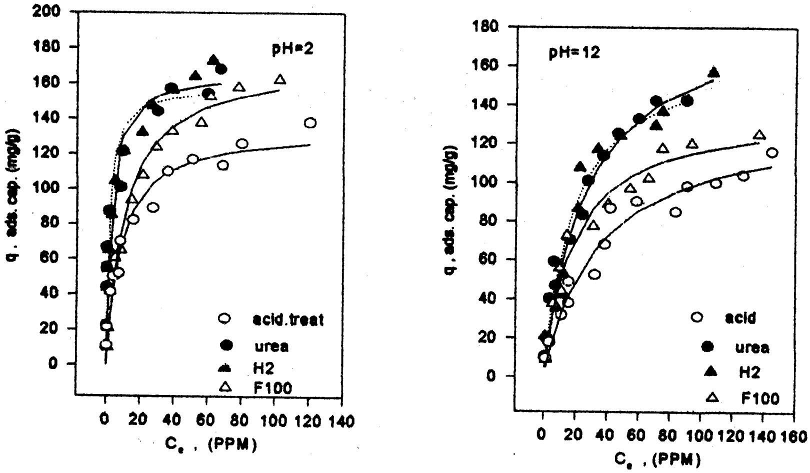

Fig. 5. p-Cresol: Langmuir fit

Table-4 shows the comparison of Q_{max} in different carbons. As expected, by treating with urea and hydrogen the electron density of the basal layers of the carbon increased, London dispersion forces between the aromatic ring of the solute and the basal planes increased and so Q_{max} is high. By treating with acid, the electron density and Q_{max} is low.

TABLE-4
COMPARISON OF Qmax IN DIFFERENT CARBON

Carbon	Q_{max}			
	pH = 2	pH = 8	pH = 10	pH = 12
Untreated F100	174	175	161	138
Urea treated F100	174	—	—	157
H_2 treated F100	178	—	—	167
Acid treated F100	138	—	—	129

Conclusion

The adsorption capacity of untreated and treated commercially available activated carbons for an aromatic compound, in different pH conditions of solution, was investigated. It was found that the uptake of the molecular forms of the aromatic solute was dependent on the surface area 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) showed that the affinity and the Q_{max} depend on the electron density of the solute and carbon. Different treatments change the adsorption capacity of the carbon.

REFERENCES

1. R.S. Juang, F.C. Wu and R.L. Tseng., *J. Chem. Eng. Data,* **41,** 487 (1996).
2. H.A, Arafat, M. Franz and N.G. Pinto, *Langmuir,* **15,** 5997 (1999).
3. A. Derylo-Marczewska and S.W. Marczewska, *Langmuir,* **15,** 3981 (1999).
4. F. Rodriguez-Reinoso, M. Molina-Sabio and M.T. Gonzalez, *Langmuir,* **13,** 2354 (1997).
5. H.P. Boehm, *Advances in Catalysis,* **16,** 179 (1966).
6. C.A. Leon, L.R. Radovic, P.A. Thrower, (Ed.), Marcel-Dekker, New York, p. 213 (1994).
7. J.W. Hassler, Chemical Publishing Co., Inc, New York, p. 127 (1951)
8. R.W. Coughlin and F.S. Ezra, *Environmental Science and Technology,* **2,** 291 (1968).
9. T.M. Ward and F.W. Getzen, *Environmental Science and Technology,* **4,** 64 (1970).
10. A. Derylo-Marczewska and M. Jaroniec, Surface and Colloid Science, **14,** 301 (1987).
11. L.R. Radovic, J.A. Schwarz and C.I. Contescu (Eds.), Marcel-Dekker, New York (1999).
12. C. Hsieh and H. Teng, *J. Colloid and Interface Sci.,* **230,** 171 (2000).
13. S.Nouri, F. Haghseresht and G.Q. Lu; *Inter. J. Engg. Sci.,* **12,** 67 (2001.)
14. S. Nouri, *Journal of Amir Kabir,* **13,** 26 (2002).
15. S. Nouri, *Adsorption Science and Technology;* **19** (2001) (in press).
16. F.W. Getzen and T.M. Ward, *Journal of Colloid and Interface Sci.,* **31,** 441 (1969).
17. M.R. Rosene and M. Manes, *J. Phy. Chem.,* **81,** 1651 (1977).
18. G. Muller, C.J. Radke and J.M. Prausnit, *J. Phy. Chem.,* **84,** 369 (1980).
19. *Idem, J. Colloid and Interface Sci.,* **103,** 466 (1985).
20. *Idem, J. Colloid and Interface Sci.,* **103,** 484 (1985).
21. J.S. Noh and J.A. Schwarz, *J. Colloid and Interface Sci.,* **130,** 157 (1989).
22. V.L. Snoeyink, W.J. Weber and H.B. Mark, *Environmental Science and Technology,* **3,** 919 (1969).

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