



Effect of Different Treatment on the Adsorption of p-Cresol by Activated Carbon

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Abstract

Adsorption of p-Cresol by three activated carbons (one untreated and two treated) was carried out at 301 K and at controlled pH conditions. By treating the activated carbon the PZC and adsorption capacity (Q_{\max}) of carbon change. The adsorption capacity of each carbon, by using the homogenous Langmuir-Freundlich model, was found to comparing the effect of different treatment. At pH lower than pK_a of p-cresol (molecular form), it was observed that 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. Treating by H_2 increase the PZC and treating by H_2SO_4 decrease this factor. At higher pH (in ionic form), it was found that the electrostatic forces played a significant role on the extent of adsorption. In this condition the adsorption of the solute dependent on the concentration of anionic form of the solute. 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 PZC of the carbon.

Introduction

Organic compounds constitute a very large group of potentially carcinogens pollutants. Many of them are recognized and are known to be toxic to the environment. Among the available methods for removing these pollutants, adsorption on activated carbon is still one of the most preferred methods. 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 [1] and the latter arises from the variety of functional groups (mainly in the form of carbon-oxygen) that exist on the surface. The traditional use of activated carbon in both water and wastewater treatment is very well known.

Carbon adsorbents materials are very versatile due to their high surface area, 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. 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 activated car-

bons precursors [2].

The significance of the carbon surface chemistry in the adsorption process was first raised by some authors [3]. A decade later, other authors [4,5] shed significant light into the effects of surface carbon-oxygen groups and the sorbate-sorbent p-p interactions on the adsorption mechanism of organic compounds. 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 [6]. 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 our previous works the effects of pH on the adsorption capacity of different activated carbons were investigated [7-9].

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,

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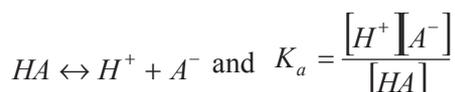
the solution conditions, referring to its pH, ionic strength and the adsorbate concentration [10,11]. It is well understood that cost-effective removal of organic pollutants can not be achieved by relying on the physical properties of activated carbons alone.

Many organic pollutants are weak electrolytes and therefore the solution pH affects both the surface charge and the adsorbate chemistry. For non-electrolytes, the effect of the surface chemistry is found to be more significant [12]. The total interaction potential in such complex systems is grouped into London dispersion forces and electrostatic force [13]. 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 the last few decades a number of authors have investigated the effects of pH on the adsorption of aromatic compounds [5,8,10,13-18].

In this work the adsorption behaviour of p-Cresol on the untreated and treated 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.

Theoretical

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



Taking the negative log of the equilibrium would yield the pK_a of the solute.

Using the Langmuir-Freundlich Equation (Eq.1)

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

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} corresponding to complete

coverage ($\theta = \frac{q_{eq}}{Q_{max}}$) and C_{eq} is the equilibrium solution concentration.

Characterization of the Activated Carbon

For characterization of the carbon 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 [19]. The ultramicropore volumes (V_{ulmic}) of the carbon was obtained by applying the Dubinin-Radushkevich equation (DR) to CO_2 adsorption isotherms obtained at 273 K [20].

The water adsorption data were analyzed by fitting the water adsorption isotherms to equation below, the DS-2 equation [21].

$$c(Q_0 - q)(1 - kq) = q/(P/P_0)$$

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.

The adsorption data were shown in Table 1.

Table 1
Adsorption Data

Solute	SBET ($m^2 \times g^{-1}$)	V_{tot} ($cm^3 \times g^{-1}$)	V_{mic} ($cm^3 \times g^{-1}$)	V_{ulmic} ($cm^3 \times g^{-1}$)	Q_0 mg/g ⁻¹
BDH	1118	0.618	0.416	0.282	72.5

Experimental

The granular activated carbons (GAC) used in this work are untreated BDH and BDH treated with H_2 and acid (H_2SO_4) from BDH Chemicals. 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 (A.R. Grade)- Ajax Chemicals.

To observe the effect of different treatment on the adsorption of activated carbon, Untreated BDH is treated with H_2 and H_2SO_4 .

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 reach-

ing equilibrium conditions, the residue concentrations of the solute, after filtration were then measured spectrophotometrically, using Jasco-V550 spectrophotometer (for PC between 285 & 310 nm).

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.

Vapor Adsorption

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.

The $pH_{(PZC)}$ (PZC = Point of zero charge) of the carbons was determined as described in our previous works [9,10]. 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 $pH_{(PZC)}$. In the $pH=pH_{(PZC)}$ the surface of car-

bon is neuter. In pH higher than $pH_{(PZC)}$ it's 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. Table 2 shows PZC of the carbons.

Table 2
PZC of the Carbons

Carbon	B.D.H.	H ₂ treated	Acid treated
PZC	10.1	12.2	6.4

Results and Discussion

Figure 1 shows the fitted and experimental isotherms of the p-Cresol (PC) in different activated carbons at pH=2 & pH=12, plotted using a mass based solid concentration, q_{eq} (in mgrams of the solute adsorbed per gram of carbon) versus the liquid concentration, C_{eq} (in ppm), respectively. Considering the pK_a of the p-cresol (PC), ($pK_a = 10.2$) in pH=2 it is in molecular form. One observes that as the solutions pH is increased the adsorption capacity of each carbon is decreased. The effect of pH must be considered from its combined effects on the carbon surface and on the solute molecules. The adsorption capacity of the carbon for the solute in their molecular form was dependent on the electron density of the solute. 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:

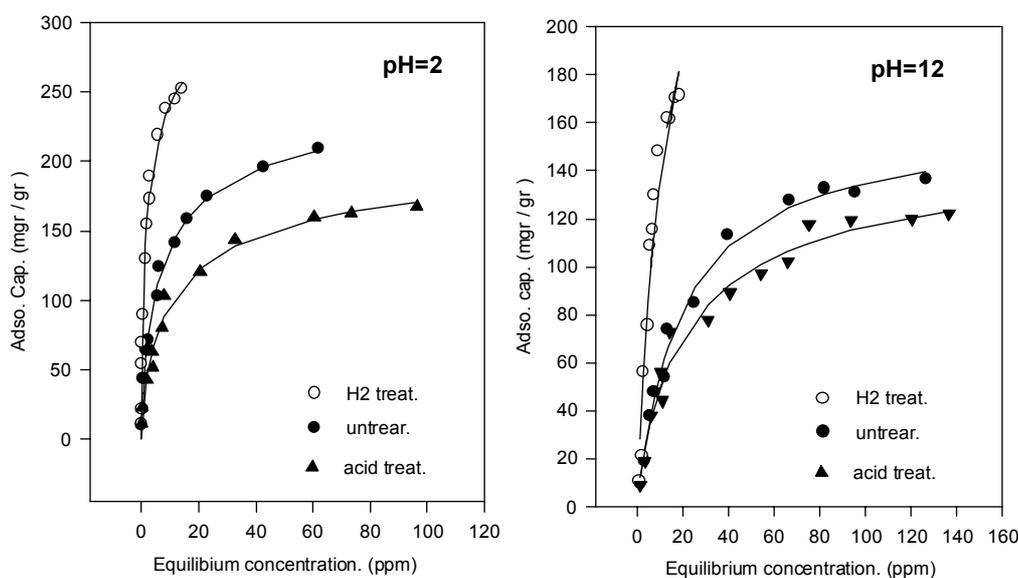


Fig. 1. Fitted and Exp. isoth. in different carbon at pH=2 & pH=12.

In pH higher than $pH_{(pzc)}$ of the carbons, carbon surface is negatively charged. This pH is also well above the pK_a of the PC (Table 3), 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 and ionic forms of the solute.

Table 3
Properties of the solute

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

Figure 2 shows the adsorption isotherms of PC in H_2 treated and acid treated carbon.

One observes that as the solutions pH is increased, the concentration of the anionic form of p-cresol is increased, it would mean a greater degree of electrostatic repulsive forces, the adsorption capacity of the carbons are expected to be lower.

All isotherms were fitted into the linear form of the Langmuir-Freundlich isotherm Equations to calculate Q_{max} . Table 3 shows the variation of Q_{max} for each carbon in different pH.

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.

To observe the effect of different treatment on the adsorption of activated carbon, Untreated BDH is treated with H_2 and H_2SO_4 .

H_2 treatment reduces carboxylic and hydroxide groups and effect on the electron density by increasing it. By oxidation and dehydration with H_2SO_4 , carbonyl and carboxyl groups increase on the surface of the carbon so there is a decrease on electron density. The adsorption isotherms of treated carbons are shown in Figure 2.

Table 4 shows the comparison of Q_{max} in different carbons. As expected, by treating with H_2 the electron density of the basal layers of the carbon increased, so London dispersion forces between the aromatic ring of the solute and the basal planes increased and Q_{max} is high. By treating with acid, the electron density and Q_{max} is low.

Figure 3 shows the variation of Q_{max} with PZC of carbon. By increasing the PZC of the carbon, Q_{max} increase.

Conclusions

The adsorption capacity of untreated and treated commercially available activated carbons for an aromatic compound, in different solution pH conditions, was investigated. Different treatment changes the

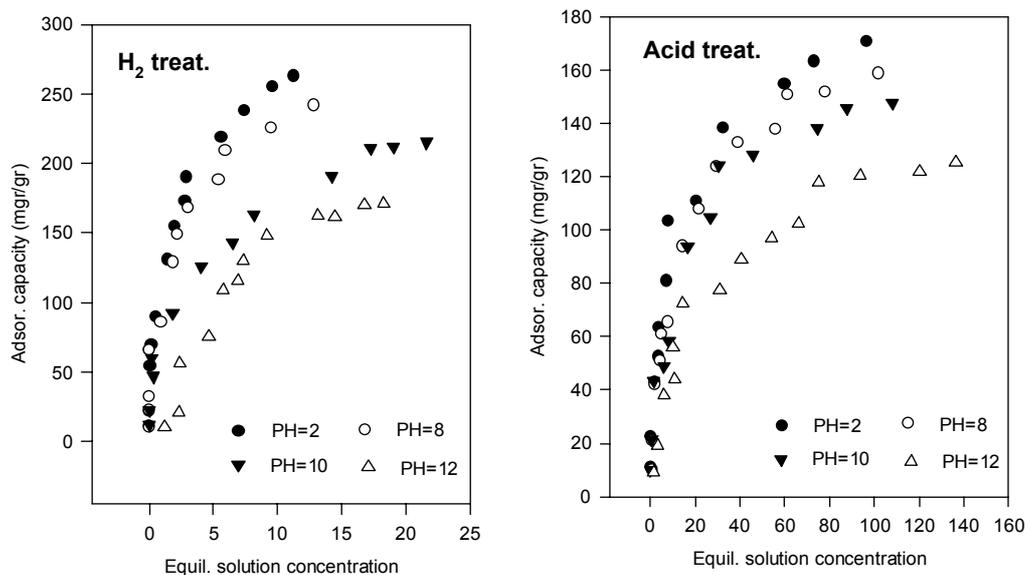


Fig. 2. Adsorption isoth. in H_2 treat. & acid treat. at diff. pH Equil. solution concentration.

Table 4
Variation of Q_{max} in different carbon with pH

Q_{max}				Carbon
PH = 12	PH = 10	PH = 8	PH = 2	
160	210	259	259	Untreated B.D.H.
291	295	299	355	H2 treated B.D.H.
150	202	207	217	Acid treated B.D.H.

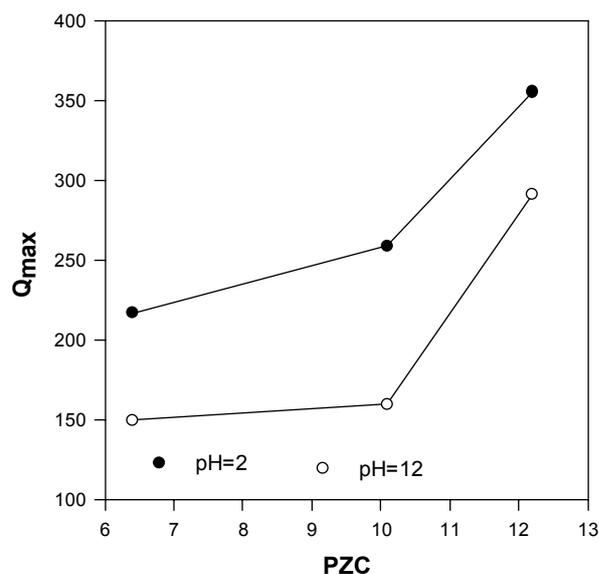


Fig. 3. Variation of Q_{max} with PZC for each carbon.

PZC of the carbon and so the affinity and adsorption capacity of the carbon.

The fitted parameters (obtained from Langmuir-Freundlich equation) showed that the affinity and the Q_{max} depend to the electron density of the solute and carbon.

In low pH 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.

Different treatment changes the adsorption capacity and PZC of the carbon.

References

- Derylo-Marczewska, A. and A.W. Marczewska Langmuir, 1999. 15: p. 3981.
- Rodriguez-Reinoso, F., M. Molina-Sabio, and M.T. Gonzalez, Langmuir, 1997. 13: p. 2354.
- Hassler, J.W. 1951, Chemical Publishing CO., INC.: New York. p. 127.
- Coughlin, R., W. and F.S. Ezra. Environmrntal Science and Technology, 1968. 2: p. 291.
- Ward, T.M. and F.W. Getzen, Environmenmtal Science and Technology, 1970. 4: p. 64.
- Hsieh, C. and H. teng. Journal of Colloid and Interface Science, 2000. 230: p. 171.
- Nouri, S., Adsorption Science & Technology; 2002, vol. 20 No.9, p. 917
- Nouri, S., F. Haghseresht and G. Q. Lu; Journal of Amir Kabir, 2002, vol. 13, no. 49, p26
- Nouri, S., F. Haghseresht and M. Lu, Iranian Journal of Science and Technology, 2002, Summer A2, 26, p. 371.
- Nouri, S., F. Haghseresht and G. Q. Lu; Adsorption Science & Technology; 2002, vol. 20 No.1, p. 1.
- Nouri, S., F. Haghseresht; Adsorption Science & Technology; 2002, vol. 20 no.4, p. 417
- Radovic, L.R., et al., Carbon, 1997. 35(9): p. 1339.
- Radovic, L.R., Surface Chemistry og Activated Carbon Materials: State of the Art and Implications for Adsorption, in Surfaces of Nanoparticles and Porous Materials, J.A. Schwarz and C.I. Contescu, Editors. 1999, Marcel Dekker: New York.
- Getzen, F.W. and T.M. Ward. Journal of Colloid and Interface Science, 1969. 31: p. 441.
- Rosene, M.R. and M. Manes. Journal of Physical Chemistry, 1977. 81: p. 1651.
- Muller, G., C.J. Radke, and J.M. Prausnit. J. Phy. Chem., 1980. 84: p. 369.
- Muller, G., C.J. Radke, and J.M. Prausnitz. Journal of Colloid abd Interface Science, 1985. 103: p. 466.

18. Muller, G., C.J. Radke, and J.M. Prausnitz. Journal of Colloid and Interface Science, 1985. 103: p. 484.
19. Gregg, S. J.; Sing, K. S.W. (1982) Adsorption, Surface Area and Porosity; Academic Press, London.
20. Marsh, H., (1987), Carbon, 25, 49.
21. Barton, S. S.; Evans, J. B.; MacDonald, J. A. F., (1991), Carbon, 29 (8), 1009.

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