

Aqueous-Phase Adsorption of Phenolic Compounds on Activated Carbon

H. I. Maarof, B. H. Hameed and A. L. Ahmad

*School of Chemical Engineering, Engineering Campus,
Universiti Sains Malaysia, Seri Ampangan, Nibong Tebal,
14300 Seberang Perai Selatan, Pulau Pinang, Malaysia.
E-mail: chbassim@eng.usm.my*

ABSTRACT

Laboratory batch studies were conducted on adsorption of phenol, 3-chlorophenol and o-cresol from aqueous solution by Norit Granular Activated Carbon (NAC 1240). The effect of various initial concentrations and time of adsorption on phenols adsorption process were investigated. The time required for adsorbates to reach equilibrium condition was about 25 h for range of initial phenols concentration between 25-200 mg/l. A maximum percentage of removal of 90% phenol and 99% of 3-chlorophenol and o-cresol were obtained under adsorption operating conditions of 30°C, 120 rpm, 25 h adsorption time and initial solute concentrations of 25 and 50 mg/l. It was observed that an increase in initial solute concentration results in increase of phenols uptake from liquid to solid phase. The suitability of Langmuir and Freundlich model were evaluated to estimate the monolayer capacity values of the activated carbon used for each sorbate-sorbent system. The adsorption behaviour of phenolic compounds on NAC 1240 was best described by Langmuir isotherm model in the whole range of initial concentrations studied. The order of adsorption capacity among the phenolic compounds was o-cresol > 3-chlorophenol > phenol. The values of adsorption capacity of 270.3, 166.7 and 161.3 mg/g were obtained for o-cresol, 3-chlorophenol and phenol, respectively.

Keywords: Adsorption; phenolic compounds; Langmuir and Freundlich models; activated carbon

1.0 INTRODUCTION

The presence of phenol and chlorinated phenol in industrial wastewater stream is stringently regulated at low limit of concentration before it could be discharged to the environment. Since phenolic substances are toxic and harmful to human and aquatic life, the removal of these pollutants from waste effluent becomes environmentally important. Additionally, phenol has been classified as one of the primary pollutants as enacted by Department of Environment (DOE), Malaysia in Environmental Quality Act 1979 (Sewage and Industrial Effluent) which should be treated to be less than 1 ppm for inland water discharge. Several methods have been proposed in literatures on techniques for removal phenolic compounds from wastewater such as photocatalytic, microbial degradation, chemical-biological oxidation and catalytic oxidation process (Canton, et al., 2003; Feng and Li, 2003; Ksibi, et al., 2003; Seetharam and Saville, 2003; Tukač, et al., 2003). However, the adsorption process appears to be the most applicable method for removing trace amount of contaminant from wastewater effluent (Podkościelny, et al., 2003).

Adsorption process is broadly used for removal of odor, oil, colours and organic contaminants from liquid-phase system. The potential of granular and powdered activated carbon have been proven as an effective adsorbent used in adsorption technology over the century. It provides large surface area, high adsorption capacity and high degree of surface reactivity (Malik, 2003). However, the adsorption system relies on some other factors which include the nature of the adsorbate and adsorption condition such as pH and temperature. The physical properties of adsorbate depend on its polarity, hydrophobicity and the molecular size (Salame and Bandosz, 2003; Weber, 1985)

The objective of the present study was to investigate the adsorption equilibrium of phenolic compounds namely, phenol, 3-chlorophenol and o-cresol on granular activated carbon. Laboratory batch system was conducted to evaluate the adsorption capacity of the adsorbent using both Langmuir and Freundlich isotherm model. The effects of contacts time and initial adsorbate concentration were studied for the particular adsorbate-adsorbent system.

2.0 MATERIAL AND METHOD

The adsorbent used was Norit Granular Activated Carbon 1240 (NAC 1240). This commercial activated carbon is produced by steam activation of selected grades of coal. The properties of NAC 1240 were characterized using Autosorb I (Quantachrome, USA) and presented by Table 1. The activated carbon was dried overnight in the oven at temperature of 110°C to remove any moisture content. Phenol (>99.5%) was purchased from Merck, Germany while 3-chlorophenol (>95%) and o-cresol (99.5%) were obtained from Fluka, Switzerland. Their physical properties are summarized in Table 2.

Table 1.
Properties of the NAC 1240

Property	Value
Multi-point BET, m ² /g	7.783 × 10 ²
Langmuir surface area, m ² /g	1.503 × 10 ³
Average pore diameter, nm	2.716

Table 2.
Physical Properties of the Phenolic Compounds

Component	Phenol	3-Chlorophenol	O-cresol
Molecular Weight	94.11	128.56	108.13
Boiling Point	181.4 °C	214 °C	190.8 °C
Specific Gravity	1.071	1.268	1.048
Solubility* (H ₂ O)	8.2	2.6	2.5

* per 100 parts by weight of water (g/100g)

A 1000 ppm adsorbate stock solution was prepared by dissolving a desired amount of solute in deionized water in a volumetric flask. Single component experimental test was conducted using conventional batch mode system. The stock solution was then diluted to 8 different solute concentrations in a range between 25-200 mg/l in 250 ml volumetric flask. 0.2 g of adsorbent was added to a series of 250 ml glass-stoppered flasks filled with 200 ml diluted solutions. The glass-stoppered flasks were then placed in a water bath shaker and shaken at 120 rpm and constant temperature of 30 °C until equilibrium condition was attained. At desired time interval, the remaining concentrations of all samples were analyzed using Uv/Vis spectrophotometer (Shimadzu, UV-1601)

The amount of solute adsorbed per unit weight of activated carbon (mg/g) was calculated according to the equation:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (1)$$

where C_o and C_e are initial and equilibrium adsorbate-concentration (mg/l), respectively, V is volume of solution (l) and W is weight of adsorbent (g).

3.0 RESULTS AND DISCUSSION

3.1 Effect of Initial Concentration

The adsorption of phenol, 3-chlorophenol and o-cresol reached the equilibrium condition after 25 min adsorption time. Previous data on the adsorption kinetics of phenolics compounds using activated carbon have shown a wide range of adsorption time. Tseng et al. (2003) reported that the adsorption of phenol using pinewood-based activated carbons was complete after 4 days. While, Jung, et al. (2001) found that a batch studied on adsorption of phenol and chlorophenol using four different commercial activated carbons reached the equilibrium state within 1 h. In the present study, the percentage of phenol adsorbed at the equilibrium time was almost 90%, whereas 99% for both 3-chlorophenol and o-cresol for initial concentration of 25 and 50 mg/l. The percentage of adsorption decreased as the initial concentration increased. Figures 1-3 show the amount of solute adsorbed for all the three phenolics

components. It could be observed that an increase in initial concentration of solute results in increasing of solute uptake. Higher initial concentration would increase the overall the mass transfer driving force of adsorbate between liquid and solid phase (Banat, et al., 2000). As a result, there is an increase in interaction of adsorbate and adsorbent which consequently, enhance the adsorption process.

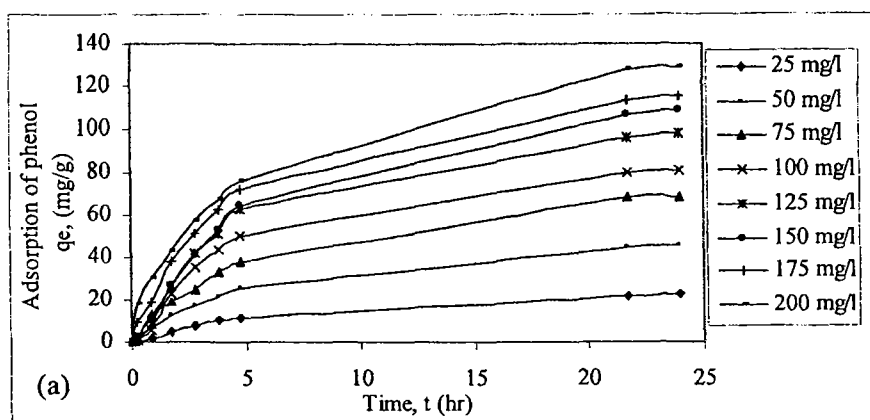


Fig.1. Effect of initial concentrations of phenol on the adsorption onto NAC 1240 at 30 °C

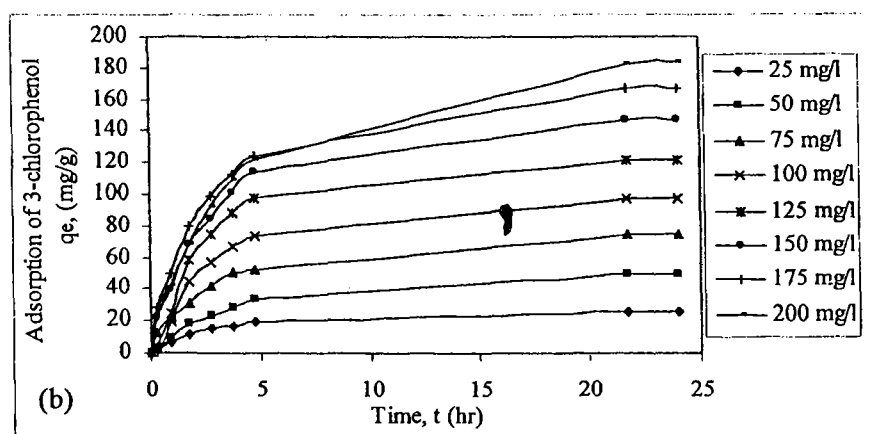


Fig.2. Effect of initial concentrations of 3-chlorophenol on the adsorption onto NAC 1240 at 30 °C

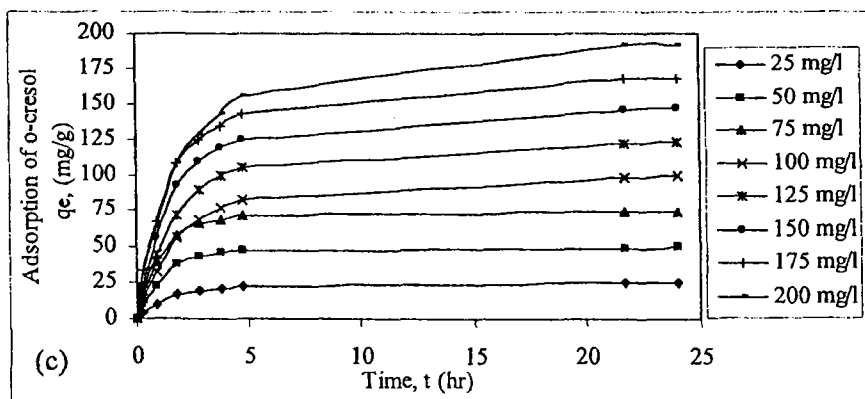


Fig.3. Effect of initial concentrations of o-cresol on the adsorption onto NAC 1240 at 30 °C

Adsorption Isotherm

The adsorption isotherm defines the functional equilibrium distribution with concentration of adsorbate in solution at constant temperature (Weber Jr., 1985). It is very useful to explain the interaction between adsorbate and adsorbent and important for prediction in modeling procedures of adsorption system. Figure 4

shows the typical adsorption isotherm which indicates that the systems studied were a nonlinear relationship characteristic of favourable adsorption.

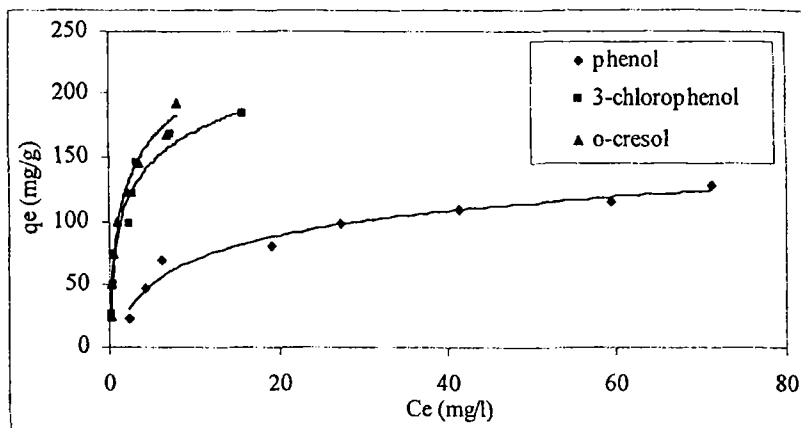


Fig.4. Adsorption isotherm of phenolic compounds by NAC 1240 at 30 °C.

The adsorption equilibrium data were then analyzed by Langmuir and Freundlich isotherm models. Both models were frequently used in literatures to describe the relationship between the amount of solute adsorbed and its equilibrium concentration for monolayer adsorption system. The linear form of Langmuir isotherm is represent by,

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_e} \quad (2)$$

where, q_e is the isotherm amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), Q (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ as shown in Figure 5.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , defined as, (Weber and Chakkravorti, 1974)

$$R_L = \frac{1}{(1 + bC_o)} \quad (3)$$

where, C_o is the highest initial solute concentration and b is the Langmuir's adsorption constant (l/mg).

The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

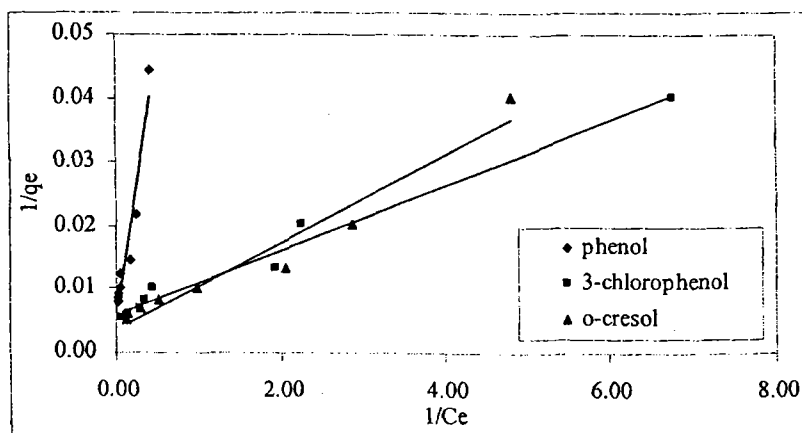


Fig.5. Langmuir adsorption isotherm of phenolic compounds adsorption on NAC 1240 at 30 °C.

The linear form of the Freundlich isotherm model is according to the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F , $(\text{mg/g})(\text{l/mg})^{1/n}$ and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. The values of K_F and $1/n$ can be obtained from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$ as shown in Figure 6.

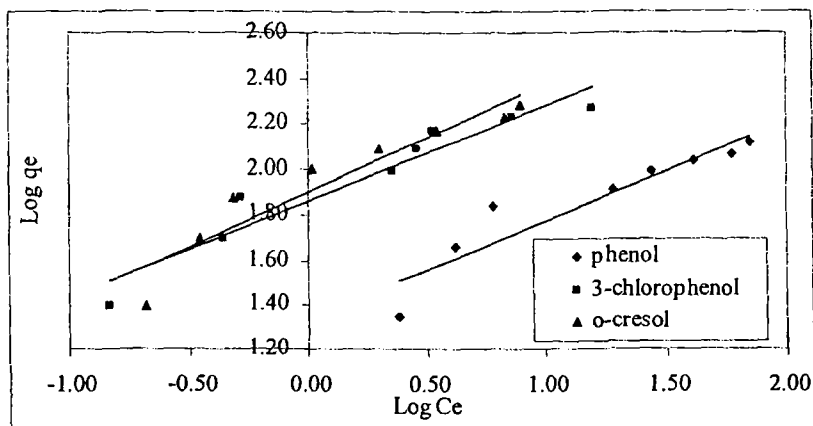


Fig.6. Freundlich adsorption isotherm of phenolic compounds adsorption on NAC 1240 at 30 °C.

The Langmuir and Freundlich constants are summarized in Table 3. By comparing the correlation coefficient values, R^2 of the linear plots, it could be observed that the adsorption equilibrium data of phenolic compounds was best described by Langmuir isotherm model as compared to Freundlich model. The calculated dimensionless separation factors, R_L are 0.062, 0.004 and 0.009 for phenol, 3-chlorophenol and o-cresol, respectively. The values are less than 1 and greater than 0, indicate that the present adsorption systems were favourable for the range of initial concentration studied.

Table 3.
Langmuir and Freundlich constants for the adsorption of phenolic compounds.

Component	Langmuir Isotherm Model			Freundlich Isotherm Model		
	Q (mg/g)	b (l/mg)	R^2	K_F (mg/g) (l/mg) ^{1/n}	n	R^2
Phenol	161.290	0.075	0.93	3.855	2.344	0.88
3-Chlorophenol	166.667	1.177	0.98	6.420	2.382	0.92
O-cresol	270.270	0.536	0.95	6.667	2.096	0.90

It is also apparent that the adsorption capacity, Q , (mg/g) increased with the order of o-cresol > 3-chlorophenol > phenol. The solubility of solute in the solvent/water has a significant effect to the adsorption process. The solubility of phenolic compound in this present studied follow this order, phenol > 3-chlorophenol > o-cresol. The higher of solute polarity as well as its solubility to the respect of solvent will decrease the tendency of adsorbate to be adsorbed from that aqueous phase. The bonding between adsorbate and water must be broken before the adsorption process can occurred (Weber Jr., 1985). Basically, greater solubility provides stronger bonding between adsorbate and adsorbent. Thus, phenol with the higher solubility as compared to 3-chlorophenol and o-cresol has the lowest adsorption capacity. The effect of solute solubility in water explained the adsorption capacity of phenolic compound studied which followed the trend, phenol < 3-chlorophenol < o-cresol.

4.0 CONCLUSIONS

Phenol, 3-chlorophenol and o-cresol were found to adsorb strongly onto NAC 1240. The experimental batch study indicates that equilibrium time required for the adsorption of phenolic compound on NAC 1240 was almost 25 hours. Adsorption behavior of the three adsorbate-adsorbant systems was described very well by Langmuir isotherm model. The adsorption capacity of the particular system was found to be affected by the solubility of the adsorbate.

5.0 ACKNOWLEDGMENT

The authors acknowledge the research grant provided by Universiti Sains Malaysia, Penang that resulted in this article.

6.0 REFERENCES

1. Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O., Adsorption of Phenol by Bentonite. *Environ. Pollut.*, 107, 391-398, (2000).
2. Canton, C., Esplugas, S. and Casado, J., Mineralization of Phenol in Aqueous Solution by Ozonation using Iron or Copper Salts and Light. *Appl. Catal., B* 43(2), 139-149, (2003).
3. Feng, Y.J., and Li, X.Y., Electro-Catalytic Oxidation of Phenol on several Metal-oxide Electrodes in Aqueous Solution. *Water Res.*, 37(10), 2399-2407, (2003).
4. Jung, M.W., Ahn, K.H., Lee, Y., Kim, K.P., Rhee, J.S., Park, J.T. and Paeng, K.J., Adsorption Characteristics of Phenol and Chlorophenols on Granular Activated Carbon (GAC). *Microchem. J.* 70, 123-131, (2001).
5. Ksibi, M., Zemzemi, A. and Boukchina, R. Photocatalytic Degradability of Substituted Phenols over UV Irradiated TiO₂. *J. Photochem. and Photobiol., A* 159(1), 61-70, (2003).
6. Malik, P.K., Use of Activated Carbons Prepared from Sawdust and Rice-husk for Adsorption of Acid Dyes: a case study of Acid Yellow 36. *Dye. Pig.*, 56, 239-249, (2003).
7. Podkościelny, P., Dądrowski, A. and Marijuk, O.V., Heterogeneity of Active Carbons in Adsorption of Phenol Aqueous Solutions, *Appl. Surface Sci.*, 205, 297-303, (2003).
8. Salame, I.I. and Bandosz, T.J., Role of Surface Chemistry in Adsorption of Phenol on Activated Carbons. *J. Colloid and Interface Sci.*, 264, 307-312, (2003).
9. Seetharam, G.B. and Saville, B.A. Degradation of Phenol using Tyrosinase Immobilized on Siliceous Supports. *Water Res.*, 37(2), 436-440, (2003).
10. Tseng, R.L., Wu, F.C. and Juang, R.S., Liquid-phase Adsorption of Dyes and Phenols using Pinewood-based Activated Carbons. *Carbon*, 41, 487-495, (2003).
11. Tukač, V., Hanika, J. and Chyba, V. Periodic State of Wet Oxidation in Trickle-Bed Reactor. *Catalysis Today*, Volume 79-80, 427-431, (2003).
12. Weber Jr., W.J. In *Adsorption Technology: A Step-by-step Approach to Process Evaluation and Application*; Slekjo, F. L., New York: Marcel Dekker, Inc., 1-35, (1985).
13. Weber, T.W. and Chakkravorti, P. Pore and Diffusion Models for Fixed-bed Adsorbers. *AIChE J.* 20, 228, (1974).