SINGLE AND BINARY ADSORPTION OF PHENOL AND 3-CHLOROPHENOL ONTO GRANULAR ACTIVATED CARBON

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ABSTRACT

Removal of phenol and 3-chlorophenol from single and bisolute diluted aqueous solution through adsorption on commercial granular activated carbon were experimentally investigated. The laboratory batch system studies were conducted at temperature of 30°C in water-bath shaker at 120 rpm rotation speed and for initial concentrations of 25-200 mg/l. The effects of initial concentration and adsorption time were evaluated. Single equilibrium data for both phenolic compounds were best described by Langmuir isotherm model. Thus, the extended Langmuir isotherm was applied to predict the extent of binary adsorption process using the previously obtained adsorption parameters of both single solute systems. The competitive adsorption behaviour between the two solutes has been found to be effected mainly by the molecular size, solubility and polarity of the adsorbate.

Keywords *: activated carbon, adsorption isotherm, binary adsorption, phenol, 3-chlorophenol.*

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1. Introduction

A fast growing of chemical and petrochemical industries over the world has generated a large amount of destructive waste containing organic contaminant. The concentration of phenol and chlorinated phenol has been found ranged between 6 to 7000 ppm in industrial wastewater streams. The contamination of surface and ground water by trace amount of phenolic compounds cause severe affect to the aquatic life as well as human health. Therefore, 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 discharged. Many efforts have been proposed on methods for removal of phenolic compounds from industrial effluent such as photocatalytic, microbial degradation, chemical-biological oxidation and catalytic oxidation process.[1-4]

Adsorption method is widely used for removal of odor, oil, colours and organic contaminants from liquid-phase system. This process has been proven as an effective method for bringing down trace amount of organic contaminants to the required low limit. The potential of granular and powdered activated carbon has been verified as an effective adsorbent used in adsorption technology. It provides large surface area, high adsorption capacity and high degree of surface reactivity.[5] However, the adsorption system relies on some other factors which include the nature of the adsorbate. The physical properties of adsorbate depend on its polarity, hydrophobicity and the molecular size.[6,7]

In the actual industrial case studies, the effluent stream contains a mixture of several impurities. Thus, multi-component adsorption system is the most commonly process applied in wastewater purification.[8] Recently, multi-component adsorption process has been the

subject of interest among the researchers.[8] Therefore, this studies was performed to investigate the adsorption equilibrium of phenolic compounds namely, phenol and 3-chlorophenol on granular activated carbon. Further, the constants parameters obtained from single adsorption equilibrium data were used to predict the binary adsorption behaviour of phenol and 3-chlorophenol. The effects of contacts time and initial adsorbate concentration were studied for the particular adsorbate-adsorbent system.

2. Experimental

2.1 Materials and chemicals

The adsorbent used was Granular Activated Carbon 1240 (NAC 1240) supplied by Norit, Nederland B.V., The Netherlands. 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 I. Phenol (>99.5% purity) was purchased from Merck, Germany while 3CP (>95% purity) was obtained from Fluka, Switzerland. Their physical properties are summarized in TABLE II.

TABLE I: 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 II: Physical Properties of the Adsorbates.

Component	Phenol	3-Chlorophenol
Molecular Weight	94.11	128.56
Boiling Point	181.4 °C	214 °C
Specific Gravity	1.071	1.268
Solubility* (H_2O)	8.2	2.6

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

2.2 Single adsorption system

Single system test was conducted using conventional batch system. Several different initial concentrations between 25-200 mg/l were filled in a series of 250 ml glass-stoppered conical flasks. 0.2 g of adsorbent was added to flasks filled with 200 ml aqueous solutions. The glass-stoppered conical flasks were then placed in a water bath-shaker and shaken at 120 rpm and constant temperature of 30 °C. At desired time interval, the remaining concentrations of all samples were analyzed using UV/Vis spectrophotometer (Shimadzu, UV-1601) until equilibrium condition was attained.

2.3 Binary adsorption system

For binary adsorption system, several initial concentrations of phenol solution were prepared in 8 different glass-stoppered conical flasks with the presence of constant initial concentration of 25 mg/l of 3-chlorophenol in each flask. Next, the experiment was carried out following the steps as for single system adsorption process. The remaining concentrations of both solutions were also analyzed using UV/Vis spectrophotometer (Shimadzu, UV-1601)

through the multi-component determination option. This model of UV/Vis spectrophotometer equipped with operational analysis of up to 8 different components simultaneously. The experiments were repeated for other constant initial concentrations of 3-chlorophenol, which are 100 and 200 mg/l. The tests were repeated over again in order to study the adsorption behaviour of 3-clorophenol in different constant initial concentrations of phenol (25, 100 and 200 mg/l).

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. Results and discussion

3.1 Effect of Initial Concentration

The equilibrium time required by single solute adsorption of phenol and 3-chlorophenol were about 25 hours. The percentage of phenol and 3-chlorophenol adsorbed at this equilibrium time were almost 90%, and 99%, respectively for initial concentrations of 25 and 50 mg/l. The percentage of removal decreases as the initial concentration of solute increase. This is due to the limited adsorption sites for bulk solution of higher initial concentration of solute to adsorb when the system reached the equilibrium stage. Besides, it could be observed that an increase in initial concentration of solute results in increasing in the amount of solute uptake (mass of adsorbate/mass of adsorbent). Higher initial concentration would increases the overall the mass transfer driving force of adsorbate between liquid and solid phase.[9] As a result, there is an increase in interaction of adsorbate and adsorbent which consequently, enhance the adsorption process.

3.2 Single system

The adsorption isotherm defines the functional equilibrium distribution with concentration of adsorbate in solution at constant temperature.[7] It is very useful to explain the interaction between solute and adsorbent and important for prediction in modeling procedures of adsorption system. Several models (Langmuir, Freundlich and Brunauer, Emmett and Teller isotherm) were used to fit the equilibrium adsorption data of the present study. It has been found that the collected data was fitted very well using Langmuir isotherm models. The Langmuir equation is presented by:

$$q_e = \frac{bq^o C_e}{1 + bC_e} \quad (2)$$

where, q_e is the isotherm amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), q^o (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. The theoretical model was derived by following several important assumptions:

(i) Molecules are adsorbed at a fixed number of well-defined sites.
(ii) Each site can hold one adsorbate molecule; monolayer adsorption
(iii) All sites are energetically equivalent

(iv) There is no interaction between molecules adsorbed on neighboring sites

The linearized equation of Langmuir model is as shown by Equation 3. The constant value of q^o will be obtained from the slope of linear plot of $1/q_e$ versus $1/C_e$ as shown by FIGURE III.

$$\frac{1}{q_e} = \frac{1}{q^o b C_e} + \frac{1}{q^o} \tag{3}$$

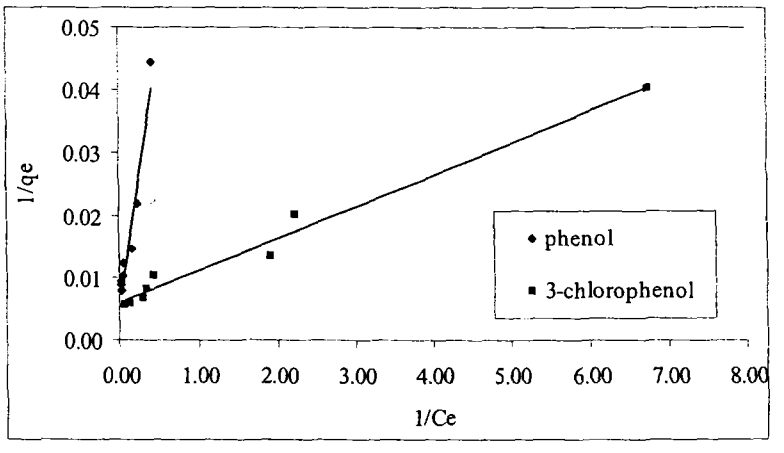

FIGURE I: Langmuir Adsorption Isotherm of Phenolic Compounds Adsorption on NAC 1240 at 30 °C.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as[10],

$$R_L = \frac{1}{(1 + bC_o)} \tag{4}$$

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).
The Langmuir constants are summarized in TABLE III. The correlation coefficient values, R^2 of the linear plots proved that the adsorption equilibrium data of phenolic compounds were well described by Langmuir isotherm model. The calculated dimensionless separation factors, R_L are 0.062 and 0.004 for phenol and 3-chlorophenol, 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 III: Langmuir Constants for the Adsorption of Phenol and 3-Chlorophenol.

Component	q^o (mg/g)	b (l/mg)	R^2	R_L
Phenol	161.290	0.075	0.93	0.062
3-Chlorophenol	166.667	1.177	0.98	0.004

The adsorption capacity, q°, (mg/g) of 3-chlorphenol is higher than phenol. This is due the different of nature of adsorbates. The higher of phenol polarity as well as its solubility to the respect of solvent used decrease its tendency to be adsorbed from that aqueous phase.[7] Therefore, the adsorption capacity of phenol is slightly lower as compared to 3-chlorophenol.

3.3 Extended Langmuir model

Langmuir competitive model was applied to predict the extent of binary adsorption process using the previously obtained adsorption parameters of both single solute systems. It is the most generally used model in multi-component system, which permitted derived from the basis of single component Langmuir model (Equation 2). This model assumes the similar assumption as for single solute Langmuir model. The extended Langmuir is presented by the following equation.[8]

$$q_e|_i = \frac{q_i^o b_i C_i}{1+\sum_{k=1}^{n} b_k C_k} \tag{5}$$

where C_i is the equilibrium concentration of species i and C_k is the equilibrium concentration of all other adsorbing species in the solution, while q_i^o, b_i and b_k are constants obtained from single component studies for particular adsorbent-adsorbate system. Therefore, the amount of solute adsorbed were calculated by substituting the constant values in TABLE I into the Equation 6 and presented by FIGURE II and III for each different system.

$$q_{e,1} = \frac{q_1^o b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{6}$$

$$q_{e,2} = \frac{q_2^o b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{7}$$

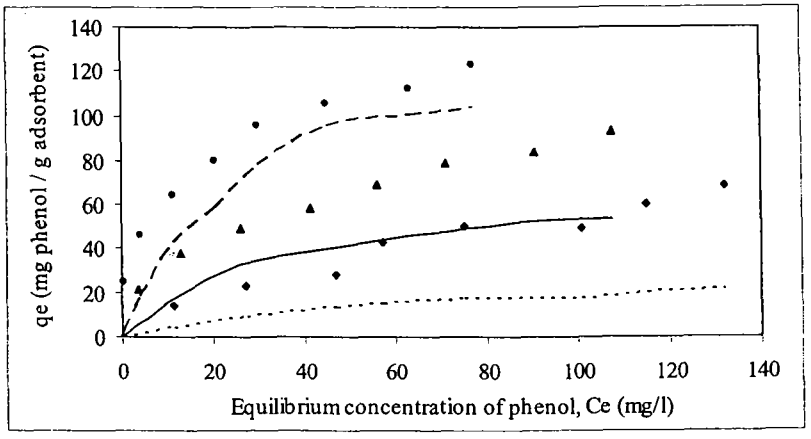

FIGURE II: Extended Langmuir Analysis for Phenol in Binary System.
●, (phenol + 25 mg/l 3CP) experimental; ▲, (phenol + 100 mg/l 3CP) experimental; ♦, (phenol + 200 mg/l 3CP) experimental; - - - (phenol + 25 mg/l 3CP) calculated; —— (phenol + 100 mg/l 3CP) calculated; ---- (phenol + 200 mg/l 3CP) calculated.

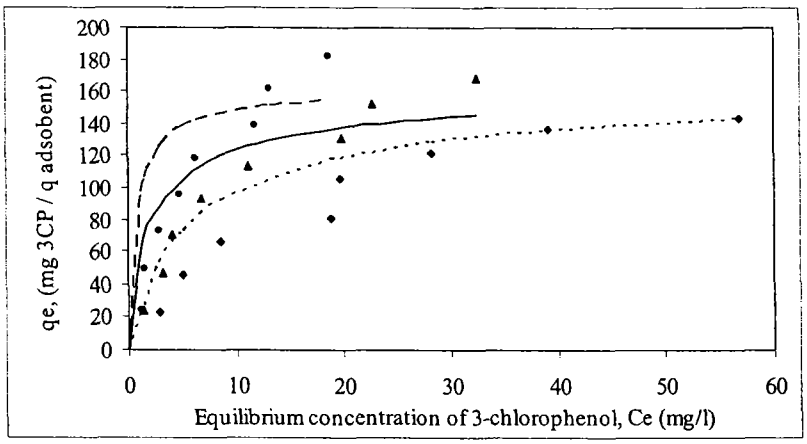

FIGURE III: Extended Langmuir Analysis for 3-Chlorophenol in Binary System.
●, (3CP + 25 mg/l phenol) experimental; ▲, (3CP + 100 mg/l phenol) experimental;
♦, (3CP + 200 mg/l phenol) experimental; - - - (3CP + 25 mg/l phenol) calculated;
—— (3CP + 100 mg/l phenol) calculated; ---- (3CP + 200 mg/l phenol) calculated.

By comparing the experimental data for all systems, it could be observed that the presence of 3-chlorophenol in binary system give a significant effect for the adsorption of phenol. However, the influence seems to be considerably small for adsorption of 3-chlorophenol in the presence of phenol solute. It is obvious that 3-chlorophenol have higher tendency to be adsorbed on NAC 1240 as compared to phenol. Therefore, the presences of 3-chlorophenol species in the system give a strong influence to overall adsorption process. Such behaviour is significantly explained by the nature of the adsorbates. 3-chlorophenol has a lower molecular polarity as well as its solubility than phenol (TABLE II). Therefore, the stronger the affinity of 3-chlorophenol to the adsorbent rather than water/solvent results a greater extent of adsorption process of 3-chlorophenol as compared to phenol. Khan et al.[8] have reported a similar observation, where chlorophenol was adsorbed strongly as compared to phenol from aqueous solution. It was explained due to strong polarity, large size and heavy molecules of chloro-derivatives.

Based on FIGURE II, the correlation between calculated and experimental data were good for phenol in 25 mg/l 3-chlorophenol but were not well fitted to the other cases which, with the presence of high initial concentration of 3-chlorophenol. The presence of high initial concentration of 3-chlorophenol is likely creating a significant competitive and interactive process between the solutes.

On the other hands, the equilibrium data results in good agreement between predicted values and the experimental observation for all systems of 3-chlorophenol in the binary system of phenol and 3-chlorophenol. Thus, the extended Langmuir model could described the adsorption behaviour of 3-chlorophenol in binary systems of the present study. The adsorption of 3-chlorophenol was thoroughly independent on the interaction of phenol molecules in binary solution of 25, 100 and 200 mg/l of phenol. This is further clarified the basic assumption of Langmuir model, where no interaction and equal independent competition were occurred in the binary aqueous phase solution.

3.4 Modified Extended Langmuir

The extended Langmuir model mentioned above was then improved and modified by Jain and Snoeyink who have developed a model that predicts sorption equilibrium, which based

on sorption without competition.[11] They assumed that a portion of adsorption takes place without competition because not all adsorption sites are available to all species. This was attributed to the chemical nature of sites and adsorbates. Therefore, they proposed an additional term to account for the competition in Langmuir theory. The first term on the right-hand side of Equation 8 refers to the amount of solute 1 adsorbed without competition with solute 2 and is given by the difference between maximum loading of the species, proportional to (q°_1-q°_2), while second term gives the amount of species 1 adsorbed in competition with 2, as described by applying the competition to the Langmuir model. The theoretical value of amount of solute adsorbed using Jain and Snoeyink modified extended Langmuir model was compared to the experimental data and was presented by FIGURE IV and V.

$$q_{e,1} = \frac{\left(q_1^o - q_2^o\right) b_1 C_{e,1}}{1 + b_1 C_{e,1}} + \frac{q_2^o b_1 C_{e,1}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{8}$$

$$q_{e,2} = \frac{q_2^o b_2 C_{e,2}}{1 + b_1 C_{e,1} + b_2 C_{e,2}} \tag{9}$$

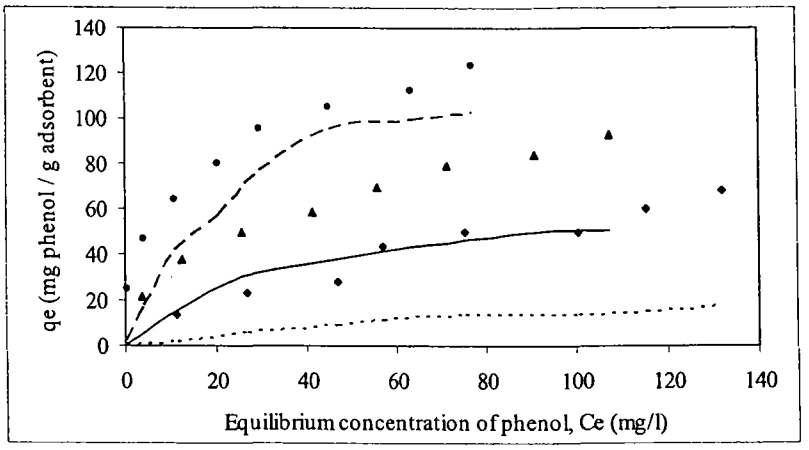

FIGURE IV: B. Jain and Snoeyink Modified Extended Langmuir Analysis for Phenol in Binary System.

●, (phenol + 25 mg/l 3CP) experimental;
▲, (phenol + 100 mg/l 3CP) experimental; ♦, (phenol + 200 mg/l 3CP) experimental;
- - - (phenol + 25 mg/l 3CP) calculated;
— (phenol + 100 mg/l 3CP) calculated; ---- (phenol + 200 mg/l 3CP) calculated.

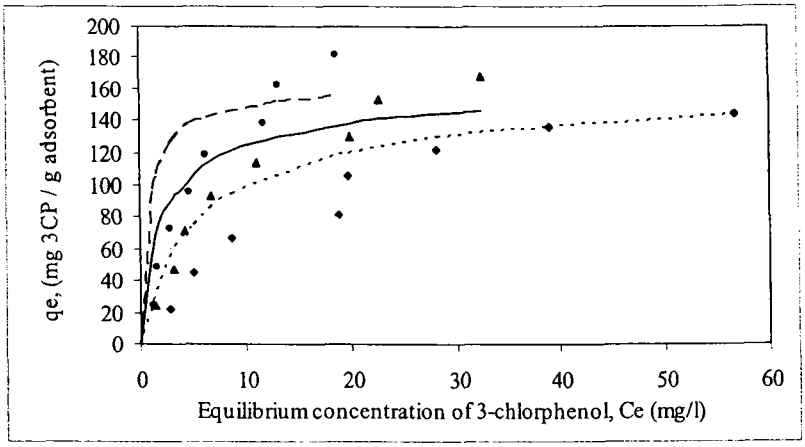

FIGURE V: B. Jain and Snoeyink Modified Extended Langmuir Analysis for 3-Chlorophenol in Binary System.
●, (3CP + 25 mg/l phenol) experimental; ▲, (3CP + 100 mg/l phenol) experimental; ♦, (3CP + 200 mg/l phenol) experimental; - - - (3CP + 25 mg/l phenol) calculated; — (3CP + 100 mg/l phenol) calculated; ---- (3CP + 200 mg/l phenol) calculated.

The model provides relatively similar observation on the adsorption system of phenol with the presence of low initial concentration of 3-chlorophenol as compared to the previously discussed model. It specified that in this case the interaction of phenol was occurred without competition with 3-chlorophenol, in view of the fact that low initial concentration of phenol does not give a significant effect to the overall adsorption process of the system. In addition, for adsorption of 3-chlorophenol in binary systems with the presence of phenol, the model prediction proposed by Jain and Snoeyink also represents fairly similar trend as the modified extended Langmuir model that has been discussed previously. The model fitted the experimental data quite good although the points are scattering. It proved that the presence of phenol in the binary aqueous solution does not give any significant to the adsorption of 3-chlorophenol. In overall, this model performs in accordance with the basis of Langmuir assumption but does not improve the extended Langmuir model for all the systems studied. The difference between maximum loading of the two species that proportional to $(q^{\circ}_1-q^{\circ}_2)$, is considerably small, resulting to this conclusion. Similar finding was observed by Choy, et al.[11] in the study of multi-component sorption of acid dyes using Filtrasorb 400. They reported that the model was not provided a satisfactory correlation of the experimental data.

4. Conclusions

Single component of phenol and 3-chlorophenol were found to adsorb strongly onto NAC 1240. The experimental batch study indicates that equilibrium time required for the adsorption of single phenolic compound on NAC 1240 was almost 25 hours. Adsorption behavior of both adsorbate-adsorbent systems was described very well by Langmuir isotherm model. The binary system of phenol in low concentration of 3-chlorophenol was well described by extended Langmuir model. The binary systems of 3-chlorophenol with the presence of phenol species with the concentration ranged between 25 to 200 mg/l was also well predicted by extended Langmuir and B. Jain and Snoeyink modified extended Langmuir model. It gives the impression that there is no interaction and equal independent competition between both species in binary adsorption process.

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6. References

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