

## LIQUID PHASE ADSORPTION ISOTHERM OF NONYL PHENOL ON ACTIVATED CARBON

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**ABSTRACT.** *In this work, the excess adsorption isotherm of nonyl phenol was measured by a combination of conventional techniques but analysed by using Langmuirian-type monolayer adsorption theory. The results showed that the excess isotherm obeyed the Langmuirian type monolayer theory and the individual equilibrium adsorption is well represented by Langmuirian type of adsorption.*

**KEYWORDS.** adsorption isotherm, nonyl phenol, activated carbon

### INTRODUCTION

Nonyl phenol is an important chemical which is widely used in various industries. For example, it is commonly used as an intermediate for the synthesis of: nonionic and anionic surfactants; antioxidants in rubber and plastics, lube oil additives, phenolic resins, rubber processing chemicals and PVC plasticizers; shale and clay stabilizers in drilling muds; in petroleum de-emulsifiers as well as in fungicides (Prager, 1995).

However, if its waste products especially phenols are improperly disposed of into environment such as rivers, the polluted water caused by this compound is very toxic to aquatic life. Therefore, removal of the products from waste-water is important.

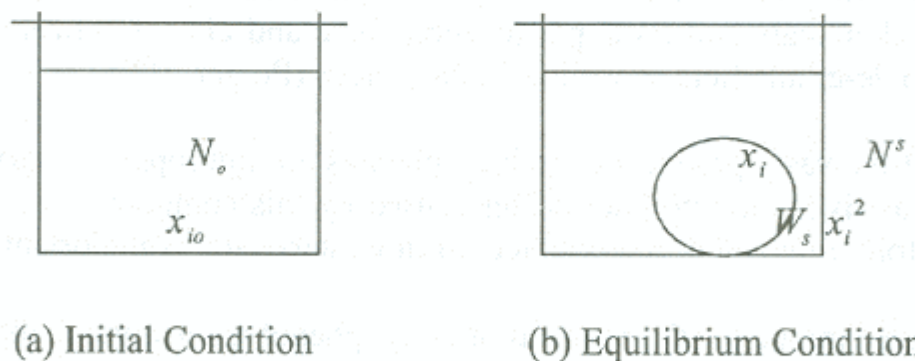
Adsorption technique for the removal of nonyl phenol from water is more feasible as it is usually present at relatively low concentrations. A number of commercially absorbents such as polymeric resin, activated carbon and porous silicate are currently available. However, literature review (Dabrowski *et al.*, 1990; Masel, 1996; Perry, 1977; Ismadji *et al.*, 2000; Perrich, 1981), indicates that activated carbon is more widely used as an absorbent for the removal of organic and inorganic contaminants from water than other materials due to its high capacity of adsorption, large surface area and porosity.

Various isotherm models are available for expressing adsorption processes (Carter, 1966; Ruthven, 1984; Masel, 1996; Perry, 1977). In this work, adsorption equilibrium is critically considered and discussed. The measurement and interpretation of sorption equilibria are the most important initial steps in the analysis of any sorption separation. In cases where

equilibrium is not closely approached, minor errors in the measurement of the static isotherm can lead to substantial errors in the dynamic loading and breakthrough time (Bono *et al*, 1989; 2003; Farhadpour, 1996a; 1984; 1988 & 1996b). Adsorption isotherm measurement includes gas phase adsorption system and liquid phase adsorption system. For the gas system, classical static gravimetric and Brunauer-Emmett-Teller (BET) theory is used for measuring adsorption but it is impeded by the unavoidable capillary condensation of the saturated vapour (Bono, 1989). Meanwhile, in the liquid system, the method used for gas system is not suitable since the adsorbed phase is not open to direct measurement such as concentration and volume change, due to the requirement for details of physical properties of adsorbent. In addition, most of the physical properties such as solid density especially activated carbon are not well known so far. The primary objective of this investigation is to study the adsorption isotherm for nonyl phenol, water and activated carbon system.

## MATERIALS AND METHODS

Both nonyl phenol and powdered commercial activated carbon used in this research were of industrial grade. The adsorption isotherm is determined by contacting with a known quantity of solution with initial mass fraction  $x_{io}$  and with a known mass,  $W_s$ , of the dry adsorbent in a closed vessel (Bono, 1989; Bono *et al*, 2003; Chu *et al*, 2003; Dabrowski, 1990; Farhadpour *et al*, 1996; 1984; 1988; 1996; Nagy, 1991; Ismadji *et al*, 2000) (Fig. 1) and the free liquid fraction  $x_i$  is determined after equilibrium has been achieved.



**Figure 1. Excess Isotherm Measurement**

The experimentally determined quantity is normally,

$$\Gamma_i = \frac{N_o(x_{io} - x_i)}{W_s} \quad i = 1, \dots, N \quad (1)$$

which is a measure of relative strength of adsorption or excess adsorption of a component.



The isotherms for the system nonyl phenol – water/activated carbon were determined by these techniques at room temperature. The solutions were made up by weight using pure distilled water. Prior to contact with the liquid, the activated carbon powder was ensured to be free from moisture and their dry weight  $W_s$  measured and recorded. All the activated carbon used was fresh carbon, which means it contained no nonyl phenol. A known weight  $W_o$  of a liquid with an initial weight fraction  $w_{io}$  was added to the activated carbon. The suspension was stirred using the magnetic stirrer for at least 45 minutes and was equilibrated for a minimum of 24 hours. At equilibrium, the samples of the free liquid were withdrawn through filter paper. The equilibrium mass fraction  $w_i$  was measured by a differential refractometer.

Nonyl Phenol was diluted into different weight fractions  $w_{io}$  and the initial refractive indices were read using a refractometer, model 2WAJ, and were recorded. Mass for 100 ml of each of the solutions so-prepared was measured and recorded.

100 mL of solution was then poured into separate 250 mL Erlenmeyer flasks with standard ground glass joints. Each Erlenmeyer flask contained exactly 5 g of activated carbon and a magnetic stirring bar was placed into each flask. The flasks were sealed and were stirred vigorously for approximately 45 minutes. The suspensions were then left to equilibrate for 48 hours. Subsequently, these suspensions were filtered. The refractive index for each individual equilibrated sample was read and recorded. These values were used to determine the final concentration value (mass fraction) for each sample with the aid of a calibration curve which had been obtained earlier.

By using the formula in equation (1), the adsorption of nonyl phenol on activated carbon was calculated and used for isotherm plot.

## RESULTS AND DISCUSSION

In most of the cases (Bono,1989; Bono *et al*, 2003;Chu *et al*, 2003; Farhapour & Bono,1996; Farhapour & Bono,1984; Farhapour & Bono,1988 & 1996) where the adsorption

isotherm is taken as  $N_o(x_{io} - x_i)/W_s$ , the equilibrium curve could be grossly in error. This may be close to the true value if  $x_i$  is very small. But the question is how small a value of can be considered as small. Therefore, by using a simple material balance (Table 1), equation 3 was established.

**Table 1. Material Balance of adsorption in liquid phase**

For each adsorbent, $W_s$	Initial: total mole of component i	Equilibrium condition : total mole of component i
Liquid	$x_{io} \cdot N_o$	$(N_o - N_s \cdot W_s) x_i$
Solid	0	$x_i^s \cdot N_s \cdot W_s$
Total component i	$x_{io} \cdot N_o$	$(N_o - N_s \cdot W_s) x_i + x_i^s \cdot N_s \cdot W_s$

$$x_{io} \cdot N_o = (N_o - N_s \cdot W_s) x_i + x_i^s \cdot N_s \cdot W_s \quad (2)$$

and rearranged to yield equation (3)

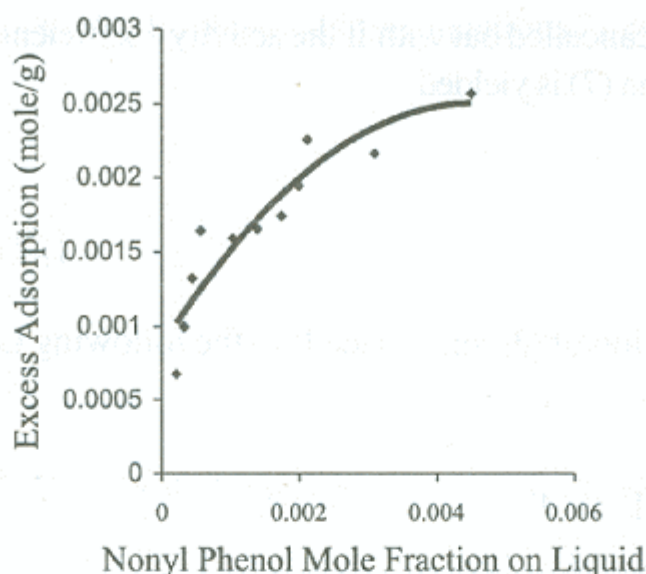
$$\frac{N_o(x_{io} - x_i)}{W_s} = N_s(x_i^s - x_i) \quad (3)$$

By considering a binary mixture and taking into account of the material balance of table 1, equation (1) can be rearranged to

$$\Gamma_i = \frac{N_o(x_{io} - x_i)}{W_s} = (1 - x_1)n_1^s - n_2^s x_1 \quad (4)$$

The experimental excess isotherm are presented in Figure. 2.





**Figure 2. Excess adsorption isotherm for {nonylphenol-water} on activated carbon at 25°C.**

The isotherm may conform to type 2 classical classification of Schay and Nagy (Oscik, 1982). The shape of this excess isotherm shows that it is a favorable type of adsorption. The

value  $N_s$  can be taken as  $N_o(x_{io} - x_i)/W_s$  in between  $x_i = 0$  to where excess isotherm reach the maximum value. Over the value for where excess isotherm less the maximum, the monolayer theory should be used (Bono, 1989; Bono *et al*, 2003; Chu *et al*, 2003).

The theory is based on the nature of adsorption to predict the absolute individual adsorption from the knowledge of the excess isotherm alone. At the simplest level, binary adsorption (Bono, 1989; Bono *et al*, 2003; Chu *et al*, 2003; Farhadpour *et al*, 1996a; 1984; 1988 & 1996b) can be viewed as an exchange reaction as shown in equation (5),



Under these assumptions, it can be established by an analysis analogous to that used in the classical theory of surface adsorption. The equilibrium constant for the above exchange reaction can be defined as shown in equation (6),

$$K = \frac{x_1^s x_2 \gamma_1^s \gamma_2}{x_1 x_2^s \gamma_1 \gamma_2^s} \quad (6)$$

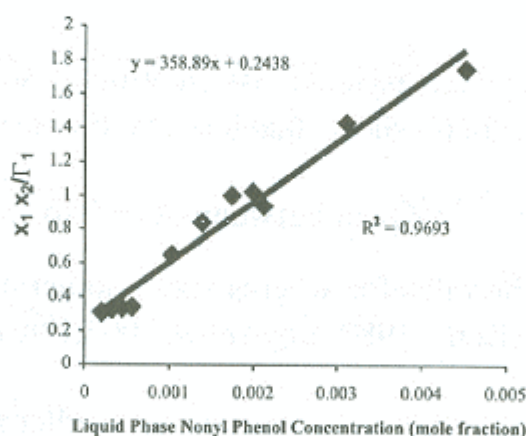
For systems where can be cancelled out with if the activity coefficient in the bulk and adsorbed phase are identical, equation (7) is yielded

$$K = \frac{x_1^s x_2}{x_1 x_2^s} \quad (7)$$

The combination of equation of (3) and (7) leads to the following Langmuir-type expression as shown in equation (8),

$$\frac{x_1 x_2}{\Gamma_i} = \frac{1}{N_s} x_1 + \frac{1}{N_s} \frac{1}{(K-1)} \quad (8)$$

Then, a plot of versus yielded a straight line as shown in Fig.3.



**Figure 3. Excess isotherm of nonyl phenol-water onto activated carbon according Langmuir monolayer theory at 25 !.**

It shows that all the data satisfactory fit the Langmuir relation indicating the adsorption of nonyl phenol from wastewater on activated carbon as the monolayer adsorption where value of  $N_s$  and  $K$  are obtained from the least square method (Table 2).

**Table 2. Saturation value of adsorption  $N^s$  and adsorption equilibria constant  $K$  according to Langmur monolayer theory**

$N_s$	1/358.89
$K$	1473.10

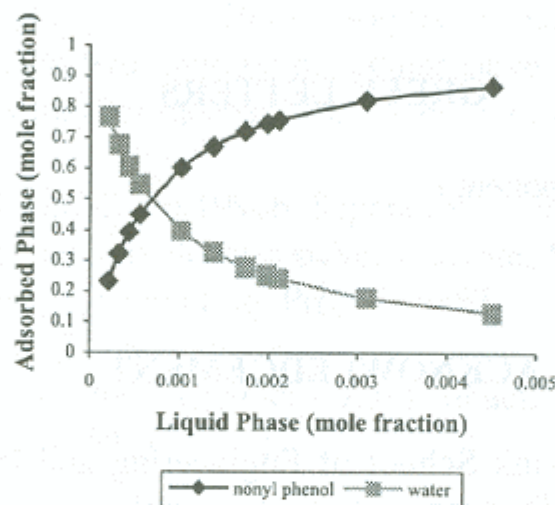
The individual isotherm can also be obtained from equation (7), rearranged and then yielding equation (9) and (10),

$$x_1^s = \frac{Kx_1}{\{1 + (K - 1)x_1\}} \quad (9)$$

and

$$x_2^s = 1 - x_1^s \quad (10)$$

and the adsorption isotherms for nonyl phenol and water on activated carbon at 25 °C are then presented in Fig. 4.



**Figure 4. Individual adsorption isotherm for nonyl phenol and water on activated carbon at 25 °C..**

## CONCLUSION

The experimental measurement of the adsorption isotherm for liquid mixture of nonyl phenol and water was carried out. It was shown that the absolute adsorption of nonyl phenol can only be approximated by the easily measured excess adsorption isotherm,  $\Gamma_i$  at liquid concentration below a critical mole fraction  $x_i$ , where excess isotherm reached a maximum value. At higher nonyl phenol concentrations over the value of where excess isotherm falls below the maximum, the excess and absolute adsorption isotherm deviate significantly and the use of the excess isotherm can lead to significant error. Consequently, the monolayer theory was proposed and the results obtained are shown to be satisfactory fitted to Langmuirian type of adsorption.

## NOMENCLATURE



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- $K$  equilibrium constant  
 $n_1^s$  absolute adsorption of component 1  
 $n_2^s$  absolute adsorption of component 2  
 $x_i$  mass fraction of  $i$  in bulk fluid  
 $x_1^s$  mass fraction of 1 in adsorbed fluid  
 $x_2^s$  mass fraction of 2 in adsorbed fluid  
 $W_s$  weight of solid  
 $N_s$  total mole of components absorbed.  
 $N_o$  total mole of solution

## GREEK LETTERS

- $\Gamma_i$  excess adsorption of component  $i$

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