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# Adsorption Isotherms for Phenol Onto Activated Carbon

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This laboratory study investigated the effectiveness of two types of activated carbons (ACs), NORIT Granular Activated Carbon (NAC 1240) and NORIT Granular Activated Carbon D10 (NAC D10), for the removal of phenol from aqueous solutions. The study was carried out under batch mode at different initial concentrations (10–60 mg/l) and at temperature of 30 °C. The adsorption isotherm parameters for the Langmuir and Freundlich models were determined using the adsorption data. It was found that both the Langmuir and the Freundlich isotherms described well the adsorption behavior of phenol on NAC D10, while the Freundlich isotherm described very well the adsorption of phenol on NAC 1240.

**Keywords:** Activated carbon (AC), adsorption, Langmuir and Freundlich isotherm models, phenol, and wastewater treatment.

## INTRODUCTION

Phenol and phenolic derivatives are the organic chemicals that appear very frequently in wastewater from almost all heavy chemical, petrochemical, and oil refining industries.

Large amounts of wastewater are usually generated during the manufacturing and processing stages of organic chemicals. The concentration of these organic matters in wastewater usually exceeds the level for safe discharge. Thus, the removal of organic compounds from wastewater has become a

priority in the management of wastewater treatment systems in chemical, petrochemical, and oil industries.

Various methods have been proposed for the removal of phenolic compounds in wastewater. These methods are often based on biochemical oxidation and solvent extraction (Streat 1998). The main limitation of these methods, however, is their low efficiency in the removal of trace-level phenols. Among the more established of these methods is the *catalytic wet air oxidation* (CWAO) which permits detoxification of hazardous substances at relatively mild conditions

**Table 1. Properties of Norit Activated Carbons, NAC 1240 and NAC D10**

Property	Value	
	NAC 1240	NAC D10
Multi-point BET, $m^2/g$	$7.783 \times 10^2$	$4.851 \times 10^2$
Langmuir surface area, $m^2/g$	$1.503 \times 10^3$	$9.914 \times 10^2$
Total pore volume, $cm^3/g$	0.529	0.343
Average pore diameter, $nm$	2.716	2.828

temperature and pressure conditions (less than 200°C and 100 bar) by using active oxidation catalysts (Imamura 1999, Matatov-Meytal and Sheintuch 1998, Levec 1997).

Likewise, a *two-step adsorption-oxidation process* for the treatment of aqueous phenolic effluents has also been reported (Polaert et al. 2002). This process is based on the use of activated carbon (AC), as adsorbent in the first step and as oxidation catalyst in the second step, in a single bifunctional reactor. The major advantage of this process is the reduction of heat consumption right at the regeneration-oxidation step, wherein a minimal amount of liquid is heated and pressurized.

Adsorption technology, however, is the method currently used for removing phenols at low concentrations. For this purpose, *nonpecific sorbents* such as activated carbons (ACs), metal oxides, silica, and ion exchange resins, have been used as well (Furuya et al. 1996, Dargaville et al. 1996, Shu et al. 1997). The major advantage of AC adsorption is that the treated adsorbent can easily be separated from the treated liquid stream. This characteristic allows easy and flexible process operation as well as reduction in process costs.

The removal of phenols from aqueous solutions may be carried out using commercial ACs (Jung et al. 2001, Colella and Armenante 1998, Uranowski et al. 1998, Ania et al. 2002) or ACs prepared from coconut shells (Iwasaki et al. 2002), date fruit pits (Abdulkrim et al. 2002), plum kernels (Wu et al. 1999), and palm seed coats (Rengaraj et al. 2002).

Thus, this study aimed to investigate, experimentally, the adsorption of phenol on two types of commercial ACs: NORIT Granular Activated Carbon (NAC 1240) and NORIT

Granular Activated Carbon D10 (NAC D10). Laboratory batch isotherm studies were conducted to evaluate the adsorption capacity of both AC types. Both the Langmuir and the Freundlich isotherm models were tested for their applicability.

## EXPERIMENTAL

### Chemical and materials

The two adsorbents used in this study were the NORIT Granular Activated Carbon (NAC 1240) and NORIT Granular Activated Carbon D10 (NAC D10). NORIT Nederland B.V. generously provided the AC samples for this study. Table 1 compares the most important properties of these two ACs.

Both carbon types were washed several times with distilled water (DW) to remove carbon fines and then dried at 110°C for 24 h. To prevent moisture readsorption by the dried carbons, they were stored with a silica gel inside a sealed bottle. Phenol (>99.5%) from Merck KGaA of Germany was used as adsorbate for the study.

### Adsorption procedure

The adsorbate stock solution was prepared by mixing a known amount of pure, crystalline solid adsorbate with deionized water to yield various desired concentrations. The adsorption experiments were carried out isothermally in static mode at  $30^\circ\text{C} \pm 1^\circ\text{C}$ .

The experiments were conducted by adding an amount of adsorbent fixed at 0.20 g to a series of 250-ml glass-stoppered flasks filled with 200 ml of diluted solutions (10–60 mg/l). These stoppered flasks were then placed in a

thermostatic shaker bath and shook at 120 rpm until equilibrium was attained. The initial and equilibrium concentrations of all liquid samples were analyzed using a UV/Vis spectrophotometer (Shimadzu UV/Vis 1601 Spectrophotometer, Japan). The amount of adsorbate on an AC sample was calculated according to the following equation:

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

where  $C_o$  and  $C_e$  are the initial and equilibrium liquid concentrations (mg/l), respectively;  $V$  is the volume of solution (l); and  $W$  is the weight of adsorbent (g).

## RESULTS AND DISCUSSION

### Adsorption time

Figures 1 and 2 show typical concentration-time profiles ( $C/C_o$  vs.  $t$ ) for the adsorption of phenol on NAC 1240 and NAC D10 at different initial concentrations, respectively. It is evident from Figure 1 that the curves obtained for NAC 1240 at the initial stage drop sharply in less than 3 h when almost 85% of the phenol had been removed, then gradually decrease until equilibrium was attained at around 24 h. For NAC D10, however, the curves drop sharply in less than 3 h when almost 96% of the phenol had been removed and equilibrium was attained in less than 24 h (refer to Figure 2).

The adsorption data for the uptake of phenol versus contact time at different initial

concentrations for both adsorbents, NAC 1240 and NAC D10 are presented in figures 3 and 4, respectively. Results indicate that the adsorption process can be considered fast because the largest amount of phenol attached to the adsorbent within the first 3 h of adsorption. It can also be seen that an increase in initial phenol concentration results in increased phenol uptake.

### Initial phenol concentration

The adsorption of phenol by activated carbons increases as the initial phenol concentration increased as shown in figures 3 and 4. Increasing the initial phenol concentration would increase the mass transfer driving force and, therefore, the rate at which phenol molecules pass from the bulk solution to the particle surface.

This reaction would result in higher phenol adsorption. However, the percentage adsorption of phenol at equilibrium is almost constant over the whole range of initial concentrations for both activated carbons as shown in Figure 5. These results suggest that both ACs are very effective for phenol adsorption.

### Adsorption Isotherms

Figure 6 shows the adsorption isotherms, the relationship between the amount of phenol adsorbed per unit mass ( $q_e$ ) of NAC 1240 and AC D10, and their final concentrations in aqueous phase ( $C_e$ ). The plots of phenol uptake against the equilibrium concentration indicate that adsorption increases with concentration.

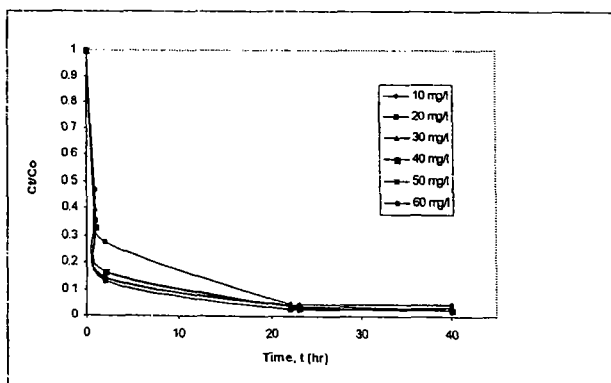


Figure 1. Concentration Time Profile of Phenol Adsorption on NAC 1240 at Different Initial Concentrations

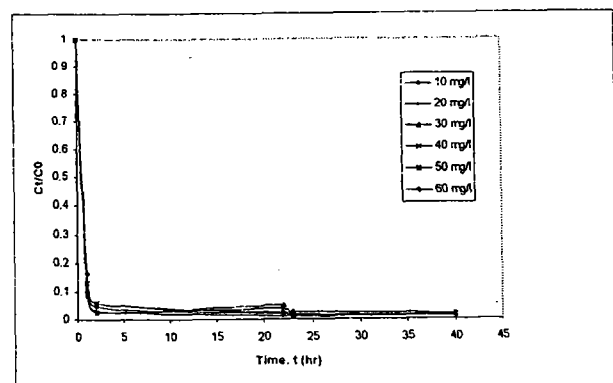


Figure 2. Concentration Time Profile of Phenol Adsorption on NAC D10 at Different Initial Concentrations

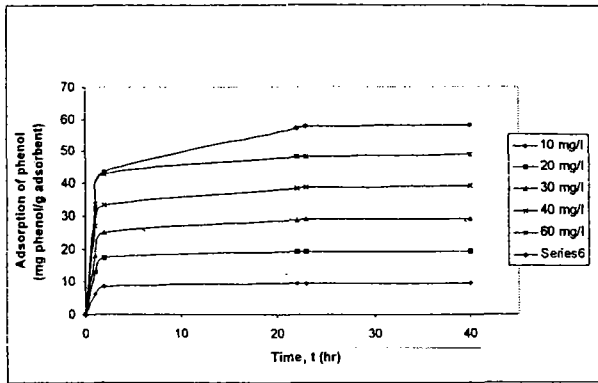


Figure 3. Adsorption of Phenol on NAC 1240 vs. Contact Time at Different Initial Concentrations at 30°C

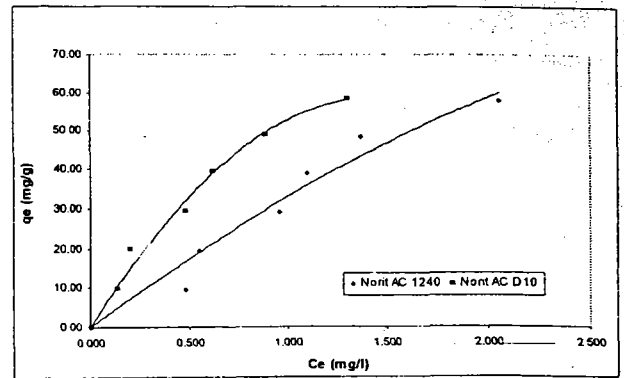


Figure 6. Adsorption Isotherm of Phenol on Both NAC 1240 and NAC D10

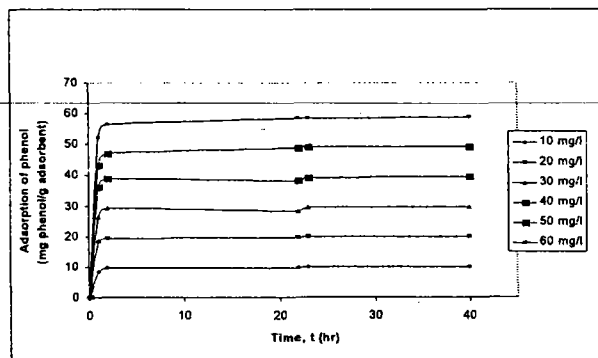


Figure 4. Adsorption of Phenol on NAC D10 vs. Contact Time at Different Initial Concentrations at 30°C

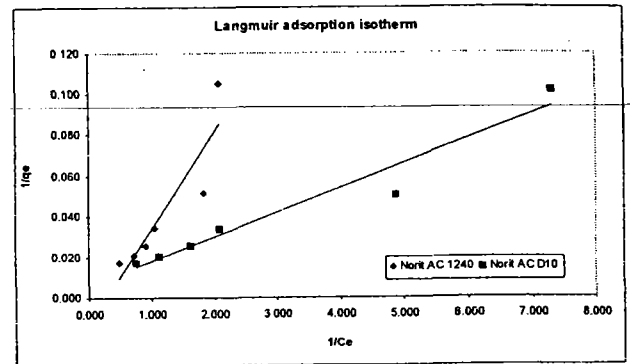


Figure 7. Langmuir Isotherm for Phenol Adsorption on NAC 1240 and NAC D10

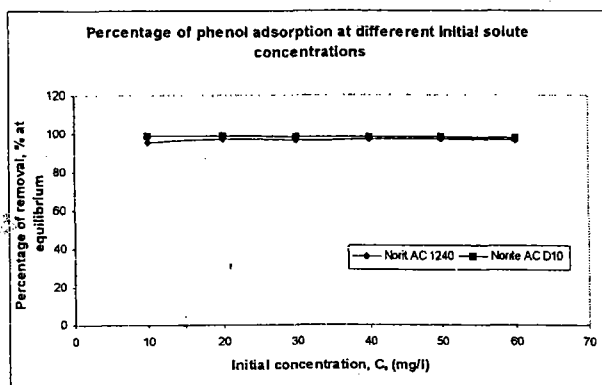


Figure 5. Relationship of Initial Phenol Concentration and Its Percent Adsorption for Both ACs

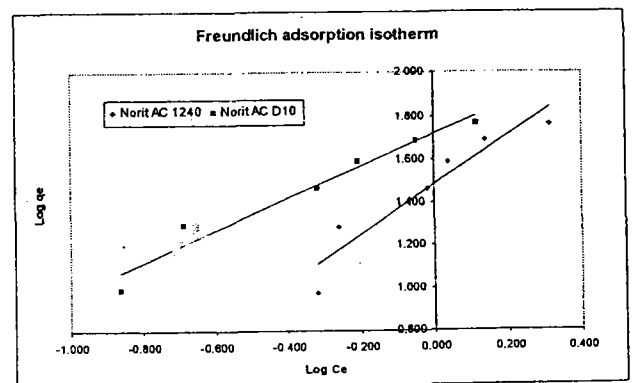


Figure 8. Freundlich Isotherm for Phenol Adsorption on NAC 1240 and NAC D10

**Table 2. Langmuir and Freundlich Constants for the Adsorption of Phenol on Activated Carbon**

Type of AC	Langmuir Isotherm Model			Freundlich Isotherm Model		
	Q (mg/g)	b (l/mg)	Correlation Coefficient, $R^2$	$K_F$ (mg/g)(l/mg) <sup>1/n</sup>	n	Correlation Coefficient $R^2$
NAC 1240	-74.074	0.285	0.829	30.395	0.87	0.899
NAC D10	166.667	0.5	0.946	52.589	1.337	0.958

Several models have been published to describe the experimental data of adsorption isotherms. Of these models, the Langmuir and Freundlich models are the most frequently employed.

Thus, in the present work, both models were used to describe the relationship between the amount of phenol adsorbed and the corresponding equilibrium concentration.

The following relation can represent the linear form of the Langmuir isotherm model:

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

where  $q_e$  is the isotherm amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/l), and  $Q$  (mg/g) and  $b$  (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively.

These constants (summarized in Table 2) 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 7. The applicability of the Langmuir isotherm suggests the monolayer coverage of phenol on the surface of NAC D10. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor,  $R_L$  defined by Hall et al. (1996) and McKay et al. (1987) as

$$R_L = \frac{1}{(1 + KC_0)} \quad (3)$$

where  $C_0$  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 value of

$R_L$  for NAC D10 was found to be at 0.0322, which suggests that the adsorption system was favorable.

The linear form of the Freundlich isotherm model is given by the following equation:

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

where  $K_F$  (mg/g)(l/mg)<sup>1/n</sup> and  $1/n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively, of the sorbent. The values of  $K_F$  and  $1/n$  can be obtained from both intercept and slope, respectively, of the linear plot of the experimental data of  $\log q_e$  versus  $\log C_e$  as illustrated in Figure 8.

The Langmuir constants  $Q$  and  $b$  and the Freundlich constants  $K_F$  and  $1/n$  are given in Table 2.

The  $R^2$  values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models describe well the adsorption behavior of phenol on NAC D10; while the Freundlich isotherm model describe very well the adsorption of phenol on NAC 1240. Similar results were previously reported for the adsorption of phenol on granular AC (Jung et al. 2001) and on organobentonites (Lin and Cheng 2002).

The negative value for the Langmuir isotherm constant for NAC 1240 indicates the inadequacy of the isotherm model to explain the adsorption process, since this constant is indicative of both the surface binding energy and monolayer coverage.

It is clear in Table 2 that the overall  $K_F$  value of NAC D10 is greater than NAC 1240, which means that the adsorption capacity of NAC D10 is greater than NAC 1240. The results show that the adsorption on the ACs used in this study is independent of the surface area (refer to Table 1).

It is well known that matching the pore size of adsorbent and the size of adsorbate molecule should be considered when explaining the adsorption process. The phenol molecular diameter is in the range of approximately 0.8–1.0 nm (Lange 1985). The average pore diameter of the ACs are approximately 2–3 times those of phenol, which means that it is easy for phenol to diffuse into the inner pores of the ACs and adsorb on the internal surfaces. Thus, the range of pore sizes is appropriate for phenol to adsorb and is not an important factor in the adsorption process.

The adsorption tendency between the ACs used, however, cannot be explained by such physical properties as surface area and pore diameter. Therefore, the adsorption characteristics of phenol on NAC 1240 and NAC D10 may be interpreted in terms of their chemical aspects.

It had been reported that the adsorption of phenol on ACs may imply an electron donor-acceptor complex or may even involve dispersion forces between  $\pi$ -electrons in phenol and  $\pi$ -electrons in ACs (Coughlin and Ezra 1986). Al-Degs et al. (2000) also explained that the differences in the capacities of adsorbents for the same adsorbate were caused by former's surface properties.

Activated carbon has high-adsorption capacity for reactivity towards a wide range of organic pollutants. This reactivity arises from the complexity of its chemical surface groups compared to those of other surfaces.

## CONCLUSIONS

Phenol was found to adsorb strongly on the surface of both commercial ACs, NAC 1240 and NAC D10.

The equilibrium time for the adsorption of phenol on NAC D10 was achieved in almost 3 h when up to 96% of phenol had already been removed from the aqueous solution. In contrast, the equilibrium time for NAC 1240 was attained in 24 h when up to 85% of phenol had been removed.

Both the Langmuir and Freundlich isotherm models described well the adsorption behavior of phenol on NAC D10; while the Freundlich

isotherm described well the isotherm adsorption of phenol on NAC 1240. The value of the dimensionless separation factor,  $R_L$  for NAC D10 was found to be at 0.0322. This value confirms that the present adsorption system reveal favorable.

## ACKNOWLEDGMENT

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## NOTATION

$b$	adsorption energy constant of the Langmuir adsorption isotherm	l/mg
$C_e$	equilibrium liquid-phase concentration	mg/l
$C_o$	initial liquid-phase concentration	mg/l
$K_F$	Freundlich isotherm constant related to the adsorption capacity	(m/g)(l/mg) <sup>1/n</sup>
$n$	Freundlich isotherm constant related to adsorption intensity	
$Q$	maximum surface coverage (formation of monolayer) of sorbent	mg/g
$q_e$	equilibrium solid-phase adsorbate concentration	mg/g
$R^2$	correlation coefficient	
$R_L$	dimensionless separation factor	
$V$	volume of solution	l
$W$	weight of adsorbent	g

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