

## Adsorption of Phenol Using Activated Carbon Adsorbent from Waste Tyres

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### ABSTRACT

The adsorption of phenol, from aqueous solutions on activated carbon from waste tyres, was studied in a batch system at different initial concentrations (100-500mg/L) at 30°C for 48 hours. The activated carbon was prepared using the two-step physiochemical activation, with potassium hydroxide (KOH) at ratio KOH/char = 5. The carbonization process was done at 800°C for 1 hour with nitrogen flow rate 150ml/min, followed by the activation with the carbon dioxide flow rate 150ml/min at 800°C for 2 hours. The adsorption isotherms were determined by shaking 0.1g of activated carbon with 100ml phenol solutions. The initial and final concentrations of phenol in aqueous solution were analyzed using the UV-Visible Spectrophotometer (Shimadzu, UV-1601) at a wavelength of 270nm. Experimental isotherm data were analyzed using the Langmuir and Freundlich isotherm models. The equilibrium data for phenol adsorption could fit both isotherm models well with the R<sup>2</sup> value of 0.9774 and 0.9895, respectively. The maximum adsorption capacity of the adsorbent obtained from the Langmuir model was up to 156.25 mg/g.

**Keywords:** Adsorption, phenol, activated carbon, adsorption capacity

### ABBREVIATIONS

- $C_o$  = initial adsorbate concentration, mg/L
- $C_e$  = equilibrium adsorbate concentration, mg/L
- $C_t$  = adsorbate concentration at time, mg/L
- $K_f$  = empirical constants depending on several environmental factors, (mg/g)(L/mg)<sup>1/n</sup>
- $K_L$  = Langmuir constant related with affinity of the points of union (L/mg)
- $n$  = empirical parameter representing the energetic heterogeneity of the adsorption sites
- $Q^o$  = maximum adsorption capacity corresponding to complete monolayer coverage (mg/g)
- $q_e$  = adsorption capacity at equilibrium solute concentration,  $C_e$  (mg/g)
- $R^2$  = correlation coefficient
- $V$  = volume of solution, L
- $w$  = weight of adsorbent, g

### INTRODUCTION

Phenol and related compounds are toxic to human and aquatic life, creating an oxygen demand in receiving waters. Chronic toxic effects, due to the phenol pollution reported in humans, include vomiting, anorexia, difficulty in swallowing, liver and kidney damage, headache, fainting and other mental disturbances (Fawell, 1988). The demand for the removal of organic compounds including phenol has been increased by the increasing the industrial wastewaters. The Department

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of Environment (DOE) of Malaysia has set the maximum concentration of phenol as 0.001mg/L for standard A and 1.0mg/L for standard B in the industrial effluent discharge to Malaysia inland waters (Environment Quality Act, 2001).

These organics compounds are considered as priority pollutants since they are harmful to organisms at low concentrations, and can be toxic when present at elevated levels and are suspected to be carcinogens (Ozkaya, 2006). Therefore, it is necessary to remove phenol from industrial effluents before discharging them into the water stream. The adsorption by activated carbon (AC) is the most frequently used treatment method to separate toxic pollutant from water environment. In waste water treatment, activated carbon is powerful adsorbent because it has a large surface area and pore volume which allows the removal of organic compounds, heavy metal ions and colours (Hsieh and Teng, 2000). Although activated carbon adsorption is considered as the best available technologies for the removal of organic compounds, it is still considered highly expensive based on the market price of the commercial activated carbon available. Therefore, more inexpensive and effective activated carbon adsorbents need to be found for removal of phenol in wastewater treatment so that the strict regulation on the concentration of phenol in wastewater can be implemented.

Recently, there has been an increasingly amount of literature devoted to the study of preparation activated carbon from agricultural and solid wastes for cheaper adsorbent which can be used in removing organic compounds such as phenol (Mukherjee *et al.*, 2006; Kennedy *et al.*, 2007; Wu *et al.*, 2006; Tseng *et al.*, 2006; Srivastava *et al.*, 2006; Tanthapanichakoon *et al.*, 2005; Ariyadejwanich *et al.*, 2003; Miguel *et al.*, 2003; Nakagawa *et al.*, 2004). In relation to the literature studies, it was proven that activated carbons prepared from waste tires are considered as highly mesoporous among solid wastes, and they have a remarkably high adsorption capacity for large molecules (Tamai *et al.*, 1999). In some applications, especially those involving large molecules or macromolecules which cannot easily penetrate into the micropores (<2 nm diameter) and adsorb onto them, the activated carbons should possess not only micropores but also interconnecting mesopores (Hsieh and Teng, 2000; Tamai *et al.*, 1999).

The purpose of this work was to determine the adsorption potential prepared activated carbon from waste tires to be used to remove phenol from wastewater. Laboratory batch isotherm studies were conducted to evaluate the adsorption capacity of the activated carbon adsorbent. The effects of contact time and initial phenol concentration were also investigated. Langmuir and Freundlich isotherm models were tested for their applicability with the experimental data.

## MATERIALS AND METHODS

### *Preparation of Activated Carbon Using the Physiochemical Activation Method*

The experiments started with the carbonization of waste tires. Approximately 100 gram of waste tires (diameter = 0.425 mm) was put on the tray and placed inside the batch muffle furnace. The temperature was increased from the ambient temperature to 800°C and kept for 1 hour under nitrogen flow rate. The char product was then cooled down to room temperature and stored in a desiccator.

The experiment was continued with an impregnation procedure. The tyre char was dispersed uniformly in the KOH solutions in a stainless steel beaker with water:KOH:char equal to 5:5:1 by mass, denoted as the KOH/char ratio = 5. The beaker was immersed in a constant temperature shaker bath. The mixing was performed at 30°C for 3 hr to make sure that potassium hydroxide pellets were completely dissolved. For dehydrating purposes, the beaker was then placed inside an oven at 110°C for 24 hours for dehydrating purpose.

The chemically treated char was placed inside a batch muffle furnace reactor and heated at 800°C under the nitrogen flow of 150 ml/min. After the temperature had reached the setting point, the gas flow was switched to carbon dioxide at the flow rate of 150 ml/min for 2 hours. The activated products were then cooled under the nitrogen flow to room temperature. The sample was then poured to a beaker containing 0.1M HCl (250cm<sup>3</sup>) and stirred for 1 hour. They were finally washed with hot water until the conductivity of the filtrate became less than 10µs. This was to ensure that all the KOH used for activation had been removed before the carbon was taken for adsorption study. The carbon was dried at 105°C until it was bone dry and stored in a dessicator.

#### *Procedures for the Adsorption Experiments*

The activated carbon was characterized for its adsorption capacity using phenol. A phenol solution of 1500mg/m<sup>3</sup> concentration was prepared in an appropriate volumetric flask. The stock solution was diluted to the desired initial concentrations (100-500 mg/L) for batch equilibrium studies. About 0.1g of activated carbon was introduced into a 100ml of 100 to 500mg/L of phenol solution, and kept in a laboratory shaker for 48 hours at 30°C. The samples were withdrawn at appropriate time interval, using a glass syringe to determine the residual concentration of the solutions. For high concentrations, 0.1 cm<sup>3</sup> of the solution was withdrawn and diluted to 50 cm<sup>3</sup> using deionized water before determining the residual concentration using UV-Spectrophotometer at 270nm wavelength for phenol.

The amounts of adsorbates adsorbed at time,  $q_t$  and at equilibrium condition,  $q_e$  were calculated using Equations (1) and (2) below.

$$q_t = \frac{(C_o - C_t)V}{w} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{w} \quad (2)$$

Where  $C_o$  and  $C_e$  are initial and equilibrium adsorbate concentrations, mg/L.  $C_t$  is the adsorbate concentration at time, mg/L.  $V$  is volume of solution, L and  $w$  is weight of adsorbent, g.

## RESULTS AND DISCUSSION

#### *Textural Characterization of the Prepared Activated Carbon*

The BET surface area of the prepared activated carbon was found to be 273.26m<sup>2</sup>/g, with a total pore volume of 0.585cm<sup>3</sup>/g. The average pore diameter was found to be 5.84nm. This indicates that the pores on the prepared activated carbon are in the meso range.

*Fig. 1* shows the SEM image of the char and the prepared activated carbon. Metals on the surface of the char could clearly be seen in the SEM images of the char. However, after the activation process, the SEM images showed that the inorganic components on the surface of the prepared activated carbon were partially removed. The pore development was also increased after the activation process, as shown in the SEM images of the prepared activated carbon.

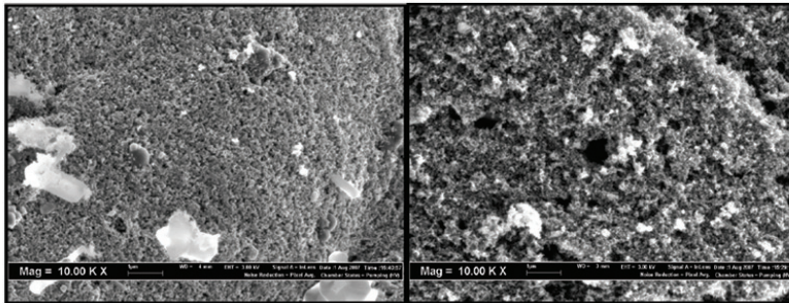


Fig. 1: SEM image of (a) tyre char and (b) activated carbon at 10Kx magnification

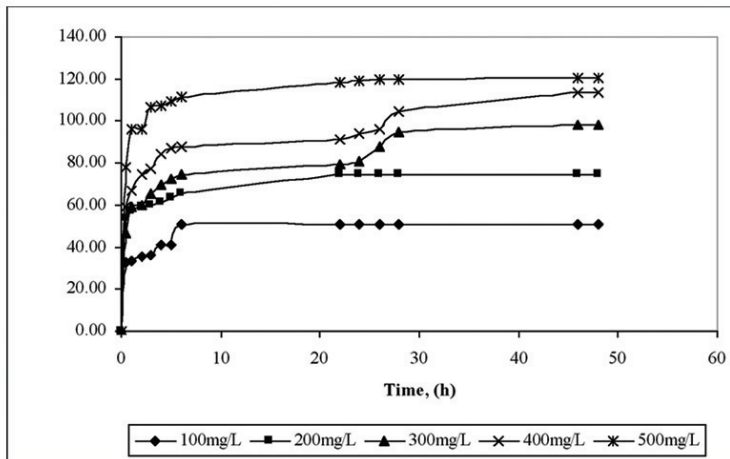


Fig. 2: Effect of initial phenol concentration on the adsorption of phenol onto the prepared activated carbon

#### Effect of Initial Concentration Phenol

The effect of the initial concentration phenol, on the adsorption capacity, as a function of time, is shown in Fig. 2. The amount of phenol adsorbed per unit weight of adsorbent increased with the increase in the phenol concentration. This means, when the initial concentration increased from 100 to 500 mg/L, the adsorption capacity also increased from 50.62 mg/g to 120.80 mg/g. It was because the initial concentration plays an important role which provided the necessary driving force to overcome the resistances to the mass transfer of phenol between the aqueous and the solid phases (Srivastava *et al.*, 2006). The interaction between phenol and the prepared activated carbon adsorbent was also found to enhance with the increase in the initial concentration. Thus, it can be concluded that higher initial concentration enhances the adsorption uptake of phenol.

#### Effect of Contact Time

Aqueous phenol solutions, with different initial concentrations ranging from 100 to 500 mg/L, were kept in contact with the adsorbents for 48 hour. The available adsorption results reveal that the uptake of the adsorbate is fast at the initial stage of the contact period, and it then becomes slower near to the equilibrium. The rate of adsorption is nearly constant between of these two stages

of the uptake (Srivastava *et al.*, 2006). It is because the number of adsorption sites available is higher at the initial stage of contact time, and the driving force for the mass transfer is also greater. Therefore, it is much easier for the adsorbate to reach the adsorption site. After a lapse of time, the number of active sites becomes less and the adsorbent becomes crowded inside the particles, and thus impeding the movement of the adsorbate (Kennedy *et al.*, 2007). This fact is in agreement with the results presented in *Fig. 2*. The fastest removal was showed at the initial concentration of 100 mg/L, which is within 6 hours to reach equilibrium. For the initial concentrations of 200 and 300 mg/L, the equilibrium was achieved within 22 and 28 hours, respectively. Meanwhile, for high initial concentration of 400 and 500 mg/L, it gradually increased to attain equilibrium at 46 hour.

### Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium (Roostaei and Tezel *et al.*, 2004). The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. The amount of phenol adsorbed at equilibrium, was plotted against the equilibrium condition,  $C_e$ , as shown in *Fig. 3*. The result shows that the value of  $q_e$  is increased with the increase in the concentration of phenol.

The adsorption isotherm of phenol onto the prepared activated carbon was fitted by several well-known isotherms models, namely the Langmuir and Freundlich models, to assess their utility. The Langmuir model is obtained under the ideal consumption of a totally homogeneous adsorption surface, whereas the Freundlich model is suitable for a highly heterogeneous surface. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration.

### Langmuir Isotherms

The Langmuir adsorption isotherm is often used for adsorption of the solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all the isotherms describing adsorption, and it is often expressed as:

$$q_e = \frac{Q^o K_L C_e}{(1 + K_L C_e)} \quad (3)$$

Where:

$q_e$  = Adsorption capacity at equilibrium solute concentration,  $C_e$  (mg/g)

$C_e$  = Concentration of adsorbate in solution (mg/L)

$Q^o$  = Maximum adsorption capacity corresponding to complete monolayer coverage (Mg/g)

$K_L$  = Langmuir constant related with affinity of the points of union (L/mg)

The above equation can be rearranged to create the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q^o K_L} + \frac{C_e}{Q^o} \quad (4)$$

The linear form can be used for the linearization of experimental data by plotting  $C_e/q_e$  against  $C_e$ . Meanwhile, the Langmuir constant  $Q^o$  and  $K$  can be evaluated from the slope and intercept of linear equation, respectively, as shown in *Fig. 4*. The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor,  $R_L$ , defined as:

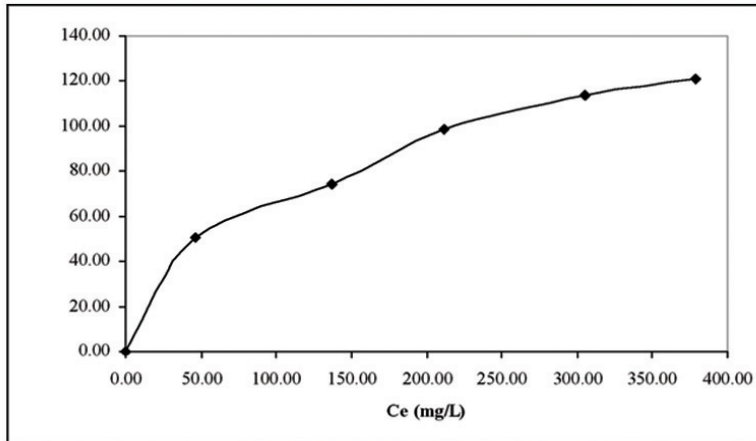


Fig. 3: Equilibrium adsorption isotherm of phenol onto prepared activated carbon at 30°C

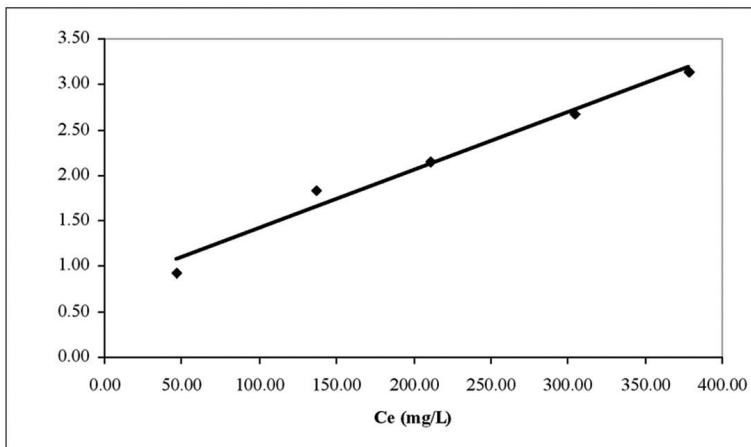


Fig. 4: Langmuir adsorption isotherm of phenol onto activated carbon at 30°C

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (5)$$

Where  $C_o$  is the highest initial solute concentration. The  $R_L$  value implies the adsorption to be favourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ). The value of  $R_L$  was found to be 0.1947 and this confirmed that prepared activated carbon is favourable for the adsorption of phenol under conditions used in the present study (Aktas and Cecen, 2007).

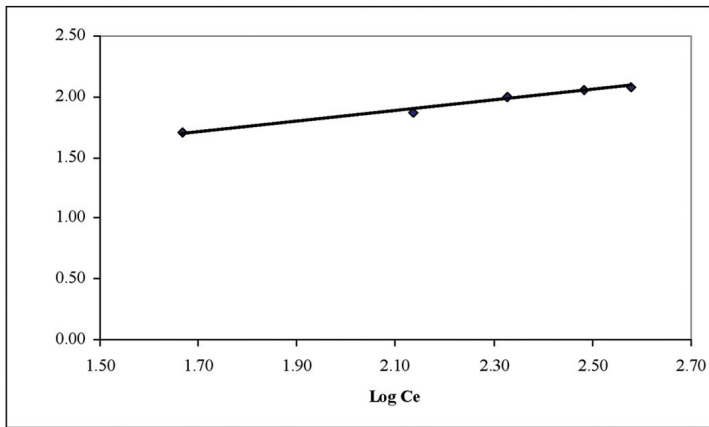


Fig. 5: Freundlich adsorption isotherm of phenol onto activated carbon at 30°C

#### Freundlich Isotherms

The Freundlich isotherm is the earliest known relationship describing the adsorption equation which is often expressed as:

$$q_e = K_f C_e^{1/n} \quad (6)$$

Where:

$q_e$  = Adsorption capacity at equilibrium solute concentration,  $C_e$  (mg/g)

$C_e$  = Concentration of adsorbate in solution (mg/L)

$K_f$  = Empirical constants depending on several environmental factors

$n$  = Empirical parameter representing the energetic heterogeneity of the adsorption sites

The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

A plot of ( $\log q_e$ ) against ( $\log C_e$ ) yields a straight line which indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope and the intercept of the linear plot of the experimental data, as shown in Fig. 5. The value of  $n$  indicates favourable adsorption when  $1 < n < 10$ . The  $n$  value was found to be 2.3348. Therefore, the present adsorption systems appear to be favourable (Ozkaya, 2006).

The Langmuir constants  $Q^o$  and  $K_L$  and the Freundlich constants  $K_f$  and  $n$  are given in the Table 1. Both isotherm models were found to fit the adsorption data of the prepared activated carbon with correlation coefficient,  $R^2$  value 0.9774 and 0.9895, respectively. The adsorption capacity of the adsorbent was obtained from the Langmuir model up to 156.250 mg/g. This result shows that the prepared activated carbon in this study has a very high adsorption capacity as compared to the other works listed in Table 2. This is probably be due to the different activation methods used, which eventually resulted in different surface characteristics (Aktas and Cecen, 2007).



TABLE 1  
Langmuir and Freundlich isotherm constants for phenol on the prepared activated carbon at 30°C

Type of adsorbent	Langmuir isotherm model				Freundlich isotherm model		
	$Q^o$ (mg/g)	$K_L$ (1/mg)	Correlation Coefficient, $R^2$	$R_L$	$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	n	Correlation Coefficient, $R^2$
Activated carbon	156.250	0.0083	0.9774	0.1947	2.6717	2.3348	0.9895

TABLE 2  
Comparison of the maximum monolayer adsorption capacity of phenol onto activated carbon adsorbents from waste tires

Adsorbent	Maximum adsorption capacity (mg/g)	Method of activation	References
Activated carbon	156.25	Physiochemical activation	Present work
Tyre rubber derived carbon	106.00	Steam activation	(Miguel <i>et al.</i> , 2003)
Activated carbon	43.06	Steam activation	(Laszlo <i>et al.</i> , 1997)

## CONCLUSIONS

The experimental data of the adsorption studies on phenol using prepared activated carbon was described well by both Langmuir and Freundlich isotherm models. This indicates that the adsorption of phenol from aqueous solutions could be either monolayer or multilayer. The adsorption capacity of the adsorbent, obtained from the Langmuir model, was up to 156.25 mg/g. The present study concludes that the production of the activated carbon adsorbents, from waste tire rubber, can provide a two-fold environmental and economic benefit; a recycling path is created for waste vehicles tires and new low-cost adsorbents are produced for commercial use in wastewater treatment.

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