

Research Article

Phenol Adsorption from Simulated Wastewater on Rice Husk Activated Carbon and Granular Activated Carbon

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Abstract

Background: Phenol has been classified as hazardous pollutant and its presence in natural water is considered as a serious threat to human health and overall water quality. The major source of phenol pollution in the aquatic environment is wastewater from petroleum and petrochemical industries. **Objective:** This study aims to investigate the adsorption efficiency of granular activated carbon (GAC) and activated carbon prepared from rice husk (RHAC), a low-cost agricultural by product, in removing phenols from simulated wastewater. **Methods:** Batch adsorption studies were conducted to study the effect of various parameters such as initial concentration, agitation time, adsorbent dose and solution pH on phenol removal. Equilibrium data were analyzed by the Langmuir, Freundlich, Temkin and Hurkin-Jura. The adsorption kinetics were studied using the pseudo-first-order and second-order kinetics models. The mechanism of the adsorption process was determined from the intraparticle diffusion model. **Results:** The efficiency of GAC and RHAC on removal of phenol was 95% and 90% respectively at an agitation time of 6 hr, a pH 6, 150 rpm, an adsorbent dose of 5 g/L, initial phenol concentration of 50 mg/L and a temperature of 20°C. Acidic pH was more favorable for the removal of phenol. Increasing initial concentration of phenol decreases the percentage removal. The adsorption isotherm models fitted the data in the order: Freundlich > Langmuir > Temkin isotherms. The pseudo-second-order kinetic model best described the adsorption process. **Conclusion:** The results showed that the prepared activated carbon was an effective adsorbent for removal of phenol as a low-cost and an alternative adsorbent.

Keywords: Adsorption, phenol, Granular activated carbon, Rice husk, Wastewater

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INTRODUCTION

Phenols are generally considered to be one of the toxic pollutants discharged into surface even at low concentrations. The major source of phenol pollution in the rivers are effluent wastewaters from pharmaceuticals, rubber, dye, surfactants, fertilizers, explosives, paints, petroleum, and petrochemical industries.⁽¹⁾ Their public health impacts due to exposure to low levels in water are liver damage, mouth ulcers, and haemolytic anaemia. Phenol affects kidneys, lungs, and vascular system.⁽²⁾ The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1mg/L.⁽³⁾ World Health Organization (WHO) recommends the permissible phenolic concentration of 0.001 mg/l in potable water.⁽⁴⁾

Several physico-chemical treatments have been proposed for efficient phenol removal, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis, etc.), adsorption⁽⁵⁾, electrochemical oxidation, wet oxidation, heterogeneous photocatalysis⁽⁶⁾ and biological treatments.⁽⁷⁾

Adsorption process is efficient for the removal of organic matter from waste effluents. Adsorption has been found to be superior compared to other techniques for water reuse in terms of flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.⁽⁸⁾

Activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants. The high adsorption capacities

of activated carbons are usually related to their high-surface-area, pore volume, and porosity.⁽⁹⁾ In addition, the adsorption capabilities of activated carbons strongly depend on the activation method and the nature of source materials. Many researchers have shown that activated carbon is an effective adsorbent for organic compounds removal, especially for phenolic compounds.⁽¹⁰⁾ However, its high initial cost and difficulty in regeneration make it less economically viable as an adsorbent and limit its use. Many researchers examined the feasibility of using cheaper raw materials of agricultural waste origin to prepare activated carbon⁽¹¹⁾ such as corn cob⁽¹²⁾, sun flower seed hull⁽¹³⁾, coconut husk⁽¹⁴⁾, soybean straw⁽¹⁵⁾, sugarcane bagasse⁽¹⁶⁾, rice and husk.^(17,18)

Rice husk is an agricultural waste and a by-product of the rice milling industry about more than 100 million tonnes, 96% of which is generated in the developing countries. The utilization of this source of agricultural waste would solve both a disposal problem as well as access to a cheaper material for adsorption in water pollutants control system⁽¹⁹⁻²⁰⁾

The present study aimed to compare the adsorption of phenol by active carbon prepared from rice husk (RHAC) and commercial granular activated carbon (GAC). The equilibrium and kinetic data of the adsorption were studied.

METHODS

Study setting: The present study was an experimental study performed in the laboratory of Chemical Engineering Department, Faculty of Engineering, Alexandria University and Pharos University, Alexandria, Egypt.

Study design: Batch adsorption experimental study was employed for the removal of phenol onto activated carbon prepared from rice husk and granular activated carbon.

Analyses: Stock solution of phenol (1000 mg/L) was prepared using double-distilled water. All solutions were prepared fresh whenever required. Phenol was analyzed by UV-vis spectrophotometer (UV Shimadzu, Japan) at a wavelength of 269 nm. The pH of the solution was adjusted using 0.1M hydrochloric acid and 0.1 M sodium hydroxide. All chemicals used were of analytical reagent grade and purchased from Merck.

Materials: Two different types of activated carbon were used in this study: Commercial granular activated carbon (GAC) and activated carbon prepared from Rice husks (RHAC). GAC had an average particle size of 0.8 mm to 1 mm. The moisture content was 4.136% and the iodine value was 550mg/g. Bulk density of GAC was 590.13 kg/L. GAC was dried for 2 h in an oven at 110 °C, then packed and stored in stoppered bottles for use.

Rice husks were obtained from local Rice Mill in Egypt. Rice husks were washed thoroughly with double distilled water to remove any dirt, then oven-

dried at about 110 °C for 6 h. The dried rice husks were subjected to thermal carbonization in a muffle furnace at 800 °C for 1 h. The samples obtained, were ground in a ball mill and sieved to obtain the particles size of 0.5mm to 0.8mm. The product was adequately cooled and stored in a vacuum desiccator until required. The moisture content of RHAC was 6.335% and the iodine value was 320mg/g. Bulk density of RHAC was 480 kg/ L.

Experimental Procedure

Batch experiments: Batch experiments were carried out to study the effect of various operating parameters on the adsorption process. For each experimental run, a known concentration of phenol of 100ml volume was taken in a glass stoppered conical flask (250 mL) and shaken at the rate of 150 rpm with a known amount of adsorbent using temperature-controlled horizontal shaker kept at 20 °C.

Adsorption experiments: Batch adsorption experiments were carried out in a series of stoppered conical flasks (250ml). Weighted amounts of GAC and RHAC were introduced into the bottles containing various concentrations of phenol (50-250 mg/l). The total volume of the solution was 100 ml. The conical flasks were agitated in a temperature-controlled horizontal shaker at a constant speed of 150 rpm at 20°C to reach the equilibrium time. The effects of contact time, initial concentration of phenol (50–250 mg/l), solution pH (2–10) and adsorbent doses (2–6 g / L) were studied. The pH measurements were made using a pH meter

The percentage removal of phenol from solution was calculated by the following equation⁽²¹⁾:

$$\text{Removal \%} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

Kinetics of adsorption was determined by analyzing adsorptive uptake of the phenol from the solution at different time intervals and calculated from the following equation⁽²¹⁾:

$$q_t = \frac{(C_i - C_t)}{m} \times V \quad (2)$$

Batch tests were carried out to compare the adsorptive capacity of GAC and RHAC. Equilibrium adsorption capacity was calculated from the following relationship⁽²¹⁾

$$q_e = \frac{(C_i - C_e)}{m} \times V \quad (3)$$

Where, C_i is the initial phenol concentration, C_t is the phenol concentration at time (t), C_e is the phenol concentration at equilibrium time, V (L) is the volume of solution and m (g) is the weight of adsorbent.

Statistical Analysis

Each experiment was carried out in duplicate and the average of two values was used in the calculations. The maximum difference between the two values was less than 3% of the mean.

Chi-square statistic test and the average percentage errors were used.⁽²²⁾ The average percentage errors indicate the fit between the experimental and calculated values of adsorption capacity used for plotting isotherm

curves. The average percentage errors (APE) were calculated according to the following equation:⁽²²⁾

$$APE(\%) = \frac{100}{N} \times \frac{\sum_{i=1}^N |(q_{e \text{ experimental}} - q_{e \text{ calculated}})|}{q_{e \text{ experimental}}} \quad (4)$$

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculation from models, with each squared difference divided by the corresponding data obtained by calculation from models:⁽²²⁾

$$X^2 = \sum_{i=1}^N \frac{(q_{e \text{ experimental}} - q_{e \text{ calculated}})^2}{q_{e \text{ calculated}}} \quad (5)$$

Where q_e , calculated is the calculated adsorbate concentration at equilibrium (mg/g), q_e , experimental is

the measured adsorbate concentration at equilibrium (mg/g), N is the number of data points.

RESULTS

Effect of contact time: Figure 1 shows the effect of contact time on the removal percentage of phenol by GAC and RHAC. The removal of phenol increased with increase in contact time for both GAC and RHAC. The adsorption was rapid during the initial 3 hr and then reached equilibrium at 6 hr. No significant change in phenol removal was observed after 4 hrs. The removal of phenol by RHAC was slightly less than that by GAC. The removal percentage of phenol onto GAC and RHAC was 90% and 83% respectively.

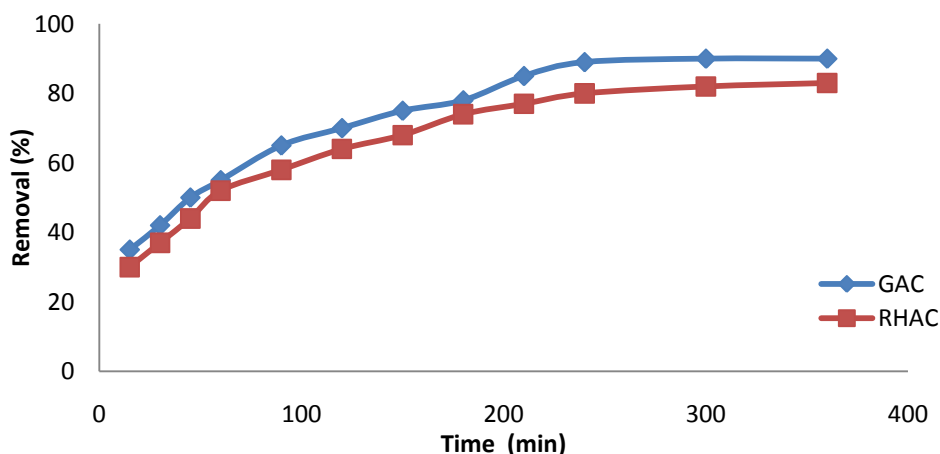


Figure1: Effect of contact time on the adsorption of phenol on RHAC and GAC (pH 6, temperature 20 °C, adsorbent dose 5g/L, phenol concentration 100 mg/L)

Effect of solution pH: The pH of the sorption medium is one of the most significant parameters in the adsorption process. The pH primarily affects the degree of ionization of the phenolic adsorbate and the surface properties of the adsorbent, i.e. the functional groups on the carbon surface. Figure 2 illustrates the

effect of solution pH on the removal percentage of phenol in the pH range of 2-10. The results show that the highest phenol removal was achieved at pH 6, with a phenol removal of 92% and 80% for GAC and RHAC, respectively at phenol initial concentration of 100 mg/l.

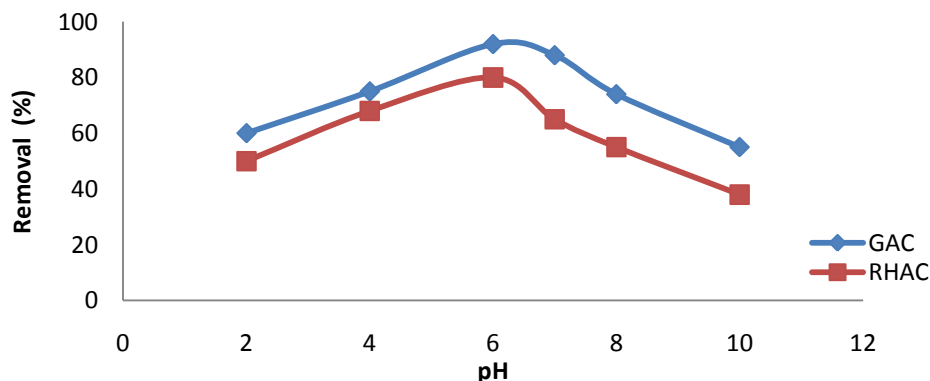


Figure 2: Effect of solution pH on the removal of phenol by RHAC and GAC (phenol concentration 100 mg/L, temperature 20 °C, adsorbent dose 5g/L contact time 6h)

Effect of adsorbent dose: Figure 3 shows the effect of adsorbent dose on removal percentage of phenol. Amount of adsorbent carried out was 2–6 g/L at 6 hr of agitation time using 100 ml of phenol concentration at pH 6 and 150 rpm shaking speed and at a temperature of 20 °C. Figure 3 illustrates that the percentage removal of phenol increases by increasing

the amount of the adsorbent for both GAC and RHAC. Removal percentage of phenol onto GAC were 78% and 95% for dosage of 2 g/L and 6 g/L, respectively, while the removal percentages of phenol onto RHAC were 67% and 82% for dosage of 2 g/L and 6 g/L, respectively.

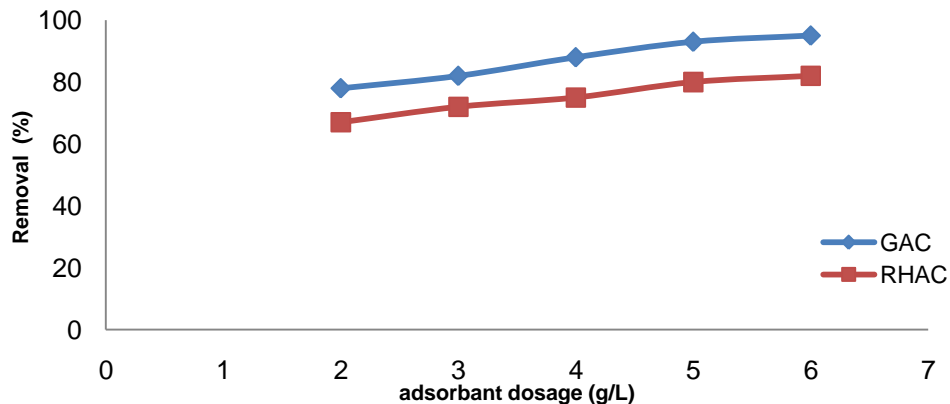


Figure 3: Effect of adsorbent dose on the removal of phenol by RHAC and GAC (pH 6, temperature 20 °C, phenol concentration 100mg/L)

Effect of initial concentration: Figure 4 presents the effect of initial concentration of phenol on the removal percentage of phenol onto GAC and RHAC within a range of 50-250 mg /L. The results reveal that the removal percentage decreases as the initial phenol concentration is increased. The removal percentage of

phenol onto GAC and RHAC was 95% and 90%, respectively at an initial phenol concentration of 50 mg/L, while a percentage removal of phenol of 75% and 65% was determined onto GAC and RHAC respectively at an initial phenol concentration of 250 mg/L.

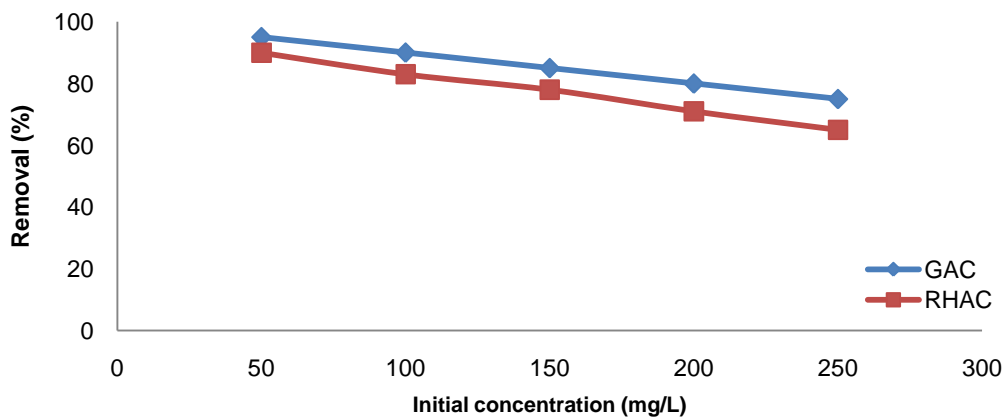


Figure 4: Effect of initial concentration on the removal of phenol by RHAC and GAC (pH 6, temperature 20 °C, adsorbent dose 5g/L, contact time 6h)

Adsorption isotherms: Adsorption isotherms indicate how the adsorbate is distributed between the liquid phase and the solid phase when the adsorption process reaches equilibrium state. In this study, Langmuir,

Freundlich, Temkin and Hurkins -Jura adsorption isotherms were applied to the equilibrium data of adsorption of phenol onto both GAC and RHAC. The Langmuir equation ⁽²³⁾ is valid for monolayer sorption

on a surface with a finite number of identical sites and is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (6)$$

Where Q_m (mg g^{-1}) is the monolayer adsorption capacity, and K_L (L mg^{-1}) the equilibrium adsorption constant related to the energy of adsorption.

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium factor R_L that is defined as:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (7)$$

The adsorption is considered as irreversible when $R_L = 0$, favourable when $0 < R_L < 1$, linear when $R_L = 1$, and unfavorable when $R_L > 1$.

Freundlich isotherm ⁽²⁴⁾ is an empirical equation assuming heterogeneous adsorptive energies on the adsorbent surface, which can be written

$$\text{Ln}q_e = \text{Ln}K_F + \frac{1}{n} \text{Ln}C_e \quad (8)$$

Where, K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The value of $0 < 1/n < 1.0$ exhibits the favourability of adsorption onto activated carbons ⁽²⁵⁾. Temkin isotherm ⁽²⁶⁾ takes into account the adsorbent-adsorbate interactions. the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

The Temkin isotherm is expressed as:

$$q_e = B_T \ln K + B_T \ln C_e \quad (9)$$

Harkin–Jura isotherm model ⁽²⁷⁾ accounts to multilayer adsorption and can be explained with the existence of a heterogeneous pore distribution. Harkin–Jura model is expressed as follows:

$$\frac{1}{q_e^2} = \frac{B_2}{A} - \frac{1}{A} \log C_e \quad (10)$$

Where A is the Harkins–Jura isotherm parameter, B_2 is the Harkins–Jura isotherm constant.

The linear fits of the adsorption equilibrium data at 20 °C of phenols on GAC and RHAC predicted from the four isotherms models were plotted in figure 5 and figure 6 respectively.

The best-fit model was determined by the correlation coefficients (R^2), the average percentage error APE (%), and chi test (X^2). The isotherm parameter values and correlation coefficients R^2 values, X^2 and APE (%) are listed in Table 1.

According to the fitting results listed in Table 1, the correlation coefficients of the three models Freundlich, Langmuir, and Temkin, were higher than 0.95. However, when APE (%) and X^2 were considered, the Freundlich isotherm model appeared to be much more applicable than the Langmuir and Tempkin isotherms. The correlation coefficient of Temkin isotherm equation ($R^2 = 0.977$) is lower than that obtained for the Freundlich isotherm model ($R^2=0.998$) and Langmuir isotherm ($R^2 =0.984$) for adsorption of phenol on GAC. The correlation coefficient of Freundlich, Langmuir and Temkin isotherm equation for adsorption of phenol on RHAC were 0.992, 0.992, and 0.988, respectively.

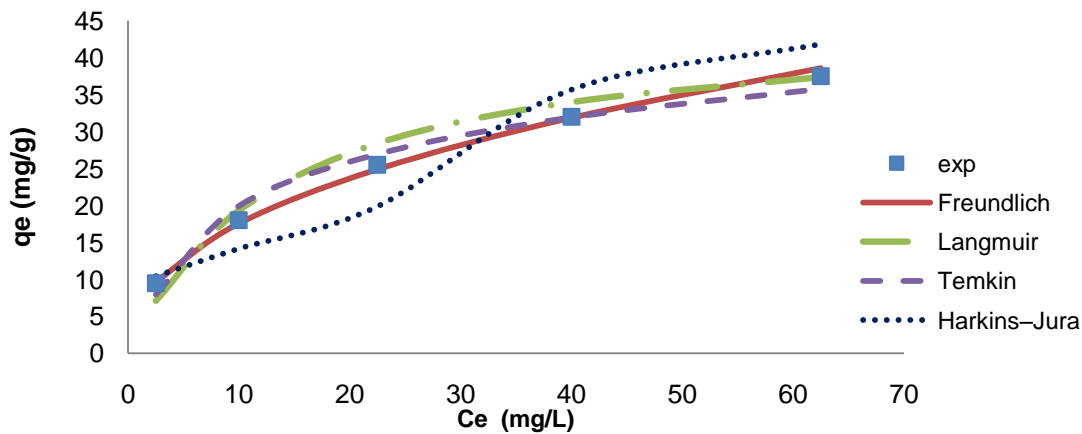


Figure 5: Equilibrium isotherms for the removal of phenol by GAC (Predicted and experimental data of equilibrium adsorption 20 °C)

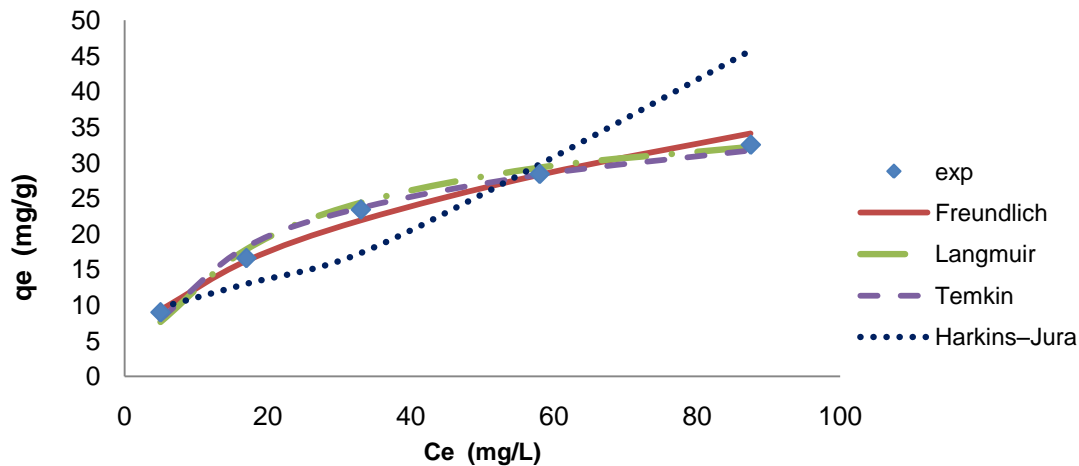


Figure 6: Equilibrium isotherms for the removal of phenol by RHAC (Predicted and experimental data of equilibrium adsorption at 20 °C)

Table 1: Adsorption isotherm parameters, error analysis values and correlation coefficients calculated for various adsorption models at 20 °C for phenol on GAC and RHAC

Isotherms models	Isotherms parameter	Adsorbents	
		GAC	RHAC
Langmuir $\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e$	$Q_m(\text{mg/g})$	45.45455	40
	K_L	0.074074	0.047259
	$(\text{mg/g})(\text{L/mg})^{1/n}$		
	R_L	0.212598	0.297358
	R^2	0.984	0.992
	X^2	1.316813	0.393044
	APE (%)	10.12524	4.849892
	$1/n$	0.429	0.454
	$K_f(\text{L/mg})$	6.548	1.44
	R^2	0.998	0.992
Freundlich $\text{Ln}q_e = \text{Ln} K_f + \frac{1}{n} \text{Ln}C_e$	X^2	0.060107	0.197084
	APE (%)	2.025094	3.479745
	$B_T(\text{L/mg})$	8.639	8.28
	$K_i(\text{J/mol})$	1.004525	0.527496
Temkin $q_e = B_T \text{Ln}K + B_T \text{Ln} C_e$	R^2	0.977	0.988
	X^2	0.648514	0.273318
	APE (%)	7.5099	4.78394
	A	142.8571	111.1111
Harkins-Jura $\frac{1}{q_e} = \frac{B_2}{A} - \frac{1}{A} \log C_e$	B_2	1.714286	1.888889
	R^2	0.872	0.866
	X^2	3.563224	7.07486
	APE (%)	15.2549	20.1212

Adsorption Kinetic Models: The adsorption rate data for phenols onto the GAC and RHAC were analysed using two kinetic models pseudo-first-order-equation and pseudo-second-order-equation. The pseudo-first-order model was expressed by Lagergren⁽²⁸⁾ as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

where q_e and q_t (mg/g) are the amounts of phenol adsorbed at equilibrium and at any time, t (min), respectively, and k_1 (1/min) is the adsorption rate

constant. The plot of $\ln(q_e - q_t)$ versus t is shown in figure 7. The values of k_1 , correlation coefficient R^2 , the experimental q_e and calculated q_{cal} values obtained from the linear plots are given in Table 2. The R^2 values were 0.953 and 0.969 for phenol of initial concentration of 100 mg/l onto GAC and RHAC respectively. The experimental q_e values 16.6 mg/g did not agree with the calculated values 12.3mg/g showing that the adsorption of phenol on the RHAC was not a first-order reaction.

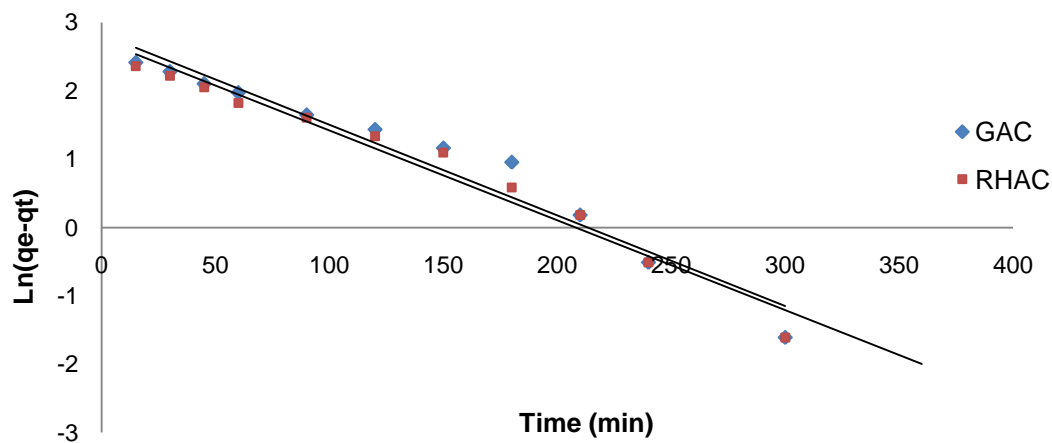


Figure 7: The pseudo-first order model for adsorption of phenol on GAC and RHAC (adsorbent dose 5g/L, initial concentration of phenol 100 mg/L)

The pseudo-second-order model ⁽²⁹⁾ can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

where k_2 is the second-order rate constant. The values of t/q_t are plotted against t as shown in figure 8, q_e and k_2 are calculated from the slope and intercept of the plot.

They are listed in Table 2. The pseudo-second-order model fits the experimental data for phenol, the R^2 values are 0.992, 0.993 for adsorption of phenol on GAC and RHAC respectively and the experimental and calculated values were found to be in good agreement.

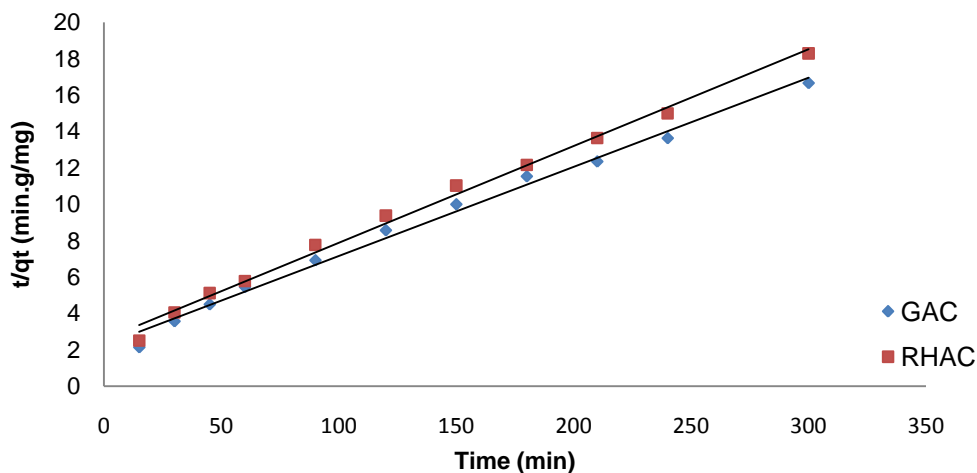


Figure 8: The pseudo-second order model for adsorption of phenol on GAC and RHAC (adsorbent dose 5g/L, initial concentration of phenol 100 mg/L)

Adsorption Mechanism: The kinetic results were then analyzed by using intraparticle diffusion model to identify the diffusion mechanism and rate controlling steps affecting the kinetics of adsorption. The intraparticle diffusion equation explained by Weber and Morris ⁽³⁰⁾ can be written as:

$$q_t = k_{diff} t^{0.5} + C \quad (13)$$

where q is the amount of phenol adsorbed (mg/g) at time t , k_{diff} is intraparticle diffusion constant (mg/g min^{0.5}), and C is the intercept which represents the value of the thickness of the boundary layer. Figure 9 illustrates the plots of q_t versus $t^{0.5}$. The constants were calculated and listed in Table 2. As can be seen from Figure 9, the linear lines did not pass through the origin and this shows that intraparticle diffusion was not the only rate limiting mechanism in the adsorption process.

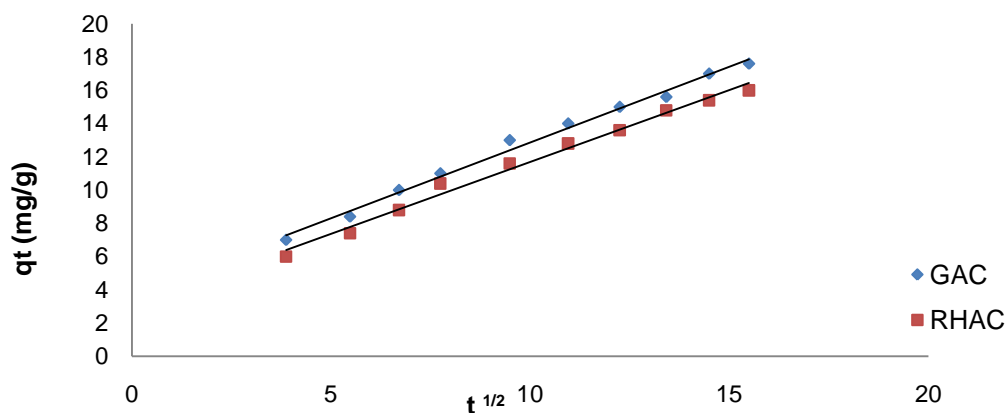


Figure 9: Intraparticle diffusion model for adsorption of phenol on GAC and RHAC (adsorbent dose 5g/L, initial concentration of phenol 100 mg/L)

Table 2: Pseudo-first-order model, pseudo-second-order model and intraparticle diffusion constants and correlation coefficients for adsorption of phenol on GAC and RHAC at 20 ° C

Adsorbent	qe mg/g	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		
		q mg/g	cal mg/g	K ₁ 1/min	R ²	q mg/g	cal mg/g	K ₂ 10 ⁻³ g/mg. min	R ²	C
GAC	18	16.96	0.013	0.953	20.4	1.066	0.992	3.759	0.911	0.992
RHAC	16.6	12.37	0.013	0.969	18.52	1.144	0.993	3.033	0.865	0.989

DISCUSSION

Effect of contact time

Contact time is an important parameter to determine the equilibrium time of adsorption process. Initially the number of vacant active sites available is higher and the driving force for the mass transfer is greater. Therefore, the adsorbate reaches the adsorption site with ease. As time progresses the number of available free active sites becomes less and the adsorbate molecules are collected at the surface thus impeding the movement of the adsorbate leading to nonlinear adsorption. This can be accounted for the decrease in adsorption rate after 4 hr. and was well exhibited by plateau lines at 6 h of adsorption showing that the process has reached the steady-state condition (figure1). Similar phenomena were previously observed.⁽³¹⁻³²⁾

Effect of adsorbent dosage

The percentage removal of phenol highly increases with the increase in adsorbent dose from 2g/L to 5 g/l after which the removal increases slightly (figure 3). These results were in agreement with Kumar S. et al⁽³⁴⁾ who stated that an increase in the phenol percentage removal with an increase in the adsorbent dosage can be attributed to the increase in the availability of surface area of mesopores for

adsorption and, hence, the availability of more adsorption sites.

Effect of initial concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of the phenol between the aqueous and solid phases. The percentage removal of phenol was found to decrease with increasing the initial concentrations of phenol in the solution onto both GAC and RHAC (figure4). The higher removal at lower concentrations may be due to the presence of more available sites on the adsorbent. However, at higher concentrations the number of phenol ions in the solution is relatively higher than available sites on the adsorbent for adsorption.^(35, 36) Previous researchers revealed that the phenol uptake from the solution was related to the mass driving force effect which permits more adsorbates to pass through from the bulk phase boundary to the carbon surface.^(37, 38)

Effect of pH of the solution

Phenol was better adsorbed to both adsorbents GAC and RHAC at pH 6. This behavior can be explained considering the nature of the adsorbent at different pH. Phenol adsorption can largely be related to the type and ionic state of the functional groups of the adsorbents and also on the phenol chemistry in solution. The decrease in phenol adsorption from pH 6 to 2 was accounted to the increased H⁺ adsorption on

the carbonyl sites, which suppresses phenol adsorption on these sites. The decrease in the phenol adsorbed from pH 6 to 10.0 on the other hand, was attributed to both greater solubility of dissociated phenol at $\text{pH} > \text{pK}_a$ and increased repulsion forces between the dissociated form of the adsorbate and the carbon surface (figure 2). A similar trend of pH effect was observed for the adsorption of phenol on activated carbon-commercial grade and laboratory grade.⁽³⁹⁾ The pK_a value for phenol is 9.89, so the adsorbing species above this pH is mostly anionic.⁽³⁾ Therefore, the adsorption decrease at high pH values 10 due to ionization of adsorbate molecules. The reason could be also due to the repulsions between the negative surface charge and the anionic phenolate anions in solution. While, at acidic pH 6 the percentage removal was higher because phenol was undissociated. The low pH value range 2-5, additional protons were introduced in the solution and competed for the carbonyl sites, so the adsorption was reduced at low pH.^(10,40)

Adsorption Isotherm models

Adsorption isotherm reveals the relationship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a solution at a constant temperature under equilibrium condition. It provides the information about the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations.⁽⁴¹⁾ In the present study, four isotherm models have been used in fitting the equilibrium data, namely, Langmuir and Freundlich, Temkin and Hurkin-Jura isotherm models. The results showed that the n values obtained from the Freundlich model were greater than one representing that the adsorption process onto GAC and RHAC was favourable for phenol. Predicted and experimental isotherms are shown in Figure 5 and 6. It is clear from these figures and from the average percentage error values (Table 1) that there is a good agreement between the experimental and predicted values, suggesting that the Freundlich model is valid for the experimental equilibrium data. Freundlich isotherm is more suitable for the experimental results than the Langmuir, Temkin and Hurkin-Jura because of the lower average percentage error values. These results agree with previous studies on the adsorption of chlorophenols with different adsorbents, where the Freundlich model was fitting the experimental data better than the Langmuir model.^(42, 43)

Adsorption kinetics

Kinetic study is one of the most important methods to evaluate the efficiency of adsorption. It describes the rate of adsorbate uptake onto adsorbents and the equilibrium time. The present study suggests that the studied adsorption systems follow the second-order-rate equation instead of the first-order one. Besides, regression coefficients between experimental and calculated values were obtained for the first-order

rate model $R^2 = 0.953$ and 0.969 , while second order rate model $R^2 = 0.992$ and 0.993 were also obtained for adsorption of phenol onto GAC and RHAC respectively. Mohan et al., has reported the pseudo-second-order rate equation for the adsorption of pyridine-derivative.⁽⁴⁴⁾ Wu et al., pointed out that the pseudo-second-order model was suitable for the adsorption of lower molecular weight adsorbates on smaller adsorbent particles.⁽⁴⁵⁾ Similar observations have previously been reported.⁽⁴⁶⁻⁴⁸⁾

The adsorption process of the adsorbate molecules from the bulk liquid phase onto the adsorbent surface is presumed to involve three stages: (1) mass transfer of the adsorbate molecules across the external boundary layer; (2) intraparticle diffusion within the pores of the adsorbent; (3) adsorption at a site on the surface. The intraparticle diffusion model proposed by Weber and Morris.⁽³⁰⁾ If intraparticle diffusion occurs, then q_t versus $t^{1/2}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved. The intra-particle diffusion model is used to investigate the diffusion controlled adsorption system. The obtained results indicate that intraparticle diffusion was not the only rate limiting mechanism in the adsorption process (figure 9). The existence of an external layer diffusion process could be deduced by the fact that these plots do not pass through the origin⁽⁴⁹⁾. Similar results have previously been reported.^(50, 51)

CONCLUSIONS

Granular activated carbon and activated carbon prepared from rice husk were found to be good adsorbents for the removal of phenol from aqueous solution. The equilibrium time of adsorption is 6 h. The equilibrium data fitted well in the Freundlich model of adsorption. The kinetics of phenol adsorption onto RHAC and GAC followed the pseudo-second-order model. These results revealed that the rice husk activated carbon could be employed as a low-cost alternative to commercial activated carbon in the removal of phenol from wastewater.

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