



Isothermal studies on adsorption of acenaphthene on activated carbon obtained from rice husk

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ABSTRACT

Rice husk, agricultural waste material of environmental impact, was carbonized at temperatures of 300 - 600°C in an oven for 2h, after which its adsorption capacities was investigated for the adsorption of acenaphthene in synthetic aqueous solution, at increasing concentrations (50–150mg/L). The yields of carbon obtained from the raw rice husk ranged from 20 - 40 % (w/w), while the adsorption capacities of rice husk increased with increasing carbonization temperature and increasing initial concentration of acenaphthene. The removal efficiencies of the rice husk increased from 71.37 - 80.56% as the carbonization temperature increased from 300-600°C, but decreased with increasing initial concentration of acenaphthene. The adsorption equilibrium data obtained, fitted well to the Freundlich, Langmuir, Temkin and Dubnin-Radushkevich isotherms with minimum correlation coefficient (R^2) of 0.9981, 0.9262, 0.9667 and 0.9215, respectively. The error analysis showed the order of suitability of the isotherm models selected to be Temkin > Freundlich > Dubnin-Radushkevich > Langmuir. This study shows that carbons rice husk possesses favourable potency of being used as activated carbon for the removal of acenaphthene from wastewater.

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Introduction

Municipal wastewater typical comprises of domestic water, industrial water and storm water run offs, which vary in characteristics depending on the locations, nature and number of industries available in a given location [1]. Discharge of wastewater effluent containing organic pollutants into natural surface water poses serious risk to aquatic organisms and human beings, besides imparting a carbolic odour to the receiving water [2, 3, 4]. Generally, wastewaters are treated through the primary, secondary and tertiary treatment facilities, depending on the source, to meet standards acceptable for reuse or discharge; however, organic waste constituents of wastewater, such as polycyclic aromatic hydrocarbons (PAHs), are defying these age-long treatment processes [3, 4].

PAHs are classified as priority organic pollutants (POPs) due to their carcinogenic, mutagenic and toxic properties [5-8]. They bear sizeable percentages of organic constituents of industrial wastewater and as result are not removed, efficiently, by conventional physiochemical methods such as coagulation, flocculation, sedimentation, filtration or ozonization [9-15]. Moreover, they must be removed from effluent to acceptable standards in order to minimize their effects on the underground water [16]. Adsorption processes, using industrial activated carbon, have been attempted to remove organic pollutants but the challenge of regenerating the spent adsorbent and the related high cost of the regeneration process have not given then adsorption process the deserved extensive applications [17-23]. Hence, an alternative method for the removal of organic pollutants from wastewaters using low-cost solid residues, such

as husks and shells from agricultural activities is attracting research interest [24-25].

Rice (*Oryza sativa L*) is one of the widely grown foods in the world with global production forecast for years between 2004 and 2005 were 397.8 million tonnes [26]. Rice bran, (husker hull), which is mainly the pericarp of the rice grain, forms 10 % by weight of the raw rice and serves as animal feed in some countries except the countries such as like the United State of America. Rice husk is commonly disposed by open-air burning and this causes environmental pollution, although the resulting ashes have been investigated as possible additives to cement. Until recent, Rice husk has been applied as adsorbent for removal of pollutants in wastewater and nearly 100 percent effectiveness of heavy metal removal have been recorded in some works [27-30]. The candidate adsorbates considered in this study is acenaphthene which is a common 3-Ring PAHs found in the environment particularly coal tar [31]. It is a white, needle-like solid with a molecular weight of 154.21 and its melting and boiling points are 93.4 and 279 °C, respectively.

The purpose of this study is to investigate the effectiveness of adsorbent produced from rice husk, agricultural waste, for the removal of acenaphthene from simulated wastewater under the effect of carbonization temperature and initial concentration using various adsorption isotherms.

Materials and Methods

Equipment and Reagents

The equipment used in this study include nut-cracker, mortar and pestle, magnetic stirrer and mechanical shaker fixed with sieves, while the analytical instruments used include furnace (Model 18A, Italy), and Gas Chromatography

(PerkinElmer Auto-System) coupled with mass spectroscopy/flame ionization detector (GC-MS/FID). The glasswares used were washed with detergent, rinsed diluted nitric acid and copious amount of distilled water. The reagents used sodium bicarbonate (NaHCO_3), phosphoric acid (H_3PO_4 , 85%), acetone (BDH Chemicals Ltd) and acenaphthene (Merck).

Sampling

The natural precursor used in the study, rice husk, was obtained from Arowomole Rice Mill, Ogbomosho, Oyo State, Nigeria. After the collection, the rice husk was sorted to remove stones, shaft and debris before being washed with distilled water and later dried to constant weight in the oven at a temperature of 105°C overnight [24]. The dried samples were then stored in dry container prior to carbonization.

Carbonization and Activation

Carbonization is essentially employed to convert the material to char and opens the pores of the char for adsorption process. 1000g of rice husk was weighed and then carbonized at different temperature (300, 500 and 600°C), individually, with Vecstra Furnace (Model 184A, Italy) for 2h [24]. The resulting charred material was weighed to determine the percentage yield which was calculated from the relation (1). Carbonized rice husk sample was weighed, soaked in excess phosphoric acid (H_3PO_4) for 3 h and then charged into the oven at temperature of 200°C for 24 h to ensure proper adsorptive drying. The Carbonized rice husk sample were removed from the furnace, allowed to cool for 2h, and then washed with bicarbonate solution (NaHCO_3 , 168 g/L). The resulting mixture was further washed with distilled water until the pH reached neutral point between 6.9 and 7.0, after which the sample was sieved and dried in the furnace at 105°C to constant weight [24].

$$\text{Percentage Yield (\%)} = \left[\frac{W_F}{W_I} \right] \times 100 \quad (1)$$

where W_I = Initial weight before carbonization and W_F = Final weight after carbonization

Adsorption Study

50 mg of acenaphthene was added to 300 ml of acetone in 1000 ml flask and the mixture was carefully stirred with magnetic stirrer for 10 min after which 700 ml of distilled water was added to the mixture piece-meal and further shaken thoroughly to facilitate thorough dissolution of the adsorbates to produce 50 mg/L of acenaphthene according to [15]. The procedure was repeated for the preparation of the 75, 100, 125 and 150 mg/L of acenaphthene under this study, respectively. 1 g of rice husk adsorbent was weighed into a 250 mL conical flask containing 50 mL of acenaphthene solution (50 mg/L) and the mixture was covered and agitated on mechanical shaker at 400 rpm for 3h, after which the content was centrifuged at 500 rpm for 20 min. The supernatant solution was decanted into sample bottles and stored for analyses. The process was repeated for simulated wastewater containing; 75, 100, 125 and 150mg/L of acenaphthene respectively, for the adsorbent carbonized at various temperatures (300 - 600°C).

Chromatographic analysis

The unadsorbed concentration of acenaphthene in the supernatant was quantified using gas chromatography coupled with flame ionization detection (GC-FID). A HP-5 capillary of 30 cm with internal diameter of $0.25\ \mu\text{m}$ and $0.25\ \mu\text{m}$ film thickness was used. The column temperature was 60°C for 2 min to 320°C programmed at $10^\circ\text{C}/\text{min}$. Nitrogen was used as carrier gas with a flow rate of 35 psi hydrogen and air flow rates

were 22 and 28 psi, respectively. Injector port and detection temperature were 250°C and 320°C , respectively. $1.0\ \mu\text{L}$ Sample was injected before analysis.

Adsorption Capacity

The adsorption capacities of the materials carbonized at different temperature were determined using

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

where q_e is the concentration of the adsorbed solute (mg/g), C_0 is the initial concentration of the adsorbate in the solution (mg/L); C_e is the final concentration of the adsorbate (mg/L), V is the volume of the solution (mL) and W is the mass of the adsorbent (g). The removal efficiency (RE %) of each adsorbent at different concentration of selected adsorbate was calculated according to equation 3 [32].

$$RE(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

where C_0 and C_e have the same definition described earlier.

Adsorption Isotherm Models

Adsorption isotherm equations were employed to describe the experimental sorption data obtained in this study. These isotherm models are characterized by parameters, which state the surface properties and affinity of the adsorbent [33]. These parameters can be evaluated from graphical plotting of the experimental data using Excel Microsoft Office tool. Using linear regression, the suitability of the selected adsorption isotherms are validated with their corresponding correlation coefficients (R^2) obtained [34]. Thus the data obtained in this study were fitted to Freundlich, Langmuir, Temkin and Dubnin-Radushkevich isotherms in order to understand the adsorption process under the influence of varying carbonization temperature.

Langmuir Isotherm Model

The linearized form of the Langmuir Isotherm equation is expressed in equation 4,

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{1}{Q_L} C_e \quad (4)$$

where C_e (mg/L) is the equilibrium concentration of the adsorbates, q_e (mg/L) is the amount of adsorbate adsorbed per unit mass of adsorbent. Q_L and K_L are related adsorption capacity and rate of adsorption respectively and were

determined by plotting $\frac{C_e}{q_e}$ against C_e .

Freundlich Isotherm Model

The Freundlich Isotherm equation is an empirical expressed in linear logarithmic form [35]

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

A plot of $\ln q_e$ against $\ln C_e$ was used to determine the Freundlich constants, K_f and $\frac{1}{n}$.

Temkin Isotherm equation

This equation focuses on the effects of indirect adsorbate-adsorbate interaction on adsorption [36]. It is expressed as:

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where A and B are the Temkin Constants which are evaluated by plotting q_e against $\ln C_e$. B was further determined from the expression

$$B = \frac{RT}{b} \quad (7)$$

where b is related to the heat of adsorption, T is the adsorbate room temperature and R is the universal gas constant ($8.314 \text{ mol}^{-1}\text{K}^{-1}$).

Dubnin-Radushkevich Isotherm (D-R)

Dubnin-Radushkevich Isotherm equation is commonly expressed in linear logarithmic form as:

$$\ln q_e = \ln Q_{DR} - K \varepsilon^2 \quad (8)$$

$$\text{where } \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (9)$$

The adsorption of acenaphthene present in wastewater onto the activated carbon produced from rice husk was investigated in this study. Dubnin-Radushkevich Isotherm constants, 'k' and 'Qm' (mgg^{-1}) were evaluated by plotting $\ln q_e$ against R^2 .

Mean free energy of adsorption

The mean free energy of adsorption (E) is the free energy change when one mole of adsorbate is transferred to the surface of the adsorbent from infinity in the solution [37]. It was calculated from the values of 'K', which is related to the adsorption energy (J mol^{-1}), and obtained from the plot of Dubnin-Radushkevich using the relation [37].

$$E = \frac{1}{\sqrt{2K}} \quad (10)$$

Error analysis

The error analysis; Average Relative Error (ARE) and Average Relative Standard Error (ARS), was employed in this study in order to find the best correlation between the non-linear isotherm equations and experimental data points [35]. ARE and ARS values were expected to be very low for a given isotherm model to be favourable, particularly under the linear method [33]. The error analysis was achieved using the expressions given by [33].

$$ARE = \left[\frac{\sum |q_c - q_e|}{q_e} \right] \quad (11)$$

The average relative standard error (ARS)

$$ARS = \sqrt{\frac{\sum \left[\frac{(q_c - q_e/q_e)^2}{n-1} \right]}{n-1}} \quad (12)$$

Where q_e is the calculated quantity of naphthalene adsorbed onto the adsorbent and q_c is the experimental data and 'n' is the number of experimental data points.

Results and Discussion

Effect of Carbonization and activation on carbon yield

The yields (%), as determined from eq (1), obtained after carbonization of the raw rice husk at 300-600 °C, were generally less than fifty percent (50%), except at 500 °C (55%) (Table 1). These values do not follow fixed pattern with respect to the temperature, however, these values compare well with the values reported for similar agricultural wastes such as Pistachio (20%), Almond (38%), Hazelnut (52%) and Walnut (57%) [38]. Moreover, irrespective of the temperature selected for the production of activated carbon from agricultural source, the percent yield does not relate, directly, to the effectiveness of the

carbon for the removal of the targeted adsorbate, though it is significant to their commercial utilizations [38]. Phosphoric acid was employed as the activant for the activation process of the carbonized rice husk (RH) due to its effectiveness in enhancing activated carbon surface area [17]. Table 1 shows the percentage washed-off, which ranged between 8.5–12.85 % and increased with increasing carbonization temperature, 300 – 600 °C. The overall results show that the activant (H_3PO_4) has less effect on the yield of the activated carbon under the influence of carbonization temperature as observed by [17].

Effect of carbonization temperature and initial concentration on removal efficiency of activated carbon

The effect of initial concentrations (50 – 150mg/L) of acenaphthene on the removal efficiencies of the rice husk with respect to different range of carbonization temperature is shown in Figures 1. The efficiencies (71.37 - 80.56 %) recorded for the removal of acenaphthene at various temperatures generally decreases with increasing concentration, but increased for the increasing carbonization temperature at a particular initial concentration. This indicates that rice husk may be more efficient in removing lower concentration of acenaphthene from wastewater, therefore, can be utilized to remove traces of such pollutant in the treatment of wastewater targeted for medical and scientific uses.

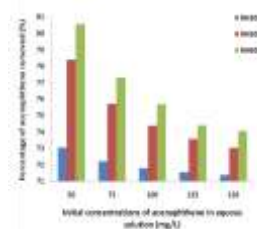


Figure 1: Removal Efficiency (RE %) of Rice Husk activated carbon at different initial concentrations of acenaphthene in wastewater

Effect of carbonization temperature and initial concentration on Freundlich Isotherm Model

Figure 2 shows the plots of $\ln q_e$ versus $\ln C_e$ used for determining the Freundlich isotherm parameters for acenaphthene adsorption onto rice husk at varying carbonization temperatures. Freundlich isotherm parameters obtained for the adsorption of acenaphthene with the selected adsorbents carbonized at varying temperature (300 - 600 °C) are shown in Tables 2.

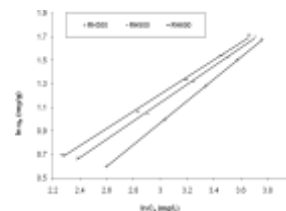


Figure 2: Freundlich adsorption isotherm of acenaphthene onto rice husk

Effect of carbonization temperature and initial concentration on Langmuir Isotherm model

Figures 3 shows the plots of C_e/q_e versus q_e using linear method to determine the Langmuir isotherm parameters for acenaphthene adsorption, onto the rice husk at varying carbonization temperatures. The Langmuir isotherm model is well fitted to the experimental data obtained for the study and the values of Q_L range from 13.37 – 45.97 molg^{-1} (Table 2).

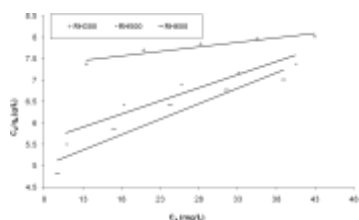


Figure 3: Langmuir adsorption isotherm of acenaphthene onto rice husk

Effect of carbonization temperature and initial concentration on Temkin Isotherm model

Temkin isotherm parameters, B , Q_A and b , (Table 2) and their corresponding correlation coefficients (R^2) were obtained from the plot of q_e versus $\ln C_e$ (Figure 4).

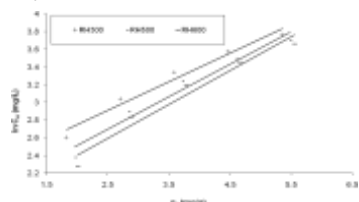


Figure 4: Temkin adsorption isotherm of acenaphthene onto rice husk

The large values of correlation coefficients (R^2) obtained for the adsorption of acenaphthene onto rice husk adsorbent range from 0.9667 - 0.9754 and decreases as the carbonisation temperature increases from 300 - 6000C. Since these values compare well with the correlation coefficients (R^2) obtained for Langmuir isotherm model, it suggests that Temkin Isotherm model can be applied to the study of adsorption capacity of rice husk carbons for the removal of acenaphthene in wastewater [37]. The heat of adsorption of acenaphthene, however, increases from 764.65 - 920.56 Jmol⁻¹ as the carbonization temperature increases from 300 - 6000C.

Effect of carbonization temperature and initial concentration on Dubnin-Radushkevich Isotherm Model

Values of Dubnin-Radushkevich (D-R) Isotherm Model obtained from the plot of $\ln q_c$ and E_2 (Figure 5) for the adsorption of acenaphthene onto rice husk at varying temperature of 300 - 6000C are shown in Table 2.

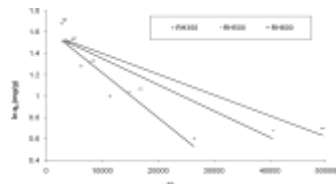


Figure 5: Dubnin-Radushkevich adsorption isotherm of acenaphthene onto rice husk

Similarly, the application of this isotherm to the study of adsorption of acenaphthene was based on its large values of correlation coefficients, R^2 , (0.9215 - 0.9445) which compare well with correlation coefficients obtained for Langmuir isotherm. Q_T obtained for the adsorption of acenaphthene decreases (5.334 - 5.180 mg/g) with increasing carbonization temperature of the adsorbents produced from rice husk (RH) (Table 3). The mean free energy of adsorption (E) obtained for the adsorption of acenaphthene range from 35.36-158.11 Jmol⁻¹.

Error Analysis

The results of the error analysis of isotherm equations for the adsorption of acenaphthene onto rice husk (RH) are shown in Table 3. The Average Relative Error (ARE) obtained for Freundlich, Temkin and Dubnin-Radushkevich are less than one

(<1), while Average Relative Standard error (ARS) for Temkin (1.0 - 1.17) and Freundlich (1.07 - 1.16) are lower than those obtained for Dubnin-Radushkevich (1.14 - 1.40) and Langmuir (4.48 - 19.72). The order of suitability is given as Temkin > Freundlich > Dubnin-Radushkevich > Langmuir. The lower values of ARS for Temkin and Freundlich compare well with each other and, thus, proposed as suitable isotherm models for fitting experimental data obtained for the adsorption of acenaphthene from wastewater onto the adsorbents produced from rice husk (RH), at various carbonization temperature (300 - 6000C).

Discussion

The yield of raw materials during carbonization is generally expected to reduced due to the greater decomposition of biomass at higher temperature, though, this may not directly relate to the efficiency of carbon in removing the targeted adsorbate but may be significant to their commercial utilization [38-39]. However, this is not considered as impediment in this preliminary study. Furthermore, the overall results showed that the activation process has effect on the yield of activated carbon obtained from RH and this indicates that, in relation to higher temperatures, more biomass that is oxidizable might have been produced at higher temperature, given the reduction trend when the carbons were activated with a strong oxidizing agent like H₃PO₄ [39]. Phosphoric acid has been used in activating carbon produced from Pecan shells, Peanut hulls, Almond shells and Coconut shells, [40-42] that share similar physical characteristic with rice husk.

This study further shows that the removal efficiencies of rice husk investigated for the adsorption of acenaphthene increased with increasing carbonization temperature but decreased with increased initial concentrations. This may be attributed to the partition coefficients (Log K_{ow}) of acenaphthene (3.989) which is relatively higher than that of naphthalene (3.36), the first in the homologous series of PAHs. This trend has been reported to be a factor that influences the adsorption of polyaromatic hydrocarbons in aqueous medium onto activated carbon [44].

The effect of carbonization temperature on Freundlich isotherm model revealed that the value of 'n' ranges from 1.08 - 1.38; this satisfies the condition $1 < n < 10$, which shows that it is a favourable adsorption [45]. The large values of R^2 (0.997 - 1.000) also showed that the Freundlich model is good for describing the adsorption of acenaphthene onto rice husk. The suitability of this model is an indication of heterogeneity of the adsorbents [36]. The effect of carbonization temperature on Langmuir isotherm model showed that Q_L range from 13.37 - 45.97 molg⁻¹, corresponds to decrease in adsorption capacity of the rice husk as the carbonization temperature increases, and this suggests that the adsorption process in this study is physisorption [22].

Generally, the correlation coefficients (R^2) of the activated carbons are high (0.9262 - 0.932), particularly for the Langmuir isotherm model, and suggests that rice husk activated carbons exhibits a monolayer reaction with constant activation energy [33-35]. Moreover, Temkin isotherm is generally applied to the study of dye [33, 36-37], and the adsorption heat values of Db-86 (dye) unto carbon produced from orange peels which ranged from 355.9 to 680.8 Jmol⁻¹ [37] are fairly less than those obtained in this study (764.65 - 920.56 Jmol⁻¹). Similarly, the adsorption heat of phenol (79.78 Jmol⁻¹) unto activated carbon derived from Rattan Sawdust [46] is less than the adsorption

heat of acenaphthene in this study. The large values of correlation coefficients (R^2) obtained for the adsorption of acenaphthene onto the adsorbents under study range from 0.9667 to 0.9766. It suggests, the experimental data of isotherms are very well described by both Langmuir and Temkin models.

The essential characteristic of the Dubinin-Radushkevich isotherm is the estimation of the mean free energy of adsorption (ϵ) often defined as the free energy change involved in the transfer of one mole of adsorbate onto the surface of adsorbent [34]. The closeness of mean free energy of adsorption observed in this study indicates that physico-adsorption play significant roles in the adsorption of acenaphthene from aqueous solution [37]. Moreover, the values of mean free energy of adsorption observed in this study fall between 5 and 40 KJmol⁻¹; and this confirms the type of adsorption involved in the study is physisorption (physical sorption), which usually takes place at low temperature [21, 47].

Conclusion

The following conclusions could be made based on the analysis of the results obtained from adsorption of acenaphthene from synthesised wastewater onto activated carbon produced from rice husk.

- Carbonization temperature and acid activation affect the yield of activated carbon produced from rice husk.
- The removal efficiencies of the rice husk adsorbents generally rank above 70% and are influenced by increasing carbonization temperature particularly at lower concentration of acenaphthene.
- Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherm models described well the equilibrium adsorption of acenaphthene onto activated carbon derived from rice husk

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Table 1: Effect of carbonization and acid activation on rice husk

Activated Carbon	Yield after Carbonization (%)	Washed-off after Acid Activation (%)
RH300	20	8.50
RH500	55	9.50
RH600	40	12.85

Table 2: Isotherm Models parameters for acenaphthene adsorption onto rice husk

Isotherm	Parameters	RH300	RH500	RH600
Freundlich	N	1.08	1.29	1.38
	K_f (mg/g)	0.1635	0.3091	0.3836
	R^2	0.9999	0.9987	0.9981
Langmuir	Q_L (molg ⁻¹)	45.97	15.82	13.37
	K_L (Lmol ⁻¹)	0.0031	0.0127	0.0175
	R^2	0.9262	0.9306	0.9320
Temkin	B	2.9683	2.5815	2.4656
	A	0.1321	0.1888	0.2214
	b (Jmol ⁻¹)	764.65	879.23	920.56
	R^2	0.9754	0.9693	0.9667
Dubnin-Radushkevich	K_T (10 ⁻⁴)	0.4	0.2	0.2
	Q_T (mg/g)	5.334	5.187	5.180
	E (Jmol ⁻¹)	35.36	158.1351	158.11
	R^2	0.9443	0.9273	0.9215

' K_f ' and 'n' are Freundlich parameters; ' Q_L ' and ' K_L ' are Langmuir parameters; A, B and b are Temkin parameters, ' Q_T ' and ' K_T ', are Dubnin–Radushkevich parameters; ' R^2 ' is the correlation coefficient while 'E' is the adsorption energy (J mol⁻¹).

Table 3: Error analysis of isotherm equation models for the adsorption of acenaphthene onto rice husk activated carbon

Adsorbent	Freundlich		Langmuir		Temkin		D-R	
	ARE	ARS	ARE	ARS	ARE	ARS	ARE	ARS
RH 300	0.944	1.16	14.43	19.72	0.955	1.17	0.802	1.40
RH 500	0.901	1.10	4.07	5.67	0.940	1.15	0.698	1.20
RH 600	0.88	1.07	3.19	4.48	0.670	1.00	0.669	1.14