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Isothermal studies of adsorption of acenaphthene from aqueous solution onto activated carbon produced from rice (*Oryza sativa*) husk

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ABSTRACT

Rice husk (RH), which is an agricultural waste material of environmental impact, was carbonized at 300–600°C in an oven for 2 h, after which its adsorption capacities were investigated for the adsorption of acenaphthene in synthetic aqueous solution with various concentrations (50–150 mg/L). The yields of carbon obtained from the raw RH ranged from 20 to 40% (w/w), while the adsorption capacities of RH increased with increasing carbonization temperature (300–600°C) and increasing initial concentration of acenaphthene (50–150 mg/L). The removal efficiencies (REs) of the RH increased from 71.37 to 80.56% as the carbonization temperature increased from 300 to 600°C, but decreased with increasing initial concentration of acenaphthene. The adsorption equilibrium data obtained fitted well to Freundlich, Langmuir, Temkin and Dubinin–Radushkevich isotherms with minimum correlation values of 0.998, 0.926, 0.966 and 0.922, respectively, although they generally decreased with increasing carbonization temperature. The error analysis showed the order of suitability of the isotherm models selected to be Temkin > Freundlich > Dubinin–Radushkevich > Langmuir. This study therefore indicates that activated carbon developed from RH possesses high potency of being used as activated carbon for the removal of acenaphthene from wastewater.

Keywords: Adsorption; Acenaphthene; Dubinin–Radushkevich; Freundlich; Langmuir; Rice husk; Temkin

1. Introduction

Municipal wastewater typically 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 [2–4]. 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 such as polycyclic aromatic hydrocarbons (PAHs), present in wastewater, are defying these age-long treatment processes.

PAHs are classified as priority organic pollutants (POPs) due to their carcinogenic, mutagenic and toxic properties [5–8]. They bear sizeable percentages of

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organic constituents of industrial wastewater, and as a result they 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 was 397.8 million tonnes [26]. Rice bran, (husker hull), which is mainly the pericarp of the rice grain, forms 10% weight by weight (w/w) of the raw rice. It is widely used as animal feed in various countries except the USA, where it is used for other industrial applications. Rice husk (RH) is commonly disposed in open-air burning and this causes environmental pollution, although the resulting ashes have been investigated as possible additives to cement. Furthermore, RH has been applied as adsorbent for the removal of pollutants in wastewater and higher effectiveness (nearly 100%) of heavy metals removal has been recorded in various studies [27–30]. The candidate adsorbate considered in this study is acenaphthene which is a common 3-ring PAHs found in coal tar and the environment particularly [31]. It is a white, needle-like solid with a molecular weight of 154.21 as well as melting and boiling points of 93.4 and 279℃, respectively. This study investigates the effectiveness of the adsorbent produced from RH for the removal of acenaphthene from simulated wastewater under the effect of carbonization temperature and initial concentration using various adsorption isotherms.

2. Materials and methods

2.1. Equipment and reagents

The equipment used in this study include nutcracker, mortar and pestle, magnetic stirrer and mechanical shaker fixed with sieves, furnace (Model 18A, Italy) and electronic weighing machine while the analytical instruments used include gas chromatography (PerkinElmer Autosystem) coupled with mass spectroscopy/flame ionization detector (GC–MS/FID). The glasswares used were washed with detergent and rinsed with diluted nitric acid and copious amount of distilled water, since the reagents to be used include hydrocarbon. The reagents used were sodium bicarbonate ($NaHCO_3$), phosphoric acid (H_2PO_4, 85%), acetone (BDH Chemicals Ltd.) and acenaphthene (Merck).

2.2. Sampling and sample processing

The RH, obtained from Arowomole Rice Mill, Ogbomosho, Oyo State, Nigeria, 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℃ overnight [24]. The dried samples were then stored in dry container prior to carbonization.

2.3. Carbonization and activation

Carbonization is essentially employed to convert carbonaceous material to char and this eventually opens the pores of the char for adsorption process. Thousand grams of RH was carbonized at different temperature (300, 500 and 600℃), individually, in Vecstar Furnace (Model 184A, Italy) for 2 h [24] and the resulting charred material was weighed to determine the percentage yield calculated from the relation (Eq. (1)). The carbonized RH sample was weighed, soaked in excess phosphoric acid (H_3PO_4) for 3 h and then charged into the oven at 200℃ for 24 h to ensure proper adsorptive drying. The sample was later removed from the furnace, allowed to cool to room temperature and then washed with bicarbonate solution ($NaHCO_3$). The resulting mixture was further washed with distilled water until the pH reached neutral point (6.9–7.0), sieved and dried in the furnace at 105℃ to constant weight [24].

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

Where W_I = initial weight before carbonization and W_F = final weight after carbonization.

2.4. Preparation of adsorbates and adsorption study

Fifty milligrams of acenaphthene was added to 300 mL of acetone and the mixture was carefully stirred with magnetic stirrer for 10 min, to allow proper dissolution. Seven hundred millilitres of distilled water was added to the mixture piecemeal and further shaken thoroughly to further facilitate thorough dissolution of the adsorbates and thus 50 mg/L of acenaphthene was produced according to [15]. RH adsorbent (1 g) was weighed into a 250 mL conical flask containing 50 mL of 50 mg/L acenaphthene solution and the mixture was covered and agitated on mechanical shaker at 400 rpm for 3 h, after which the content was centrifuged at 500 rpm for 20 min. The supernatant solution was decanted into sample bottles and stored for analysis. The procedure was repeated for 75, 100, 125 and 150 mg/L of acenaphthene and subsequently for the adsorbent carbonized at various temperatures (300–600˚C).

2.5. Analytical measurement

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 and 0.25 μm of film thickness was used. The column temperature was 60˚C for 2 min to 320˚C programmed at 10˚C/min. Nitrogen was used as the 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 and 320˚C, respectively. Sample (1.0 μL) was injected before analysis and calibration standard was run to check column performance peak height and resolution. The limits of detection of the compound were identified mainly by its retention time. The abundance of quantification of analyte with respect to authentic PAH standard detection limits was derived from replicate procedure.

2.6. Quantification values

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

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

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 in the solution quantified with GC–FID (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 by using Eq. (3) [32].

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

where C_0 and C_e have the same definition described earlier.

2.7. Adsorption isotherm models

Adsorption isotherm equations that are applicable to single solute 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 Microsoft Office Excel tool. The best fit of the isotherm equations was further determined using linear regression and their suitability was validated with their correlation coefficients (R^2) obtained [34]. Thus, the data obtained in this study were fitted to selected adsorption isotherms such as Freundlich, Langmuir, Temkin and Dubinin–Radushkevich, in order to understand the adsorption process under the influence of various carbonization temperature and the initial concentrations of the adsorbates.

2.8. Langmuir isotherm model

The linearized form of the Langmuir isotherm equation is expressed as:

$$C_e/q_e = \frac{1}{Q_L K_L} + \frac{1}{Q_L} C_e \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbates and 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 C_e/q_e against C_e.

2.9. Freundlich isotherm model

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

$$\text{In} q_e = \text{In} K_f + 1/n \, \text{In} C_e \tag{5}$$

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

2.10. Temkin isotherm equation

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

$$q_e = B \text{In} A + B \text{In} C_e \tag{6}$$

where A and B are the Temkin constants which are evaluated by plotting q_e against $\text{In} C_e$.

B was further determined from the expression

$$B = RT/b \tag{7}$$

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

2.11. Dubinin–Radushkevich isotherm (D–R)

Dubinin–Radushkevich isotherm equation is commonly expressed in linear logarithmic form as:

$$\text{In}q_e = \text{In}Q_{DR} - K\varepsilon^2 \tag{8}$$

where

$$\varepsilon = RT\text{In}\left(1 + \frac{1}{C_e}\right) \tag{9}$$

The adsorption of acenaphthene present in wastewater onto the activated carbon produced from RH was investigated in this study. Dubinin–Radushkevich isotherm constants, 'K' and 'Q_{DR}' (mg g^{-1}), were evaluated by plotting Inq_e against R^2.

2.12. Mean free energy of adsorption

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

$$E = 1/\sqrt{2K} \tag{10}$$

2.13. Error analysis

The error analyses, average relative error (ARE) and average relative standard error (ARSE), were employed 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].

$$\text{ARE} = \left[\sum |(q_c - q_e)/q_e|\right] \tag{11}$$

The ARSE

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

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

3. Results and discussion

3.1. Effect of carbonization and activation on carbon yield

The yields (%) obtained after carbonization of the raw RH at 300–600°C, were generally less than 50%, except at 500°C (55%) (Table 1). These values do not follow fixed pattern with respect to the temperature, however, they compare well with the yields reported for similar agricultural wastes such as pistachio (20%), almond (38%), hazelnut (52%) and walnut (57%) [38]. Moreover, Kazemipour et al. [38] noted that 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. H_3PO_4 was employed as an activant for the activation process in this study due to its effectiveness in enhancing activated carbon surface area [17]. Table 1 shows the percentage washed-off, which ranged between 8.5 and 12.85% and it increased with increasing carbonization temperature, 300–600°C. The overall results show that H_3PO_4 had less effect on the yield of the activated carbon obtained as observed by Johns et al. [17].

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

The effect of initial concentrations (50–150 mg/L) of acenaphthene on the REs of the RH with respect to the range of carbonization temperature (300–600°C) is shown in Fig. 1. The REs (71.37–80.56%) recorded

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

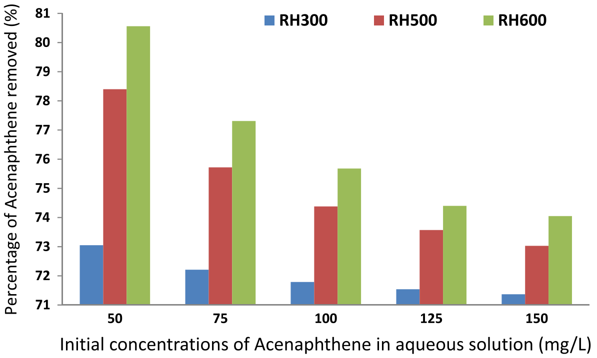

Fig. 1. Removal efficiency (RE %) of rice husk activated carbon at different initial concentrations of acenaphthene in wastewater.

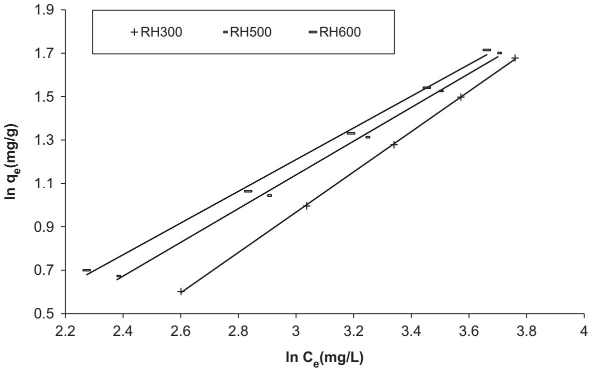

Fig. 2. Freundlich adsorption isotherm of adsorption of acenaphthene onto rice husk carbonized at 300–600℃.

at various temperatures generally decreased with increasing concentration, but increased for the increasing carbonization temperature at a particular initial concentration. This indicates that RH 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.

3.3. Effect of carbonization temperature and initial concentration on isotherm models

Fig. 2 shows the plots of Inq_e vs. InC_e used for determining the Freundlich isotherm parameters. Freundlich isotherm parameters obtained for the adsorption of acenaphthene with the selected adsorbents carbonized at varying temperature (300–600℃) are shown in Table 2. Fig. 3 shows the plots of C_e/q_e vs. q_e, and the linear method was used to determine the Langmuir isotherm parameters adsorption. The Langmuir isotherm model was well fitted to the experimental data obtained for the study, and the values of Q_L ranged from 13.37 to 45.97 mol g^{-1} (Table 2).

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 vs. InC_e (Fig. 4). The large values of correlation coefficients (R^2) obtained for the adsorption of acenaphthene onto RH adsorbent range from 0.9667 to 0.9754 and decreased as the carbonization temperature increased

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 (mol g^{-1})	45.97	15.82	13.37
	K_L (L mol^{-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 (J mol^{-1})	764.65	879.23	920.56
	R^2	0.9754	0.9693	0.9667
Dubinin–Radushkevich	K_T (10^{-4})	0.4	0.2	0.2
	Q_T (mg/g)	5.334	5.187	5.180
	E (J mol^{-1})	35.36	158.14	158.11
	R^2	0.9443	0.9273	0.9215

Notes: '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 Dubinin–Radushkevich parameters; 'R^2' is the correlation coefficient, while 'E' is the adsorption energy (J mol^{-1}).

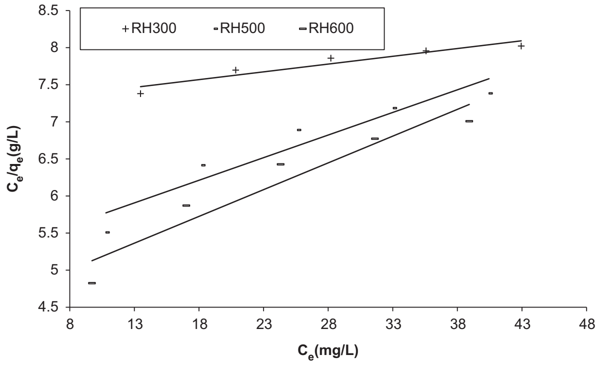

Fig. 3. Langmuir adsorption isotherm of adsorption of acenaphthene onto rice husk carbonized at 300–600°C.

from 300 to 600°C. 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 RH carbons for the removal of acenaphthene in wastewater [37]. The heat of adsorption of acenaphthene, however, increased from 764.65 to 920.56 J mol^{-1} as the carbonization temperature increased from 300 to 600°C. Dubinin–Radushkevich (D–R) isotherm model parameter was obtained from the plot of Inq_c and E^2 (Fig. 5) for the adsorption of acenaphthene onto RH at varying temperature of 300–600°C (Table 2). Similarly, the application of this isotherm to the study of adsorption of acenaphthene was based on the large values of R^2 (0.9215–0.9445), which compare well with correlation coefficients obtained for Langmuir isotherm. 'Q_T' (5.334–5.180 mg/g) obtained decreased with increasing carbonization temperature of the adsorbents produced from RH (Table 3). The mean free energy of adsorption (E) obtained ranged from 35.36 to 158.11 J mol^{-1}.

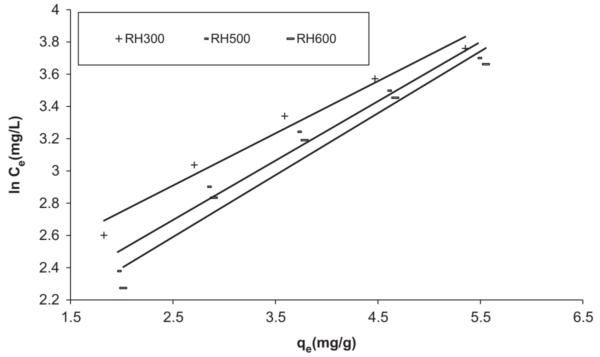

Fig. 4. Temkin adsorption isotherm of adsorption of acenaphthene onto rice husk carbonized at 300–600°C.

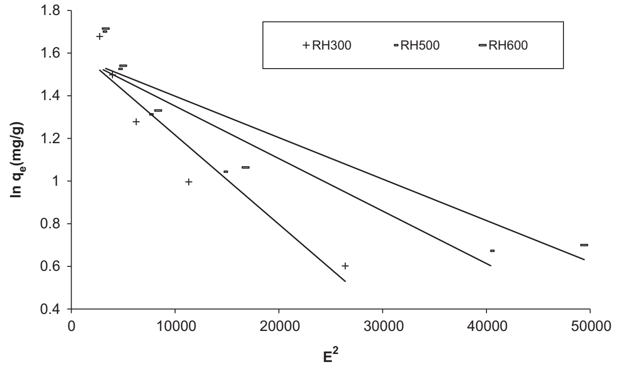

Fig. 5. Dubinin–Radushkevich adsorption isotherm of adsorption of acenaphthene onto rice husk carbonized at 300–600°C.

3.4. Error analysis

The error analysis of the selected isotherm equations for the adsorption of acenaphthene onto RH are shown in Table 3. The AREs obtained for Freundlich, Temkin and Dubinin–Radushkevich were less than one (<1), while ARSEs for Temkin (1.0–1.17) and Freundlich (1.07–1.16) were lower than those obtained for Dubinin–Radushkevich (1.14–1.40) and Langmuir (4.48–19.72). The order of suitability is given as Temkin > Freundlich > Dubinin–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 RH, at various carbonization temperature (300–600°C).

3.5. Discussion

The yield of raw materials during carbonization is generally expected to reduce due to the greater decomposition of biomass at higher temperature, though this may not directly relate to the efficiency of carbon in the removal of 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 are oxidizable might have been produced at higher temperature, given the reduction trend when the carbons were activated with a strong oxidizing agent such as H_3PO_4 [39]. Phosphoric acid has been used in activating carbon produced from pecan shells, peanut hulls, almond shells and coconut shells which share similar physical characteristic with RH [40–42].

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

	Adsorption isotherm models							
	Freundlich		Langmuir		Temkin		D–R	
Adsorbent	ARE	ARS	ARE	ARS	ARE	ARS	ARE	ARS
RH300	0.944	1.16	14.43	19.72	0.955	1.17	0.802	1.40
RH500	0.901	1.10	4.07	5.67	0.940	1.15	0.698	1.20
RH600	0.88	1.07	3.19	4.48	0.670	1.00	0.669	1.14

Note: ARE, average relative error; ARS, average relative standard error.

This study further shows that the REs of RH 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 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 to 1.38, and this satisfies the condition $1 < n < 10$, which showed that it is a favourable adsorption [45]. Furthermore, the large values of R^2 (0.997–1.000) showed that the Freundlich model is good for describing the adsorption of acenaphthene on RH adsorbent. The suitability of this model is an indication of heterogeneity of the adsorbents [36]. Moreover, the effect of carbonization temperature on Langmuir isotherm model showed that 'Q_L' range from 13.37 to 45.97 mol g^{-1}, which corresponds to decrease in adsorption capacity of the RH as the carbonization temperature increases, suggests that the adsorption process in this study is physisorption [22].

Generally, the correlation coefficients (R^2) of the activated carbons were high (0.9262–0.932) and such high degree of R^2, particularly for the Langmuir isotherm model, suggests that RH activated carbons exhibits a monolayer reaction with constant activation energy [33–35]. Temkin isotherm is generally applied to the study of dye [33,36,37], and the values of heat of adsorption of Db-86 (dye) onto activated carbon produced from orange peels ranged from 355.9 to 680.8 J mol^{-1} [37] and they are lesser than those obtained in this study (764.65–920.56 J mol^{-1}). Similarly, the heat of adsorption of phenol (79.78 J mol^{-1}) onto activated carbon derived from rattan sawdust [46] is less than the heat of adsorption of acenaphthene in this study. The large values of correlation coefficients (R^2) obtained for the adsorption of acenaphthene onto RH adsorbent ranged from 0.9667 to 0.9766. Since these values compare well above 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 activated carbon produced from RH for the removal of acenaphthene in wastewater.

The essential characteristic of the Dubinin–Radushkevich isotherm model is the estimation of the mean free energy of adsorption (ε) which is often defined as the free energy change involved in the transfer of one mole of adsorbate onto the surface of adsorbent [34]. Nemr et al. [37] suggested that the closeness of mean free energy of adsorption, as observed for the adsorption of acenaphthene onto RH300, RH500 and RH600, indicates that physicosorption plays significant roles in the adsorption of the adsorbate from the wastewater. Moreover, the mean free energy of adsorption observed in this study ranged between 5 and 40 K J mol^{-1}, and this corroborates the type of adsorption involved in the study to be physisorption (physical sorption), which usually takes place at low temperature [21,47]. Furthermore, the applicability of this isotherm to the study of adsorption of acenaphthene was based on the large value of its correlation coefficients (R^2).

4. Conclusion

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

- Carbonization temperature and acid activation affect the yield of activated carbon produced from RH.
- The REs of the RH 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 RH.
- Temkin isotherm is the most suitable to describe the adsorption study of acenaphthene onto RH.
- The adsorption type involved in the study is physisorption (physical sorption), which usually takes place at low temperature.

Conflict of interest

The authors have declared no conflict of interest.

Abbreviations

RH — rice husk
RH300 — rice husk carbonized at 300°C
RH500 — rice husk carbonized at 500°C
RH600 — rice husk carbonized at 600°C

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