

**ARTICLE INFO** 

Article history:

15 May 2012:

Keywords

Adsorption,

Freundlich,

Temkin.

Acenaphthene,

Received: 1 February 2012;

Received in revised form:

Accepted: 24 May 2012;

Dubnin-Radushkevich,

Langmuir, Rice husk,

Available online at www.elixirpublishers.com (Elixir International Journal)

**Chemical Engineering** 

Elixir Chem. Engg. 46 (2012) 8461-8467



# Isothermal studies of adsorption of acenaphthene from aqueous solution onto activated carbon produced from rice (*Oriza Sativa*) husk

Abass Olanrewaju Alade<sup>1</sup>, Omotayo Sarafadeen Amuda<sup>2</sup>, Afolabi Tinuade Jolaade<sup>2</sup> and Asiata Omotayo Ibrahim<sup>2</sup> <sup>1</sup>Department of Chemical Engineering Ladoke Akintola University of Technology, Ogbomosho, Nigeria. <sup>2</sup>Analytical/Environmental Chemistry Unit, Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomosho, Nigeria.

Ogdomosno, Nig

ABSTRACT Rice husk, agricultural waste material of environmental impact, was carbonized at temperatures of  $300 - 600^{\circ}$ 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 values of 0.9981, 0.9262, 0.9667 and 0.9215, respectively, although, generally decreases with increasing carbonization temperature. 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 high potency of being used as activated carbon for the removal of acenaphthene from wastewater.

#### © 2012 Elixir All rights reserved.

## 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.

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), electronic weighing machine and

Tele: E-mail addresses: osamuda@lautech.edu.ng © 2012 Elixir All rights reserved

<sup>8461</sup> 

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<sub>3</sub>), phosphoric acid (H<sub>2</sub>PO<sub>4</sub>, 85%), acetone (BDH Chemicals Ltd) and Acenaphthene (Merck).

### Sampling and Sample processing

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  $^{0}$ 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<sub>3</sub>PO<sub>4</sub>) for 3 h and then charged into the oven at temperature of 200 <sup>0</sup>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<sub>3</sub>, 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].

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

where  $W_{I}$  = Initial weight before carbonization and  $W_{F}$  = Final weight after carbonization

#### **Preparation of Adsorbates and Adsorption Study**

50 mg of acenaphthene was added to 300 ml of acetone in 1dm<sup>3</sup> standard flask and the mixture was carefully stirred with magnetic stirrer for 10 mins, in order to allow proper dissolution, 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 50 mg/L acenaphthene solution and the mixture was covered and agitated on mechanical shaker at 400 rpm for 3hrs, after which the content was centrifuged at 500 rpm for 20 mins. The supernatant solution was decanted into sample bottles and stored for analyses. The process was repeated for 75, 100, 125 and 150mg/L of acenaphthene and subsequently for the adsorbent carbonized at various temperatures.

#### **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  $\mu$ m and 0.25  $\mu$ m film thickness was used. The column temperature was 60  $^{\circ}$ C for 2 min to 320  $^{\circ}$ C programmed at 10  $^{\circ}$ C/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  $^{0}$ C and 320  $^{0}$ C, respectively. 1.0  $\mu$ L Sample 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.

#### **Quantification Values**

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

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

where  $q_e$  is the concentration of the adsorbed solute (mg/g),  $C_o$  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 according to equation 3 [32].

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

where  $C_o$  and  $C_e$  have the same definition described earlier.

#### **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 Excel Microsoft Office tool. The best fit of the isotherm equations were further determined using linear regression and their suitability is validated with values of the correlation coefficients ( $\mathbb{R}^2$ ) 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 as:

$$\frac{C_{e}}{q_{e}} = \frac{1}{Q_{L}K_{L}} + \frac{1}{Q_{L}}C_{e}$$
 (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  $C_e/q_e$  against  $C_e$ .

#### **Freundlich Isotherm Model**

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

$$Inq_e = InK_f + \frac{1}{n}InC_e \qquad (.5)$$

A plot of  $Inq_e$  against  $InC_e$  was used to determine the Freundlich constants,  $K_f$  and 1/n.

#### **Temkin Isotherm equation**

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

$$q_e = BInA + BInC_e \tag{6}$$

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

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

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

#### Dubnin-Radushkevich Isotherm (D-R)

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

$$Inq_{e} = InQ_{DR} - K\varepsilon^{2}$$
(8)
where  $\varepsilon = RTIn\left(1 + \frac{1}{C_{e}}\right)$ 
(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<sup>-1</sup>) were evaluated by plotting  $Inq_e$  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<sup>-1</sup>), and obtained from the plot of Dubnin-Radushkevic using the relation [37].

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

#### **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].

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

The average relative standard error (ARS)

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

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.

#### **Results and Discussion**

#### Effect of Carbonization and activation on carbon yield

The yields (%), as determined from eqn (1), obtained after carbonization of the raw rice husk at 300-600  $^{0}$ C, were generally less than fifty percent (50%), except at 500  $^{0}$ 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 <sup>0</sup>C. The overall results show that the activant (H<sub>3</sub>PO<sub>4</sub>) 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 - 150 mg/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.

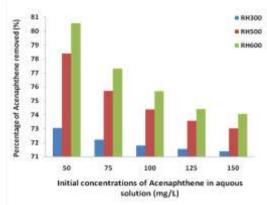
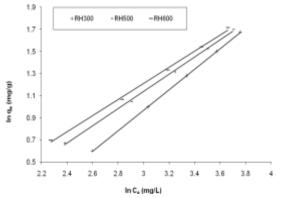
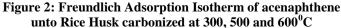


Figure 1: Removal Efficiency (RE %) of Rice Husk activated carbon at different initial concentrations of Acenaphthene in wastewater

Effect of carbonization temperature and initial concentration on Freundlich Isotherm Model

Figure 2 shows the plots of  $Inq_e$  versus  $InC_e$  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  $^{\circ}C$ ) are shown in Tables 2.





# Effect of carbonization temperature and initial concentration on Langmuir Isotherm model

Figures 3 shows the plots of Ce/q<sub>e</sub> versus q<sub>e</sub> 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<sup>-1</sup> (Table 2).

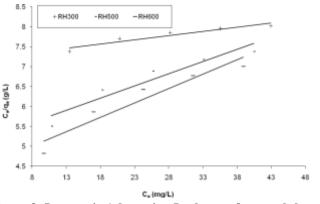


Figure 3: Langmuir Adsorption Isotherm of acenaphthene unto Rice Husk carbonized at 300, 500 and 600 <sup>o</sup>C Effect of carbonization temperature and initial concentration on Temkin Isotherm model

Temkin isotherm parameters, B,  $Q_A$  and b, (Table 2) and their corresponding correlation coefficients (R<sup>2</sup>) were obtained from the plot of  $q_e$  versus InC<sub>e</sub> (Figure 4). The large values of correlation coefficients (R<sup>2</sup>) obtained for the adsorption of acenaphthene unto rice husk adsorbent range from 0.9667 -0.9754 and decreases as the carbonisation temperature increases from 300 - 600<sup>o</sup>C. Since these values compare well with the correlation coefficients (R<sup>2</sup>) 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<sup>-1</sup> as the carbonization temperature increases from 300 - 600<sup>o</sup>C.

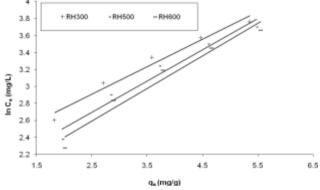
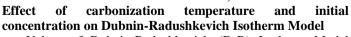


Figure 4: Temkin Adsorption Isotherm of acenaphthene unto Rice Husk carbonized at 300, 500 and 600<sup>o</sup>C



Values of Dubnin-Radushkevich (D-R) Isotherm Model obtained from the plot of In  $q_c$  and  $E^2$  (Figure 5) for the adsorption of acenaphthene unto rice husk at varying temperature of 300 - 600<sup>o</sup>C are shown in Table 2. 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 35.36–158.11Jmol<sup>-1</sup>.

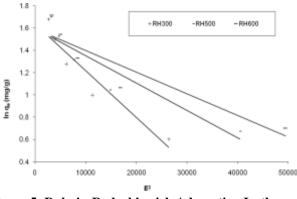


Figure 5: Dubnin-Radushkevich Adsorption Isotherm of acenaphthene unto Rice Husk carbonized at 300, 500 and 600  $^{\circ}C$ 

#### **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 are suitable isotherm models for fitting experimental data obtained for the adsorption of acenaphthene from wastewater unto the adsorbents produced from rice husk (RH), at various carbonization temperature (300 - $600^{0}$ C).

#### 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 H<sub>3</sub>PO<sub>4</sub> [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 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 unto 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 – 45.97molg<sup>-1</sup>, 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) and such high degree of  $\mathbb{R}^2$ , particularly for the Langmuir isotherm model, 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 values of heat of adsorption of Db-86 (dve) unto carbon produced from orange peels which ranged from 355.9 to 680.8 Jmol<sup>-1</sup> [37] are fairly less than those obtained in this study  $(764.65 - 920.56 \text{ Jmol}^{-1})$ . Similarly, the heat of adsorption of phenol (79.78 Jmol<sup>-1</sup>) unto 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 unto the adsorbents understudy range 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 rice husk for the removal of acenaphthene in wastewater.

The essential characteristic of the Dubinin-Radushkevich isotherm is the estimation of the mean free energy of adsorption (ɛ) often defined as the free energy change involved in the transfer of one mole of adsorbate unto the surface of adsorbent [34]. Nemr et al., [37], suggested that the closeness of the values of mean free energy of adsorption as observed for the adsorption of acenaphthene unto RH300, RH500 and RH600 indicate that physico-sorption play significant roles in the adsorption of the adsorbate from the wastewater. Moreover, the values of mean free energy of adsorption observed in this study fall between 5 and 40 KJmol<sup>-1</sup>; and this confirms the type of adsorption involved in the study is 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<sup>2</sup>)

#### Conclusion

The following conclusions could be made based on the analysis of the results obtained from adsorption of acenaphthene from synthesised wastewater unto 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 Dubnin-Radushkevich isotherm models described well the equilibrium adsorption of acenaphthene unto activated carbon derived from rice husk

• Temkin isotherm is the most suitable to describe the adsorption study of acenaphthene unto rice husk.

## References

1. ESCWA, Waste – water treatment technologies: A general review, Economic and Social Commission for Western Asia, United Nations, New York, U.S.A. 2003.

2. D.H.F. Liu, B.G. Liptak, Wastewater Treatment, Lewis Publishers. Boca Raton, FL. 2000.

3. O. S. Amuda, A. O. Alade, Coagulation/flocculation process in the treatment of abattoir wastewater. Desalination, 196, 22-31, 2006.

4. P. S. Kunwar, M. Amrita, S. Sarita, O. Priyanka, Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material. J. Hazard. Mater. 2008, 150, 626–641.

5.J. Arrey, Environmental Chemistry, PAHs and Related Compounds, Vol. 3, Springer, Berlin. 1998.

6. E. Manoli, C. Samara, Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. Trends Anal. Chem., 1999, 18, 417–428

7. B. Finlayson-Pitts, J. Pitts, Chemistry of the upper and lower atmosphere: theory, experiments, and applications, Academic Press. 2000.

8. A.D. Pereira Netto, J.C. Moreira, A.E.O.D. Xavier, G. Arbilla, L.F.V. Ferreira, A.S. Oliveira, J. Barek, Avaliac,a<sup>\*</sup>o da contaminac,a<sup>\*</sup>o humana por hidrocarbonetos polici<sup>\*</sup>clicos aroma<sup>\*</sup>ticos (PAHs) e seus derivados nitrados (NPAHs): uma revisa<sup>\*</sup>o metodolo<sup>\*</sup>gica. Qui<sup>\*</sup>m. Nova. 2000, 23: 765–773

9. R. Pitt, B. Roberson, P. Barron, A. Ayyoubi, S. Clark, Storm water treatment at critical areas: The multi-chambered treatment train (MCTT). U.S. Environmental Protection Agency, Water Supply and Water Resource Division. National Risk Management Research Laboratory. EPA 600/R-99/017. Cincinnati, OH. 1999.

10. S. McCready, D. J. Slee, G. F. Birch, S. E. Taylor, The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. Marine Pollut. Bull, 2000, 40 (11), 999-1006.

11. E. Naffrechoux, E. Combet, B. Fanget, L. Paturel, F. Berthier, Occurrence and fate of PAHs from road runoff in the south drainage basin of Annecy Lake. Polycyclic Arom. compd., 2000, 18 (2) 149–159.

12. G. Witt, Occurrence and transport of polycyclic aromatic hydrocarbons in the water bodies of the Baltic Sea. Marine Chemistry, 2002, 79, 49–66

13. B. Vrana, A. Paschke, P. Popp, Polyaromatic hydrocarbon concentrations and patterns in sediments and surface water of the Mansfeld region, Saxony-Anhalt, Germany. J. Environ. Monitor. 2001, 3, 602–609.

14. H. M. Hwang, G. D. Foster, Characterization of polycyclic aromatic hydrocarbons in urban storm water runoff flowing into the tidal Anacostia River. Environ. Pollut, 2006,140, 416-426.

15. R. Crisafully, M.A.L. Milhome, R. M. Cavalcante, R. M. Silveira, E. R. Keukeleire, R. F. Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. Biores. Technol, 2008, 99, 4515-4519.

16. WHO, Polycyclic aromatic hydrocarbons. In Guidelines for drinking-water quality. 2nd Ed. Vol. 2. Health criteria and other

supporting information, Geneva, World Health Organization, pp. 123 – 152. 1998.

17. M. M. Johns, W. E. Marshall, C. A. Toles, Agriculture byproducts as granular activated carbons for adsorbing dissolved metals and organics. J. Chem. Technol. Biotechnol. 1998, 71(2), 131-140.

18. S. B. Lalvani, T. Wiltoski, A. Hubner, A. Weston, N. Mandich, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. Carbon, 1998, 36, 1219–1226.

19. C. A. Toles, W. E. Marshall, M. M. Johns, Phosphoric acid activation of nutshells for metals and organic remediation: Process optimization. J. Chem. Technol. Biotechnol. 1998, 72(30), 255-263

20. C. A. Toles, W. E. Marshall, M. M. Johns, L. H. Wartelle, A. McAloon, Acid activated carbons from almond shells: Physical, chemical and adsorptive properties and estimated cost of production. Biores. Technol. 2000, 71(1), 87-92.

21. D. O. Cooney, Adsorption designer for wastewater treatment. Lewis Publishers, London, England, UK, 1999.

22. S. A. Dastgheib, D. A. Rockstraw, Pecan shell activated carbon: synthesis, characterization, and application for the removal of carbon from aqueous solution. Carbon, 2001, 39(12), 1849-1855.

23. L. H. Wartelle, W. E. Marshall, Nutshells as granular activated carbons: physical, chemical and adsorptive properties. J. Chem. Technol. Biotechnol. 2001, 76, 451-455.

24. O. S. Amuda, A. O. Ibrahim, Industrial wastewater treatment using natural materials as adsorbent. African Journal of Biotechnology, 2006, 5 (16), 1483 – 1487.

25. S. Laohaprapanon, M. Marques, W. Hogland, Removal of Organic Pollutants from Wastewater Using Wood Fly Ash as a Low-Cost Sorbent CLEAN – Soil, Air, Water 2010, 38 (11), 1055–1061.

26. Economic Research Service (ERS). Briefing: Rice. United States Department of Agriculture. 2004. http://www.ers.usda.gov/briefing/rice/.

27. M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption Studies on Rice Husk: Removal and Recovery of Cd (II) from Wastewater. Bioresource Tech., 2003, 86, 147-149.

28. K.K. Wong, C. K. Lee, K. S. Low, M. J. Haron, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solution. Chemosphere, 2003, 50, 23-28.

29. A.A.M. Daifullah, B. S. Girgis, H. M. H. Gad, Utilization of agro-residues (rice husk) in small wastewater treatment plants. Mater. Lett. 2003, 57:1723-1731.

30. P. Subramaniam, N. A. Khan, S. Ibrahim, Rice husk as an adsorbent for heavy metals. Proceedings of International Conference on Water and Wastewater (ASIAWATER 2004) Kuala Lumpur, Malaysia. 2004.

31. I.L. Finar, Organic Chemistry Vol 1, (6<sup>th</sup> Ed) Pearson Education. Singapore Pte Limited 2005, 793.

32. O.S. Amuda, F.E. Adelowo, M.O. Ologunde, Kinetics and equilibrium studies of adsorption of chromium (VI) ion from industrial wastewater using *Chrysophyllum albidum* 

(Sapotaceae) seed shells. *Colloids and Surfaces B: Biointerfaces.* 2009, 68, 184–192.

33. R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao, M. Tan, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite. Chemical Engineering Journal, 2009, 145, 496-504.

34. A.E. Nemr, Potential of pomegranate husk carbon for Cr (VI) removal from wastewater: kinetic and isothermal studies. J. Hazard. Mater. 2009, 161, 132-141.

35. W.H. Cheung, Y. S. Szeto, G. McKay, Enhancing the adsorption capacities of acid dyes by chitosan nano particles. Biores. Technol. 2009, 100, 1143–1148

36. A. Olgun, N. Atar, Equilibrium and kinetic adsorption study of Basic Yellow 28 and Basic Red 46 by a boron industry waste. J. Hazard. Mater. 2009, 161, 148–156

37. A. E. Nemr, O. Abdelwahab, A. El-Sikaily, A. Khaled, Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. J. Hazard. Mater., 2009, 161, 102–110.

38. M. Kazemipour, M. Ansari, S. Tajrobehkar, Removal of lead, cadmium, zinc and copper from industrial wastewater by carbon developed from walnut, hazelnut almond, pistachio shell and apricot stone. J. Hazard. Mater. 2008, 150, 322 – 327.

39. O. Ioannidou, O. Zabaniotou, Agricultural residues as precursors for activated carbon production – A review. Renewable and Sustainable Energy Reviews 2007, 11, 1966 – 2002.

40. A. N. A. El-Hendawy, S. E. Samra, B. S. Girgis, Adsorption characteristics of activated carbons obtained from corncobs. Colloid Surface A: Physicochem Eng Aspects. 2001, 180, 209–221.

41. M. Ahmedna, W. E. Marshall, A. A. Husseiny, R. M. Rao, I. Goktepe, The use of nutshell carbons in drinking water filters for removal of trace metals. Water Res., 2004, 38, 1062–1068.

42. O. S. Amuda, A. A. Giwa, I. A. Bello, Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon, Biochem. Eng. J., 2007, 36, 173-181.

43. L. C. Bornemann, R. S. Kookana, G. Welp Differential sorption behaviour of aromatic hydrocarbons on charcoal prepared from different temperatures from grass and wood. Chemosphere 2007, 67, 1033–1042.

44. J. Lemic, M. Tomasevic–Canovic, M. Adamovic, D. Kovacevic, S. Milicevic, Competitive adsorption of polycyclic aromatic hydrocarbons on organo–zeolites. Microporous and Mesoporous Mater. 2007, 105, 317 – 323

45. J.R. Rao, T. Viraraghavan, Biosorption of phenol from an aqueous solution by Aspergillus niger biomass. Biores. Technol. 2002, 85, 165.

46. B.H. Hameed, A.A. Rahman, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. J. Hazard. Mater. 2008, 160: 576–581.

47. V. J. Inglezakis, S. G. Poulopoulo, Adsorption, Ion Exchange and Catalysis: Design, Operations and Environmental Applications. Elsevier, Amsterdam, The Netherlands. 2006.

Table 1: Effect of Carbonization and acid activation on Rice husk

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

Table 2: Isotherm Models parameters for Acenaphthene adsorptio	n onto rice husk
--	------------------

· · · · · · · · · · · · · · · · · · ·		· · · · · · · · · ·		<b>I</b>
Isotherm	Parameters	RH300	RH500	RH600
Freundlich	Ν	1.08	1.29	1.38
	$K_{f}(mg/g)$	0.1635	0.3091	0.3836
	$\mathbb{R}^2$	0.9999	0.9987	0.9981
Langmuir	$Q_L (molg^{-1})$	45.97	15.82	13.37
	$K_L$ (Lmol <sup>-1</sup> )	0.0031	0.0127	0.0175
	$\mathbf{R}^2$	0.9262	0.9306	0.9320
Temkin	В	2.9683	2.5815	2.4656
	А	0.1321	0.1888	0.2214
	b (Jmol <sup>-1</sup> )	764.65	879.23	920.56
	$\mathbf{R}^2$	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 <sup>-1</sup> )	35.36	158.1351	158.11
	$R^2$	0.9443	0.9273	0.9215

 $K_{\rm F}^{\rm 0.9243}$  0.9275 0.9275 0.9215 'K<sub>F</sub>' and 'n' are Freundlich parameters; 'Q<sub>L</sub>' and 'K<sub>L</sub>' are Langmuir parameters; A, B and b are Temkin parameters, 'Q<sub>T</sub>' and 'K<sub>T</sub>', are Dubnin–Radushkevich parameters; 'R<sup>2'</sup> is the correlation coefficient while 'E' is the adsorption energy (J mol<sup>-1</sup>).

# Table 3: Error Analysis of Isotherm Equation Models for the Adsorption of Acenaphthene onto Rice Husk activated carbon

Adsorbent	Freun	dlich	Langmuir		Ten	Temkin		D-R	
	ARE	ARS	ARE	ARS	ARE	ARS	ARI	E ARS	
RH 300	0.944	1.16	14.43	19.72	0.955	1.17	0.80	2 1.40	
RH 500	0.901	1.10	4.07	5.67	0.940	1.15	0.69	8 1.20	
RH 600	0.88	1.07	3.19	4.48	0.670	1.00	0.66	9 1.14	

ARE (Average Relative Error), ARS (Average Relative Standard Error)