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Batch equilibrium and kinetic studies of naphthalene and pyrene adsorption onto coconut shell as low-cost adsorbent

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ABSTRACT

This study investigated the use of coconut shell as a non-conventional and low-cost adsorbent for the removal of naphthalene and pyrene from synthetic waste water. Coconut shells were used to adsorb naphthalene and pyrene at varying initial naphthalene and pyrene concentrations, adsorbent dosage, particle size and agitation time. The results of the batch equilibrium adsorption studies revealed that adsorption capacity decreased with increase in particle size and increased with increase in adsorbent dosage. The equilibrium adsorption data were analysed by two-parameter models of Langmuir and Freundlich and three-parameter models of Redlich-Peterson, Sips and Toth isotherms. The results showed that the equilibrium adsorption data for naphthalene and pyrene sorbent systems fitted well with all the tested adsorption isotherm models which can adequately describe the adsorption behaviour of naphthalene and pyrene onto coconut shell. The adsorption kinetic data obtained at 100 mg/l initial naphthalene and pyrene concentrations were analysed using Lagergren pseudo-first order, Elovich and intraparticle diffusion rate equations. The rate equations fitting showed that the adsorption kinetic data generally fit the three rate equations tested from which the rate constants and diffusion rate constants were estimated. However, the Lagergren pseudo first-order rate equation gave the best fit and, thus the process followed the first-order rate kinetics. Therefore, coconut shells being an agricultural waste product have the potential to be used as a low-cost adsorbent for the removal of organic pollutant from waste water.

Keywords: Adsorbent; Adsorption; Adsorption isotherms; Adsorption kinetics; Coconut shell

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical species with two to six fused benzene rings. They are an important family of toxic hazardous and long-persistent environmental pollutants that have been found to be carcinogenic and mutagenic [1–4]. PAHs originate from natural and anthropogenic sources. Anthropogenic sources include industrial processes, crude oil refineries, incinerators, urban run-offs, engine exhausts, domestic heating systems, incomplete combustion of fossil fuels, cooking process and smoke. Natural sources are terrestrial coal

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deposits, forest fires and volcanic eruptions [3,5–7]. The main sources of PAHs in surface waters are atmospheric deposition, runoffs from contaminated soil and deposition from sewage discharges [8]. Due to the hydrophobicity of most PAH, they have low water solubility and can therefore exist and accumulate in soils or water for a long period of time [3,9]. The ever increasing demand for water has caused considerable attention to be focused towards recovery and re-use of waste waters [10]. The removal of these kinds of pollutants from the environment cannot be accomplished by traditional methods [7]. It is now universally recognized that adsorption technology provides a feasible and effective method for the removal of pollutants from contaminated water resources and waste waters [11,12]. Activated carbons are the most commonly used adsorbents in the adsorption process due to their high adsorption capacity, high surface area and high degree of surface reactivity; however, regeneration is difficult and expensive [13].

In recent years, extensive research is now focused on new, efficient, low-cost and easily obtainable natural materials, e.g. clay materials [14], plant residue materials [15] and agricultural by-products like orange [16,17] and banana peels [16,18], spent tea leaves [19], tamarind fruit shell [20], soya bean hull [21], cotton seed hull, corn cobs [22] and pine barks, [23] as adsorbents.

The objective of this study is to investigate the potential of coconut shells, an abundantly available agricultural by-product as a non-conventional and low-cost adsorbent to remove naphthalene and pyrene from synthetic waste water. The effects of adsorbent particle size, adsorbent dosage, initial naphthalene and pyrene concentrations and agitation time on the adsorption were studied. The kinetic data were checked for Lagergren pseudo first-order, Elovich and intra-particle diffusion kinetic model equations from which the rate constants were evaluated. The sorption equilibrium data were correlated with two-parameter models of Langmuir and Freundlich as well as three-parameter models of Redlich-Peterson, Sips and Toth adsorption isotherms and the maximum adsorption capacity was estimated.

2. Materials and methods

2.1. Chemicals and stock solution

Naphthalene and pyrene (99% pure, chemical grade), being products of Sigma-Aldrich, USA, was purchased from a chemical store in Lagos, Nigeria. Due to the low water solubility of naphthalene and pyrene (polyaromatic hydrocarbons), the water–methanol solution was used as the aqueous solution. A stock solution was prepared by dissolving 1 g each of naphthalene and pyrene in de-ionized water–methanol solution. The water–methanol solution was composed of 50 ml of methanol and 950 ml of de-ionized water. From this original stock solution, six test solutions with various concentrations (50, 100, 150, 200, 250 and 300 mg/l) were prepared with de-ionized water.

2.2. Adsorbent and preparation of adsorbent

Coconut shells, a waste product of coconut fruit pulp to be used as adsorbent, were obtained from a local market in Benin-City, Nigeria. The coconut shells were sundried and then reduced to small-sized particles by grinding using a serrated disk grinder. The powdered particles were sieved to obtain different desired average particle sizes (0.125–0.422 mm). They are washed thoroughly with sterilized de-ionized water and dried in the oven for 2–3 h at 60°C. The physical and chemical compositions of brown coconut shell are given in Table 1. Analysis of the chemical composition showed that coconut shells are mainly composed of cellulose, hemicelluloses, lignin and other carbohydrates. Literature report has shown that the composition of agricultural by-products has a strong influence on the final porous and chemical features of the solid products obtained from pyrolysis and activation [4]. Cabal et al. [4] observed that high contents of cellulose yield predominantly microporous materials, whereas high content of lignin favours the development of a macroporous structure. Thus, coconut shell exhibits a combination of large quantities of cellulose and lignin, which makes the material a potential candidate for use as adsorbents as well as in the preparation of activated carbons probably with well-developed micro- and macroporosity [24].

2.3. Batch adsorption studies

Batch adsorption studies were carried out by adding a known amount of powdered coconut shell (PCS) (2 g) into a number of 250 ml Erlenmeyer conical flasks containing a known volume (100 ml) of synthetic waste water with different initial naphthalene and pyrene concentrations (100–500 mg/l). The pH of waste water was maintained at 7 by adjusting with 0.1 M H_2SO_4 and 0.1 M NaOH as the case may be. The flasks were placed in a rotary mechanical shaker for 2 h at a speed of 180 rpm and a temperature of 30°C so as to reach equilibrium. Prior to analysis, samples were filtered to separate adsorbent from the adsorbate and minimize interferences. At time $t = 0$ and equilibrium, the naphthalene and pyrene concentrations were

Table 1
Isotherm constants of different adsorption isotherms for naphthalene adsorption data

Isotherm model	Isotherm constants						R^2
	q_m (mg/g)	b (L/mg)	K_f (mg/g)	m	n	β	
Langmuir	24.3	0.0025	–	–	–	–	0.8318
Freundlich	–	–	0.2336	–	4.543	–	0.8256
Redlich–Peterson	−0.3559	0.4326	–	–	–	0.986	0.8323
Toth	0.2423	8.436	–	0.3584	–	–	0.8324
Sips	1.124	14.34	–	–	15.44	–	0.8297

determined quantitatively by the spectrophotometric method at an absorbance wavelength of 276 nm [4] and 320 nm [25], respectively, using UV-visible spectrophotometer. The amount of adsorption at equilibrium, q_e (mg/g) was calculated according to Eq. (1) [26]:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o and C_e (mg/l) are the initial and final (equilibrium) concentrations of naphthalene and pyrene in waste water. V (ml) is the volume of the waste water and W (g) is the mass of dry adsorbent (PCS) used. Kinetic studies for the adsorption of naphthalene and pyrene were carried out at 30˚C with an initial concentration ranging between 50 and 300 mg/l. The amount of adsorption at time t, q_t, was calculated according to Eq. (2) [27]:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

where C_t is the concentration of naphthalene and pyrene, respectively, in waste water at time t.

3. Results and discussion

3.1. Effect of agitation time and initial concentration

Fig. 1 shows the effect of agitation time on the adsorption of naphthalene and pyrene for an initial naphthalene and pyrene concentration of 100 mg/l, respectively. It could be seen that the respective adsorption of naphthalene and pyrene increased with increase in agitation time until equilibrium was reached at 100 min. Similar observations have been reported [28–30]. In this work, it was observed that the period of equilibrium increased to 120 min after which desorption occurred. The effects of initial naphthalene and pyrene concentrations on its adsorption by coconut shell are shown in Fig. 2. It could be seen that the respective amount of naphthalene and pyrene adsorbed per unit mass of adsorbent increased with the increase in initial concentration; however, the percent removal decreased with the increase in initial concentration.

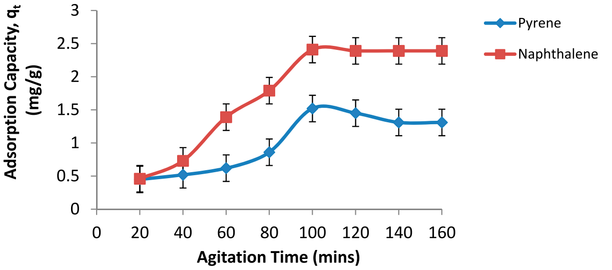

Fig. 1. Effect of agitation time on the adsorption of naphthalene and pyrene from aqueous solution onto coconut shell. Bars indicate the average of triplicate samples while error bars show the standard deviation.

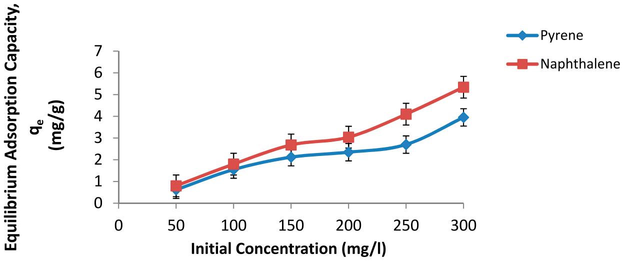

Fig. 2. Effect of initial concentration on the adsorption of naphthalene and pyrene from aqueous solution onto coconut shell. Bars indicate the average of triplicate samples while error bars show the standard deviation.

3.2. Effect of adsorbent particle size and adsorbent dosage

Fig. 3 shows the effect of particle size on the respective adsorption of naphthalene and pyrene by coconut shell. It is seen that the adsorption capacity of coconut shell for both naphthalene and pyrene increases with an increase in particle size from 0.075

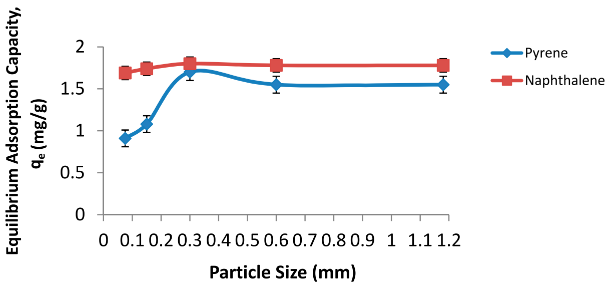

Fig. 3. Effect of particle size on the adsorption of naphthalene and pyrene from aqueous solution onto coconut shell. Bars indicate the average of triplicate samples while error bars show the standard deviation.

to 1.18 mm. However, the maximum adsorption capacity was attained with a particle size diameter of 0.3 mm. This indicates that the removal of naphthalene and pyrene increases as the particle size diameter decreases. Similar observations have been reported for the adsorption of phenol [10,31]. Decrease in particle size increases the percentage removal due to an increase in surface area as well as micropore volume [10,32]. Smaller particle size means more interior surface and micropore volume and hence more will be the area of active sites for adsorption [10]. Also for larger particles, the diffusion resistance to mass transfer is higher and most of the internal surfaces of the particle may not be utilized for adsorption and consequently, the amount of naphthalene and pyrene adsorbed is small [10,28,33]. Small particles are better for naphthalene and pyrene removal from liquid waste effluents. However, one cannot use small particle sizes in a continuous packed-bed adsorber because of higher pressure drops that will be encountered [10]. The percentage removal of naphthalene and pyrene with various adsorbent doses is shown in Fig. 4. The percentage removal of naphthalene and pyrene marginally increased with an increase in adsorbent dosage from 1 g to 8 g. Nonetheless, from this figure, it is evident that the percent (%) removal of naphthalene reaches its constant value at a dose of around 5 g/l. However, for pyrene, the percentage removal increases beyond this dose and reaches maximum at the adsorbent dose of about 6 g/l. This observation indicates that the adsorption capability of naphthalene by the coconut shell is more than that of pyrene. At a particular dose within this range, the % removal of naphthalene is more than that of pyrene, which indicates the higher energy of adsorption in case of pyrene than that of naphthalene [31]. As the % removal for both the compounds attains almost a constant value at the adsorbent dose of 5 g/l or above, the optimum adsorbent dose has been considered as 5 g/l.

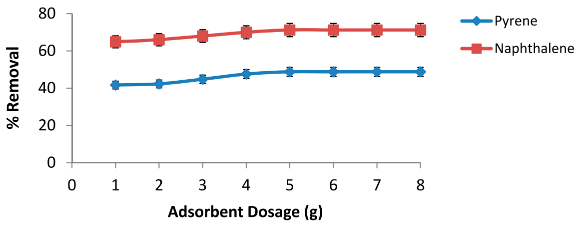

Fig. 4. Effect of adsorbent dosage on percent removal of naphthalene and pyrene from aqueous solution. Bars indicate the average of triplicate samples while error bars show the standard deviation.

3.3. Adsorption Isotherms

The adsorption isotherm is probably the best method to determine the amount of adsorbate that an adsorbent can retain and that remains in the solution at equilibrium [28]. Langmuir and Freundlich isotherms are two-parameter isotherms commonly used for the study of pollutant adsorption on activated carbon, while Toth isotherm, Redlich-Peterson isotherm and Sips isotherm are three-parameter isotherms models being used. According to the Langmuir isotherm, adsorption occurs at homogenous sites and forms a monolayer. In other words, once an adsorbate is attached to a site, no further adsorption can take place. The Langmuir isotherm equation is given in Eq. (3):

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{3}$$

where $q_{\max}$ and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. A dimensionless equilibrium parameter called separation factor, R_L, is used to study the applicability of Langmuir adsorption isotherm and this is given in Eq. (4):

$$R_L = \frac{1}{(1 + b C_o)} \tag{4}$$

where C_o is the initial concentration of naphthalene and pyrene. The separation factor (R_L) indicates the isotherm shape as follows: $R_L<1$ unfavourable, $R_L>1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable and $R_L = 0$ irreversible.

The Freundlich isotherm, on the other hand, assumes that adsorption takes place on heterogeneous sites with different distributions of energy levels. The Freundlich isotherm model is given in Eq. (5):

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and n are Freundlich constants. K_f is roughly an indicator of the adsorption capacity and n is the adsorption intensity.

The Redlich-Peterson isotherm equation contains three parameters and incorporated the features of the Langmuir and Freundlich isotherms [34,35]. This isotherm equation is as given in Eq. (6):

$$q_e = \frac{q_m C_e}{1 + bC_e^{\beta}} \tag{6}$$

Toth isotherm model is a three-parameter model that describes adequately the heterogeneous systems [28]. The model is given as (Eq. (7)):

$$q_e = \frac{q_m C_e}{(b + C_e^m)^{1/m}} \tag{7}$$

where q_m is the total adsorption capacity, m is the dissociation parameter and b is the adsorption equilibrium constant.

Sips isotherm model is also a three-parameter model that is represented as [36,37]:

$$q_e = \frac{q_m b C_e^{1/n}}{1 + b + C_e^{1/n}} \tag{8}$$

The data obtained from the batch adsorption experiment were fitted to Langmuir (Eq. (3)), Freundlich (Eq. (5)), Redlich-Peterson (Eq. (6)), Toth (Eq. (7)) and Sips (Eq. (8)) isotherm models (plot of q_e vs. C_e) using the non-linear fitting routine of MATLAB software package as shown in Figs. 5 and 6, for naphthalene and pyrene, respectively. The values of Langmuir constants (q_m, m, b), Freundlich constants (n, K_f) and Redlich-Peterson constants (β, q_m and b), Toth constants (q_m, m, b) and Sip constants (b, q_m, n) estimated from the plot are presented in Tables 1 and 2 for naphthalene and pyrene, respectively. The results in Fig. 5 and Table 1, shows that all the two- and three-parameter adsorption isotherm models adequately fitted the experimental adsorption data. The maximum adsorption capacity (q_m) and the energy of adsorption (b) obtained from Langmuir for naphthalene are 24.3 mg/g and 0.0025 L/mg, respectively, while for pyrene (q_m) is 5.52 mg/g and b is 0.0091 L/mg. These values indicate that coconut shell has a greater adsorption capacity for naphthalene than pyrene. Tsyntsarski et al. [38] obtained 18.75 and 29.95 mg/g as the maximum monolayer adsorption capacity of activated carbon derived from coal tar pitch/furfural and apricot stones for the adsorption of naphthalene, respectively. While, Agarry and Aremu [24] and Alade et al. [39] have correspondingly reported a value of 5.32 and 13.643 mg/g as the maximum adsorption capacity of orange peels and activated carbon derived from milk bush kernel shell (MB_{300}) for the adsorption of naphthalene, respectively.

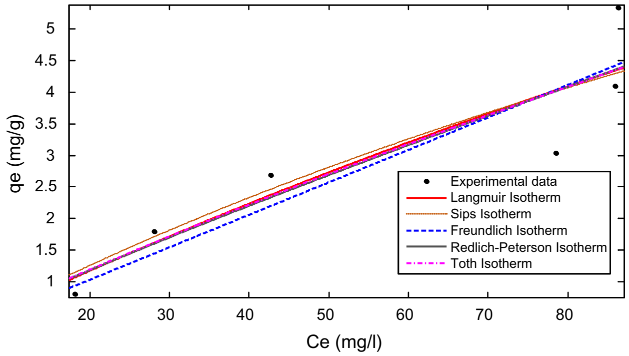

Fig. 5. Different adsorption isotherms model fitted to the equilibrium adsorption data for naphthalene.

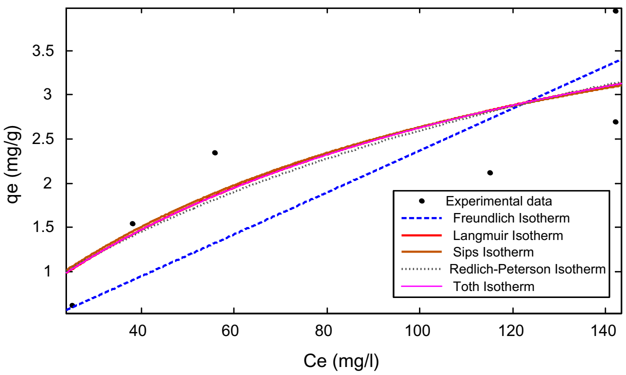

Fig. 6. Different adsorption isotherms model fitted to the equilibrium adsorption data for pyrene.

The separation factor (R_L) of Langmuir isotherm obtained in this study for naphthalene and pyrene was in the range 0.57–0.89 and 0.27–0.69, respectively. These values indicate the applicability and favourability of the Langmuir isotherms. For Freundlich isotherm, the value of $n > 1$ is a favourable adsorption condition [40] and when $1 < n < 10$, it is beneficial adsorption [10]. The Freundlich constants obtained for naphthalene are K_f (= 0.2336 mg/g) and n (= 4.543), and for pyrene K_f is 0.0097 mg/g and n is 0.4182. From other studies in the literature, the value of ($K_f : n$) obtained for the adsorption of naphthalene onto other adsorbents are: 7.52:0.086 for ripe orange peels [17]; 1.57:1.90 for orange peels [24]; 0.060:0.64 for coconut shell [41]; 0.025:1.47 for rice husk [41]; 030:1.12 for sugarcane bagasse [41]; 0.043:0.94 for activated carbon derived from flamboyant pod (FB_{300}) [39] and 0.077:1.19 for activated carbon derived from milk bush kernel shell (MB_{300}) [39] While Crisafully et al. [26] have also reported that the values of n for

Table 2
Isotherm constants of different adsorption isotherms for pyrene adsorption data

Isotherm model	Isotherm Constants						R^2
	q_m (mg/g)	b (L/mg)	K_f (mg/g)	m	n	β	
Langmuir	5.52	0.0091	–	–	–	–	0.7139
Freundlich	–	–	0.0097	–	0.4102	–	0.5799
Redlich–Peterson	−0.963	1.042	–	–	–	0.989	0.7097
Toth	4.995	100.1	–	0.9844	–	–	0.7139
Sips	0.6577	8.013	–	–	11.1	–	0.7133

the adsorption of naphthalene onto sugar bagasse, green coconut shell, chitin and chitosan are 1.02, 0.15, 2.00 and 0.75, respectively and Chang et al. [42] reported a ($K_f : n$) value of 4.215:1.074 for naphthalene adsorption onto zeolite adsorbent. Furthermore, the value of ($K_f : n$) obtained for pyrene adsorption onto other adsorbents are: 1.8:4.545 for pulverized coke [43]; 110:3.225 for pulverized activated carbon [43] and 170:2.564 for activated carbon [44].

Generally, the similar high correlation coefficient (R^2) value obtained for the fitting of two-parameter models of Langmuir and Freundlich isotherms and three-parameter models of Redlich-Peterson, Sip and Toth's isotherms to naphthalene and pyrene adsorption data indicates that these isotherms can suitably describe the adsorption behaviour of naphthalene and pyrene onto coconut shell. Chang et al. [42] gave a similar report that both Langmuir and Freundlich isotherms can suitably describe the adsorption process of naphthalene onto zeolite adsorbent.

3.4. Adsorption kinetics

To investigate the kinetics of naphthalene and pyrene adsorption onto coconut shell, adsorption rate constants were determined using Lagergren pseudo-first order, Elovich and intraparticle diffusion models. The Lagergren pseudo-first-order kinetic model equation [35,45] is represented in an integral form as given in Eq. (7):

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \tag{9}$$

The adsorption rate constant, k, can be measured by plotting $\ln(q_e - q_t)$ vs. t, as shown in Fig. 7.

It is seen that a straight line plot was obtained which indicates the applicability of Lagergren pseudo-first-order model. Table 3 shows the values of R^2 (correlation coefficient) and the rate constants for the Lagergren pseudo-first-order kinetic model. The rate constant ($k_{ad} = 0.008\,\text{min}^{-1}$) for naphthalene adsorption is greater than that for pyrene ($k_{ad} = 0.006\,\text{min}^{-1}$) and this suggests that the coconut shells has a greater rate of naphthalene adsorption than that of pyrene adsorption. The reason for this observation may be due to difference in molecular size of the organic pollutant. Mondal and Balomajumder [31] reported a similar observation for the adsorption of resorcinol and phenol by granular-activated carbon.

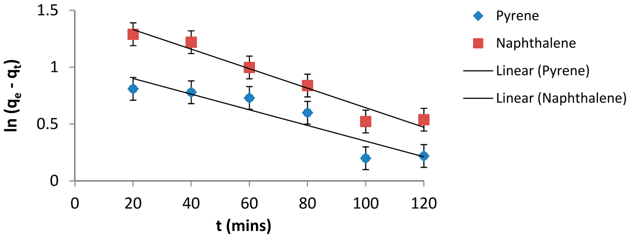

Fig. 7. Lagergren pseudo-first-order model fitted to the adsorption kinetics data of naphthalene and pyrene. Bars indicate the average of triplicate samples while error bars show the standard deviation.

The Elovich equation [7,46] is generally expressed as in Eq. (8):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{10}$$

To simplify Elovich equation, Chien and Clayton [47] assumed $\alpha\beta_t >> 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Eq. (8) becomes [48]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{11}$$

where α is the initial adsorption rate (mg/g min) and β is the desorption constant (g/mg).

The rate constants (α and β) are estimated from the plot of q_t vs. ln t as shown in Fig. 8. It could be seen that a linear relationship was obtained which also indicates the applicability of Elovich model. The R^2 and rate constants values are presented in Table 3. It could be seen that the Elovich rate constants

Table 3
Rate constants of some adsorption kinetic models and correlation coefficient (R^2)

Pollutant	Lagergren pseudo-first-order			Elovich			Intraparticle diffusion	
	K_{ad}	q_e	R^2	α	β	R^2	K_p	R^2
Naphthalene	0.008	4.49	0.953	0.072	0.838	0.922	0.273	0.915
Pyrene	0.006	2.82	0.858	0.049	1.652	0.725	0.154	0.843

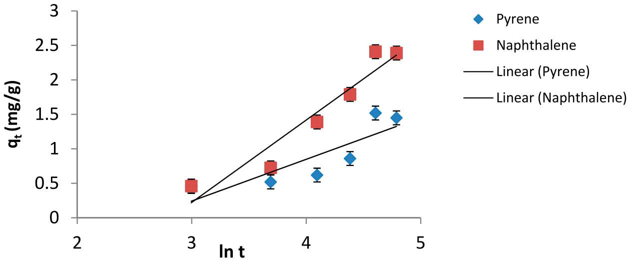

Fig. 8. Elovich model fitted to the adsorption kinetics data of naphthalene and pyrene. Bars indicate the average of triplicate samples while error bars show the standard deviation.

($\alpha = 0.072$ mg/g min, and $\beta = 0.838$ g/mg) for naphthalene adsorption are greater than those for pyrene where α is 0.049 mg/g min, and β is 1.652 g/mg. These values also suggest that the initial adsorption rate of naphthalene on coconut shell is faster than that of pyrene, while the rate of desorption of pyrene from coconut shell is greater than that of naphthalene.

Generally, between the Lagergren pseudo-first-order and Elovich models, the higher R^2 value (0.953 and 0.858) for Lagergren pseudo-first-order makes it a better fit to the adsorption kinetic data of naphthalene and pyrene than Elovich model. Thus, the adsorption of naphthalene and pyrene onto coconut shell follows a first-order kinetic process.

The adsorption steps include the transport of adsorbate in bulk phase and in solid phase. The initial transport of adsorbate to macropores is fast, then transport to mesopores is medium and finally there is slow diffusion into micropores. In general, intra-particle diffusion transport is considered as a rate-limiting step in case of adsorption on porous solid adsorbent from aqueous solution, if system is well mixed. In adsorption of naphthalene and pyrene onto coconut shell, there is the possibility of intra-particle diffusion. The Lagergren pseudo-first-order and Elovich kinetic models cannot identify the diffusion mechanisms and the kinetic results were then subjected to analysis by the intra-particle diffusion model of Weber and Morris [49] given in Eq. (10):

$$q_t = K_p t^{1/2} \tag{12}$$

where K_p is the intra-particle diffusion rate constant (mg/g min$^{-½}$).

The plot of sorption q_t vs. square root of time ($t^{1/2}$) should be linear and if it passes through the origin then the intra-particle diffusion will be the sole rate-limiting process [13,50].

In the present study, it was found that the plots of q_t vs. square root of time ($t^{1/2}$) exhibited an initial linear portion followed by a plateau which occurred after 100 min (Fig. 9). The curved portion of the plots seems to be due to the boundary layer diffusion and the linear portion as a result of intraparticle diffusion with the plateau corresponding to the equilibrium [7]. Values of the intraparticle diffusion constant, k_p, were obtained from the slopes of the linear portions of the plots and are presented in Table 3. The correlation coefficients (R^2) value of the intra particle diffusion model for naphthalene and pyrene are 0.915 and 0.843, respectively. These relative high values suggest that the sorption of naphthalene and pyrene onto coconut shell may be followed by the intraparticle diffusion up to 100 min. It is important to note that the value of k_p of pyrene is less than that of naphthalene. This indicates that the rate of removal of pyrene will be less than that of naphthalene.

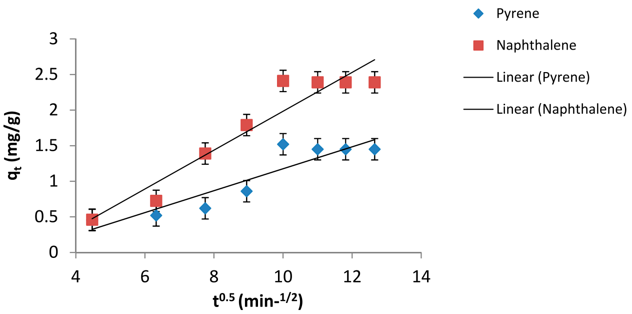

Fig. 9. Intraparticle diffusion model fitted to the adsorption kinetics data of naphthalene and pyrene. Bars indicate the average of triplicate samples while error bars show the standard deviation.

4. Conclusion

The adsorption of naphthalene and pyrene from synthetic waste water using coconut shells has been investigated under different conditions in batch and equilibrium modes. The monolayer adsorption capacity of coconut shell determined for naphthalene adsorption ($q_m = 24.3\,\mathrm{mg/g}$) was reasonably higher than that for pyrene ($q_m = 5.52\,\mathrm{mg/g}$) adsorption at pH 7 and at a particle size of 0.60 mm. The kinetics of naphthalene and pyrene adsorption nicely followed Lagergren first-order rate expression and demonstrated that intraparticle diffusion plays a significant role in the adsorption mechanism. Langmuir, Freundlich, Redlich-Peterson, Toth and Sip adsorption isotherms could be used to describe both naphthalene and pyrene sorption equilibrium. The treatment is simple and economic. The batch adsorption equilibrium and kinetic data thus generated may be used for designing an economically viable treatment plant for naphthalene and pyrene effluents using batch or stirred tank reactors.

References

[1] T. Garcia, R. Murillo, D. Cazorla-Amoros, A.M. Mastral, A. Linares-Solution, Role of the activated carbon surface chemistry in the adsorption of phenanthrene, Carbon 42 (2004) 1683–1689.

[2] C.O. Ania, B. Cabal, C. Parida, A. Arenillas, J.B. Parra, F. Rubiera, J.J. Pis, Effects of activated carbon properties on the adsorption of naphthalene from aqueous solutions, Appl. Surface Sci. 253 (2007) 5741–5746.

[3] C.K. Ahn, S.H. Woo, J.M. Park, Enhanced sorption of phenanthrene on activated carbon on surfactant solution, Carbon 46 (2008) 1401–1410.

[4] B. Cabal, T. Budinova, C.O. Ania, B. Tsyutsarski, J.B. Pana, B. Petrova, Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods, J. Hazard. Mater. 161 (2009) 1150–1156.

[5] A.M. Mastral, T. Garcia, M.S. Callen, M.V. Navarro, J. Galban, Removal of naphthalene, phenanthrene and pyrene by sorbents from hot gas, Environ. Sci. Technol. 35 (2001) 2395.

[6] N. Irha, E. Teinemaa, Behaviour of three—to four ring PAHs in the presence of oil shale ash and aluminosilicate matter, Polycyclic Aromat. Compd. 22(3–4) (2002) 663–671.

[7] O. Gok, A.S. Ozcan, A. Ozcan, Adsorption kinetics of naphthalene on to organo—sepiolite from aqueous solutions, Desalination 220 (2008) 96–107.

[8] D.M. Wassenberg, R.T. Di Giuliio, Synergistic embryo toxicity of polycyclic aromatic hydrocarbon receptor agonists with Cytochrome P4501 A inhibitors in *Fundulus Heteroclitus*, Environ. Health Perspect. 17 (2004) 1658–1664.

[9] M.K. Chung, M.T.K. Tsui, K.C. Cheung, N.F.Y. Tam, M.H. Wong, Removal of aqueous phenanthrene by brown seaweed *Sargassum hemiphyllum*: Sorption-kinetic and equilibrium studies, Sep. Purif. Technol. 54 (2007) 355–362.

[10] A. Annadurai, S.R. Babu, K.P.O. Mahesh, T. Murugesan, Adsorption and biodegradation of phenol by chitosan-immobilized *Pseudomonas putida* (NICM 2174), Bioprocess. Eng. 2 (2000) 493–501.

[11] T.J. Bandosz, Activated Carbon Surfaced in Environmental Remediation, in: T.J. Bandosz (Ed), Interface Science and Technology Series, Elsevier, New York, 2006.

[12] W.T. Tsai, C.W. Lai, T.Y. Su, Adsorption of bisphenol-A from aqueous solution onto minerals and carbon adsorptions, J. Hazard. Mater. 134 (2006) 169–175.

[13] A. Ozcan, A.S. Ozcan, Adsorption of Acid Red 57 from aqueous solutions onto surfactant modified sepiolite, J. Hazard. Mater. 125 (2005) 252–259.

[14] M. Khalid, G. Joly, A. Renaud, P. Magnoux, Removal of phenol from water by adsorption using Zeolites bain, Ind. Eng. Chem. Res. 43(17) (2004) 5275–5280.

[15] B. Chen, M. Yuana, H. Liu, Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent, J. Harzad Mater. 188 (2011) 436–442.

[16] G. Annadurai, R.S. Juang, D.J. Lee, Adsorption of heavy metal from water using banana and orange peels, Water Sci. Technol. 47 (2002) 185–190.

[17] C.N. Owabor, J.E. Audu, Studies on the adsorption of naphthalene and pyrene from aqueous medium using ripe orange peels as adsorbent, Global J. Pure Appl. Sci. 16 (2010) 131–139.

[18] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, W. Shao, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, Zinc, Cobalt and Nickel. Colloids Surf. A: Physicochem. Eng. Asp. 317 (2008) 512–521.

[19] B.H. Hameed, Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solution, J. Hazard. Mater. 161 (2009) 253–259.

[20] S.R. Popuri, A. Jammala, K.V.N. Reddy, K. Abburi, Biosorption of hexavalent chromium using tamarind (Tamarinddus indica) fruit shell—a comparative study, Electronic. J. Biotechnol. 3 (2007) 358–367.

[21] W.E. Marshall, L.H. Wartelle, D.M. Boler, C.A. Toles, Metal ion adsorption by soybean hulls modified with citric: A comparative study", Environ. Technol. 21(6) (2000) 601–607.

[22] Z. Reddad, C. Gerente, Y. Andres, P. Lecloirec, Adsorption of several metal ions onto a low cost biosorbent: Kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[23] Y. Li, B. Chen, L. Zhu, Enhanced sorption of polycyclic aromatic hydrocarbons from aqueous solution by modified pine bark, Bioresour. Technol. 101 (2010) 7307–7313.

[24] S.E. Agarry, M.O. Aremu, Batch equilibrium and kinetic studies of simultaneous adsorption and biodegradation of naphthalene by orange peels immobilized *Pseudomonas aeruginosa* NCIB 950, J. Bioremed. Biodegrad. 3(2) (2012) 138–141.

[25] P. Kubat, S. Cívíš, A. Muck, J. Barek, J. Zima, Degradation of pyrene by UV radiation, J. Photochem. Photobiol. A: Chem. 132 (2000) 33–36.

[26] R. Crisafully, M.A. Milhome, R.M. Cavalcante, E.R. Silveira, D. Keukeleire, F. Nascimento, Removal of some polycyclic aromatic hydrocarbons from petrochemical waste water using low-cost adsorbents of natural origin, Bioresour. Technol. 99 (2008) 4515–4519.

[27] Y. Xun, Z. Shu-ping, Z. Wei, C. Hong-you, D. Xiao-Dong, L. Xin-Mei, Y. Zi-Feng, Aqueous dye adsorption on ordered malodorous carbons, J. Colloid Interface Sci. 310 (2007) 83–89.

[28] M.A. Dabhade, M.B. Saidutta, D.V.R. Murthy, Adsorption of phenol on granular activated carbon from nutrient medium: Equilibrium and kinetic study, Int. J. Environ. Res. 3(4) (2009) 557–568.

[29] C. Parvathi, T. Maruthavanan, S. Sivamani, C. Prakash, C.V. Koushik, Role of tapioca peel activated carbon (TPAC) in decolourisation of Red Brown C4R reactive dye, Indian J. Sci. Technol. 3(3) (2010) 290–292.

[30] B.K. Hamad, A-Md. Noor, A.A. Rahim, Removal of 4-chloro-2-methoxyphenol from aqueous solution by adsorption to oil palm shell activated carbon activated with K2CO3. J. Phys. Sci. 22(1) (2011) 39–55.

[31] P. Mondal, C. Balomajumder, Treatment of resorcinol and phenol bearing waste water by simultaneous adsorption biodegradation (SAB): Optimization of process parameters, Int. J. Chem. Reactor Eng. 5(S1) (2007) 1213–1228.

[32] A. Kumar, S. Kumar, S. Kumar, D.V. Gupta, Adsorption of phenol and 4- nitro phenol on granular activated carbon in basal salt medium: Equilibrium and kinetics, J. Hazard. Mater. 147 (2007) 155–166.

[33] N.R.K. Lakshimi, K. Krishbaiah, A. Ashutosh, Colour removal from a dye stuff industry effluent using activated carbon, Indian J. Chem. Technol. 1 (1994) 13–19.

[34] O. Redlich, D.L.A. Peterson, Useful adsorption isotherm, J. Phys. Chem. 63 (1998) 1024–1029.

[35] G. McKay, Y.S. Ho, Orption of lead (II) ions on peat, Water Res. 33 (1999) 578–584.

[36] R. Sips, On the structure of a catalyst surface, J. Chem. Phys. 16 (1948) 490–495.

[37] I.O. Oboh, E.O. Aluyor, T.O.K. Audu, Adsorption isotherms for sorption of nickel (ii) ions onto agricultural waste materials, J. Nig. Soc. Chem. Eng. 26 (2011) 115–122.

[38] B. Tsyntsarski, B. Petrova, T. Budinova, N. Petrov, L. Velasco, C.O. Ania, Characterization and application of activated carbon from biomass and coal wastes for naphthalene removal, Bull. Chem. Commun. 43(4) (2011) 552–557.

[39] A.O. Alade, O.S. Amuda, T.J. Afolabi, A.A. Okoya, Adsorption of naphthalene onto activated carbons derived from milk bush kernel shell and flamboyant pod, J. Environ. Chem. Ecotoxicol. 4(7) (2012) 124–132.

[40] R.E. Treybal, Mass Transfer Operation, 10th ed., McGraw-Hill, New York, 1998.

[41] D. Pal, Adsorption of polycyclic aromatic hydrocarbons using agricultural wastes-effect of lignin content, in: International Conference on Chemical, Ecology and Environmental Sciences (ICEES'2012) Bangkok, March 17–18, 2012.

[42] C.-F. Chang, C.-Y. Chang, K.-H. Chen, W.-T. Tsai, je.-L. Shie, Y.-H. Chen, Adsorption of naphthalene on zeolite from aqueous solution, J. Colloid Interface Sci. 277 (2004) 29–34.

[43] S. Ahn, D. Werner, H.K. Karapanagioti, D.R. Mcglothlin, R.N. Zare, R.G. Luthy, Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke, and activated carbon, Environ. Sci. Technol. 39 (2005) 6516–6526.

[44] R.W. Walters, R.G. Luthy, Equilibrium adsorption of polycyclic aromatic hydrocarbons from water onto activated carbon, Environ. Sci. Technol. 18 (1984) 395–403.

[45] S. Lagergren, Zur theorie der sogenannte, adsorption geloster stoffe, Kungliga Svenska vetenskap-sakademiens, Handlingar 24 (1898) 1–39.

[46] M.J.O. Low, Kinetics of chemisorptions of gases on solids, Chem. Rev. 60 (1960) 267–312.

[47] S.H. Chien, W.R. Clayton, Application of Eloviich equation to the kinetics of phosphate release and sorption in soils, Soil Sci. Soc. Am. J. 44 (1980) 265–268.

[48] D.L. Sparks, Kinetics and mechanisms of chemical reactions at the soil mineral/water interface in: D.L. Sparks (Ed.), Soil Physical Chemistry, CRC press, Boca Raton, FL, 1999, pp. 135–192.

[49] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanitary Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.

[50] K.G. Bhattacharyya, A. Sharma, Azadirachta indica leaf powder as an effective biosorbent for dyes: A case study with aqueous Congo red solutions, J. Environ. Manage. 71 (2004) 217–229.