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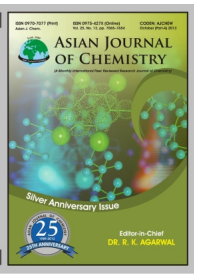

Equilibrium and Kinetic Studies of Sorption of Polycyclic Aromatic Hydrocarbons from Water Using Rice Husk Activated Carbon

S.M. YAKOUT[1,2,*], A.A.M. DAIFULLAH[2] and S.A. EL-REEFY[2]

[1]Biochemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
[2]Hot Laboratories Centre, Atomic Energy Authority, 13759 Inshas, Cairo, Egypt

*Corresponding author: Tel: +966558448693; E-mail: sobhy.yakout@gmail.com

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The uptake of polycyclic aromatic hydrocarbons (*viz*., naphthalene, phenanthrene and pyrene) by rice husk activated carbon was comparable to conventional adsorbent, powdered activated carbon and higher than all other agricultural and industrial adsorbents. Polycyclic aromatic hydrocarbons showed similar behaviour regarding kinetics after 24 h. Polycyclic aromatic hydrocarbon removal follow the order naphthalene < phenanthrene < pyrene. Molecular weight and solubility play vital role in the adsorption of polycyclic aromatic hydrocarbon on rice husk activated carbon. The results pointed to the occurrence of intraparticle mechanism in all cases. The isotherm models which best represented the data obtained were Freundlich for naphthalene, Redlich-Peterson for phenanthrene and Langmuir for pyrene. These observations suggest that rice husk activated carbon have great potential as biosorbents to remove polycyclic aromatic hydrocarbons from water.

Key Words: Polycyclic Aromatic Hydrocarbons, Activated carbon, Adsorption, Water treatment.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are stable organic molecules which consist of fused aromatic rings and comprise only carbon and hydrogen atoms. Polycyclic aromatic hydrocarbons are generally produced as byproducts in incomplete combustion of fuel, coal, oil, garbage, wood, organic substances, polymers, *etc*. Due to their chemical persistence and semi-volatile nature, PAHs can transport long distance in air and water and are difficult to biodegrade. Once inside the human body, PAHs can pass easily through cell membranes and are readily adsorbed into cells since they are rich in carbon and they are hydrophobic. Some PAHs are capable of interacting with DNA to promote mutagenic and carcinogenic responses. Sixteen PAHs are on the US-EPA's priority pollutants list[1]. Adsorption treatment provides a simple approach for effective removal of organic pollutants from the aquatic environment. For the adsorptive removal of PAHs from water, various kinds of adsorbents have been researched, including wood fiber[2] and leonardite[3] due to their low costs. Walters and Luthy[4] have shown that the adsorption of PAHs onto porous carbon is much stronger than that onto soils, sediments and suspended organic matters, suggesting that porous carbon may be suitable for removing polycyclic aromatic hydrocarbons from aquatic environments.

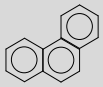
Yuan *et al*.[5] found that the petroleum coke-derived porous carbon is most effective in adsorbing these PAHs[5]. The adsorption of PAHs onto activated carbon from various media such as oil[6,7], gaseous phase[8,9] and water[10,11] has been reported. Activated carbon has also been used for groundwater treatment in numerous cases.

The objectives of this work are to evaluate the effectiveness of activated carbon-prepared from locally available material (rice husk) for a number of polycyclic aromatic hydrocarbons in aqueous solution, namely, naphthalene (NA), phenanthrene (PH), pyrene (PY) from water and to better understand the adsorption of PAHs onto this carbon.

EXPERIMENTAL

In adsorption experiments, analytical-grade naphthalene, phenanthrene and pyrene , HPLC-grade acetone and distilled water Milli-Q were used. These three PAHs were selected due to their common presence in petroleum wastewaters and their troublesome properties. These are taken as representatives for 2, 3 and 4 rings of polycyclic aromatic hydrocarbons. The environmental and biological behaviors of the 3 PAHs studied are best described by some of their physico-chemical properties, presented in Table-1. It can be seen that these substances have low solubility in water and it tends to be even lower when the number of aromatic rings is increased. Thus, the PAH stock

TABLE-1
PHYSICOCHEMICAL PROPERTIES OF PAHS STUDIED

Compound	Structure	m.f.	m.w. (g/mol)	b.p. (°C)	Solubility (mg/L) [Ref. 55]	log K_{ow}
Naphthalene		$C_{10}H_8$	128.17	218	31.7	3.30
Phenanthrene		$C_{14}H_{10}$	178.23	340	1.29	4.57
Pyrene		$C_{16}H_{10}$	202.26	404	0.135	5.18

solution was prepared in acetone. The solutions used in the isotherms and kinetics experiments and in the construction of analytical curves were prepared immediately prior to use, by diluting the stock solution and adjusting the acetone concentration to 30 % v/v.

Adsorbents: Adsorbents used in the removal of three PAHs were classified into two categories according their sources:

(a) Adsorbents from industrial by-products: The residue (B-1) is a by-product from paint industry, supplied by Pakin Co., Mostorod, Egypt. Where the animal bones were pyrolyzed for 5 h at 800 °C to produce the residue, its constituents dependent on the animal type (*e.g.*, camel, buffaloes or cattle) and its food. The residue (B-2) is discarded from the sugar refinery of the Sugar & Integrated Industries CO., Giza, Egypt. The chemical composition of (B-2) mainly is tricalcium phosphate (73.5 %), calcium carbonate (8.5 %), carbon (9.5 %), volatile matter (16.5 %). Pyrolysis residue is a by-product of domestic waste incineration and was supplied by PKA (Pyrolysis-Kraft-Anlagan)-Co., Germany.

(b) Adsorbents from agricultural wastes: Peat moss was obtained from Belbaes, Egypt and used without any pretreatment. The activated rice husk activated carbon (RHAC), was prepared by impregnating 40 g of rice husk with 100 mL of 40 % (v/v) H_3PO_4. This mass was heated gradually up to 673 K within 2 h and soaked at this temperature for 3 h. After cooling the carbonized mass was washed several times with bidistilled water until pH 6.5 and dried at 110 °C. For comparison, a conventional adsorbent, powdered active carbon (PAC) was purchased from El-Nasr Pharmaceutical Chemicals Co., Egypt.

Adsorbents were sieved to a constant particle size of 590 μm. The BET surface area was determined by N2 adsorption isotherms at 77 K using a Gemini 2375 V3.03 instrument (Micromeritics). Ash content (wt. %) was determined from gravimetric measurement[12]. About 1 g of homogenized powdered samples (A) was heated up to 900 °C at a rate of 10/°C min. The measurement was performed in air and final weight was determined as (B). Then,

$$\text{Ash content (wt. \%)} = (B/A) \times 100 \quad (1)$$

The BET-surface area, ash content and the elemental analysis of these sorbents are listed in Table-2.

The analysis of PAH was performed using HP 6890-GC with split-splitless injector and flame ionization detector. Carrier gas nitrogen (99.999 %) with flow rate 1.5 mL min^{-1} was used. The sample injection volume was 5 μL, in pulsed splitless. A Ultra 2 ; 50 m* 0.2 mm (i.d) 0.11 μm film thickness (5 % phenyl methyl siloxane). The oven temperature was programmed from 45 °C (holding time1min) to 190 °C at 30 °C min^{-1} to 310 °C at 3 °C min^{-1} holding the final temperature for 1 min.

Adsorption studies: Glass bottles provided with screw caps and thermostated shaker water bath set to operate at 200 rpm at 28 ± 1 °C. The utilization of acetone as cosolvent was efficient for the solubilization of the PAHs in aqueous medium, in the concentration range used in this work[13].

To select a particular adsorbent to be used for all the experimental work, single dosage experiments were carried out by contacting 5 mL of mixture solution of initial concentration (C_o = 8 mg/L for each compound) with 10 mg of each material (B-1, B-2, peat moss, pyrolysis residue, RHAC, PAC) in the glass bottles. The bottles were then shaken for 24 h at (25 ± 1) °C. The residual concentration (C_e) in the filtrate was measured.

For the adsorption kinetics experiments, 5 mL aliquots (8 mg/L) of each PAH (naphthalene, phenanthrene and pyrene) with 2 mg of activated RHAC were mixed and shacked at different time intervals (1, 2, … Up to 7 days). Then, each mixture was filtered and the residual concentration was determined. The aim was to determine the equilibrium time for each adsorption system.

Adsorption isotherms experiments were done by mixing various masses of activated rice husk (0.1 to 7 mg) with 5 mL of each solute (8 mg/L) in glass bottles. The bottles were shaken at (25 ± 1) °C until equilibrium and the residual concentration was measured. Adsorption isotherms of phenanthrene were

TABLE-2
PROPERTIES OF VARIOUS SORBENT MATERIALS USED

Adsorbent	C (%)	H (%)	N (%)	Cl (%)	S (%)	Ash (%)	S_{BET} (m^2/g)
B-1	10.8	1.3	3.6	1.9	n.a	81.5	72.9
B-2	9.5	n.a	n.a	n.a	n.a	n.a	35.1
Peat moss	45.7	4.8	3.5	2.5	3.4	3.8	6.4
Pyrolysis residue	34.1	1.12	1.71	0.44	0.35	54.7	40
RHAC	58.5	3.4	2.9	1.9	2.1	3.8	446
PAC	77.4	2.4	0.9	-	-	5.9	560.3

n.a: not available; RHAC = Rice husk activated carbon; PAC = Powdered active carbon.

determined at various temperatures 25, 35 and 45 °C to decide if the adsorption process is exothermic or endothermic.

The amount of PAHs adsorbed at equilibrium, q_e (mg g^{-1}) was calculated based on mass balance using the following equation:

$$q_e = V(C_o - C_e)/m \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of PAHs (mg L^{-1}) in water, respectively. V is the total volume of solute solution (mL), m is the mass of adorbent used (g).

RESULTS AND DISCUSSION

Comparison of adsorbents: Fig. 1 provides a comparison of the total adsorption capacity of the three polycyclic aromatic hydrocarbons (PAHs) under investigations, in one mixture in aqueous solution for the different investigated adsorbents. The results are presented in weight capacity, q_e (mg/g). Based on the data obtained, the amount adsorbed from PAH mixture by activated RHAC are comparable to that obtained by the manufactured powdered activated carbon (PAC). Both are higher than other adsorbents used. Therefore, RHAC was used as an adsorbent material for the removal of the three compounds (naphthalene, phenanthrene and pyrene).

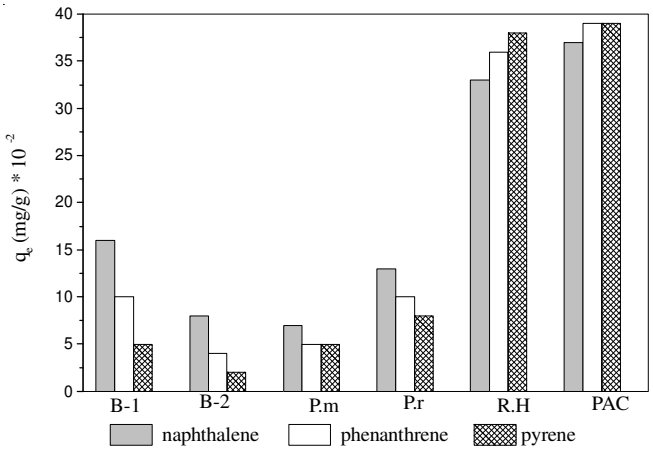


Fig. 1. Adsorption of PAH by B-1, B-2, peat moss (P.m), pyrolysis residue (P.r), RHAC and PAC

Equilibrium time and adsorption rate: The adsorption kinetics study was carried out to determine the time required for the adsorption equilibrium to be reached, conditions under which there is no variation in adsorption capacity. The kinetic curves obtained can be seen in Fig. 2. Adsorption of all PAHs appeared to have similar behaviour regarding kinetics. The removal curves are single, smooth and continuous leading to saturation. It is noted that after one day of contact between the adsorbent RHAC and the PAHs, the adsorption process tends to reach the equilibrium state. The time to reach equilibrium of 24 h for PAH solution systems was in good agreement with previous results[5].

Weber *et al.*[14] kinetic models were tested to determine the kinetic rate in the adsorption process of each PAH onto the RHAC, as well as the mechanisms involved.

$$q_t = K\, t^{0.5} \quad (3)$$

where q_t are the amounts of PAHs adsorbed (mg g^{-1}) at time t (h), k(K,(mg/g $h^{0.5}$) is Morris constant rate constant. The adsorption rate, K was calculated[15] and listed in Table-3. According to the Weber *et al.* model, to elucidate the diffusion mechanism, if a linear curve is obtained and it passes through the origin, the predominant mechanism for the adsorption is diffusion[16]. In this work, the behavior of the q_t *versus* $t^{0.5}$ graph is initially linear, indicating that the diffusion process occurs. However, it was not the only rate-controlling step. A remarkable dependence exists between the observed K values and the number of aromatic rings (or molecular weight). It is clear that, as the number of aromatic rings increases, the removal capacity increases and the adsorption rate k increases too. The sequence has the order: naphthalene < phenanthrene < pyrene. When the amount of solute adsorbed is expressed in molar units instead of weight units as in column (b) in Table-3, the K' values for the three components have a similar order as above. This can be explained by the fact that not only the molecular weight has the predominant effect on the adsorption rate but also there are some factors should be considered. *e.g.*, solubility in water. The solubility order is naphthalene > phenanthrene > pyrene whereas the rate order: naphthalene < phenanthrene < pyrene. *i.e.*, as the solubility increases, the adsorption rate decreases.

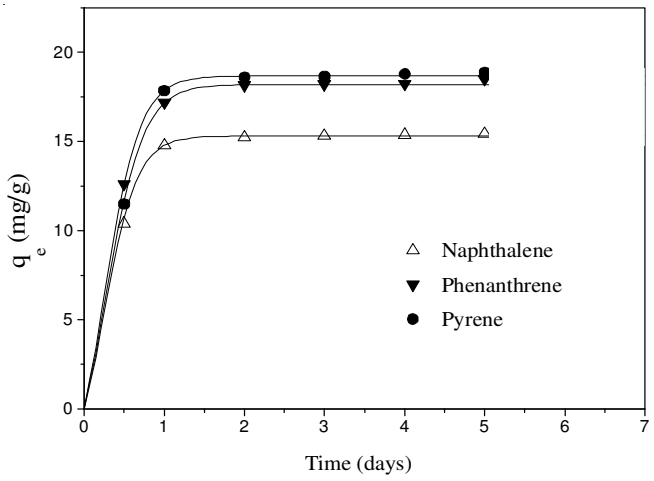


Fig. 2. Equilibrium uptake of PAH compounds on R.h

TABLE-3
ADSORPTION RATES OF POLYCYCLIC AROMATIC HYDROCARBON STUDIED

PAH	K (mg/g $h^{0.5}$) $\times 10^{-3}$	K´ (mmol/g $h^{0.5}$) $\times 10^{-3}$
Naphthalene	101.5	0.7919
Phenanthrene	156	0.8752
Pyrene	200	0.99

Adsorption isotherms: Study of adsorption equilibrium isotherms is an important step in investigating adsorption processes since it makes it possible to identify the relationship between the amounts of analyte adsorbed and in solution, after equilibrium is reached[17].

As shown in Fig. 3, initially the isotherm rose rapidly over the initial stage of adsorption where low C_e and q_e values existed. This behaviour indicates that there were plenty of readily accessible sites available on RHAC adsorbent. Eventually a slow approach to equilibrium at high concentrations occurred. As more sites are filled, it becomes difficult for the

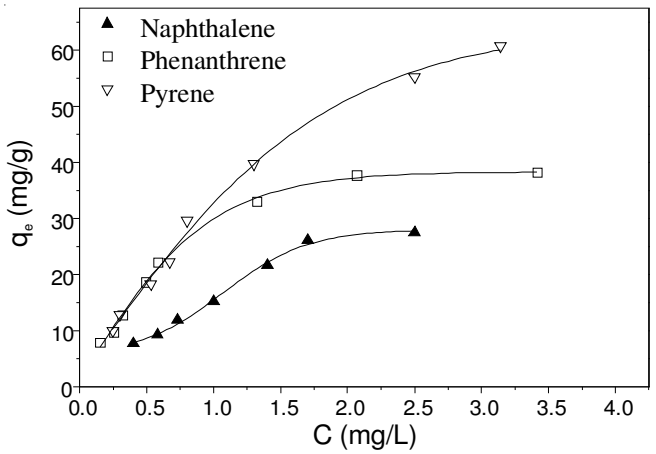


Fig 3. Adsorption isotherms of PAH compounds on RHAC

solute molecules to find a site for adsorption and/or the difficulty of molecules in penetrating the layer of adsorbed metal ion already covering the surface sites. As result, the rate of adsorption decreases giving a plateau covers a wide range of solution concentrations.

Although linear regression has been widely used to estimate the isotherm parameters, the way the linearization of non-linear isotherm expressions is done may lead to different changes in error distributions[18] and vioxlation of the normality suppositions of the least-square method, which makes linearization an in appropriate approach[19]. A computer program has been used for the estimation of coefficients based on non-linear optimization technique. The value of the mean absolute percentage error[20].

The following equation has been selected as a test criterion for the fit of the correlation[21] and used to estimate the isotherm parameters of Langmuir, Freundlich, Toth and Redlich-Peterson models for a better understanding of the interactions between adsorbent materials and organic adsorbates. The results presented in Table-4.

$$\% \text{ err} = \left(\frac{q_e(\text{experimental}) - q_e(\text{predicted})}{q_e(\text{experimental})} \times 100 \right) \quad (4)$$

Langmuir adsorption isotherm: The Langmuir isotherm is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species[17]. The adsorbent is saturated after one layer of adsorbed molecules is formed on the adsorbent surface[22]. The Langmuir isotherm is represented by

$$q_e = \frac{q^0 b C_e}{1 + b C_e} \quad (5)$$

where q^o is the monolayer capacity of the adsorbent (mg g^{-1}) and b is the Langmuir adsorption constant related to the energy of adsorption (L mg^{-1}). In this work, the Langmuir isotherm best fits the experimental data for lower values of C_e, indicating that initially the adsorption process occurs as a monolayer phenomenon. However, this mechanism does not persist under higher concentration ranges and in these cases the adsorption seems to be a multilayer process. Polycyclic aromatic hydrocarbons adsorption from wastewaters has been investigated else-where by using Al-MCM-41[23], mesoporous organosilica[24] and zeolite[25] as adsorbents and the results are compared to those obtained in this work. Intensity of adsorption and Langmuir adsorption constant KL, calculated for each adsorption system, are given in Table-5.

Freundlich adsorption isotherm: The Freundlich isotherm model takes multilayer and heterogeneous adsorption into account[22]. The Freundlich isotherm model is given by

$$q_e = K_f C_e^{1/m_f} \quad (6)$$

where K_f (L mg^{-1}) and n_f are Freundlich isotherm constants, indicative of the saturation capacity and intensity of adsorption. It is well known that "$1/n_f$" values between 0.1 and 1 indicate a favorable adsorption[22]. As shown in Table-6, all 1/n values lower than unity, that implies stronger interaction between RHAC adsorbent and PAHs.

Polycyclic aromatic hydrocarbons adsorption from wastewaters has been investigated by using different substances *e.g.*, chitosan, chitin, sugar bagasse, coconut shells, immature coal-leonardite and mesoporous organosilica[3,13,24]. The intensity of adsorption and the Freundlich adsorption constant KF calculated for each adsorption system are given in Table-5.

TABLE-4
PARAMETERS OF ISOTHERMS MODELS

PAHs	Langmuir			Freundlich			Toth				Redlich-Peterson			
	q^o	b	% err	K_f	1/n	% err	q_T	K_T	n_T	% err	a_R	B_R	B	% err
Naphthalene	63.6	0.34	7.0	15.7	0.71	6.5	86.9	0.33	0.68	9.55	25.5	0.58	0.76	8.1
Phenanthrene	50.4	1.02	7.3	24.8	0.55	12.8	39.4	1.06	2.3	4.82	45.6	0.54	1.4	4.6
Pyrene	104.5	0.44	4.3	29.8	0.71	6.6	109.3	0.43	0.96	4.4	262.7	7.6	0.4	9.1

TABLE-5
LANGMUIR PARAMETERS FOR ADSORPTION OF PAHS ON VARIOUS KINDS OF ADSORBENTS

Adsorbent	T (°C)	Solute	Langmuir parameters		Reference
			b (L mg^{-1})	q^o (mg g^{-1})	
Al-MCM-41	25	Naphthalene	0.214	106.24	23
Zeolite	–		0.005	769.231	25
Periodic mesoporous organosilica	28 ± 1		6.273	46.641	24
Rice husk activated carbon	28 ± 1		0.34	63.6	This work
Al-MCM-41	28 ± 1	Pyrene	1.184	371.68	23
Periodic mesoporous organosilica	28 ± 1		0.228	2601.504	24
Rice husk activated carbon	28 ± 1		0.44	104.5	This work

TABLE-6
FREUNDLICH PARAMETERS FOR ADSORPTION OF PAHS OBTAINED BY VARIOUS KINDS OF ADSORBENTS

Adsorbent	Solute	Freundlich parameters		Reference
		K_f	$1/n_f$	
Sugar cane bagasse	Naphthalene	13	0.98	13
Green coconut shells		23	1.34	13
Chitin		138	0.05	13
Chitosan		2	1.39	13
Zeolite		4.215	1.074	25
Periodic mesoporous organosilica		0.277	0.974	24
Rice husk activated carbon		15.7	0.71	This work
Sugar cane bagasse	Pyrene	170	0.15	13
Green coconut shells		140	0.99	13
Chitin		120	0.14	13
Chitosan		50	0.21	13
Immature coal (leonardite)		10	0.62	3
Periodic mesoporous organosilica		0.119	1.682	24
Rice husk activated carbon		29.8	0.71	This work

Redlich-Peterson isotherm: Redlich-Peterson is an empirical equation, with three parameters, which is capable of representing adsorption equilibrium over a wide concentration range[26]. This equation has the form:

$$q_e = \frac{a_R C_e}{1 + b_R C_e^{\beta}} \quad (7)$$

where a_R (L mg^{-1}), b_R (L mg^{-1}) and β are the isotherm constants. This equation is an empirical one and reduces to Henry's law, Freundlich or Langmuir under appropriate condition[19]. The Redlich-Peterson model incorporates the characteristics of Langmuir and Freundlich isotherms into a single equation. Two limiting behaviors exist, *i.e.*, Langmuir form for β equal to 1 and Henry's law form for β equal to 0[26]. The β values are far from unity in adsorption of naphthalene, phenanthrene and pyrene (Table-4). This means that the data can't preferably be fitted with the Langmuir model for these PAHs.

Toth isotherm: Toth has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of his equation is best suited to multilayer adsorption similar to BET isotherms, which is a special type of Langmuir isotherm and has very restrictive validity. The Toth mode equation[27] given as

$$q_e = \frac{q_T K_T C_e}{[1 + (K_T C_e)^{n_T}]^{1/n_T}} \quad (8)$$

where q_T, K_T and n_T are the isotherm constants. The application of this equation is best suited to multilayer adsorption similar to BET equation[21]. The parameters obtained for Toth isotherms are shown in Table-3 and were used to identify the models that best fit the experimental data

In general, the data obtained from the adsorption isotherms experiments appeared to be well represented by all theoretical models tested. It was found that the Freundlich isotherm for naphthalene, Redlich-Peterson isotherm for phenanthrene and Langmuir isotherm for pyrene gave an excellent overall fit. Among the three -parameter models investigated in this study, the better known Radlick-Peterson isotherm[28] gave the worst fitting for pyrene with (% err = 9.1), if compared to the rest of models. Whereas, the rarely used Toth isotherm[27] gave much better fitting for pyrene with (% err = 4.4) only. Although the latter model provided a satisfactory fit to the isotherm data for phenanthrene over most of the concentration range, the newest Redlich-Peterson isotherm model[21] is much better. It is worth to note that the % err of the two-parameter isotherms is always higher (less fitting) than that of three or four parameters isotherms in case of phenanthrene. The reverse status is noticed in case of naphthalene, where the two-parameter models provided a satisfactory fit to the isotherm data over most of the liquid concentration range. In conclusion, we can decided that the fitting can be improved independent on the number of isotherm parameters.

Conclusion

The adsorption behavior of selected PAHs from organic-free, deionized water onto various adsorbent materials has been examined. Two-, three and four parameters adsorption isotherm equations were applied to find the best fitting for representing adsorption data of naphthalene, phenanthrene and pyrene onto activated rice husk. The adsorption affinity depends on the solute shape and the separation factor as well as the solubility and molecular structure. The adsorption process is favourable and indicates a normal trend associated with physical adsorption *i.e.*, exothermic.

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