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Removal of selected polycyclic aromatic hydrocarbons from aqueous solution onto various adsorbent materials

S.M. Yakout[a,*], A.A.M. Daifullah[b]

[a]*Biochemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
Email: sobhy.yakout@gmail.com
[b]*Atomic Energy Authority, Hot Laboratories Centre, Cairo 13759, Egypt*

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ABSTRACT

Adsorption of three polycyclic aromatic hydrocarbons (PAH) in one mixture, namely naphthalene (NA), phenanthrene (PH), and pyrene (PY), was tested using various adsorbent materials: Bone charcoal (B-1 and B-2), Peat Moss (PM), Pyrolysis Residue (PR), Activated Rice Husk (RH), and powdered activated carbon (PAC). It was found that adsorption capacity RH carbon for PAH is comparable with the conventional adsorbent (PAC). Kinetics, equilibrium, and thermodynamic studies were carried out for the adsorption of selected PAH on RH carbon in single-component systems. Two days are sufficient contact time between each solute and the RH carbon. Intraparticle mechanism was proved for all compounds. Langmuir, BET, Freundlich, Redlick–Peterson, Toth, Generalized and Fritz–Schlünder isotherm equations were studied. It was found that the Freundlich isotherm for NA, Generalized isotherm for PH and BET isotherm for PY gave an excellent overall fit. The fitting was improved independent on the number of isotherm parameters. The calculated values of dimensionless separation factor R_L of NA, PH, and PY were between 0 and 1 supporting the adsorption of PAH compounds onto RH carbon is very favorable. The results indicated the exothermic nature of PH adsorption onto RH carbon. Thermodynamic parameter was determined. Comparison with other studies was investigated.

Keywords: Adsorption; Polycyclic aromatic hydrocarbons (PAH); Activated rice husk; Adsorption isotherms and water treatment

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of organic compounds produced as a result of pyrolysis during coal conversion processing, which have been identified in liquid effluents from several coal conversion facilities [1]. Another important source of these pollutants in the air is known to be tobacco smoke [2]. Because PAH have low aqueous solubilities, these compounds exist in waters and wastewaters primarily as species adsorbed onto suspended matter rather than as dissolved species [3]. 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

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*Corresponding author.

carcinogenic responses. Sixteen PAHs are on the US-EPA's priority pollutants list [4]. Activated carbon adsorption offers the most efficient processes available for removing certain organics and inorganics from wastewater. The capacity of activated carbon for a certain type of pollutant is important for designing adsorption contacting systems [5]. However, recognized that activated carbon is an expensive material for a large number of countries, particularly if they depend only on importation from the few leading producing countries. Thus, it becomes necessary to identify new, preferably more natural, more abundant and cheaper materials to prepare activated carbon.

In this study, various low cost locally available industrial and agricultural wastes were evaluated for the removal of naphthalene (NA), phenanthrene (PH), and pyrene (PY). These three PAHs were selected due to their common presence in petroleum wastewaters and their troublesome properties. These are taken as representatives for two, three, and four rings of PAH. Moreover, NA and PH are included in the composition range of kerosene which is known to be a very important diluent in the hot laboratories center due to its regular uses in the "Purex Process". The equilibrium, kinetics, and thermodynamic data of the adsorption process were analyzed to study the adsorption characteristics and the mechanism of adsorption.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical grade and were used without any further purification. Analytical-grade NA, PH, PY, and HPLC-grade acetone were used. Double-distilled water was used throughout this study. The standard stock solutions of PAH were prepared by dissolving 8 mg of pure compound in a least amount of acetone, transferring to a 100 ml volumetric flask and completing to the mark with a reagent water. The analysis of PAH was performed by EPA 610–GC method using HP 6890–GC with split–splitless injector and flame ionization detector (GC–FID) [6].

2.2. Adsorbents

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

2.2.1. Adsorbents from industrial by-products

The residue (B-1) is a by-product from paint industry, supplied by Pakin CO., Mostorod, Egypt. The animal bones were pyrolysed for 5 h at 800°C to produce the residue. The residue constituent is 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 (PR) is a by-product of domestic waste incineration and was supplied by PKA (Pyrolysis-Kraft-Anlagan)-Co., Germany.

2.2.2. Adsorbents from agricultural wastes

Peat moss (PM) was obtained from Belbaes, Egypt and used without any pretreatment. Activated Rice Husk (RH), was prepared by impregnating 40 g. of RH 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 activated carbon (PAC) was purchased from El-Nasr Pharmaceutical Chemicals CO., Egypt.

All adsorbents were sieved to a constant particle size of 590 μm. The BET surface area was determined by N_2 adsorption isotherms at 77 K using a Gemini 2375 V3.03 instrument (Micromeritics). Ash content (wt.%) was determined from gravimetric measurement [7]. About 1.0 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,

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

The BET-surface area, ash content and the elemental analysis of these sorbents are listed in Table 1.

Table 1
Some data on the various sorbent materials

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
PM	45.7	4.8	3.5	2.5	3.4	3.8	6.4
PR	34.1	1.12	1.71	0.44	0.35	54.7	40
RH	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.

2.3. Sorption experiments

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 ($C_0 = 8$ mg/l for each compound) with 10 mg of each material (B-1, B-2, PM, PR, RH, PAC in a glass bottle provided with a screw cap. The bottles were then shaken for 24 h at (25 ± 1)˚C. The residual concentration (C_e) in the filtrate was measured using GC–FID.

2.4. Adsorption Isotherms

Adsorption isotherms were done by mixing various masses of RH carbon. (0.1–7 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 PH were determined at various temperatures 25, 35, and 45°C to decide whether the adsorption process is exothermic or endothermic.

In all cases, the adsorptive capacity (q_e) was calculated as follows:

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

where C_0 and C_e are the initial and equilibrium concentrations of PAHs (mgl^{-1}) in water, respectively. V is the total volume of solute solution (l), m is the mass of adsorbent used (gm).

3. Results and discussion

3.1. Comparison of adsorbents

Fig. 1 provides a comparison of the total adsorption capacity of the three PAH under investigations, in one mixture in aqueous solution for the different investigated adsorbents. Based on the data obtained, the amount adsorbed from PAH mixture by RH carbon are comparable with that obtained by the manufactured PAC. Therefore, RH was used as an adsorbent material for the removal of the three compounds (NA, PH and PY).

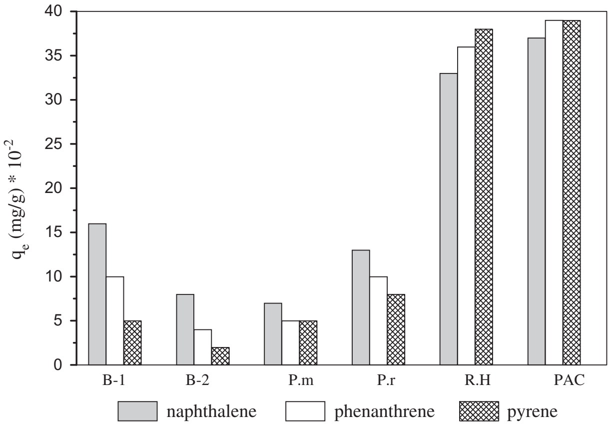

Fig. 1. Adsorption of PAH by B-1, B-2, PM, PR, RH and PAC represented by weight capacity, q_e (mg/g).

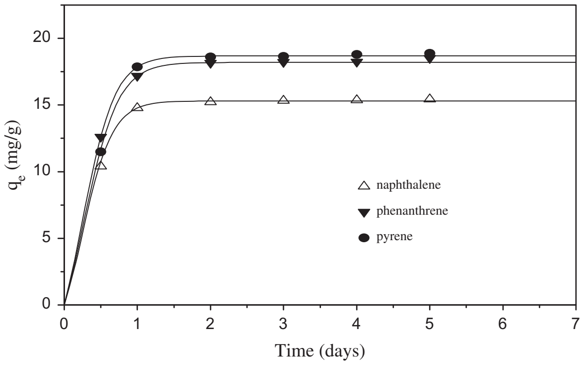

Fig. 2. Equilibrium uptake of PAH compounds.

3.2. Equilibrium time and adsorption rate

Fig. 2 shows the variation of the uptake expressed by the weight capacity q_e (mg/g), of NA, PH, and PY on RH carbon in terms of time (days). It was clear that two days are sufficient contact time between each solute and the RH sorbent. The time to reach equilibrium of 24 h for PAH solution systems was in good agreement with previous results [8].

Weber and Morris kinetic models were tested to determine the kinetic rate in the adsorption process of each PAH onto the RH carbon, as well as the mechanisms involved [9].

$$q_t = K \times t^{0.5} \tag{3}$$

where q_t are the amounts of PAHs adsorbed (mg g^{-1}) at time t (h), K, (mg/g h$^{0.5}$) is Morris constant rate constant. The adsorption rate, K was calculated [10]

Table 2
Adsorption rates of PAH studied

PAH	K (mg/g h$^{0.5}$)×10^{-3}	log K_{ow}
NA	101.5	3.30
PH	156	4.57
PY	200	5.18

Table 3
The constants of two; three and four-parameter isotherms

Solute		NA	PH	PY
Langmuir	q^o	63.6	50.4	104.5
$q_e = \frac{q^o b C_e}{1+bC_e}$	b	0.34	1.02	0.44
	%err	7.0	7.3	4.3
BET	Q^o	52.1	14.76	106.4
$q_e = \frac{Q^o B C_e}{(C_s - C_e)\left[1+(B-1)\left(\frac{C_e}{C_S}\right)\right]}$	B	12.7	5.64	1,720
	%err	6.7	36.6	4.22
Freundlich	K_f	15.7	24.8	29.8
$q_e = K_f C_e^{1/n_f}$	n_f	1.4	1.8	1.4
	%err	6.5	12.8	6.6
Redlick–Peterson isotherm	a_R	25.5	45.6	262.7
$q_e = \frac{a_R C_e}{1+b_R C_e^{\beta}}$	B_R	0.58	0.54	7.6
	B	0.76	1.4	0.4
	%err	8.1	4.6	9.1
Toth isotherm	q_T	86.9	39.4	109.3
$q_e = \frac{q_T K_T C_e}{[1+(K_T C_e)^{n_T}]^{1/n_f}}$	K_T	0.33	1.06	0.43
	n_T	0.68	2.3	0.96
	%err	9.55	4.82	4.4
Generalized isotherm	a_1	14.8	216.0	16.9
$q_e = \frac{a_1 a_2 C_e}{(1+a_2 C_e)^M}$	a_2	1.87	0.231	3.7
	M	0.5	2.6	0.46
	%err	10.0	4.52	7.4
Fritz–Schlünder	α_1	28.7	45.1	90.65
$q_e = \frac{\alpha_1 C_e^{\beta_1}}{1+\alpha_2 C_e^{\beta_2}}$	α_2	1.5	0.992	1.4
	β_1	0.71	0.53	1.8
	β_2	1.6	1.42	1.1
	%err	7.2	4.6	5.3

and listed in Table 2. According to the Weber and Morris 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 [11]. In this work, the behavior of the q_t vs. $t^{0.5}$ graph is initially linear, indicating that the diffusion process occurs. However, it was not the only rate-controlling step as line did not passes through the origin. The adsorption rate sequence has the order: NA > PH > PY. This different degree of adsorption may be explained in terms of the hydrophobic character of the three PAH. The n-octanol/water partition coefficient (log K_{ow}) is a well-known indicator of the hydrophobicity of an organic compound. As shown in Table 2 log K_{ow} values are directly related to observed adsorption rates. Good relations between log K_{ow} and adsorption rates were found in a system containing hydrophobic solutes and a hydrophobic adsorbent [12]. The hydrophobicity of an organic compound can be varied by the structure and functional group of the compound.

3.3. Adsorption Isotherms

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

The adsorption equilibrium data (Figs. 3 and 4) were fitted with several well-known isotherm models. A computer program has been used for the estimation of coefficients based on nonlinear optimization technique. The value of the mean absolute percentage error [13]:

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

has been selected as a test criterion for the fit of the correlation [14]. The best fitting (i.e., the lower %err) for each compound was presented by shadow in Table 3. A comparison of the experimental and theoretical data for NA by Langmuir, Freundlich, and BET isotherm equations shown in Fig. 3 and by Redlick–Peterson, Toth, Generalized and Fritz–Schlünder isotherm equations shown in Fig. 4. The results of the fitting procedure were presented in Table 3. It was found that the Freundlich isotherm for NA, Generalized isotherm for PH and BET isotherm for PY gave an excellent overall fit. Among the three-parameter models investigated in this study, the better known

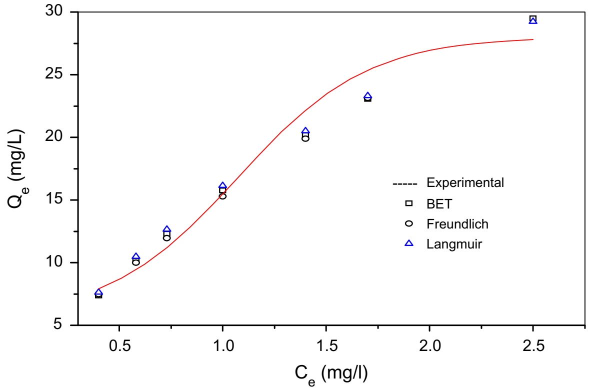

Fig. 3. Comparision of the experimental and theoretical data of PH adsorption (two parameters isotherms).

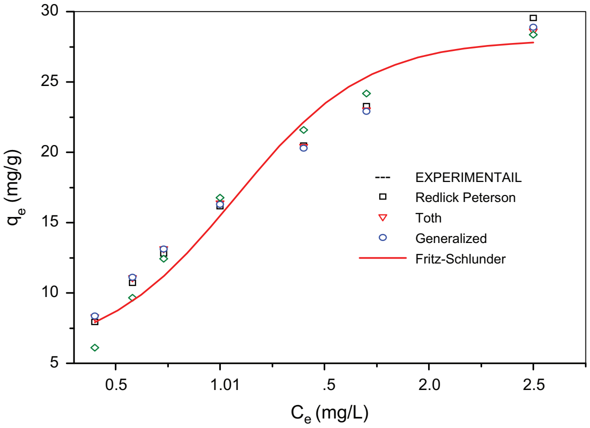

Fig. 4. Comparsion of the experimental and theoretical data of PH adsorption (three and four parameters isotherms).

Radlick–Peterson isotherm [15] gave the worst fitting for PY with (%err = 9.1), if compared with the rest of models. Whereas, the rarely used Toth isotherm [16] gave much better fitting for PY with (% err = 4.4) only and somewhat better than the Fritz–Schlünder isotherm [17]. Although the latter model provided a satisfactory fit to the isotherm data for PH over most of the concentration range, the newest Generalized isotherm model [14] 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 PH. The reverse status is noticed in case of NA, where the two-parameter models provided a satisfactory fit to the isotherm data over most of the liquid concentration range. Neither of three or four parameters isotherms described accurately the flat portion of the experimental isotherm curve. The empirical four-parameter Fritz–Schlünder isotherm [17] was tried with the expectation that the introduction of a fourth parameter would enhance the fit to the flat portion of the isotherm. Although use of this isotherm did not improve the overall fit, yielding a (%err = 7.2) close to or higher than those obtained with the two-parameter isotherms, it did not improve somewhat the fit at high concentrations. Therefore, Freundlich fit was selected as shown for adsorption system of NA:RH due to the (% err = 6.5) only. In conclusion, we can decide that, the fitting can be improved independent on the number of isotherm parameters.

3.4. Dimensionless separation factor

The adsorption isotherm process favorability was also checked using the dimensionless separation factor (R_L) and the values were calculated using adsorption affinity constant, b, of Langmuir isotherm by the following equation, [18,19]

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

If the value of R_L lies between 0 and 1 ($0 < R_L < 1$), the adsorption process is favorable. If the value of R_L lies beyond one ($1 < R_L$), the adsorption process is not favorable. Whereas if the R_L value equals unity (i.e., $R_L = 1$), then the process is linear and if R_L attains a value of zero ($R_L = 0$), and then, the adsorption process is irreversible in nature [20]. The isotherm shape for NA, PH, and PY was determined to decide whether the adsorption process of each adsorption system is favorable or unfavorable [21]. The calculated value of R_L of NA, PH, and PY was 0.27, 0.22, and 0.1, respectively, z lying between 0 and 1. The experimental and calculated results of the adsorption process are the evidences supporting the isotherm condition and hence it could be concluded that the adsorption of PAH compounds onto RH carbon is very favorable. In addition, the lower values of R_L indicate that the interaction between PAH molecules and the RH carbon may be due to relatively strong chemical forces of attraction [22].

3.5. Temperature effect

The uptake of PH obtained at 25, 35, and 45°C is shown in Fig. 5. It is clear that, the adsorbent RH carbon indicates a normal trend associated with physical adsorption, that is, an increase in the temperature, will result in a reduction in the equilibrium adsorptive capacity [23]. The Freundlich parameters K_f and n_f and Langmuir constants q^o and b are calculated and listed in Table 4.

The thermodynamic parameters of the adsorption process, such as free energy of adsorption ΔG, enthalpy of adsorption ΔH and entropy of adsorption ΔS, were determined using Van't Hoff equation [24,25] by plotting ln K vs. $1/T$ for different temperatures at 298, 308 and 318 K (Fig. 6) as follows: [24,25]

$$\ln k = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{6}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

where ΔG is the change in the Gibbs free energy (kJ/mol); ΔH is the change in enthalpy (kJ/mol), and ΔS is the change in entropy (kJ/mol K), R = gas con-

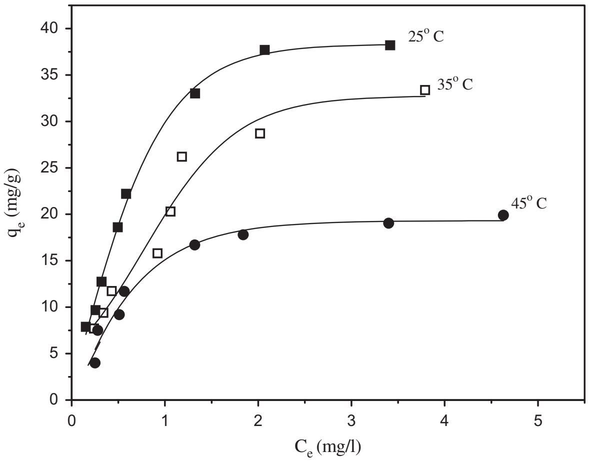

Fig. 5. The uptake of PH obtained at 25, 35, 45°C.

Table 4
Effect of temperature on adsorption capacity of PH

Temperature (°C)	K_f	n_f	q^o	b
25	24.4	1.8	50.4	1.2
35	18.43	1.76	41.6	0.91
45	11.93	2.16	32.3	0.74

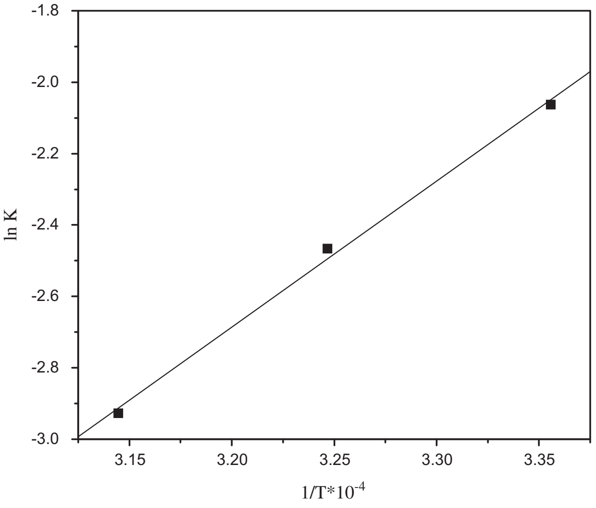

Fig. 6. Van't Hoff equation of PH.

stant (1.98 cal/mol K), T = thermodynamic temperature (K). k is the equilibrium constant obtained from the product of Langmuir constant, b and Langmuir monolayer adsorption capacity, q^o normalized with respect to the surface area, S of RH carbon ($K = q^o b/S$).[26] The thermodynamic parameters calculated according to Eqs. (6) and (7) are listed in Table 5. The estimated value of ΔH^o for the PH:RH system was –8180.5 cal/mole. The negative value of the enthalpy change confirms the exothermic nature of the adsorption of PH on RH carbon [27]. The increase in the value of $+\Delta G^o$ with increasing temperature indicates that the sorption of PH on to RH carbon becomes more favorable at low temperature [28]. The negative values of ΔS^o suggests a decrease randomness at the solid/solution interface during the adsorption process [24,27].

Table 5
The thermodynamic parameters of PH

Temperature (K)	ΔH^o (cal/mol)	ΔS^o (cal/mol.deg.)	ΔG^o (cal/mol)
298	}−8180.5	−31.6	1,229
308		−31.5	1,519
318		−31.6	1,861

3.6. Comparison with previous work

PAHs adsorption from wastewaters has been investigated by using different substances: chitosan, chitin, sugar bagasse, coconut shells, immature coal–leonardite and mesoporous organosilica [29–31], Al–MCM-41 [32], mesoporous organosilica [31] and zeolite [33]. Intensity of adsorption and Langmuir adsorption constant q^o, calculated for each adsorption system, are given in Table 6. The Freundlich adsorption constant K_F calculated for each adsorption system are given in Table 7. The results in both tables are compared with those obtained in this work. In general, the PAH uptake capacities on RH carbon are comparable to some adsorbents and far exceeded the uptake capacities of others. Some materials show outstanding PAH adsorption capacities compared to our materials. However, a fair and objective evaluation concerning the potential of any material as an adsorbent at commercial level should consider its local availability, as this factor closely related with cost minimization. Egypt has abundantly available agricultural waste, such as RH, which has very little economic value and in fact, often creates a serious problem of disposal for local environment. To achieve an economically feasible and effective treatment of organic-contaminated water, the utilization of such unused resources from an agricultural waste as an alternative adsorbent for PAH removal is highly desirable.

Table 6
Langmuir parameters for adsorption of PAHs on various kinds of adsorbents

Adsorbent	T (°C)		Langmuir parameters		Reference
			b ($\mathrm{l\,mg^{-1}}$)	q^o ($\mathrm{mg\,g^{-1}}$)	
Al–MCM-41	25	NA	0.214	106.24	[32]
Zeolite	–		0.005	769.231	[33]
PMO	28 ± 1		6.273	46.641	[31]
RH carbon	28 ± 1		0.34	63.6	This work
Al–MCM-41	28 ± 1	PY	1.184	371.68	[32]
PMO	28 ± 1		0.228	2601.504	[31]
RH carbon	28 ± 1		0.44	104.5	This work

Table 7
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	NA	13	0.98	[29]
Green coconut shells		23	1.34	[29]
Chitin		138	0.05	[29]
Chitosan		2	1.39	[29]
Zeolite		4.215	1.074	[33]
PMO		0.277	0.974	[31]
RH carbon		15.7	0.71	This work
Sugar cane bagasse	PY	170	0.15	[29]
Green coconut shells		140	0.99	[29]
Chitin		120	0.14	[29]
Chitosan		50	0.21	[29]
Immature coal (leonardite)		10	0.62	[30]
PMO		0.119	1.682	[31]
RH carbon		29.8	0.71	This work

4. Conclusion

The adsorption behavior of selected PAH 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 NA, PH and PY onto activated RH. The adsorption affinity depends on the solute shape and the separation factor as well as the solubility and molecular structure. The adsorption process is favorable and indicates a normal trend associated with physical adsorption, that is, exothermic.

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