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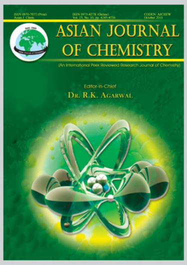

Enhanced Sorption of Phenanthrene from Water by Modified Peat and the Thermodynamic Analysis

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In this study, the sorption processes of phenanthrene from aqueous solutions using natural and surfactant modified peat were investigated. The effects of initial concentration, contact time and temperature on the amount of phenanthrene adsorbed were studied and the mechanism involved was discussed. Good correlation coefficients were obtained for the pseudo-second-order kinetic model, showing that the sorption process of phenanthrene by peats followed the pseudo-second-order rate expression. The sorption capacity of peat increased with enhanced hydrophobicity and decreased surface negative charge. Equilibrium sorption studies showed that the sorption process was better described by the Langmuir isotherm in comparison to the Freundlich and Tempkin isotherm. The thermodynamic parameters were evaluated and the sorption of phenanthrene by peats was found to be spontaneous and exothermic. Evidently, modified peat has a great potential application in the effective remediation of polluted groundwater.

Key Words: Modified peat, Phenanthrene, Adsorption, Kinetics, Thermodynamics.

INTRODUCTION

Water pollution by hydrophobic organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), is a worldwide concern. The high bioaccumulation and possible carcinogenicity of polycyclic aromatic hydrocarbons may have long-lasting effects on animals and humans[1,2]. Polycyclic aromatic hydrocarbons mainly arise from incomplete combustion processes of organic matter, industrial processes and petroleum seeps. Given their organophilicity and bioavailability, polycyclic aromatic hydrocarbons can enter natural water by accumulating in sediments, suspension solids and organisms[3-5]. An effective and affordable method for wastewater treatment and water body reclamation needs to be developed.

Extensive studies have been conducted for discovering methods to remove hydrophobic organic pollutants from water. One effective method is adsorption. A previous study has revealed that the brown seaweed *Sargassum hemiphyllum* is an effective sorbent for removing aqueous phenanthrene[6]. More than 90 % of aqueous phenanthrene could be removed under certain conditions. The shaking rate and temperature influence the sorption rates, but not the maximum sorption capacities. In another study, a pine bark modified by three chemical treatments (*i.e.*, Soxhlet extraction, alkaline saponification and acid hydrolysis) has shown a great potential for removal of polycyclic aromatic hydrocarbons[7]. The adsorption of polycyclic aromatic hydrocarbons strongly depends on the organic content and surface characteristics of the adsorbent, particularly hydrophobicity. Hence, surface modification would be a valid method for significantly improving the sorption capacity. The surfactant cetyltrimethyl ammonium bromide is used as a structure-directing agent for modifying materials. The surface properties could be changed by introducing long-carbon-chain groups[8-10].

The purpose of the current study is to invent a low-cost biosorbent that can remove polycyclic aromatic hydrocarbons from aqueous solutions. Peat was used as the adsorbent and cetyltrimethyl ammonium bromide as modifier. The potential sorption capacities of peat and cetyltrimethyl ammonium bromide-modified peat for adsorbing phenanthrene, a nonpolar neutral polycyclic aromatic hydrocarbon, was experimentally investigated. To better understand the adsorption mechanism and make it more efficient, adsorption kinetics and thermodynamics were used to analyse the adsorption process of polycyclic aromatic hydrocarbons by natural and modified peat.

EXPERIMENTAL

Fibric peat was obtained from the Jixiang Peat Co. (Jilin, China). Table-1 shows some of its physicochemical properties. The cetyltrimethyl ammonium bromide modifier was purchased from the Lingfeng Chemical Reagent Co. (Shanghai,

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF PEAT

Sorbent	Ash content (%)	Organic matter (%)	Humic substance content (%)	Cation exchange capacity (meq g^{-1})	Dry density (g cm^{-3})	pH
Natural fibric peat	15.5	83.2	48.8	0.414	0.36	5.3
Modified fibric peat	14.2	85.7	31.2	-	0.40	6.4

China). Phenanthrene (> 98.9 % purity) was purchased from the Accu Standard Chemical Co. (CT, USA). Phenanthrene had a molecular weight of 178.2 g mol^{-1}, an aqueous solubility of 1.1 mg L^{-1} at 25 ºC and a partition coefficient (l g K_{ow}) of 4.447.

Preparation of cetyltrimethyl ammonium bromide-modified peat: Prior to the sequential modification procedure, the peat (as supplied) was crushed, ground, sieved (120-180 µm), washed with deionized water to remove any adhering impurities and oven dried at 65 ºC. About 1 g of pretreated natural fibric peat (NP) was mixed with 500 mL of 2 g L^{-1} cetyltrimethyl ammonium bromide solution for 4 h at 25 ºC under 190 rpm agitating conditions. The modified fibric peat (MP) was separated from the solution by suction filtration and washed with deionized water until no macroscopic bubble was observed in the eluate. The modified fibric peat was then dried for 6 h at 65 ºC. Afterwards, the hydrogen ion from the carboxyl and hydroxyl groups of natural fibric peat was replaced by the long-carbochain of cetyltrimethyl ammonium bromide, which enhanced the hydrophobicity of natural fibric peat[10].

Adsorption experiments: phenanthrene has low water solubility. Hence, the phenanthrene stock solutions were prepared at high concentrations in high-performance liquid chromatography (HPLC)-grade methanol. The intraday available aqueous solutions of phenanthrene used in the isotherm and kinetics experiments were prepared by dissolving the desired amount of stock solutions and adjusting them to the desired concentration with deionized water. The concentration of methanol in the aqueous solution was always less then 1 % by volume to avoid cosolvent effects on adsorption.

The adsorption of phenanthrene was carried out in batch experiments. Screw-cap vials (50 mL) sealed with polytetrafluoroethylene film and an orbital shaker device set to operate at 190 rpm were used in the experiments. Controls without sorbent were prepared in the same way to account for possible loss of phenanthrene other than adsorption by the natural fibric peat and modified fibric peat. A glass-fiber filter, which had a proven negligible sorption of polycyclic aromatic hydrocarbons, was used to separate the sorbent from the solution.

The kinetic experiments were conducted by mixing 50 mL of aqueous phenanthrene solutions (1 mg L^{-1}) with the desired amount of sorbents at 25 ºC at various time intervals between 5 and 360 min. About 0.03 g of sorbent was added for adsorption. The sorption isotherms were obtained at 25, 35 and 45 ºC. About 50 mL of aqueous phenanthrene solutions with different initial concentrations corresponding to 100, 300, 500, 700, 900 and 1100 µg L^{-1} were mixed with the desired amount of sorbent. After agitation for 4 h, the adsorbent was removed by the glass-fiber filter and the respective solutions were analyzed by HPLC. The amount of phenanthrene adsorbed by the sorbent was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where, q_e is the amount of phenanthrene adsorbed (µg g^{-1}); C_o and C_e are the solute concentrations before and after sorption, respectively (µg L^{-1}); V is the volume of the experimental solution (L); and m is the amount of sorbent (g).

Instrumental analyses: The quantification of phenanthrene was performed using a Hitachi (Tokyo, Japan) D2000 HPLC system equipped with an Agilent (Santa Clara, CA, US) Li Chroshper polycyclic aromatic hydrocarbon reverse-phase column (25 cm × 3 mm, 5 µm) at 30 ºC. The detection at 251 nm was performed using an ultraviolet detector at an isocratic operation (1 mL min^{-1}) of the mobile phase comprising 93/7 (v/v) methanol/water.

Data analyses: Usually, the determination coefficient R^2 is the only scientific criterion for the best fitting isotherm for the experimental data. R^2 could greatly reflect the experimental quantitative relation. However, R^2 is unable to show error distributions, reducing the credibility of evaluation results.

In the present study, both R^2 and the standard error (SS) were used to statistically analyse how well the experimental data fitted each model using the following equation. The two optimal rules are maximising the determination coefficient and minimizing the standard error (SS) is calculated as:

$$SS = \left[\frac{1}{N} \sum_{i=1}^{N} \left(\frac{q_{e\,exp} - q_{ecalc}}{q_{eclac}} \times 100 \right)^2 \right]^{\frac{1}{2}} \quad (2)$$

where, q_{eexp} is the experimental amount of adsorbed phenanthrene (µg g^{-1}), q_{ecalc} is the calculated amount of adsorbed phenanthrene (µg g^{-1}) and N is the number of experiment plots.

RESULTS AND DISCUSSION

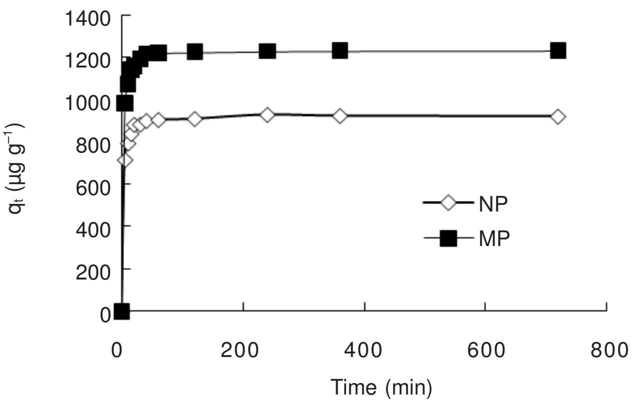
Adsorption kinetics: The effect of contact time on the amount of phenanthrene adsorbed on the natural fibric peat and modified fibric peat from the aqueous solution is shown in Fig. 1. The adsorption of phenanthrene onto both natural fibric peat and modified fibric peat appears to be kinetically similar. In the first 0.5 h, the adsorption efficiency rapidly increases. The adsorption process tends to reach the equilibrium state after 1 h of contact between the adsorbent and phenanthrene. The equilibrium sorption capacity of natural fibric peat is 964 µg g^{-1}, whereas that of modified fibric peat is 1279 µg g^{-1}. The phenanthrene removal efficiency and adsorption rate on modified fibric peat are higher than those on natural fibric peat.

Two kinetic models, pseudo-first-order and pseudo-second-order equations, are used to fit the experimental data. The rate equation for the pseudo-first-order model is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

TABLE-2
PARAMETERS OF THE PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETIC MODELS

Sorbent	C_0 (μg L^{-1})	q_e (μg g^{-1})	Pseudo-first-order		Pseudo-second-order		
			k (min^{-1})	R^2	q_e (μg g^{-1})	k_2 (g $μg^{-1}$ min^{-1})	R^2
NP	890	964	4.56 E-2	0.95	1000	3.85E8	0.99
MP	890	1279	2.44 E-2	0.75	1250	2.60E9	0.99



The pseudo-second-order kinetic model equation is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{4}$$

where, q_t and q_e are the amounts of phenanthrene adsorbed (μg g^{-1}) at time t (min) and at equilibrium, respectively. k_1 and k_2 [g (μg $min)^{-1}$] are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

Table-2 shows that the linear correlation of the curve analyzed by the pseudo-second-order kinetic equation is better. All the correlation coefficients R^2 of the pseudo-second-order kinetic model are more than 0.99 and the calculated q_e' values agree with the experimental q values. Therefore, this adsorption mechanism associated with the removal of phenanthrene by natural fibric peat and modified fibric peat probably involves a concentration- and adsorption time-dependent process. The fiting of results of phenanthrene to the pseudo-second-order kinetic model shows that the kinetic rates and sorption amount on modified fibric peat are greater than those on natural fibric peat.

Adsorption isotherms: The next goal has been to identify the relationship between the amounts of analyte adsorbed and in the solution after equilibrium. For this purpose, the equilibrium adsorption data obtained were fitted to the linear forms of the Freundlich, Langmuir and Tempkin isotherm equations[11]:

Langmuir : $q_e = \frac{K_L C_e}{(1 + a_L C_e)}$; linear form : $\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$,

Freundlich: $q_e = K_F C_e^{b_F}$; linear form: $\ln q_e = \ln K_F + b_F \ln C_e$,

Tempkin : $q_e = \frac{RT}{b}(\ln AC_e)$;linear form: $q_e = B \ln A + B \ln C_e$,

where, q_e is the amount of polycyclic aromatic hydrocarbons adsorbed (μg g^{-1}); C_e is the equilibrium solution concentration of polycyclic aromatic hydrocarbons (μg L^{-1}); K_L and a_L are the Langmuir constants; K_F and b_F are the Freundlich constants; A and B are the Tempkin constants and B = RT/b.

The values of the Langmuir, Freundlich and Tempkin constants are presented in Table-3 for the sorption of phenanthrene onto natural fibric peat and modified fibric peat at 298, 308 and 318 K. Fig. 2 shows plots comparing the theoretical Langmuir isotherm, empirical Freundlich isotherm and Tempkin isotherm with the experimental data for the sorption of phenanthrene onto natural fibric peat and modified fibric peat at 298 K. As shown in Table-3 and Fig. 2, the Langmuir and Freundlich isotherms have the best regression fitting for the degree of relationship. The sorption of phenanthrene onto natural fibric peat using the Freundlich isotherm has a high coefficient of determination and low standard error, which takes heterogeneous adsorption processes into account. On the other hand, the Langmuir isotherm has a better fitting for the phenanthrene adsorption process on the modified fibric peat. The Langmuir isotherm accounts for monomolecular layer adsorption and is based on the assumption that adsorption occurs place at specific homogeneous sites within the adsorbent[12,13]. The better fit with the Langmuir isotherm is probably due to the fact that the modification enhanced the stability of the surface characteristics of the peat.

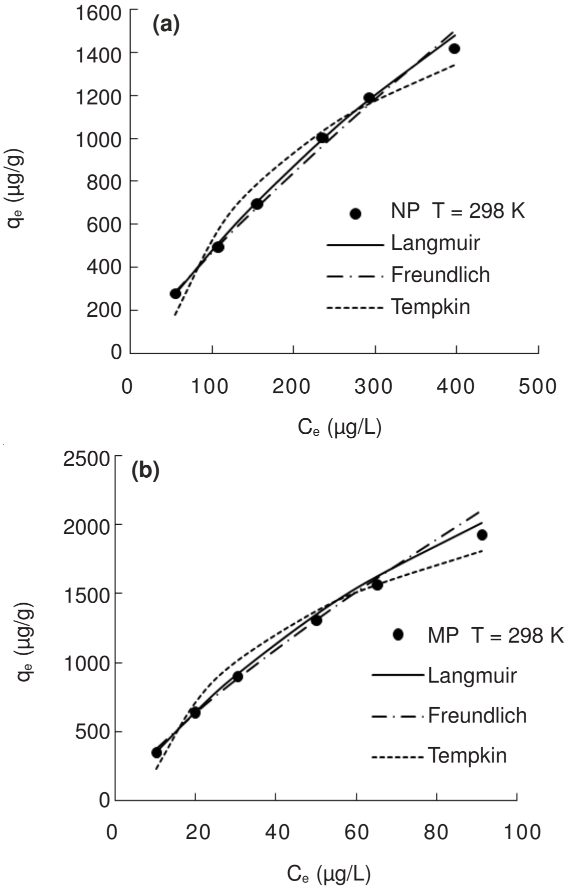


Fig. 2. Isotherms for the sorption of PHE onto (a) natural fibric peat and (b) modified fibric peat at 298 K.

TABLE-3
PARAMETERS OF ISOTHERM MODELS

Isotherm	Sorbent	T (K)	298	308	318
Langmuir	NP	q_m (μg g^{-1})	4791	3236	2469
		K_L (L μg^{-1})	0.00105	0.00136	0.00158
		R^2	0.9688	0.9899	0.9950
		SS	2.25	2.95	2.65
	MP	q_m (μg g^{-1})	5005	3333	3196
		K_L (L μg^{-1})	0.00741	0.00836	0.00524
		R^2	0.9997	0.9994	0.9939
		SS	2.87	0.91	5.06
Tempkin	NP	A (L μg^{-1})	0.02433	0.02404	0.02107
		B	590.34	488.03	445.41
		R^2	0.9667	0.9815	0.9889
		SS	23.74	15.31	9.79
	MP	A (L μg^{-1})	0.1329	0.1122	16.6226
		B	724.78	487.59	487.59
		R^2	0.9715	0.9761	0.9861
		SS	22.46	20.19	10.15
Freundlich	NP	b_F	0.834	0.816	0.715
		K_F (μg g^{-1}) (L μg^{-1})$^{1/n}$	60.83	40.86	33.95
		R^2	0.9924	0.9862	0.9964
		SS	3.25	4.86	5.14
	MP	b_F	0.842	0.786	0.746
		K_F (μg g^{-1}) (L μg^{-1})$^{1/n}$	185.2	116.9	63.03
		R^2	0.9971	0.9972	0.9965
		SS	4.55	4.45	4.98

NP = Natural fibric peat; MP = Modified fibric peat.

Thermodynamic parameters: The Gibbs free energy change (ΔG), the enthalpy change (ΔH) and the entropy change ΔS were used to consider the energy and entropy factors of the adsorption processes. As shown in Table-4, the negative values of ΔG and ΔH confirm the spontaneous nature of phenanthrene sorption onto natural fibric peat and modified fibric peat and the exothermic sorption reaction. The sorption of phenanthrene by modified fibric peat is easier because the process has lower ΔG values. ΔG decreases with increased temperature, indicating that a high temperature has inhibition effects on adsorption.

TABLE-4
THERMODYNAMIC PARAMETERS

Sorbent	T (K)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})
NP	298	-4.04	-32.59	-13.75
	308	-3.72		
	318	-3.39		
MP	298	-8.81	-84.78	-34.19
	308	-8.31		
	318	-7.12		

NP = Natural fibric peat; MP = Modified fibric peat.

Conclusion

Cetyltrimethyl ammonium bromide-modified peat was efficient in the adsorption of phenanthrene from aqueous solutions. The equilibrium sorption capacity of modified fibric peat was 1279 μg g^{-1}, whereas that of natural fibric peat was 964 μg g^{-1}. The pseudo-second-order kinetic equation best represented the adsorption kinetics data of the adsorption of phenanthrene at 298 K. The adsorption reached equilibrium in 1 h. The models that best fitted the obtained data were the Freundlich model for phenanthrene adsorption onto the natural fibric peat and the Langmuir model for that onto the modified fibric peat. The thermodynamic parameters show that the sorption processes of phenanthrene onto both natural fibric peat and modified fibric peat was spontaneous and exothermic.

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