Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1015304

57 (2016) 145–150
January

Taylor & Francis
Taylor & Francis Group

Analysis of sorption efficiency of activated carbon for removal of anthracene and pyrene for wastewater treatment

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Received 5 October 2014; Accepted 16 November 2014

ABSTRACT

The potential carcinogenicity and mutagenicity has placed polycyclic aromatic hydrocarbons (PAHs) on top priority calling for immediate management strategies. The present study draws its rationale that industries should opt for sustainable and economically viable solutions. The powdered activated carbon (PAC) is applied as adsorbent for removal of anthracene and pyrene under ambient conditions. Aliquot of batch run on GC–MS demonstrated progressively increasing percentage removal of anthracene and pyrene with increase in time. Further, pyrene shows a slower but regular increase in adsorption with distinct equilibrium at 100 min. However, anthracene depicts simultaneous adsorption–desorption pattern with multiple equilibriums. This suggests that pyrene is more stable due to its higher molecular weight and boiling point resisting its diffusion into adsorbent. The maximum removal of >99% is achieved after contact of 4 h between adsorbate and adsorbent. The fitness of pseudo-first-order kinetics suggests the linear and direct relationship of pyrene with time. Furthermore, the agreement of experimental data to Elovich model proposes chemisorption as the preferred mode of action for removal of PAHs on the surface of PAC. The study concludes that activated carbon is a successful alternate for efficient removal of PAHs from wastewater. Therefore, it can be adapted by industries as a sustainable remediation.

Keywords: Batch adsorption; Chemisorption; Activated carbon; Polycyclic aromatic hydrocarbons; Wastewater treatment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) pose serious environmental hazard due to persistent nature. Incomplete combustion of hydrocarbons and fossil fuel leads to formation of PAHs [1]. PAHs are also present in many common foods and are significant component of tobacco smoke [2]. Major sources of PAHs include vehicular emissions, forest fires, wood burning,

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Presented at the International Conference on Business, Economics, Energy and Environmental Sciences (ICBEEES) 19–21 September 2014, Kuala Lumpur, Malaysia

agricultural residue burning, asphalt roads, coal tar, tobacco smoke, incineration, and hazardous waste sites [3]. PAHs are also found in leafy plants, such as lettuce, spinach, tea, smoked meat, and fish [2].

PAHs are very toxic in nature with mutagenic and carcinogenic effects [2,4]. Pyrene, anthracene, phenanthracene, and fluoranthene have been found in very high concentrations in drinking water [5]. Various physical, chemical, and biological techniques are used to for removal of PAHs from the wastewater [6,7]. Wastewater treatment through adsorption method is quite effective because it is economically effective, economically feasible, and insensitive to most of the toxic pollutants [8].

Powdered- and granular-activated carbons are typical carbon adsorbents. These are non-graphitic, non-graphitizable carbons with a highly disordered microstructure. Other forms of carbons are also used as adsorbents such as activated carbon fibers, fabrics, and felts prepared from coal, petroleum pitch, viscose, or rayon. Carbon adsorbents have a porous carbon structure, which contains small amounts of different heteroatoms such as oxygen and hydrogen. Some activated carbons also contain variable amounts of mineral matter (ash content) depending on the nature of the raw material used as precursor [9].

2. Materials and methods

2.1. Reagents

Anthracene and pyrene were procured from Merck Chemical Co. Analytical reagent grade n-hexane was used. Powdered activated carbon procured from Merck was used as an adsorbent. Stock solutions of anthracene and pyrene were prepared in n-hexane. Characteristics of anthracene and pyrene are given in Table 1.

2.2. Batch adsorption experiments

Anthracene and pyrene solutions of 15 ml were made in contact with 0.1 g of sorbent in a conical flask until equilibrium was achieved. Dynamic contact between the activated carbon and the solutions of anthracene and pyrene was carried out on a mechanical shaker at 210 rpm at room temperature. Samples were filtrated through filter papers (Whatman Grade 40 Circles, 125 mm) to take out the activated carbon in order to have accuracy in the analysis. The samples were then analyzed to measure the quantity of sorbate to determine the extent of sorption.

2.3. Analysis of pyrene and anthracene

GC–MS-QP5050 gas chromatograph–mass spectrometer was used to analyze the concentration of anthracene and pyrene. Separation was achieved using DB-5 ms capillary column with 30 m length, 0.25 mm diameter, and 0.25 µm film thickness. Helium was used as carrier gas. Separation was taken place in an oven temperature gradient: 70˚C initial, held for 2 min, increased from 240 to 280˚C/min, and held for 5 min. Qualitative and quantitative analyses were undertaken by similarity search using computer library and also by calibrating against the standard solutions. Concentrations of anthracene and pyrene adsorbed by activated carbon at equilibrium are determined by using a mass balance equation:

$$q_e = (C_i - C_e)/S \tag{1}$$

where q_e is the concentration of anthracene and pyrene adsorbed on activated carbon at equilibrium, C_i is the initial concentration of anthracene and pyrene in the solution (mg/l), and C_e is the equilibrium concentration

Table 1
Characteristics of anthracene and pyrene

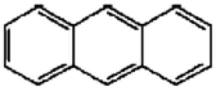
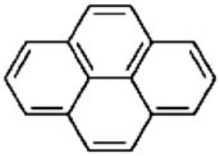
PAH	Structure	Molecular weight (g/mol)	Solubility 25˚ (mg/dm^3)	Melting point (˚C)	Boiling point (˚C)
Anthracene ($C_{14}H_{10}$)		178.22	0.045	215–219	340
Pyrene ($C_{16}H_{10}$)		202.26	0.13	151.2	404

Table 2
Parameters of pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models

Model	Parameters	Anthracene	Pyrene
Pseudo-first-order	K_1 (1/min)	-1×10^{-5}	-1×10^{-5}
	q_e (mg/dm^3)	142.69	142.26
	R^2	0.9786	0.9844
Pseudo-second-order	K_2 (1/min)	−11.833	−0.6307
	q_e (mg/dm^3)	1.48	∞
	R^2	0.0607	0.0605
Elovich	b (g/mg)	−1.096	−0.8651
	a (g/mg min)	0.8061	0.7112
	R^2	0.7605	0.889
Intraparticle diffusion	A	1.7611	1.2075
	$\log K_{\mathrm{id}}$	−2.0799	−0.8027
	R^2	0.9865	0.931

or final concentration of anthracene and pyrene in solution (mg/l). The dose concentration S, is expressed by:

$$S = m/v \tag{2}$$

where v is the initial volume (L) of anthracene and pyrene solutions used, and m is the mass of adsorbent used (g).

The percent adsorption (%) and distribution ratio (K_d) are calculated using Eqs. (3) and (4), respectively:

$$\%\,\text{adsorption} = C_i - C_e/C_i \times 100 \tag{3}$$

$$K_d = \text{amount of PAH in adsorbent}/\text{amount of PAH in solution} \times 1/S \tag{4}$$

The percent adsorption and K_d are correlated by the following equation:

$$\%\,\text{adsorption} = 100\ K_d/K_d + 1/S \tag{5}$$

3. Results and discussion

3.1. Effect of contact time

Effective variation of time on adsorption of anthracene and pyrene by activated carbon is studied. Adsorption of anthracene and pyrene is studied at the time interval of 5 min for total period of 5 h. Table 2 shows the concentration of anthracene and pyrene in the sample after adsorption on activated carbon, adsorbed concentration, and percent adsorption. It is clear from Table 2 that the adsorption capacity increases with increase in contact time. It has been noticed that the equilibrium for anthracene and pyrene have been attained in 4 h 5 min and 4 h 10 min, respectively.

Comparison of % adsorption of anthracene and pyrene is shown in Fig. 1 which summarizes the difference in rate of adsorption of both PAHs on same time interval. A linear relationship has been obtained for pyrene which shows that the adsorption of pyrene is directly dependent on contact time. It is clear that the adsorption of pyrene increases with increase in contact time. Although, the adsorption of anthracene also increases with time, adsorption rate is very slow in beginning. However, as the contact time is increased, rate of adsorption is also increased and so equilibrium for anthracene and pyrene is achieved almost at the same time.

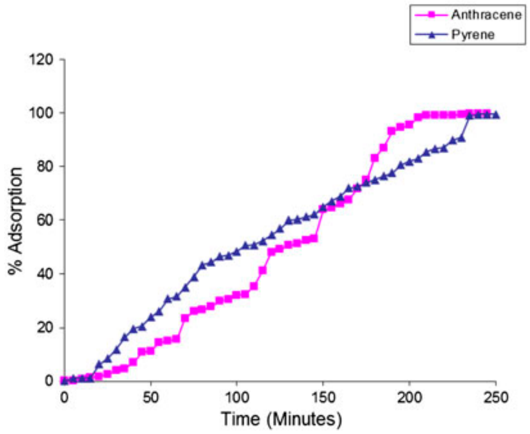


Fig. 1. Comparison of % adsorption of anthracene and pyrene.

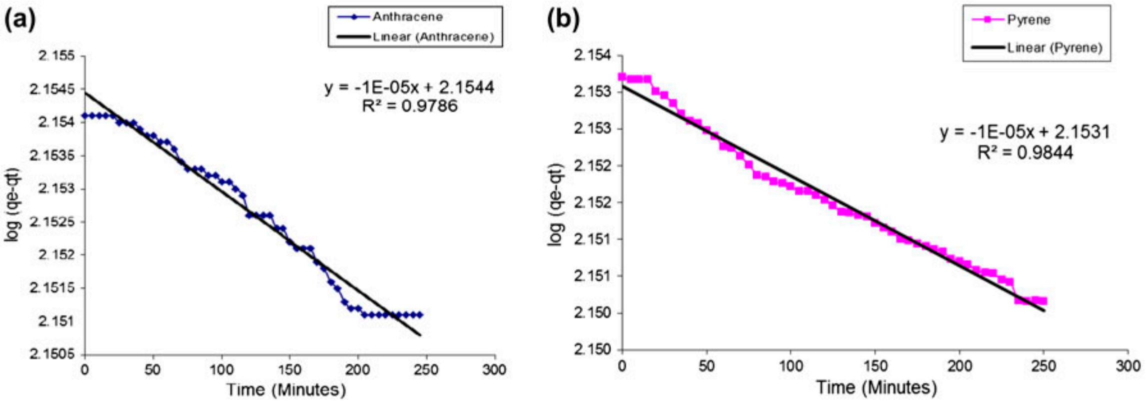


Fig. 2. Pseudo-first order kinetics model for (a) anthracene and (b) pyrene.

3.2. Adsorption kinetics and isotherms

Predicting the sorption rate for a given system is one of the important factors in the adsorption system design as the sorption kinetics controls the retention time and the reactor dimensions. The sorption rate constants are important physicochemical parameters to evaluate the quality of adsorbents [10]. Sorption kinetics applied to optimize the correlation for the equilibrium curve may be described as given below:

3.2.1. Pseudo-first-order kinetics

Kinetic study of adsorption experiments showed that the sorption of anthracene and pyrene on to activated carbon follow the pseudo-first-order as shown in Fig. 2(a) and (b) at various contact time. From these plots, linear relationships between ln $(q_e - q_t)$ and t for anthracene and pyrene have been established with significant correlation coefficients of 0.9786 and 0.9844, respectively, suggesting that the sorption of anthracene and pyrene are the pseudo-first-order reaction.

3.2.2. Pseduo-second-order kinetics

Pseudo-second-order kinetics was also applied on the adsorption data of anthracene and pyrene as given in Fig. 3(a) and (b). However, the coefficient correlations of 0.4082 and 0.0605 clearly indicate that the pseudo-second-order kinetics is not fit for adsorption of anthracene and pyrene on activated carbon.

3.2.3. Elovich model

Fig. 4(a) and (b) show plots of the Elovich equation for anthracene and pyrene. In this case, a linear relationship was obtained for anthracene and pyrene sorbed q_t, and ln t, with correlation coefficients 0.7605 and 0.889, respectively. It is evident that the Elovich equation better describes the adsorption kinetics of these PAHs on to activated carbon, whereas an

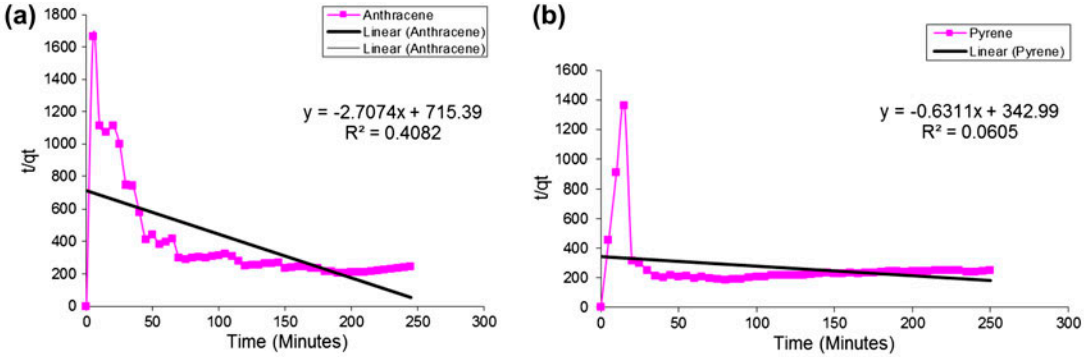


Fig. 3. Pseudo-second-order kinetics model for (a) anthracene and (b) pyrene.

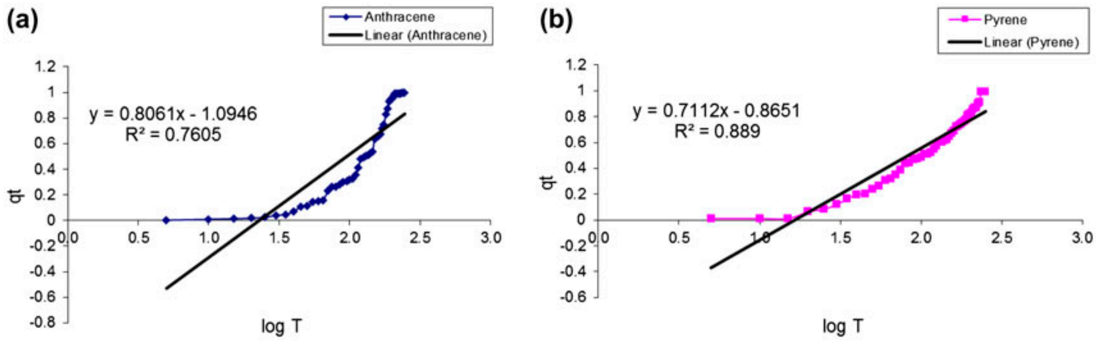


Fig. 4. Plot of Elovich model for adsorption of (a) anthracene and (b) pyrene.

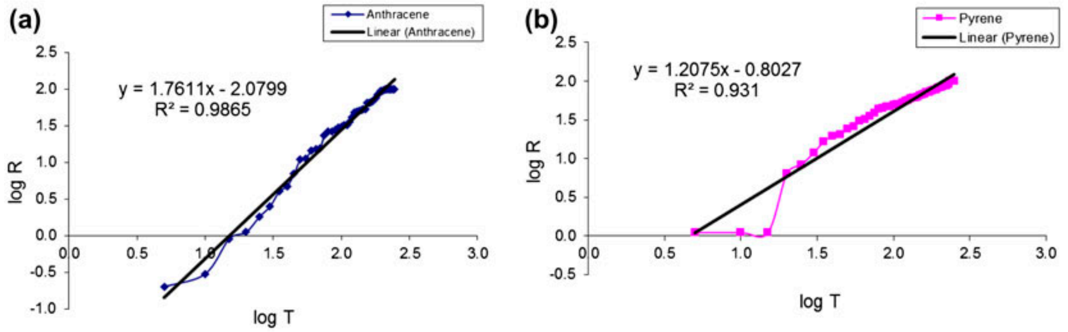


Fig. 5. Plot of intraparticle diffusion model for adsorption of (a) anthracene and (b) pyrene.

expression for a pseudo-second-order kinetic reaction could not be shown.

3.2.4. Intraparticle diffusion model

Intraparticle diffusion model for adsorption of anthracene and pyrene on to activated carbon are represented in Fig. 5(a) and (b), respectively. A linear relationship between log R and log t is shown with correlation coefficients of 0.9865 and 0.931. Intraparticle diffusion model also provides a very good description of the sorption of anthracene and pyrene on to activated carbon with high correlation coefficients.

Parameters of pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models are given in Table 2.

4. Conclusion

The results of kinetic sorption of PAH from aqueous solutions indicate that the rate-determining step of PAH extraction is the sorbent-phase diffusion. The rate of adsorption is high at the contact for first five minutes and after that the rate of adsorption becomes consistent till the equilibrium is achieved.

Elovich, intraparticle diffusion models, and pseudo-first-order kinetic equations provided the best fit for the sorption of anthracene and pyrene on to activated carbon. These models seem to be more appropriate due to their high correlation coefficients than pseudo-second-order kinetics model. These models provided an appropriate data fitting based on the statistical correlation coefficients, however, the Elovich correlation coefficient had the lowest value.

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