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Adsorption of anthracene using activated carbon and *Posidonia oceanica*

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Abstract The aim of this work was to examine the static capacity of adsorption of anthracene by *Posidonia oceanica* and activated carbon. The effect of experimental parameters pH and contact time on the anthracene adsorption onto cited materials was investigated in detail. The results showed that the anthracene removal on both *P. oceanica* and activated carbon was unaffected in the pH range of 2–12. The equilibrium data fit well to the Langmuir model with a maximum adsorption capacity of 8.35 mg/g and 0.14 mg/g, respectively with activated carbon and *P. oceanica*.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemical compounds consisting of carbon and hydrogen, arranged in the form of two or more aromatic rings. They are mainly originated from the incomplete combustion of fossil fuels, petrochemical industry and biomass burning. PAHs become ubiquitous contaminants in the environment (Jacques et al., 2008; Sartoros et al., 2005; Ye et al., 2011). Indeed, PAHs are stable and persistent in the environment due to their low aqueous solubility, low volatility and their slow response to biodegradation (Sartoros et al., 2005; Cheung et al., 2008; Nkansah et al., 2011). These compounds are considered as priority pollutants since they are harmful to organisms at low concentrations (Nkansah et al., 2011) and many of them have been classified as hazardous pollutants because of their potential to harm human health (Karim and Husain, 2010). Consequently, PAHs have raised great environmental concern all over the world to be an environmental potential problem. In addition, water resources management is a predominant problem for future development in the Arabian Gulf region, while water demand will continue to increase and the amount of available fresh water is limited. Thus the reuse of treated waste

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water effluents constitutes one of the solutions to solve this problem (Hamoda et al., 2004).

The removal of PAHs from wastewater is currently performed by physical, chemical and biological treatments (Yan and Urmila, 2004). In fact, the biological process usually requires a considerably long time to break down organic pollutants to an acceptable level of PAHs. The adsorption method is considered to be an effective method for the wastewater treatment due to its low cost, simplicity of design, ease of operation and insensitivity to toxic pollutants. Therefore, this last decade, there has been an increasing interest to find cheap and easily provided natural adsorbent. *Posidonia oceanica* (*P. oceanica*) an endemic marine magnoliophyta is found in the Mediterranean Sea (Demirak et al., 2011). It is a local biomass abundant on the coasts of Tunisia (Douissa et al., 2013; Khiari et al., 2011), has shown its effectiveness in removing organic and inorganic pollutants (Cengiz et al., 2012; Demirak et al., 2011; Douissa et al., 2013; Dridi et al., 2011; Dural et al., 2011).

The present work aims to present the usage of a sustainable environmental waste, *P. oceanica*, and activated carbon as promising precursors for the removal of anthracene from wastewaters. The effects of some parameters such as pH and contact time on the adsorption of the anthracene/*P. oceanica* or activated carbon system have been examined. Secondly a modeling of the isotherms of adsorption has been under taken by fitting the parameters of the Langmuir and Freundlich models.

2. Experimental

2.1. Materials

2.1.1. Anthracene

Anthracene (molecular weight 178.23 g mol^{-1}; melting point: 216–218 °C; boiling point: 340 °C) was purchased from Aldrich (Fig. 1).

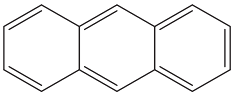

Figure 1 Molecular structure of anthracene.

2.1.2. Posidonia oceanica

The *P. oceanica* balls were collected from the Monastir beach (Tunisia). The collected material was washed with tap and distilled water to remove salt, impurities and epiphytes, and then dried at 60 °C for 3 days. The resulting material was crushed to produce homogeneous particles of size 50 μm.

2.1.3. Activated carbon

Commercial activated carbon was used in this study: a granular activated carbon (GAC) supplied by Merck Germany (2–8 mesh).

2.2. Methods

2.2.1. Effect of the initial pH

The adsorption of anthracene by the activated carbon or *P. oceanica* was studied over a pH range of 2–12 at 25 ± 1 °C. Initial concentration of anthracene was 4 mg/L. The influence of the initial solution pH was studied by shaking, in different brown flasks, 0.3 g of sorbent and 30 mL of the anthracene solution (4 mg/L) at different pHs. The flasks were agitated for 20 min with a constant stirring speed of 150 rpm. The solution pH was adjusted at the desired value by adding a small amount of HCl (0.1 M) or NaOH (0.1 M).

After the adsorption step, the solid phase was separated by filtration. The final concentration of anthracene in the solution was analyzed using a UV–Vis spectrometer (BECKMAN DU 800) at 252 nm wavelength. The adsorbed amount of anthracene at equilibrium, qe (mg/g) was calculated by the following expression:

$$q_e = \frac{(C_0 - C_e)}{m} \cdot V \tag{1}$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentration of anthracene solution, respectively. V (L) is the volume of the solution, and m (g) is the mass of adsorbent used.

2.2.2. Effect of contact time

In order to determine the contact time necessary for establishment of adsorption equilibrium, the adsorbed quantity of anthracene on activated carbon is measured as a function of the contact time corresponding to adsorption equilibrium. Adsorption studies were carried out by agitating 30 mL of anthracene solution (4 mg/L) with 0.3 g of adsorbent in a 50 mL brown flask at room temperature (25 ± 1 °C). The amount of adsorbed anthracene was determined at different time intervals (5–60 min).

2.2.3. Adsorption isotherms

The adsorption experiments were carried out at room temperature (25 ± 1 °C) and at natural pH. The brown flasks containing 30 mL of desired anthracene concentration (Table 1) with 0.3 g of adsorbent were mechanically agitated with a constant stirring rate of 150 rpm. After sharking, the samples were filtered and residual concentration of anthracene in the filtrate was estimated at $\lambda_{\max} = 252$ nm using a UV–Vis spectrometer (BECKMAN DU 800).

2.3. Theoretical

The equilibrium study on adsorption has provided information on the capacity of the adsorbent. The adsorption isotherms describe how solutes interact with adsorbents and express the surface properties and affinity of the adsorbent. The adsorption isotherm generally fits the Langmuir or Freundlich model (Cherifi et al., 2009; Freundlich, 1906; Hameed and Rahman, 2008; Langmuir, 1916; Montanher et al., 2005; Woodard, 2001).

2.3.1. Langmuir model

Langmuir model assumes that the maximum adsorption capacity consists of a monolayer adsorption, that the adsorption energy is distributed homogeneously over the adsorbent surface and that there are no interactions between adsorbed molecules. Langmuir equation is (Langmuir, 1916; Kobya, 2003)

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{2}$$

Table 1 Anthracene concentration (mg/L).

Sample	1	2	3	4	5	6	7	8	9	10	11
Concentration (mg/L)	0.33	1.33	2	2.66	4	16.66	33.33	50	66.66	83.33	100

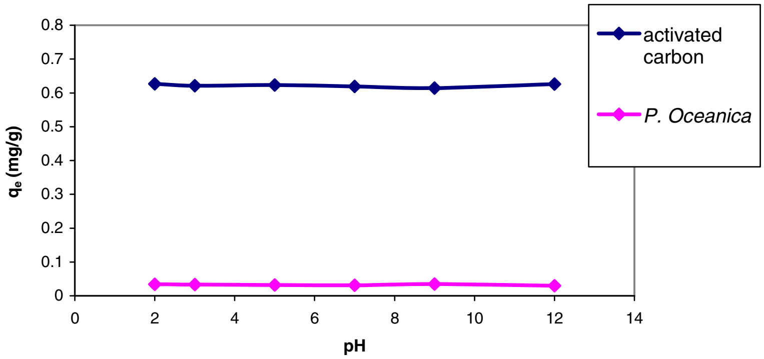

Figure 2 Effect of pH on anthracene adsorption onto activated carbon and *Posidonia oceanica*.

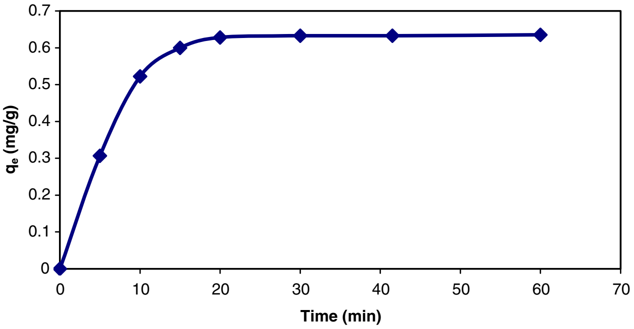

Figure 3 Effect of contact time on anthracene adsorption.

Where q_e, $q_{\max}$, K_L and C_e are the amount adsorbed at equilibrium (mg/g), maximum adsorption capacity (mg/g), Langmuir constant (L/mg) and the concentration of adsorbate at equilibrium (mg/L), respectively.

The linear form of the Langmuir isotherm can be represented by the following equation (Hameed and Rahman, 2008):

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

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter R_L as follows:

$$R_L = \frac{1}{1 + K_L \times C_0} \tag{4}$$

When C_0 is the highest initial solution concentration. The value of R_L indicates the type of isotherm to the reversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

2.3.2. Freundlich model

The Freundlich model assumes a heterogeneous surface with a non-uniform distribution of adsorption over the surface of adsorbent. The Freundlich model can be expressed by the equation (Freundlich, 1906; Kobya, 2003)

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

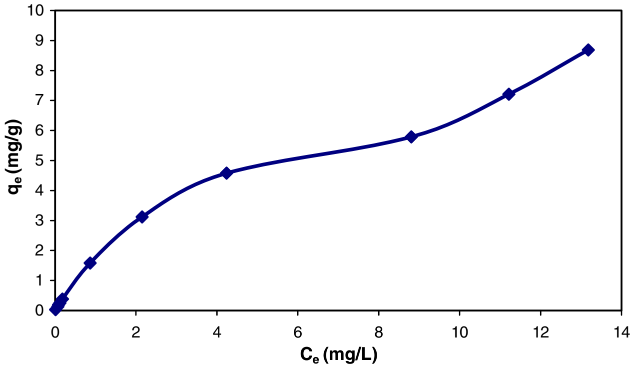

Figure 4 Adsorption isotherm of anthracene onto activated carbon.

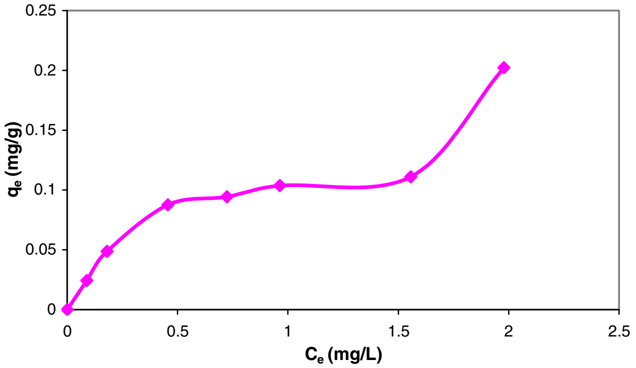

Figure 5 Adsorption isotherm of anthracene onto *Posidonia oceanica*.

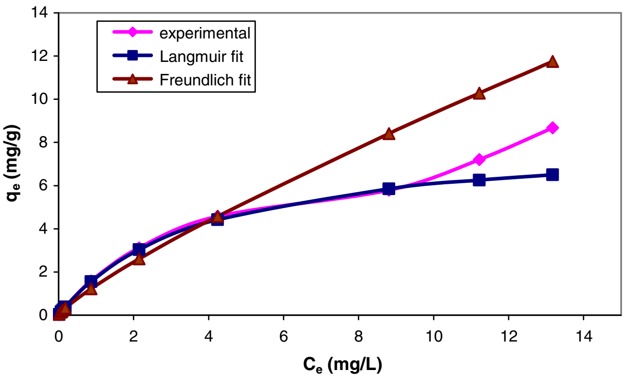

Figure 6 Langmuir and Freundlich isotherms fitted to experimental sorption of anthracene onto activated carbon.

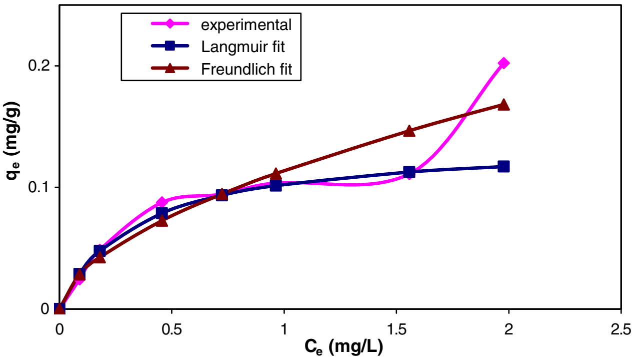

Figure 7 Langmuir and Freundlich isotherms fitted to experimental sorption of anthracene onto *Posidonia oceanica.*

Where K_F and n are Freundlich constant. K_F and n values can be determined from a linear plot of log q_e versus log C_e.

$$\log q_e = \log K_F + (1/n)\log C_e \tag{6}$$

3. Results and discussion

3.1. Effect of the initial pH

To study the influence of pH on the adsorption capacity of activated carbon and *P. oceanica* for anthracene, experiments were performed at room temperature and anthracene initial concentration of 4 mg/L using different initial solution pH values, varying from 2 to 12. The obtained results of anthracene removal at different pH solution values are shown in Fig. 2.

It is clear that anthracene was unaffected by varying pH of solution. A similar trend of pH effect was observed for the adsorption of anthracene on activated carbon and *P. oceanica*. Thus medium pH was used to study the adsorption isotherms.

3.2. Effect of contact time

The effect of the contact time on the removal of anthracene by activated carbon is shown in Fig. 3. It was observed that the adsorbed amount of anthracene increased with the increase of contact time. The removal of anthracene was rapid in the initial stage of the contact time and gradually decreased with lapse of time until equilibrium. The fast adsorption at initial stage may be due to the availability of uncovered surface area and the remaining active sites on the adsorbents. Optimum contact time was found to be 30 min. The equilibrium time considered for the further work has been taken as 30 min to ensure steady state.

3.3. Adsorption isotherms

The equilibrium of adsorption is one of the important physicochemical aspects for the evaluation of the adsorption process as a unit operation. The adsorption isotherm studies were conducted by varying the initial concentration of anthracene from 0.33 to 100 mg/L (Table 1) while the adsorbent mass in each sample was kept constant. Figs. 4 and 5 depict the adsorption isotherm (q_e versus C_e) and show that the adsorption capacity increased with increasing equilibrium of anthracene concentrations and eventually attained a constant value before remounting.

3.3.1. Modeling of isotherms

In order to obtain information on the properties and mechanism of the adsorption process, the experimental results of anthracene adsorption on activated carbon and *P. oceanica* are commonly fitted to the Langmuir and Freundlich model (Eq. (2), Eq. (5), Figs. 6 and 7). The calculated constants using linear forms (Eqs. ()()(3)–(5)), are given in Table 2 for the two materials. The value of R_L is found to be 0.036 and 0.077 for activated carbon and *P. oceanica,* respectively suggesting a favorable adsorption of anthracene on the used materials. Although correlation coefficients (R^2) (Table 2) of both equations (Eqs. (2) and (5)) are considerably well obtained with two adsorbents (activated carbon and *P. oceanica*). The Langmuir model exhibited a better fit to the adsorption data than the Freundlich model. K_F and n of the Freundlich isotherm constants showed the tendency of anthracene uptake from the adsorption medium with the high capacity of the activated carbon. All n values were greater than unity, indicating that anthracene adsorption was favorably adsorbed by the activated carbon and *P. oceanica.*

Figs. 6 and 7 confirmed that the suitable isotherm for our experimental equilibrium curves was the Langmuir one. Thus

Table 2 Isotherm constants for adsorption of anthracene onto *Posidonia oceanica* and activated carbon.

Sorbents	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
Posidonia oceanica	0.14	2.97	0.99	1.74	8.78	0.92
Activated carbon	8.35	0.26	0.99	1.20	1.37	0.98

we can notice that the better anthracene retention was achieved onto activated carbon.

The maximum capacity, $q_{\max}$, defines the total capacity of the anthracene adsorbent. The maximum equilibrium adsorption capacity values were determined as 8.35 mg/g and 0.14 mg/g for activated carbon and *P. oceanica*, respectively.

4. Conclusions

On the basis of the described results a number of conclusions can be proposed:

The adsorption of anthracene on activated carbon and *P. oceanica* was not influenced by the initial pH variation.

Adsorption equilibrium was reached within short period (30 min).

The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium data were best described by the Langmuir isotherm model.

Results showed that activated carbon can be effectively used as an adsorbent for the removal of anthracene. Adsorption capacity was 8.35 mg/g and 0.14 mg/g for activated carbon and *P. oceanica*, respectively.

Marine waste, *P. oceanica,* is a sustainable natural resource and eco-friendly material due to its large use as raw material for many applications such as waste water treatment. *P. oceanica* can be used as a precursor material for the preparation of activated carbon. The preparation of activated carbon from *P. oceanica* is an economically promising twofold. The endemic species in the Mediterranean Sea would be utilized and the production of activated carbon for the treatment of wastewaters would be achieved at low cost. The present study offers an alternative usage of *P. oceanica* accumulated on the beach in the industrial wastewater treatment.

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