Polycyclic aromatic hydrocarbons sorption on soils: Some anomalous isotherms

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Abstract

The sorption of four polycyclic aromatic hydrocarbons (PAHs), namely acenaphthene (Ac), phenanthrene (Ph), anthracene (An), and fluoranthene (Fl), on soil has been investigated. The kinetics of the sorption is characterised by the presence of two distinct periods. A fast initial stage followed by a second slower sorption process. Various kinetic models (i.e., Elvoich, Lagergren, second order and double exponential models) have been used to fit experimental data. The sorption equilibrium of individual PAHs has been assessed in the 298–333 K temperature range. Unlike Ac, Ph at 333 K and An and Fl at any temperature showed anomalous isotherms. The reason seems to rely on the "trapping" of dissolved PAHs by soil organic matter (SOM) released to water. This abnormal trend was not experienced when the isotherms were obtained for four PAHs mixture. Apparently, the most soluble Ac was capable of binding all the released material so no effect was thereafter observed.
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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a group of over 100 different chemicals that are formed during the incomplete burning of fuels, garbage or other organic substances such as tobacco, plant material or meats. PAHs can also be found in coal tar, bitumen, crude oil, creosote and roofing tar. The distribution of PAHs in the environment is extensive and the general public may be exposed to PAHs found in soil/dust, air, water, food or household products. 17 PAHs have been identified as being of greatest concern with regard to potential exposure and adverse health effects on humans [1].

Exposure to PAH-containing substances increases the risk of cancer in humans. The carcinogenicity of PAHs is associated with the complexity of the molecule (i.e., increasing number of benzenoid rings) and with metabolic activation to reactive diol epoxide intermediates and their subsequent covalent binding to critical targets in DNA [2].

The hydrophobicity of PAHs induces the fast sorption of these substances onto soil particulates, especially if solid organic matter (SOM) is included in the composition of the former. Accordingly, data on the equilibrium and dynamic behaviour of the sorption process is of fundamental importance in terms of correctly assessing the contamination of soils by these substances. In spite of the large number of studies focused on the sorption of PAHs onto soils, most of the investigations have been carried out under a unique set of experimental conditions. Thus, the influence of some important operating variables (pH, temperature, etc.) has not normally been assessed. Additionally, not many works have been dealing with equilibrium models, consequently, there is a clear lack of data on equilibrium modelling of PAHs adsorbed on soils. Pan et al. [3] have recently applied the Freundlich isotherm to the sorption of phenanthrene on soil. These authors have suggested the importance of the organic matter structure on sorption capacity, however, most of works just determine a partition coefficient with no further investigations on the nature and shape of the isotherms.

This study is intended to provide some insights into the sorption of four PAHs, namely acenaphthene (Ac), phenanthrene (Ph), anthracene (An) and fluoranthene (Fl) on soil, either individually or in a mixture of them. The influence of key variables like pH and temperature has been investigated. The possible effect of dissolved organic matter has been considered to explain some of the results obtained. Finally, different models have been

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Nomenclature

A_C	adjustable parameter in Caurie isotherm model
A_{OSW}	adjustable parameter in Oswin isotherm model
C	PAH concentration in water (mg L^{-1})
C_e	PAH concentration in water at equilibrium (mg L^{-1})
D_1	adjustable parameter in the double exponential kinetic equation
D_2	adjustable parameter in the double exponential kinetic equation
f_C	organic fraction of soil (g g^{-1})
k	kinetic constant in the second order kinetic equation (min^{-1})
k_1	kinetic constant in the double exponential kinetic equation (min^{-1})
k_2	kinetic constant in the double exponential kinetic equation (min^{-1})
K_C	adjustable parameter in Caurie isotherm model
K_D	distribution coefficient defined as the ratio Q_e (g g^{-1}) to C_e (mg L^{-1})
K_F	adjustable parameter in Freundlich equation
K_{OC}	carbon normalized distribution coefficient
K_{OSW}	adjustable parameter in Oswin isotherm model
K_{P1}	adjustable parameter in Peleg isotherm model
K_{P2}	adjustable parameter in Peleg isotherm model
m_{Ads}	soil concentration (g L^{-1})
n	adjustable parameter in Freundlich equation
n_1	adjustable parameter in Peleg isotherm model
n_2	adjustable parameter in Peleg isotherm model
pH$_{2.5}$	pH of a suspension soil:water with ratio 2.5:1 (w/w)
Q	PAH concentration in soil (μg g^{-1})
Q_e	PAH concentration in soil at equilibrium (μg g^{-1})
t	time (min)
t_o	adjustable parameter in Elovich equation
z_o	adjustable parameter in Lagergren equation

Greek symbols

α	adjustable parameter in Elovich equation
β	adjustable time constant parameter in Lagergren equation (min^{-1})
λ	adjustable parameter in Oswin isotherm model
$\chi_{2.5}$	conductivity of a suspension soil:water with ratio 2.5:1 (w/w) (μS cm^{-1})

applied to both the equilibrium and dynamics of the mixture sorption.

2. Experimental

2.1. Materials

The soil used in this study was taken from a location close to the town of Villafranca de los Barros (Badajoz, Southwest of Spain) where a refinery is tentatively to be constructed in the

Table 1
Particle size distribution of soil

Particle size distribution (radii in mm)	Percentage
>1.25	13.4
1.00 > r > 1.25	5
0.80 > r > 1.00	43.2
0.32 > r > 0.80	1.2
0.15 > r > 0.32	10
0.10 > r > 0.15	10.5
0.05 > r > 0.10	10.5
<0.05	6.2

near future. Thus, the sorption properties of the soil to potential PAHs spillage are therefore more realistically considered. Homogenization of soil was achieved by crushing and sieving of the previously dried soil (110 °C for three days). Particle size distribution is depicted in Table 1. This study was conducted by discarding the biggest fraction.

pH$_{2.5}$ and $\chi_{2.5}$ (i.e., pH and conductivity at a water:soil ratio of 1:2.5, w/w) were determined using a Radiometer Copenhagen pH-meter and a Crison 524 conductivity meter. These values were 7.9 and 253 μS cm^{-1}, respectively.

The organic matter content was determined by two different methods. First, the weight loss due to combustion at 510 °C was evaluated in the presence of air. After 24 h of heating the weight loss was 5.53%. However, although this technique is commonly used to determine the organic fraction in solids, other processes different to organic matter combustion might proceed (i.e., carbonate decomposition). Consequently, the oxidizable organic carbon was also monitored by oxidation in the presence of dichromate and sulphuric acid and further titration with ferrous iron [4]. With this method the percentage of oxidizable organic matter was 4.58%, quite close to the value given by the combustion method. The concentration of humic (HA) and fulvic (FA) acids in the soil was determined by digestion with NaOH. Thus, 5 g of soil were soxhlet extracted with a NaOH (0.1 M) solution for one hour, the supernatant containing the HA and FA extracts were analysed for total organic carbon (TOC) content by using a Shimazdu TOC-V/SSM analyser. Acidification of the sample with HCl to pH 1.5 led to the precipitation of HA. Accordingly the percentages of FA and HA in soil were 1.28 and 0.53%, respectively, the rest of organic matter apart of HA and FA is considered to be humin and/or black carbon.

Acenaphthene, phenanthrene, anthracene and fluoranthene (Sigma–Aldrich) were used as received. Saturated solutions were obtained by vigorous stirring of an excess of PAHs in MilliQ ultrapure water in the dark. After three days the non-dissolved fraction of PAHs was removed from solution by consecutive filtrations on Schleicher & Schuell 589^3, 2° filtration paper and 0.47 mm diameter Millipore membranes (MF Millipore 0.45 μm). If required, the pH of the solution was modified by addition of perchloric acid or a sodium hydroxide solution.

2.2. Sorption experiments

The sorption of PAHs from aqueous solution onto soil was performed using the batch equilibrium technique. All the lab

glassware was firstly saturated with the PAHs solution for one day and rinsed thereafter with pure water. As a consequence, sorption of PAHs onto walls is minimized to some extent. In any case, blank runs were always conducted.

For kinetic experiments a 2.5 L jacketed glass reactor was used. Initial aqueous concentrations of PAHs were within the following ranges: Ac = 0.89–2.8 ppm; Ph = 0.16–0.65 ppm; An = 4.4–21 ppb; Fl = 38–71 ppb. The suspension was continuously stirred at a constant temperature (298 K) to reach equilibrium in most of cases. At various time intervals, samples were taken and PAH concentration was analysed after filtration. The amount of PAH adsorbed at any time was calculated from the mass balance between the liquid and the solid.

For the determination of sorption isotherms, a solution of single PAHs or a mixture of them was contacted with varying amounts of soil in 25 mL closed vials. The system was kept at constant temperature (298–333 K) and shaken for a time enough to achieve equilibrium conditions (one week). Simultaneously to isotherm determinations, vials containing the PAHs solution in the absence of soil were also placed in the shaker to account for potential losses due to photolysis, hydrolysis, volatilization, wall adsorption, etc. Direct comparison of blank runs and vials containing the soil allowed for the calculation of the amount of PAH adsorbed. Unlike kinetic experiments, isotherm curves were obtained by triplicate.

2.3. Analysis

Aqueous PAHs were analysed by injecting 25 μL of a sample previously centrifuged (Eppendorf microcentrifuge set at 12600 rpm) into a HPLC system (Rheodyne injector, 1050 Hewlett Packard pump, 1046A, Alltech Prevail C18 column (4.6 mm × 150 mm), Hewlett Packard fluorescence detector, Chromjet Spectra Physics integrator) in isocratic mode using an acetonitrile–water mixture 70:30 (v/v) as mobile phase.

3. Results and discussion

3.1. Kinetic experiments

Before studying the equilibrium of PAHs sorption on the soil, some preliminary kinetic experiments were carried out to ascertain the minimum time required to achieve steady state conditions, i.e., equilibrium conditions. These experiments were conducted by using a mixture of the four PAHs in the presence of different amounts of soil. Fig. 1 illustrates the evolution profiles of the adsorbed PAHs concentration versus time for dynamic sorption experiments carried out at 298 K and with no modification of solution pH. As observed from this figure, PAH uptake values (in terms of total amount of PAH removed from liquid) at steady state conditions follow the order Ac > Ph > Fl > An, i.e., the same order as the solubility
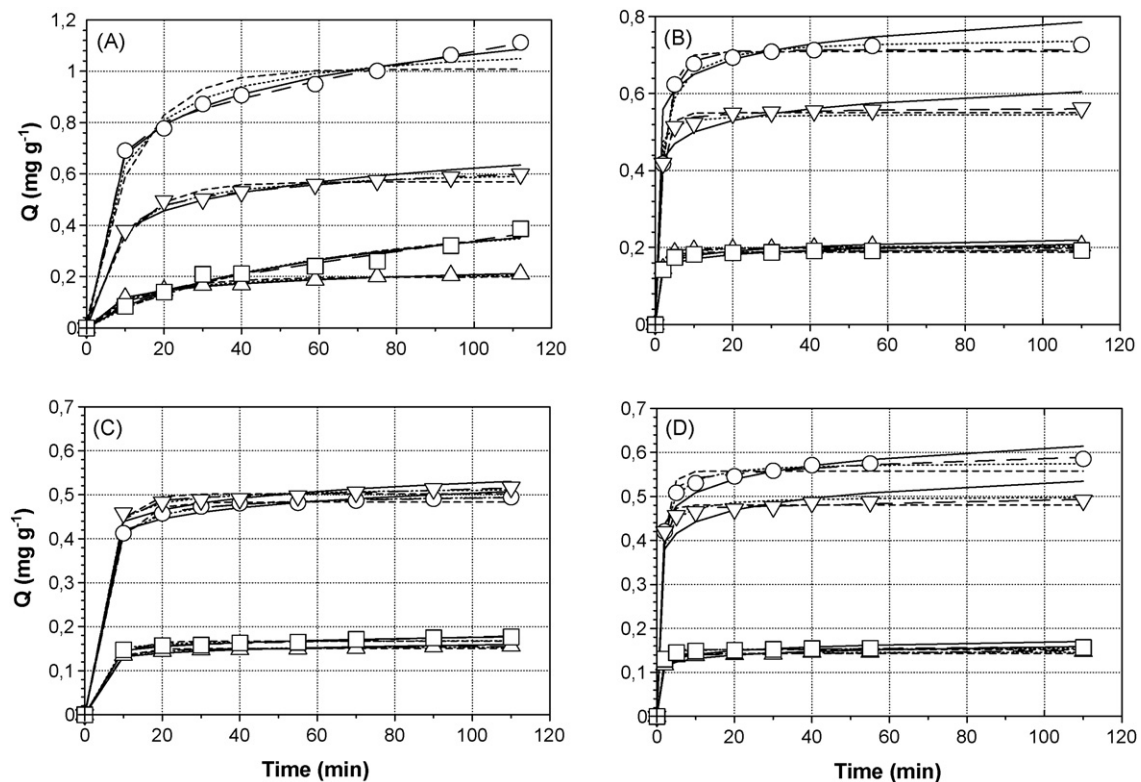

Fig. 1. Dynamic sorption of PAHs on soil. Experimental conditions: $T = 298$ K, pH 6.0. Initial PAHs concentration in ppm: (A) soil = 0.5 g L^{-1}, $C_{Aco} = 0.89$, $C_{Pho} = 0.16$, $C_{Ano} = 4.4 \times 10^{-3}$, $C_{Flo} = 3.8 \times 10^{-2}$. (B) Soil = 2.0 g L^{-1}, $C_{Aco} = 2.2$, $C_{Pho} = 0.52$, $C_{Ano} = 1.3 \times 10^{-2}$, $C_{Flo} = 4.5 \times 10^{-2}$. (C) Soil = 3.0 g L^{-1}, $C_{Aco} = 2.2$, $C_{Pho} = 0.56$, $C_{Ano} = 1.8 \times 10^{-2}$, $C_{Flo} = 6.3 \times 10^{-2}$. (D) Soil = 4.0 g L^{-1}, $C_{Aco} = 2.8$, $C_{Pho} = 0.65$, $C_{Ano} = 2.1 \times 10^{-2}$, $C_{Flo} = 7.1 \times 10^{-2}$. Symbols: (◯) acenaphthene; (△) phenanthrene; (▽) anthracene ($Q \times 100$); (□) fluoranthene ($Q \times 10$). Solid line: Elovich equation; dashed line: modified Lagergren equation; dotted line: second order kinetics; long dashed line: double exponential model.

in water: acenaphthene = 4.46 ppm, phenanthrene = 1.28 ppm, fluoranthene = 0.26 ppm and anthracene = 0.065 ppm [5]. The previous observation means that the increasing solubility of PAHs allows for a higher amount of sorbate to be available for sorption, i.e., a higher driving force. Likely, if the isotherms had been obtained with the same initial concentration of the four PAHs, the results would have been different (see the partition coefficient determination in the adsorption of the PAH mixture). Hence, the capacity of PAH to be accumulated in the soil does depend on parameters like K_{OW} or K_{OC} while the amount of PAH adsorbed/absorbed is highly related to the driving force present in the process.

Also as observed from Fig. 1, there is an initial fast period of sorption where the PAHs uptake is almost complete followed by a second slow stage in which the uptake steadily increases up to equilibrium conditions. The first stage could represent the sorption of PAHs onto more accessible sites within the soil matrix. Accordingly, this stage becomes faster as the soil concentration is increased from 0.5 (Fig. 1A) to 4.0 g L^{-1} (Fig. 1D), thus providing a higher number of sites for easy binding. Note that, for comparison purposes, the graph corresponding to 3.0 g L^{-1} (Fig. 1C) should be discarded as the first sample was taken too late in time (see for instance Fig. 1B with a lower soil concentration).

Thereafter, with the exception of the experiment carried out with the lowest soil concentration, equilibrium conditions are achieved. The values of PAH concentration in soil at equilibrium (Q_e) are higher for the experiment carried out with 0.5 g L^{-1} of soil (Fig. 1A), for the rest of experiments, at steady state conditions, the values of Q_e are quite similar regardless of the soil concentration (a slight decrease of Q_e is obtained as soil concentration is increased).

The kinetics of the sorption was modelled by using several simplistic mathematical expressions, as follows:

Elovich equation : $Q = \alpha \log(t + t_o) - \alpha \log(t_o)$ (1)

Lagergren modified equation : $Q = Q_e[1 - \exp(-\beta(t + z_o))]$ (2)

Second order kinetics : $Q = \dfrac{Q_e^2 kt}{1 + Q_e kt}$ (3)

Double exponential model :

$$Q = Q_e - \frac{D_1}{m_{Ads}} \exp(-k_1 t) - \frac{D_2}{m_{Ads}} \exp(-k_2 t)$$ (4)

where Q and Q_e, stand for the PAH concentration at any time and at equilibrium in soil, respectively, t is time and m_{Ads} is the soil concentration. The rest of symbols are adjustable parameters for each model [6,7]. By minimization of the squared errors (Error^2 = $(Q_{e(exp)} - Q_{e(model)})^2$) the fitted parameters obtained are shown in Table 2. The appropriateness of each model was assessed by calculating the percentage of error (Error% = 100/NP × ABS[$(Q_{e(exp)} - Q_{e(model)})/Q_{e(exp)}$]). As a rule of thumb, the double exponential method shows the lowest Error% values.

Obviously, the optimized parameters are dependent on the initial guess (i.e., they can derive from an absolute or relative minimum of the function) and consequently they have to be taken with caution. In any case a rough linear correlation is found for some parameters. For instance, with the exception of the run conducted with 0.5 g L^{-1} of soil (Fig. 1A), the parameter α seems to remain constant regardless of the soil concentration used.

Q_e values derived form the Lagergren model and second order kinetics indicates a slight decrease of this parameter as soil concentration is increased. However, given the high number of parameters to be fitted, Q_e from the double exponential model did not follow a clear trend.

The parameters representative of the PAH sorption rate, like β or k, clearly indicates an increase of sorption velocity as the soil concentration is increased. Data obtained in the experiment carried out with 3 g L^{-1} of soil were discarded because the first sample was taken too late in time.

3.2. Equilibrium experiments

Once the equilibrium time was assessed, the equilibrium isotherms of the system PAH–soil were obtained by carrying out experiments in two ways: sorption of single PAH and sorption in a mixture of four PAHs.

3.2.1. Equilibrium sorption of single PAHs

Fig. 2 illustrates the equilibrium sorption curves for single PAHs obtained at three different temperatures. Acenaphthene isotherms show a typical L$_3$ or S$_1$ type profiles of Giles classification [8]. Thus, at 298 and 313 K there is an initial sorption stage (up to C_{eq} = 0.6–0.8 ppm) where the sorption follows a sorption favourable shape (concave shape), thereafter a sharp increase in Q_e is experienced for increasing values of C_{eq} (type L$_3$), this is typical of finely divided non-porous materials, as it is the case [9]. When temperature is raised to 333 K, the first step disappears and a typical type S isotherm (non-favourable) is obtained. Phenanthrene isotherms at 298 and 313 K also are of S type. This behaviour has previously been reported for similar systems as for instance the sorption of fluorene onto titania particles [10]. Regarding the temperature influence, from Fig. 2 it is inferred a positive effect of this parameter on the acenaphthene uptake for temperatures above 313 K. In any case, as commented next, this parameter involves the development of parallel processes which make difficult the correct interpretation of temperature influence.

The sorption isotherms corresponding to phenanthrene show an anomalous behaviour. When temperature is varied from 298 to 313 K the sorption capacity of soils diminishes, which is a typical trend in sorption processes, however, a further increase of temperature to 333 K leads to an isotherm showing negative slopes, i.e., the lower the PAH concentration in soil the higher the phenanthrene aqueous equilibrium concentration.

Sorption of Ph at 333 K and An and Fl at any temperature leads to anomalous isotherms since PAH uptake on soil decreases dramatically as the aqueous equilibrium concentration increases from a critical value. The reason for this anomalous

Table 2
Optimization of parameters in the modelling of PAHs sorption kinetics

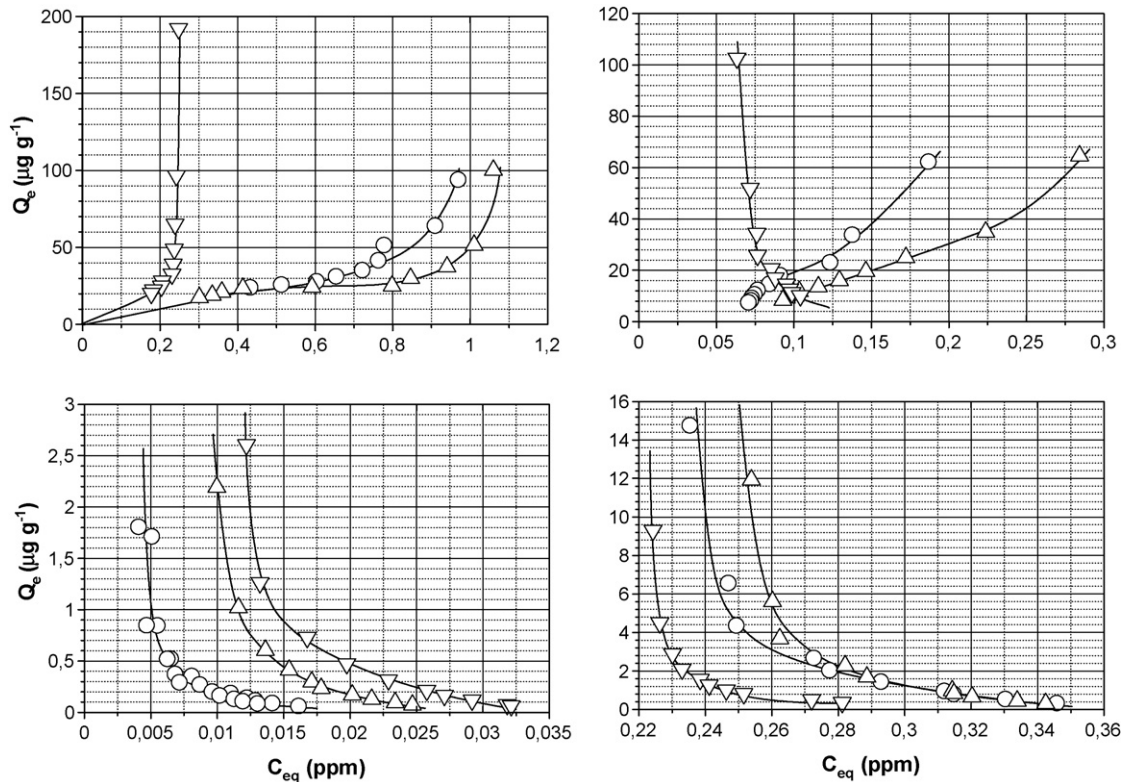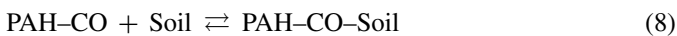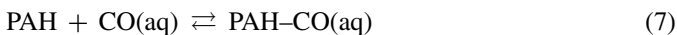|	Acenaphthene				Phenanthrene				Anthracene				Fluoranthene			
	$0.5\,\mathrm{g\,L^{-1a}}$	$2.0\,\mathrm{g\,L^{-1a}}$	$3.0\,\mathrm{g\,L^{-1a}}$	$4.0\,\mathrm{g\,L^{-1a}}$	$0.5\,\mathrm{g\,L^{-1a}}$	$2.0\,\mathrm{g\,L^{-1a}}$	$3.0\,\mathrm{g\,L^{-1a}}$	$4.0\,\mathrm{g\,L^{-1a}}$	$0.5\,\mathrm{g\,L^{-1a}}$	$2.0\,\mathrm{g\,L^{-1a}}$	$3.0\,\mathrm{g\,L^{-1a}}$	$4.0\,\mathrm{g\,L^{-1}}$	$0.5\,\mathrm{g\,L^{-1a}}$	$2.0\,\mathrm{g\,L^{-1a}}$	$3.0\,\mathrm{g\,L^{-1a}}$	$4.0\,\mathrm{g\,L^{-1a}}$
Elovich																
α	0.394	0.130	0.0839	0.102	0.090	3.8×10^{-2}	2.6×10^{-2}	2.6×10^{-2}	2.3×10^{-3}	1.1×10^{-3}	8.8×10^{-4}	8.8×10^{-4}	3.8×10^{-2}	3.6×10^{-3}	2.9×10^{-3}	2.8×10^{-3}
t_o	0.197	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	0.503	2.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	0.2535	2.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}	15.246	2.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
Error^2	2.3×10^{-2}	2.5×10^{-2}	7.5×10^{-4}	2.7×10^{-3}	7.4×10^{-5}	8.4×10^{-4}	6.9×10^{-5}	3.6×10^{-4}	4.1×10^{-7}	5.9×10^{-7}	1.1×10^{-7}	6.2×10^{-7}	3.7×10^{-5}	6.8×10^{-6}	2.1×10^{-7}	5.6×10^{-6}
Error%	1.5	5.1	1.6	2.5	1.3	4.0	1.7	3.6	3.5	4.3	1.9	4.6	5.6	3.6	1.1	4.4
Lagergren																
Q_e	1.008	0.709	0.483	0.558	0.199	0.198	0.151	0.143	5.6×10^{-3}	5.5×10^{-3}	5.0×10^{-3}	4.8×10^{-3}	4.1×10^{-2}	1.9×10^{-2}	1.7×10^{-2}	1.5×10^{-2}
z_o	0.317	6.2×10^{-3}	4.7×10^{-3}	4.7×10^{-3}	0.367	2.1×10^{-3}	1.9×10^{-3}	1.0×10^{-3}	0.368	2.1×10^{-3}	1.9×10^{-3}	9.9×10^{-4}	2.913	2.9×10^{-3}	1.5×10^{-3}	4.9×10^{-3}
β	8.5×10^{-2}	0.432	0.185	0.662	6.8×10^{-2}	0.641	0.221	0.843	9.6×10^{-2}	0.641	0.221	0.843	1.6×10^{-2}	0.683	0.201	0.956
Error^2	3.8×10^{-2}	1.4×10^{-3}	4.9×10^{-4}	3.0×10^{-3}	8.5×10^{-4}	1.3×10^{-4}	8.2×10^{-5}	9.9×10^{-5}	4.2×10^{-7}	1.6×10^{-7}	9.7×10^{-8}	1.6×10^{-7}	5.2×10^{-5}	1.4×10^{-6}	3.2×10^{-6}	8.2×10^{-7}
Error%	6.6	1.5	1.4	3.2	5.1	1.8	1.8	2.3	3.8	2.1	2.1	2.7	8.1	1.8	3.1	2.0
Second order																
Q_e	1.121	0.745	0.491	0.578	0.224	0.205	0.156	0.146	6.2×10^{-3}	5.5×10^{-3}	5.2×10^{-3}	0.005	5.3×10^{-2}	0.0193	0.017	1.5×10^{-2}
k	0.116	1.01	1.601	2.284	0.432	6.528	4.071	13.97	25.34	600	126	350	0.320	100	50	200
Error^2	0.012	2.7×10^{-3}	4.1×10^{-5}	4.1×10^{-4}	1.7×10^{-4}	1.2×10^{-4}	1.5×10^{-5}	2.4×10^{-5}	7.9×10^{-8}	3.9×10^{-7}	2.7×10^{-8}	1.7×10^{-7}	4.5×10^{-5}	1.2×10^{-6}	2.1×10^{-6}	2.0×10^{-7}
Error%	3.7	2.2	1.4	1.0	2.1	1.6	0.7	1.0	1.3	2.6	0.9	2.4	7.4	1.2	2.5	2.7
Double exponential																
Q_e	1.441	0.713	0.494	0.604	0.224	0.202	0.394	0.3367	6.2×10^{-3}	5.6×10^{-3}	0.114	0.084	0.170	1.9×10^{-2}	0.29	0.015
D_1	0.359	0.132	3.0×10^{-2}	0.264	0.0598	6.8×10^{-3}	0.125	6.9×10^{-2}	2.1×10^{-3}	1.5×10^{-4}	5.5×10^{-2}	1.7×10^{-3}	5.9×10^{-3}	6.2×10^{-4}	0.138	2.8×10^{-3}
k_1	0.219	0.229	3.2×10^{-2}	0.672	0.176	4.7×10^{-2}	3.9×10^{-4}	0.924	0.176	4.2×10^{-2}	3.3×10^{-5}	0.98	9.3×10^{-2}	2.7×10^{-2}	8.8×10^{-5}	0.724
D_2	0.361	0.226	0.217	3.5×10^{-2}	5.2×10^{-2}	9.2×10^{-2}	7.2×10^{-2}	9.8×10^{-2}	9.6×10^{-4}	2.6×10^{-3}	2.0×10^{-3}	0.039	7.9×10^{-2}	9.0×10^{-3}	8.6×10^{-3}	6.8×10^{-4}
k_2	6.9×10^{-3}	0.647	0.241	1.4×10^{-2}	1.8×10^{-2}	0.691	0.235	5.3×10^{-4}	1.8×10^{-2}	0.690	0.286	2.7×10^{-5}	1.5×10^{-3}	0.698	0.309	8.2×10^{-2}
Error^2	1.5×10^{-3}	8.6×10^{-4}	2.4×10^{-5}	9.2×10^{-4}	4.9×10^{-5}	4.1×10^{-5}	1.3×10^{-5}	2.6×10^{-5}	4.9×10^{-8}	6.9×10^{-8}	3.3×10^{-8}	7.7×10^{-8}	2.4×10^{-5}	4.2×10^{-7}	1.4×10^{-7}	3.8×10^{-7}
Error%	1.2	1.3	0.3	1.7	1.1	0.9	0.9	1.7	1.4	1.1	0.2	0.9	8.0	1.4	0.6	0.5

[a] m_{Ads}.

Fig. 2. Equilibrium isotherms for the sorption of PAHs on soil (pH 6.0). Symbols: (◯) 298 K; (△) 313 K; (▽) 333 K. (Acenaphthene: up-left; phenanthrene: up-right; anthracene: down-left; fluoranthene: down-right.)

tendency seems to rely on the presence of organic chelating agents in the soil used capable of being released to the aqueous matrix. The sorption of contaminants onto soils might involve several phases, leading to the progress of distinct simultaneous processes. Thus, the following reaction scheme might take place:

$$PAH(aq) + Soil \rightleftarrows PAH–Soil \tag{5}$$

$$Soil–CO \rightleftarrows CO(aq) + Soil \tag{6}$$

$$PAH + CO(aq) \rightleftarrows PAH–CO(aq) \tag{7}$$

$$PAH–CO + Soil \rightleftarrows PAH–CO–Soil \tag{8}$$

In the above mechanism, CO stands for the organic material associated to soils capable of complexing the aromatic hydrocarbon [11]. Equilibrium (6) is hypothesised to be very sensitive to temperature. An increase in temperature shifts the equilibrium to the release of complexing agents (CO) from soil to water.

Thus, in the case of phenanthrene sorption at 313 K, formation of the complex PAH–CO is higher than at 298 K and, consequently, the isotherm curve indicates a lower sorption extent at 313 K than at 298 K.

Raising the temperature to 333 K involves a drastic influence of aqueous CO. Hence, at 333 K the amount of CO released and the subsequent formation of the complex PAH–CO predominates over the sorption of Ph onto soils. As a consequence, an increase of the amount of soil involves a higher fraction of PAH retained in solution in the form PAH–CO. From the results obtained it is suggested that equilibrium (8) does not exist or is displaced to the left.

The possible variation in PAHs fluorescence due to the formation of the complex PAH–CO was assessed by completing two parallel determinations. On one hand a solution of PAHs was made by using pure water, on the other hand, water previously shaken with soil and filtered was used to prepare a second PAHs solution. PAHs analysis in both solutions revealed no loss of fluorescence when the results were compared. Likely dilution of samples with the mobile phase used in the HPLC analysis could displace the equilibrium (7) to the left or, alternatively, the complex PAH–CO shows a similar fluorescence to the isolated polycyclic aromatic hydrocarbons. The presence of released CO in water was confirmed after scanning the UV/vis spectra of water vigorously shaken with soil and further comparison with pure water (Fig. 3). Also TOC analysis of the previous water corroborated the leaching of organic material to the water bulk (i.e., TOC = 19 ppm after 12 h stirring of 100 mL of pure water containing 2 g of soil).

Given the lower solubility of anthracene and fluoranthene if compared to acenaphthene or phenanthrene, the effect of dissolved CO was more pronounced for the former PAHs. Thus, released CO was capable of partially complex An and Fl (i.e., anomalous isotherms) to a considerable extent regardless of the temperature.

Amazingly, CO did not lead to obtaining anomalous isotherms in the case of acenaphthene. The reason seems to rely on the relatively high solubility of this PAH. Thus, a small part of the dissolved acenaphthene would eventually complex all the released CO so the ratio Acenaphthene–CO to "free" acenaphthene would be sufficiently low to be neglected.
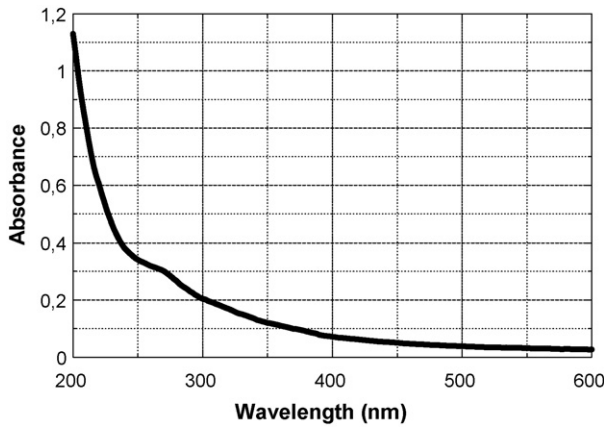
Fig. 3. Absorbance of water after vigorous stirring with soil and further filtration.

3.2.2. Equilibrium sorption of PAH mixtures

Given the apparent different effects that CO causes on single PAHs sorption, it was decided to investigate the sorption of PAH mixtures and the influence of different operating parameters.

Fig. 4 illustrates the isotherm profiles of acenaphthene, phenanthrene, anthracene and fluoranthene obtained from their mixtures at different temperatures. As observed, some important differences were experienced if compared these results and those obtained with individual PAHs. Thus, the most relevant difference is the absence of anomalous isotherms in the case of phenanthrene (at 333 K), fluoranthene or anthracene.

The reason of the above findings seems to be the much higher solubility of acenaphthene if compared to the rest of PAHs. Thus,

similarly to the sorption of acenaphthene individually, a small fraction of this PAH would be sufficient to trap the dissolved CO, so no effect of the latter could be envisaged in the sorption of the rest of less soluble PAHs.

At observed from Fig. 4, the sorption of acenaphthene either in the mixture of 4 PAHs or as a single solute is similar. Small differences in the curves are obtained at temperatures of 298 and 313 K while a sharp increase in sorption capacity at 333 K is experienced. An analogous analysis can be adopted in the case of phenanthrene. Contrarily, the sorption capacity of the soil to remove anthracene and fluoranthene from the water matrix seems to be less dependent on temperature.

The isotherms depicted in Fig. 4 were modelled by considering the peculiar shape of the curves. The following expressions were used [12]

$$\text{Freundlich:} \quad Q_i = K_F C_i^n \tag{9}$$

$$\text{Oswin:} \quad Q_i = K_{OSW} \left[\frac{A_{OSW} C_i}{1 - A_{OSW} C_i} \right]^\lambda \tag{10}$$

$$\text{Peleg:} \quad Q_i = K_{P1} C_i^{n1} + K_{P2} C_i^{n2} \tag{11}$$

$$\text{Caurie:} \quad Q_i = \exp(A_C + K_C C_i) \tag{12}$$

In the above equations Q_i and C_i stand for the ith-PAH concentration in the soil and water, respectively. The rest of symbols are adjustable parameters in each model.

Table 3 shows the optimized parameters found at different temperatures as well as Error^2 and Error%.
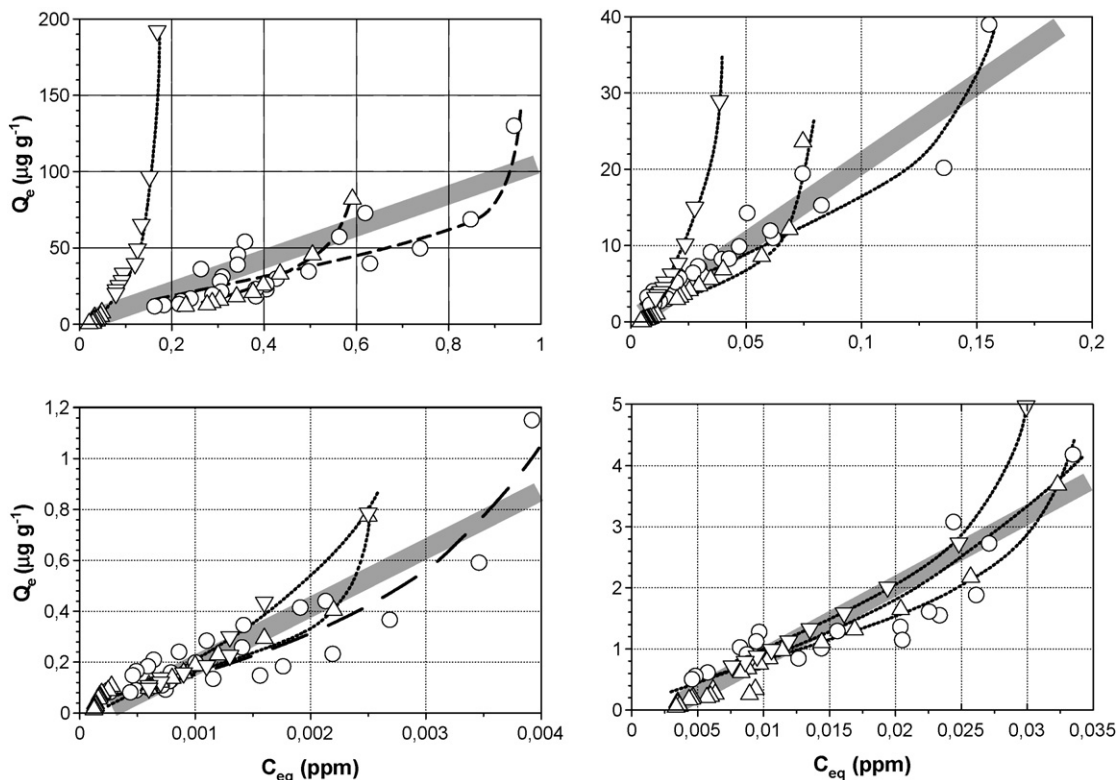

Fig. 4. Equilibrium sorption of PAH mixtures on soil (pH 6.0). Symbols: (○) 298 K; (△) 313 K; (▽) 333 K. (Acenaphthene: up-left; phenanthrene: up-right; anthracene: down-left; fluoranthene: down-right.) Dashed line: Peleg equation; dotted line: Oswing equation; long dashed line: Caurie equation.

Table 3
Optimization of parameters in the modelling of PAHs sorption equilibrium

	Acenaphthene			Phenanthrene			Anthracene			Fluoranthene		
	298 K	313 K	333 K	298 K	313 K	333 K	298 K	313 K	333 K	298 K	313 K	333 K
K_F	107.1	316.5	2.05×10^5	183.4	1383.3	2.05×10^5	713.3	1383.37	2.05×10^5	216.2	543.6	1250
n	1.28	2.66	3.96	0.94	1.66	2.69	1.21	1.28	2.06	1.23	1.47	1.60
$Error^2$	4463	260.2	1572.1	165.2	56.8	51.6	0.30	0.059	0.039	3.93	0.50	0.78
$Error\%$	26.3	61.8	32.7	17.1	33.9	39.2	35.9	32.1	31.4	19.4	32.9	14.8
K_{OSW}	37.0	19.7	27.8	15.06	4.82	32.0	17.9	0.21	36.7	1.49	7.98	1.63
A_{OSW}	1.01	1.47	5.4	5.62	12.5	12.5	17.9	376.4	27.4	26.6	10.4	29.0
λ	0.41	0.76	0.82	0.47	0.59	1.27	1.17	0.47	1.47	0.49	1.19	0.59
$Error^2$	3091.6	65.6	89.0	129.4	23.7	1.42	0.29	0.01	0.008	2.22	0.46	0.045
$Error\%$	31.5	35.6	5.9	20.1	269	3.8	35.6	38.9	11.7	11.3	43.1	4.4
K_{P1}	495.8	30.5	1.9×10^5	495.8	1453	192718	495.8	1453	192718	108.2	541.9	1227
n_1	36.4	0.70	3.9	36.4	2.60	2.67	36.4	1.62	2.05	1.22	1.47	1.60
K_{P2}	78.9	788.9	1.9×10^5	183.4	1140.2	192718	713.4	1140	192718	108.26	1224	1227
n_2	0.94	4.88	7.35	0.94	1.62	7.4	1.21	1.27	7.41	1.22	10883	3.55
$Error^2$	2718.9	45.1	1569.8	165.2	55.9	49.7	0.30	0.058	0.0386	3.93	0.50	0.78
$Error\%$	27.4	48.1	32.5	17	35.4	38.5	35.9	32.9	31	19.4	33.1	14.6
A_C	2.47	0.88	0.41	1.49	−0.18	0.55	−2.42	−3.1	−2.61	−0.89	−1.41	−0.94
K_C	2.38	5.94	28.47	13.49	43.17	73.4	622.9	1092	956.8	67.94	85.16	83.9
$Error^2$	3814.8	67.6	731.2	208.9	52.4	4.56	0.18	0.042	0.0151	2.34	1.14	0.21
$Error\%$	30.3	62.0	21.1	31.4	282	8.3	30.0	45.9	14.4	11.8	99.6	4.8

As seen in Table 3, the general trend is that Oswing model produces the lowest errors. However, model parameter correlations with temperature are more evident for the Freundlich and Caurie models.

Additionally, from Fig. 4, if experiments for acenaphthene and phenanthrene conducted at 333 K are ruled out, it is inferred a certain linear trend of the sorption isotherms. The linear trend is especially plausible if neglecting the points with the highest C_{eq} values (likely these points present the highest analytical errors). Taking into account this linearity, the apparent equilibrium partitioning of PAHs between soil and water (K_D) can be easily calculated from the slopes. These slopes were $K_D = 108, 200, 200$ and 94 (μg PAH g^{-1} soil/mg PAH L^{-1} water) for acenaphthene, phenanthrene, anthracene and fluoranthene, respectively. Some correlations relating the partitioning of PAHs between soil and water and certain physical chemical properties have been previously reported [13,14]. To assess if some of these relationships applies in this study, the carbon-normalized distribution coefficient K_{OC} value was computed as:

$$K_{OC} = \frac{K_D}{f_C} \qquad (13)$$

where f_C is the organic fraction of the soil. Walter et al. [13] proposed the following correlation:

$$\log K_{OC} = 0.62 \log K_{OW} + 0.70 \qquad (14)$$

Calculations derived from this study showed that expression (14) did correlate acceptably the K_{OC} and K_{OW} values for the PAHs studied but fluoranthene. Thus, the equation ($\log K_{OC} - 0.7$)/$\log K_{OW}$ led to values of 0.654, 0.631 and 0.635 for acenaphthene, phenanthrene and anthracene. In the case of fluoranthene, the previous expression gave a value of 0.49, far

away from the slope of 0.62. K_{OW} values were taken from Cai et al. [15].

Given the particular behaviour of fluoranthene, with just three remaining PAHs, suggesting additional correlations is rather audacious. In any case, given the literature values reported, a priori, other potential relationship can be proposed for the pairs K_{OC}–molecular surface, K_{OC}–F number (F = number of double bonds + number of primary and secondary carbons − 0.5 × number of non-aromatic rings) or K_{OC}–L/B number (L/B represents the ratio of maximized length to breadth of the rectangle enclosing the PAH molecule).

Finally, once the influence of the temperature has been analysed, another important operating variable like the sorption pH was investigated. The results obtained for the equilibrium isotherms of PAHs carried out at initial pHs of 3, 6 and 9.
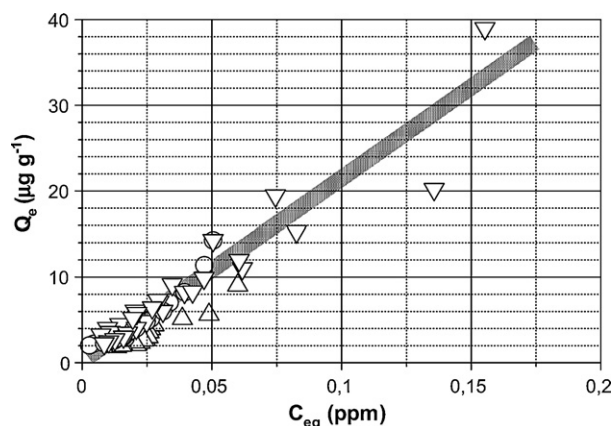

Fig. 5. Equilibrium sorption of PAH mixtures on soil (phenanthrene). $T = 298$ K. Symbols: (△) pH 3; (▽) pH 6; (○) pH 9.

No appreciable effect of pH was experienced in the sorption isotherms of the PAHs studied. The latter results are the consequence of the low tendency of PAHs to be ionized or protonated and the low influence of pH on the surface properties of the soil studied. As an example Fig. 5 shows the phenanthrene isotherms obtained at different pH.

4. Conclusions

The following conclusions can be derived from this work:

- The kinetic experiments of the PAHs sorption onto soil show that the process is quite fast (almost complete in just 10–20 min). The hydrophobic nature of PAHs involves a rapid transference of PAH from the aqueous phase to the SOM.
- When mixing the soil and pure water, a fraction of SOM lixiviates to the water bulk. The main consequence is the trapping of dissolved PAHs by the released organic species which induces the appearance of anomalous isotherms for individual PAHs (case of phenanthrene at 333 K and anthracene and fluoranthene).
- If isotherms are conducted by mixing of the four PAHs used in this work, the anomalous trend disappears. It seems that acenaphthene (the most soluble PAH) is capable of immediately removing the lixiviated organic material so no effect is experienced thereafter.

Acknowledgements

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