

Study of Pyrene Adsorption on Brazilian Soils

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Most studies that involve the adsorption of polycyclic aromatic hydrocarbons (PAHs) in soils are made in regions of temperate or cold climate. Since in tropical countries the characteristics of the pedological processes and the resultant soils are quite different, there is a lack of such studies with Brazilian soils. In this work, the adsorption of pyrene was studied in five representative Brazilian soils: Argissolo, Latossolo Vermelho Acriférico, Latossolo Vermelho Amarelo, Neossolo Quartzarênico and Vertissolo. In this work, Langmuir's isotherms were found to Argissolo and Latossolo Vermelho Amarelo, Langmuir-Freundlich isotherms to Neossolo Quartzarênico and linear isotherms to Vertissolo. We observed that the presence of the swelling clays may contribute to the increase of the amount of Pyrene adsorbed on the soil (Q), such as happened in the Vertissolo.

Keywords: pyrene, Brazilian soils, adsorption isotherms

Polycyclic aromatic hydrocarbons (PAHs) in soils and sediments are considered to be persistent and to possess low mobility [1]. Due to their known toxic, mutagenic and carcinogenic effects [2], remediation of PAH-contaminated soils and sediments is an important environmental issue [3]. Adsorption is known to be one of the main processes that determines their availability and fate in soils [4]. Accurate information on adsorption characteristics in terms of equilibrium partition and mass transfer rates are therefore important when predicting the availability of contaminants for uptake, degradation and mobility [5]. The adsorption of hydrophobic organic contaminants (HOCs), like PAHs, in a soil-water system is believed to be ruled by a mechanism where these non-ionic organic carbon (NOC) molecules distribute into the soil organic matter (SOM) phase [6, 7]. It has been generally accepted that the NOC adsorption increases with increasing SOM content. Soils with high organic matter content serve as a huge sink of these compounds, and effectively limit NOC availability in environment [8, 9]. In addition, adsorption is known to be dependent on the characteristics of SOM. For different soils, carbon-normalized distribution coefficients (K_{oc}) of a NOC may range over an order of magnitude. These facts can be attributed to differences in the composition in SOM, such as polarity and aromaticity [10, 11, 12].

Thus, in the present study, we seek to determine the effects of different soil components on adsorption of pyrene on several soils and the distribution coefficient of pyrene on the soil, i.e. the fraction that stayed in the soil.

Pyrene was selected as model hydrophobic non ionic PAH because it exhibits a high hydrophobicity (and consequently it has a high tendency to accumulate on SOM), it is a compound of environmental concern, and it has been frequently used as model contaminant in transport and environmental fate studies [13].

Experimental part

Pyrene (99%) was purchased from Aldrich. Their stock solutions were prepared using ethanol:water solution 20% (v/v) in 0.01 mol L⁻¹ CaCl₂ plus 0,01 mol L⁻¹ NaN₃ solution. CaCl₂ was used as background electrolyte, and NaN₃ was used as biocide to eliminate microbial degradation of Pyrene.

Adsorption experiments were conducted at 25°C using a batch technique. Solid to solution ratios were chosen to ensure that 15 to 100% of the pyrene mass was adsorbed. Approximately 2.5 g of soil materials were weighed into 125 mL Pyrex tubes, and a 50 mL aliquot of pyrene solution was added. The centrifuge tubes were tightly sealed with Teflon lined screw caps. Teflon tape was used on the threads of the centrifuge tubes to minimize possible losses by volatilization. Control samples without any soil material were also prepared in the same way and used as controls to account for possible losses due to volatilization and sorption of pyrene to the centrifuge tube walls.

To reach the equilibrium state the samples were allowed to equilibrate in the dark at room temperature for 20 h under continuous mixing on a reciprocating gyratory shaker. After the 20 h equilibration period, the samples (including control samples) were centrifuged for 15 min at 150000g. Supernatants were then sampled and analysed by synchronous fluorescence spectroscopy.

Synchronous fluorescence spectra were measured in a 1.0 cm quartz cell pre-washed with the sample. The synchronous fluorescence emission was recorded using a spectrofluorimeter (Perkin Elmer, LS45). For pyrene the maximum excitation and emission wavelengths measured were 332 and 373 nm, respectively, and so a $\Delta\lambda$ of 41 nm was used to acquire the synchronous fluorescence spectra. Fixed slit widths of 10.0 nm were used. No adsorption of pyrene onto the quartz cell was observed. To

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Table 1
SOME CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE STUDIED BRAZILIAN SOILS

Brazilian Soil Taxonomy	USA Soil Taxonomy	Clay	Organic carbon g kg^{-1}	pH	CEC cmolc kg^{-1}	V %
Argissolo (P)	Kandiudult	160	7.8	5.2	5.4	52
Latossolo Vermelho acriférrico (LVwf)	Acrudox	720	21.4	5.4	8.6	21
Latossolo Vermelho Amarelo (LVA)	Kandiudox	260	17.4	4.1	8.9	12
Neossolo quartzarênico (RQ)	Quartzipsamment	40	1.8	5.4	1.5	53
Vertissolo (V)	Hapludert	460	5.6	7.8	30.7	100

control instrument stability, the Raman peak of water at 348 nm was used. Also, lamp decay was controlled by measuring the fluorescence intensity of pyrene standard solutions. As said above, to monitor the loss of pyrene, control tubes with no soil present were prepared for each concentration level. The losses of pyrene by photochemical decomposition, volatilization, and sorption on Pyrex tubes were found to be negligible.

Five soils were used in this study: Argissolo (P), Latossolo Vermelho acriférrico (LVwf), Latossolo Vermelho Amarelo (LVA), Neossolo Quartzarênico (RQ) and Vertissolo (V). These names correspond to the Brazilian Soil Taxonomy. Their equivalents in USA Soil Taxonomy are also indicated in table 1. These soils differ with respect to origin, texture, and SOM content. Samples were taken from A horizon and were collected from the 0 to 10 cm layer. All soils were air-dried and sieved to 40 μm .

The soils were sampled and analyzed according to Embrapa soil analysis methods [14]. Soil pH was measured in a 1:2.5 soil to water suspension. Organic carbon content was determined by wet combustion with potassium dichromate acidic solution and back-titration with ferrous ammonium sulfate. Particle size distribution was determined after sample dispersion with NaOH 1 mol L^{-1} stirred at high speed. Sand (2-0.53 mm) was separated by sieving. Clay (< 0.002 mm) was measured in the supernatant (pipette or densimeter method) and silt (0.53-0.002 mm) was calculated by difference.

Exchangeable Ca and Mg were extracted with KCl 1 mol L^{-1} and determined by complexometric titration with EDTA. Exchangeable Na and K were extracted with Mehlich 1 and determined by photometry. Exchangeable Al was extracted with KCl 1 mol L^{-1} and determined by acid-base titration. H was extracted with calcium acetate 0.5 mol L^{-1} and also determined by acid-base titration. Cation Exchange Capacity (CEC) was calculated by the sum of Ca, Mg, Na, K, Al and H.

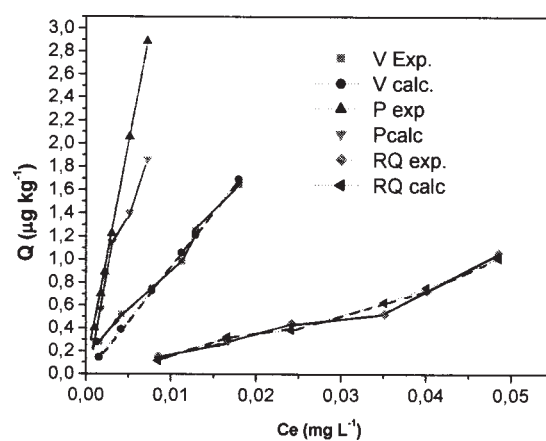
In previous studies, the equilibrium time to adsorption process was determined in each soil [15]. Most often, the equilibrium time was 1280 min.

F and Tukey test were employed as statistic tests. Minitab (10,0), Origin (6,0) and SAS (9,0) programs were used. Adjustments of model isotherms to experimental data were obtained with IsoFit software.

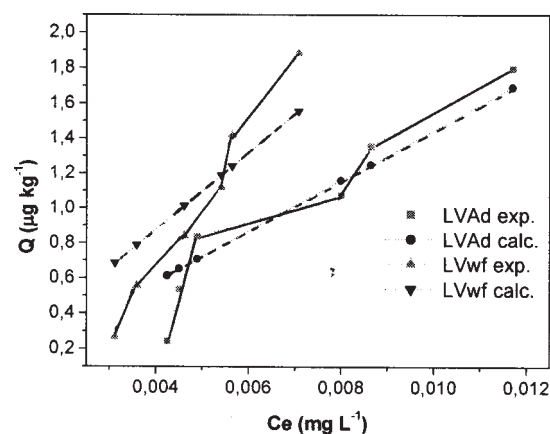
Results and discussion

Table 1 shows some chemical and physical characteristics of the studied Brazilian soils. In general, it can be observed that most soils are acidic, since most of Brazilian soils were subjected to high weathering conditions [16]. As a consequence, cation exchange capacities (CEC) of the soils are low. The exception is the

Vertissolo that was developed over calcareous parent material and had highest pH, base saturation (V%) and CEC. Soil organic carbon content ranged from 1.8 to 21.4 g kg^{-1} . The mineralogical composition (data not shown) showed a predominance of kaolinite in most of the soils. The Latossolo Vermelho showed also the presence of iron



a)



b)

Fig. 1. Adsorption isotherms obtained to a) Vertissolo (V), Argissolo (P), Neossolo Quartzarênico (RQ) b) Latossolo Vermelho Amarelo (LVA) and Latossolo Vermelho acriférrico (LVwf)

oxides (hematite and goethite) in large quantities. The Vertissolo showed a predominance of 2:1 secondary silicates (montmorillonite) and also kaolinite. The adsorption isotherms of the five soils are presented in figure 1.

Table 2
PHYSICO-CHEMICAL DATA OF SOILS - EXPERIMENTAL AND CALCULATED PARAMETERS RELATED TO PYRENE ADSORPTION ON THEM

a)

Parameter	P	LVwf	LVA	RQ	V
foc	0.0078	0.0214	0.0174	0.0018	0.0056
Kd exp.	341.4	24.97	46.24	15.75	159.7
Kd calc.	283.46	219.68	144.97	18.9	94.11
Koc	43769.23	1166.82	2657.47	8750	34946.42
ΔG°	-261.14	-17.12	-19.26	-221.8	-255.64
Isotherm	Langmuir	Linear	Langmuir partition	Langmuir Freundlich	Linear
R2	0.9860	0.9910	0.9590	0.9740	0.9950

b)

Criteria	Freundlich	Freundlich Partition	Langmuir	Langmuir - Freundlich	Langmuir Partition	Linear
P						
R2	0.962	0.962	0.986	0.962	0.973	0.941
AICc	-19.226172	-9.222146	-21.111619	-9.297373	-11.108282	-17.961578
LVwf						
R2	0.982	0.982	0.982	0.975	0.982	0.9910
AICc	74.695785	84.696004	74.709646	71.92441	69.69578	69.69578
LVA						
R2	0.919	0.919	0.919	0.913	0.959	0.919
AICc	-12.575767	-2.575762	-5.48870	-4.649277	-17.575773	-17.575773
RQ						
R2	0.932	0.932	0.932	0.974	0.932	0.932
AICc	-21.951881	-26.95188	-21.951014	-14.124733	-11.951884	-26.951883
V						
R2	0.985	0.983	0.981	0.983	0.99	0.995
AICc	-16.427249	-25.46844	-23.196461	-15.292131	-21.361811	-26.283273

AICc - Corrected Akaike Information Criterion [19].

Table 3
PARAMETERS FROM LANGMUIR, LANGMUIR-FREUNDLICH AND LANGMUIR WITH PARTITION ISOTHERMS OBTAINED FROM THE FITTING TO THE EXPERIMENTAL ADSORPTION CURVES OF PYRENE ON THE STUDIED SOILS

Soils	Langmuir		Langmuir Freundlich			Langmuir Partition		
	b	Q0	b	Q0	1/n	b	Q0	kp
P	98.3642	4.4447	0.7988	95.298	0.7572	99.1865	4.3843	2.3106
LVwf	2.29×10^{-04}	$9.59 \times 10^{+05}$	4.28×10^{-02}	2.30×10^{-04}	1.9982	6.54×10^{-06}	1.20×10^{-07}	219.6819
LVA	0.6107	2.3837	0.1376	611.5402	1.2728	8.97×10^{-10}	0.0205	144.7977
RQ	1.56×10^{-03}	1206.8	0.7312	73.8751	1.291	5.07×10^{-07}	28026.3	18.8871
V	13.9876	8.0521	0.5794	75.0882	0.8376	0.9666	318.6029	1.36×10^{-03}

Their respective K_d are presented in table 2a), together with organic matter fraction (f_{oc}), experimental K_d , K_d obtained from the isotherm model that better explained each adsorption curve, partition coefficient normalized by organic carbon (K_{oc}), Gibbs free energy (ΔG°). For each soil, in table 2a), is indicated also the adsorption isotherm that better fits each adsorption curve and R2 (correlation value between experimental results and model isotherms) is given. In table 2b) R2 and AICc (Corrected Akaike Information Criterion) are given for the five soils and for all the tested isotherms.

Starting with K_d values, K_{oc} was calculated. The soils presented different K_d and K_{oc} values. The correlation with K_d and f_{oc} is negative (-0.3139). This result showed us that in Brazilian soils organic matter is not the main responsible for adsorption [17, 18].

These last values were used to compute the Gibbs free energy. The Gibbs free energy calculated indicated that all processes were spontaneous.

After the comparison between experimental data and data fitted with isotherms models, we concluded that the adsorption process was best described by Langmuir theory (Langmuir or Langmuir derived isotherms), as is shown in

table 3 and 4. The b parameter of Langmuir equation describes the maximum adsorption capacity of soils. The correlation between b and K_d is positive (0.9570) what indicates that Langmuir model is suitable to describe adsorption in Brazilian soil. On other hand, the correlation between K_f of Freundlich equation and K_d is negative (0.3760), as presented in table 5.

Furthermore, although Vertissolo and Argissolo have similar organic matter content their K_{oc} values are very different. Comparing the readsorption process and the clay content, the K_{oc} of Vertissolo is minor than that of Argissolo. In Langmuir theory, all adsorption sites are similar and do not occur any competition to sites. However, in Vertissolo with its high montmorillonite content Pyrene adsorption in interlayer space it is possible and so it is Pyrene dimer formation, due to the extra intra-lamellar space of this clay. Because of this, this adsorbent is different and no ideal and their adsorption sites are different too. This fact contradicts Langmuir theory and that's way this theory can not be applied to Vertissolo.

The isotherm that better explained pyrene behavior in Argissolo was Langmuir isotherm. However, as can be observed from fig. 1a), for the higher concentrations, a

Table 4
PARAMETERS FROM FREUNDLICH AND FREUNDLICH WITH PARTITION ISOTHERMS OBTAINED FROM THE FITTING TO THE EXPERIMENTAL ADSORPTION CURVES OF PYRENE ON THE STUDIED SOILS

Soils	Freundlich		Freundlich Partition		
	kf	1/n	kf	1/n	Kp
P	74.4142	0.7456	73.4835	0.7442	1.5538
LVwf	4.03x10 ⁺⁰⁵	1	140.8594	0.9993	79.0759
LVA	144.7905	0.9999	143.4901	1	1.3132
RQ	18.9010	1	1.75x10 ⁻⁰⁷	0.8022	18.9008
V	44.8500	0.8281	6.7196	0.5919	54.8072

Table 5
CORRELATION BETWEEN b FROM LANGMUIR EQUATION AND k_f FROM FREUNDLICH EQUATION WITH K_d VALUES AND FITTING OF ISOTHERMS TO EXPERIMENTAL DATA

Correlation of kd with b			Correlation of kf with kd	
Langmuir	Langmuir Freundlich	Langmuir Partition	Freundlich	Freundlich Partition
0.9570	0.6015	0.91199	-0.3760	-0.1715

strong deviation between experimental and model calculated data occurs. We have some explanation for that.

Langmuir theory is the base theory to others adsorption theories, as the linear theory. Langmuir theory considers monolayer uptake; adsorption sites have a plane surface and with a fix number of identical active sites where competition between adsorbent molecules for the adsorption sites does not exist.

As mentioned above, at high pyrene concentrations and appropriated conditions (namely space) its dimerization often occurs. Then if pyrene dimer formation occurs the adsorbed dimer modifies the nature of the adsorption sites, what is in clear contradiction with Langmuir theory and so experimental data would never be totally justified by the Langmuir theory. Another possible explanation is the fact that adsorption sites have a fixed and finite number for Argilssolo. However, at high concentrations the competition of pyrene molecules to the adsorption sites occurs. The higher the concentration, the bigger is this competition. Because adsorption sites have limited adsorption capacity, the saturation of sites was observed from Ci = 60 µg L⁻¹ of pyrene.

To Vertissolo soil the linear isotherm model fits well and fully explains pyrene behavior in this soil. This is true even for high concentrations, where any deviation occurs due to adsorption of pyrene molecules in interlayer space. This result is corroborated by b values for Argissolo and Vertissolo that are 98.36 , 13.98 respectively, as can be seen in table 3.

Latossolo Vermelho Amarelo and Latossolo Vermelho acriférico soils have similar organic carbon content and their isotherms have been compared too. For Latossolo Vermelho Amarelo, the isotherm presents very different behavior from all other soils. The adsorption isotherm obtained for this soil has an S like shape. Looking at the isotherm (fig. 1b)) we can easily conclude that the process occurs in two steps. First step is observed for low concentrations and the second one for the highest pyrene concentrations. The first study undertaken to understand the processes on this soil started by obtaining Log K_d. In this isotherm for low concentrations, the soil presents low pyrene affinity and apparently the prevalent process was liquid phase water uptake on adsorptive sites. For high concentrations, we suggest that for the remaining adsorption sites, a competition processes between pyrene uptake and solvent uptake was established. For these high concentrations, pyrene adsorption was the prevalent

process. This soil presented also the second lowest K_{oc} and a b of 0.6107 that indicated that although this is one of the soils with highest organic mater content it present a low K_{oc} when compared with all other soils. This can be explained by the advanced oxidation stage of the soil organic matter.

A similar behavior of that of Latossolo Vermelho Amarelo occurs also for Latossolo Vermelho acriférico. For Latossolo Vermelho acriférico the isotherm that better explains the soil/pyrene behavior is the linear isotherm (R² - 0,9910). For this soil the lowest K_d, K_{oc}, b and ΔG^o(-17,12) values were found. Although this process is still spontaneous, this is the lowest value for all soils. However, this soil has the highest organic matter and iron contents. Similarly to the other latosol, the organic matter for this soil is also in an advanced oxidation state because these are old formation well structured soils. It is possible that the high iron content form with organic matter a complex and so the adsorption sites are occupied for pyrene adsorption. In other sites, the iron forms an inner sphere complex with pyrene by the iron that was coordinated to pyrene.

Neossolo Quartzarênico is basically formed by sand; it has low organic matter content whose distribution has a non regular profile. Since they have low porosity, silicates do not constitute adsorption sites for non ionic compounds and prevent in this way intra particular diffusion and consequently adsorption. The analysis of b from Langmuir model indicates that this soil has low adsorption capacity and that the isotherm that better fits experimental data is the dual Langmuir-Freundlich isotherm model, because the adsorption sites are in fact different. The comparison between theoretical and experimental model shows an R² of 0.9740.

Literature usually refers to adsorption specific sites, an equations that usually describe this process are Langmuir and Freundlich isotherms, since they both describe high adsorption capacity and competitive adsorption.

Conclusions

We could observe that the studied soils present physico-chemical properties and K_{oc} values very much different and so those soils can not be seen as the same representative category for pyrene adsorption.

Langmuir isotherm is the one that best describes adsorption for Argissolo soil. However, for high concentration, adsorption sites saturated already and significant deviations to Langmuir model occur.

We verified also that the organic matter content was not the only responsible for the dynamic equilibrium of the adsorption process. The presence of expansible clays may also contribute for the Q increase in soils, as was the case of Vertissolo soil.

For Latossolo Vermelho Amarelo a two steps process was observed. Those steps are directly related with the availability of adsorption sites and the process presented an S shape isotherm.

On Neossolo Quartzarênico experiments, a low content and irregular organic matter distribution was observed. Comparing with other studied soils the variation on organic carbon on the five replicates samples of Neossolo Quartzarênico led to a low K_{oc} and on standard deviation increase.

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