



## Modelling single compound adsorption onto porous and non-porous sorbents using a deformed Weibull exponential isotherm

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### ABSTRACT

A new isotherm equation, the Brouers–Sotolongo isotherm (BSI), a deformed (Weibull) exponential equation was used to describe adsorption equilibrium of phenol and methylene blue (MB), respectively onto a non-porous adsorbent, *Posidonia oceanica* fibres and two porous adsorbents, chemically and physically activated carbons (ACs) prepared from vetiver roots. The adsorption characteristic parameters obtained were also calculated using classical adsorption isotherm, i.e. the Langmuir isotherm (LI), Freundlich isotherm (FI) and Redlich–Peterson isotherm (RPI). Using only  $R^2$  to determine the best-fitting model was not sufficient, calculation of the error deviation using both the Marquardt's percent standard error (MPSE) and the average relative error (ARE) was also done. For the case of phenol, and among all studied models, the BSI involving adsorption on a heterogeneous surface is definitely the most suitable one to satisfactorily describe biosorption of phenol on posidonia, but as well adsorption of phenol on the ACs giving the highest squared correlation coefficients and the lowest MPSE. For posidonia and as well for the ACs, when MB is the adsorbate, the RPI is the best-fitting model.

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### 1. Introduction

In the last decade, a large number of papers have been devoted to model adsorption process involved in the removal of pollutants from contaminated waters [1–4]. It has been found that like activated carbons (ACs), in many instances, natural biological materials; as well biomass wastes can be used for water treatment purposes [5–7]. The isotherm, describing the retention of a substance on a solid at various concentrations at a constant temperature is a major tool to predict the efficiency of a sorbent to remove a given pollutant from polluted waters. The isotherm data are traditionally fitted with either the Langmuir isotherm (LI) or the Freundlich isotherm (FI) [8,9]. The Redlich–Peterson isotherm (RPI) tending to the two previous isotherms at low and high value of solute concentration, respectively has been as well used with some success [10,11]. These formulas are however essentially empirical, indeed, the physical situation is generally very far from the one postulated by Langmuir which derives its equation supposing that the adsorption takes place on a homogeneous surface. Con-

trary to the proposed Langmuir picture, the sorption mechanism should be dominated by the most energetically active sites and it is the nature of the non-Gaussian energy distribution of these sites which determines the shape of the isotherm. Following the work of Brouers and Sotolongo on the statistical properties of physical complex systems, it has been recently demonstrated how the exponent of the FI could be related to an exponential distribution of sorption energies (energy landscape). A deformed exponential (Weibull) isotherm, namely the Brouers–Sotolongo isotherm (BSI) has been proposed to analyse sorption processes on highly heterogeneous systems [12]. In the present paper, the validity of the use of the BSI equation for describing isotherms of phenol and methylene blue (MB) adsorption, respectively, onto ACs prepared from vetiver (*Vetivera zizanoides*) roots and posidonia leaf sheath fibres (*Posidonia oceanica*) is investigated.

### 2. Materials and methods

#### 2.1. Biomass preparation

*P. oceanica* leaf sheaths (basal parts of leaves of the Mediterranean seagrass) were collected from Chott–Meriem bay (Sousse, Tunisia). The fibres are manually separated, washed thoroughly

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**Table 1**  
Textural characteristics of the vetiver roots ACs

Samples	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{mi}}$ (m <sup>2</sup> /g)	$V_{\text{mi}}$ (m <sup>3</sup> /g)	$V_{\text{me}}$ (cm <sup>3</sup> /g)	$V_{\text{tot}}$ (cm <sup>3</sup> /g)	$V_{\text{mi}}/V_{\text{tot}}$ (%)	$D_p$ (nm)
Vet-H <sub>2</sub> O	1185	894	0.36	0.33	0.69	52	2.16
Vet-P1	1272	737	0.39	0.80	1.19	33	2.83

with distilled water to remove salt and then dried in an oven at 40 °C for 48 h to a constant weight, without altering the polymeric composition of the fibres. After drying, the biomass was blended in a waring blender to get homogenous particle size (2 mm sieve) and stored in dessicator.

## 2.2. Activated carbons preparation

The ACs were obtained from vetiver roots collected in Guadeloupe. Vetiver roots were initially dried at 105 °C for 48 h using a drying oven, then ground and sieved to several particle sizes ranging from less than 0.2 to 1 mm. The fraction with a particle size ranging between 0.4 and 1 mm was retained for the whole of handling. In this experiment, two conventional methods of preparation of AC were used.

For physical activation, approximately 5 g of pre-treated vetiver roots were initially pyrolyzed in a furnace Thermolyne F-21100 under nitrogen atmosphere at 800 °C for 1 h with a heating rate of 10 °C/min. Coals thus prepared, were then activated with steam under a nitrogen atmosphere at 800 °C for 12 h with a heating rate of 10 °C/min in the same furnace giving sample vet-H<sub>2</sub>O.

For chemical activation, 3 g of the raw material was impregnated in phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) 85% for 24 h, in order to facilitate the access of the acid inside the particles [13–15]. Impregnation ratio;  $X_P$  (g H<sub>3</sub>PO<sub>4</sub>/g precursor): 1:1 is used giving sample: vet-P1. After impregnation, the sample was dried for 4 h at 105 °C in a drying oven. The sample thus dried was pyrolyzed under nitrogen flow at 600 °C for 1 h. After cooling, until ambient temperature, the AC thus obtained was washed with distilled water until stabilization of the pH, and then dried overnight using a drying oven at 105 °C.

The ACs were characterized by N<sub>2</sub> adsorption at 77 K using a Micromeritics ASAP-2020 analyzer. The manufacturer's software provided BET surface area ( $S_{\text{BET}}$ ) of the carbons by applying the BET equation to the adsorption data. The microporous surface ( $S_{\text{micro}}$ ) and micropore volume ( $V_{\text{mi}}$ ) were evaluated by the  $t$ -plot method, and mesopore volume ( $V_{\text{me}}$ ) was estimated by the Barrett–Joyner–Halenda (BJH) method. The textural characteristics of the ACs are presented in Table 1.

## 2.3. Adsorbate solution preparation

Two organic molecules have been used as models in this study: MB and phenol (analytical grade, Merck). Synthetic solutions for each sorbate were prepared separately by dissolving accurately weighted amount of dye (1000 mg/L) in distilled water and subsequently diluted to obtain the required concentrations. Spectrophotometric scanning of dilute dye solutions was performed and absorbance maxima were fixed at 660 nm for MB and 270 nm for phenol.

## 2.4. Equilibrium liquid-phase sorption experiments

Equilibrium adsorption experiments with MB and phenol were carried out using batch technique. For posidonia fibres, adsorption experiments were carried out by shaking 0.5 g of fibres with 50 mL of dye solution (i.e. 10 g/L) for the desired dye concentration and under initial solution pH (5.2 for phenol and 6 for MB). Studies were conducted at 30 ± 2 °C using a thermo-regulated water bath oper-

ating at 100 rpm. For vetiver-derived ACs, a fixed amount of carbon (40 mg) was weighted into conical flasks containing 100 mL of different initial concentrations (50–300 and 20–100 mg/L of MB and phenol, respectively). The flasks were then stoppered and agitated at 25 °C until to reach equilibrium time, previously determined by kinetics tests.

At equilibrium, after filtration (case of ACs) and centrifugation at 4000 rpm for 2 min (case of posidonia fibres), MB and phenol residual concentrations were estimated using the spectrophotometric technique at their respective absorbance wavelength maxima.

Then, in order to monitor dye and phenol removal, biosorption capacity at equilibrium time ( $Q_e$ ) will be determined according to the following equation:

$$Q_e = (C_0 - C_e) \frac{V}{M} \quad (\text{mg/g}) \quad (1)$$

where  $C_0$  and  $C_e$  are, respectively, the initial and equilibrium liquid-phase concentrations of the adsorbate (mg/L),  $V$  the solution volume (L) and  $M$  the mass of the dried adsorbent (g).

## 2.5. Isotherm modelling studies

Non-linear analysis of isotherm data is an interesting mathematical approach for describing adsorption isotherms at a constant temperature for water and wastewater treatment applications and to predict the overall sorption behaviour under different operating conditions. Indeed, as different forms of the equation affected  $R^2$  values more significantly during the linear analysis, the non-linear analysis might be a method of avoiding such errors [16,17].

In the present study, four different isotherm models were tested under two different adsorption systems (i.e. porous and non-porous sorbent media using phenol and MB as sorbate molecules) namely, the commonly used Langmuir [18], Freundlich [19] and Redlich–Peterson [20], and the newly elaborated BSI. The non-linear analysis was carried out using the SPSS 13.0 mathematical software.

### 2.5.1. Langmuir isotherm (LI)

The Langmuir model is valid for monolayer sorption a surface with a finite number of similar active sites. The well-known expression of the Langmuir model is given by the following equation:

$$Q_e = \frac{Q^0 K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $Q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of adsorbed phenol or dye per unit weight of biomass and the residual concentration in solution at equilibrium, respectively.  $Q^0$  is the maximum amount of the dye per unit weight of biomass to form a complete monolayer on the surface bound and  $K_L$  is a constant related to the affinity of the binding sites (L/mg).

### 2.5.2. Freundlich isotherm (FI)

The empirical Freundlich equation based on sorption onto a heterogeneous surface is given below by the following equation:

$$Q_e = K_F (C_e)^{1/n} \quad (3)$$

where  $K_F$  and  $n$  are the Freundlich constants characteristic of the system.  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) and  $n$  are indicators of adsorption capacity and adsorption intensity, respectively.

### 2.5.3. Redlich–Peterson isotherm (RPI)

The Redlich–Peterson model incorporates the features of the LI and FI into a single equation and presents a general isotherm equation as follows:

$$Q_e = \frac{A_{RP} C_e}{1 + K_{RP} C_e^\beta} \quad (4)$$

where  $A_{R-P}$  ( $\text{L/mg}$ ) $^\beta$  and  $K_{R-P}$  ( $\text{L/g}$ ) are the RPI constants. The exponent,  $\beta$ , as it lies between 0 and 1, has two limiting behaviours: Langmuir form for  $\beta = 1$  and Henry's law form for  $\beta = 0$ .

### 2.5.4. Brouers–Sotolongo isotherm (BSI)

One of the earlier attempts to formulate a theory of adsorption on a non-uniform surface is due to Langmuir who suggested the extension of the simple LI to irregular surfaces.

The surface is assumed to comprise a finite number of patches of sites of equal energy. In that case, if one assumes a continuous range of energies and replace the summation by an integral, the isotherm may be written:

$$\frac{q_c}{q_m} = \int \frac{K(E, T) C_e}{1 + K(E, T)} g_K(K) dK \quad (5)$$

with

$$K(E, T) \sim \exp\left(\frac{E_s}{kT}\right) \quad (6)$$

The distribution of local Langmuir coefficients can be obtained from the distribution of sorption energies  $g_{E_0}(E_s)$  using the following equality of probability theory:

$$g_{E_s}(E_s) dE_s = g_K(K) dK \quad (7)$$

If one assumes that the sorption energies are distributed according to the distribution

$$g_{E_s}(E_s) \sim \exp\left(\frac{E_s}{E_0}\right) \quad (8)$$

(i.e. that the local sorption energies have an exponentially small probability to be large) it is straightforward to show that  $g_K(K)$  is given by a power-law Pareto probability distribution

$$g_K(K) \sim kTK^{-1-\alpha} \quad \text{with} \quad \alpha = \frac{kT}{E_0} \quad (9)$$

Using this distribution, the result of the integration is:

$$\frac{q_c}{q_m} = \left(\frac{C_e}{1 + C_e}\right) F\left(\alpha, \alpha, 1 + \alpha, \frac{1}{1 + C_e}\right) \quad (10)$$

which tends to the Freundlich law when  $C_e \rightarrow 0$

$$\frac{q_c}{q_m} = K_0 C_e^\alpha \quad \text{with} \quad K_0 = \pi\alpha \csc[\pi\alpha] \quad (11)$$

One can show for more realistic sorption energy distribution having an exponential asymptotic behaviour that the characteristic energy is related to the quantities characterizing the distribution such the expectation value and the width. For more realistic distribution having the asymptotic exponential behaviour, it has been shown that the quantity  $E_0$  is a measure of the width of the distribution of sorption energies.

The parameter is therefore a meas-thermal equilibrium Gaussian homogeneity at temperature  $T$ . For  $E_0 > kT$ , the sorption system is heterogeneous and  $\alpha < 1$ . For low  $C_e$ , it coincides with the Freundlich exponent  $1/n$ . Heuristic arguments borrowed from the theory of Lévy stable distributions and of the theory maximum

entropy suggest that a good choice for the averaged isotherm, when the sorption energy distribution is given by a function having the asymptotically the exponential behaviour [21], is given by a deformed exponential (Weibull) function (BSI):

$$q_c = Q_m(1 - \exp(-K_w C_e^\alpha)) = Q_m \left( K_w C_e^\alpha - \frac{1}{2}(K_w C_e^\alpha)^2 + O(C_e^\alpha)^3 \right) \quad (12)$$

The parameters  $Q_m$ ,  $K_w$  and  $\alpha$ , which can be determined by a non-linear fitting procedure, have a clear physical meaning:  $Q_m$  ( $\text{mg/g}$ ) is the saturation value,  $K_w$  ( $\text{L/mg}$ ) is the BSI constant, and the exponent  $\alpha$  (dimensionless) is a measure of the width of the sorption energy distribution and therefore of the energy heterogeneity of the surface.

A power-law Freundlich behaviour is expected only for  $C_e \ll K_w^{1/\alpha}$ . For  $C_e \sim K_w^{1/\alpha}$ , the isotherm exhibits a cross-over corresponding to a saturation effect towards the maximum adsorption. The isotherm appears to have a Langmuir behaviour. This can be misleading when  $\alpha$  is different from unity.

### 2.6. Error estimation

In the present research, the average relative error (ARE) deviation [22], the Marquardt's percent standard error (MPSE) deviation [23] tests were used to estimate the goodness of the fit of the studied models. The related equations are given by Eqs. (13) and (14), respectively.

$$\text{ARE} = \frac{1}{N} \sum \left| \frac{(Q_{e,\text{cal}} - Q_{e,\text{exp}})}{Q_{e,\text{exp}}} \right| \times 100 \quad (13)$$

$$\text{MPSE} = \sqrt{\frac{\sum [(Q_{e,\text{exp}} - Q_{e,\text{cal}})/Q_{e,\text{exp}}]^2}{N - P}} \times 100 \quad (14)$$

where  $N$  is the number of experimental data points,  $Q_{e,\text{cal}}$  ( $\text{mg/g}$ ) is the theoretically calculated adsorption capacity at equilibrium,  $Q_{e,\text{exp}}$  ( $\text{mg/g}$ ) is the experimental adsorption capacity at equilibrium and  $P$  is the number of parameters in each isotherm model.

If data from the model are similar to the experimental data, both ARE and MPSE will give small values. Hence, in order to confirm the best-fitting isotherm for each adsorption system, it is necessary to analyse the data using three error estimation functions:  $R^2$  (determined from the non-linear analysis), ARE and MPSE.

## 3. Results and discussion

The equilibrium data for MB and phenol adsorption onto fibrous ACs from vetiver roots and posidonia fibres were analysed by non-linear curve fitting analysis using Langmuir, Freundlich, Redlich–Peterson and the newly established model: the BSI.

For all studied models, the accuracy of the fit with experimental data was determined based on  $R^2$ , MPSE and ARE. Modelling results were considered suitable to satisfactorily describe the biosorption process if the squared correlation coefficient was greater than 95% and/or the percent deviation error for both MPSE and ARE was less than 10%.

### 3.1. Adsorption isotherm modelling onto non-porous medium: *P. oceanica* fibres

The equilibrium modelling results related to the biosorption of MB and phenol onto raw posidonia fibres using the Freundlich, Langmuir, Redlich–Peterson and Brouers–Sotolongo, in addition to

**Table 2**

Isotherm modelling results related to the adsorption of phenol and MB onto raw *Posidonia oceanica* fibres

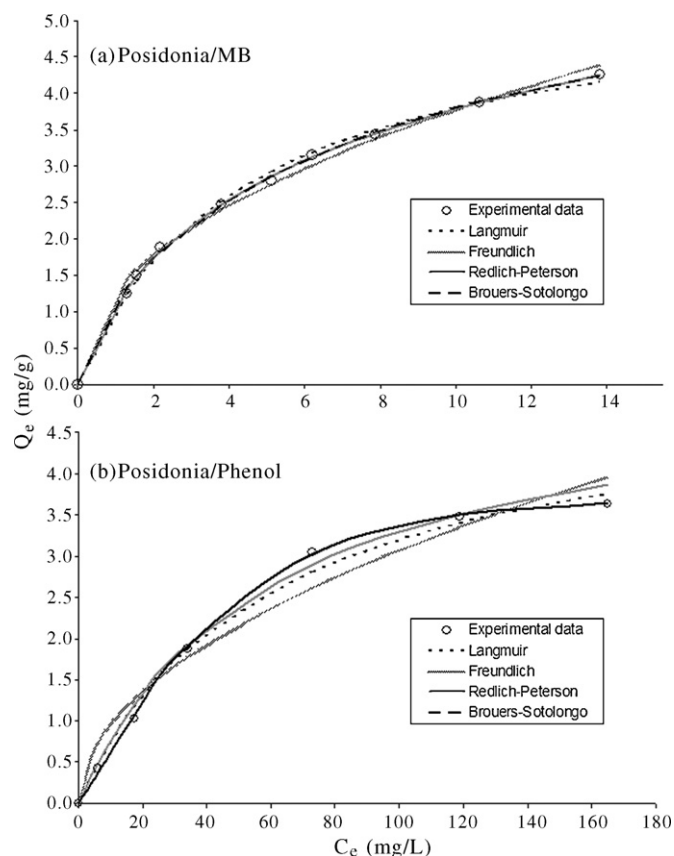
Parameters	Phenol	Methylene blue
<b>Langmuir isotherm</b>		
$Q^0$ (mg/g)	5.085	5.518
$K_L$ (L/mg)	0.017	0.220
$R^2$	0.990	0.995
MSPE	0.911	0.350
ARE	6.077	2.563
<b>Freundlich isotherm</b>		
$K_F$ ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	0.295	1.281
$n$	1.966	2.134
$R^2$	0.948	0.989
MPSE	3.892	0.685
ARE	21.142	4.236
<b>Redlich–Peterson isotherm</b>		
$A_{RP}$ (L/mg) $^\beta$	0.089	1.663
$K_{RP}$ (L/g)	0.017	0.528
$\beta$	1.000	0.808
$R^2$	0.990	0.999
MPSE	1.112	0.227
ARE	7.214	1.363
<b>Brouers–Sotolongo isotherm</b>		
$Q_{\text{max}}$ (mg/g)	3.689	5.415
$K_w$ ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	0.014	0.233
$\alpha$	1.123	0.716
$R^2$	0.999	0.998
MPSE	0.745	0.282
ARE	2.462	1.699

the error calculations, are mentioned in Table 2. The graphic correlation between the experimental data and the theoretical models for the adsorption systems are given in Fig. 1a and b for MB and phenol, respectively.

First of all, from Table 2, the experimental data were better described by the BSI for phenol and the RPI for MB. In addition, it is obvious that the Freundlich model is not suitable to fit the isotherm curves for both sorption systems. Indeed, according to the Freundlich related results, the use of this model provides the lowest  $R^2$  and the highest MPSE and ARE. Such trend is quite logical since the Freundlich equation is a pure exponential one, which means that when  $C_e \sim \infty$ ,  $Q_e$  will also extend to  $\infty$ . However, for both MB and phenol adsorption systems, since there is a clear saturation plateau, the calculated  $Q_e$  will necessary tend towards a constant (i.e. maximum adsorption capacity).

For the case of phenol, the BSI model gives the best fit by providing the highest non-linear  $R^2$  (99.9%) and the lowest MPSE (0.74) and ARE (2.46). Such trend would probably enlighten the energetic heterogeneity at the interface adsorbent (raw *P. oceanica* fibres)/adsorbate (phenol). Indeed, under the used experimental conditions (pH 5.2 and temperature equal to 30 °C), the interactions involved in such sorption case would be between phenol molecules and posidonia cell surface via different possible interactions mainly electrostatic, electron donor–acceptor interactions and/or hydrophobic bonds between aromatic phenolic ring and both carboxyl and hydroxyl groups [24]. Thus, such tendency would lead to a heterogenous sorption energy landscape, explaining therefore the good fit of the BSI model and the quite high  $\alpha$  exponent (1.12).

By the way, it is necessary to point out that using only  $R^2$  to determine the best-fitting model is not sufficient and could lead to some ambiguities. Indeed, the results in Table 2, dealing with phenol, showed that based on  $R^2$  both LI and RPI seem to be adequate. However, the calculation of the error deviation using both MPSE and ARE revealed that the LI model is more suitable to describe the



**Fig. 1.** Isotherm modelling of MB (a) and phenol (b) adsorption onto raw *Posidonia oceanica* fibres at 30 °C.

sorption phenomenon of phenol onto *P. oceanica* fibres by giving lower error estimation values. Therefore, using only  $R^2$ , even if it is estimated via a non-linear analysis is not always an appropriate tool to evaluate the goodness of the fit of an isotherm model.

On the other hand, modelling the results of MB adsorption showed that the highest squared correlation coefficients (99.9%) and the lowest MPSE (0.22) and ARE (1.36) are given by the RPI model. Furthermore, it is interesting to analyse the RPI exponent  $\beta$  to determine if it is more approaching the LI or the FI. Hence, with  $\beta$  equal to 0.81, it is clear that the special form of the RPI in such case is the LI, which assumes a monolayer coverage of MB onto posidonia surface via electrostatic attractions between cationic MB molecules and anionic carboxyl and hydroxyl groups within the posidonia biopolymers (mainly lignin and cellulose) [25].

On the other hand, it is also clear in that case (i.e. between RPI and BSI for MB adsorption), that  $R^2$ , by itself, is not sufficient to determine the most suitable model.

### 3.2. Adsorption isotherm modelling onto porous media: activated carbons from vetiver roots

For the ACs, all curves rise steeply at low concentration, and quickly approach a plateau at high concentration for MB (Fig. 2), while for phenol the plateau is reached gradually (Fig. 3). For both vet-H<sub>2</sub>O and vet-P1 ACs, the amount of adsorbed MB is higher than the one of phenol (Table 3). Such behaviour can be explained by the ACs textural characteristics. Indeed, both prepared ACs have a large specific surface area; 1185 and 1272 m<sup>2</sup>/g and an average pores diameter of 2.16 and 2.83 nm for vet-H<sub>2</sub>O and vet-P1, respectively, allowing them to accommodate the MB molecule. Due to the lower molecular mass of phenol (MW=94.11) and molecu-

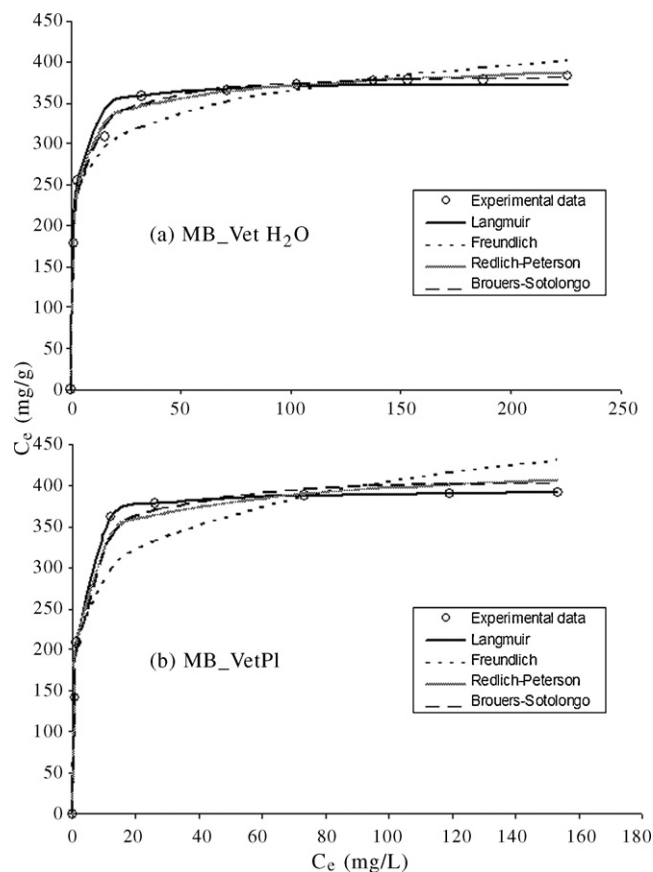


Fig. 2. Isotherm modelling of methylene blue adsorption onto vet-H<sub>2</sub>O (a) and vet-P1 (b) at 25 °C.

Table 3

Isotherm modelling results related to the adsorption of phenol and MB onto chemically (vet-P1) and physically (vet-H<sub>2</sub>O) activated carbons from vetiver roots

Parameters	Phenol		Methylene Blue	
	Vet-H <sub>2</sub> O	Vet-P1	Vet-H <sub>2</sub> O	Vet-P1
<b>Langmuir isotherm</b>				
$Q^0$ (mg/g)	145.464	74.445	375.295	393.73
$K_L$ (L/mg)	0.124	0.058	0.683	0.935
$R^2$	0.992	0.986	0.964	0.970
MSPE	0.255	0.376	0.456	0.510
ARE	1.838	2.793	2.620	4.377
<b>Freundlich isotherm</b>				
$K_F$ ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	43.957	14.853	215.742	206.496
$n$	3.675	3.022	8.739	6.842
$R^2$	0.942	0.950	0.903	0.897
MPSE	0.608	0.722	0.961	1.970
ARE	3.773	5.141	5.725	11.021
<b>Redlich–Peterson isotherm</b>				
$A_{RP}$ (L/mg) <sup><math>\beta</math></sup>	18.038	4.330	363.175	476.944
$K_{RP}$ (L/g)	0.124	0.059	1.188	1.485
$\beta$	1.000	0.996	0.956	0.952
$R^2$	0.992	0.986	0.988	0.987
MPSE	0.183	0.378	0.250	0.603
ARE	1.306	2.840	1.530	3.952
<b>Brouers–Sotolongo isotherm</b>				
$Q_{\text{max}}$ ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ )	129.255	59.928	382.280	405.062
$K_w$ (L/mg)	0.163	0.049	0.634	0.617
$\alpha$	0.772	1.032	0.388	0.423
$R^2$	0.995	0.996	0.985	0.979
MPSE	0.176	0.204	0.357	0.921
ARE	1.007	1.216	2.145	4.955

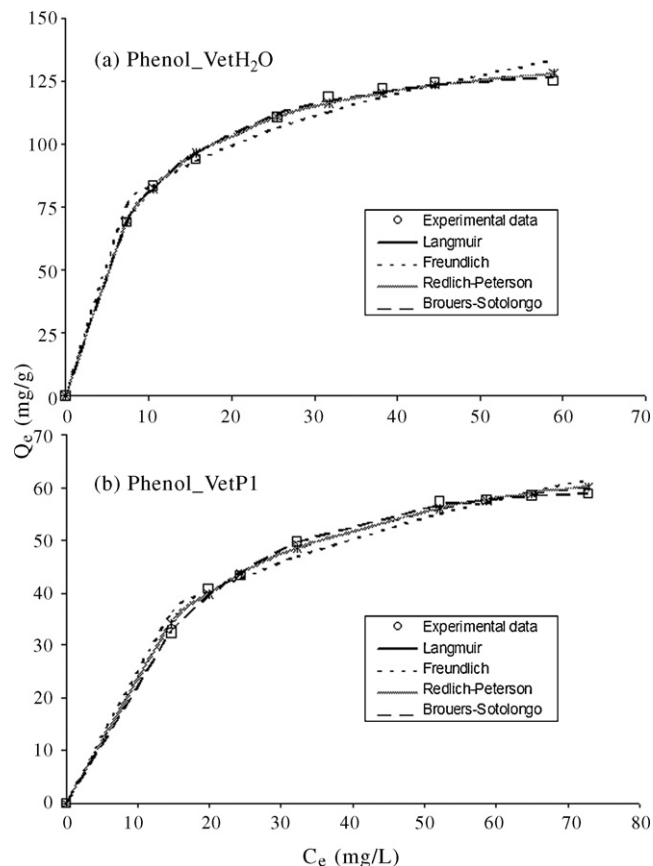


Fig. 3. Isotherm modelling of phenol adsorption onto vet-H<sub>2</sub>O (a) and vet-P1 (b) at 25 °C.

lar size <0.62 nm, when compared to the molecular mass of MB (MW = 373.9, molecular size <1.4 nm) a highest amount of phenol is adsorbed on vet-H<sub>2</sub>O according to the lowest average pores diameter of this AC sample. Indeed, vet-H<sub>2</sub>O has a higher percentage of micropore volume ( $V_{mi}/V_{tot}$ ) 52% (33% of micropore volume for vet-P1) suitable for phenol adsorption.

On the other hand, the larger average pore diameter of vet-P1 and mesopore volume leads to a higher amount of MB adsorbed [26,27] on vet-P1 (Fig. 3a and b; Table 3).

The results from the application of the four models are listed in Table 3. As observed for the *P. oceanica* fibres, the Redlich–Peterson model is the most adapted for fitting adsorption isotherms of MB on the ACs, the highest values of  $R^2 = 98.8\%$  and  $98.7\%$ , respectively are obtained for vet-H<sub>2</sub>O and vet-P1. Moreover, the lowest values of ARE (1.53 and 3.92) for vet-H<sub>2</sub>O and vet-P1, respectively, and MPSE value (0.25) for vet-H<sub>2</sub>O, are provided by this model. However, for phenol adsorption the BSI model assuming adsorption on a heterogeneous surface is the best-fitting equation. It provides the best  $R^2$  values (99.5% and 99.6% for vet-H<sub>2</sub>O and vet-P1, respectively) and the lowest values of ARE (1.007 and 1.216) and MPSE (0.176 and 0.204), respectively for vet-H<sub>2</sub>O and vet-P1. Indeed, ACs have strong heterogeneous surfaces. This heterogeneity of AC surfaces stems from two sources known as geometrical and chemical ones [28]. Geometrical heterogeneity is a result of differences in size and shape of pores, cracks, pits and steps. Chemical heterogeneity is associated with different functional groups such as carbonyls, phenols, lactones, aldehydes, ketones, quinines, hydroquinones, anhydrides or etheral structures and delocalized electrons of the graphitic structure determining the apparent chemical character of an AC surface [29]. Both chemical and geometrical heterogeneities contribute strongly to the adsorption of phenol on ACs [28].

On the other hand, considering the modelling behaviour of both BSI and FI isotherms, which are used to estimate the heterogeneity within the sorption system, it is clear that the BSI is the most performing model. Indeed, when the isotherm curve has an obvious saturation plateau, the commonly used Freundlich model became inappropriate at all. However, in such condition, the BSI is still suitable to show satisfactory fit to the experimental data. Thus, for any sorption equilibrium phenomenon, ending with a saturation regime, the widely used FI and its surface heterogeneity assumption will be no longer appropriate, especially if the BSI model gives a clear and physically reliable idea on the energy landscape heterogeneity of the studied sorption system.

### 3.3. Mechanistic interpretations of the involved sorption systems through isotherm modelling

It is believed that the isotherm shape can provide qualitative information on the nature of the solute surface interaction based on the nature of the solute–surface interaction. Although the FI involves adsorption on heterogeneous surfaces, our curves could not be fitted using the FI, since a plateau regime was observed in all studied sorption systems (both porous and non-porous sorbents).

For the case of phenol, and among all studied models, the BSI involving adsorption on a heterogeneous surface is definitely the most suitable one to satisfactorily describe biosorption of phenol onto posidonia fibres but as well adsorption of phenol on the ACs giving the highest squared correlation coefficients and the lowest MPSE and ARE (Tables 2 and 3). Nevertheless, for posidonia and as well for the ACs, when MB is the adsorbate, the BSI did not show the best fit to the experimental curves, based on the error deviation calculation, which pointed out that the RPI is the best-fitting model. However, based on the fact that error estimation differences between those two models is too small and, that the RPI is a pure empirical equation, contrary to the BSI model which is providing parameters with physical meanings, the last one would be the most interesting fitting-model. Indeed, it is not sufficient to “mathematically” fit experimental data, but essentially to find out a suitable equation showing a good fit to isotherm curves and providing probable explanations to the studied adsorption phenomenon, based on the variation of its constants. As well, the small BSI  $\alpha$ -value for MB sorption confirms the best fitness of the LI model (as a special case of RPI when  $\beta \approx 1$ ) for MB adsorption since less heterogeneity is deduced from the BSI related assumption.

Overall, the present study had shown two different behaviours related to the nature of experimented pollutant. In that context, for posidonia which is a non-porous adsorbent and as well for the ACs which are porous ones, from the difference between the exponent  $\alpha$  related to the phenol adsorption and the one calculated for MB adsorption, it is obvious that, energetically, there is more heterogeneity when phenol is involved and less when MB is the adsorbate.

For posidonia, such a trend could be explained by the fact that with MB electrostatic attractions are the main sorption mechanism [25]. For the case of phenol adsorption on posidonia, electron donor–acceptor, electrostatic and hydrophobic interactions could be involved, which leads to a heterogeneous energy landscape in this sorption system [24].

MB electrostatic interactions with the surface of ACs are also the main sorption interactions [30–32]. The adsorption mechanisms of phenol on the ACs should be dominated by interactions similar to the one involved in adsorption of phenol on posidonia. Such an observation indicates that the porous network only play a role on the adsorption capacity (15–50 times larger for the ACs) but not on

the adsorption mechanism. Our study confirm the results obtained by several works indicating that in liquid adsorption on solids, the role of surface functionalities increases significantly relative to pore size distribution or surface area and in many cases dominates [28]. The pore volume of carbon does not decide about phenol adsorption solely in the range of low equilibrium concentrations. The influence of surface functionalities is meaningful. Indeed phenol adsorption is governed by several interactions, such as, (i)  $\pi$ – $\pi$  dispersion interactions between the basal plane of the carbon and the aromatic ring of the adsorbate [33], (ii) electron donor–acceptor intercalations between the aromatic phenolic ring and the basic surface oxygens [34], (iii) electrostatic attraction and repulsion when ions are presented and [28] (iv) solvent effect [35], reflecting the heterogeneity of the adsorption energies.

## 4. Conclusion

The new BSI equation, as well, the LI, FI and RPI were used to described adsorption equilibrium of phenol and MB, respectively onto a non-porous adsorbent, *P. oceanica* fibres and two porous adsorbents, ACs prepared from vetiver roots. Using only  $R^2$  to determine the best-fitting model was not sufficient, calculation of the error deviation using both the MPSE and the ARE allow us to determine the best-fitting model. Indeed, according to the Freundlich related results, the use of this model provides the lowest  $R^2$  and the highest MPSE and ARE, since the adsorption curves have a clear saturation plateau.

Overall, the present study shown two different behaviours related to the nature of experimented pollutant. For posidonia, which is a non-porous adsorbent, and as well for the ACs, which are porous ones, the RPI model was the best-fitting model when MB was the solute molecule whereas BSI was the best equation to describe phenol adsorption. The BSI model could provide adsorption capacity values in agreement with the maximum amount absorbed and the alpha parameters calculated reflected the adsorption energies heterogeneity. This study confirms the key role played by of surface functionalities in phenol adsorption mechanism.

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