NON-LINEAR MODELLING OF PHENOL ADSORPTION USING POROUS AND NON-POROUS LOW COST SORBENTS

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ABSTRACT

Three isotherm models were used to describe adsorption equilibrium of a toxic chemical compound, phenol, onto a non porous adsorbent (Mediterranean *Posidonia oceanica* fibres) and a porous adsorbent, activated carbon prepared from Caribbean *Vetiveria zizanoides* roots. The adsorption characteristic parameters obtained were calculated using classical adsorption isotherm, i.e. the Langmuir (LI), Freundlich (FI) and Redlich-Peterson (RPI) isotherms. Calculation of the error deviation was performed using both R^2 and the average relative error (ARE). Thus, among the studied models, the Langmuir equation involving adsorption on a homogeneous actives site is definitely the most suitable modelling tool to satisfactorily describe biosorption of phenol on Posidonia and vetiver-derived activated carbon, by providing the highest squared correlation coefficients and the lowest ARE.

Keywords: adsorption; isotherm, activated carbons, posidonia, phenol modelling, surface heterogeneity

INTRODUCTION

Phenol is a very toxic and hazardous chemical compound. Indeed, many phenol-based substances are confirmed or suspected human carcinogens (Gupta et al., 1998). Worldwide, phenolics are present at different concentrations (0.002 – 2.6 mg/L) in the effluents generated from many industries such as petroleum refineries, pulp and paper mills, dyes, pharmaceuticals, plastics and rubber-production factories.

As one of the most common organic pollutants of industrial wastewater, phenol had to be removed before being discharged into receiving water streams. Commonly,

biodegradation (Santos and Linardi, 2004; Margesin et al., 2005), membrane separation (Kujawski et al., 2004) and chemical oxidation (Ovejero et al., 2005) are the most widely used techniques to treat phenol-containing wastewater. But for the developing countries, the use of these technologies on great scale is not possible mainly for economic reasons. Hence, low cost, efficient and eco-friendly techniques are required and the most appropriate method seems to be adsorption onto cheap matrix. In the literature there are many materials reported as phenol adsorbent such as activated carbon derived from bioresources (Bertoncini et al., 2003; Tancredi et al., 2004) activated sludge (Aksu and Gönen, 2004), pumice (Akbal, 2005) and clay materials (Al-Asheh et al., 2003).

The focus of this research was to model the phenol sorption phenomenon onto *P. oceanica* fibres and an activated carbon from Vitiver biomass, within an overall comparative study on the sorption onto porous and non-porous media.

2. MATERIALS AND METHODS

2.1. Biomass Preparation

Posidonia oceanica (L.) delile 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 with distilled water to remove salt and then dried in an oven at 40°C for 48 hours to a constant weight.

2.2. Activated Carbons Preparation

The activated carbon (AC) was 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 the chemical activation, 3 g of the raw material was impregnated in phosphoric acid (H_3PO_4) 85% for 24 h, in order to facilitate the access of the acid inside the particles (Sabio et al., 2004). Impregnation ratio; X_P (g H_3PO_4 /g precursor): 1:1. After impregnation, the sample is dried for 4 h at 105°C in a drying oven. The sample thus dried is pyrolyzed under nitrogen flow at 600°C for 1 h. After cooling, until ambient temperature, the AC thus obtained is washed with distilled water until stabilization of the pH, and then dried overnight using a drying oven at 105°C.

2.3. Phenol Solution Preparation

Synthetic solution of analytical grade phenol (Merck, Germany) was prepared by dissolving an accurately weighted amount (1000 mg/L) in distilled water and subsequently diluted to obtain the required concentrations. Spectrophotometric scanning of dilute solutions was performed, and absorbance maximum was fixed at 270 nm.

2.4. Isotherm Sorption Assays

Equilibrium Adsorption experiments with 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 phenol solution (i.e. 10 g/L) for the desired concentration and under initial solution pH (5.2). Studies were conducted at 30±2°C using a thermo-regulated water bath operating at 100 rpm. For vetiver derived activated carbons, a fixed amount of carbon (40 mg) was weighted into conical flasks containing 100 mL of different initial concentrations (20-100 mg/L) of phenol. The flasks were then agitated at 25°C until to reach equilibrium time, previously determined by kinetics tests.

At equilibrium, after filtration (case of activated carbons) and centrifugation at 4000 rpm for 2 min (case of posidonia fibres), phenol residual concentrations were estimated using the spectrophotometric technique.

Thereafter, in order to monitor phenol removal, biosorption capacity at equilibrium time (*Qe*) will be determined according to the following equation:

$$Qe = \left[(Co - Ce) \times V / M \right] \qquad (mg / g) \qquad (1)$$

Where *Co* and *Ce* are, respectively, the initial and equilibrium liquid-phase concentrations of the adsorbate (mg/L), *V* the solution volume (L), and *M* is the mass of the dried adsorbent (g).

2.5. Modelling Theoretical Background

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 R² values more significantly during the linear analysis, the non-linear analysis might be a method of avoiding such errors (Ho and Wang, 2004; Kumar and Sivanesan, 2005).

In the present study, three isotherm models were tested under two different adsorption systems (i.e. porous and non porous sorbent media using phenol as sorbate molecule)

namely, Langmuir (1918), Freundlich (1906) and Redlich-Peterson (1959). 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 on to a surface with a finite number of similar active sites. The well-known expression of the Langmuir model is given by Eq. (2):

$$Qe = (Q^o . K_L . Ce) / (1 + K_L . Ce) \qquad (2)$$

where Qe (mg/g) and Ce (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 Eq. (3):

$$Qe = K_F . (Ce)^{1/n} \qquad (3)$$

where K_F and n are the Freundlich constants characteristic of the system. K_F [(mg/g)*(L/mg)$^{(1-n/n)}$] 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 Langmuir and Freundlich isotherms into a single equation and presents a general isotherm equation as follows:

$$Qe = (A_{R-P} . Ce) / (1 + K_{R-P} . Ce^{\beta}) \qquad (4)$$

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

2.6. Error Estimation

In the present research, the average relative error deviation (ARE) (Kapoor, 1989) test is used to estimate the goodness of the fit of the studied models. The related equation is given by Eq. (5):

$$ARE = \frac{1}{N} \sum \left| (Qe_{cal} - Qe_{exp}) / Qe_{exp} \right| \times 100 \tag{5}$$

Where N is the number of experimental data points, Qe_{cal} (mg/g) is the theoretically calculated adsorption capacity at equilibrium, Qe_{exp} (mg/g) is the experimental adsorption capacity at equilibrium.

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

3. RESULTS AND DISCUSSION

3.1. Adsorption Isotherm Modelling onto Posidonia Fibres

The equilibrium modelling data of phenol sorption onto raw Posidonia fibres using the Freundlich, Langmuir and Redlich-Peterson, in addition to the error calculations, are mentioned in Table 1.

Table 1: **Isotherm modelling calculation related to the phenol sorption onto raw *Posidonia oceanica* fibers**

Langmuir model	
Q° (mg/g)	5.085
KL (L/mg)	0.017
R^2	**0.990**
ARE	**6.077**
Freundlich model	
K_F ($mg^{1-1/n}L^{1/n}g^{-1}$)	0.295
n	1.966
R^2	0.948
ARE	21.142
Redlich-Peterson model	
A_{RP} L/mg$)^{\beta}$	0.089
K_{RP} (L/g)	0.017
β	1.000
R^2	**0.990**
ARE	7.214

The graphic correlation between the experimental data and the theoretical models for the adsorption systems are given in Fig. 1.

First of all, from Table 1, the experimental data were better described by the Langmuir model by providing the highest R^2 (99.0%) and the lowest ARE (6.077%), which supposes an eventual monolayer adsorption of phenol molecules onto the biomass surface. Besides, it is obvious that the Freundlich model is not suitable to fit the isotherm curves for such sorption system. Indeed, according to the Freundlich related results, the use of this model provides the lowest R^2 and the Highest ARE. Such trend is quite logical since the Freundlich equation is a pure exponential one, which means that when $Ce \sim \infty$, Qe will also extend to ∞. However, for the phenol adsorption phenomenon, since there is a saturation plateau, the calculated Qe will necessary tend towards a constant (i.e. maximum adsorption capacity).
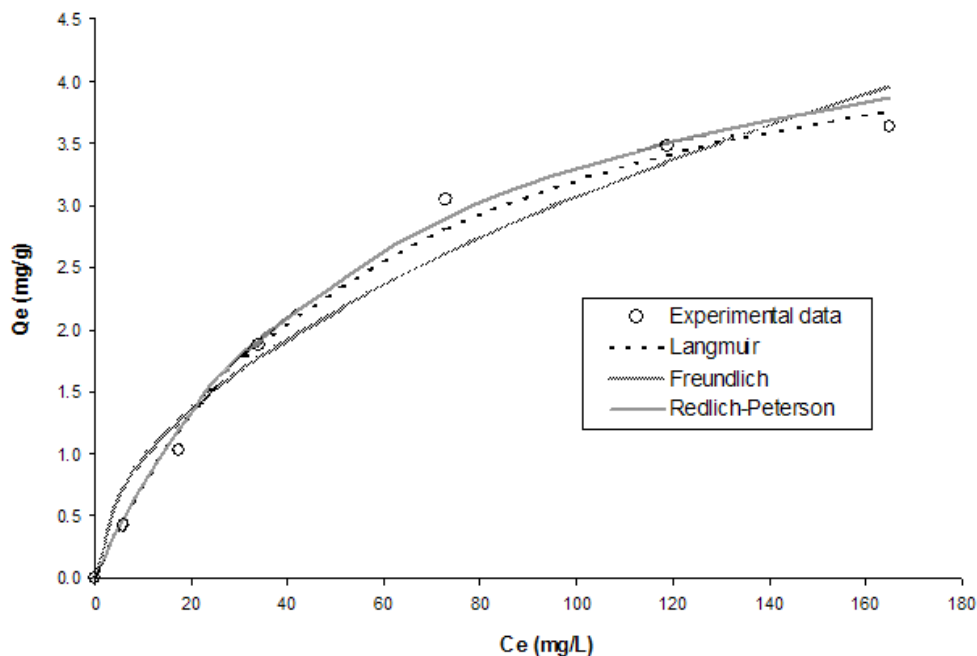

Figure 1: Isotherm modelling of phenol adsorption onto raw *Posidonia oceanica* fibres at 30°C

3.2. Adsorption Isotherm Modelling onto Vetiver Roots-Derived Activated Carbon

In addition to its acid activation, the experimented carbon has two other textural characteristics, i.e. a large specific surface area (1272 m²/g) and an average pores diameter of 2.83 nm, which would enhance the sorption capacity of the activated carbon (Dabowski et al., 2005).

The results from the application of the isotherm equations are depicted in Fig. 2 and listed in Table 2.
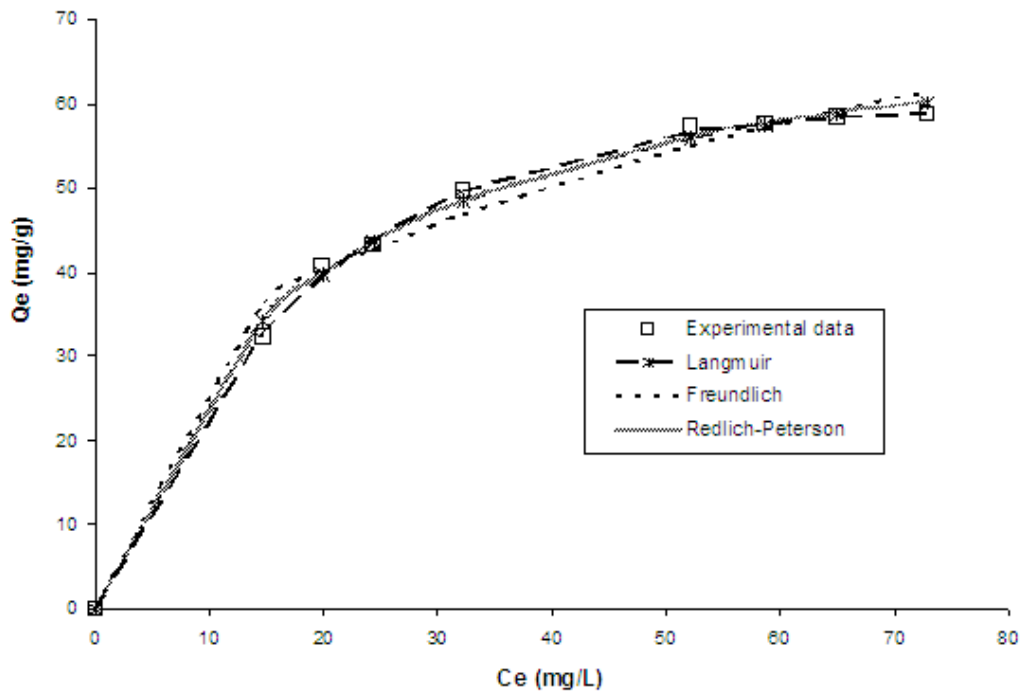
Figure 2: Isotherm modelling of phenol adsorption onto chemically activated vetiver roots at 30°C

Table 2: Isotherm modelling calculation related to the phenol sorption onto chemically activated carbons from vetiver roots

Langmuir model	
$Q^{°}$ (mg/g)	74.445
KL (L/mg)	0.058
R^2	**0.986**
ARE	**2.793**
Freundlich model	
K_F ($mg^{1-1/n}L^{1/n}g^{-1}$)	14.853
n	3.022
R^2	0.950
ARE	5.141
Redlich-Peterson model	
A_{RP} L/mg)$^{\beta}$	4.330
K_{RP} (L/g)	0.059
β	0.996
R^2	**0.986**
ARE	2.840

As observed for the phenol sorption onto Vetiver carbon, the Langmuir isotherm model is the best-fitting equation, assuming therefore an adsorption process involving homogeneous active sites. Indeed; it provides the best R^2 value (98.6%) and the lowest values of ARE (2.79%). In addition, statistically spoken, the Redlich-Peterson is as much performing since it provides the same R^2 (98.6%) and an insignificant higher ARE value (2.84%). Such behaviour is mathematically justified since the Redlich-Peterson equation is a special case of the well-known Langmuir one, when the exponent β is quite equal to unity (0.996 in the present case).

On the other hand, since the experimental isotherm curve (*Cf.* Fig. 2) has a saturation plateau, the commonly used Freundlich model became inappropriate to fit. 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. The only case in which this model will be useful is when low concentrations and pressures are involved, which would limit the eventual interpretation of the overall sorption phenomenon.

4. CONCLUSION

The Langmuir, Freundlich and Redlich-Peterson isotherms were used to describe adsorption equilibrium of phenol onto a non porous adsorbent, *Posidonia oceanica* fibres and a porous adsorbent, activated carbons prepared from vetiver roots. The results showed that, for both case, the use of the Freundlich model provides the lowest R² and the Highest ARE values, since the adsorption curves have a clear saturation plateau. Besides, for posidonia biomass (non porous adsorbent), and as well for the vetiver activated carbon (porous adsorbent), the Langmuir model was the best fitting model to satisfactorily describe phenol adsorption, suggesting that, as far as phenol is the sorbate, the porous nature of the matrix does not induce any changes in the energy landscape (i.e. most of the active sites have the same affinity towards the phenol molecules).

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