

Uptake of phenol from aqueous solutions by adsorption in a *Pinus pinaster* bark packed bed

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Abstract

The adsorption of phenol from aqueous solutions using a column packed with pre-treated *Pinus pinaster* bark was studied. The influence of the inlet phenol concentration (0.01 or 0.1 g/L) and the flow rate (6, 15.6 or 30 mL/min) on the breakthrough curves was analysed. An increase in the flow rate, decreased the time necessary to reach the breakthrough point and, for the highest inlet concentration, the dynamic capacity of the bed, from 7.5 to 0.4 min and from 0.38 to 0.15 mg phenol/g o.d. bark, respectively, at 0.1 g/L. The LUB Design Approach was used to determine the equivalent length of unused bed. The lower LUB values, which imply a better utilization of the bark bed, were obtained at the higher flow rate. A model which considered the effect of axial dispersion was successfully used to describe the fixed-bed operation behaviour for the lower flow rates. For the lowest inlet phenol concentration, the axial dispersion coefficient increased significantly when the flow rate increased.

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1. Introduction

Adsorption systems have been rapidly gaining importance as wastewater treatment processes to produce high quality effluents with low concentration of dissolved organic compounds. The most frequently employed adsorption technique is the process performed on a fixed bed of granular activated carbon, due to ease of operation and no carbon loss problem [1]. However, activated carbons are expensive and, therefore, their use may imply carrying out regeneration and reactivation procedures.

The search for new and innovative treatment techniques has focused attention on the adsorption capacities of other adsorbents, such as agricultural by-products and lignocellulosic residues [2–5], which are readily available and do not need to be regenerated due to their low cost. Numerous studies on the

sorption of metals and organic pollutants by these alternative adsorbents in batch systems have been reported [3,6]. However, the adsorption on continuous flow fixed-bed columns is often preferred, since it is simple to operate, gives high yields and can be scale-up from a laboratory process [7]. In order to design and operate fixed-bed adsorption processes successfully, the adsorption equilibrium and dynamics for specified systems must be known; that is, the breakthrough curves under specified operating conditions must be predictable. The shape of this curve is determined by the shape of the equilibrium isotherm and it is influenced by the individual transport processes in the column and in the adsorbent.

Phenol and its derivatives appear in the effluents from many industries, such as coking, synthesis rubber, pharmaceuticals, petrochemical, paper, textiles and wood [5]. Because of their toxicity, their prevention or removal is extremely important [8,9].

To reduce the use of phenol in the preparation of phenol-formaldehyde (PF) adhesives for the wood industry, we have studied the use of lignocellulosic materials, such as *Pinus pinaster* bark tannins and acetosolv lignin, to partially replace phenol in the formulation of adhesives for plywood manufacture, obtaining good results [10,11]. On the other hand, in a previous

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Nomenclature

a	mass-transfer area per unit bed volume (m^{-1})
C	outlet phenol concentration (g/L)
C_0	inlet phenol concentration (g/L)
d_p	particle diameter (m)
D_L	axial dispersion coefficient (m^2/min)
e_i	i th experimental data point
erf	error function
E	absolute errors
k	kinetic coefficient in Lin–Wang model (min^{-1})
k_f	mass-transfer coefficient in the liquid phase (m/h)
L	bed length (m)
LES	length of the ideal fixed-bed adsorber (cm)
LUB	equivalent length of unused bed (cm)
m	weight of oven-dried bark (g)
n	ratio between void and non-void fraction of the bed
N	number of the data points
q	phenol concentration in the stationary phase
Q	flow rate of phenol aqueous solution (mL/min)
Re	Reynolds number
s_i	i th model-predicted value
Sc	Schmidt number
Sh	Sherwood number
t	operating time (min)
$t_{\text{breakthrough}}$	breakthrough time for a concentration of 1 mg/L (min)
t_{min}	minimum time to saturate the bed (min)
v	interstitial velocity of the carrier fluid (m/min)
V	total volume referred to the unit transversal area of the void bed
V_{min}	minimum volume to saturate the bed per unit transversal area (m^3/m^2)
W_e	dynamic capacity of the bark (mg of phenol adsorbed/g of oven-dried bark)
W_{sat}	amount of adsorbed phenol at the saturation of bed (mg of phenol adsorbed/g of oven-dried bark)
X	fraction of phenol remaining in aqueous solution
Y	fraction of phenol adsorbed
z	distance from the inlet of the mobile phase
<i>Greek letters</i>	
ε	void fraction of the bed
τ	adsorption time when C is one-half of C_0 (min)

work [12], we have investigated the adsorption of phenol by pine bark in batch mode as an alternative technology for its removal from wastewaters. The aim of the present work was to study the adsorption of phenol by pine bark in continuous mode using a packed bed column. In order to analyse the column dynamics in the sorption process, the influence of the flow rate and the inlet phenol concentration on the breakthrough curves was investigated.

2. Materials and methods

P. pinaster bark from a local sawmill was air-dried to a moisture content close to equilibrium (approximately 15%). It was ground in a hammer mill to a size below 2 mm. The adsorption experiments were carried out with the fraction of particle size between 0.5 and 1 mm. Prior to adsorption experiments, in order to polymerise and immobilise the water-soluble phenolic compounds, the ground bark was treated with formaldehyde in acid medium under previously optimised conditions [13]: A 1:4 (v/v) mixture of 37% formaldehyde and 0.2N H_2SO_4 was heated to 50 °C, bark was added in the ratio of 4 g of bark per 10 mL of formaldehyde, and after stirring at 50 °C for 2 h, the bark was filtered out with a Büchner funnel, washed with distilled water until the pH of the filtrate was approximately of 4, and air-dried. Finally, prior to adsorption experiments the pre-treated bark was soaked in water for 24 h and the floating particles were removed.

Packed bed experiments were performed at room temperature (approximately 20 °C) in a cylindrical Pyrex glass column with a height of 23.7 cm and an internal diameter of 1.86 cm. Glass-wool was placed in the upper and lower part of the column to retain the adsorbent. The effective bed length was 15 cm, being the length-to-diameter ratio 8.06. The bulk density and void fraction of the bed were determined, with values of 0.63 g/cm^3 and 0.505, respectively. Bulk density was calculated as the ratio between the oven-dried weight of bark and its bulk volume, which was determined by displacement after immersion in *n*-heptane [14].

A phenol solution of known concentration (0.01 or 0.1 g/L) was pumped through the stationary bed of bark in an up flow mode using a peristaltic pump at flow rates of 6, 15.6 or 30 mL/min .

One of the most important parameters influencing the adsorption capacity is the pH of the solution. In a previous batch study [12], it was found that the higher sorption percentage was obtained at the pH of the phenol solution (approximately 4.5). Therefore, since *P. pinaster* bark has acid character [12], it was not necessary to precondition the bark.

The phenol concentration of the effluent was measured by means of a HP5890 Series II chromatograph with FID detector and a capillary column HP-1 [12], and the amount of phenol retained by the bark was then calculated. In each adsorption experiment effluent samples were taken at predetermined times until the inlet phenol concentration was attained in the outlet stream.

3. Results and discussion

In a previous work [12], the static adsorption of phenol from aqueous solutions using *P. pinaster* bark was studied, and the influence of solid/liquid ratio (1/50 and 1/100 g/mL), pH (4.5–9.5), initial concentration of phenol (0.01, 0.1 and 1 g/L) and contact time on the adsorption capacity of the bark has been analysed. The percentage of phenol adsorbed was greater for the higher solid/liquid ratio and for the lower pH, but decreased when the initial phenol concentration was increased. Phenol adsorption kinetics was described using a model based on the

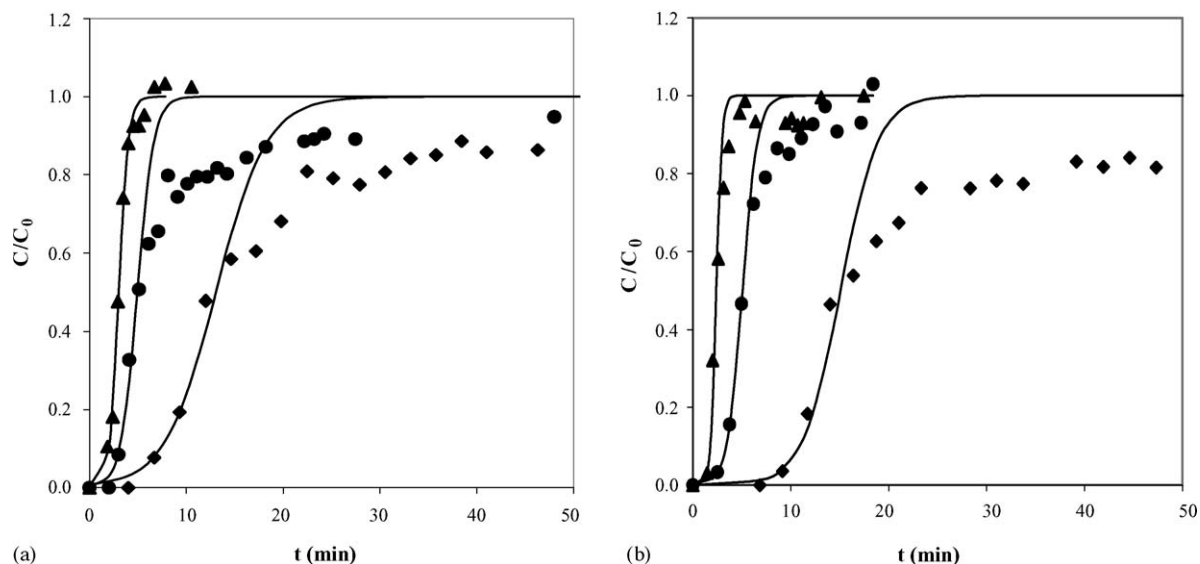


Fig. 1. Experimental and calculated (Eq. (4)) breakthrough curves for the adsorption of phenol on *Pinus pinaster* bark for an inlet concentration of (a) $C_0 = 0.01$ g/L and (b) $C_0 = 0.1$ g/L (◆, 6 mL/min; ●, 15.6 mL/min; ▲, 30 mL/min; lines, Eq. (4)).

control of mass transfer within the pores of the bark and the equilibrium data were satisfactorily fitted by the BET and Freundlich isotherms.

Since in practice the sorption of pollutants is carried out more economically in a continuous mode, the present work investigates the ability of pine bark in a packed bed column to remove phenol from aqueous solutions using the lower initial phenol concentrations of those previously essayed.

3.1. Effect of flow rate and inlet phenol concentration

The effect of the flow rate on the sorption of phenol by the bark was investigated. The breakthrough curves developed under the three different flow rates (6, 15.6 and 30 mL/min) are presented in Fig. 1a and b for inlet phenol concentrations of 0.01 and 0.1 g/L, respectively. As can be observed, initially, the phenol was rapidly adsorbed on the bark and the effluent (from the upper part of the bed) was almost free of solute. As the phenol solution continued to flow, the bark was progressively saturated with phenol and, therefore, the outlet concentration started to increase until the saturation point was reached.

In practice, system operation is interrupted when the effluent concentration reaches a certain level, called breakthrough concentration, above which it is not profitable to continue the operation. Although the experiments were performed until the saturation of the bed, when calculating the characteristic parameters of the system, a breakthrough concentration of 1 mg/L was considered [15]. The experimental breakthrough times, determined from Fig. 1a and b, are shown in Table 1. As can be observed, the breakpoint decreased when flow rate increased, and more significantly for the higher inlet phenol concentration, the service time of the bark bed being then reduced.

In addition, decreasing flow rate resulted not only in the breakthrough time increasing but also in the breakthrough curve broadening, which in turn resulted in an increase in the difference between the breakthrough time and the saturation time.

Once the breakthrough time ($t_{\text{breakthrough}}$) was determined, the dynamic capacity of the bark (W_e), i.e. the amount of phenol adsorbed on the bark at the breakpoint, was calculated (Table 1) as:

$$W_e \left(\frac{\text{mg of phenol adsorbed}}{\text{g of oven-dried bark}} \right) = \frac{(C_0 - C)Q t_{\text{breakthrough}}}{m} \quad (1)$$

where C and C_0 are the outlet and inlet phenol concentrations, respectively, Q the flow rate of the phenol aqueous solution and m is the weight of oven-dried bark.

It can be observed that at the lower inlet concentration, the capacity is independent of the flow rate, however, at the higher concentration, an increase of the flow rate from 6 to 30 mL/min, implied a decrease in the dynamic capacity of approximately 60%. The use of high flow rates reduces the contact time between the phenol solution and the bark, thus allowing less time for adsorption to occur, which leads to an earlier breakthrough of phenol, as the breakthrough time values indicate (Table 1).

As regards the inlet concentration, for the higher flow rates, an increase in the inlet concentration diminished the breakthrough time, due to the high phenol concentration which saturated the bark more quickly. At the flow rate of 6 mL/min, the inlet concentration in the range essayed had no influence on the break-

Table 1

Experimental breakthrough time, dynamic capacity of the bark and equivalent length of unused bed (LUB) for the flow rates and inlet phenol concentration essayed

Q (mL/min)	C_0 (g/L)	$t_{\text{breakthrough}}$ (min)	W_e (mg phenol/g o.d. bark)	LUB (cm)
6	0.0102	7.17	0.0354	10.35
15.6	0.0111	3.03	0.0383	10.56
30	0.0103	1.76	0.0377	6.10
6	0.1020	7.45	0.3768	9.27
15.6	0.1020	0.74	0.1027	9.11
30	0.1130	0.43	0.1479	7.77

through time; nevertheless, the dynamic capacity of the bark increased with an increase of concentration from 0.01 to 0.1 g/L (Table 1). A high concentration gradient provides a high driving force for the adsorption process, which may explain why higher adsorption capacities were achieved at the highest phenol concentration.

3.2. Determination of unused bed length

Apart from the breakthrough time of a bed of specified height, other parameter for the design of an adsorber is the equivalent length of unused bed (LUB), which can be obtained by analysis of the breakthrough curves according to Eq. (2):

$$\text{LUB} = \left(1 - \frac{W_c}{W_{\text{sat}}}\right) L \quad (2)$$

where L is the bed length and W_{sat} is the adsorbed phenol at the saturation of bed. It is used to determine the length of a full-scale adsorbent bed as the sum of the length of the ideal fixed-bed adsorber (LES), i.e. the stoichiometric length of bed needed to produce the desired adsorption capacity of the bed, based on ideal step-function behaviour, plus the LUB, as additional length.

The LUB Design Approach assumes that the adsorption bed is long enough to produce constant-pattern behaviour and that the system is governed by a convex isotherm [16]. In a previous work [12], the experimental equilibrium data for the adsorption of phenol by *P. pinaster* bark fitted to the Freundlich isotherm, and, therefore, the last assumption is true. The LUB was determined from the breakthrough curves, obtaining the results shown in Table 1. It can be observed that the best utilization of the bed (the lower values of LUB) was achieved for the experiments performed at the highest flow rate. Thus, the percentages of the adsorption capacity used at the breakthrough time were approximately 60 and 50% for 0.01 and 0.1 g/L, respectively.

3.3. Mathematical modelling of breakthrough curves

The model adopted in the present study for predicting the breakthrough curves was proposed by Lin and Wang [15] to describe the phenol adsorption by an Amberlite resin. The model assumes that the rate of decrease in the fraction of adsorbed phenol (Y) is proportional to Y and to the fraction of phenol remaining in the aqueous solution and passing through the stationary bark bed ($X = C/C_0$):

$$-\frac{dY}{dt} = kYX \quad (3)$$

Considering that τ is the time corresponding to a phenol removal of 50% ($X = 0.5$) and that $Y = 1 - X$, the integrated form of Eq. (3) becomes:

$$\frac{C}{C_0} = \frac{1}{1 + \exp[k(\tau - t)]} \quad (4)$$

Table 2
Fitted values of the kinetic parameters of Eq. (5)

Q (mL/min)	τ (min)	$1/k$ (min)	r^2
$C_0 = 0.01$ g/L			
6	13.0	2.615	0.97
15.6	4.9	0.842	0.96
30	3.0	0.497	0.95
$C_0 = 0.1$ g/L			
6	15.1	1.898	0.94
15.6	5.1	0.760	0.99
30	2.4	0.284	0.94

which can be linearised as:

$$t = \tau + \frac{1}{k} \ln \left(\frac{C}{C_0 - C} \right) \quad (5)$$

Regressing the experimental values of t on $\ln [C/(C_0 - C)]$ afforded lines with r^2 values larger than 0.94, allowing the estimation of the parameters k and τ . Table 2 lists the values of k and τ obtained for each inlet concentration of phenol and flow rate used, and Fig. 1a and b shows the experimental data together with the calculated ones by means of Eq. (4). It can be observed that there is a good fit of the model equation to the data only for the experiments carried out at the highest flow rate (30 mL/min), independently of the inlet phenol concentration used. For the experiments at 6 and 15.6 mL/min, the breakthrough curves obtained were asymmetrical and the model, which assumes an ideal plug flow behaviour that implies symmetrical breakthrough curves, only predicts satisfactorily the breakthrough curves for $t \leq \tau$.

Axial dispersion is one of the mechanisms responsible for the broadening of concentration profiles in fixed-bed adsorbers [17] and, therefore, it has been taken into account in the modelling of the breakthrough curves obtained at low flow rates.

The governing equation for predicting the fixed-bed dynamics, with provision for axial dispersion (D_L), is:

$$\frac{\partial(vC)}{\partial z} - D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial t} + \frac{1}{n} \frac{\partial q}{\partial t} = 0 \quad (6)$$

where v is the interstitial velocity of the carrier fluid, C and q the phenol concentration in the mobile and stationary phase, respectively, z the distance from the inlet of the mobile phase, $n = \varepsilon/(1 - \varepsilon)$, where ε is the void fraction of the bed and t is the operating time.

The assumptions associated with the above equation are: (a) no chemical reactions occur in the column; (b) only mass transfer by convection is significant; (c) radial dispersion is negligible; (d) the temperature in the column is uniform and invariable with time; (e) the flow rate is constant and invariable with the column position.

For a long fixed bed, initially free of solute and with a constant inlet concentration, C_0 , the solution of Eq. (6) is [18]:

$$\frac{C}{C_0} = \frac{1}{2} \left\{ 1 + \operatorname{erf} \left[\left(\frac{vL}{4D_L} \right)^{1/2} \frac{V - V_{\text{min}}}{(VV_{\text{min}})^{1/2}} \right] \right\} \quad (7)$$

Table 3
Fitted values of the kinetic parameters of Eq. (7) and liquid phase mass-transfer coefficients

Q (mL/min)	v ($\times 10^{-2}$ m/min)	D_L ($\times 10^{-3}$ m ² /min)	V_{\min} (m ³ /m ²)	r^2	E (%)	$(k_{fa})_{\text{exper}}^a$ (h ⁻¹)	$(k_{fa})_{\text{correl}}^b$ (h ⁻¹)
$C_0 = 0.01$ g/L							
6	4.37	2.11	0.319	0.97	4.79	–	335.3
15.6	11.37	6.08	0.327	0.95	5.58	–	461.3
30	21.86	–	–	–	–	327.9	700.6
$C_0 = 0.1$ g/L							
6	4.37	1.80	0.387	0.94	8.16	–	335.3
15.6	11.37	1.84	0.304	0.98	4.14	270.9	461.3
30	21.86	–	–	–	–	470.4	700.6

^a Eq. (9).

^b Eq. (10).

where $\text{erf}(x)$ is the error function of x , V the total volume referred to the unit transversal area of the void bed ($V = v\epsilon t$), V_{\min} the minimum volume to saturate the bed per unit transversal area ($V_{\min} = v\epsilon t_{\min}$) and L is the bed length.

The model parameters, D_L and V_{\min} , for the adsorption of phenol on *P. pinaster* bark were obtained fitting the experimental data to Eq. (7) using TABLECURVE[®] program with r^2 being larger than 0.94. The values obtained for both inlet concentrations and the three flow rates used are presented in Table 3. The breakthrough curves calculated using Eq. (7) are shown as lines in Fig. 2a and b together with the experimental data. Calculated curves are in reasonably good agreement with experimental data, as shown in the figures. A statistical assessment of the agreement between experimental and calculated breakthrough curves was made by computing absolute errors (E) using the following equation:

$$E = \frac{\sum |e_i - s_i|}{N} \quad (8)$$

where e_i is the i th experimental data point, s_i refers to the corresponding model-predicted value and N is the number of data

points. A summary of the fractional E calculated is given in Table 3.

The axial dispersion coefficient, D_L , is affected by molecular diffusion and by the dispersion related with fluid flow [19]; thus, this parameter is expected to increase with increasing flow rate, as is the case for the experiments carried out at the lowest inlet phenol concentration, 0.01 g/L. Moreover, for this concentration the volume treated until saturation, V_{\min} , remained nearly constant, whereas for an inlet concentration of 0.1 g/L an increase in the flow rate decreased V_{\min} .

Assuming that only external film mass transfer is of importance during the early part of the breakthrough curve, solving for C as a function of z with the corresponding boundary conditions and evaluating the resulting equation at the end of the bed ($z = L$) results [20]:

$$\frac{C}{C_0} = \exp \left\{ \frac{vL}{2D_L} - \left[\left(\frac{vL}{2D_L} \right)^2 + \frac{(1-\epsilon)k_{fa}L^2}{\epsilon D_L} \right]^{1/2} \right\} \quad (9)$$

In order for this method to work, it is necessary to consider that the flow rate in the bed must be large enough and/or the

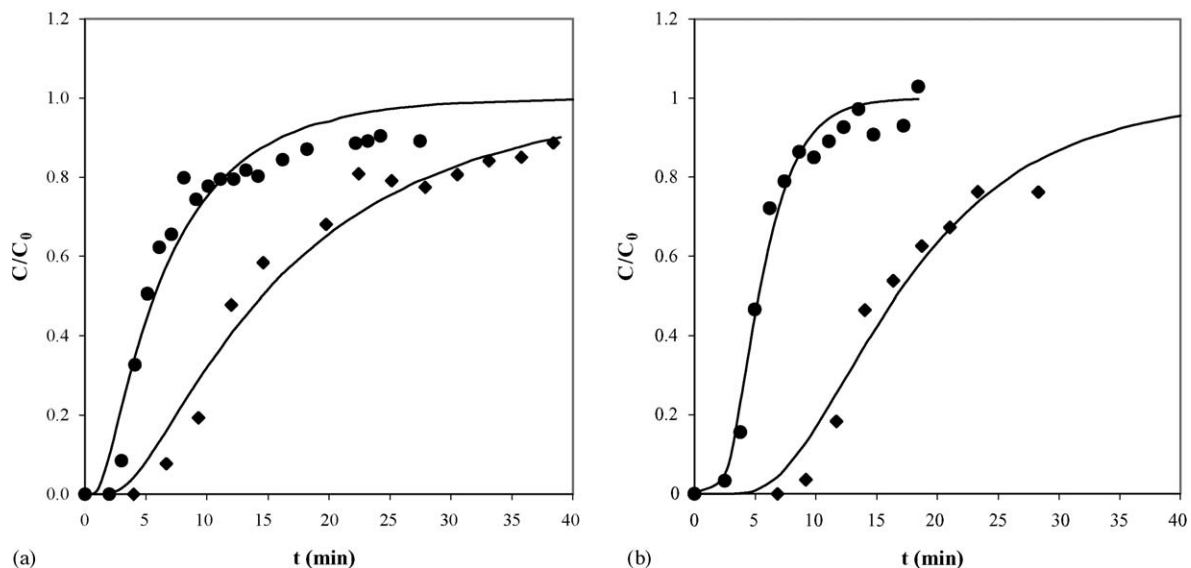


Fig. 2. Experimental and calculated (Eq. (7)) breakthrough curves for the adsorption of phenol on *Pinus pinaster* bark for an inlet concentration of (a) $C_0 = 0.01$ g/L and (b) $C_0 = 0.1$ g/L (◆, 6 mL/min; ●, 15.6 mL/min; lines, Eq. (7)).

bed short enough to generate a non-zero value of C/C_0 . The mass-transfer coefficient in the liquid phase (k_f) was determined from Eq. (9) for those experiments that verified that assumption, obtaining the results shown in Table 3. As it was expected, the coefficient increased when the flow rate was increased from 15.6 to 30 mL/min for the higher inlet concentration. For a fixed flow rate of 30 mL/min, the mass-transfer coefficient decreased when the inlet phenol concentration was diminished.

The volumetric mass-transfer coefficients in the liquid phase, k_f , were also estimated using the following correlation for Reynolds number (Re) of 0.0015–55 [21]:

$$Sh = \frac{1.09}{\varepsilon} Re^{1/3} Sc^{1/3} \quad (10)$$

where Sh and Sc are, respectively, the Sherwood and the Schmidt numbers. The value of phenol diffusivity in aqueous solution is $1 \times 10^{-9} \text{ m}^2/\text{s}$, the particle diameter (d_p) was taken as the mean value in the range (0.5–1 mm) and the mass-transfer area per unit bed volume was calculated as: $a = 6(1 - \varepsilon)/d_p$. The values of k_f calculated using Eq. (10) are shown in Table 3. When experimental and predicted values of $k_f a$ are compared, it is found that the volumetric mass-transfer coefficients based on the liquid film only are significantly higher than those determined from the experimental breakthrough curves. This indicates that the solid-phase mass-transfer resistance exists and may have some influence on the breakthrough curve [1].

4. Conclusions

The sorption of phenol from aqueous solutions on a packed bed of *P. pinaster* bark was investigated in a continuous mode. It has been found that the adsorption of phenol is influenced by the inlet phenol concentration as well as by the flow rate. Both the breakthrough time and the dynamic capacity of the bark decreased when the flow rate was increased, especially for the higher inlet concentration, probably due to an insufficient residence time of the phenol solution in the column. However, it should be noted that the use of low flow rates would result in long overall processing times that may not be desirable in practice when large volumes of phenol-contaminated wastewater have to be processed.

The equivalent length of unused bed (LUB) was determined using the LUB Design Approach. The results showed that the LUB increases by decreasing the flow rate.

The breakthrough curves have been satisfactorily described using different models. A theoretical model which involves two parameters was used satisfactorily for the experiments carried out at the highest flow rate. However, for the lower flow rates, it was necessary to employ a model which considered the effect of axial dispersion. The experimental external film mass-transfer coefficients have been calculated and the comparison with the predicted ones has demonstrated that there may be some influence of solid-phase mass transfer.

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