

Biodegradation (2010) 21:379–392  
 DOI 10.1007/s10532-009-9308-5

ORIGINAL PAPER

## Removal of organic compounds by a biofilm supported on GAC: modelling of batch and column data

Cristina Quintelas · Bruna Silva ·  
 Hugo Figueiredo · Teresa Tavares

Received: 20 February 2009 / Accepted: 22 October 2009 / Published online: 1 November 2009  
 © Springer Science+Business Media B.V. 2009

**Abstract** The performance of a biofilm of *Arthrobacter viscosus* supported on granular activated carbon on the retention of organic compounds was evaluated. The presence of functional groups on the cell wall surface of the biomass that may interact with the organic compounds was confirmed by Fourier transform infrared spectroscopy, to assess the applicability of this system to the removal of those compounds. The batch assays showed that the removal percentage decreases with the increasing initial concentration. The removal of phenol ranged from 99.5 to 93.4%, the chlorophenol removal ranged from 99.3 to 61.6% and the *o*-cresol removal ranged from 98.7 to 73.5%, for initial concentrations between 100 and 1,700 mg/L. The batch data were described by Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich, Sips and Toth model isotherms and the best fit for the retention of phenol and for the retention of *o*-cresol was obtained with the Sips model, while for chlorophenol, the best fit was obtained with the Freundlich model. The column tests showed that the retention performance followed the order: phenol > chlorophenol > *o*-cresol, and increased with the increasing initial organic compound concentration. Data from column runs were described by

Adams–Bohart, Wolborska and Yoon and Nelson models with good fitting for all the models.

**Keywords** *Arthrobacter viscosus* · Biodegradation · Biosorption · Hazardous compounds

### List of symbols

$Q_e$ (mg/g)	Ratio between mass of compound sorbed by the biofilm and the mass of GAC, at the equilibrium
$Q_{\max}$ (mg/g)	Maximum mass of compound sorbed per mass of GAC
$C_e$ (mg/L)	Concentration of compound in solution at equilibrium
$b$ (L/mg)	Langmuir adsorption equilibrium constant
$K_f$	Capacity of adsorption
$n$	Intensity of adsorption
$K_R$ (L/g), $a_R$ (L/mg) and $\beta$	Redlich–Peterson constants. $\beta$ varies between 0 and 1
$K_S$ (L <sup>bs</sup> mg <sup>1-bs</sup> /g), $a_S$ (L/mg) <sup>bs</sup> and $b_S$	Sips isotherm parameters
$K_t$ (mg/g), $a_t$ and $t$	Toth isotherm constants
$B_D$	Related to the mean free energy of sorption per gram of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution

C. Quintelas (✉) · B. Silva · H. Figueiredo · T. Tavares  
 IBB-Institute for Biotechnology and Bioengineering,  
 Centre of Biological Engineering, University of Minho,  
 Campus de Gualtar, 4710-057 Braga, Portugal  
 e-mail: [cquintelas@deb.uminho.pt](mailto:cquintelas@deb.uminho.pt)

$T$	Temperature (K)
$R$	Universal gas constant
$k_{AB}$	Kinetic constant (L/(mg·min)) for the Adams–Bohart model
$N_0$	Saturation concentration (mg/L) for the Adams–Bohart model
$C_0$	Inlet compound concentration (mg/L)
$C$	Effluent compound concentrations (mg/L)
$C_s$	Compound concentration at the solid/liquid interface (mg/L)
$D$	Axial diffusion coefficient (cm <sup>2</sup> /min)
$v$	Is the migration rate (cm/min)
$\beta_a$	Kinetic coefficient of the external mass transfer (min <sup>-1</sup> )
$\beta_0$	External mass transfer coefficient with a negligible axial dispersion coefficient $D$
$k_{YN}$	Rate constant (min <sup>-1</sup> )
$\tau$	Time required for 50% adsorbate breakthrough (min)
$T$	Breakthrough time (min)

## Introduction

The chemical pollution caused by the presence of heavy metals and organic compounds in the environment is, at present, one of the most serious problems faced by nature. This pollution can cause changes in physical (turbidity, colour, temperature, viscosity, surface tension), chemical (chemical oxygen demand, pH, acidity, alkalinity, dissolved oxygen, toxicity level, nutrients) and biological characteristics of an aquatic medium compromising the water quality for human consumption. A variety of industries including olive mills, oil refineries, plastics, leather, paint, pharmaceutical and steel industries are responsible for the presence of phenolic compounds in wastewaters. Cresol is used in disinfectants and fumigants, in the manufacture of synthetic resins, in photographic developers and in explosives. This compound is highly toxic, corrosive and causes nervous system depression (Tallur et al. 2006). Chlorophenols are

used in petrochemical refinery, plastic, pesticide, herbicide, fiberglass manufacturing and coal conversion industries, hence, they are present in the respective effluents. General weakness, fatigue, ataxia, headache, anorexia, sweating, hyperpyrexia, nausea, vomiting, tachycardia, abdominal pain, terminal spasms and death characterize acute poisoning by dichlorophenol (Sathishkumar et al. 2007).

The conventional treatments, physical or chemical, applied to the removal of hazardous compounds are effective but present several limitations that include excessive usage of chemicals, expensive plant requirements, high operational costs and sensitivity to variations in the wastewater input (Prigione et al. 2008). The development of a robust, highly competitive process, with high performance and efficiency, based on the ability of certain biological materials to accumulate and eventually to transform molecules from effluents by physico-chemical or metabolic reactions, is strongly recommended. This process would include a biosorption step followed by a biodegradation step, depending on the microorganism ability to degrade the pollutants. The main advantages of such system are the reusability of biomaterial, low operating cost, improved selectivity for specific pollutants, short operation time and no production of secondary compounds which might be toxic (Munigasavalli et al. 2007).

Several authors have been studying biosorption applied to the removal of organic compounds from wastewaters. Wu and Yu (2006, 2007) used a fungus, *Phanerochaete chrysosporium*, for the removal of phenol and chlorophenols. A wider approach was used by Tallur et al. (2006) who studied the biodegradation of *p*-cresol using *Bacillus* sp. Moreover, the fungus *Trametes versicolor* was used for the treatment of phenol and *o*-cresol contaminated wastewaters (Ryan et al. 2007). Bacteria tend to retain strongly many organic compounds including dyes, phenolics and pesticides. According to Xiao et al. (2007), as the interior plasma membrane is impermeable to organic pollutants, the bacterial cell wall is expected to be the primary element responsible for organic biosorption.

Bacteria spend most of their natural existence growing as a biofilm. It is possible that the presence of a suitable substrate for attachment is all that is required to trigger biofilm formation (Jefferson 2004). Biofilms have also been used for the treatment

of wastewaters contaminated with organic contaminants (Quintelas et al. 2006; Wicke et al. 2007). The use of activated carbon for the removal of organic compounds was extensively studied by several authors (Cañizares et al. 2006; Mourão et al. 2006; Li et al. 2002). Aktas and Çeçen (2007) studied the adsorption and desorption of chlorophenol on activated carbon and activated sludge. The use of bacteria supported on activated carbon allows combining the good capabilities of both to retain and/or degrade organic compounds and, eventually, a synergistic effect is expected between support and biofilm.

The design and analysis of the adsorption process require equilibrium characterization. Sorption equilibria provide fundamental physicochemical data to evaluate the applicability of the sorption process as a unit operation and to describe the fixation capacity of the biosorbents. The prediction of the concentration–time profile or breakthrough curve for the effluent to be treated is one of the requirements for a successful design of a column adsorption process.

The main focus of this study was the evaluation of the retention ability of a biofilm of *Arthrobacter viscosus* supported on granular activated carbon (GAC), for the removal of organic compounds from liquid solutions.

The presence of functional groups in the suspended biomass that may have a role in the retention process was confirmed by Fourier transform infrared spectroscopy aiming to evaluate the applicability of this microorganism to the removal of organic compounds. The removal ability was investigated using batch and column studies. All the equilibrium isotherms for the biosorption of phenol, chlorophenol and *o*-cresol by the biofilms were described by Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich, Sips and Toth isotherms. The dynamic behaviour of the columns with respect to the inlet organic compound concentration was analysed by the Adams–Bohart, Wolborska and Yoon and Nelson models.

## Materials and methods

### Materials

The bacterium *A. viscosus* (CECT 908) was obtained from the Spanish Type Culture Collection of the

University of Valência. The organic compounds solutions were prepared by diluting extra pure *o*-cresol (Riedel–de Haen), phenol and chlorophenol (Merck) in distilled water. Glassware used for experimental purposes were washed in 60% nitric acid and subsequently rinsed with deionised water to remove any possible interference by other compounds. The support was GAC from MERCK, characterised by N<sub>2</sub> adsorption (77 K) with an ASAP Micromeritics 2001. This support has an average particle size of 2.5 mm, a Langmuir area of 1,270 m<sup>2</sup>/g and an average pore diameter of 2 nm.

### Methods

#### *Fourier transform infrared spectroscopy*

Infrared spectra of suspended biomass, with and without previous contact with the organic compound, were obtained using a Fourier transform infrared spectrometer (FTIR BOMEM MB 104). For the FTIR study, biomass were centrifuged and dried (24 h at 60°C), followed by weighting. Then, 10 mg of finely ground biomass was encapsulated in 100 mg of KBr (Riedel) in order to prepare translucent sample disks. Background correction for atmospheric air was used for each spectrum. The resolution was 4 cm<sup>-1</sup> and a minimum of five scans were conducted for each spectrum with the range between 500 and 4,000 wavenumbers.

#### *Batch biosorption*

The biofilm formation was prepared according to previous studies (Quintelas and Tavares 2001, 2002). A medium with 10 g/L of glucose, 5 g/L of peptone, 3 g/L of malt extract and 3 g/L of yeast extract was used for growth and maintenance of the microorganism. Bacteria are always harvested during the exponential phase of the growth curve, as described in previous publications. The biosorption isotherms for the organic compounds by the biofilm supported on GAC were obtained from batch experiments at 28°C. The experiments were performed with 250 mL Erlenmeyer flasks containing 150 mL of the organic compound solution and 1.5 g of GAC covered with biofilm. The concentrations tested ranged between 100 and 1,000 mg/L, for phenol, between 100 and 1,500 mg/L, for chlorophenol and between 150 and 1,700 mg/L, for

*o*-cresol. The flasks were rotated at a constant rate of 150 rpm until equilibrium was reached. Previous assays were made to determine the time needed for equilibrium to be reached (5 days). Samples of 5 mL were taken after reaching equilibrium, centrifuged at 2,500g during 5 min and the supernatant liquid was analysed for the organic compounds using spectrometry with the 4-aminoantipyrine method (Clesceri et al. 1989). This method is based on the fact that phenolic compounds react with 4-aminoantipyrine in alkaline solution, in the presence of ferricyanide to produce a red reaction product.

### Column biosorption

All experiments were conducted in triplicate. GAC was placed in Erlenmeyer flasks of 250 ml with 150 ml of distilled water. It was sterilised at 120°C for 20 min to release the air inside the pores. Then, it was placed in mini-columns (internal diameter = 2 cm, height = 30 cm) for open system studies. The microorganism culture and the nutrient broth, composed by glucose, peptone, yeast extract and malt extract, were pumped through at a flow rate of 25 mL/min, according with previous works of this group (Quintelas and Tavares 2001, 2002). The high flow rate used (25 mL/min) allows the formation of a compact biofilm, resistant to the erosion stress promoted by hydrodynamic forces. After biofilm formation, beds were washed out and 5 L of the organic compound solutions with concentrations between 10 and 100 mg/L, were passed through the columns with a flow rate of 5 mL/min for 17 h. At the end of each run, columns were washed out and samples of the effluent were seeded in Petri plates with nutrient agar to assess the metabolic activity of the microorganism. Organic compound concentration at the inlet and at the outlet of the columns was systematically measured by spectrometry with the 4-aminoantipyrine method (Clesceri et al. 1989).

## Modelling

### Adsorption isotherm models

Equilibrium isotherm equations are used to describe experimental sorption data. The equation parameters

and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into the sorption mechanism, the surface properties and the affinity of the sorbent (Gerente et al. 2007). Six isotherm equations have been tested in the present study and are presented in Table 1. The simplest method to determine isotherms constants for two parameter isotherms (Langmuir, Freundlich and Dubinin-Radushkevich) is to convert the equation to a linear form and then to apply linear regression. For the other equations, the model parameters were estimated by non-linear regression using MATLAB and EXCEL software.

### Modelling column biosorption data

#### *The Adams–Bohart, Wolborska and Yoon and Nelson models*

The prediction of the concentration–time profile or breakthrough curve for the effluent to be treated is one of the requirements for a successful design of a column adsorption process. The Adams–Bohart, Wolborska and Yoon and Nelson models can be used to predict the behavior of breakthrough curves. All parameters are referred to in the Nomenclature section, in order of appearance.

*The Adams–Bohart model* In 1920, Bohart and Adams (1920) established the fundamental equations that described the relationship between  $C/C_0$  and  $t$  in a flowing system for the adsorption of chlorine on charcoal. The proposed model assumes that the adsorption rate is proportional to the residual capacity of the activated carbon and to the concentration of the sorbing species. The mass transfer rates obey the following equations:

$$\frac{\partial q}{\partial t} = -k_{AB}qC_b \quad (1)$$

$$\frac{\partial C_b}{\partial Z} = -\left(\frac{k_{AB}}{U_0}\right)qC_b \quad (2)$$

Two assumptions are made for the solution of these differential equations system:  $t \rightarrow \infty$  and  $q \rightarrow N_0$ . When the differential equations system is solved, the following equation is obtained with parameters  $k_{AB}$  and  $N_0$ :

**Table 1** Isotherm models used to represent the sorption equilibria

Isotherm model	Equation	Theory	Reference
Langmuir	$Q_e = (Q_{\max}bC_e)/(1 + bC_e)$	Establishes a relationship between the amount of gas sorbed on a surface and the pressure of gas. Assumes monolayer coverage of adsorbate over a homogenous adsorbent surface	Langmuir 1918
Freundlich	$Q_e = K_f C_e^{1/n}$	This exponential equation assumes that as the adsorbate concentration in solution increases so does it on the adsorbent surface. Can be applied to nonideal sorption on heterogeneous surfaces as well as to multilayer sorption	Freundlich 1906
Redlich–Peterson	$Q_e = (K_R C_e)/(1 + a_R C_e^b)$	This isotherm model incorporates features of both the Langmuir and the Freundlich isotherms and may be used to represent adsorption equilibria over a wide concentration range	Redlich and Peterson (1959)
Sips	$Q_e = (K_S C_e^{1/bs})/(1 + a_S C_e^{1/bs})$	Is also called Langmuir–Freundlich isotherm, and the name derives from the limiting behaviour of the equation. At low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry’s law. At high sorbate concentrations, it predicts a monolayer sorption capacity, characteristic of the Langmuir isotherm	Sips 1948
Toth	$Q_e = (K_T C_e)/[(a_T + C_e)^{1/n}]$	Derived from potential theory, it is used in heterogeneous systems. It assumes a quasi-Gaussian energy distribution, i.e. most sites have an adsorption energy lower than the peak of maximum adsorption energy	Toth 1971
Dubinin–Radushkevich	$Q_e = q_D \exp(-B_D [RT \ln(1 + 1/C_e)]^2)$	The characteristic sorption curve is related to the porous structure of the sorbent	Dubinin and Radushkevich 1947

$$\ln \frac{C}{C_0} = k_{AB} C_0 t - -k_{AB} N_0 \frac{Z}{U_0} \tag{3}$$

From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of  $\ln C/C_0$  against  $t$  at a given bed height and flow rate.

*The Wolborska model* Wolborska (1989) proposed another model for the description of adsorption dynamics using mass transfer equations for diffusion mechanisms in the range of the low-concentration of the breakthrough curve. The mass transfer in the fixed bed sorption is described by the following equations:

$$\frac{\partial C_b}{\partial t} + U_0 \frac{\partial C_b}{\partial Z} + \frac{\partial q}{\partial t} = D \frac{\partial^2 C_b}{\partial Z^2} \tag{4}$$

$$\frac{\partial q}{\partial t} = -v \frac{\partial q}{\partial Z} = \beta_a (C_b - C_s) \tag{5}$$

Three assumptions are made for the solution of this differential equation:  $C_s \ll C_b$ ,  $v \ll U_0$  and axial diffusion negligible  $D \rightarrow 0$  as  $t \rightarrow 0$ . The solution can be approximated to:

$$\ln \frac{C}{C_0} = \frac{\beta_a C_0}{N_0} t - \beta_a (C_b - -C_s) \tag{6}$$

with

$$\beta_a = \frac{U_0^2}{2D} \sqrt{((1 + 4\beta_0 D/U_0^2) - 1)}. \tag{7}$$

The author observed that in short beds or at high flow rates of solution through the bed, the axial diffusion is negligible and  $\beta_a = \beta_0$ . The migration rate of the steady-state front satisfies the Wicke’s law:

$$v = \frac{U_0 C_0}{N_0 + C_0} \tag{8}$$

The expression of the Wolborska model is equivalent to the Adams–Bohart relation if the coefficient  $k_{AB}$  is equal to  $\beta_a/N_0$ . So, the drawing of  $\ln C/C_0$  versus  $t$  would also give information on this model.

*The Yoon and Nelson model* In 1984, Yoon and Nelson (1984) developed a simple model for describing the adsorption and breakthrough of adsorbates with respect to activated carbon. The basis of this model is the assumption that the rate of decrease in the probability of

adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and to the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model can be expressed by the following equation:

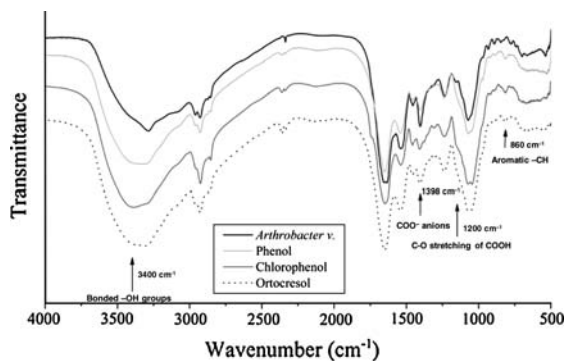
$$\ln \frac{C}{C_0 - C} = k_{YN}t - \tau k_{YN} \quad (9)$$

The values values of  $k_{YN}$  and  $\tau$  can be calculated from the plot of  $\ln (C/(C_0 - C))$  versus  $t$ .

## Results and discussion

### FTIR spectral analysis

The FTIR spectra of suspended *A. viscosus* biomass, with and without previous contact with each organic compound, in the range of 500–4,000  $\text{cm}^{-1}$  were taken to confirm the presence of functional groups that might be responsible for the biosorption process and presented in Fig. 1. As seen in this figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. Band shifts were observed for the signals at 3,400  $\text{cm}^{-1}$  (bonded hydroxyl groups; Mungasavalli et al. 2007), 1,398  $\text{cm}^{-1}$  (indicative of  $\text{COO}^-$  anions), 1,200  $\text{cm}^{-1}$  (C–O stretching of COOH) and at 860  $\text{cm}^{-1}$  (aromatic –CH stretching peak) (Tunali et al. 2006). These changes observed in the spectrum indicated the possible involvement in biosorption process of those functional groups on the surface of the biomass. These results allow the continuation of this study, as the selected biomass presents the needed properties for good biosorption performance.

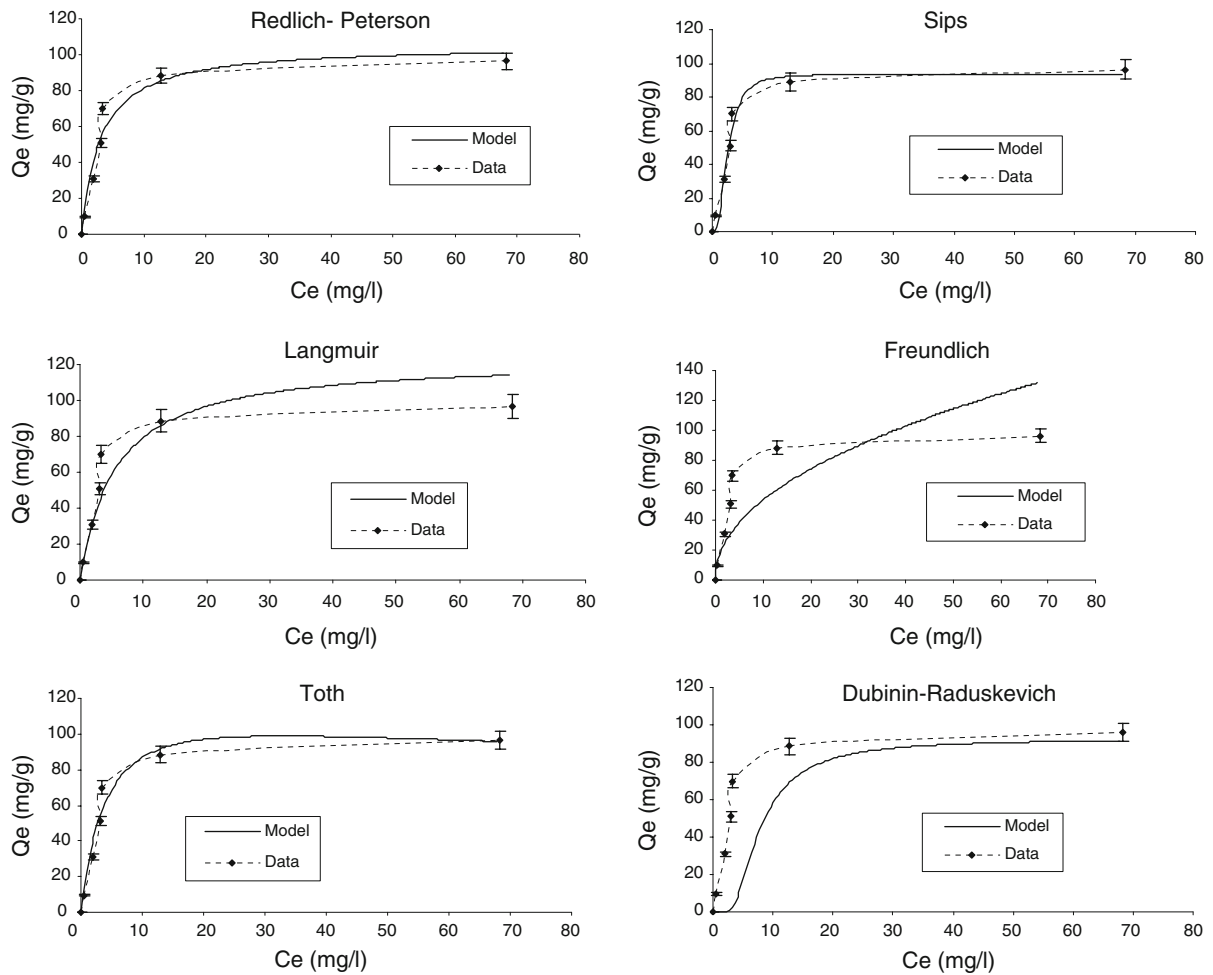


**Fig. 1** FTIR spectra of *Arthrobacter viscosus* before and after organic compound contact

### Batch biosorption studies

The adsorption isotherms express the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at constant temperature (Sathishkumar et al. 2007) or, in other words, the amount adsorbed per unit mass of adsorbent as a function of the equilibrium concentration in solution (Mourão et al. 2006). The retention capacity of organic compounds by a biofilm of *A. viscosus* supported on GAC was analysed using different isotherm models: Langmuir, Freundlich, Redlich–Peterson, Sips, Toth and Dubinin–Radushkevich. The sorption capacity was correlated with the variation of surface area and porosity of the support. Higher surface area and pore volume would result in higher retention capacity (Sathishkumar et al. 2007). Because of this, GAC with a biofilm presents improved characteristics of a good sorbent.

Equilibrium data were experimentally determined for the organic compounds phenol, chlorophenol and *o*-cresol and the results are shown in Figs. 2, 3 and 4. The experimental assays were made using solutions of initial phenol concentration between 100 and 1,000 mg/L, solutions of initial chlorophenol concentration between 100 and 1,500 mg/L and solutions of initial *o*-cresol concentration between 150 and 1,700 mg/L. The results showed that the removal percentage of the organic compounds decreased as the initial concentration of organic compound was increased (Table 2). Phenol removal ranged from 99.5 to 93.4%, the chlorophenol removal ranged from 99.3 to 61.6% and the *o*-cresol removal ranged from 98.7 to 73.5%, for the range of initial concentrations of each organic compound used. Padmesh et al. (2005) and Horsfall Jr et al. (2006) explain this phenomenon. The first authors affirm that this decrease is based on the fact that at lower concentration, the ratio of the initial number of moles of the compound to the available surface area may be lower and subsequently the fractional sorption becomes independent of the initial concentrations or, in other words, at higher concentrations the available sites become fewer compared with the number of moles of compound present and hence the removal percentage is dependent of the initial concentration. The second authors affirm that at higher concentrations, the reduced average distance between the species to be adsorbed affects the

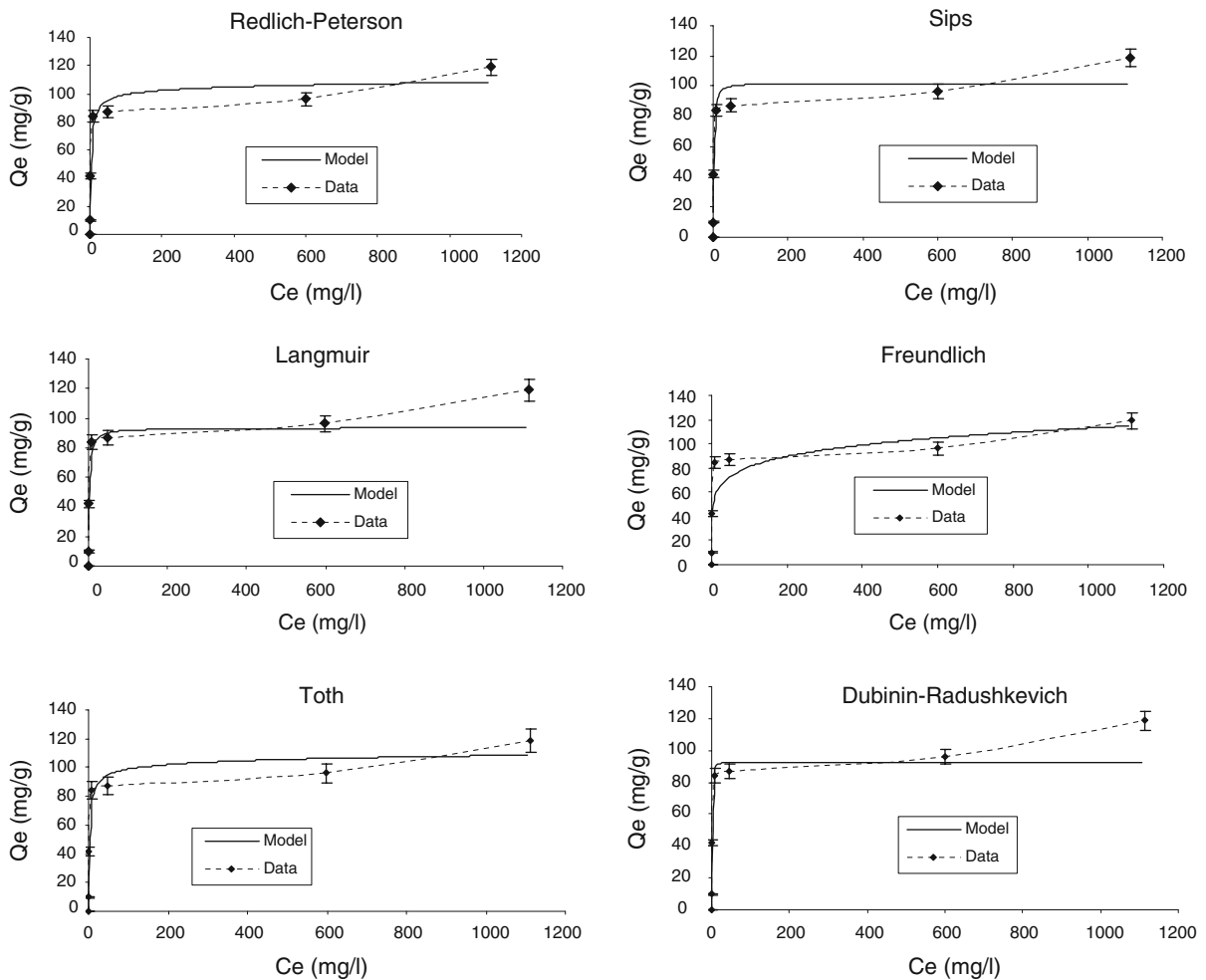


**Fig. 2** Comparison between the experimental results and those predicted by different models for the phenol adsorption isotherms

charge distribution of their neighbours, thus altering the ability of the species to migrate to the biomass surface, which results in reduced fixation. Despite of the fact that the removal percentage decreased with the initial concentration, the total amount adsorbed increases with the same factor.

Comparing values of removal percentage for similar initial concentrations (values highlighted on Table 2), it may be registered a removal percentage of 99.1% of *o*-cresol, against a removal percentage of 93.4% for the phenol and 80.8% for the chlorophenol. The higher affinity between the biofilm and the *o*-cresol seems to be the reason for that behaviour. The different removal values can be explained by the differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity between the

three organic compounds tested (Streat et al. 1995). Studies developed by Brasquet et al. (1997) showed that the adsorbability of organic compounds increased with molecular size and decreased with the number of heteroatoms. The molecular sizes of chlorophenol, *o*-cresol and phenol are 128.6, 108.1 and 94.1, respectively. The biosorption performance described in the present report, for the batch studies, followed the order: *o*-cresol > phenol > chlorophenol and it can be concluded that the results are in agreement with the study developed by Brasquet et al. (1997): the compound with higher number of heteroatoms (chlorophenol) showed the worst results and between phenol and *o*-cresol the best results were obtained for the compound with higher molecular size, *o*-cresol.



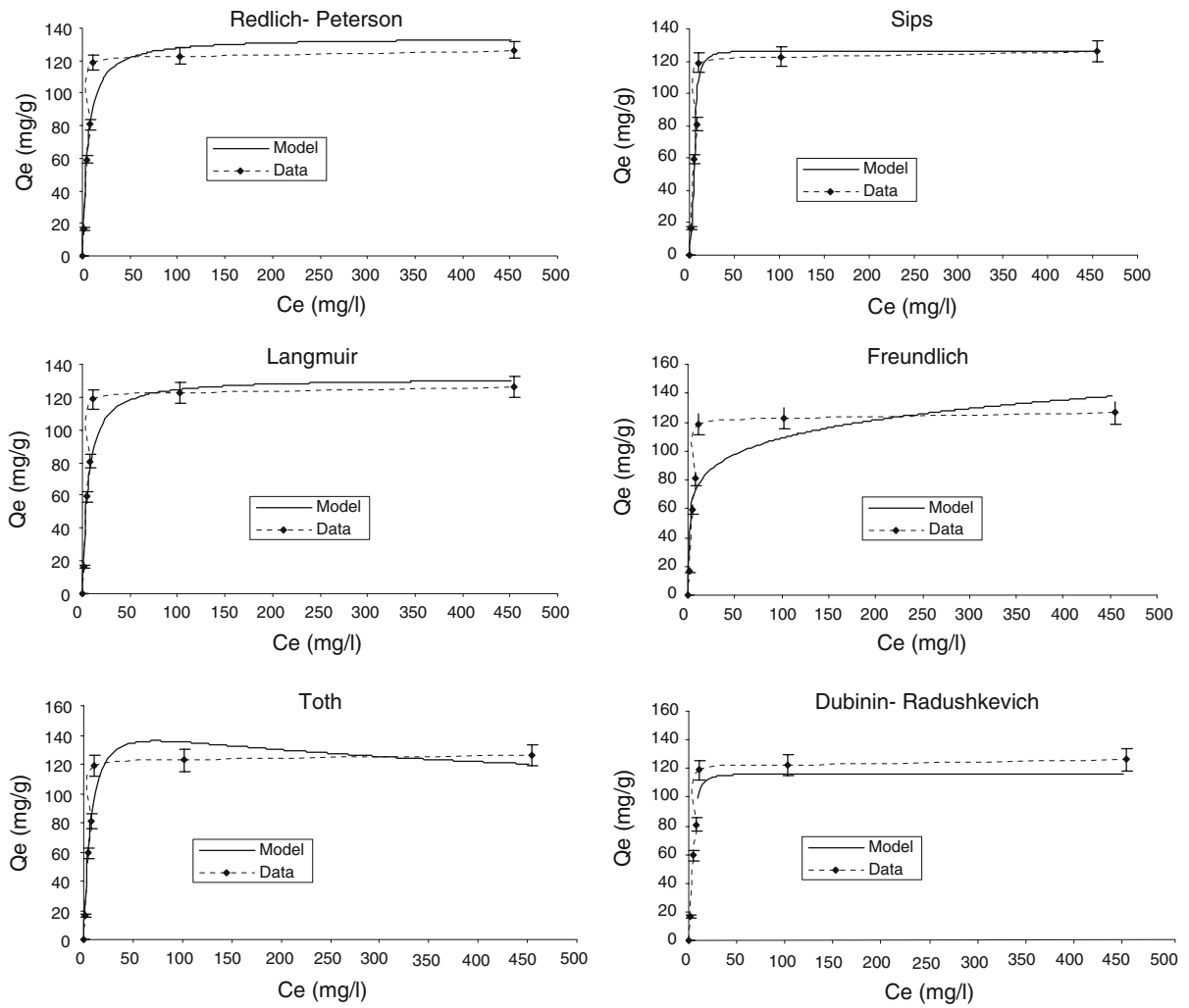
**Fig. 3** Comparison between the experimental results and those predicted by different models for the chlorophenol adsorption isotherms

A comparison between the performance of a biofilm supported on GAC and the performance of other adsorbents/biosorbents was made and is presented on Table 3. The activated carbon has been used for the treatment of organic compounds solution (Aktas and Çeçen 2006, 2007; Lu and Sorial 2004; Hamdaoui and Naffrechoux 2009). The *A. viscosus* biofilm supported on GAC presents better results in terms of removal percentage than the activated carbon by itself, for the three compounds under study. Several reports showed that the microorganisms are able to degrade organic compounds (Thawornchaisit and Pakulanon 2007; Rao and Viraraghavan 2002; Denizli et al. 2005; Ziagova and Liakopoulou-Kyriakides 2007). The biofilm supported on GAC probably combines the adsorption by GAC with the biosorption and possible

degradation by the microorganisms, resulting in a more effective and resilient treatment system for aqueous solutions with relevant concentrations of some specific organic compounds. The *A. viscosus* ability to degrade the organic compounds under study was assessed by parallel assays in which all the experimental parameters were the same as before, but in which the biofilm was used in its suspended form, without GAC to act as support and or as adsorbent. Degradation occurred for phenol and for *o*-cresol but not for chlorophenol. Moreover, the degradation was detected just after a much longer period (13 days) than the one needed for biosorption/adsorption to reach equilibrium (5 days).

The best fit for the biosorption equilibrium of phenol was obtained with the Sips model, followed





**Fig. 4** Comparison between the experimental results and those predicted by different models for the *o*-cresol adsorption isotherms

**Table 2** Equilibrium concentrations and removal percentages of phenol, chlorophenol and *o*-cresol, obtained for different initial concentrations of the organic compound (28°C, 150 rpm)

Phenol			Chlorophenol			<i>o</i> -Cresol		
$C_0$ (mg/L)	$C_{eq}$ (mg/L)	Rp (%)	$C_0$ (mg/L)	$C_{eq}$ (mg/L)	Rp (%)	$C_0$ (mg/L)	$C_{eq}$ (mg/L)	Rp (%)
96.6	0.47	99.5	100.1	0.71	99.3	167.5	2.20	98.7
310.1	2.00	99.4	421.1	1.64	99.6	596.8	4.86	99.2
511.6	3.07	99.4	848.6	7.53	99.1	816.2	7.69	99.1
702.7	3.32	99.5	916.3	46.73	94.9	1,198.6	10.57	99.1
897.6	12.82	98.6	1,030.8	197.89	80.8	1,329.6	102.24	92.3
1,031.7	68.29	93.4	1,560.2	598.45	61.6	1,717.2	454.50	73.5

by the Redlich- Peterson and Toth models (Fig. 2). For the chlorophenol, the best fit was obtained with the Freundlich model (Fig. 3) while for the *o*-cresol

the best fit was achieved with the Sips model (Fig. 4). The isotherm parameters are presented on Table 4. For all the organic compounds used, the Langmuir

**Table 3** Uptake and removal percentages obtained for different biosorbents/adsorbents

Compound	Initial conc. (mg/L)	Adsorbent/biosorbent	Uptake (mg/g)	Removal (%)	Reference
Phenol	110	Sewage sludge	94	–	Thawornchaisit and Pakulanon (2007)
	1	<i>Aspergillus niger</i>	–	66	Rao and Viraraghavan (2002)
	500	<i>Pleurotus sajor caju</i>	89.4	–	Denizli et al. (2005)
	200	Activated carbon	–	63.1	Aktas and Çeçen (2006)
	500	<i>A. viscosus</i> /GAC	50.9	99.4	This work
2,4-Dichlorophenol	163	<i>Pseudomonas</i> sp.	–	11	Ziagova and Liakopoulou-Kyriakides (2007)
2-Chlorophenol	200	Activated carbon	–	80.3	Aktas and Çeçen (2007)
4-Chlorophenol	100	Activated carbon (GAC)	–	60	Hamdaoui and Naffrechoux (2009)
	421	<i>A. viscosus</i> /GAC	–	99.6	This work
4-Cl- <i>m</i> -cresol	144	<i>Pseudomonas</i> sp.	–	8	Ziagova and Liakopoulou-Kyriakides (2007)
<i>o</i> -Cresol	1,000	Activated carbon (GAC)	–	30	Lu and Sorial (2004)
	200	Activated carbon (GAC)	–	75	Lu and Sorial (2004)
	1,200	<i>A. viscosus</i> /GAC	–	99.1	This work

isotherm model does not fit well the data obtained. An important assumption in Langmuir adsorption isotherm is the independence of the process on the available adsorption sites and Doshi et al. (2007) affirm that the deviation from this isotherm may be traced to the failure of this assumption suggesting that probably the energetically most favourable sites are occupied ahead. Gerente et al. (2007) affirm that the importance of obtaining the “best-fit” isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the design of treatment systems.

#### Column biosorption data

##### *Application of the Adams–Bohart and the Wolborska models*

According to Malkoc et al. (2006), the Adams–Bohart model is based on the surface reaction theory and it assumes that equilibrium is not instantaneous; therefore, the rate of the sorption is proportional to the fraction of sorption capacity that still remains on the sorbent. The Wolborska model is based on the general equations of mass transfer for diffusion mechanisms in the range of the low-concentration of the breakthrough curve (Hamdaoui 2006). These sorption models (Adams–Bohart and Wolborska)

were used to describe the experimental data. This approach was focused on the estimation of characteristic parameters, such as maximum adsorption capacity ( $N_0$ ) and kinetic constant ( $k_{AB}$ ) of Adams–Bohart model and kinetic coefficient of the external mass transfer ( $\beta_a$ ) of Wolbraska model. After applying Eq. (3) (or Eq. (6)) to the experimental data for different inlet organic compound concentrations, a linear relationship between  $\ln C/C_0$  and  $t$  was obtained. Values of  $N_0$ ,  $k_{AB}$  and  $\beta_a$  were calculated from the  $\ln C/C_0$  versus  $t$  plots at all inlet organic compound concentrations, as presented in Table 5 together with the respective correlation coefficients. The value of maximum adsorption capacity ( $N_0$ ) increased with increasing inlet organic compound concentration, as expected, for all the organic compounds tested. The value of  $\beta_a$  is also an effective coefficient which reflects the effect of both mass transfers in liquid phase and axial dispersion as defended by Aksu and Gönen (2004). These authors verified that this coefficient is positive and strongly influenced by the flow rate, since increased turbulence reduces the film boundary layer surrounding the immobilized particles. During the experimental work described here the flow rate was the same for all the experimental assays, and because of that the value of  $\beta_a$  remained in the same order of magnitude. The predicted and experimental breakthrough curves, with respect to the inlet organic compound

**Table 4** Adsorption isotherm constants and adjustment regression parameter for the models considered and for the three organic compounds

	$Q_{\max}$	$b$	$R^2$	
<b>Langmuir</b>				
Phenol	123.46	0.18	0.99	
Chlorophenol	93.46	0.51	0.97	
<i>o</i> -Cresol	131.58	0.18	0.98	
	$K_f$	$n$	$R^2$	
<b>Freundlich</b>				
Phenol	18.09	2.12	0.89	
Chlorophenol	41.53	6.91	0.92	
<i>o</i> -Cresol	52.78	6.34	0.87	
	$q_D$	$B_D$	$R^2$	
<b>Dubinin–Radushkevich</b>				
Phenol	97.83	0.050	0.99	
Chlorophenol	92.30	0.0045	0.98	
<i>o</i> -Cresol	116.33	0.022	0.97	
	$K_R$	$a_R$	$\beta$	$R^2$
<b>Redlich–Peterson</b>				
Phenol	35.12	0.33	1.00	0.95
Chlorophenol	42.06	0.47	0.97	0.95
<i>o</i> -Cresol	26.28	0.20	1.00	0.99
	$K_S$	$a_S$	$b_S$	$R^2$
<b>Sips</b>				
Phenol	8.02	0.086	2.60	0.98
Chlorophenol	30.42	0.30	1.37	0.96
<i>o</i> -Cresol	2.28	0.020	2.43	0.98
	$K_t$	$a_t$	$t$	$R^2$
<b>Toth</b>				
Phenol	209.20	5.41	0.86	0.96
Chlorophenol	37.22	-0.71	1.20	0.85
<i>o</i> -Cresol	87.22	2.15	1.03	0.96

concentration, are shown in Fig. 5. The model fitted well to the experimental data, for all the inlet concentrations, for phenol and *o*-cresol. For the chlorophenol, and for the highest concentration used (100 mg/L), the discrepancies verified between the experimental and the predicted data are higher (data not showed). Although the Adams–Bohart (or Wolbraska) model provides a simple and comprehensive

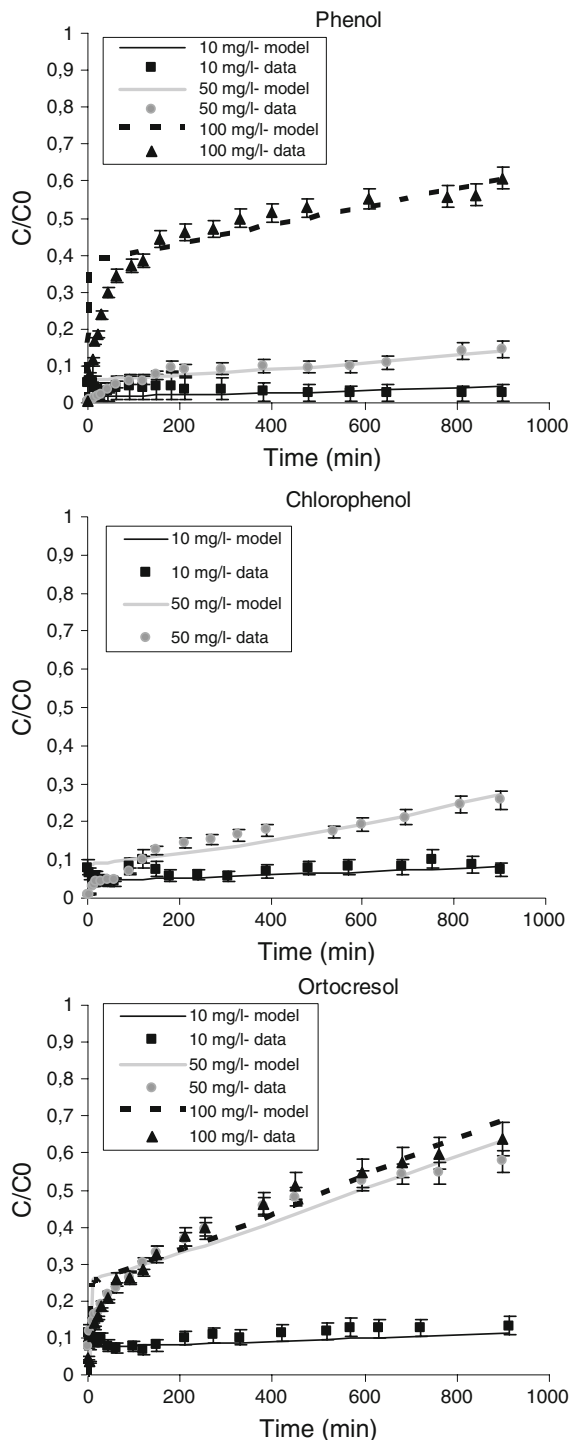
**Table 5** Parameters predicted by the Adams–Bohart and Wolborska models and adjustment regression parameter at different inlet organic compound concentrations

$C_0$ (mg/L)	$N_0$ (mg/L)	$k_{AB}$ (L/(mg.min))	$\beta_a$ (L/min)	$R^2$
<b>Phenol</b>				
10	2,651.8	6.27E-5	0.17	0.85
50	7,962.4	1.89E-5	0.15	0.85
100	10,792.5	4.52E-6	0.049	0.83
<b>Chlorophenol</b>				
10	1,765.8	9.31E-5	0.16	0.89
50	5,294.6	2.22E-5	0.12	0.87
100	10,061.3	1.21E-5	0.12	0.83
<b><i>o</i>-Cresol</b>				
10	3,340.3	3.73E-5	0.13	0.85
50	4,723.7	1.38E-5	0.065	0.90
100	8,604.3	7.08E-6	0.061	0.94

approach to sorption-column tests, its validity is limited to the range of conditions used.

*Application of the Yoon and Nelson model*

The Yoon and Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each sorbate molecule is proportional to the probability of sorbate sorption and to the probability of sorbate breakthrough (Vijayaraghavan and Prabu 2006). The Yoon and Nelson model not only is more straight forwarded than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent or the physical properties of adsorption bed (Hamdaoui 2006). This model was applied to describe the breakthrough behavior of three different organic compounds on biofilm supported on GAC. The values of  $k_{YN}$  and  $\tau$  were determined from  $\ln[C/(C_0-C)]$  against  $t$  plots at different inlet chromium concentrations varied between 10 and 100 mg/L. These values are listed in Table 6. The values for the kinetic constant ( $k_{YN}$ ) have the same order of magnitude for all the organic compounds. It is expected that the value of  $\tau$  may decrease with the increase on the inlet concentration, because the higher the inlet concentration the lower the saturation period. This is verified in the experimental assays described here. The theoretical curves are compared with the corresponding experimental data in Fig. 6 and it could be concluded that the experimental



**Fig. 5** Comparison between the experimental results and those predicted by the models for the different inlet solute concentrations, according to the Adams–Bohart (or Wolbraska) model, for all the organic compounds

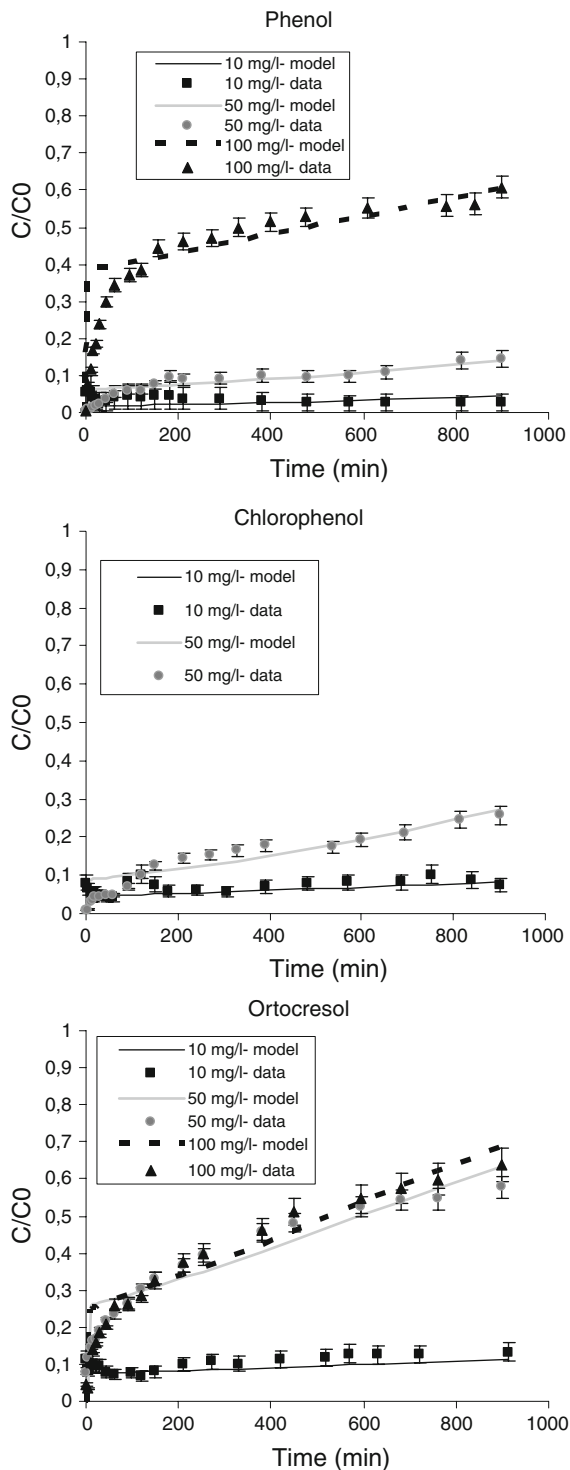
**Table 6** Parameters predicted from the Yoon and Nelson model and adjustment regression parameter at different inlet organic compound concentrations

$C_0$ (mg/L)	$\tau$ (min)	$k_{YN}$ ( $\text{min}^{-1}$ )	$R^2$
<b>Phenol</b>			
10	3,998.40	0.0010	0.97
50	2,711.70	0.0010	0.87
100	486.80	0.0010	0.86
<b>Chlorophenol</b>			
10	4,318.57	0.0007	0.87
50	1,554.93	0.0015	0.85
100	1,282.79	0.0019	0.90
<b><i>o</i>-Cresol</b>			
10	5,020.60	0.0005	0.85
50	594.67	0.0018	0.90
100	530.52	0.0021	0.94

breakthrough curves were followed very closely by the Yoon–Nelson model, for all the concentrations tested. The discrepancies found for the inlet concentration of 100 mg/L, for chlorophenol, with the Adams–Bohart and Wolbraska are also found for the Yoon and Nelson model, limiting the application of these models.

## Conclusions

A biofilm of *A. viscosus* supported on GAC was tested, in batch and column studies, for the removal of phenol, chlorophenol and *o*-cresol with promising results. The presence of functional groups on the cell wall surface of the biomass that may interact with the organic compounds were previous confirmed by FTIR, to assess the applicability of this system to the removal of organic compounds. The batch biosorption studies showed that the phenol removal ranged from 99.5 to 93.4%, the chlorophenol removal ranged from 99.3 to 61.6% and the *o*-cresol removal ranged from 98.7 to 73.5%, for the range of initial concentrations of each organic compound used. The best fit for the biosorption of phenol was obtained with the Sips model, followed by the Redlich–Peterson and Toth models, for the chlorophenol, the best fit was obtained with the Freundlich model and for the *o*-cresol the best fit was achieved with the Sips



**Fig. 6** Comparison between the experimental data and those predicted by the models for the different inlet solute concentrations, according to the Yoon and Nelson model, for all the organic compounds

model. The modelling of the biosorption process allows the successful design of a column adsorption process aiming a future industrial usage. Data from column runs were described by Adams–Bohart, Wolborska and Yoon and Nelson models, with good agreement for both models.

**Acknowledgments** This work was supported by Fundação para a Ciência e Tecnologia (FCT-Portugal), under programme POCTI/FEDER (POCTI/CTA/44449/2002). Cristina Quintelas gratefully acknowledges the Fundação para a Ciência e Tecnologia (FCT-Portugal) for a Post-Doc grant.

## References

- Aksu Z, Gönen F (2004) Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochem* 39:599–613
- Aktas O, Çeçen F (2006) Effect of type of carbon activation on adsorption and its reversibility. *J Chem Technol Biotechnol* 81:94–101
- Aktas O, Çeçen F (2007) Adsorption, desorption and bioregeneration in treatment of 2-chlorophenol with activated carbon. *J Hazard Mater* 141:769–777
- Bohart G, Adams EQ (1920) Some aspects of the behaviour of charcoal with respect to chlorine. *J Am Chem Soc* 42:523–544
- Brasquet C, Subrenat E, Le Cloirec P (1997) Selective adsorption on fibrous activated carbon of organics from aqueous solutions: correlation between adsorption and molecular structure. *Water Sci Technol* 35:251–259
- Cañizares P, Carmona M, Baraza O, Delgado A, Rodrigo MA (2006) Adsorption equilibrium of phenol onto chemically modified activated carbon F400. *J Hazard Mater B131*: 243–248
- Clesceri LS, Greenberg AE, Trussell RR (1989) Standard methods for the examination of water and wastewater, 17th edn. American Public Health Association, Washington
- Denizli A, Cihangir N, Tuzmen N, Alsancak G (2005) Removal of chlorophenols from aquatic systems using the dried and dead fungus *Pleurotus sajor caju*. *Bioresour Technol* 96:59–62
- Doshi H, Ray A, Kothari IL (2007) Bioremediation potential of live and dead *Spirulina*: spectroscopic, kinetics and SEM studies. *Biotechnol Bioeng* 96:1051–1063
- Dubinín MM, Radushkevich LV (1947) The equation of the characteristic curve of activated charcoal. *Dokl Akad Nauk SSSR* 55:327–329
- Freundlich H (1906) Adsorption in solutions. *Phys Chemie* 57:384–410
- Gerente C, Lee VKC, Le Cloirec P, McKay G (2007) Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review. *Rev Environ Sci Bio/Technol* 37:41–127
- Hamdaoui O (2006) Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns. *J Hazard Mater B138*:293–303

- Hamdaoui O, Naffrechoux E (2009) Adsorption kinetics of 4-chlorophenol onto granular activated carbon in the presence of high frequency ultrasound. *Ultrason Sonochem* 16:15–22
- Horsfall M Jr, Ogban F, Akporhonor EE (2006) Sorption of chromium (VI) from aqueous solution by cassava (*Manihot sculenta* CRANZ) waste biomass. *Chem & Bio* 3:161–173
- Jefferson K (2004) What drives bacteria to produce a biofilm? *FEMS Microbiol Lett* 236:163–173
- Langmuir I (1918) Adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc* 40:1361–1403
- Li L, Quinlivan PA, Knappe DRU (2002) Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon* 40:2085–2100
- Lu Q, Sorial GA (2004) Adsorption of phenolics on activated carbon—impact of pore size and molecular oxygen. *Chemosphere* 55:671–679
- Malkoc E, Nuhoglu Y, Dundar M (2006) Adsorption of chromium (VI) on pomace—An olive oil industry waste: batch and column studies. *J Hazard Mater* B138:142–151
- Mourão PAM, Carrott PJM, Ribeiro Carrott MML (2006) Application of different equations to adsorption isotherms of phenolic compounds on activated carbons prepared from cork. *Carbon* 44:2422–2429
- Mungasavalli DP, Viraraghavan T, Jin Y-C (2007) Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*: batch and column studies. *Colloids Surf A* 301:214–223
- Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M (2005) Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla filiculoides*. *J Hazard Mater* B125:121–129
- Prigione V, Varese GC, Casieri L, Marchisio VF (2008) Biosorption of simulated dyed effluents by inactivated fungal biomasses. *Bioresour Technol* 99:3559–3567
- Quintelas C, Tavares T (2001) Removal of chromium (VI) and cadmium (II) from aqueous solution by a bacterial biofilm supported on granular activated carbon. *Biotechnol Lett* 23:1349–1353
- Quintelas C, Tavares T (2002) Lead (II) and iron (II) removal from aqueous solution: biosorption by a bacterial biofilm supported on granular activated carbon. *J Res Environ Biotechnol* 3:196–202
- Quintelas C, Sousa E, Silva F, Neto S, Tavares T (2006) Competitive biosorption of ortho-cresol, phenol, chlorophenol and chromium (VI) from aqueous solution by a bacterial biofilm supported on granular activated carbon. *Process Biochem* 41:2087–2091
- Rao JR, Viraraghavan T (2002) Biosorption of phenol from an aqueous solution by *Aspergillus niger* biomass. *Bioresour Technol* 85:165–171
- Reddlich O, Peterson DL (1959) A useful adsorption isotherm. *J Phys Chem* 63:1024
- Ryan D, Leukes W, Burton S (2007) Improving the bioremediation of phenolic wastewaters by *Trametes versicolor*. *Bioresour Technol* 98:579–587
- Sathishkumar M, Binupriya AR, Kavitha D, Yun SE (2007) Kinetic and isothermal studies on liquid-phase adsorption of 2, 4-dichlorophenol by palm pith carbon. *Bioresour Technol* 98:866–873
- Sips R (1948) Combined form of Langmuir and Freundlich equations. *J Chem Phys* 16:490–495
- Streat M, Patrick JW, Camporro Perez MJ (1995) Sorption of phenol and pchlorophenol from water using conventional and novel activated carbon. *Water Res* 29:467–472
- Tallur PN, Megadi VB, Kamanavalli CM, Ninnekar HZ (2006) Biodegradation of p-cresol by *Bacillus* sp. strain PHN 1. *Curr Microbiol* 53:529–533
- Thawornchaisit U, Pakulanan K (2007) Application of dried sewage sludge as phenol biosorbent. *Bioresour Technol* 98:140–144
- Toth J (1971) State equations of the solid-gas interface layer. *Acta Chim Acad Sci Hung* 69:311–328
- Tunali S, Çabuk A, Akar T (2006) Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. *Chem Eng J* 115:203–211
- Vijayaraghavan K, Prabu D (2006) Potential of *Sargassum wightii* biomass for copper(II) removal from aqueous solutions: application of different mathematical models to batch and continuous biosorption data. *J Hazard Mater* B137:558–564
- Wicke D, Bockelmann U, Reemtsma T (2007) Experimental and modelling approach to study sorption of dissolved hydrophobic organic contaminants to microbial biofilms. *Water Res* 41:2202–2210
- Wolborska A (1989) Adsorption on activated carbon of p-nitrophenol from aqueous solution. *Water Res* 23:85–91
- Wu J, Yu H-Q (2006) Biosorption of phenol and chlorophenols from aqueous solutions by fungal mycelia. *Process Biochem* 41:44–49
- Wu J, Yu H-Q (2007) Biosorption of 2, 4-dichlorophenol by immobilized white-rot fungus *Phanerochaete chrysosporium* from aqueous solutions. *Bioresour Technol* 98:253–259
- Xiao L, Qu X, Zhu D (2007) Biosorption of nonpolar hydrophobic organic compounds to *Escherichia coli* facilitated by metal and proton surface binding. *Environ Sci Technol* 41:2750–2755
- Yoon YH, Nelson JH (1984) Application of gas adsorption kinetics-II. A theoretical model for respirator cartridge service life and its practical applications. *Am Ind Hyg Assoc J* 45:509–516
- Ziagova M, Liakopoulou-Kyriakides M (2007) Kinetics of 2, 4-dichlorophenol and 4-Cl-m-cresol degradation by *Pseudomonas* sp. cultures in the presence of glucose. *Chemosphere* 68:921–927