Modelling of fixed bed biosorption columns in continuous metal ion removal processes. The case of single solute local equilibrium

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A modelling approach for a fixed bed biosorption column is presented. The developed model includes the solute bulk movement through the void space of the bed, a solute dispersion term for simulating cases of non ideal flow, and sorption terms expressed by the appropriate sorption isotherm. The main assumption of the model is that biosorption equilibrium is rapid and no mass transfer resistances exist in the liquid and solid phase. The resulting second order non-linear partial differential equation describes the performance of a column filled with biosorbent material and used to remove single solute metal ions from dilute solutions. The model predicts the optimum expected operation of the bed by simulating breakthrough and concentration profile curves, under different operating conditions. Sensitivity analysis of the operating parameters, revealed that the most important of them are the sorption capacity and the sorption intensity of the biosorbent material as these terms are expressed through the Freundlich's isotherm coefficients.

1. INTRODUCTION

Adsorption is well-known and widely used industrial separation process in which chemical molecules are selectively bound on the surface of a solid phase. Traditional sorbent materials such as zeolites, granular activated carbon (GAC), silica and alumina have been used extensively in industrial scale gas and liquid separation processes. In the light of searching for inexpensive, renewable, alternative natural sorption materials the use of metabolically active or inactive microbial biomass as sorbent material has been proposed. The term biosorption has been adopted to describe the phenomenon of sequestering metal ions from aqueous solutions by different microorganisms such as bacteria, fungi, algae and yeast. Biosorption, has been extensively documented in the literature, over the last three decades, for many types of

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microbial biomass. In the last few years, the industry has shown also an increasing interest in applying biosorption as the key component of a waste water treatment technology, for achieving the effluent horizon values imposed by the increasingly more stringent environmental effluent standards. Biosorption is among the candidate alternative technologies for achieving low metal effluent concentrations at reasonable cost, especially for high volume - low concentration applications. Pilot scale units installed at different industrial sites have provided with promising results.5

Most of the experimental data reported in literature refer to results from small scale batch experiments (shaking flasks), of single, binary or multi-element synthetic metal ion solutions, on different biomass types, correlating the metal uptake capacity through an isotherm equation. In few cases, small-scale laboratory systems have been set up, (usually fixed bed columns), with attempt to correlate their performance to the design and scale up of an integrated metal decontamination process. The reasons for the limited mathematical modelling work on biosorptive systems reported in the literature are primary the following:

- The studies on biosorption have focused for many years mostly on the microbiological aspects of process, whereas the engineering view for developing an applied novel waste water treatment technology has been overlooked.

- Biosorption process itself is complex. Predictive modelling of biosorption in micro scale molecular level, with sorption or ion exchange reactions between metal ions and cell components is difficult. The mechanism of such interactions is not well elucidated, the microbial surface is highly heterogeneous, and the metal sequestering also depends on several other parameters such as metal ion chemistry, the nature of the microbial biomass, solution pH, anion or cation co-ion effects, presence of organic molecules etc. In addition, other phenomena such as bioprecipitation, bioreduction/biooxidation, may also contribute significantly to the metal uptake mechanism when metabolically active biomass is used. The complex matrix of the waste water in industrial applications, may also interfere significantly in the sequestering process, in a way that can not be predicted beforehand and almost inevitably by reducing the metal uptake capacity as compared to that estimated from pure, single element, chemically defined metal solutions.

- Modelling of adsorption as a separation process is complex itself. In many cases empirical models are used for design and the process scale up is based on experimental data obtained from similarly configured lab scale units, (usually packed beds). Complete models and detailed design equations for the most common process configurations such as batch fixed beds and fluidised beds are complicated due to the fact that the sorption process is a non steady state operation concerning the solute concentration on the solid and liquid phase. Mathematical modelling of such systems although is more often based on simple material balances and mass transfer phenomena from the liquid to the solid phase, usually results in a system of non-steady state partial differential equations, in the general case of non linear form. These equations, can only be solved by applying advanced numerical analysis methods. Therefore, as the solution is not provided in simple explicit form, (except for some simple cases), the manipulation of the model is difficult. In addition, the parameters involved in modelling continuous fixed bed columns, (axial dispersion coefficient, mass transfer coefficients in liquid and solid phase, kinetic constants, etc.), are difficult to be measured experimentally from batch or continuous systems. Therefore, reliable parameter values should either be calculated from generalised expressions, or be estimated by fitting the
model equations to data obtained experimentally. This multivariable fitting procedure is mathematically cumbersome, many times arbitrary, and the values obtained are not always easily scaleable to large systems.

Development of reliable process design and modelling tools for biosorption technology is important for simulating the results obtained from currently running systems. In addition, model sensitivity analysis will reveal the significance of each process parameter, leading to optimisation of process efficiency. The scale up criteria and wastewater treatment costs should also be considered for any industrial scale applications. Principles from chemical reactor design, separation processes, applied environmental biotechnology, and numerical analysis methods should be combined for successful modelling.

So far, biosorption modelling in batch mode systems has been studied thoroughly for the case of immobilised biomass particles of *Rhizopus arrhizus*. The outcome of the model is a kinetic profile curve (predicted or fitted to experimental data), which converges to the sorption equilibrium values. Although, batch systems are not likely to be used in industrial applications, the manipulation of batch models reveals the model mathematical complexity, even for the simplest configuration. Nevertheless, it provides the basis for tackling more complex systems.

A summary of possible contacting configurations for biosorptive systems has been presented elsewhere. Continuous contacting configurations, such as fixed bed columns (canisters), similar in operation to activated carbon and ion exchange resins, are more likely to be used in industrial applications. Metabolically active or inactive microbial biomass can be immobilised by different techniques (encapsulation, biofilm formation, etc.) to formulate biosorbent particles, similar in the behaviour to ion exchange resins. The performance of such columns is described through the concept of the breakthrough curve, which is the concentration profile of the sorbate at the column exit as a function of time. The time of breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation of a sorption column. Mathematical models for fixed beds, originate mainly from activated carbon sorption processes and ion exchange or chromatographic applications. Although, models for ordinary sorption columns have been studied extensively, modelling of continuous biosorption contacting configurations has not been examined in depth. Only recently, experimental breakthrough data for Cd biosorption have been treated theoretically.

The present paper aims to contribute to the mathematical modelling of biosorption process design, for a packed bed column configuration. The model examines the limited case described by the concept of rapid equilibrium. Under this concept, the model predicts the maximum anticipated "life duration" or best performance for a biosorption column used for sequestering a single solute from a solution. Although mass transfer limitations, both in liquid and solid phase, exist in most sorption processes, the developed model provides new information about the importance of key process operating parameters.
2. FIXED BED DESIGN

2.1. Principles

2.1.1. The breakthrough concept

In the simplest type of adsorption processes in which an adsorption column is used to remove a trace impurity from a process stream or waste water, the main requirement for rational design is an estimate of the dynamic or breakthrough capacity of the bed. In such systems the adsorbable impurity is strongly adsorbed with a favourable isotherm and the concentration profile therefore rapidly approaches constant-pattern form. The constant-pattern assumption provides the basis of a very simple design method, which permits reliable scale-up from small-scale laboratory experiments. Thus, a breakthrough curve and in particular the width of the sorption zone are important characteristics for describing the operation of a fixed bed biosorption column. A typical sketch of a breakthrough curve is presented in Figure 1, (for downflow mode of operation). The width of the sorption zone is shown in grey colour. At the early stages of the operation the solute is retained at the top of the column, and the most of the sorbent material is unsaturated, (white area). As the operation continues, a sorption zone is developed (grey area). This reaction zone moves downward, while saturated material is left behind (black area). At the beginning of breakthrough, at which the lower end of the sorption zone touches the bottom of the column, the total volume treated is represented by $V_b$. From this point afterward, the concentration of the solute at the exit increases constantly. The operation of the column can be continued until the exhaustion point ($t_e, or V_e$), at which the sorption zone has reached the exit of the column.

2.1.2. Length of unused bed (LUB)

The length of the unused bed (LUB) is defined by the equation,\(^{16}\):

$$LUB = \left(1 - \frac{t_1}{t_2}\right) L \tag{1}$$

where $L$ is the length of the fixed bed and the time parameters $t_1$ and $t_2$ are defined by the integrals, (see also figure 1):

$$t_1 = \int_0^b \left(1 - \frac{C}{C_0}\right) dt = \text{dark area} \tag{2} \quad t_2 = \int_0^\infty \left(1 - \frac{C}{C_0}\right) dt = \text{dark + light area} \tag{3}$$

The time $t_b$ is the breakthrough time at which the effluent concentration reaches its maximum permissible discharge level. This level is usually considered to be between 1 to 5% of the feed solute concentration. In some cases time parameters $t_1$ and $t_2$ are substituted by $t_b, t_e$ respectively.
Figure 1. A typical breakthrough curve showing the movement of the adsorption zone, breakthrough and exhaustion time.

3. DESIGN BASED ON EXPERIMENTAL DATA

The length of sorption zone can be calculated from the experimental breakthrough curve, for the system being studied, by applying material balance equations and implementing the maximum solute uptake capacity. It should be noted that the total mass of pollutant entered the column from the beginning to the completion of breakthrough is \((V_e - V_b)C_0\). At the same period, the solute that escaped removal can be calculated by the integral below the breakthrough curve from the points \(V_b\) to \(V_e\). Thus the solute removed \((M_r)\) in the reaction zone is:

\[
M_r = (V_e - V_b)C_0 - \int_{V_b}^{V_e} CdV
\] (4)
Mr is also given by the product $A_s \delta \rho_p q_o$, where $A_s$ is the superficial area of the bed, $\rho_p$ the fixed density of the bed, $q_o$ the maximum solute uptake capacity, and $\delta$ the width of reaction zone. Combining with equation 4 and solving for $\delta$ gives:

$$
\delta = \frac{(V_e - V_b)C_0 - \int_{V_b}^{V_e} CdV}{A_s \rho_p q_o}
$$

(5)

The integral in equation 5, should be calculated by numerical approximations from experimental breakthrough data.

Empirical models applied for the results obtained from ion exchange columns, resulted the equation 6 which describes the breakthrough curve in terms of $t_b$, $t_m$ and $\beta$.

$$
\frac{C}{C_0} = 1 - \exp \left[ - \left( \frac{t - t_b}{t_m} \right) ^\beta \right]
$$

(6)

where $t_b$ is the experimental breakthrough time, $t_m$ is the time when $C/C_0 = 0.632$, and $\beta$ is a curve shape factor. The parameter $\beta$ can be estimated by fitting a set of experimental data to the linear logarithmic form of the equation. Application of the equation 6 requires experimental breakthrough data, which in many cases might not be available. In addition, such mathematical expression does not predict the performance of the column when various operating parameters are changed, thus no information for the scale up of the process are provided. Further details on designing of fixed bed columns are given elsewhere.

Dimensionless numbers and correlation equations applied for the design of fixed bed columns

Two different velocities can be defined for the liquid flowing into the column. The superficial velocity based on the total volume of the column (or based on the empty volume), and the interstitial velocity based on the void volume of the packed bed, defined by the equations:

$$
\nu_{\text{superficial}} = \frac{F}{A} \quad (7)
$$

$$
\nu_{\text{interstitial}} = \frac{F}{A \varepsilon} \quad (8)
$$

where $F$ is the volumetric flow rate (cm$^3$/min), $A$ is the cross sectional area of the column (cm$^2$) and $\varepsilon$ is the porosity of the bed. The velocity mentioned in the ADR equation in the following paragraphs is the interstitial velocity.

Three forms of particle Reynolds numbers have been used in correlation equations for a liquid flow through a fixed bed:

$$
N_{Re} = \frac{D_p G}{\mu} \quad (9)
$$

$$
N_{Re} = \frac{D_p G}{\mu \varepsilon} \quad (10)
$$

$$
N_{Re} = \frac{D_p G}{\mu (1 - \varepsilon)} \quad (11)
$$
where $G$ is the superficial mass flow rate for the solution, (mass per time per surface area, e.g. gr/min cm$^2$), $\varepsilon$ is the bed porosity, and $\mu$ is the absolute viscosity of the flowing liquid, (gr/cm min) and $D_p$, the particle diameter (cm).

The axial dispersion coefficient for the liquid flowing in the fixed column can be calculated by the correlation coefficient $^{22}$:

$$\frac{D_h}{\mu} = \frac{N_{Re}}{0.20 + 0.011 N_{Re}^{0.48}} \quad 10^{-3} < N_{Re} < 10^{3}$$

(12)

Finally, the pressure drop in the column can be calculated by the equation $^{16}$:

$$f = \left(\frac{2 R_p}{L}\right) \frac{\Delta P}{\rho_f (\varepsilon \mu)^2}$$

(13)

where $\varepsilon \mu$ is the superficial fluid velocity (cm/min), $L$ is the bed length (cm), and $\Delta P$ is the bed pressure drop (gr/cm min$^2$).

The $f$ coefficient can be calculated by the Ergun equation:

$$f = \left(\frac{1 - \varepsilon}{\varepsilon}\right) \left(\frac{150(1 - \varepsilon)}{N_{Re}} + 1.75 \right)$$

(14)

In equations 12 and 14 the Reynolds number used is the one calculated from equation 9.

4. MATHEMATICAL MODELLING OF FIXED BEDS

A design approach based on a mathematical model preliminary relies on the solution of the material balance equations for the solute being adsorbed by the solid phase. What is required, is to determine the expected performance of a fixed column through the prediction of the breakthrough curve. For the case of a biosorption column the sorbent material is composed of biological material. The biosorbent particles can be native or immobilised biomass particles similar to the particles developed in previous works $^{9,23}$.

Models for sorption phenomena, and material balance equations have been summarised and reported in an excellent review paper $^{24}$. The movement of a solute in a column type reactor is generally described by the three dimensional generalised advection-dispersion-reaction (ADR) equation $^{24,25}$:

$$\frac{\partial C}{\partial t} = \text{div} (D_h \text{ grad } C) - v \text{ grad } C + \left(\frac{\partial C}{\partial t}\right)_r + S(C)$$

(15)

The subscript $r$ denotes reaction that affects the solute concentration. The reaction under consideration for the case of biosorption is solute retention by the biomass solids, a heterogeneous-phase, mass transfer process.

The above equation is a generalised three dimensional non steady state material balance equation for a solute being transported by diffusion, bulk flow, and depleted from the solution by
a sorption reaction. For generality, a solute production term is also included. The solution of this equation describes the performance and process dynamics of a sorption column.

Simplification of the general ADR equation to one spatial axial dimension (z) for a single solute, subject only to sorption without any other fluid-phase reaction or source term, yields the following equation.

\[
\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \rho_s (1 - \varepsilon) \left( \frac{\partial q}{\partial t} \right)
\]

(16)

The most important term of this material balance equation, is the rate of the solute uptake by the biosorbent, \( \frac{\partial q}{\partial t} \). Various methods can be used to characterise this term. All methods consist of describing two general components:

(i) the aqueous-solid equilibrium phase distribution relationship, (i.e. the sorption isotherms),

and

(ii) the rate at which this equilibrium is approached.

4.1. Local equilibrium models

The most simplistic approach to model sorption phenomena, is to assume that the time scale associated with the microscopic processes of mass transfer to the sorption site and subsequent sorption is very much smaller than that associated with the macroscopic processes of fluid transport. This effectively assumes that the equilibrium prevails locally, and is approached rapidly. Putting that in other words, this concept implies, that for the case of a fixed column, the rate of change of the sorbed phase concentration, \( q \), at any point \( z \), is instantaneously reflected by the rate of change of the solution phase concentration, \( C \), at that point. Therefore, it is assumed that mass transfer limitation in the liquid and solid phase are negligible and the sorption reaction is rapid. This approach yields the so called local equilibrium models, (LEM), which are presented in table 1. The general equation (16a), which describes the local equilibrium model, is a special case of equation (16).

The most simple local equilibrium model, assumes that the equilibrium distribution between the solid phase and the fluid phase is linear. In this case a linear isotherm equation is applied and the partial derivative \( \frac{\partial q}{\partial C} \) can be substituted by the partitioning coefficient \( K_p \) (The partial derivative is equal to the derivative \( \frac{dq}{dC} \) as \( q \) is only a function of \( C \) in this model).

\[
q = K_p C \quad \quad \quad \quad \quad \quad \quad \frac{dq}{dC} = K_p
\]

(17) (18)

The linear local equilibrium model (LLEM), shown in equation 23, is a very popular modelling method for column configurations, due in part to the simplicity of its solution, which can be obtained analytically, and differs simply by a constant from any solution to the conservative form of the advection-dispersion equation. Although the LLEM version of ADR equation has been widely employed for describing solute retardation by sorption in subsurface systems, it has become increasingly apparent that this model frequently fails to provide adequate representation of the effect of sorption processes on solute transport. Inclusion of more sophisticated non-linear equilibrium models, such as the Freundlich or Langmuir isotherms, often
provides better representation of sorption phenomena, especially over extended equilibrium concentration ranges\textsuperscript{24}.

If the Freundlich isotherm is used to describe the sorption term, then a local equilibrium model is obtained by substituting the term \( \frac{\partial q}{\partial C} \) by the equation (20):

\[
q = K_F C^n \quad (19) \quad \frac{dq}{dC} = K_F n C^{n-1} \quad (20)
\]

Similarly, for the case of Langmuir isotherm the term \( \frac{\partial q}{\partial C} \) can be substituted by the derivative of Langmuir isotherm:

\[
q = Q^* \frac{C}{1 + bC} \quad (21) \quad \frac{dq}{dC} = \frac{Q^* b}{(1 + bC)^2} \quad (22)
\]

A nonlinear equilibrium isotherm generally precludes analytical solution of equation 16a, thereby complicating model solution and application. In addition in many models the term of the axial dispersion coefficient is neglected before proceeding to the solution. A detailed review of the analytical solutions of the ADR equation for many special cases, is available elsewhere\textsuperscript{16}.

Table 1

<table>
<thead>
<tr>
<th>LOCAL EQUILIBRIUM MODELS</th>
</tr>
</thead>
<tbody>
<tr>
<td>FIXED COLUMN REACTOR CONFIGURATION</td>
</tr>
<tr>
<td>( \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} + u \frac{\partial C}{\partial z} - \frac{\rho_s (1 - \varepsilon)}{\varepsilon} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} ) \quad (16a)</td>
</tr>
<tr>
<td>LINEAR ISOTHERM</td>
</tr>
<tr>
<td>( \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{\rho_s (1 - \varepsilon)}{\varepsilon} K_P \frac{\partial C}{\partial t} ) \quad (23)</td>
</tr>
<tr>
<td>FREUNDLICH ISOTHERM</td>
</tr>
<tr>
<td>( \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{\rho_s (1 - \varepsilon)}{\varepsilon} K_F n C^{n-1} \frac{\partial C}{\partial t} ) \quad (24)</td>
</tr>
<tr>
<td>LANGMUIR ISOTHERM</td>
</tr>
<tr>
<td>( \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - \frac{\rho_s (1 - \varepsilon)}{\varepsilon} \frac{Q^* b}{(1 + bC)^2} \frac{\partial C}{\partial t} ) \quad (25)</td>
</tr>
</tbody>
</table>

The model developed and solved by the authors, has the advantage that non linear isotherms can be incorporated in the model and there is no need to eliminate the term of axial dispersion coefficient for the solution of the model\textsuperscript{26}. 
4.2. Rate Models

The assumption that the equilibrium is attained instantaneously, (local equilibrium models), is not always valid. There are cases, such as the sorption of hydrophobic organic compounds on soil\textsuperscript{27,28}, and the sorption of Uranium\textsuperscript{9} by \textit{Rhizopus Arrhizus} where the equilibrium is attained after several hours.

For all these cases, the term $\frac{\partial q}{\partial t}$ should be approximated by rate models. The most significant rate models have been summarised elsewhere\textsuperscript{24,27}. Two of the most popular used are the dual resistance diffusion model and pore diffusion model\textsuperscript{29}.

5. SOLUTION OF THE ADR EQUATION FOR THE CASE OF LOCAL EQUILIBRIUM

The ADR equation is a partial differential equation of parabolic type. The implementation of a non-linear sorption isotherm precludes its analytical solution. Thus numerical methods should be used.

\textit{Problem description}

The effluent solute concentration of a fixed bed biosorption column, as a function of time and the other operating parameters, is to be known, (breakthrough curve). At the beginning of the column operation the sorbent material of the column is assumed to be fresh or completely regenerated, for the entire column length. At time $t=0$ waste water containing a single solute is pumped introduced in a downward mode through the column as shown in figure 1.

\textit{Model assumptions}

The main model assumptions are the following:

(i) The concept of rapid equilibrium has been applied in all cases.
(ii) Operation is isothermal, which is valid for the cases of sorption from dilute solutions. Wastewater treatment by biosorption is applicable mainly to large volume low concentration solutions. Thus, this assumption is almost always valid. Indirectly, isothermal operation, implies that the sorption parameters, (coefficients of sorption equilibrium equation), are constant along the column length and duration of column service life.
(iii) Treatment of single solute wastewater. The model can be extended to describe multi-solute sorption phenomena, assuming that the appropriate sorption equilibrium equations are provided and competition effects among the species can be expressed analytically through a multi-solute isotherm equation.
(iv) Uniform bed packing. Uniform bed porosity throughout the column length. Hydraulic defects such as short-circuiting or channelling effects are not considered.
(v) Solute dispersion to the radial direction is negligible,
(vi) No radial velocity gradient. Uniform $u_z$ in any cross section of the bed and along the column length.

\textit{Equations}

The one dimensional local equilibrium cases of ADR equation have been used (equations 23 or 24 or 25) with the appropriate initial and boundary conditions.

\textit{Initial and boundary conditions}

Solving the ADR equation (equation 16a), requires the definition of one initial and two boundary conditions which can be formulated as follows\textsuperscript{28,30,31}.
Initial condition \( t \leq 0 \quad C_i = 0 \quad 0 < z < L \) \hspace{1cm} (26)

1\textsuperscript{st} boundary condition \( t > 0 \quad C = C_{i,\text{initial}} \quad z = 0 \) \hspace{1cm} (27)

2\textsuperscript{nd} boundary condition \( t > 0 \quad \frac{\partial C}{\partial z} = 0 \quad z = L \) \hspace{1cm} (28)

The second boundary condition denotes that at lengths longer than \( L \), solute transfer does not take place because no sorbent material is present.

**Solution method**

The authors have developed a solution method based on the application of the finite differences method for the solution of the material balance equation\(^{26}\). The methods of Euler or Crank-Nicolson have been used for the discretisation of the space and time derivatives\(^{52}\).

It is important to notice that at any point of the column, the concentration of the solute in the liquid phase is both a function of time and the position of it along the column length, because the system is at non steady state concerning the liquid and solid phase solute concentrations.

### 6. RESULTS AND DISCUSSION

The column dynamic response for the case of Cu biosorption by immobilised *Rhizopus arrhizus* assuming rapid equilibrium has been studied. The Freundlich isotherm has been used to describe Cu equilibrium distribution between the liquid and solid phase. The operating conditions summarised in Table 2 have been selected as a "typical" data set, around which model sensitivity analysis has been performed.

The column length and the internal diameter, are representative of a small scale laboratory column. Longer columns could also be selected. The bed porosity depends on the packaging arrangement and on the radius of the biosorbent particles used. Biosorbent particles are likely to have a density value slightly higher than that of water, (as described\(^{33}\) by the BIO-CLAIM\textsuperscript{TM} system), whereas the immobilized particles developed by the research group of Tsezos have a density value of about 0.773 gr/cm\(^3\). Wastewater, at a flow rate of 1 lt/min, loaded with 100 ppm Cu is assumed to be pumped downflow through the column. The mathematical expression to present the sorption isotherm is the Freundlich equation with the appropriate constants\(^{34}\). The axial dispersion coefficient \( D_h \) has been estimated by the correlation equation 12 for the conditions described above, while pressure drop \( \Delta P \) and \( f \) factor, have been calculated from equations 13 and 14 respectively.

Preliminary runs of the computer program had the aim to identify the conditions that would allow increased accuracy and solution stability. Although, no significant difference on the solution accuracy has been observed, between the Euler and Crank-Nicolson methods, the later has been used in all cases.

A broad range of sensitivity analysis has been performed by changing each time one of the values of the operating parameter or sorption characteristics of a fixed column and monitoring the breakthrough response of the system. The following tables and figures summarise the results obtained from the sensitivity analysis of the model. Length of unused bed (LUB) has been calculated from equation 1 after numerical calculation of \( t_1 \) and \( t_2 \) from equations 2 and 3 respectively.
Table 2
Operational data of a supposed laboratory scale column (base point).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length (L)</td>
<td>20 cm</td>
</tr>
<tr>
<td>Column internal diameter (ID)</td>
<td>2 cm</td>
</tr>
<tr>
<td>Column length/ internal diameter (L/ID)</td>
<td>10/1</td>
</tr>
<tr>
<td>Bed porosity (ε)</td>
<td>0.25</td>
</tr>
<tr>
<td>Biosorbent particles density (ρs)</td>
<td>1.1 gr/cm³</td>
</tr>
<tr>
<td>Fluid flow rate</td>
<td>1000 cm³/min</td>
</tr>
<tr>
<td>Initial solute concentration (C₀)</td>
<td>100 mg/l</td>
</tr>
<tr>
<td>Isotherm type</td>
<td>Freundlich</td>
</tr>
<tr>
<td>Metal Ion</td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Freundlich exponent (n)</td>
<td>0.782</td>
</tr>
<tr>
<td>Freundlich coefficient (K₊)</td>
<td>0.991 mg/gr dry biomass</td>
</tr>
<tr>
<td>Immobilised Particles Diameter(Dₚ)</td>
<td>0.1 cm</td>
</tr>
<tr>
<td>Flow density (ρ₁)</td>
<td>1000 gr/l</td>
</tr>
<tr>
<td>Absolute viscosity (μ)</td>
<td>0.6 gr/min cm</td>
</tr>
<tr>
<td>Interstitial velocity</td>
<td>1273 cm/min</td>
</tr>
<tr>
<td>Superficial mass flow (G)</td>
<td>31830 gr/min cm²</td>
</tr>
<tr>
<td>Nᵣₑ=DₚGμ</td>
<td>5300</td>
</tr>
<tr>
<td>Dₑ (estimated from eq. 12)</td>
<td>3 10⁻³ cm²/min</td>
</tr>
</tbody>
</table>

The parameter, which affects most significantly the breakthrough of the column, has been shown to be the exponent of the Freundlich equation. This value is characteristic of the sorption intensity. At values <<1, a highly favourable equilibrium pattern is observed, which means a preference of the solute to be sorbed at the solid phase at concentrations multiple of that of the liquid phase. Thus, the length of the sorption zone is narrow. At values of the exponent near but less than 1, the sorption zone is wider as the sorption intensity is weaker. For constant Freundlich coefficient value, the increase at the value of the Freundlich exponent, means indirectly an increase of the available sorption capacity for low solute concentrations. Thus, later breakthrough and exhaustion times are observed. A non-uniform behavior is observed at the exponent value of 0.5, (Table 3 and Figure 2).

The coefficient of the Freundlich equation is the second important parameter. It indicates the sorption capacity of the biosorbent material. The higher this value (for constant exponent), the higher is the capacity of the biosorbent material. Thus, as it was expected increased values of Freundlich’s coefficient result in longer breakthrough and exhaustion times, without affecting the width of the sorption zone, (Table 3 and Figure 3).

The effect of the axial dispersion coefficient is well known from the studies of its effect on the reaction efficiency of plug flow chemical reactors. From the engineering point of view, a small axial dispersion coefficient is required for higher column performance. The ideal limit would be plug flow pattern. High dispersion coefficient values result in flattening of the breakthrough curve as shown in figure 4. In the simulated results, as the axial dispersion coefficient decreases, the breakthrough curves becomes steeper and the length of unused bed shorter, (Table 4 and Figure 4).
Table 3
Effect of isotherm parameters on breakthrough curves

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Breakthrough time (min)</th>
<th>Exhaustion time (min)</th>
<th>% Length of unused bed</th>
<th>(1-t/t_c)*100%</th>
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<tr>
<td>Exponent of Freundlich equation</td>
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Figure 2. Effect of Freundlich exponent on breakthrough curves.
Figure 3. Effect of Freundlich coefficient on breakthrough curves.

Figure 4. Effect of axial dispersion coefficient on the breakthrough curve.
Table 4
Effect of various parameters on the operation of the column.
Results obtained by ADR model for rapid equilibrium

<table>
<thead>
<tr>
<th>Parameter variation</th>
<th>Breakthrough time (min)</th>
<th>Exhaustion time (min)</th>
<th>% Length of unused bed</th>
<th>($1-t/t_0$)*100%</th>
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</thead>
<tbody>
<tr>
<td>Base point (set values of Table 2)</td>
<td>18.6</td>
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<td>Bed porosity (dimensionless)</td>
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<td>0.10</td>
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<tr>
<td>Axial dispersion coefficient (dm²/min)</td>
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<td></td>
<td></td>
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<td>1.1</td>
<td>4.3</td>
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<tr>
<td>Solute concentration (ppm)</td>
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<td></td>
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<td>Sorbent density (gr/cm³)</td>
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<tr>
<td>Column length (dm)</td>
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<td>Internal column diameter (dm)</td>
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<td>109.1</td>
<td>134.9</td>
<td>6.6</td>
<td>19.1</td>
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</tbody>
</table>
The change of bed void volume revealed that as bed porosity increases, the breakthrough and exhaustion time decrease, because less sorbent material is present in the bed, the void volume of the column is higher, therefore, the sorption front moves faster toward the exit of the column. This behaviour has been quantified in table 4. The length of unused bed also increases as the porosity of the bed increases.

The increase of the flow rate with constant solute concentration decreases the useful column operation time (for constant bed capacity). Thus, as the fluid flow rate increases the breakthrough and the exhaustion times decrease. Increase at the column flow rate reflects also to increase of the interstitial velocity of the fluid in the column. This might affect the axial dispersion coefficient, resulting possibly in the flattening of the breakthrough curve. In our work increase of flow rate has not been interrelated to simultaneous changes of the axial dispersion coefficient values.

For constant column sorption capacity it is expected that the saturation of the column will occur earlier as the solute concentration increases, and thus an earlier breakthrough curve is expected. This behaviour has been verified.

According to the simulated results obtained, the density of the biosorbent material is also significant to the breakthrough time. An increase on the biosorbent density results in an increase in breakthrough time due to the presence of more sorbent material in the column and thus the higher sorption capacity of the system.

It is obvious that the increase of column length, results to higher sorption capacity of the bed thus to a later breakthrough. A linear relationship between breakthrough time and column length has been observed. This observation has been verified experimentally in the biosorption literature.15

A comparative way of presenting sensitivity analysis data is shown in Figure 5. The relative importance of the various parameters can be identified by plotting the relative change of the value of interest (i.e. breakthrough time) against the relative change in the value of the parameter under investigation. The percentage relative changes have been calculated from the formula:

$$\% \frac{dx}{x} = \frac{x_{\text{new}} - x_{\text{base point}}}{x_{\text{base point}}} \times 100\%$$

The origin of the axis correspond to the base point selected previously (see Table 2). The breakthrough time at the base point is 18.56 min. The x axis shows, the percentage deviation from the base point of the variable under consideration. In y axis the percentage change of the breakthrough time from the base point breakthrough time is presented. From Figure 5, it is clear that the most important operating parameter is the sorption intensity and the sorbent uptake capacity, as expressed by the Freundlich exponent and coefficient respectively. The effect of column length is the same as of the Langmuir coefficient, which is in agreement with the common sense that doubling the column length is equivalent to doubling the maximum uptake capacity. Presenting sensitivity analysis data in such normalising way reveals the relative significance of the parameters in the model. Nevertheless, the plot may be misleading because the easiness of changing one parameter by 10% might not be as easy as for the other parameters. For example 10% change of the flow rate may represent a flow disturbance, whereas 10% change of the Freundlich equation coefficient might require the development of a new sorbent material with higher uptake capacity.
Figure 5. Sensitivity analysis plot showing the relative importance of various parameters on the breakthrough time of a fixed bed column.

7. CONCLUSIONS

A modelling approach to simulate the operation of a fixed bed biosorption column has been presented. Although the model is restricted for the case described by the concept of local equilibrium, it simulates the optimum performance expected from a sorption column under different operating conditions. The breakthrough curves predicted are steep because the overall sorption rate in the model is considered infinite. This is actually an ideal situation for maximum exploitation of the sorption capacity of a column. The importance of the sorbent high uptake capacity has been demonstrated. In addition, the flattening effect of the axial dispersion on the breakthrough curves has been also observed. Experimental validation of the results predicted from the model is difficult to be obtained, as in most of the cases mass transfer resistances in solid and/or liquid phase determine the overall sorption rate. In cases where the sorbent particles are fine, highly porous and the flow regime is turbulent, the operation of a column is believed to approach that predicted from the model, without in any case exceeding that. Therefore, the assumption of rapid equilibrium provides one of the two extremes for the operation of sorption columns. The other extreme condition would be flow without sorption reaction.

The presented model, provides the background for developing more complex models. The core ADR equation remains the same, whereas it should be completed with the equations describing liquid and solid phase mass transfer phenomena. Sorption reaction kinetic coefficients should also be used if the sorption time scale is comparable to the diffusion time scale. Preliminary results from
extension of the model to implement mass transfer resistances in the liquid and solid phase have revealed much more earlier breakthrough curves with more flattening pattern concentration profiles.

NOMENCLATURE

\( A_s \)  
Superficial area of the bed (cm\(^2\))

\( b \)  
Langmuir isotherm parameter (cm\(^3\)/mg)

\( C_s \)  
Solution phase solute concentration (mg of solute / cm\(^3\) of solution)

\( C_0, C_{\text{initial}} \)  
Initial solute concentration at the feed (mg/l)

\( D_h \)  
Hydrodynamic dispersion coefficient (cm\(^2\)/min),

\( \varepsilon \)  
Bed porosity, void volume per unit total volume (dimensionless)

\( F \)  
Volumetric flow rate (l/min)

\( f \)  
\( f \) coefficient

\( G \)  
Superficial mass flow rate (gr/cm\(^2\) min)

\( K_p \)  
Partitioning coefficient

\( L \)  
Column length (cm)

\( LUB \)  
Length of unused bed (cm)

\( M_r \)  
Solute removed in the reaction zone

\( N_{Re}, N_{Re}', N_{Re}'' \)  
Reynolds number (dimensionless)

\( q \)  
Volume averaged sorbed-phase solute mass per solid-phase mass (mg solute/gr sorbent).

\( q_0, Q^0 \)  
Maximum solute uptake capacity of the solid phase

\( r \)  
subscript denotes reaction that affects the solute concentration

\( R_p \)  
Biosorbent particle radius (cm)

\( \rho_b \)  
Biosorbent material bulk density (gr/cm\(^3\)),

\( S(C) \)  
Fluid-phase solute source term (mg of solute / cm\(^3\) min)

\( t \)  
Time (min)

\( t_t \)  
Time parameter until the breakthrough point

\( t_e \)  
Time parameter until the exhaustion point

\( t_b \)  
Breakthrough time (min)

\( t_e \)  
Exhaustion time (min)

\( t_m \)  
Time when \( C/C_0 = 0.632 \), (min)

\( u \)  
One dimensional fluid phase interstitial velocity (cm/min),

\( v \)  
Pore velocity vector (cm/min)

\( z \)  
Space direction (cm)

\( \beta \)  
Curve shape factor (dimensionless)

\( \delta \)  
Width of reaction zone (cm)

\( \Delta P \)  
Column pressure drop (gr/cm min\(^2\))

\( \mu \)  
Absolute viscosity of the wastewater (gr/cm min)

\( \rho_b = \rho_s(1-\varepsilon) \)  
Fixed density of the bed (biosorbent mass per unit bed volume, gr /cm\(^3\))

\( \rho_s \)  
Biosorbent material density (g/cm\(^3\))
REFERENCES

