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Dynamic Simulation and Experimental Validation of Single and Multi-Metallic Solutions in the Biosorption of Heavy Metals in Membrane Reactors: An Overview

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ABSTRACT

In this paper an overview on the use of membrane reactors to immobilise micro-organisms in a stirred tank reactor during continuous heavy metal biosorption tests is presented. Experimental data were collected in different operation conditions of pH and biomass concentration both with single and binary metal solutions in membrane reactor apparatus using Sphaerotilus natans as biosorbent. A dynamic model is developed on the base of equilibrium adsorption data obtained by batch biosorption tests carried out in different operation conditions. Comparison among experimental data and simulated profiles provides the base for implementation of dynamic model as a fundamental mathematical tool in process design of continuous biosorption systems. Multi-metallic biosorption experimental data and simulations evidenced the adsorbent selectivity following the general order Pb>Cu>Cd. Multi-stage configuration allows metal removal to be increased and it is a possible alternative to separate the different metals contained in real polluted waste streams in the different stages according to their affinity for the adsorbent active sites. © 2002 SDU. All rights reserved.

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1. INTRODUCTION

Biosorption is an innovative technology to remove heavy metals from wastewater based on the property of certain kinds of inactive and dead biomasses to bind and concentrate these pollutants from even very dilute aqueous solutions (Vegliò and Beolchini, 1997; Volesky, 2000). Biosorbent materials usually used for these studies are wastes resulting from agricultural and industrial activities, from water biological purification plants, seaweed and specially propagated biomasses of fungi, yeast and bacteria.

The mechanisms of metal uptake can be various and simultaneous such as physical adsorption, ion exchange, complexation and surface micro-precipitation (Vegliò and Beolchini, 1997).

The main advantages of biosorption, compared to conventional technologies such as precipitation and ion exchange, are:
- cost effectiveness when a waste is used as adsorbent;
- possibility of using conventional process configuration as fixed bed column generally after the biosorbent immobilization;
- possibility of recovering metals;
- reduction of residual waste volume because the exhausted biomass can be easily burned.

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The materials generally used in biosorption have poor mechanical properties so that a preliminary immobilisation step is generally required to modify cells or biological fragments, with low density and mechanical strength, into adsorbent particles with proper dimensions, stability and resistance, permitting their use in conventional fixed bed columns. Nevertheless immobilisation presents some disadvantages with respect to free cells: first of all the cost required for immobilisation which can be a strict limitation for a wider application of biosorption whose main advantages is the low cost of the adsorbent. Immobilisation can also negatively affect biosorption in terms of increasing mass diffusion resistance and decreasing adsorption capacity for carrier-biomass physico-chemical interactions (Vegliò *et al.*, 1998).

An alternative operative configuration to perform a continuous biosorption process is a membrane reactor obtained by coupling a stirred tank reactor (STR) and an ultrafiltration-microfiltration (UF/MF) tangential flow membrane modulus. The membrane system is able to retain free cells and it is permeable to metallic species (Barba *et al.*, 2000; Vegliò *et al.*, 2000; Beolchini *et al.*, 2001). This operative configuration allows a continual separation of biosorbent particles and treated solution also providing a suitable system to keep in contact biomass and heavy metals improving thus the adsorption efficiency.

Along with the process design of a continuous biosorption apparatus, the other discriminating factor in the development of a depuration process is the selectivity of the adsorbent. In fact real polluted waste streams are usually characterised by the presence of various heavy metals, alkaline and alkaline-earth metals. The selectivity of the adsorbent is assumed to be dependent on the specific nature of the active sites present on the surfaces and can be partially enhanced by specific physico-chemical treatments. Nevertheless analysis of different experimental adsorption data reported in the literature, not only onto biological matrices but also onto inorganic natural adsorbents (such as soils and clays), shows the occurrence of a general selectivity series both in single and multi-metallic systems.

In the present paper an overview of the main results obtained in biosorption studies of heavy metals carried out on membrane reactors are reported here. The main challenges of biosorption applications have been described proposing an experimental apparatus to perform a continuous biosorption process also describing a dynamic modelling suitable as a means to understand the physico-chemical phenomena into the reactor.

Biosorption of single and binary metal systems is performed and simulated in single and two stages membrane reactors. In particular a specially propagated biomass of *Sphaerotilus natans*, a filamentous gram-negative bacterium generally present in biological depuration plants, has been used in these experimental tests.

2. MATERIALS AND METHODS

2.1. Biomass

The *Sphaerotilus natans* is a gram-negative bacterium isolated from the waste streams of a water purification plant (Solisio *et al.*, 2000). The cultivation medium consists of meat peptone (7.5g/l) and yeast extract (7.5g/l) and the operating conditions in a bioreactor vessel of one liter are 25°C and 1atm with an air flux rate of 0.5l/min: the cultural media has been selected as reported in previous works (Solisio *et al.*, 2000). The biomass growth was controlled by dry weight measurements. The biomass produced was separated by centrifugation, washed by distilled water, lyophilised (Vegliò *et al.*, 1999) and stored.

2.2. Biosorption tests in batch reactor

Biosorption batch tests onto *Sphaerotilus natans* were performed under different operating conditions of pH and biomass concentration with lead, copper, zinc and cadmium as heavy metals both in single (Esposito *et al.*, 2001; Pagnanelli *et al.*, 2002a) and binary systems (Pagnanelli *et al.*, 2002b).

Single metal system biosorption tests (Esposito *et al.*, 2001; Pagnanelli *et al.*, 2002a) were carried out by using an experimental procedure named as Subsequent Addition Method (S.A.M.) (Pagnanelli et al., 2000), which allows the whole isotherm to be obtained at a constant equilibrium pH using only one sample, saving time, reagents and biomass. This experimental procedure consists of successive spikes of a heavy metal concentrated solution to a cellular suspension kept under magnetic stirring. After each metal addition, residual metal concentration was determined by ICP (Inductively Coupled Plasma Spectrophotometer) on samples collected when the system has reached equilibrium conditions (30 minutes). Additional tests without biomass were performed to evaluate the possible contribution of metal precipitation. Metal specific uptake q (mg/g of lyophilized biomass) was then calculated by the mass balance of the metallic ion in the system (Pagnanelli *et al.*, 2000).

Heavy metal biosorption tests in binary systems investigated the couples Cu-Cd, Cu-Pb and Cu-Zn with various initial molar ratios (4:1, 2:1, 1:1, 1:2 and 1:4) (Pagnanelli *et al.*, 2002b). A known amount of lyophilised biomass was weighted and re-hydrated under magnetic stirring at constant temperature (25°C) for 1 hour. Then a precise volume of a concentrated solution containing two metals with different initial molar ratios, was added to the re-hydrated cellular suspension. The pH was monitored by a pH-meter and kept constant by NaOH additions during all the time necessary to reach equilibrium (30 minutes). The solid adsorbent was separated by centrifugation and the liquid was analysed to determine the residual metal concentration by ICP. The initial metal concentration was determined by blanks reproducing the samples with the same metal and NaOH additions but without biomass.

2.3. Biosorption tests in membrane reactor

A biosorption trial was performed as follows: the lyophilised biomass at different concentration levels was introduced in a temperature controlled glass reactor (volume 200 ml, temperature 30°C). The dead biomass suspension was fed through a membrane module by a peristaltic pump (tangential velocity 0.3 m/s; trans-membrane pressure 200 kPa). A polysulfone membrane was used with 100,000 Da molecular weight cut off (MWCO) and a total area of 36 cm². The metal solution was then fed to the reactor by a second peristaltic pump. The flux decreasing (F) was monitored during time and by this way the reactor operated at a constant volume. As a consequence the first peristaltic pump (which feeds the metal solution) was manually controlled in order to have a constant reactor volume. Figure 1 shows schematically the experimental system used.
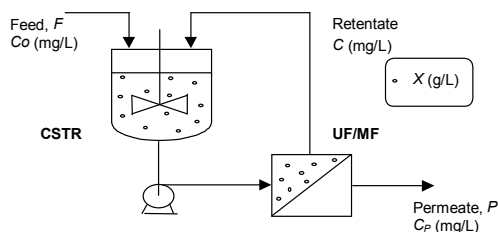

Figure 1. Schematic representation of a membrane reactor

pH was also controlled at a fixed value according to operating conditions and kept constant by continuous additions of NaOH 0.1 and/or 0.01N. Different samples of permeate and retentate were collected during time and analysed. In the case of permeate, no cell harvesting was needed because all cells were completely retained by the membrane. In the case of retentate, cells were separated by centrifugation at 8000g for 10 minutes and then copper concentration was determined by Atomic Absorption Spectrophotometer (Vegliò *et al.*, 2000; Beolchini *et al.*, 2001).

A centred factorial design was implemented for single system biosorption with pH, biomass concentration and inlet copper concentration as factors. Preliminary binary biosorption test of copper and lead solutions was performed at pH 5 with a biomass concentration (X) of 1g/l.

3. DYNAMIC MODEL AND EXPERIMENTAL VALIDATION

3.1. Single metal system

A dynamic model of biosorption in a membrane reactor system was developed considering the following hypotheses:
➢ a constant reactor volume (V) and then the same feed and permeate flow rates (F=P),
➢ zero metal retention coefficients (σ) that means that metal concentration in the permeate (C_P) and in the retentate (C_R) are the same and the membrane cannot adsorb the metals (retentate (C_R) and reactor (C) metal concentration are also assumed to be equal)

$$\sigma = 1 - \frac{C}{C_R} = 0 \qquad (1)$$

➢ biomass concentration (X), pH and temperature constant in the reactor
➢ a perfect mixing reactor
➢ no bulk diffusion effect
➢ an equilibrium process being the adsorption kinetic very fast (Vegliò *et al.*, 1998) with respect with the residence time (τ=V/F)

where:
V   reactor volume (l)
F   feed solution containing heavy metals (l/h)
P   permeate flow rate (l/h)
X   biomass concentration (g/l)
σ retention coefficient (dimensionless)
C   heavy metal concentration in the permeate (mg/l)
C_R heavy metal concentration in the retentate (mg/l)
τ residence time in the continuous reactor (h)

The dynamic model is then obtained under these assumptions by the metal mass balance in the system:

$$FC_0 - FC - rV = V\frac{dC}{dt} \qquad (2)$$

where:
C_0 metal concentration in the feed solution (mg/l)
r   rate of metal uptake (mg/l h)

The rate of metal uptake can be related to the specific metal uptake q (mg/g) considering a constant
biomass concentration in the reactor if the membrane can retain all cells and no degradation phenomena occur then, r = d(qX)/dt = X dq/dt.
When biosorption of a single metal system is considered in a reactor a simple Langmuir isotherm can be used to represent the equilibrium conditions:

$$q_i = \frac{q_{max,i}b_iC_i}{1+b_iC_i} \qquad (3)$$

where $q_{max,i}$ (mmol/g) and b_i (l/mmol) are the equilibrium adjustable parameters, which can be related (Langmuir, 1918) to the maximum specific metal uptake and to the equilibrium constant of metal-active site species respectively.

The equilibrium parameters for the single component metallic system for different conditions of pH and biomass concentration were obtained by batch tests (Table 1) (Esposito *et al.*, 2001; Pagnanelli *et al.*, 2002a,b).

Table 1
Equilibrium parameters for the three models estimated on single and binary metal systems (Esposito *et al.*, 2001; Pagnanelli *et al.*, 2002a,b)

Model 1	pH	$q_{max,i}$ (mmol/g)		b_i (l/mmol)
Pb	4	0.39		670
	5	0.65		41
Cu	4	0.18		17
	5	0.65		18
Cd	4	0.06		50
	5	0.23		40
Model 2	pH	η_i		η_j
Cu-Cd	4	30		2
	5	23		5.5
Cu-Pb	4	2900		4
	5	8.4		55
Model 3	pH	Q_{max} (mmol/g)	B_i (l/mmol)	B_j (l/mmol)
Cu-Cd	4	0.18	28	8
	5	0.68	15	4.2
Cu-Pb	4	0.19	100	120
	5	0.67	12	40

Coupling the metal material balance (2) and the equilibrium equations (3) a first order differential equation was then obtained and numerically solved (MathCAD 2000 Professional Software) considering a step perturbation in the metal feed concentration.

$$\frac{dC}{dt} = \frac{F(C_0 - C)}{V\left(1 + \dfrac{q_{i,max} b_i X}{(1 + bC)^2}\right)} \tag{4}$$

The experimental validation of the formulated dynamic model was carried out by performing a factorial design with pH, biomass concentration and inlet metal concentration as factors. The simulation curves were then obtained by introducing in the dynamic model (2) an empirical time depending function accounting for the permeate flux decline generally observed in membrane systems (Beolchini *et al.*, 2001):

$$F(t) = a - d \cdot t^c \tag{5}$$

where a, d and c are the adjustable parameters determined by a non linear regression of the experimental data.

The experimental data and the relative simulated curves (these last obtained by solving equations 2, 3, 4 and 5 with the appropriate equilibrium parameters shown in Table 1) were reported as an example for a constant pH (pH 4) at two different biomass concentrations (X = 1 and 5g/l) in Figure 2, and for a constant biomass concentration (X=3g/l) at different pH (4, 5 and 6) in Figure 3. In each graph, the permeate copper concentration profiles and the permeate flux decline were reported (as experimental data and fitted or simulated curves). The comparison among experimental data and blank simulation (obtained by resolving the same equations for X=0g/l) evidenced the good performances of *Sphaerotilus natans* in removing copper from

aqueous solutions especially for the higher level of the tested factors pH and biomass concentration.
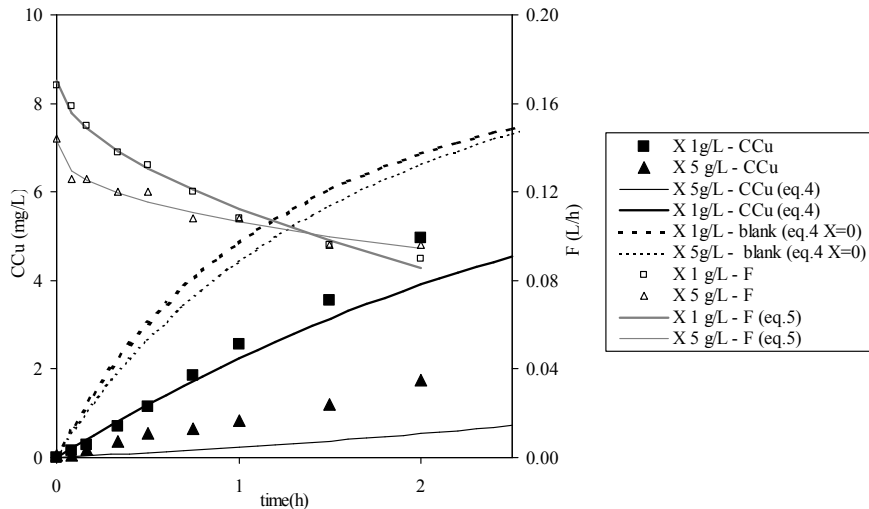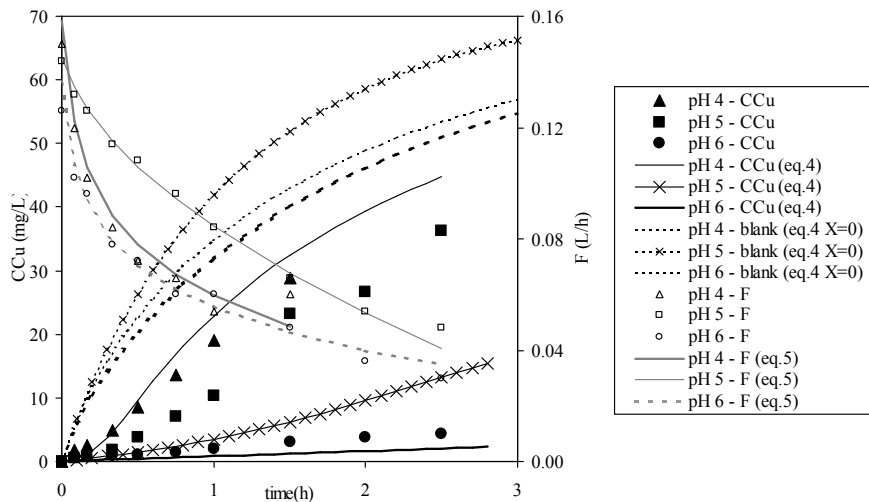

Figure 2. Experimental data of permeate flux decline (F) and copper permeate concentration (CCu) during biosorption tests in a membrane reactor at pH 4 for two different biomass concentrations (X 1g/l and 5g/l). Comparison with simulated curves obtained by solving equation 4 accounting for permeate flux decline by eq. 5 and considering the equilibrium parameters reported in Table 1 for eq. 3. Blank simulation were also reported considering X=0 in eq.4.

Figure 3. Experimental data of permeate flux decline (F) and copper permeate concentration (CCu) during biosorption tests in a membrane reactor with X 1g/l for different pH (4, 5 and 6). Comparison with simulated curves obtained by solving equation 4 accounting for permeate flux decline by eq. 5 and considering the equilibrium parameters reported in Table 1 for eq. 3. Blank simulation were also reported considering X=0 in eq.4.

As for the comparison among experimental data and simulation of the permeate concentration, a quite good agreement is obtained when low biomass and inlet metal concentration were considered and therefore a low metal concentration was reported in the permeate. Anyway as the feed metal concentration and the biomass concentration increase the agreement between experimental and simulated results diminishes. This detachment required further experimental investigation to develop a more detailed dynamic description of the

biosorption phenomenon. In particular the observed decline in the permeate flow rate can be related to a partial cell disruption due to mechanical stressing conditions in the reactor and the generation of cell fragments, which could be responsible of pore plugging. The decrease of biomass concentration during continuous biosorption in membrane reactor was observed by Chang and Chen (1999) that studied regarding a series of hollow filter microfiltration devices using *Pseudomonas aeruginosa* as adsorbent material for Pb, Cu and Cd ions: for an analogous apparatus, where the biomass concentration in suspension was found to decrease during time. Another phenomenon relating to biomass degradation, which was experimentally observed is the change of the metal retention coefficient on the membrane during time in different ways according to the different operating conditions (Figure 4): this experimental evidence was obtained by monitoring the copper concentration in the permeate and retentate during an experimental test.
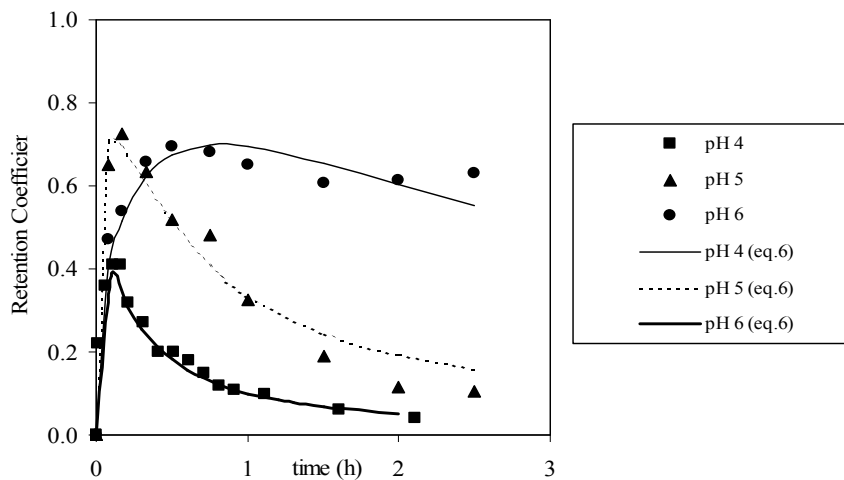

Figure 4. Metal retention coefficient profiles (as experimental data and fitted curves by eq. 6) for different equilibrium pH (4, 5 and 6).

This fact may be explained by considering that cell fragments produced for the shear stress in the membrane reactors, can liberate in solution different cellular matters present into the microbial cells. These organic compounds may have a complexing action with respect to copper (II) and at the same time they can be retained by the membrane reactor: in this manner the retention coefficient appears to be larger than zero as assumed in the dynamic model (2). In any case the assumption of $\sigma = 0$ appears to be no realistic in the experimental system investigated.

Finally, biosorption is characterised by a non-constant metal uptake as the biomass concentration in solution changes (due to microbial cell degradation and the adsorption phenomena on the membrane). This fact is also probably due to aggregation phenomena occurring at high biomass concentration and the complexation properties of the organic compounds released in solution for cell damaging. This can be another source of detachment among dynamic simulation and experimental data because the equilibrium parameters used are referred to a fixed constant value of biomass concentration, while active bulk biomass concentration in the membrane reactor may change during time.

A model implementation was then developed by considering an empirical fitting of the experimental data of the metal retention coefficient during time in the different operative conditions. The following model was used to fit the experimental data reported in Fig.4:

$$\sigma = \alpha t^{-\beta}\left(1 - \exp(-\gamma t)\right) \tag{6}$$

where parameters α, β and γ were estimated by non linear regression techniques. This empirical correlation is a simple tool to take into account the σ variation with time. Nevertheless, a deeper investigation is in progress to obtain a deterministic modeling of this phenomenon.

A further simple correlation was then introduced between active bulk biomass concentration and σ

$$X = X_0 (1-\sigma) \tag{7}$$

where X_0 is biomass concentration at the beginning of the process. The assumption that biomass disruption and σ variation with time are strictly linked is also observed in the case of *Arthrobacter* sp. (Beolchini *et al.*, 2001), where biomass disruption and σ variation were hypothesised to vary both with a first order kinetics, and the two kinetic constants were estimated by non linear regression techniques. This dynamic model without any additional parameter (except those directly fitted on separate set of experimental data as for σ) can represent adequately metal concentration in the permeate for different operative conditions as reported for example in Figure 5.
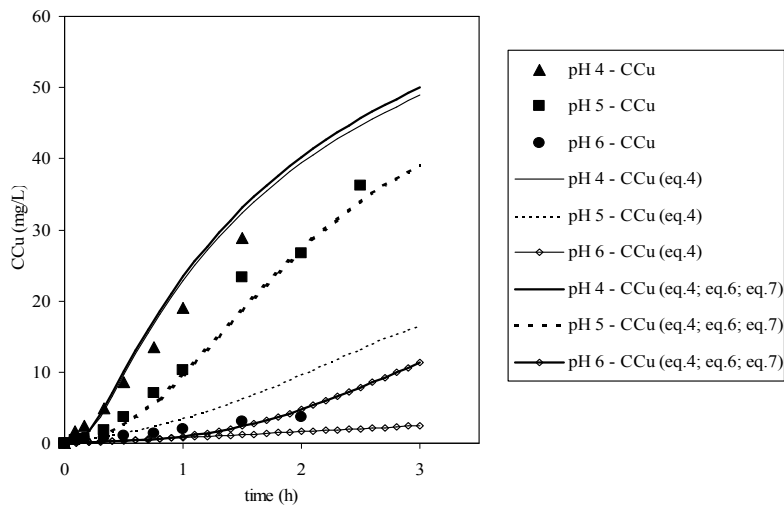

Figure 5. Experimental data of permeate flux decline (F) and copper permeate concentration (CCu) during a biosorption tests in a membrane reactor with X 1g/l for different pH (4, 5 and 6). Comparison among experimental data and simulated curves obtained by solving eq. 4 combined with eq. 5 and considering or not the metal retention coefficient and biomass concentration changes during time (eq. 6 and eq. 7).

3.2. Multi-metallic systems

The actual application of biosorption technology to real waste stream requires the study of multi-metallic systems (Pagnanelli *et al.*, 2000b; Sag *et al.*, 2000) by means of dynamic simulation and relative experimental validation.

When biosorption of binary metal system is considered, the equilibrium metal concentrations in the solid (q_i) and in the liquid phase (C_i) can be calculated according to different Langmuir type competitive models, which can be written according to the general equation:

$$q_i = \frac{\alpha_i C_i}{1 + \beta_i C_i + \gamma_j C_j} \tag{8}$$

where the subscript *i* and *j* are referred to two different metals and α, β and γ are the equilibrium parameters.

The difference among these models lies in the adjustable parameters fitting (Pagnanelli *et al.*, 2002a,b).

The simplest way to represent biosorption of multi-metallic systems is a prediction by using mathematical equations containing only parameters obtained from single metal isotherms. Model 1 are predictive model with the adjustable parameters determined from single metal systems data (Table 2) according to the traditional Langmuir equation (4).

Table 2
Adjustable parameters for three competitive Langmuir type models (equation 8): $q_{max,i}$ and b_i are the equilibrium parameters estimated on single metal data by equation 4, while the correction parameters η_i as well as Q_{max} and B_i were estimated on binary metal system equilibrium data.

Parameters	Model 1	Model 2	Model 3
α_i	$q_{max,i}\,b_i$	$q_{max,i}\,b_i/\eta_i$	$Q_{max}B_i$
β_i	b_i	b_i/η_i	B_i
γ_j	b_j	b_j/η_j	B_j

Predictive models cannot describe adequately adsorption of multi-metallic system due to non ideal competition among adsorbates. The addition of further correction coefficients into the classical competitive Langmuir isotherm (3) makes this model more flexible and representative of the complexity of multi-metallic systems. Additional correction parameters fitted on multi-metallic equilibrium data were then added in Model 2.

On the other side Model 3 adjustable parameters were all fitted on binary metal system equilibrium data.

In Figures 6 and 7 two 3D plots were reported which represent binary metal systems of Cu-Cd and Cu-Pb at pH 5 and X 1g/l according to Model 3.
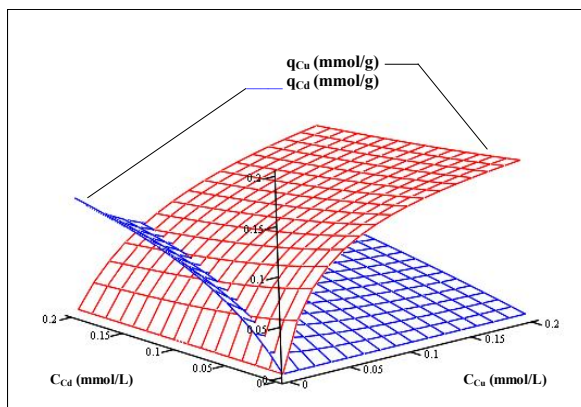

Figure 6. 3D plot for Cu-Cd binary system biosorption onto *Sphaerotilus natans* (X 1g/l; pH 5) represented by Model 3 (Tables 1-2).
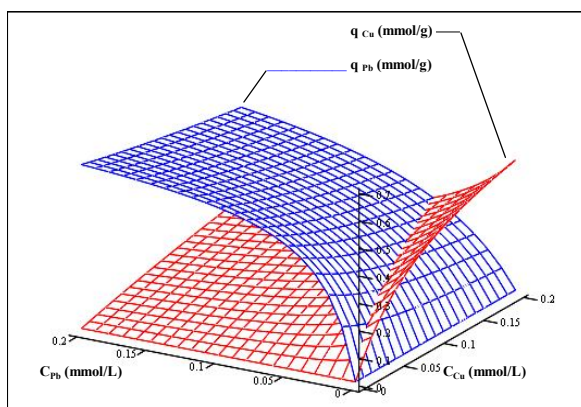

Figure 7. 3D plot for Cu-Pb binary system biosorption onto *Sphaerotilus natans* (X 1g/l; pH 5) represented by Model 3 (Tables 1-2).

These two figures were reported to outline a general affinity series observed not only for biosorbents but also for different inorganic matrices as soils, clays and others. According to this affinity order, lead and copper have major affinity than cadmium; when binary systems are

considered copper uptake is scarcely influenced by increasing cadmium concentrations, while cadmium uptake is negatively affected by the presence of copper in solution. In the same way lead is scarcely affected by copper, which on the contrary is influenced by increasing lead concentration in solution. This trend is more evident when pH is increased being the competition among heavy metals masked by that for hydrogen ions at low pH value. This quite general selectivity series can be explained according to various theoretical hypotheses: considering the different affinities of the sites for aquo- and hydroxo-complexes (Spark *et al.*, 1995), supposing a complexation mechanism on the base of the strict analogy between affinity series and first hydrolysis constant (Smith and Martell, 1976) or according to the ASAB theory of Pearson (Pearson, 1969). The affinity series puts in evidence the importance of metal speciation on the adsorption selectivity, which can even predominate on the specific adsorbent characteristics.

A dynamic simulation of binary biosorption in membrane reactor is then obtained combining the metal mass balances with an equilibrium model accounting for the presence of different metals in solutions. The system of differential equations is then numerically solved considering a step perturbation for both metals in the feed:

$$\frac{dC_1}{dt} = \frac{(C_{01} - C_1)}{\tau} - X \frac{dq_1}{dt} \tag{9}$$

$$\frac{dC_2}{dt} = \frac{(C_{02} - C_2)}{\tau} - X \frac{dq_2}{dt} \tag{10}$$

$$\begin{cases} C_{1,input} = 0 \\ C_{2,input} = 0 \end{cases} \text{for t<0} \quad \text{and} \quad \begin{cases} C_{1,input} = C_{01} \\ C_{2,input} = C_{02} \end{cases} \text{for t} \geq 0 \tag{11}$$

where q_1 (mmol/g) and q_2 (mmol/g) are the specific metal uptake for the two metals, C_1 (mmol/l) and C_2 (mmol/l) are the metal concentrations in the permeate and in the reactor.

As in the case of single metal system biosorption, also for binary solutions the formulated model was compared with experimental data collected using Cu-Pb system at pH 5 and X=1g/l considering an empirical equation for the permeate flux decline (Figure 8).
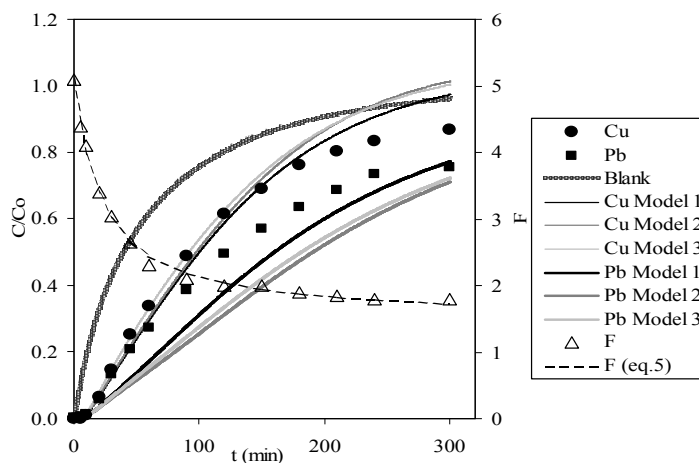

Figure 8. Experimental data of permeate flux decline (F) and copper and lead permeate dimensionless concentrations (C/C$_0$) during a biosorption tests in a membrane reactor with X 1g/l and pH 5. Comparison among experimental data and simulated curves obtained by solving eq.9-11 using different equilibrium competitive models (Model 1, Model 2 and Model 3) (Table 2) considering the permeate flux decline (eq.5) and the metal retention coefficient and biomass concentration changes during time (eq. 6 and eq. 7).

Experimental data show that, according to the affinity series observed in batch tests both in single and binary solutions, lead is more retained by the biomass in comparison with copper which reaches the feed concentration level in the permeate faster than Pb. Considering the specific trend of copper and lead retention coefficients fitted by empirical equations (Figure 9), a simple predictive Langmuir type model (Model 1) represents adequately the experimental data (Figure 8).
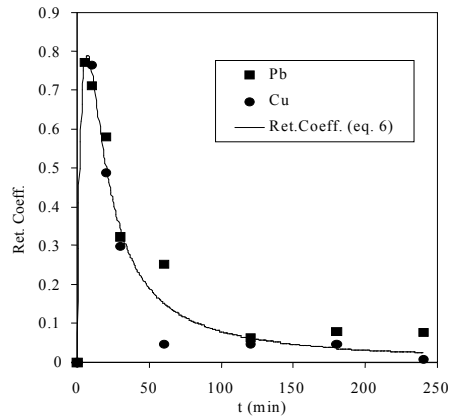

Figure 9. Metal retention coefficient (Ret. Coeff.) for copper and lead binary system as experimental data and fitted curve by eq. 6.

The dynamic model formulation reported here was also used to simulate experimental data reported in the literature for continuous multi-metallic biosorption in a similar membrane reactor apparatus (Chang and Chen, 1999). In particular the permeate concentration profiles for a ternary metal system containing Pb, Cu and Cd were considered and a predictive Langmuir type equilibrium model was used on the base of the single metal system parameters reported by the authors. The system of three differential equations was solved numerically with the following input parameters reported in the paper: the same feed concentration for all three metals $C_0=200\mu M$; 1 liter reactor volume; 7.3g/l biomass concentration; a constant influent and permeate flow rate 350ml/h. In the simulation according to the observation made by the authors that the bulk biomass concentration decreases during time, the initial biomass concentration was corrected by a constant $\theta=0.6045$ assuming a real biomass concentration in the reactor smaller than the initial one as the authors observed experimentally. The simulations so obtained were compared in Figure 10 with the experimental data reported in the literature.
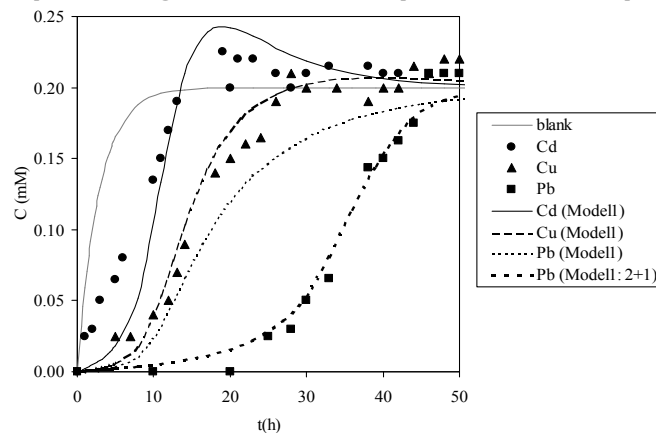

Figure 10. Experimental data (Chang and Chen, 1999) and simulated profiles of metal permeate concentrations for continuous biosorption onto *Pseudomonas aeruginosa* of Pb-Cu-Cd ternary solutions in a membrane reactor. As for the equilibrium models, simulation were performed using a Model 1 extension to ternary systems for Pb-Cu-Cd and also a competitive binary model for Cu-Cd coupled with single metal Langmuir equation for Pb (Model 1: 2+1).

It is possible to see that the dynamic model well represents the behaviour of copper and cadmium and in particular the presence of the overshoot regions for these metals with the lower affinity. This particular trend can be explained by considering that biosorption is an equilibrium phenomenon. In the first stages of biosorption, the metal with the major affinity (Pb) present in the multi-metallic solution is preferentially adsorbed by the solid so that its concentration in the liquid is very low. As a consequence the other metals present in solution can adsorb themselves as lead wasn't in solution: in particular copper, being the metal with the second major affinity starts to adsorb as if it was in a single component system and then the same for cadmium which is the metal with the minor affinity.

As time goes, being the reactor continuously fed by a multi-metallic solution, lead concentration in solution increases and lead ions start to replace the copper and cadmium ions previously adsorbed on the solid phase. As a consequence copper and cadmium in the permeate have higher concentrations than in the feed.

As for lead profile using a Langmuir predictive competitive model (like Model 1 but for three metals) a not adequate representation of the experimental data is obtained. Starting from the experimental observation that lead biosorption in ternary metal systems was not affected by the presence of copper and cadmium in solution a single metal component Langmuir isotherm was used for lead in the dynamic formulation and a binary predictive competitive model for copper and cadmium. In this case no change is observed for copper and cadmium data reproduction, while a precise representation of the Pb data is also obtained.

3.3. Multi-metallic system in a series of membrane reactors

Performances of a series of two membrane reactors was here considered and compared with this of a single reactor to improve the removal of the metal with the minor affinity and to separate the metals by making use of the intrinsic selectivity of the biomass. Under the same assumptions made for single reactor, the dynamic model was developed for a series of two membrane reactors and binary metal solution considering the metal mass balances in the two reactors and a Langmuir competitive equilibrium model.

$$\frac{dC_{11}}{dt} = \frac{(C_{01} - C_{11})}{\tau_1} - X_1 \frac{d}{dt}\left(\frac{\alpha_1 C_{11}}{1 + \beta_1 C_{11} + \gamma_2 C_{21}}\right) \tag{12}$$

$$\frac{dC_{21}}{dt} = \frac{(C_{02} - C_{21})}{\tau_1} - X_1 \frac{d}{dt}\left(\frac{\alpha_2 C_{21}}{1 + \beta_1 C_{11} + \gamma_2 C_{21}}\right) \tag{13}$$

$$\frac{dC_{12}}{dt} = \frac{(C_{11} - C_{12})}{\tau_2} - X_2 \frac{d}{dt}\left(\frac{\alpha_1 C_{12}}{1 + \beta_1 C_{12} + \gamma_2 C_{22}}\right) \tag{14}$$

$$\frac{dC_{22}}{dt} = \frac{(C_{21} - C_{22})}{\tau_2} - X_2 \frac{d}{dt}\left(\frac{\alpha_2 C_{22}}{1 + \beta_1 C_{12} + \gamma_2 C_{22}}\right) \tag{15}$$

where in this case each metal concentration is characterised by two subscripts, the first one refers to the metal and the second to the reactor; V_1 and V_2 are the constant volumes of the two reactors, X_1 and X_2 are the relative biomass concentrations and τ_1 and τ_2 are the residence times. The differential equations reported above have to be arranged as for the single reactor resulting in a system of equations, which is solved considering a step perturbation of both metals to the first reactor. The solution of the system of differential equations was performed numerically using MathCAD 2000 Professional Software.

The simulated performances of a series of two membrane reactors were compared with those of a single stage using the Langmuir competitive parameters obtained for copper and lead biosorption onto *Sphaerotilus natans* with X 1g/l and pH 5 (Pagnanelli *et al.*, 2002b). The comparison was made using the same total volume in the single (V=1 liter) and two stage configurations (V$_1$=V$_2$=0.5 liter), the same feed concentrations C$_{01}$=C$_{02}$=0.2mmol/l and flow rate F=0.1 liter per hour. In Figure 11 the simulation curves of the permeate of both reactors were reported showing that Pb is more adsorbed than Cu in both stages and that the removal efficiency increases in the second step. In fact in the second step the breakthrough of both metals was delayed with respect to the first so that a larger volume of contaminated water can be treated giving residual metal values under the target limit.
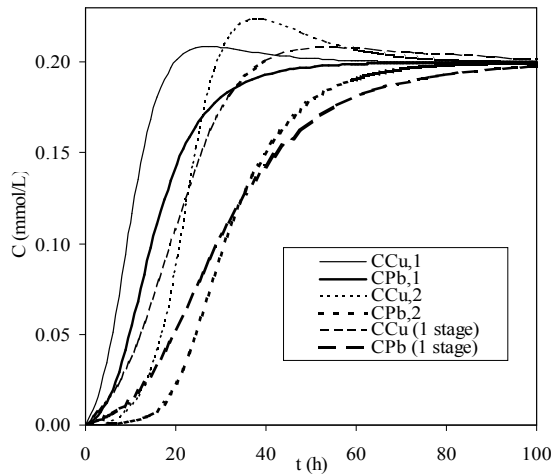

Figure 11. Liquid concentration simulated profiles vs. time for a series of two membrane reactors (C$_{Cu,1}$, C$_{Pb,1}$ from the first stage; C$_{Cu,2}$ and C$_{Pb,2}$ from the second stage) in comparison with a single stage membrane reactor (C$_{Cu}$ one stage and C$_{Pb}$ one stage) with the same total volume and biosorbent amount (Model 3 parameters for Cu-Pb biosorption onto *Sphaerotilus natans* at pH 5 and X 1g/l from Table 1).

In Figure 12 the metal concentrations in the solid were reported for both stages: in the first reactor Pb solid concentration is always higher than Cu, while in the second reactor copper uptake is at the beginning higher than Pb being the concentration of this metal very low in the first phase of adsorption (Figure 11).
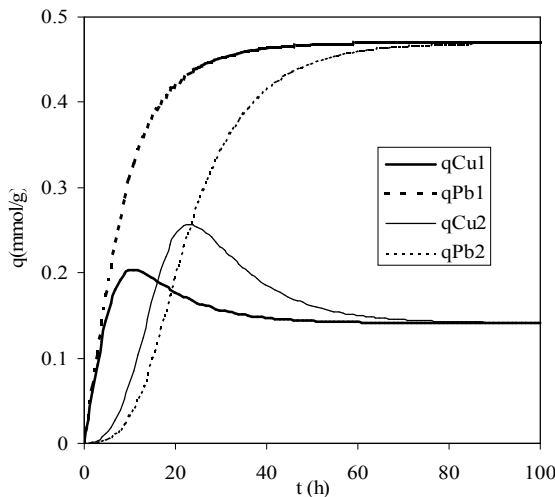

Figure 12. Solid concentration profiles (q$_{Cu,1}$, q$_{Cu,2}$, q$_{Cd,1}$, q$_{Cd,2}$) vs. time for a series of two membrane reactors using the equilibrium parameters for Cu-Pb biosorption onto *Sphaerotilus natans* (pH 5; X 1g/l).

As the feed concentration of Pb increases also in the second reactor, Pb concentration in the solid becomes higher then that of copper which was replaced as observed by the overshoot in Figure 11 and by the non monotonic trend of concentration in the solid Figure 12.

The effect of the different metal affinity could be exploited to favour metal separation in the different stages of the different metals. In fact even though the cumulative lead adsorption is higher than those of Cu and Cd in each stage, the metals with the lower affinities (Cu and Cd) have maximum concentration values in the solid comparable with those observed in single metal system experiments. So that by interrupting the continuous biosorption test at a certain predefined moment it is possible to obtain a metal separation in the different stages starting from multi-metallic systems. In Figure 11 the comparison between single and two stages was reported in terms of permeate concentrations of both metals: multi-stage configuration especially improves the removal of the metal with the lower affinity. In the two stages two different environments can be observed that work at concentration higher in the first reactor and lower in the second one with respect to the single reactor. In the reactor series the adsorption capacities were better exploited then in a single reactor with the same total volume. In fact in the first reactor working at high metal concentrations in solution the equilibrium concentration in the solid is also high according to the equilibrium Langmuir model, while in the second reactor (fed by a lower metal concentration) the metal uptake is low according to the equilibrium but also the residual concentration in the permeate is low.

By this way in the two stage configuration metal adsorption is maximised and breakthrough is delayed allowing thus to treat larger amounts of contaminated solutions according to the target limit.

The simulated profiles obtained in this theoretical study were in agreement with the experimental results reported by Chang and Chen (1999) that studied continuous biosorption of multi-metallic systems in a membrane reactor apparatus. These authors evidenced experimentally that metal removal efficiency increased in the different stages and comparing the effluent of the third reactor with that of a single reactor especially the metals with the lower affinity were removed in a higher degree: in particular Cu maximum concentration in the solid was registered in the second stage and Cd in the third one, where the initial Pb concentration in the feed solution is low. By this way metal competition can be used to separate metals in different stages according to the affinity series: in the first stage the metal with the major affinity and so on.

4. CONCLUSIONS

➤ Experimental data showed the very high sorption abilities of *Sphaerotilus natans* and the non ideal behaviour of copper retention by the membrane in the presence of biomass taken into account in the kinetic modeling, by empirical correlations. The kinetic model was able to predict experimental data under different operating conditions, even if further work is necessary to develop a deterministic modeling of copper retention by the membrane.
➤ The dynamic simulations reproduce qualitatively the experimental behaviour of multi-metallic biosorption into single and two stage membrane reactors: the metal with the minor affinity is released first, characterised by overshoot profile in the liquid permeate concentration and non monotonic trend of the concentration in the solid. When a series of reactors is employed the general performance of the system is improved especially for the metals presenting the lower affinity. Metal separation in the different stages can be improved by increasing the number of the stages on the base of the different metal affinity.

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