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Dynamics of Biodegradation Kinetics of 1,2-DCE and TCE in Bioreactor Coupled to Ultrafiltration Membrane Unit. Modeling Procedure

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Abstract

The paper presents the modeling approach to aerobic biodegradation of 1,2-dichloroethane (1,2-DCE) by the microorganism *Xanthobacter autotrophicus* GJ10, and of trichlorethylene (TCE) by the microorganism *Pseudomonas cepacia* PR131 in a bioreactor with an ultrafiltration (UF) membrane unit. The aim of the study was to estimate the kinetics of the bioprocess and to perform a parameter identification procedure. The specific growth rate was assumed to be a function of 1,2-DCE and TCE and oxygen substrate concentrations. The parameter values were estimated based on experimental data of continuous and discontinuous systems published elsewhere. For this purpose, the Particle Swarm optimization algorithm, coded in Maple 15® software, was applied. Simulations with the developed kinetic model showed new highlights and an optimal trajectory that can help to increase organochlorine wastewater treatment efficiency.

Keywords: Biodegradation of organochlorine; kinetics modeling; bioreactor with recycle; ultrafiltration membrane unit.

Резюме

Представен е подход за моделиране на процеса на микробиологично разграждане в аеробни условия на 1,2-дихлороетан (1,2-DCE) от *Xanthobacter autotrophicus* GJ10 и на трихлороетилен (TCE) от *Pseudomonas cepacia* PR131 в биореактор снабден с ултрафилтрационна мембрана. Целта на изследването е да се определи кинетиката на биопроцеса и да се извърши параметрична идентификация на модела. Беше допуснато, че специфична скорост на растеж е функция на 1,2-DCE и TCE както и от концентрации на разтворения кислород. Стойностите на параметрите са изчислени на основата на експериментални данни от непрекъснати и прекъснати операции публикувани в литературата. За тази цел беше използван алгоритъм на рояка на частиците, кодиран в MAPLE 15® софтуер. Симулациите с разработения кинетичен модел показаха нови свойства на системата и подчертаха една оптимална траектория, която може да се използва за увеличаване на ефективността на пречистване на отпадъчни води от органохлорни съединения.

Introduction

Volatile organic compounds are produced in many manufacturing processes (Scheutz *et al*, 2011; Frascari *et al.*, 2013b.), especially in the production of pesticides, plastics and paper, and thus comprise an important group in the treatment of industrial effluents (Arjoon *et al.*, 2013; Huang *et al.*, 2014). 1,2-DCE and TCE are two organochlorine compounds, well-known for their chemical stability and high toxicity (Yeh and Kastenberg, 1991). Both have similar physical and chemical properties (Table 1), and their molecular structure is com-

posed of a double bond between the carbon atoms. The maximum allowable concentration of both compounds in drinking water is 5 µg L⁻¹ (US EPA, 2009). 1,2-DCE is widely used in the production of chlorinated solvents like 1,1,1-trichloroethane, TCE and perchloroethylene (PCE), and especially in the manufacture of vinyl chloride (Gwinn *et al.*, 2011), which is an essential substance for the production of polyvinyl chloride (PVC) (Yuan *et al.*, 2015). TCE is widely used as a degreasing agent and a solvent, and has the characteristic of migrat-

Table 1. Physical and chemical properties of 1,2-DCE and TCE

Description	Units	1,2-DCE	TCE	
Molecular formula	-	$C_2H_2Cl_2$	C ₂ HCl ₃	
Molecular weight	MW(g.mol ⁻¹)	98.97	131.39 ^a	
Liquid density (25°C)	P(g.cm ⁻³)	1.253	1.460a	
Solubility in water	S(g.cm ⁻³)	8.606x10 ⁻³	1.1x10 ^{-3a}	
Dynamic viscosity (20°C)	μ(cP)	0.84	0.55	
Cinematic viscosity	ν	2.41x10 ⁻³		
Vapor pressure	V _p (torr)	79	73ª	
Fusion point	T_m (°C)	-35	-86a	
Boiling point	T _b (°C)	85	87ª	
Coefficient of octanol-water partition	K _{ow}	1.48	1.86ª	
Sorption coefficient (organic carbon)	K_{oc}	1.52	2.42ª	
Henry's Law Constant	H(atm.m³mol-1)	1.2	11.7	
Diffusion coefficient and clean air	$D_{air}(m^2.h^{-1})$	-	2.84x10 ^{-2a}	
Diffusion coefficient in pure water	D _{water} (m ² .h ⁻¹)	-	3.75x10 ^{-6a}	

^a(Pant and Pant, 2010)

ing through the soil making it a threat to groundwater (Folsom *et al.*, 1990). With respect to damage to humans, 1,2-DCE is classified as a possible human carcinogen (group B2) by the International Agency for Research on Cancer (IARC, 1999). TCE has been classified by the Agency for Toxic Substances and Disease Registry (ATSDR, 2015) as the 16th greatest potential threat to human health, setting up for a probable human carcinogen group (Group B1) (US EPA, 2001).

The treatment of wastewaters contaminated with organic compounds has been accomplished using various physical, chemical and biological methods such as:

Chemical oxidation (Vilve *et al.*, 2010; Che and Lee, 2011); reduction employing iron (Zhang *et al.*, 2011; Dror *et al.*, 2012; Fu *et al.*, 2014); photocatalytic degradation (Joo *et al.*, 2013; Lin *et al.*, 2014; Gas *et al.*, 2015; Priya and Philip, 2015); separation membranes (Oliveira *et al.*, 2001; Das *et al.*, 2006); ultrasound (Jiang *et al.*, 2002).

Aerobic and anaerobic biodegradation (Inguva and Shreve, 1999; Min and Ergas, 2006; Kocamemi and Çeçen, 2009; Frascari *et al.*, 2013a, 2013b; Yu *et al.*, 2013; Hasan and Jabeen, 2015) are natural methods of breaking down organic matter by microorganisms. They have the advantage of being

capable of completely mineralizing compounds at a low cost (Kocamemi Ceçen, 2010).

In order to group the strengths of treatments and to achieve simultaneous separation and biodegradation, the aerobic or anaerobic biodegradation methods can be performed in membrane reactors (MBR) (Inguva et al., 1998; Xing et al., 2000; Min and Ergas, 2006; Bolzonella et al., 2007). The major advantages of combining both treatments include improved control of microbiological activity, lower operational costs. where the released effluent is free of bacteria and pathogens (Cicek, 2003). Furthermore, studies have shown that microbial activity improves the flow of the solute through the membrane (Aziz et al., 1995; Inguva et al., 1998).

Min and Ergas (2006) conducted a study of biodegradation of volatile compounds: acetaldehyde, butyraldehyde and vinyl acetate. The experiment was designed in two CSTRs reactors in series coupled to an UF membrane. The biomass retained on the membrane module was returned to the first reactor through a recycle stream. The results of this approach verified the need to use a reactor that enabled a long solids residence time, under high organic content. This helped to maximize the dissolved oxygen concentration and to minimize volatilization of biodegradable products. Inguva *et al.*,

1998 also conducted experiments for biodegradation of 1,2-DCE and TCE using an UF membrane, as well as a source of biomass such as *Xanthobacter autotrophicus* GJ10 *and Pseudomonas cepacia* PR131. The results showed an improvement in the flow of 1,2-DCE and TCE through the membrane compared to the system without use of microorganisms. More particularly, the authors determined the diffusivity of the compounds 1,2-DCE and TCE in the UF membrane and the solute flows through the membrane in the presence and absence of microbial degradation of the solute into the permeate side.

The phenomena that arise during microbial activities govern the processes in reactors for wastewater treatment and have great relevance for the treatment of natural ecosystems. Phenomenological models are widely used in bioprocesses (Esser et al., 2015), being based on the formulation of hypotheses and theoretical and/or empirical correlations to describe the phenomena and inter-relations between process variables. The pioneer work of Monod (1949) on modeling of microbial growth kinetics is still considered fundamental when a substrate limitation process is described. The Monodbased expressions (see Table 2) describe the growth rate of biomass $\mu(h^{-1})$ as a function of (S) the substrate concentration, where different effects on the growth take place (Schimidell, 2001).

Considering the difficulty of measuring accurately all the variables involved in the biodegradation process, the study and application of a set of algebraic and differential equations formulated from physical, chemical and/or biological relationships between variables was a useful tool to adequately describe the process within the required range of precision (Gombert and Nielsen, 2000). Thus, an elaborate mathematical modeling should be able to predict the system output variable(s) from the input data correlated to the independent process variables.

Due to the complexity of the mechanism of diffusion in a medium, it is reasonable to estimate the diffusion coefficient of the compounds within an acceptable range of possible solutions. Therefore, the interpretation of mass-transfer phenomena in the bioreactor can be performed using empirical correlations related to the estimation parameters, such as diffusivity coefficient of the solute in the medium.

The parametric identification procedure was a critical phase of the development of the mathematical model, as it can help in the search for experimentally unknown parameters. In this relation, there are several methods, especially those based on probability techniques such as the Genetic Algorithm and Particle Swarm (Kroumov *et al.*, 2006; Schwaab *et al.*, 2008; Trigueros et al., 2010; Ghovvati *et al.*, 2015). The Particle Swarm optimization technique was developed by Kennedy and Eberhart, 1995, and was successfully applied for estimation of parameters of different models describing sophisticated phenomena of biotechnological processes (Kroumov *et al.*, 2006; Trigueros *et al.*, 2010; Feisther *et al.*, 2015).

In this context, this paper presents the development of a mathematical model able to describe the biodegradation of the compounds 1,2-DCE and TCE in an aerobic bioreactor coupled to an UF module. During the model development, the Particle Swarm global search method was applied to estimate the kinetic, stoichiometric and diffusivity parameters.

Materials and Methods

Laboratory scale. Bioreactor modeling

The biodegradation process was modeled using experimental data taken from the literature (Inguva et al., 1998). The authors used an experimental apparatus, basically consisting of a glass container and a polypropylene ultrafiltration membrane module. This UF module divided the bioreactor space into two compartments: an effluent feed chamber and a permeate chamber where the cellular biomass acted. Two strains were used by the authors: *Xanthobacter autotrophicus* GJ10 and *Pseudomonas cepacia* PR131, for degradation of 1,2-DCE and

Table 2. Kinetic models of microbial growth

+						
	Model	References	Model	References	Model	References
	$\mu = \mu_m (1 - e^{-\frac{S}{Kt}})$	Tessier (1942)	$\mu = \frac{\mu_m S}{K_S + S + S^2 / K_I}$	Andrews (1968)	$\mu = \frac{\mu_m S^n}{K_s + S^n}$	Moser (1958)
	$\mu = \frac{\mu_m S}{K_s + S}$	Monod (1949)	$\mu = \frac{\mu_m}{K_s / S + (S/K_I)^n}$	Wu et al. (1988)		

TCE, respectively. The following assumptions were considered for modeling the aerobic biodegradation of compounds: (i) the flow through the membrane was in a pseudo-steady state; (ii) the diffusivity coefficient of the solute was constant; and (iii) perfect mixing of the liquid phase.

The mass balance for a batch system (Eq.1) is given by the diffusive flux j_i (M.L⁻².T⁻¹) of the compound i (1,2-DCE and TCE) over the UF membrane.

$$j_i = K_0(S_i^A - S_i^P) (1)$$

where K_0 - is the global mass-transfer coefficient (L.T⁻¹); S_i^A -is the substrate concentration in the feed chamber; S_i^P -is the substrate concentration in the permeate chamber.

Equation 2 gives the removal rate of the compounds in the feed chamber:

$$\frac{dS_i^A}{dt} = -j_i \frac{A}{V_A} \tag{2}$$

where V_A -is the volume of the feed (L³); A is the contact surface area of the UF module (L²).

The biodegradation rate of the permeate chamber (Eq.3) considers the solution flux through the membrane plus the biological reaction rate (R_i) for each compound i (Eq.4).

$$\frac{dS_i^P}{dt} = j\frac{A}{V_P} + R_i \tag{3}$$

$$R_i = -\frac{\mu_i}{Y_{x/s_i}} X \tag{4}$$

where V_p -is the volume of the permeate chamber (L³), μ_i -is the specific growth rate of the biomass (T¹) for the "ith" compound; X -is the biomass concentration (M.L⁻³); -is the yield coefficient of conversion of "ith" compound to biomass (M.M⁻¹).

The dynamics of changes in the concentration of biomass and oxygen in the permeate chamber are given by equations 5 and 6, respectively.

$$\frac{dX}{dt} = \mu_i X \tag{5}$$

$$\frac{dC_{ox}}{dt} = K_L a_{ox} (C_{ox}^{eq} - C_{ox}) - \frac{\mu_i}{Y_{ox}} X$$
 (6)

where C_{ox} -is the oxygen concentration (ML⁻³) in the liquid phase; K_L a-is the volumetric mass transfer coefficient in the liquid phase (T⁻¹); C_{eq} -is the equilibrium concentration of the oxygen (ML⁻³) in the liquid, and Y_{oxi} -is the yield coefficient for

oxygen to biomass (MM-1) for the ith compound.

The mass transfer coefficients of the film on the feed kf^A and the permeate kf^P (LT¹) were calculated using equation 7 (Colton 1969); and K₀ (LT¹) was calculated using equation 8 (Kreulen et al., 1993).

$$kf = 0.0443 \frac{D_{AB}}{d} \left(\frac{v}{D_{AB}}\right)^{1/3} \left(\frac{\omega d^2}{v}\right)^{0.75}$$
 (7)

$$\frac{1}{K_0} = \frac{1}{kf^A} + \frac{\delta}{D_m} + \frac{1}{kf^P}$$
 (8)

where D_{AB} is the thermal diffusivity coefficient of the solute (L².T¹); ν -is the kinematic viscosity (L².T¹); d -is the length of the impeller (L); ω -is the velocity of the agitation (rotation speed, T¹); D_m - is the coefficient molecular diffusivity of the solute in the membrane (L².T¹); -is membrane thickness (L).

The molecular diffusivity coefficient (D_m) of 1,2-DCE and TCE in the Metricel membrane was determined experimentally by Inguva *et al.* (1998) and their values were 1,692.10⁻⁸ and 5,076.10⁻⁸ m²h⁻¹, respectively. The values of the parameters such as Metricel membrane thickness, diameter and contact area used by Inguva *et al*, (1998) were as follows: 89 μ m; 4,7.10⁻² m and 17,4.10⁻⁴ m², respectively. The recipient container used with a total volume of 70.10⁻⁶ m³ was maintained on a magnetic stirrer, assuming the length of the stir bar was 1.10⁻² m.

In this study, several models with different levels of sophistication were tested in order to represent the effects of substrate (1,2-DCE, TCE, and oxygen) limitation (Monod (1949), Tessier (1942) and Moser (1958)) and inhibition (Andrews (1968)) and Wu et al. (1988)). (see Table 2). The Ks_{ov} oxygen saturation constant was set at 10-4 kg m⁻³, far below the critical oxygen concentration. This ensured about 10-30% of the oxygen saturation concentration (C_{eq}) in the cultivation medium (Schimidell, 2001). The equilibrium oxygen concentration (C_{eq}) in the medium was estimated to be about 6.5 to 7.6 mg L^{-1} at the given temperature (Schimidell, 2001). This corresponded to 10 up to 15% lower concentration than the saturation concentration of the oxygen in water. The value of the volumetric mass transfer coefficient K₁ a of oxygen varied from 50 to 150 h⁻¹. The initial O₂ concentration was considered to be equal to the saturation concentration (C_{eq}) .

The kinetic and stoichiometric parameters of the kinetic model (μ_{max} , K_s and $Y_{x/s}$), and the coefficient of diffusivity D_{AB} and stirring speeds ω in the feed and permeate chambers were estimated by ap-

plying the Particle Swarm Optimization Algorithm. The mass transfer coefficients in the film (kf^A) and $kf^P)$ were calculated using the expression obtained from literature $kf = f(D_{AB}, \omega, v, d)$ (Eq.7). The overall mass transfer coefficient for 1,2-DCE and TCE was calculated using the following $K0 = f(kf^A, kf^P, D_m, \delta)$ (Eq.8).

Parameter Identification Procedure

The Particle Swarm optimization algorithm is based on the simulation of the movement of groups of animals in search for food and/or shelter, according to their individual and collective contributions. More details can be found elsewhere (Kennedy and Eberhardt, 2001).

The predefined values of algorithm parameters were as follows: 500 particles; 30 iterations; c1=c2=1.5; $\omega_{inicial}=0.9$; $\omega_{final}=0.4$. The algorithm was coded in Maple 15® software, and the ordinary differential equations were solved using the Rosenbrock method. The least squares objective function (Eq. 9) was applied to minimize the difference between the model and experimental profiles (Eq. 9).

$$FO = \sum_{i=1}^{NV} \sum_{j=1}^{NP} (y_{ij}^{\text{mod}} - y_{ij})^2$$
 (9)

where y^{mod} stands for the simulated values and y_{ij} is the experimental value of the ith dependent variable at jth data point of the independent variable. All simulations were carried out on Intel Core i7 computer (1.8 GHz 1.8 GHz cache memory) with 8 GB RAM.

Simulation Results and Discussion

Batch mode

All models applied to describe the substrate limitation (Monod, 1949; Tessier, 1942; and Moser, 1958) were evaluated based on the experimental data of Inguva *et al.*, 1998. The obtained values of their objective function and the correlation coefficient were similar (see Table 3). The values of kinetic parameters of the models Andrews, 1968, and Wu *et al.*, 1988 showed no effect of inhibition. Hence, the Monod model was further used to describe the process of biodegradation of the com-

pounds 1,2-DCE and TCE. The values of the kinetic and stoichiometric constants of this model are shown in Table 4.

The specific growth rate of the biomass was higher when 1,2-DCE (μ_{max} =0,080h⁻¹) was used. The value of the saturation constant (K_s =0,723 ppm) showed that *X. autotrophicus* GJ10 had higher affinity to the 1,2-DCE substrate. On the other hand, *P. cepacia* PR131 showed affinity to TCE (K_s =2,5 ppm). The TCE yield coefficient was higher than on DCE ($Y_{x/s}$ =0,52kg_{cell}/kg_{TCE}). The biomass initial concentration was set up in the range of 0,010-0,050 kg.m⁻³ (Table 4).

The diffusivity coefficients of 1,2-DCE and TCE in the permeate chamber (4.88×10^{-5}) and 5.65 × 10⁻⁵ m²h⁻¹, respectively) were smaller than their values in the feed chamber $(7.35 \times 10^{-5} \ 7.94 \times 10^{-5})$ m²h⁻¹, respectively). These facts can be explained by the presence of microorganisms in the permeate chamber. The mass transfer coefficients in the film (kf) for 1,2-DCE and TCE were also lower in the permeate chamber (0.010 and 0.015 m.h⁻¹, respectively) than the estimated values for the effluent feed chamber (0.068 and 0.073 m.h⁻¹, respectively). The same interpretation can be applied to the kf value. The smaller kf value corresponded to greater resistance to the mass transfer flow. This is because of the presence of microorganisms in the permeate chamber (Table 4).

The profiles presented in Figure 1 show the kinetics of biodegradation of 1,2 DCE and TCE in the feed and permeate chamber (Fig.1A and Fig.1B, respectively); the kinetics of microbial growth of *Xanthobacter autotrophicus* GJ10 associated with the 1,2 DCE utilization and the dynamics of *Pseudomonas cepacia* PR131I growth on TCE (Fig.1C and Fig.1D, respectively); DO profiles for 1,2 DCE and TCE are shown, as well (Fig.1E and Fig.1F, respectively).

Analyzing the flow profiles across the membrane (see Fig 1A, Fig.1B) two phases of state can be distinguished. Initially, the flows of 1,2 DCE and TCE had maximum and minimum values, since the concentration gradients among the two cameras

Table 3. Values of the objective function (F_{obj}) and correlation coefficient (R^2) for all tested models used in simulations

Model	Monod	l (1949)	Megee et a	al. (1972)	Tessier (1942)		Moser (1958)	
Substrate	1,2-DCE	TCE	1,2-DCE	TCE	1,2-DCE	TCE	1,2-	TCE
							DCE	
Fobj	3,5×10 ⁻²	6,7×10 ⁻³	3,3×10 ⁻³	6,7×10 ⁻³	3,3×10 ⁻²	6,4×10 ⁻³	3,3×10 ⁻³	5,3×10 ⁻³
\mathbb{R}^2	0.9933	0.9771	0.9928	0.9771	0.9923	0.9773	0.9928	0.9776

were large. Then the flow profiles followed each other up to the end of the process, where the concentrations of 1,2-DCE and TCE reached zero on both sides of the UF membrane module. The effect of substrate utilization by the cells can be indirectly seen in the dynamics of the increase in the biomass concentrations (see Fig 1C, Fig.1D). Moreover, when analyzing the biomass profiles (see Fig. 1C and 1D), the strain that had higher growth was *Pseudomonas cepacia* PR131, associated with the consumption of TCE (0.062 kg.m⁻³). The simulation results about the dissolved oxygen (DO) con-

centration profiles are in accordance with the theory and their minimum values (see Fig. 1E and 1F) correspond to the maximum value of biomass concentrations. Further, the DO concentrations approach the C_{eq} values because of the complete utilization of organic compounds. It is noteworthy that during the process neither DO concentration reached the critical values that affected cellular metabolism. The critical values for both substrates (1,2 DCE and TCE) can be obtained by using RSA methodology (see Fig. 2).

Table 4. Values of the estimated model parameters and experimental data of aerobic biodegradation of 1,2-DCE and TCE compounds in reactor supplied with UF membrane module. Batch mode.

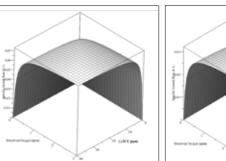
Parameters	Valu	Units	
Estimated Parameters	1.2-DCE TCE		
$\mu_{ ext{max}}$	0.080	0.035	h-1
K _s	0.723×10 ⁻³	2.5×10 ⁻³	kg.m ³
$Y_{x/s}$ D_{AB}^{F}	0.450	0.520	kg.kg ⁻¹
D_{AB}^{F}	7.35×10 ⁻⁵	7.94×10 ⁻⁵	m^2h^{-1}
D_{AB}^{P}	4.88×10 ⁻⁵	5.65×10 ⁻⁵	m^2h^{-1}
$\omega_{\rm k}$	100	100	rpm
ω_{b}	10	10	rpm
Calculated Parameters	1.2-DCE	TCE	
kf^F	0.068	0.092	m.h ⁻¹
kf^{p}	0.010	0.012	m.h ⁻¹
K0	0.006	0.0092	m.h ⁻¹

Note: Superscript symbols-"F"-stands for feed chamber; "P"-stands for permeate chamber; rpm-stands for rotation per minute.

Figure 2 shows the response surface of the specific growth rate of biomass (μ) as a function of substrates and DO concentration. It can be seen in Figure 2A that concentrations below 1.5 ppm (20% of saturation concentration) of DO value limit the growth of *X. autotrophicus* GJ10. The limiting concentration of 1,2-DCE for the same strain was found to be below 20 ppm. Figure 2B shows that a concentration below 30 ppm of TCE limits the growth of *P.cepacia* PR131, and that the value of 1.5 ppm of DO can be considered as a limiting level for the system.

Conclusions

The paper presents the modeling approach to the process of aerobic biodegradation of 1,2-DCE by the microorganism *Xanthobacter autotrophicus* GJ10 and TCE by the microorganism *Pseudomonas*



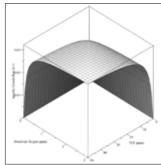


Fig. 2. Response Surface Analysis of the specific growth rate as a function of substrates: (Fig.2A) 1,2-DCE and dissolved oxygen; (Fig.2B) TCE and dissolved oxygen.

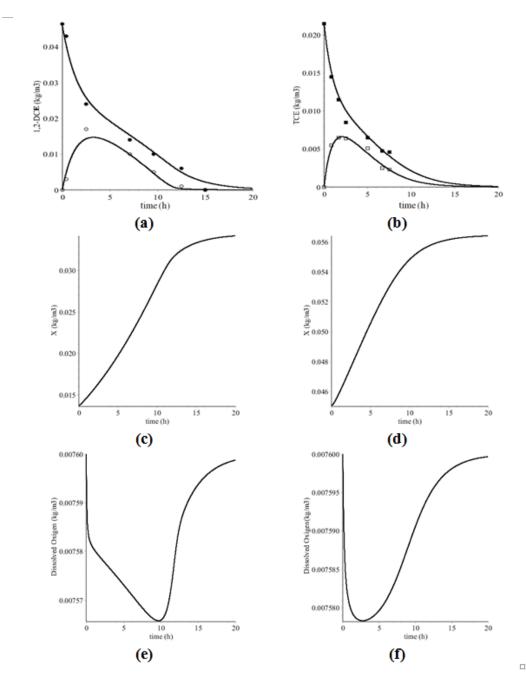


Fig. 1. Kinetics of 1,2-DCE and TCE biodegradation in reactor supplied with UF membrane module. Batch mode. (experimental data are taken from Inguva *et al.*, 1998): (A,B) compounds removal in feed and permeate: (●) 1,2-DCE in the feed chamber; (○)1,2-DCE in the permeate chamber; (□) TCE in the permeate chamber; (----) Simulation results for the feed chamber; (□)Simulation results for the permeate chamber; (C,D) simulation results for biomass growth on 1,2-DCE and TCE substrates, respectively; (E,F) simulation results of the DO -dissolved oxygen concentration in the culture medium in the presence of 1,2-DCE and TCE substrates, respectively.

cepacia PR131 in a bioreactor coupled to an UF membrane unit. The aim of the study was to estimate the kinetics of the bioprocess and to perform a parameter identification procedure based on the real experimental data published in the literature. The specific growth rate was assumed to be a function of the 1,2-DCE and TCE and oxygen substrates concentrations. The parameter values were estimat-

ed based on experimental data of batch mode. For this purpose, the Particle Swarm optimization algorithm was used, encoded in Maple 15® software. The simulation results obtained using the developed kinetic model showed new highlights and optimal trajectory that can help to increase organochlorine wastewater treatment efficiency for the bioreactor system coupled to an UF membrane module.

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