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REMOVAL OF FURFURAL FROM WASTEWATER USING MOVING BED BIOFILM REACTOR

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ABSTRACT

In this study the biodegradation process of toxic compounds such as furfural, present in petrochemical effluents is described by a phenomenological model expressed through a single differential equation which allows the description of the concentration profile through a fixed bed biofilm reactor. The mechanisms which control the mass transfer, such as the effects of dispersion, convection and reaction in the liquid phase, and of diffusion and reaction within the biofilm, are considered in this model. The reaction in the biofilm is described by Michaelis–Menten kinetics. The Finite Volume Method (FVM) is used in the discretization of the differential equation of the phenomenological model, an algorithm being developed for the numerical simulation of the biodegradation process of FURFURAL compounds under different operational conditions. The computational algorithm developed was validated by comparing the results of the numerical simulation of the biodegradation process of FURFURAL compounds with experimental data provided in the literature. The results obtained through the simulations showed that the parameters evaluated in this study influenced the biodegradation of FURFURAL compounds, and that the mathematical model and the numerical methodology adopted can be used as an efficient tool for predicting the dynamic and stationary behavior of the biodegradation process.

Keywords: Furfural, Sewage treatment, Fluidized bed reactors, Mass transfer, MBBR reactor

INTRODUCTION

The FURFURAL compounds, present in refinery and chemical industry effluents, have a high polluting potential, due to their neurotoxic, carcinogenic and teratogenic properties, representing a high risk to the environment and human health [Jo et al. 2008; Mathur et al. 200] is the maximum biodegradation reaction rate). Epidemiological studies have shown that benzene is a very hazardous pollutant, due to its confirmed carcinogenic action, being able to cause leukemia and tumors in multiple organs [Semple et al. 1998; Skov et al. 2001]. The United States Environmental Protection Agency (US EPA) has classified these compounds as priority pollutants due to their toxic properties [Jo et al. 2008; Mathur et al. 2007; Semple et al. 1998]. Many processes which involve physico-chemical principles are used for the treatment of toxic compounds. Despite the capacity of these processes to remove FURFURAL, some are technically less attractive due to the economic factor and safety reasons. Physical methods such as adsorption on activated carbon are not only expensive, but also result in saturation of the carbon requiring its regeneration or disposal in landfills. On the other hand, biological treatment is an efficient and potentially lucrative alternative for the treatment of these compounds [Amanullah et al. 1999; Bertin et al. 2007; Massalha et al. 2007]. In recent years the greatest advances in the area of biological treatment of effluents were reached through processes which use biofilms supported on inert particulate materials. According to Ulson de Souza et al. (2003) and Xavier et al. (2003), the biofilm can be defined as a set of microorganisms and extracellular products which adhere to a solid support, forming a voluminous and thick layer, with an external structure which is not completely even and uniform. The compounds disperse in the biofilm where they are consumed metabolically by the microorganisms and degraded to CO2 and water [Amanullah et al. 1999]. The bioreactors with adhered biofilm have as advantages: a greater concentration of biomass retained with greater metabolic activity; there is no requirement for the sludge to return to the biological reactor; coexistence of anoxic and aerobic metabolic activity within the same biomass ecosystem; high efficiency in BOD (biochemical oxygen demand) removal; application of a greater organic load; large area for mass transfer between the phases; more compact installations; greater capacity to tolerate recalcitrant and toxic pollutants. The ideal

operational conditions for industrial plants which aim at the biodegradation of biochemical compounds can be predicted through the modeling and numerical simulation of the phenomena involved, since the results allow the process to be described under conditions which have not been tested experimentally, thus aiding the design and optimization of the biodegradation process in real scale. In order for the numerical simulation to represent the reality, the mathematical models must adequately describe the phenomena involved in the process [Silva et al. 2005]. In order to understand the process using adhered biomass, several researchers have developed models to describe the mass transfer with biochemical reaction and the cellular growth. The others presented the development of a one-equation model which describes the concentration profile of the substrate in a fluidized bed reactor. In the development of the model the Volume Averaging Method is used for the different scales. This methodology has been employed in different areas to solve problems related to transport phenomena in porous media: dispersion in the fluid phase, internal diffusion and chemical reaction in the pores and at the surface of the catalyst, (dispersion and adsorption and reaction in the biofim. The one-equation mathematical model developed by Guelli et al. (2007a) is used in this study to describe the biodegradation process of the FURFURAL present in liquid effluents of the petrochemical industry, using biofilms. The kinetic model of the reaction in the biofilm is described by the Michaelis–Menten expression. In order validate the mathematical modeling and the numerical algorithm developed, the results obtained in this study were compared with data presented by Mohammed and Allayla (1997). The kinetic parameters obtained by Mello (2007) are used in the model for the simulation of a biofilm column in a fixed bed, using carbon particles as the biofilm support.

2. Mathematical modeling

The mathematical formulation is based on the study presented by Guelli et al. (2007a), in which a one-equation model was developed which describes the concentration profile of the substrate in a fluidized bed reactor, considering the effects of dispersion, convection and reaction in the liquid phase and diffusion and reaction within the biofilm. This mathematical model is capable of describing the mass transport with biochemical reaction in a reactor with adhered biomass, which is characterized by two scales of heterogeneity: the macroscale, comprising two distinct phases—the solid phase, known

as bioparticle (biofilm and material support) and the liquid phase (effluent present within the bioreactor), the mass transfer process occurring in two phases; and the microscale (biofilm) which includes the microorganisms. It is considered that there are also two phases in the microscale, a liquid phase which comprises the effluent together with the polymeric substances present between the microbial cells, and a solid phase, which comprises the microbial cells. In the microscale the solid phase is rigid and impermeable and, thus, mass transfer does not occur between the two phases (solid and liquid), the governing equation being written only for the liquid phase. Guelli et al. (2007a) applied the Volume Averaging Method in the governing equation for a certain chemical species, and under the boundary conditions of a microscale heterogenic system, with the aim of writing the transport equation for the intrinsic average concentration in the liquid phase. This method consists of transforming the point concentration into an average concentration valid for the whole control volume in the scale under study [Guelli et al. 2007b]. In the macroscale, the system comprises two distinct phases: the solid phase and the liquid phase; thus, equations which describe the two phases are required. The solid phase is described by the equation obtained for the biofilm (microscale), for which the effective parameters are defined in terms of the parameters of the microscale and of the biofilm structure. The equation for the transport of the chemical species of interest in the liquid phase is given by the terms for accumulation, convection, diffusion and by the reaction term, due to the consumption of the chemical species by the microorganisms suspended in the liquid phase. Through successive application of the spatial average theorem, the authors obtained an equation for the average concentration for both phases, in the microscale. Further details can be found in Guelli et al. (2007a). In this study the Michaelis–Menten kinetic model is adopted, Eq. (1). Considering that in aqueous solution, a given substrate is transformed into products following an elementary reaction A→B, and that the concentration of microorganisms is constant in the liquid phase, the term r_A'' is given by the following equation:

$$r_A'' = \frac{-R_{mA}\ C_A}{K_A + C_A} \quad (1)$$

Where R_{mA} is the maximum biodegradation reaction rate and KA is the Michaelis–Menten half-saturation constant. The one-equation model is based on the hypothesis that the mass transfer process can be characterized by a single concentration, that is, the average concentration of chemical species A. Thus,

the concentration of chemical species A in the solid phase (σ) is equal to the concentration in the liquid phase (β). When this situation is valid, the two equations of the macroscale can be summed in order to obtain the one-equation model. The equation which describes the mass transport with chemical reaction in a biofilm bioreactor, when the hypothesis of local mass equilibrium is valid, is given by Eq. (2):

$$(\varepsilon_\beta + \varepsilon_\gamma\varepsilon_\sigma)\frac{\partial\{C_A\}}{\partial t} = \nabla\cdot\left(\varepsilon_\beta D^*\cdot\vec{\nabla}\{C_A\}\right) - \vec{\nabla}\cdot\left(\varepsilon_\beta\langle v_\beta\rangle^\beta\{C_A\}\right) - \left(\varepsilon_\sigma a_v|_{\gamma k} R_{mA}\frac{\{C_A\}}{K_{A\sigma}+\{C_A\}}\right) \quad (2)$$

where,

$$D^* = Deff|_{\beta\sigma} + D \quad (3)$$

$$\varepsilon_\beta Deff|_{\beta\sigma} = (\varepsilon_\beta D_\beta I + \varepsilon_\sigma\varepsilon_\gamma Deff|_{\gamma k}) + \frac{D_\beta I}{V_\omega}\cdot\int_{A_{\beta\sigma}} n_{\beta\sigma} b_{A\beta} dA + \frac{\varepsilon_\gamma Deff|_{\gamma k}}{V_\omega}\cdot\int_{A_{\sigma\beta}} n_{\sigma\beta} b_{A\sigma} dA \quad (4)$$

$$D = -\langle\tilde{v}_\beta b_{A\beta}\rangle^\beta \quad (5)$$

The initial condition and the boundary conditions adopted for Eq. (2) are:

$$t = 0(\forall z) : \{C_A\} = 0(\text{the bed is absent of any chemical species A}) \quad (6)$$

$$\{C_A\}|_{z=0} = C_{A,o}(\text{inlet concentration}) \quad (7)$$

$$\left.\frac{\partial\{C_A\}}{\partial z}\right|_{z=Z} = 0(\text{null derived condition}) \quad (8)$$

2.1. Model parameters

In order to obtain the solution to the equation which describes the mass transport with chemical reaction in the biofilm bioreactor (Eq. (2)), and to evaluate its restrictions, some parameters must be evaluated. Some of these parameters were obtained from the literature and others were calculated from correlations found in the literature.

The macroscale total dispersion coefficient (D*) was calculated through the correlation presented by Whitaker (1999), described by Eq. (9):

$$D^* = 0.700 D_\beta\left[\frac{d_p\langle v_\beta\rangle^\beta}{D_\beta}\left(\frac{\varepsilon_\beta}{1-\varepsilon_\beta}\right)\right]^{1/2} \quad (9)$$

The porosity of the microscale liquid phase (εγ) is estimated by Fan et al. (1990), who obtained an average value of 0.70.

The specific mass of the dry biofilm (ρb) was calculated through Eq. (10), estimated by Coelhoso et al. (1992).

$$\rho_b(mg/cm^3) = 191.4 - 0.224\delta$$

This equation can only be used for biofilm thickness values lower than 593 μm.

Voice et al. (1992) determined the biofilm thickness on activated carbon particles through scanning electron microscopy (SEM) analysis; the value was in the range of 100 to 200 μm.

In this study the average value, that is, 150 μm, was used. The microscale effective diffusivity (Deff|γk), was calculated through an empirical correlation given by Fan et al. (1990), Eq. (11).

$$Deff|_{\gamma k}(m^2/s) = \frac{D_{Aw}}{\varepsilon_\gamma}\left(1 - \frac{0.43\rho_b^{0.92}}{11.19 + 0.27\rho_b^{0.99}}\right) \quad (11)$$

The macroscale effective diffusivity (Deff |βσ), was estimated through the correlation used by Guelli et al. (2007a), Eq. (12).

$$Deff|_{\beta\sigma} = \frac{D_{ls}}{\varepsilon_\beta}(0.250(1-S) + S)) \quad (12)$$

where S is a parameter calculated through Eq. (13).

$$S = \frac{\varepsilon_\gamma Deff|_{\gamma k}}{D_{ls}} \quad (13)$$

The macroscale surface area by unit of volume can be calculated by:

$$a_v|_{\beta\sigma} = \frac{6(1-\varepsilon_\beta)}{d_p} \quad (14)$$

dp being the bioparticle diameter, calculated through Eq. (15).

$$d_p = d_s + 2\delta \quad (15)$$

The convective mass transfer coefficient (h) is obtained by correlation through the Sherwood number. Wakao and Funazkri (1978), cited in Cremasco (2002), proposed the following correlation for beds with spherical particles.

$$Sh_p = \frac{d_p h}{D_{Aw}} = 2.0 + 1.1Re_p^{0.6}Sc^{1/3} \quad (16)$$

3. Numerical formulation

The equation which describes the mass transfer process, with biochemical reaction, following the Michaelis–Menten kinetics in a biofilm bioreactor (Eq. (2)), was numerically solved, in space and time by the Finite Volume Method.

In this study, a fixed structured mesh, explicit formulation and a collocated arrangement of variables, for the placement of the variables on the computational mesh, were used. In order to evaluate the properties at the control volume interfaces, the Weighted Upstream Differencing Scheme (WUDS) was employed, as discussed by Maliska (1995) and Souza et al. (2006), in order to avoid

stability problems with the numerical method. The hypotheses assumed for the model were: incompressible fluid; cylindrical coordinates; impermeable bioreactor walls with the concentration varying only in the z direction; constant physical properties; constant porosities; isothermal flow; and fluid without rotation. Also, it was assumed that the biomass concentration in suspension is negligible when compared with that of the biofilm [Kryst and Karamanev, 2001], all of the biomass present in the bioreactor being adhered to the support; spherical support particles; homogeneous biofilm, the density and thickness of the biofilm is maintained constant; quantity of immobilized microorganisms (biofilm) remains constant over time [Kryst and Karamanev, 2001]; the support is inert, with no adsorption or desorption of contaminants occurring on the support; and the system is biologically climatized, with a constant biodegradation rate over time.

Writing Eq. (2) in the one-dimensional form, considering the hypotheses listed above, and identifying the variable ⟨vβ⟩βas vβ, we obtain Eq. (17):

$$(\varepsilon_\beta + \varepsilon_\gamma K_{ad})\frac{\partial \langle C_A \rangle}{\partial t} + \varepsilon_\beta v_\beta \frac{\partial \langle C_A \rangle}{\partial z} = \varepsilon_\beta D^* \frac{\partial}{\partial z}\left(\frac{\partial \langle C_A \rangle}{\partial z}\right) - \varepsilon_\alpha r_A^* \qquad (17)$$

On integrating Eq. (17), in space and time, using the WUDS, this equation is obtained written in its general form, Eq. (18). Further details of these procedures can be obtained in Mello (2007).

The computational algorithm was written in Matlab software, and the graphs were constructed with the aid of MATLAB R12. The equation was solved following an iterative method, which was applied until the convergence criterion was satisfied. The convergence criterion adopted to interrupt the iterative process was the error for the concentration. The numerical solution is obtained in this study using a mesh of 80 control volumes in the z direction, since the solution obtained this mesh is in agreement with the solution obtained with more refined meshes.

$$A_P^*\{C_A\}|_P^{n+1} = A_P\{C_A\}|_P^n + A_E\{C_A\}|_E^n + A_W\{C_A\}|_W^n - S_P^\Phi \quad (18)$$

where the A_i coefficients are given in the equations below:

$$A_P^* = 1 \quad (19)$$

$$A_P = \left(\begin{array}{l} 1-\alpha_e \dfrac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} - \alpha_w \dfrac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} - \\ - \dfrac{\beta_e \Delta t(\varepsilon_\beta D^*)}{\Delta z^2(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} - \dfrac{\beta_w \Delta t(\varepsilon_\beta D^*)}{\Delta z^2(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} \end{array} \right) \quad (20)$$

$$A_E = \left(\frac{\beta_e \Delta t(\varepsilon_\beta D^*)}{\Delta z^2(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} - \frac{1}{2}\frac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} + \alpha_e \frac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} \right) \quad (21)$$

$$A_W = \left(\frac{1}{2}\frac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} + \alpha_w \frac{(\varepsilon_\beta v_\beta)\Delta t}{\Delta z(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} + \frac{\beta_w \Delta t(\varepsilon_\beta D^*)}{\Delta z^2(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} \right) \quad (22)$$

$$S_P^\Phi = \frac{\varepsilon_\sigma a_v R_{mA} \Delta t}{(\varepsilon_\beta + \varepsilon_\gamma \varepsilon_\sigma)} \frac{\{C_A\}|_P^n}{(K_A + \{C_A\}|_P^n)} \quad (23)$$

Table 1.

C_{A0} [mg/L][a]	10.0
ε_β [a]	0.22
ε_γ [b]	0.70
D_β [m^2/s][c]	8.6×10^{-10}
d_s [m][a]	6.5×10^{-4}
K_A [mg/L][a]	30.0
v_β [m/day][a]	2.0
R_{mA} [mg/L s][a]	4.90×10^{-5}
h [m][c]	1.98×10^{-6}
D^* [m][c]	2.94×10^{-8}
X [mgSSV/L][a]	4.13×10^{-1}
δ [m][d]	1.50×10^{-4}
z [m][a]	8.0

RESULTS AND DISCUSSION

Validation of mathematical formulation and numerical methodology

In order to validate the proposed mathematical model and the numerical methodology for the prediction of the biodegradation process of FURFURAL compounds, the numerical results obtained by the computational algorithm are compared with three different experimental situations. The results given by the authors were obtained for a fixed bed biological reactor, composed of a tank with 800 cm of height, 30 cm of width and 30 cm of depth. There is a sampling point at every 100 cm of the reactor. The support material used for the fixation of

microorganisms is sand. The parameters used for the solution of the proposed mathematical model, for the three cases under study, are given in Table 1.

Fig. 1 shows the concentration profile of toluene FURFURAL compound, obtained numerically using the proposed Table 1 Parameters used to obtain the concentration profiles.

Through the results given in Fig. 1 it is possible to observe an excellent agreement between the experimental data obtained by Mohammed and Allayla (1997) and those presented in this study. On evaluating Figure 1 it can be seen that the maximum error obtained numerically in relation to the experimental data was 14.86% for FURFURAL. These results allow us to corroborate the mathematic model and the numerical methodology, since these represent with good precision the real biodegradation process, allowing other situations to be simulated, enabling an analysis of the sensitivity of the process when the conditions of the biodegradation process are changed.

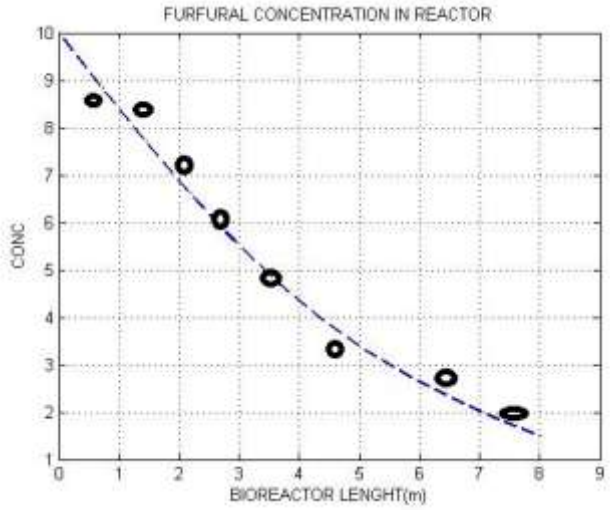

Figure 1

CONCLUSIONS

This investigation demonstrated that MBBR filled with the suspended carrier was an effective and feasible process for removal FURFURAL from waste water. The modification of biocarrier with different material produced positive outcomes in the wastewater treatment Efficiency.

Nomenclature

Ai Coefficients of the discretized equation where i=P, E, W, P* [adimensional]

Aβσ (=Aσβ) Area of the interface between phases βσ [m^2]

av|βσ Surface area by unit volume in the macroscale [m−1]

av|γκ Surface area by unit volume in the microscale [m−1]

bAβ Closure variable in phase β [m]

bAσ Closure variable in phase σ [m]

CA Concentration of chemical species A [mg/L]

CA0 Initial concentration of chemical species A [mg/L]

{CA} Average spatial concentration of chemical species A, under conditions of local mass equilibrium [mg/L]

D Hydrodynamic dispersion tensor [m^2 /s]

dA Infinitesimal element of area [m^2]

DAw Molecular diffusivity of chemical species A in water [m^2 /s]

dp Bioparticle diameter [m]

ds Average particle diameter [m]

Deff|βσ Effective diffusivity for system β−σ [m^2 /s] Deff|γκ Effective diffusivity for system γ−κ [m^2 /s]

Dβ Molecular diffusivity of chemical species A in phase β [m^2/s]

h Convective coefficient of mass transfer [m/s]

I Identity tensor [adimensional]

KA Michaelis–Menten half-saturation constant of chemical species A [mg/L]

nβσ (=nσβ), Unitary vector normal to area Aβσ [adimensional].

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