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Studies of Mass Transfer Coefficients in Denitrifying Biofilms

García López L. and Veiga M.C.
Chemical Engineering Laboratory. Faculty of Science. University of A Coruña.
Campus da Zapateira s/n. A Coruña 15071 (Spain)
Nogueira R. and Melo L.F.
Center of Biological Engineering-IBQF, University of Minho, 4700 Braga (Portugal)
e-mail address: lourdesg@mail2.udc.es

Abstract - Mass transfer coefficients within denitrifying biofilms were determined with an inert compound (LiCl) using two different flow conditions in a membrane flow cell and feeding an easily degradable substrate. The experiments were made until the biofilm reached steady state. The results obtained from the biofilm mass transfer experiments show that the biofilms grown under these two different conditions reach similar values in the steady state. However, the mass transport was higher during biofilm formation, for the biofilm developed under higher upflow velocity.

Key words: denitrifying biofilm, diffusion, flow cell, mass transfer coefficients.

INTRODUCTION

Biofilm technology is widely used in biological nitrogen removal from wastewater. In the last years, denitrifying biofilm systems are being used for nitrate removal. Mass transfer usually is limiting the development of biofilm systems (Siegriest and Gujer, 1985). It is important to understand and optimize the mass transfer mechanisms to develop biofilm reactors. In natural and industrial biofilms, convective and molecular diffusion are the predominant mechanism of transport of solutes (De Beer *et al.*, 1996). However transport between surface film and base film occurs primarily by molecular diffusion for dissolved components and by volumetric displacement for particulate components (Characklis and Marshall, 1990).

To evaluate the mass transfer coefficients within biofilms, a simplifying method can be used, where a mass balance with a non reactive tracer is applied to a biofilm adhered to a porous membrane (Kitsos *et al.*, 1992, Vieira *et al*., 1993, Brito and Melo, 1999). The inert tracer is transported through the biofilm under different flow conditions. With this method, biofilm mass transfer coefficients are studied for anaerobic and aerobic biofilm systems.

The present work was carried out to study the mass transfer coefficients in a denitrifying biofilm grown in a membrane flow cell, using two different upflow velocities, similar to the ones used in denitrifying biofilm reactors.

METHODS

Experimental system

A denitrifying biofilm was grown in a vertical flow cell (Figure 1) consisting of two chambers (I and II), separated by a hydrophilic membrane of cellulose esters, with a mass transfer area and pore diameter of $1.6 \cdot 10^{-3}$ m^2 and 0.22 µm, respectively. The flow cell was made of plexiglass with a semi-circular geometry. A centrifugal pump was connected to each chamber (circuit I and circuit II) in order to recycle the liquid continuously. Sample ports were placed in chambers I and II.

Two experiments were carried out applying two different upflow velocities to the system. An upflow rate of 0.01 $m \cdot s^{-1}$ was adjusted with a flow meter on each side of the membrane, in the first case. A differential manometer was connected to both sides of the membrane in order to have the same pressure and avoid the transport due to a pressure gradient across the membrane. In the second case, an upflow rate of 0.04 $m \cdot s^{-1}$ was given by the centrifugal pump flow. The total volume of each circuit was about 800 mL and 500 mL for the two different cases respectively.

Initially, circuit I was inoculated with a denitrifying bacterial suspension and water was pumped in circuit II. After 24 h the inoculum was replaced by medium solution fed in fed–batch mode in the first case, and in a continuous mode, using a peristaltic pump connected to circuit I, working with 4 hours of hydraulic retention time, for the second case, to promote biofilm growth during the experiments.

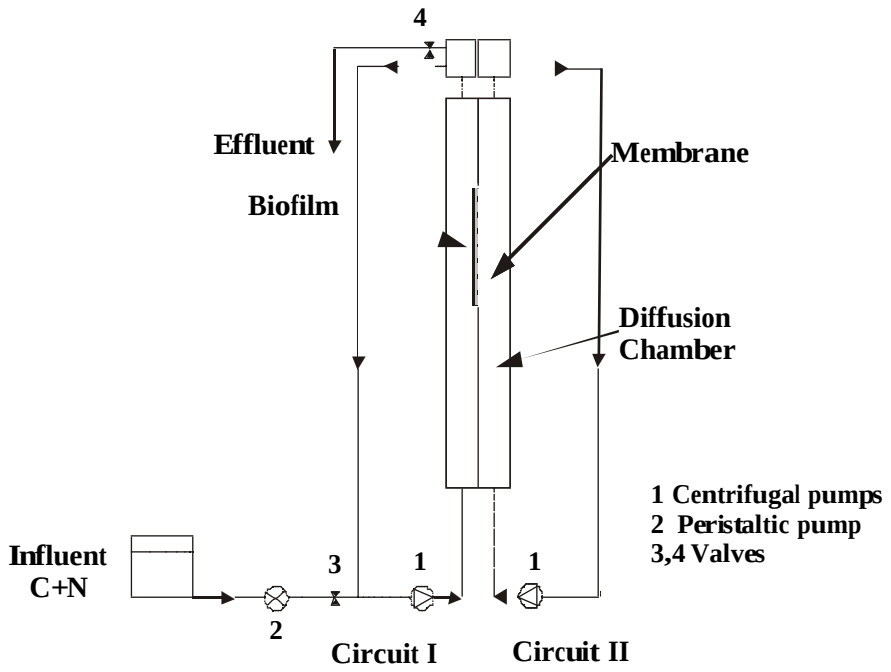

Figure 1. Mass Transfer Flow Cell Design

The nitrate concentration in the feed of the flow cell was always 50 mg N/L, with a C/N ratio of 4 and 2.25, using acetate and methanol, respectively for the two different conditions. Inorganic elements were used as nutrients in both cases. The pH was adjusted between 7.3 and 7.5. The operation temperature was 20 °C.

Mass transfer measurements were performed on the membrane cell and during biofilm growth with an inert compound, lithium chloride (Vieira *et al*., 1993, Kitsos *et al*. 1992). A fixed amount of LiCl (200 mg $Li^{+}\cdot L^{-1}$) was added to vessel I together with the medium and the mass transfer experiment started after equilibrium conditions were reached. Samples were collected at intervals of 30 min, during 8 h, in both circuits. After that, LiCl was removed from the system. Lithium concentration was measured by atomic absorption spectroscopy (Varian SpectrAA.250 plus).

Biofilm characterization

At the end of the experiments, the biofilm thickness (L_b) was determined, in the first case with a micrometer and a video camera, according to Brito and Melo (1999). In the second case, the biofilm thickness was determined with a microscope Leica Leitz DMRD at magnification of 5x0.12p and with a calibrated ocular micrometer.

The biofilm was detached from the support by ultrasound treatment. The following parameters of the biofilm were characterized. Total protein, and Total Polymers according to the methods of Lowry (Sigma kit 5656) and Dubois, respectively and dry weight (TS) by Standard Methods (1995). Biomass density represents the weight of biomass expressed as TS per unit volume of biofilm. Also, scanning electron microscopy observations were made on biofilm samples submitted to dehydration in an ethanol series (30,50,70,90 and 100%).

Evaluation of Mass Transfer Coefficients

Mass transfer coefficients were determined in the system with a nonreacting substance (LiCl), diffusing across the membrane and the biofilm attached to the membrane, assuming that the biofilm thickness remained constant during the period of the experiment (i.e., when LiCl is introduced).

A material balance for the inert compound in the system, based on Fick´s model, can be made using the following equations:

$$\frac{dC}{dt} = k_T \cdot A \cdot (C_I - C_{II}) \cdot \left(\frac{1}{V_I} + \frac{1}{V_{II}} \right) \qquad (1)$$

With the integration of (1) is possible to obtain the concentrations in both sides for each time during the experiment:

$$C_I = C_\infty + (C_I^0 - C_\infty) \cdot \exp\left(-(t - t^0) \cdot k_T \cdot A \cdot \left(\frac{1}{V_I} + \frac{1}{V_{II}}\right)\right) \quad (2)$$

$$C_{II} = C_\infty - (C_\infty - C_{II}^0) \cdot \exp\left(-(t - t^0) \cdot k_T \cdot A \cdot \left(\frac{1}{V_I} + \frac{1}{V_{II}}\right)\right) \quad (3)$$

with the concentration at infinite time:

$$C_\infty = \frac{C_I^0 \cdot V_I + C_{II}^0 \cdot V_{II}}{V_I + V_{II}} \quad (4)$$

where C^0 and C are the lithium concentrations at $t = t_0$ and $t = t$, for circuit I and II, respectively, V_I and V_{II} the volume for both circuits, A is the mass transfer area, k_T the overall mass transfer coefficient, including the biofilm, the membrane and the external mass transfer resistances, and t is the time during which the lithium accumulates in circuit II.

The value of k_T was calculated by fitting equations (2) and (3) to the measured concentrations by non-linear regression.

The biofilm mass transfer coefficient, k_b, can be calculated from the overall mass transfer coefficients, k_T, and the initial mass transfer coefficient of the membrane without the biofilm, k_T^0

$$\frac{1}{k_b} = \frac{1}{k_T} - \frac{1}{k_T^0} \quad (5)$$

The diffusion coefficient in the biofilm (D_b) results from the biofilm mass transfer coefficient and the biofilm thickness

$$D_b = k_b \cdot L_b \quad (6)$$

RESULTS AND DISCUSSION

Mass transfer studies were performed during the biofilm formation. Data were collected for 15 days at different stages of the biofilm development. All the experiments were undertaken in duplicate. The biofilm was grown under two different conditions. They were called Biofilm 1 and Biofilm 2.

Figure 2 shows one example of the several diffusion experiments conducted. The approach of the measured concentrations in both circuits as well as modelled concentration curves can be seen. From each of these experiments values for k_T and k_b could be estimated.

Figure 3 shows the evolution of the biofilm mass transfer coefficient k_b for both biofilms. In both cases, the biofilms reach a steady state after 10 days. The final value of k_b was about $1 \cdot 10^{-6}$ $m \cdot s^{-1}$. However, before steady state was achieved, the biofilm mass transfer coefficient of the lithium for the biofilm grown with the higher flow rate was 30 to 50% higher than for the biofilm grown under low flow rate. This could possibly be explained by a better interaction between the biofilm and the substrate in biofilm 2, resulting in a more compact biofilm. The results obtained from the measurement of the biofilm thickness can also corroborate this hypothesis.

Biofilm thickness was around 418 and 467 μm for biofilm 1 and 2, respectively. This results in a D_b of lithium of about 4.18 10^{-10} $m^2 \cdot s^{-1}$ and $5.83 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$, for each biofilm. These values correspond to 41% and 57% of the diffusivity of lithium in water. This agrees well with the range of relative biofilm diffusion coefficients reported by Stewart (1998) for inorganic ions, like Li^+ and NO_3^- (58 ± 24 % of the diffusion coefficient in water).

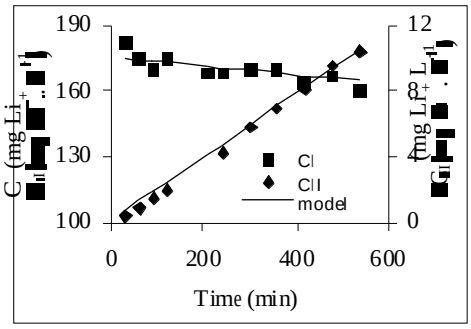

Figure 2. Example of experimental results of each side (biofilm of 2 days).

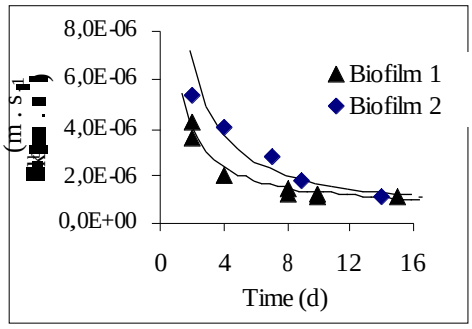

Figure 3. Biofilm Mass Transfer Coefficient.

Previous work was also performed in a laminar flow, but with a methanogenic biofilm. The internal mass transfer coefficient approached similar values (Brito and Melo, 1999). Biofilms formed under turbulent flow with *Pseudomonas fluorescens*, showed the same behaviour (Vieira *et al*., 1993).

The biofilm was characterized at the end of each experiment The specific mass of the biofilm was in the range of 29 and 49 kg dry biofilm·m^{-3} wet biofilm, for Biofilm 1 and 2, respectively. Total protein contents were 0.5 and 0.66 kg·kg^{-1} dry biofilm and total polysaccharides were 0.2 and 0.12 kg·kg^{-1} dry biofilm, respectively.

Biofilm surface was irregular and not homogenous for Biofilm 1 and regular and almost homogenous in Biofilm 2. However, SEM photographs of the both biofilms showed an irregular surface and biofilm structure of clusters and channels as described by Lewandowski *et al*. (1995).

CONCLUSIONS

A non reactive compound, LiCl, was used as tracer to estimate the biofilm mass transfer coefficients in a denitrifying biofilm, at different states of growth. The conditions were similar to those in denitrifying biofilm reactors. It was found that increasing the upflow rate, lithium diffusion was better, during the biofilm formation time. The final values achieved, for the biofilm mass transfer coefficients, were in the same order of magnitude for the all experimental studies and similar to the results previously obtained with different types of biofilms under various hydrodynamic conditions. More work is needed in order to understand this particular pattern of mass transfer results in biofilms.

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