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Analysis of polysaccharide, protein and humic acid retention by microfiltration membranes using Thomas' dynamic adsorption model

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ABSTRACT

Thomas' model has been applied in this study for the quantitative description and parameterization of the dynamic adsorption of organic foulants to membranes by analysis of the permeate concentration as a function of filtration time (or effluent volume). A hydrophilically enhanced polyvinylidene fluoride (PVDF) membrane was used with dextran (DEX), bovine serum albumin (BSA) and Aldrich humic acid (HA) that were used as model compounds representative of polysaccharides, proteins and humic substances, respectively. Thomas' model stemming from *Langmuirian* adsorption kinetics was found to give a good description of physically irreversible membrane fouling as well as the corresponding adsorption constants. The simplification of *Langmuirian* kinetics to *Linear* kinetics was found to be reasonable though with no further mathematical simplifications or approximations valid for the case of fouling of a hydrophilically enhanced PVDF membrane. *Ka*, i.e. the product of the equilibrium constant and the total adsorption capacity, is considered to be a more practicable measure of adsorption affinity than *K*. The *Ka* values of 2.09, 2.83 and 3.44 for DEX, BSA and HA, respectively, confirm that the affinity exhibited by foulants typically follows the order: humic substances > proteins > polysaccharides for hydrophilically enhanced PVDF membranes. However, the final adsorbed amount (i.e. the fouling extent) is dependent upon not only the membrane-binding affinity but also the concentration of foulant in the solution.

1. Introduction

Membrane fouling is considered to be the major drawback to wider application of microfiltration and ultrafiltration for water and wastewater treatment [1,2]. The process of membrane fouling consists, in sequence, of pore blocking and narrowing, gel layer formation and cake layer formation, of which the initial stage, i.e. the pore blocking and narrowing stage, is considered the most problematic as it leads to physically irreversible fouling [3,4], which cannot easily be removed by regular means except by addition of chemical reagents. The pore blocking and narrowing, also known as internal fouling, is mainly due to the adsorption of organic foulants such as polysaccharides, proteins and humic substances of smaller or comparable size to that of the membrane pores, which are recognized to exist widely in surface waters and wastewaters. Each of these organic groupings, i.e. the polysaccharides [5], proteins [6] and humic substances [7], have been reported to be the predominant cause of irreversible fouling. In order to clarify the relative contribution of each of these groupings to irreversible fouling, further fundamental understanding of the adsorption behavior of each of these groupings is required.

In order to quantify the expected extent of adsorption of particular organic compounds to membranes, "dynamic" rather than "static" investigations must be undertaken where the solute of interest is dissolved in a liquid stream flowing through the membrane and the extent of removal from the flowing stream assessed. Information on the extent and nature of partitioning of the solute to the membrane can then be deduced by application of mathematical models which appropriately describe the dynamic process. A few researchers [8–10] have succeeded in performing dynamic adsorption experiments and in applying appropriate models to analysis of the obtained data though, generally, with some compromise in either description of the adsorption kinetics or in development of an appropriate solution method.

The Thomas' model [11,12] is considered to be a particularly attractive approach to describe dynamic adsorption. It has a sound theoretical basis in *Langmuir* adsorption kinetics and has a precise analytical solution enabling determination of adsorption rate constants which may be used to characterize the fouling behavior. Thomas' model was derived with respect to dynamic adsorption in an adsorption column and enables description of the permeate concentration of the sorbing entity as a function of filtration time (or effluent volume). A simplified version of the analytical solution has been utilized widely in studies of the behavior of an adsorption column in the field of chromatography [13,14] and treatment of wastewaters [15], containing dye [16,17] or hazardous metal ions

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[18,19]. However, to our knowledge, few researchers have employed this model in analysis of membrane fouling. Application of Thomas' model, especially its simplified form, to the analysis of membrane fouling would be of particular value in providing a sound basis for properly describing adsorptive effects in membrane filtration and in developing predictive ability in this regard.

It should be noted that although the Thomas' model has been successfully used in describing the behavior of a sorbing solute in a conventional adsorption column, for the case of membrane fouling, the usually thin membrane coupled with the typically relatively low foulant's concentration might cast doubt upon the availability of a series of assumptions and limiting conditions involved in the establishment, derivation and simplification of the model. If the model is used without consideration of these assumptions and conditions, the selected expression might be erroneous and may yield false results, especially with respect to the determination of adsorption rate constants and equilibrium constant. Thus a systematic analysis of the applicability of Thomas' model to description of the adsorptive removal of solutes during membrane filtration and the appropriateness of the various possible simplifications in both the model and solution methods used is considered important to appropriate use of this potentially powerful model.

In this study dextran, bovine serum albumin and Aldrich humic acid with similar hydrodynamic molecular sizes were used as model compounds representative of polysaccharides, proteins and humic substances, respectively. The limiting conditions of Thomas' model were examined by the determination of adsorption constants utilizing models based on *Langmuir* kinetics and its simpler variant of *Linear* kinetics, and between the complete and simplified expressions of Thomas' model. The experimental data were obtained by constant-flow microfiltration of model organic solutions and adsorption constants obtained by nonlinear regression of experimental data based on a particular expression of Thomas' model. Furthermore, the adsorption constants of dextran, bovine serum albumin and Aldrich humic acid were compared in order to characterize the membrane fouling behaviors of polysaccharides, proteins and humic substances.

2. Theory

Two forms of Thomas' model have been derived depending on whether the adsorption isotherm is of *Langmuir* type or *Linear* type. Either the complete expression of Thomas' model or a simplified form may be developed in both cases. The relative simplicity of these expressions follows the order: complete *Langmuir* < complete *Linear* < simplified *Linear* < simplified *Langmuir* expression. The most frequently used is the simplest expression, i.e. the simplified *Langmuir* expression, while the most accurate expression, i.e. the complete *Langmuir* expression, has been rarely used due to its complexity. The derivation of expressions for these forms of Thomas' model is outlined below (c.f. [11,12] for more details).

2.1. Conservation condition

Fig. 1 is the schematic diagram of an adsorption column. The mass of organic adsorbate is denoted by total organic carbon (TOC). The mass conservation condition for constant flow through such a column is:

$$cJ\delta t = \left(c + \frac{\partial c}{\partial x}dx\right)J\delta t + \varepsilon dx\frac{\partial c}{\partial t}\delta t + dx\frac{\partial q}{\partial t}\delta t \tag{1}$$

where c (gTOC/m^3) is the concentration of foulant, J (m^3/(m^2 h)) the solution flux of filtration, t (h) the time, x (m) the distance from membrane surface in the direction of permeation, ε (m^3/m^3) the porosity, and q (gTOC/m^3) the adsorbed foulant's concentration denoted by adsorbed mass per membrane total volume.

Hence

$$\frac{\partial c}{\partial x} + \varepsilon\frac{\partial c}{\partial V} + \frac{\partial q}{\partial V} = 0 \tag{2}$$

where V (m^3/m^2) is the specific volume of permeate.

If the variables are changed into independent ones, namely:

$x = x$

$y = Jt - \varepsilon x = V - \varepsilon x$ i.e. the specific volume of solution downstream (m^3/m^2), then Eq. (2) becomes

$$\frac{\partial c}{\partial x} + \frac{\partial q}{\partial y} = 0 \tag{3}$$

2.2. Adsorption kinetics

An adsorption process is comprised of diffusion and reaction steps. Supposing diffusion is not rate-determining factor (which is the situation in most cases of interest) then, based on *Langmuir*'s assumptions, we can write:

$$\left(\frac{\partial q}{\partial t}\right)_x = J\left(\frac{\partial q}{\partial y}\right)_x = k_1(a-q)c - k_2q \tag{4}$$

where k_1 (m^3/(gTOC h)) and k_2 (h^{-1}) are rate constants and a (gTOC/m^3) the total adsorption capacity.

In the equilibrium state,

$$q_e = \frac{k_1ac_e}{k_2 + k_1c_e} = \frac{Kac_e}{1 + Kc_e} \tag{5}$$

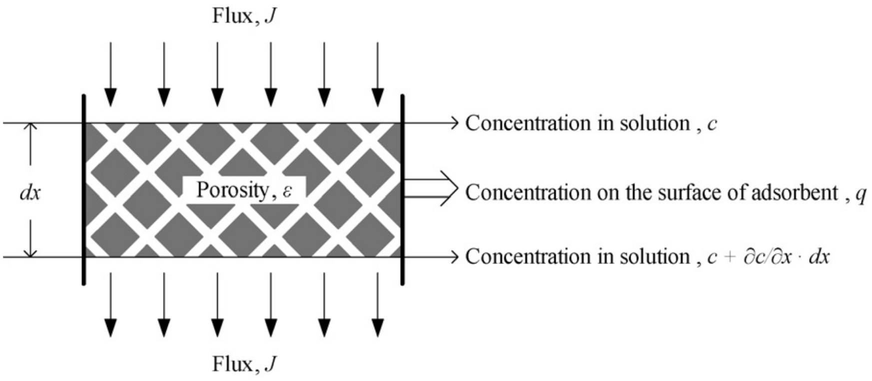

Fig. 1. Scheme of an adsorption column.