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Hollow fiber membrane contactors—A means to study the reaction kinetics of humic substance ozonation

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Abstract

This paper describes the use of membrane contactors to investigate the reaction kinetics of the ozonation of humic substances (HS). Humic substances are a collection of large, complex organic molecules in soil and surface water originating from microbial decay of dead organisms. They give and undesired yellow color to (drinking) water. A methodology based on theoretical mass transfer considerations was used to evaluate and interpret results from ozonation experiments. Mass transfer experiments were conducted in a hollow fiber membrane contactor in order to allow stationary ozonation conditions. Because mass transfer conditions for hollow fiber membranes can be controlled well and in and outgoing streams can be analyzed precisely, this way of performing ozonation enables a thorough and precise investigation of the reaction kinetics. For this purpose, an ozone resistant PVDF hollow fiber membrane module was developed. Theoretical considerations on mass transfer with and without reaction and experimental mass transfer data indicate that the initial ozonation reactions occur instantaneously compared to the diffusive ozone mass transfer. During the oxidation process the reaction rate shifts from instantaneous to fast compared to the diffusive ozone mass transfer. Even when the ozone consumption is 0.25 mol O_3/mol DOC, the enhancement factor is >2 and no ozone is found in the liquid bulk. This indicates that the reaction is at least fast. The average HS diffusion coefficients during the initial ozonation reaction can be estimated from the assumption that the reactions are instantaneous.

Keywords: Humic substances; Ozonation; Mass transfer kinetics; Membrane contactors

1. Introduction

Humic substances (HS) pose a world wide problem in drinking water production giving drinking water a yellow color. HS is the name for a cocktail of organic molecules that originate from biological degradation of dead plants and animals in the soil and surface water. The size of these molecules ranges from 1×10^3 to 1×10^6 Da and they contain a variety of functional groups like unsaturated bonds and aromatic groups. Further ketonic, alcoholic and carboxylic groups and aldehydes are found in HS molecules. A characteristic feature of humic substances is their low biodegradability. Being a product of microbial degradation processes, it has lost its value as energy source for microorganisms. Several techniques are available for efficient removal of humic substances from water, e.g. adsorption/ion exchange, coagulation/flocculation and membrane filtration [1]. The degradation of HS in an economical effective way seems to give more problems, mainly due to the low biodegradability of HS. One of the ways to overcome this problem is using ozonation as pre-treatment for biodegradation. In some places, this technique is already applied in drinking water production [2]. Most research focusing on the effect of ozonation on HS mainly address the characterization of the ozonation products. Few results, however, have been reported on the process technology involving mass transfer and reaction kinetics of the ozonation of HS. Xiong and Legube [3] describe the ozone consumption rate in presence of aquatic fulvic acids at different pH values with and without the presence of radical scavengers. Staehelin and Hoigne [4] investigated the effect of pre-ozonated HS on the radical chain reactions during

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the ozone decomposition. Langlais et al. [5] discuss in their book a few studies on the ozonation of humic substances. The molecular structure of HS is usually very complex and hard to reveal, which makes HS a subject for many studies for the characterization of the molecular structure. The fact that quantity and type of varying potentially reactive sites, each with its own reactivity, are hardly known has consequences for reaction kinetic studies. In batch-wise experiments, the reaction kinetics may change during the ozonation period making a qualitative evaluation of reaction experiments a difficult task. For this purpose an experimental setup which can be operated stationary is desirable.

In recent years, the use of membranes as gas–liquid contactors has advanced rapidly. The advantages lie in the (potentially) high interfacial area and the hydrodynamic decoupling of the phases. Also in bubbleless transport of a gas to a liquid phase membrane contactors can be of much use. Due to the low solubility of ozone in water a high contact area would be very beneficial to enhance the ozone transfer from the gas to the liquid phase. Several investigations involving the use of membrane contactors for ozone transport have been reported. Shanbhag and co-workers investigated the ozone mass transfer application of silicone hollow fiber membranes and their application for ozonation of wastewaters [6–8]. Guha and Shanbhag tested both silicone and microporous Teflon tubes and polypropylene hollow fibers in investigating a multiphase ozonation reactor [9]. Janknecht et al. [10,11] and Picard et al. [12] developed hydrophobic and hydrophilic ceramic membranes for ozonation purposes. Also a few companies, such as Gore and Pall offer membrane ozonators for several applications.

A beneficial feature of the hollow fiber/hollow fiber membrane contactor is that its surface area is known accurately. Also, the fluid dynamics and mass transfer description of a phase flowing through the hollow fibers is very accurate. Furthermore, the gas/liquid adsorption processes can be operated stationary so that the chosen experimental conditions remain constant throughout the experiments. This makes the membrane contactor a potentially useful tool for measurements in mass transfer and reaction kinetics.

In this paper, the results and evaluation of mass transfer measurements in a PVDF membrane contactor are reported which were conducted to investigate the reaction kinetics of the ozonation of HS. For this purpose, ozone resistant PVDF hollow fiber membranes and modules are prepared.

2. Theory

2.1. Mass transfer without reaction

The molar flux of a gas A, into a liquid can be described by the general equation

$$J_A = K_{ov}(c_{A,L,i} - c_{A,L}) \qquad (1)$$

For a non-wetted porous membrane, the overall mass transfer coefficient, K_{ov}, can be described by a resistance-in-series model:

$$\frac{1}{K_{ov}} = \frac{1}{S_A k_G} + \frac{1}{S_A k_M} + \frac{1}{E_A k_L} \qquad (2)$$

Here, E_A is a so-called enhancement factor which accounts for an apparent acceleration of the mass transfer coefficient due to a reaction in the liquid phase. Details on the enhancement factor are further elaborated in Section 2.3. For the mathematic approach of the transport of a gas into a liquid, several models have been developed. The most well known basic models are the film, penetration and surface renewal model. The film model assumes a stagnant liquid film near the interface and a well mixed bulk behind it. The mass transfer coefficient of the liquid is then determined by the thickness of the layer and the diffusion coefficient of the compound in the liquid (Eq. (3)). The penetration model (also known as Higbie-penetration model) assumes that a liquid-package is transported from the bulk to the interface, remains there for a certain time and then turns back to the bulk. During the time at the interface non-stationary mass transfer occurs. The mass transfer coefficient can be calculated by Eq. (4). The penetration depth of the compound in the package depends on the contact time, τ and thus the length of the membrane and the liquid velocity. This penetration depth should be small with respect to the thickness of the dimensions of the medium ($\ll 0.5 d_{m,in}$). The Danckwerts surface renewal model is a modification of the penetration model and assumes a surface age distribution with a replacement probability, s. The mass transfer coefficient can be calculated by Eq. (5). In contrast to the Higbie model, this model also covers the case that the bulk concentration differs from zero.

$$k_L = \frac{D_{A,L}}{\delta} \quad \text{(film model)} \qquad (3)$$

$$k_L(\tau) = 2\sqrt{\frac{D_{A,L}}{\pi\tau}} \quad \text{and} \quad \delta_{\text{penetration}} = 2\sqrt{D_{A,L}\pi\tau}$$
$$\text{(Higbie pen. model)} \qquad (4)$$

$$k_L = \sqrt{D_{A,L} s} \qquad \text{(sur. ren. model)} \qquad (5)$$

For a (liquid) phase flowing through the bore side of a fiber, the Graetz-Lévèque (G-L) equation gives two asymptotic correlations for the dimensionless mass transfer coefficient, the Sherwood-number, *Sh*.

$$Sh_L = 1.62\left(Re_L Sc_L \frac{d_{m,in}}{Z}\right)^{1/3} = 1.62\left(\frac{v_L d_{m,in}^2}{D_{A,L} Z}\right)^{1/3}$$
$$= 1.62 Gz_L^{1/3} \quad Gz_L > 20 \qquad (6)$$

$$Sh_L = 3.67 \quad Gz_L < 10 \qquad (7)$$