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A hybrid photocatalysis–ultrafiltration continuous process: The case of polysaccharide degradation

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ABSTRACT

A novel system is described, which involves coupling the photo-catalysis process with ultrafiltration, permitting a steady state operation with a fixed quantity of dispersed TiO_2 catalytic nano-particles. Results are presented demonstrating the good performance of the system for degradation of a typical polysaccharide (sodium alginate) dissolved in feed-water at relatively small concentration. Using a hollow-fiber UF module submerged in an aerated tank and periodic backwashing, membrane fouling is controlled and TiO_2 particles are totally retained by the membranes, thus allowing continuous "once-through" flow operation with no reject stream. Experiments carried out with catalyst concentration in the range 0.25–1.5 g/L and constant UV-A irradiation of 17.7 J/s (in a 9 L capacity system), show fairly high alginate mineralization rates with a maximum TOC removal (~75%) at TiO_2 concentration 0.75 g/L. The three backwash frequencies employed (i.e. 1 min backwashing after 5, 9, or 15 min suction period) result in approximately the same percentage TOC removal; however, the smaller frequencies are desirable as they lead to greater permeate productivity. Based on the present encouraging results, research needs are indicated for overall system improvement and optimization for various applications.

1. Introduction

Heterogeneous photocatalysis is intensively investigated as a very promising method, within the category of *Advanced Oxidation Processes* (*AOP*), capable of oxidizing a wide spectrum of organic substances, with numerous potential water treatment applications [1,2]. It is widely reported that this process is appropriate for oxidation/degradation of various organic compounds, including humic substances, proteins, pesticides, phenolic compounds, pharmaceutical substances, and dyes used in textile industry [3,4]. The photocatalytic oxidation, using UV irradiation with a TiO_2 catalyst has attracted particular attention due to many advantages, including low cost, ease of implementation and effectiveness [2,5,6]. Polycrystalline TiO_2 is the most widely used photocatalyst, in both the allotropic phases of anatase and rutile, although the anatase phase appears to be generally more photoactive [7].

The photocatalytic reactors described in the literature can be divided in two main groups: (i) reactors with TiO_2 particles dispersed in the reaction mixture (slurry type) and (ii) reactors with TiO_2 fixed on a carrier material (fixed-catalyst type). Both configurations have advantages and disadvantages [1,8,9]. Fixed-catalyst type reactors have the intrinsic advantage of not requiring a catalyst recovery operation; however, they have several drawbacks such as possible catalyst deactivation and wash out, reduced processing capacity due to mass transfer limitations, low surface area-to-volume ratio and low UV light utilization efficiency due to scattering by the immobilized photocatalyst [10,11]. Moreover, they exhibit operating inflexibility, as it is difficult to adjust the catalyst loading to the composition of the feed solution [1]. On the other hand, slurry reactor systems have relatively high surface area to reactor volume ratio and enhanced mass transfer due to the high specific surface area of the dispersed TiO_2 powders [12]; therefore, the efficiency of photocatalytic degradation is usually much higher than in the case of the fixed-catalyst reactors [1,8,9]. The major drawback of the slurry reactor systems is the requirement for an effective separation step to recover the catalyst and obtain a good quality effluent [12].

A very promising approach for dealing with the separation of photocatalyst from the reaction mixture is the photocatalytic membrane reactor (PMR), involving a membrane filtration step [8]. PMR advantages, compared to conventional photoreactors, include catalyst confinement in the reaction environment and use over a long period of time, the efficient control of the residence time of pollutants in the photoreactor, and the possibility of operating in continuous mode, simultaneously separating catalyst particles and treated effluent [1,8,13,14]. The membrane should function as a barrier for photocatalyst particle retention as well as for selective separation of the process reactants and by-products, thereby enhancing the degradation action of the ultraviolet irradiation [13]. In general, PMR can be categorized in two groups:

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(i) reactors with catalyst dispersed in the solution under treatment and (ii) reactors with catalyst supported in/on the membrane. In the former case membrane filtration may be used in a single step for catalyst recovery; however, the major disadvantage in this system is the deterioration of membrane permeability due to fouling. In the latter case, photo-oxidation occurs on the external surface and within the pores of the membrane, whilst reactants are permeating together with the carrier fluid. This mode of fluid/catalyst contact often results in a loss of photoactivity and appropriate membrane materials (resistant to UV irradiation and hydroxyl radicals) are necessary for long time applications [1].

The most often investigated PMR described in the literature are the hybrid systems coupling photocatalysis with microfiltration or ultrafiltration membranes. They have been tested for removal of various pollutants, such as dyes [8,13,15], humic acids [7,13,15,16] and fulvic acids [9,17], 4-nitrophenol [5,7,11,13], bisphenol A [2,18], chlorophenol [15], trichloroethylene [19], pharmaceuticals [6], as well as for treatment of wastewaters [7,20,21], surface waters [3,16,22], and partial disinfection of water streams [23]. Several studies with different PMR configuration [7] and characterisation of membrane properties (e.g. permeability, rejection, material) [5,6] have been conducted. Other studies [3,18] have focused on the effect of operating parameters and determination of their optimum values that lead to maximum photodegradation. A few kinetic models describing the mechanism of the photocatalytic reaction [17,24] have been also proposed, mostly involving simple first-order or pseudo first-order kinetics. It is pointed out, however, that these studies were performed in a batch operating mode [3,8] and were carried out in small-scale reactors [9,16,17,19] with solution volumes ranging from ~0.5 to ~3 L.

To the best of the authors knowledge, there are very few studies of PMR operating in a continuous mode under steady state conditions, which is desirable for practical applications; moreover, relevant performance data are scanty. Ryu et al. [15] have developed and tested a pilot-scale submerged PMR, with 500 L volume, and submerged MF membranes, for the removal of humic acids, 4-chlorophenol and dyes from water. Interestingly, an intermittent operation mode of 9 min suction and 3 min pause period appeared to be effective in preventing membrane fouling of the MF membranes in a relatively longtime continuous run. Rivero et al. [21] have reported generally satisfactory results with a process combining photocatalysis and microfiltration for grey water treatment; additionally, no significant fouling of the membranes was observed, when the PMR was operated continuously with permeate fluxes up to 60 L/m^2 h, and trans-membrane pressure (TMP) values less than 0.6 bar. Nonetheless, despite claiming continuous operation, the reported data do not support achievement of steady state conditions in these tests [21]. Chin et al. [18] have described a continuous submerged PMR for the degradation of bisphenol-A. The possibility was also reported of operating the PMR at a high flux (100 L/m^2 h), with low membrane fouling, using an intermittent permeation mode. However, it is unclear whether a steady state operation was attained in their tests [18] which were of relatively short duration (1–2 h).

Taking into account the preceding comments on the state of the art in this area, the main objective of this study is to develop a hybrid photocatalysis–ultrafiltration process, capable of operating under steady state conditions that would be attractive for practical applications. The case study considered in this paper deals with degradation of polysaccharides present in water at relatively small concentration; sodium alginate, a typical polysaccharide, is selected for this study. Polysaccharides are macromolecular biopolymeric compounds, common constituents of natural organic matter (NOM) and of extracellular polymeric substances (EPS) [25] in natural waters and waste-waters. Despite its potential practical significance, the catalytic photodegradation of these compounds has received very little attention. To our best knowledge, there are but a few studies on photocatalytic degradation of polysaccharides over TiO_2 in water, dealing with batch photocatalytic processes, which do not involve a membrane separation step. Burana-osot et al. [26] report that depolymerization of sodium alginate to 40% of its average molecular weight occurs in a photochemical UV/TiO_2 reaction at pH 7 for 3 h. Blazkova et al. [27] studied the photocatalytic degradation of sodium heparin, over TiO_2, in a physiological saline fluid and reported significant changes of the heparin macromolecule structure in acidic and neutral environment.

2. Materials and methods

2.1. Materials

Titanium dioxide, (Aeroxide® P25, Degussa-Evonik, Germany), predominantly anatase (75% anatase and 25% rutile) with a BET surface area of 50 m^2/g, an average primary particle size of 21 nm and energy band gap of 3.18 eV, was used as photocatalyst in all experiments of this study. Unless otherwise stated, all aqueous solutions were prepared using Millipore MilliQ (MQ) water with a resistivity of ~18 MΩ cm at 25 °C. To prepare a catalyst suspension, TiO_2 powder was dispersed in water and vigorously stirred for 3 h; six different concentrations of TiO_2, ranging from 0.25 to 1.5 g/L, were employed in this investigation. Sodium alginate (SA) from brown algae was purchased from Sigma–Aldrich. SA was dissolved in water to prepare a stock solution of 1800 mg/L; mixing was provided for complete SA dissolution that lasted 3 h. The feed solution concentration was adjusted with distilled water to approximately 7.5 mg/L alginate (~2.5 mg/L TOC) in all experiments. Calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$), supplied by Sigma–Aldrich, was added to the feed water to achieve a realistic feed solution. A stock solution of 345 mM Ca^{2+} was prepared and stored in the refrigerator for 2 days; then, an appropriate volume of this solution was used to obtain 1 mM Ca^{2+} final concentration. The pH of the bulk solution in the PMR was adjusted, by adding either HCl or NaOH.

Ultrafiltration membranes made of hydrofillised polyvinylidene fluoride (PVDF) with a nominal pore size of 0.04 μm were provided by Zenon Environmental Inc. Three 30 W black light blue lamps (TLD 30 W/08 BLB Philips) emitting at wavelength 365 nm were employed as UV light source.

2.2. Experimental set-up

Fig. 1 shows the continuous flow PMR system designed and constructed in this laboratory. The experimental setup is comprised of a cylindrical slurry tank with a submerged UF membrane module, positioned in the center of the tank. The latter is made of plexiglass with a working volume of 7.5 L. The membrane module of cylindrical shape consists of 300 hollow fibers with a total surface area of 0.47 m^2. UV-A irradiation of flowing fluid is provided by three BLB lamp units, hydraulically connected in series. Each UV-A lamp is encased within a borosilicate glass tube, which is placed inside a plexiglass pipe (L = 85 cm, ID = 4 cm, OD = 5 cm) thus creating an annular space for the flowing medium of irradiated volume 0.5 L. The total effective volume of the hybrid system was 9 L. The light intensity measured by a radiometer was 8.3 mW/cm^2. This value corresponds to a mean UV photon dose of 1.97 J/s per liter of system volume.

The concentrated SA solution was continuously agitated by a magnetic stirring device to prevent agglomeration of the polysaccharide, and was fed to the reactor at a constant flow rate. Simultaneously, distilled water was pumped to the reactor through a second pump to adjust the feed SA concentration. With a centrifugal pump