Full Length Article

Development and assessment of photo-catalytic membranes for water purification using solar radiation

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ABSTRACT

This paper describes a novel set-up for characterization of the performance of membranes designed for purification of water. It involves a recirculatory system, with continuous monitoring of the concentration in the water of a representative pollutant (Methylene Blue). Pressures, flow rates and temperatures are also measured. Results, in the form of rate constants for reduction in pollutant concentration, are presented for three different types of membrane, all of which incorporate relatively high surface areas of titania and have permeability values in a range making them suitable for this type of processing ($\sim 10^{-11}$ m^2). These results are rationalized in terms of the surface areas of the membranes, and the likely water flow characteristics within them. It is concluded that all of the titania surfaces within them have similar efficiencies for photo-catalytic oxidation of pollutants, but there are significant differences in the ways that the water is exposed to these surfaces, and hence in the pollutant oxidation rates. These points are relevant to the optimization of membrane design for this purpose.

1. Introduction

Photo-catalysis is promotion of a light-activated reaction involving a semiconductor illuminated with light of sufficient energy to excite electrons from the valence band to the conduction band [1–3]. If photo-generated charge separation persists, a redox reaction can occur at the surface of the catalyst; typically, this is oxygen reduction and water oxidation [4]. The results of this redox reaction are the production of highly oxidizing reactive oxygen species (ROS), which are able to oxidize organic contaminants. This photo-catalytic mechanism is well established [5–7]. Titanium dioxide (TiO$_2$) is by far the most heavily researched metal-oxide photo-catalyst, owing to its stability, abundance, affordability and suitable band positions for water oxidation and photo-generated redox reactions [8]. A number of recent studies [9–14] have been oriented towards optimization of the structure of titania films in terms of their photo-catalytic performance (including light absorption characteristics and maximization of surface area). It's also well-established [15–19] that the efficiency of titania as a photo-catalyst can be enhanced by the deposition of certain (noble) metals in finely-divided form onto the surface.

The use of TiO$_2$ nanoparticles has traditionally dominated photo-catalytic research, since their exceptionally large specific surface area gives high reaction rates [2,20,21]. However, for bulk water treatment, nanoparticle suspensions are unattractive, due to the cost and complexity of removing them in a post-treatment step. Many techniques have been employed in attempts to overcome the nanoparticle problem. For example, magnetic cores have been incorporated into TiO$_2$ structures to allow easy removal under an applied field [22]. Nanoparticles have been applied to relatively large, porous particles, to facilitate removal via sedimentation or filtering [23]. The formation of TiO$_2$ in meso-porous structures [24,25] or as thin films on immobilised materials such as ceramics [26,27] and plastics [28] have also been extensively investigated.

Overall, the use of porous photo-catalytic membranes offers the most attractive approach, provided they can be designed to offer a combination of high specific surface area and high permeability. This should allow rapid throughput of water flowing close to photo-catalytic surfaces that are being exposed to suitable radiation. Photo-catalytic reaction allows conversion of organic pathogens (and other pollutants) to harmless, fugitive species (possibly just CO$_2$ and water), avoiding the problems of clogging that often plague simple filtration systems. An ideal photo-catalytic membrane should: (a) allow high fluxes of water, to promote rapid water treatment, without clogging, (b) have high photo-catalytic efficiency, ensuring rapid water disinfection and removal of chem-

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ical contaminants, and (c) be sufficiently robust to survive service conditions, handling and repeated usage.

A number of different types of scaffold have been explored for the creation of such membranes. For example, glass fibres have been extensively used [29]. Metallic foams, particularly those based on nickel, have also been investigated, notably for inactivation of chlorella [30], degradation of pollutants in industrial wastewater [31] and breakdown of gaseous acetaldehyde [32]. There has also been work on use of the plasma electrolytic oxidation process to create relatively thick and porous TiO_2 coatings on titanium substrates, for photo-catalytic purposes [26,33–39]. Some of these studies have involved the creation of membrane structures.

Despite these activities, meaningful comparisons between the characteristics of different types of membrane are in very short supply, mainly owing to a lack of standardized testing methodologies. In general, very little work has been done on comparing different types of photo-catalytic membranes in a systematic way. In the present study, three TiO_2-based photo-catalytic membranes have been produced and a comparative assessment has been made of their performance, with and without an attempt to characterize the inherent efficiency of the surfaces concerned (i.e. to make an allowance for different surface areas and water flow patterns).

2. Experimental procedures

2.1. Production of photo-catalytic membranes

2.1.1. Ni foam structure
Ni foam was obtained from Sigma Aldrich, initially in the form of plates with dimensions $150 \times 49 \times 1.6$ mm, 95% porosity and pore dimensions of ~200–300 μm. This material was cut into circular discs of diameter 40 mm (and thickness 1.6 mm). A binder solution was made up (by mixing and stirring 1 g of poly-acrylonitrile with 20 ml dimethyl-formamide for 12 h) and then 3 ml of this solution was added to 0.5 g of TiO_2 P25 nanopowder. The Ni foam was dip coated into this solution and then dried for 6 h in air at about 100° C. This left the surfaces of the foam fairly uniformly coated with fine TiO_2 nanopowder.

2.1.2. PEO-processed Ti mesh
A sheet of fine Ti mesh, 80 wires per inch (wire diameter ~130 μm) was obtained from Alfa Aesar and cut into 40 mm diameter discs. Three of these were cold-welded together (simply subjected to pressure at room temperature) to create the membrane. A Plasma Electrolytic Oxidation (PEO) process was carried out on this sample in a Keronite™ processing facility. The electrolyte was 0.04 M sodium phosphate (Na_3PO_4). A square-wave 50 Hz AC supply was employed, with set anodic and cathodic voltages of 600 V and 250 V respectively. These created anodic and cathodic currents that were both ~14 A. Processing was carried out for 30 min. The resultant PEO layer (uniform on all of the wire surfaces) was about 15 μm in thickness.

2.1.3. Glass fibre scaffold
This material was supplied by St. Gobain, having the tradename Quartzel PCO mesh. It was used in the as-received form, after cutting discs of 40 mm diameter from the supplied sheet. It is composed of (silica-rich) glass fibres, of about 10 μm diameter. The surfaces of the fibres have been subjected to a proprietary treatment that creates a layer containing finely-dispersed TiO_2.

2.2. Microstructural characterisation

2.2.1. Scanning electron microscopy
Microstructures apparent on the free surfaces of all of the samples were examined using a JSM-5500LV scanning electron

microscope (SEM) in secondary electron (SE) imaging mode, mostly with an accelerating voltage of 5 kV and a working distance of about 5 mm.

2.2.2. Isothermal nitrogen adsorption (BET)
A MicroMeritics TriStar 3000 was used to measure the specific surface area of samples (surface regions). Samples were weighed and dried thoroughly (200 °C overnight) before use in this instrument. The sample chambers were then cooled with liquid N_2 and evacuated. Nitrogen was then introduced in controlled pressure increments, and the equilibrated pressures measured and compared with the saturation pressure, to determine the quantities of adsorbed gas. The Brunauer-Emerett-Teller (BET) adsorption isotherm was then used to determine the specimen surface area.

2.2.3. Crystal structure of titania
Previous studies have confirmed the crystallographic characteristics of the coatings produced in these studies. For example, it has been shown [38] that PEO coatings produced on Ti under similar conditions to those used here comprise about 60–80% anatase, with around 10–20% rutile and a small amorphous content. There has also been work [40] on the crystal structure of TiO_2 nanoparticles created using procedures such as those employed here for deposition on the Ni foam and the glass fibres. These have confirmed that the structure is at least predominantly anatase. All three cases are therefore similar in terms of crystal structure.

2.3. Photo-catalytic performance

A customized facility was constructed, designed to allow accurate characterization of the photo-catalytic efficiency of membranes. The set-up, which is shown schematically in Fig. 1(a), is here termed a COMPORM facility (Continuous Monitoring of Photo-catalytic Oxidation during Recirculation through Membranes). Water containing a selected (pollutant) species – Methylene Blue Dye for the work described here – is pumped around a closed system that incorporates a sealed irradiation chamber containing the membrane. The dye concentration was monitored using an in-line UV–vis spectroscopy, with an OceanOptics USB-4000 spectroscope and a flow-cell cuvette. Experiments were carried out with and without membranes present. The membranes were fitted into an O-ring sealed acrylic reactor, having a quartz window through which the sample was irradiated with simulated solar light via a Xenon-Mercury 150 W Light (with optical B40 UV–vis band-pass filter attachment). Fig. 1(b) shows the spectrum of the radiation incident on the sample (obtained by convolution of the intensity spectrum from the lamp and the transmission spectrum of the filter, both supplied by the manufacturers). It can be seen that most of the radiation was in the range 350–600 nm. In fact, with this radiation, in the absence of a photo-catalytic membrane there was no detectable degradation of the dye within the timescale of the experiments (a few hours). Temperature, flow rate and differential pressure data were also continuously monitored and logged (using LabView). Flow was controlled using a pump (MGD1000S, manufactured by TCS Micropumps Ltd.) that operated at a constant flow rate of 300 ml min^{-1}. The reactor configuration is depicted in the perspective view of Fig. 2.

Photo-catalytic efficiency was quantified using pseudo-first order rate constants, assuming Langmuir-Hinshelwood kinetics:

$$-kt = \ln\left(\frac{C}{C_0}\right) \tag{1}$$

where k is the rate constant, t is the time, C_0 is the starting concentration and C is the concentration at time t. For photo-catalytic experiments, 125 ml of water was used in a closed circuit, containing Methylene Blue dye at a starting concentration of 5 mg l^{-1}. The