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Orthogonal experimental design of titanium dioxide—Poly(methyl methacrylate) electrospun nanocomposite membranes for photocatalytic applications

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ABSTRACT

An orthogonal experimental method was designed to assess the influence of the electrospinning processing parameters on average diameter and distribution of poly(methyl methacrylate) (PMMA) fibers. Based on the orthogonal experimental design analysis, electrospun TiO_2-PMMA nanocomposites were processed with the optimal polymer processing conditions to obtain thin fibers with a high overall surface area. Further it was found that the average fiber diameter decreases from 2.0 ± 0.5 down to $1.2 \pm 0.2\,\mu m$ with increasing photocatalyst content. Moreover, the wettability of samples was independent of the filler amount, and showed strong hydrophobic behavior. Thermogravimetric analysis showed that for polymer solutions with concentrations higher than 10 wt%, there was a loss of the photocatalytic particles during processing, being more evident for the sample with 40 wt% particles present in the solution, with a loss of 8 wt% of ceramic particles. The immobilization of the TiO_2 nanoparticles in the polymer fibers led to an increase of the thermal stability. The photocatalytic performance was assessed by using methylene blue (MB). The nanocomposite electrospun fiber membranes had a remarkable photocatalytic activity, especially the one with higher amount of TiO_2, with all the MB dye being removed from the solution after 100 min, under UV. The orthogonal experimental design is an efficient way to save time and materials in the production of photocatalytic membranes.

1. Introduction

Pharmaceuticals and different micro and nanomaterials, used in daily applications, are disposed of and eventually reach rivers and groundwater. Conventional sewage treatment technologies are ineffective in the removal of such pollutants present at trace levels [1–4], demonstrating an urgent need for innovative technologies that can effectively deal with these compounds [5–7]. Photocatalysis is an alternative since it allows their rapid and efficient removal from water, transforming them into by-products with lower toxicity [5,6]. Among several semiconductor materials, titanium dioxide (TiO_2) has a band gap of ~3.10 eV [8,9], which make it a suitable photocatalyst for the degradation of organic pollutants because of its low cost, unique optical properties, and availability [10].

Catalysts can be employed either in a colloidal or in an immobilized form. The removal of such catalyst nanoparticle following water treatment is a major obstacle towards their applicability in an industrial process. Further, nanoparticle's size, large surface area-to-volume ratio and surface energy, strongly leads to agglomeration during operation, decreasing its efficiency [11,12]. For these reasons, immobilized systems are preferable in water treatment, to avoid the costly and additional final filtration process [13–15]. However, the immobilization of photocatalyst nanoparticles to a polymer scaffold is usually weak due to the low attachment of the catalyst onto the supporting material.

Electrospinning is a versatile technique to produce highly porous polymer fibrous membranes with high permeability, small pore size, high specific surface area and good interconnectivity between pores [16,17]. Synthetic polymers usually present suitable

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mechanical properties for handling and separation from reaction media. This process can be easily up-scaled for mass production of one-by-one continuous micro and nanofibers from various polymers [16–18].

Electrospinning is a straightforward effective technique to immobilize ceramic particles onto the polymer fibers. Polyamide 6 (PA6) and polyamide 12 (PA12)/titanium dioxide nanocomposite membranes were processed by electrospinning [17,19]. It was reported that for the same photocatalyst concentration, PA6 solvent casting membranes present enhanced photocatalytic performance when compared to PA6 electrospun nanocomposites. Complete degradation of the methylene blue (MB) dye solution was achieved after 170 min for the polymer films, while the electrospun membranes only degraded 70% of the dye, for the same UV radiation exposure time [19]. Electrospun membranes of TiO_2-PA12 completely removed the dye after 100 min under UV exposure, and showed suitable thermal and mechanical properties [17].

Poly(methyl methacrylate) (PMMA) is a low cost material that presents good flexibility, mechanical properties, chemical resistance, low density, high durability, and easy availability [20], which makes this polymer a good candidate to use as supporting layer for inorganic nanoparticles, such as TiO_2.

Different electrospinning parameters affect fiber formation and ultimately, the average fiber diameter and its distribution. These parameters can be divided in three main categories: (a) solution properties (viscosity, solvent properties, and polymer molecular weight; (b) jet formation parameters (applied electric filed, flow rate, needle inner diameter, temperature, and moisture). Finally, (c) the collection procedure, static or rotating drum or disc collector, and rotation speed determines the fiber diameter and orientation [16]. The number of parameters that influence the fiber diameter and average distribution is thus quite high and experimental design is a powerful tool to determine the parameters with the highest influence on fiber properties.

Orthogonal design is a mathematical method applied to design multilevel experiments, in which selective parameters are chosen to carry out sample experiments from overall experiments on the basis of orthogonality [21,22]. This method allows one to evaluate the relative importance of each factor and identifies the ideal values for various factors [21,23]. The approach not only saves experimental time to determine the optimum conditions associated to a trial and error approach, but also raw materials.

In the present work, an orthogonal experimental design was used to assess the importance of the individual electrospinning parameters in the formation of the PMMA average fiber diameter and distribution. Based on the performed analysis, the optimum electrospinning parameters were chosen to achieve TiO_2-PMMA nanocomposite fibers with a smaller average diameter, increasing the area-to-surface ratio of the membranes. Wettability, chemical and thermal properties of the pristine and nanocomposite membranes were characterized. It was found that there is a loss of photocatalytic particles during the electrospinning process, especially for higher filler concentrations. The photocatalytic performance of the pristine and nanocomposite fibers was assessed and correlated to the amount of the photocatalyst present in the fibrous membrane, by following the degradation of MB upon UV radiation exposure and compared to the performance of the TiO_2 suspension. Finally, it was found that the photocatalytic performance of the nanocomposite samples is related to the concentration of photocatalyst present in the electrospun fiber matrix and no ceramic filler was lost from the polymeric fibers during the photocatalytic experiments.

2. Experimental

2.1. Materials

High molecular weight poly(methyl methacrylate) (PMMA, Elvacite 2041, $M_w = 450\ kDa$) was supplied by Lucite International and titanium dioxide (TiO_2 P25) was supplied by Evonik. PMMA was dissolved in a solvent mixture of dichloromethane/dimethylformamide (DCM/DMF, 8/2 vol/vol) at a polymer/solvent ratio of 10/90 (w/w) and stirred at room temperature until complete dissolution. For the nanocomposites solution preparation, the desired amount of TiO_2 powder, between 0 and 40 wt% related to polymer concentration, was added to the DCM/DMF solvent mixture and was sonicated in an ultrasound bath (Soniclean, 250TD) for 4 h. After the TiO_2 dispersion, the desired amount of polymer was added to the solution and dissolved with the help of a magnetic stirrer, at room temperature, until complete dissolution.

2.2. Electrospinning

The polymer solution was placed in a commercial glass syringe (10 mL) fitted with a steel needle with different inner diameters (0.5, 1 and 1.7 mm). Electrospinning was conducted at different applied electric fields (between 0.8 kV cm^{-1} and 1.4 kV cm^{-1}) with a high voltage power supply from *Gamma High Voltage*. A syringe pump (*KDScientific*) was used to feed the polymer solution into the needle tip, and the electrospun fibers were collected on a grounded collecting plate. The distance between the needle and the collector was kept constant at 15 cm.

2.3. Experimental design

Electrospinning processing parameters affecting electrospun fiber diameter and distribution, include molecular weight, moisture, temperature, solution viscosity, applied electric field, among others [24]. An orthogonal design table L_9 was designed using Orthogonal Design Assistant II software (Sharetop Software Studio). Each orthogonal table has its own mark denoted as $L_n(t)^c$, where L represent the orthogonal table, n is the total number of experiments, t is the number of levels of each factor, and c is the maximum allowed number of factors. In this work, factors of applied electric field, polymer flow rate, and needle inner diameter, labelled as A, B and C, were investigated (Table 1).

2.4. Electrospun fiber membrane characterization

Electrospun fiber membranes were coated with a thin gold layer using a sputter coater (*Polaron,* model SC502), and their morphology was analyzed by scanning electron microscopy (SEM) (JCM-6000PLUS Neoscope, from JEOL) with an accelerating voltage of 10 kV. The fiber average diameters and their size distribution was calculated over approximately 40 fibers using SEM images at 3000× magnification and Image J software. Contact angle measurements (sessile drop in dynamic mode) were performed at room temperature in a Data Physics OCA20 device using ultrapure water as test liquid. The contact angles were measured

Table 1
Factors and levels used for the orthogonal experimental design for PMMA samples.

	Factors		
Levels	A (E/kV cm^{-1})	B (Flow rate/mL h^{-1})	C (Needle diameter/mm)
1	0.8	1	0.5
2	1.0	2	1
3	1.4	8	1.7