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Functionalisation of electrospun nanofibre membranes with titaniumdioxide nanoparticles for water treatment.

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Abstract: Electrospun nanofibre membranes have a high water flux in comparison to other microporous structures. In this research the added value of functionalisation of nanofibers with titanium dioxide nanoparticles (nTiO2) is evaluated. Titaniumdioxide nanoparticles have been used in this study because of their low cost and advanced oxidation properties. This leads to efficient removal of pathogens and recalcitrant molecules in water. Tests with nanofibre membranes functionalised with TiO_2 performed in this study showed an enhanced removal of methylene blue, used as indicator, with 40 to 80% after 6 hours illumination with UV-A.

Keywords: electrospinning; microfiltration; nanofibres; non-woven; photocatalytic; titaniumdioxide; UV-A light

Introduction

The electrospinning technique is a process for making continuous nanofibres in a non-woven form. This process spins fibres ranging from 80 nm diameter to several hundred nanometers. Nanofibres have a small pore size and a large surface area to volume ratio compared to other non-woven membranes. This and their low density and interconnected open pore structure, makes the nanofibre non-woven appropriate for a wide variety of filtration applications.

Combining nano-sized inorganic and organic materials for the production of functionalised nanofibre membranes can enhance the performance of several properties of a polymer matrix or can add immobilized functionality to a nanofibre filtration process. Electrospinning is regarded as a simple and versatile method for this purpose. The production technique enables incorporation of inorganic nanoparticles into a polymer matrix.

Titaniumdioxide nanoparticles have been used as a functional agent for the nanofibre membranes because of their antibacterial properties and the possibility to oxidize organic material offering a high efficiency at low cost. A possible application of these functionalised nanofibers is WWTP effluent filtration in view of water re-use. In order to assess these functionalised nanofibers tests with methylene blue were performed. In a later stage also tests with a standard mixture of humic acids and real waste water effluent will be performed.

Two possible ways of functionalisation are being studied: dip-coating and in-line functionalisation (Decostere et al., 2009). Two titaniumdioxide-solutions have been tested. Degussa P25 (Sigma Aldrich), offering a mixture of anatase and rutile TiO_2 in the range of 25 nm and a synthesized colloid consisting of faceted, single-crystalline, anatase TiO_2 nanoparticles with an average size of 6 nm (Mihailovic et al., 2010).

Material and Methods

The standard setup for single nozzle electrospinning consists of a syringe with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector. An electric field is applied across a PA-6 solution and a collector plate. As the solution jet travels, it is bent and split by the electric forces while the solvent evaporates with formation of fibres which are attracted to the grounded collecting plate (De Vrieze et al., 2009).

Photocatalytic activity of the nanofibre membranes functionalised with TiO_2 was assessed by photodegradation of methylene blue under UV-A irradiation. Different membranes (3.0 cm x 3.0 cm) were immersed in a methylene blue solution (10 mg/l; liquor-to-membrane ratio of 1:800) and illuminated on 40 cm distance by an ULTRA-VITALUX lamp, 13,6W UV-A (Osram) (Figure 1). Sampling was done after 2, 4 and 6h of illumination after which the concentration of the methylene blue was measured by recording its absorbance at 664 nm with a UV-Vis spectrophotometer () Unfunctionalised electrospun nanofibre membranes were considered a reference. The effect of dyeing was taken into account by repeating the methylene blue tests in absence of UV-A.

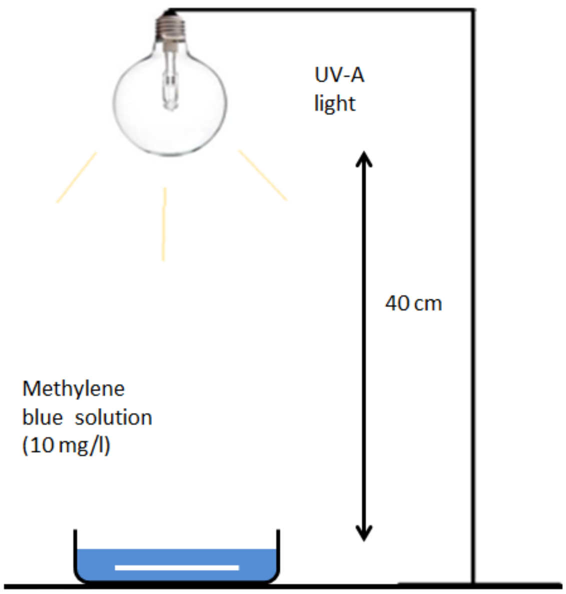

Figure 1: schematic diagram of the batch photocatalytic set-up

Colloidal 6 nm $nTiO_2$ (0,12 M) was prepared as described in Mihailović et al. (2010). The TiO_2 nanoparticles with an average dimension of 6 nm have an anatase crystal structure with an irregularly shape. TiO_2 nanoparticles were obtained in a colloid solution with a concentration of 0,12M $nTiO_2$. Until now it is not possible to obtain the TiO_2 nanoparticles in a higher concentration.

Degussa P25, a standard material in the field of photocatalytic reactions, is a TiO_2 powder containing anatase and rutile phases in a ratio of about 3 : 1. The average sizes of the anatase and rutile elementary particles are 85 and 25 nm, respectively. In this study TiO_2 Degussa P25 (MW = 79.87 g/mol, specific surface area 35-65 m_2/g, Aldrich Co., USA) was used in an aqueous suspension (0,12M and 0,50M P25 TiO_2). The advantage of using Degussa P25 is that solutions with different concentrations can be produced, allowing higher concentrations then with the 0,12M 6 nm TiO_2.

Results and Conclusions

Inline functionalisation with both P25 and $nTiO_2$ give uniform nanofibre membranes (Figure 2). According to the SEM-images, a difference on the nanofibre membrane morphology is visible between post-functionalisation with a 0,50M P25 TiO_2 and 0,12M $nTiO_2$. Whereas the $nTiO_2$ nanoparticles are very well distributed onto the individual fibres, the P25 TiO_2 is clogging together on the whole nanofibre membrane surface.

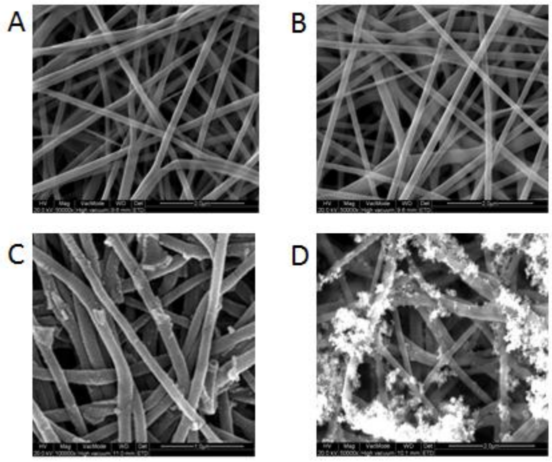

Figure 2: SEM images of A: inline functionalised membrane with 0,12M $nTiO_2$, B: inline functionalised membrane with 0,50M P25 TiO_2, C: post-functionalised membrane with 0,12M $nTiO_2$, D: post-functionalised membrane with 0,50M P25 TiO_2

The nanofibre membranes functionalised with TiO_2 showed an enhanced efficiency on the removal of methylene blue with a removal of 40% (in-line functionalisation) to 80% (post-functionalisation) of the colour after 6 hours illumination with UV-A. (Figure 3) These are promising results on lab scale.

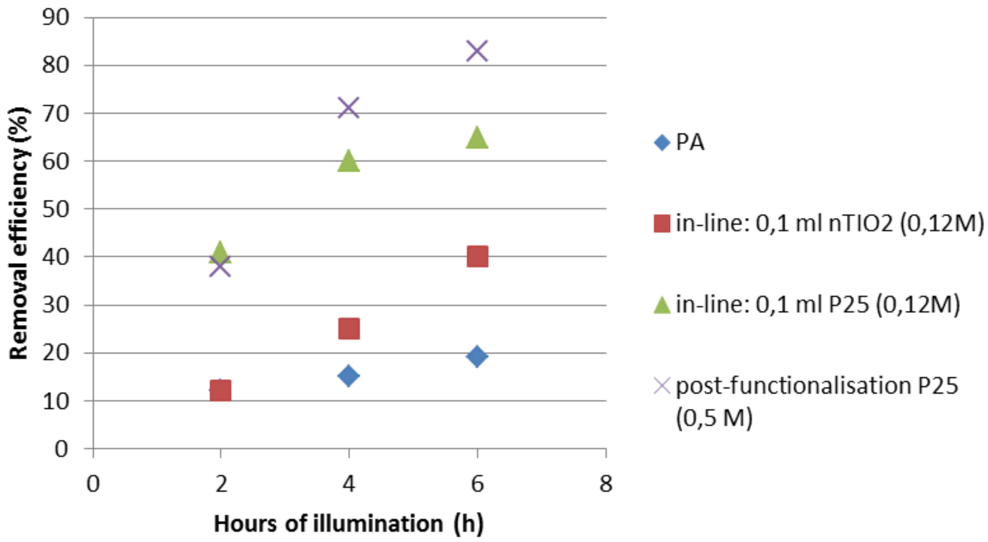

Figure 3: removal efficiency by different functionalised nanofibre membranes of methylene blue (intensity at 664 nm) after illumination with UVA. PA= non-functionalised polyamide nanofibre membrane. In-line: 0,1 ml TIO_2 added to 20 ml spinning solution.

The tests with methylene blue as an indicator revealed that dissolved organic matter degradation is possible. Possible applications could be effluent filtration in view of water discharge and re-use. The functionalised membranes with the highest photocatalytic performance can be tested in the future with e.g. a standard mixture of humic acids and/or bacteria in order to investigate the effectiveness in industrial conditions

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