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TiO_2 functionalized nanofibrous membranes for removal of organic (micro)pollutants from water

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ABSTRACT

Titania has already proven its added value for air and water treatment. The higher the surface-to-volume area, the better the performance of the TiO_2 photocatalyst. These nanoparticles are typically applied in a slurry form. The use of titania nanoparticles in suspension has, however, multiple disadvantages such as a high turbidity and complex recovery of the photocatalyst after use. Therefore, immobilization of titania nanoparticles on a porous support such as a nanofibrous membrane, can be highly valuable for water treatment. These TiO_2 functionalized nanofibrous membranes may be used not only in a membrane separation reactor, but also in a contact reactor. In this study, TiO_2 nanoparticles were immobilized on both polymer (polyamide 6) and ceramic (silica) nanofibrous membranes. Polymer nanofibers are chosen as they are the state-of-the-art material, silica nanofibers on the contrary are less studied but show additional advantages due their excellent chemical and thermal stability and can thus offer a clear benefit for a wider range of applications. Two immobilization techniques were used, namely inline functionalization and dip-coating. Inline functionalization showed to be the preferred method for polyamide 6 nanofibrous membranes, dip-coating for silica nanofibrous membranes. Complete degradation of isoproturon, an actual concern in water treatment, is shown. Even the widely available commercial TiO_2 nanoparticles allowed for a complete isoproturon removal as the result of a correct immobilization process on nanofibrous materials. This clearly opens up the high value of TiO_2 functionalized nanofibrous membranes for organic (micro)pollutants removal.

1. Introduction

Titania, a well-known photocatalyst, is widely used because of its great availability, low cost, non-toxicity, chemical and thermal stability [1]. One of the most interesting properties of titania is its photocatalytic activity under UV irradiation, producing highly oxidative hydroxyl radicals capable of oxidizing many organic (micro)pollutants [2]. This results in many applications such as self-cleaning surfaces, antibacterial surfaces, air purification and water purification [3–6]. Since many of the applications rely on surface related phenomena, a high specific surface area is desired as it enhances the performance of the photocatalyst. TiO_2 nanoparticles are thus known to show greater photocatalytic properties compared to their bulk counterpart [7,8].

Phenylurea herbicides are generally applied for agricultural applications. Isoproturon is one of the most used herbicides in Europe and due to its water solubility, low chemical and biological degradation it contaminates surface and ground water [9,10]. Heterogenous photocatalysis using TiO_2, has been considered as highly promising for waste water treatment and degradation of these herbicides [11,12]. Additionally, removal of organic components present in industrial, highly acidic effluents remains a major issue as well, which can also be tackled using TiO_2. Photocatalytic reactor configurations for water treatment can be classified into two types depending on the state of the photocatalyst: reactors

Abbreviations: PA 6, polyamide 6; MB, methylene blue; IL, inline; DC, dip-coating; H, hydrophilic.

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with suspended photocatalyst particles (slurry reactors) (1) and reactors with immobilized photocatalyst particles (2). A major disadvantages of slurry type reactors (type 1) is the additional post-separation step of the photocatalyst. An increased interest is thus seen in immobilizing the TiO_2 nanoparticles on a porous, inert support [13–17].

Nanofibrous membranes, obtained via the electrospinning process, have a high specific surface area, high porosity and small pore sizes. These unique properties make these non-woven membranes ideal for a wide range of filtration applications [18]. Moreover, they show to be an ideal highly porous support for immobilization of TiO_2 nanoparticles. Via the electrospinning process both polymeric as ceramic nanofibrous membranes can be produced [19–21]. Polymer nanofibrous membranes functionalized with TiO_2 nanoparticles have already shown to be promising for photodegradation of dissolved organic matter, humic acids and bacteria [3,22,23]. Ceramic membranes, although less exploited so far, have many advantages over polymeric membranes for filtration applications, since they have typically superior thermal properties, and a better resistance against corrosion and chemicals [24]. These membranes can thus be used for highly acidic effluents. Moreover, ceramic membranes are much less susceptible to deterioration by the attack of OH radicals, which might be a problem for long life use of polymer membranes [14]. Silica nanofibers have recently shown their added value for removal of heavy metal ions and dyes via sorption [25–27]. So far they have not yet been exploited to study the removal of micro pollutants. Functionalization of these nanofibrous membranes with TiO_2 nanoparticles results in an added functionality for removal/degradation of organic components. Additionally, functionalization with TiO_2 prevents fouling of the membranes, which is a major concern in membrane use for water treatment [24,28]. Thus TiO_2 functionalized ceramic nanofibers will be exploited here for the removal of micro pollutants from water, allowing a close contact between the highly oxidative radicals and the pollution.

The simplest approach for functionalization with TiO_2 nanoparticles is the addition of a chosen amount of the particles to the solution prior to electrospinning, namely inline functionalization. An alternative method is post-functionalization, where the membranes are functionalized with TiO_2 after production. In this study, the dip-coating process will be studied as a post-functionalization method. Both functionalization methods have their advantages and disadvantages. Inline functionalization is an easy and straightforward, one-step functionalization method, resulting in TiO_2 nanoparticles which are distributed inside the nanofibers. Dip-coating, on the contrary, is a two-step process resulting in the presence of the nanoparticles on the surface of the nanofibers and making them more accessible to the pollutants. Three challenges are encountered during surface modification, being uniformity, coating without affecting the pore sizes and possibility for industrial upscaling [18].

In this work, commercial Degussa P25 TiO_2 nanoparticles are immobilized in and on a highly porous nanofibrous support. Commercial Degussa P25 TiO_2 nanoparticles have already proven their value as photocatalyst for water treatment, but proper immobilization remains vital as it increases the applicability of these nanoparticles. Therefore, in this study both polymeric (polyamide 6) and ceramic (silica) nanofibrous membranes are functionalized with these TiO_2 nanoparticles. First, the TiO_2 loading of inline and dip-coated nanofibrous membranes are quantified using TGA, XRD and ICP-OES. Next, the photocatalytic behavior is tested by decoloring of methylene blue, an ideal test compound for a first screening of the produced membranes and their degradation efficiency. Finally, the true degradation potential of micro pollutants is tested on isoproturon using a basic set-up. Both UV–Vis spectroscopy and LC-MS are used for evaluation of the degradation of the pollutants. The removal of isoproturon is a real concern in water treatment today in view of discharge to the environment and has not yet been solved adequately. It is believed that commercial TiO_2 nanoparticles may be highly valuable when immobilized on porous polyamide or silica nanofibrous membranes for removal of various organic (micro)pollutants. Moreover, these membranes are applicable in various water treatment set-ups such as contact reactors or membrane separation reactors.

2. Experimental section

2.1. Materials

Titanium (IV) oxide (Degussa P25) was obtained from Sigma-Aldrich. It is a standard material in the field of photocatalytic reactions, having a primary particle size of 21 nm and a specific surface area of 35–65 m^2/g. The sol–gel precursor tetraethoxysilane (TEOS, reagent grade 98%) and hydrogen chloride (HCl, 37%) used as catalyst for the sols, were both obtained from Sigma-Aldrich and used as received. The solvent absolute ethanol was obtained from Fiers. Polyamide 6 (PA 6) pellets were provided by Sigma-Aldrich and used as received. The solvents formic acid (98 v%) and acetic acid (99.8 v%) were supplied by Sigma-Aldrich. The dye methylene blue and the herbicide isoproturon were also provided by Sigma-Aldrich.

2.2. Electrospinning of nanofibers

Polyamide solutions for electrospinning were prepared by dissolving 13 wt% and 16 wt% of PA 6 in a 50:50 v% formic acid:acetic acid solvent mixture. The sols were prepared using the methodology described in previous work [29–31]. The sols were prepared from a mixture of TEOS:ethanol:H_2O:HCl with a molar ratio of respectively 1:2:2:0.01. Firstly, TEOS and ethanol were mixed. Secondly, aqueous HCl was added to the solution under vigorous stirring. After completion of the hydrolysis reactions (exothermic process) the sols were heated under stirring at 80 °C. An Allihn set-up was used allowing the ethanol to reflux during 16 h. Finally, a rotary evaporator was used to evaporate the ethanol until a desired sol viscosity, in between 100 and 200 mPa.s, was reached.

Prior to electrospinning the viscosity of the solutions was measured using a Brookfield viscometer LVDV-II. The electrospinning experiments were executed on a mononozzle set-up with a rotating drum collector. For the electrospinning of the 16 wt% polyamide solutions a tip-to-collector distance (TCD) of 6 cm was used, a flow rate of 2 mL h^{-1} and a voltage in between 21 and 25 kV. The electrospinning of the 13 wt% PA 6 solution was carried out with a TCD of 10 cm, flow rate of 0.5 ml h^{-1} and a voltage in between 20 and 25 kV to obtain a stable process. For the electrospinning of the silicon oxide sols the TCD was fixed at 15 cm, the flow rate at 1 mL h^{-1} and the voltage was adjusted in between 20 and 24 kV to obtain a stable electrospinning process. All the experiments were executed at a relative humidity of 34% RH ± 10% of and a room temperature of 22 °C ± 2 °C. Nanofibrous membranes with a density of ± 10 g/m^2 were obtained.

2.3. Functionalization of nanofibers

Inline (IL) functionalization was carried out by adding varying amounts of TiO_2 nanoparticles to the electrospinning solutions prior to electrospinning. For the lower TiO_2 loadings (0.2 wt%–5 wt%), TiO_2 powder was added after preparation of the electrospinning solutions, the solutions were first stirred with a magnetic stirrer during 0.5 h and next ultrasonicated for 0.5 h, resulting in a homogenous dispersion of the nanoparticles. The electrospinning