

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Photocatalytic Membranes for Efficient Water Treatment

---

Alex T Kuvarega and Bhekie B Mamba

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/62584>

---

## Abstract

Membrane processes which combine the physical separation through filtration and pollutant degradation or antibacterial properties achieved by photocatalysis in a single unit are gaining popularity as wastewater treatment alternatives. There has been considerable progress in the development of photocatalytic membranes through incorporation of metal-oxide photocatalysts to enhance the performance of the membranes. An optimum amount of the photocatalyst should be incorporated into the membrane in order to realise reasonable photocatalytic activity with minimal consequences on water flux. Besides TiO<sub>2</sub> loading, membrane performance is also affected by light intensity and irradiation time. This chapter highlights some of the recent progresses in photocatalytic membrane fabrication, reactor configuration and membrane application in disinfection and pollutant removal from wastewater.

**Keywords:** titanium dioxide, photocatalytic membrane, photodegradation, membrane fouling, water treatment

---

## 1. Introduction

The past few decades have seen membrane-based technologies gaining global popularity largely due to the high separation efficiencies, relatively low costs, small footprint and ease of operation. A membrane is a physical porous barrier between two phases that allows substances to be selectively transported through it. The efficiency and effectiveness of a

membrane as a separation barrier depends on a number of factors, including the type of membrane, the pore structure and sizes, polarity, roughness, hydrophilicity as well as its mechanical properties [1].

In the water sector, membranes have found applications as physical barriers to specific size ranges of water contaminants. They act as filters or selective sieves, removing contaminants that are larger than the membrane pore size and allowing smaller contaminants and water molecules to pass through [2]. However, the use of membranes is without drawbacks. Membrane separation efficiency is compromised mainly due to two effects: concentration polarisation and membrane fouling. Concentration polarisation is a result of increase in concentration of the rejected suspended or dissolved solids near the membrane surface. Membrane fouling is a result of irreversible deposition of suspended or dissolved solids on the external membrane surface or membrane pores compromising the overall performance of the membrane. Once fouled, complex and often expensive cleaning procedures that affect the continuous operation of the membrane filtration process, such as forward and reverse flushing, backwashing, air scouring and back permeation, need to be performed. Although membrane systems may incur higher capital or operational costs than conventional processes (such as evaporation, use of activated carbon, deep-bed filtration, coagulation, sedimentation or chemical treatment), they are generally able to achieve superior quality water, while imposing a smaller footprint at the plant level. Fouling remediation is currently receiving much research attention in an effort to mitigate these challenges through modification of traditional membranes to improve their antifouling properties. Recently, a whole new field of study focused on membrane modification has emerged. One such innovation is the modification of membrane characteristics with nanomaterials to fine-tune performance for specific pollutant types or improve resistance to fouling.

## 2. Classification of membranes

Membrane technology has developed to a point where there are a variety of membranes tailored for specific contaminants and even different membrane configurations and technologies designed for specific industries such as milk production, beer production, desalination, solvent separation and material regeneration. Depending on their pore sizes, which determine their selectivity, membranes can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes [3] (**Table 1**). The so-called nanoporous membranes consist of a film in which molecules are transported through solution-diffusion mechanism. Transport through such membranes is driven by pressure, concentration or potential gradient across the membrane. Nanoporous membranes are typically used for processes such as reverse osmosis (RO) and, more recently, forward osmosis (FO). Nanofiltration (NF) membranes have very small pores (0.1–1 nm). Microporous membranes are used for other pressure-driven processes such as microfiltration (MF) and ultrafiltration (UF). MF membranes can separate particles between 0.1 and 10  $\mu\text{m}$ , whereas UF membranes can remove particles of size range 1–100 nm [1,4].

Filtration mode	Particle capture size	Typical contaminant removed	Typical operating pressure ranges
Microfiltration (MF)	0.1 to $10\ \mu\text{m}$	Suspended solids, bacteria, protozoa	0.1–2 bar
Ultrafiltration (UF)	0.001–0.1 $\mu\text{m}$	Colloids, proteins, polysaccharides, most bacteria, viruses (partially)	1–5 bar (cross-flow) 0.2–0.3 bar (dead-end and submerged)
Nanofiltration (NF)	0.0001–0.001 $\mu\text{m}$	Viruses, natural organic matter, multivalent ions (including water hardness)	5–20 bar
Reverse osmosis (RO)	$<0.0001\ \mu\text{m}$	Almost all impurities (including monovalent ions)	10–100 bar

**Table 1.** Operational characteristics of membranes.

### 3. Photocatalytic membranes

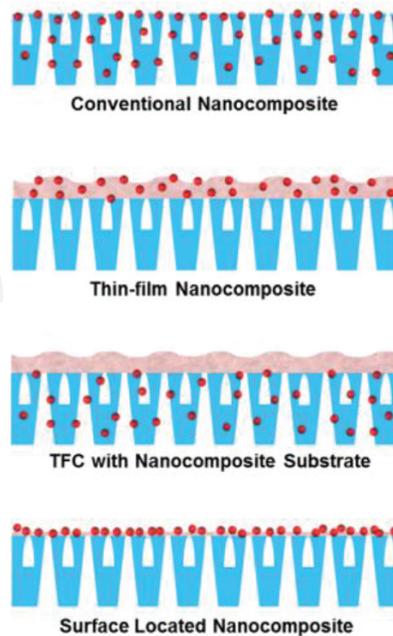
Materials in which one or more phases with nanoscale dimensions are embedded in another matrix phase are called nanocomposites. The motive behind fabricating such materials is to create synergies between the various phase constituents to result in smart materials capable of meeting or even exceeding the intended design expectations [5]. Membranes have been functionalised through incorporation of engineered nanoparticles deposited on their surfaces or embedded into their matrices to result in tailored properties such as capability to bind specific contaminants or catalyse degradation reactions. The resulting mixed matrix membranes (MMMs) play a multifunctional role in water treatment. Variables such as the nanomaterial loading, the matrix material, degree of particle dispersion, size, shape and orientation of the nanoscale phase as well as interactions between the phases have a bearing on the overall properties of the hybrid material. In photocatalytic membranes, nanoscale inorganic photocatalysts are embedded in a membrane matrix to enhance the properties of the resultant polymer.

The first attempts at combining photocatalysis with membrane technology were aimed at achieving the separation and reuse of the photocatalyst nanoparticles from the reactor slurry. However, the approach faced the usual problems of membrane fouling, photocatalyst deactivation and nanoparticle agglomeration. This stirred interest in the development of stand-alone hybrid photocatalysis/filtration water treatment processes exhibiting both photocatalytic and separation efficiency. The advantages of such innovations include the absence of any requirement for post- or pre-treatment stage, an attractive feature for upscaling the technology in membrane wastewater treatment applications [6].

Among various photocatalysts,  $\text{TiO}_2$  has been proven to be an attractive and promising semiconductor catalyst in heterogeneous photocatalysis and in advanced oxidation processes owing to its stability, low cost, availability, non-toxicity, unique photocatalytic efficiency and its promise for applications in water and wastewater treatment [7]. Several methods have recently been developed and optimised for the fabrication of  $\text{TiO}_2$ -based photocatalytic membranes. Among them are dip-coating or spin-coating of porous supports using  $\text{TiO}_2$  precursor sols, filtration of  $\text{TiO}_2$  nanofibers through glass filters followed by hot pressing or liquid phase pressurisation, hydrothermal growth of free-standing  $\text{TiO}_2$  nanowire membranes, anodisation of titanium films sputtered on to stainless steel substrates, embedding  $\text{TiO}_2$  nanoparticles into the polymeric membranes matrix, electrospinning  $\text{TiO}_2$  fibres or flat membranes by recasting, development of  $\text{TiO}_2$  layers with rapid atmospheric plasma spray coating and the fabrication of free-standing and flow-through  $\text{TiO}_2$  nanotube membranes among others [6].

Photocatalytic membranes can be broadly classified into four categories, based on the location of the nanoparticles on the membrane [8] (**Figure 1**):

1. Conventional nanocomposites
2. Thin-film nanocomposites (TFC)
3. Thin film nanocomposite with nanocomposite substrate
4. Surface-located nanocomposites

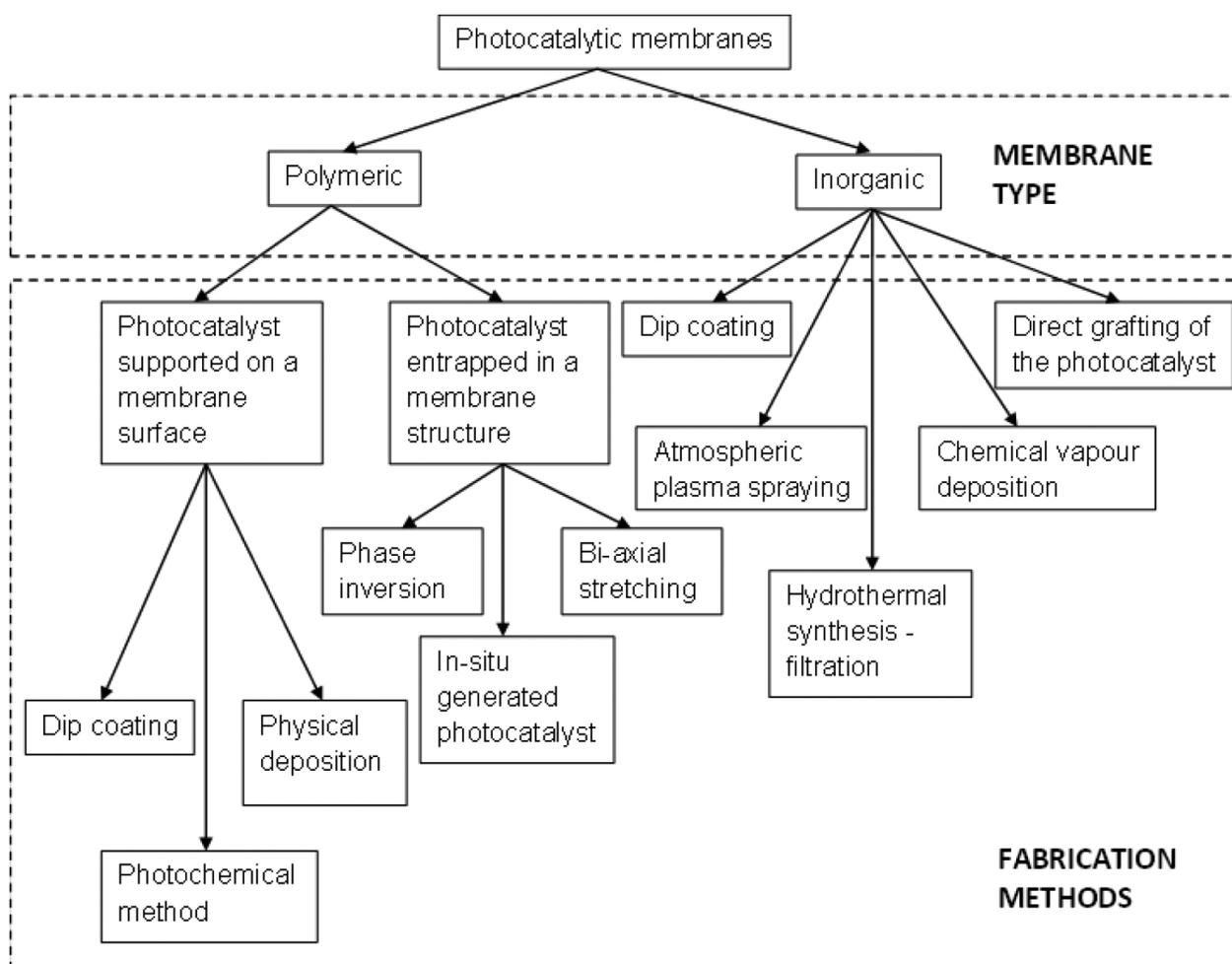


**Figure 1.** Typical type of nanocomposite membranes (The red spheres represent photocatalyst nanoparticles) (Adapted from [8], with permission from Elsevier. Copyright © 2014 Elsevier B.V.).

### 3.1. TiO<sub>2</sub>—polymer membranes

Polymer membranes have gained popularity for use in wastewater treatment and water purification. A number of polymers have successfully been used as supports for photocatalysts, and these include polymers such as polyamide, polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), sulfonated polyethersulfone (SPES), polyurethane (PU), polyethylene terephthalate (PET), polyester, polyacrylonitrile (PAN) and polytetrafluoroethylene (PTFE) [4,9].

The photocatalyst nanoparticles can either be deposited onto the membrane surface or dispersed in the polymer dope solution prior to membrane casting. Several other methods have been proposed and tried for the fabrication of polymeric and ceramic photocatalytic membranes (**Figure 2**). The overall objective is to incorporate the photocatalyst onto the membrane to impart some photocatalytic activity to the membrane.



**Figure 2.** Methods for the preparation of photocatalytic membranes.

### 3.1.1. Surface-located TiO<sub>2</sub> polymer membranes

#### 3.1.1.1. Dip-coating or self-assembly

Surface-located TiO<sub>2</sub> polymer membranes are prepared through dip-coating or self-assembly [10], chemical or photochemical processes based on chemical grafting and photopolymerisation [11] and physical deposition of a TiO<sub>2</sub> layer via ultrafiltration of a TiO<sub>2</sub> suspension through a polymer membrane [12]. In the dip-coating or self-assembly method, a layer of TiO<sub>2</sub> is coated on the surface of a membrane through dipping the membrane into a sol-gel TiO<sub>2</sub> slurry solution, followed by drying and pressing with a compressed gas. The TiO<sub>2</sub> particles tend to self-assemble on the membrane due to the anchoring effect of the functional groups (e.g. carbonyl, sulfone) located on the membrane surface or through hydrogen bonding of the membrane surface groups and TiO<sub>2</sub>. Kim et al. prepared a hybrid thin-film composite (TFC) membrane by self-assembly of TiO<sub>2</sub> nanoparticles through coordination and H-bonding interaction with the COOH functional group of aromatic polyamide thin-film layer. The TFC membrane with self-assembled TiO<sub>2</sub> nanoparticles showed photocatalytic activity towards the destruction of microorganisms. Such membranes can be used to reduce membrane biofouling [13]. In another study, reverse osmosis (RO) membranes composed of aromatic polyamide thin films underneath titanium dioxide (TiO<sub>2</sub>) nanosized particles were fabricated by a self-assembly process. Sol-gel colloidal TiO<sub>2</sub> were self-assembled on a TFC aromatic polyamide membrane containing COOH groups along its surface. The TiO<sub>2</sub> hybrid membrane was examined for its photocatalytic efficiency for the destruction of *Escherichia coli* (*E. coli*) as a model bacterium under UV light illumination. The photocatalytic bactericidal destruction was remarkably higher for the TiO<sub>2</sub> hybrid membrane under UV illumination [14]. Bae and Tak anchored sol-gel synthesised nanosized TiO<sub>2</sub> on commercial polyethersulfone microfiltration (MF) membranes with sulfonic acid (SO<sup>3</sup>-H<sup>+</sup>) groups generated on the membrane surfaces through sulfonation. The fouling mitigation effects of the membrane were investigated over a mixed liquor membrane bioreactor (MBR) system. Results showed that membrane fouling could be considerably reduced by the introduction of TiO<sub>2</sub> nanoparticles on the surface of the membranes. This can be attributed to the higher hydrophilicity of these membranes, which facilitated easy dislodging of adsorbed foulants by shear force than those on neat membranes [15]. One major challenge with the dip-coating technique is the risk of nanoparticle leaching during continuous operation or use of high pressure. The membrane performance thus deteriorates with time.

#### 3.1.1.2. Chemical grafting and photopolymerisation

In this method, appropriate monomers containing the photocatalyst to be immobilised and an initiator are photo-irradiated on a support. In a study by Razmjou et al., commercial TiO<sub>2</sub> nanoparticles were functionalised by aminopropyltriethoxysilane (APTES) to initiate coupling with PES in the dope solution, prior to casting and precipitation, to form hollow fibre membranes. Initial pure water flux was significantly enhanced while there was a small improvement in the fouling performance in comparison with the control. The modified hollow fibre membrane showed increased glass transition temperature, membrane porosity and pore

size, stiffness and hydrophilicity, whereas tensile strength and elongation at break decreased [16].

In a chemical grafting and photopolymerisation study,  $\text{TiO}_2$  was added to a suitable acrylic acid monomer and sonicated for about 20 min to facilitate the interaction between  $\text{TiO}_2$  and acrylic acid. Ethylene glycol was then added as a cross-linker, and potassium persulfate (1 wt.%) as an initiator. The PVDF support membrane was then dipped in the polymerisation solution for 2 min and placed on a glass plate. The grafted membranes were irradiated with UV light (160 W) for 15 min. The covalent attachment of  $\text{TiO}_2$  to PAA network in the membrane composite resulted in improved fouling resistance due to the hydrophilic functional groups of PAA and the photocatalytic effect of  $\text{TiO}_2$  that reduced the hydrophobic adsorption between the whey protein and the modified membrane surface [17].

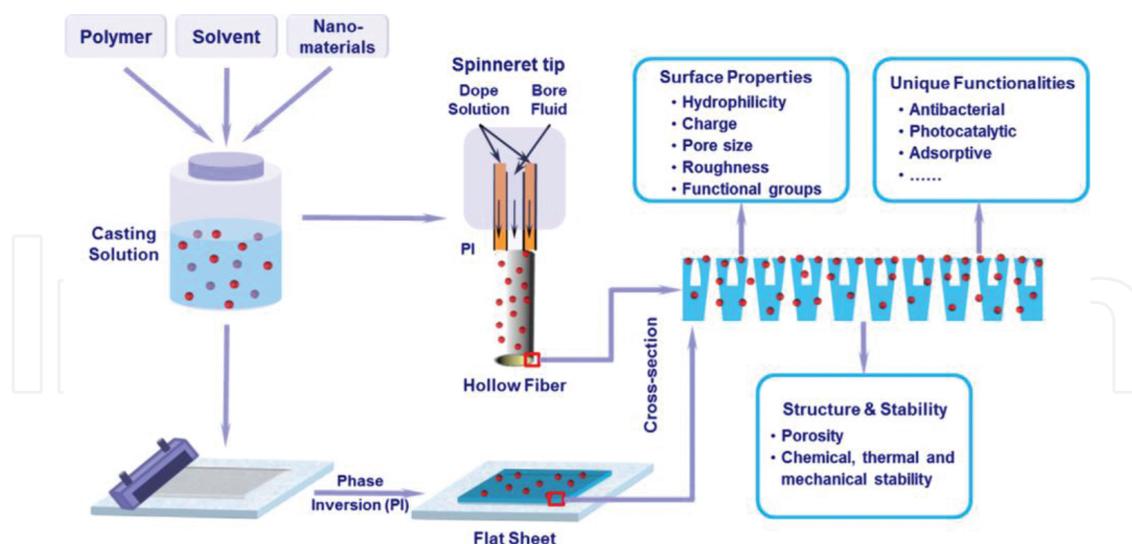
### 3.1.1.3. Physical deposition

In this method, the photocatalyst is physically deposited on the membrane surface through pressure-driven filtration of the photocatalyst suspension slurry. A photocatalyst cake builds on the surface of the membrane, the thickness of which can be controlled by varying the filtration time and operational pressure [18]. Bai et al. synthesised  $\text{TiO}_2$  nanothorn spheres and assembled them on a piece of cellulose acetate polymer membrane through compression on a dead-end filtration set-up. The resulting  $\text{TiO}_2$  nanothorn membrane was reported to exhibit a hierarchical porous structure, which gave a high water flux and a multifunctional  $\text{TiO}_2$  surface for mitigation of membrane fouling [12].

### 3.1.2. $\text{TiO}_2$ -entrapped polymer membranes

#### 3.1.2.1. Phase inversion

Phase inversion is by far the most common and popular method for synthesising nanoparticle-entrapped membranes. In this method, the preformed photocatalyst is added to the polymer dope solution to form a homogenous solution. The solution is then cast on a glass plate and immersed in a coagulation bath to effect gelation. In the dry method, the solvent is allowed to evaporate until gelation is complete after casting [8]. Phase inversion membranes may be fabricated in different forms, such as hollow fibres or flat sheets, which can be incorporated modules designed to produce optimal hydrodynamic conditions for separation (**Figure 3**).  $\text{TiO}_2$ -embedded membranes have been reported to show improved membrane properties such as porosity, wettability, permeability and antifouling propensity. Application of photocatalytic membranes requires irradiation of the membrane to activate the photocatalyst. However, sulfone group containing membranes (PES and PSf) are generally sensitive to UV radiation, and irradiation may lead to destruction of some membrane bonds. The least affected membranes are PTFE and PVDF [19].



**Figure 3.** Fabrication of conventional nanocomposite membranes through the PI process and the main effects of nano-fillers on final products. (Adapted from [8], with permission from Elsevier. Copyright © 2014 Elsevier B.V.).

Although embedding nanoparticles onto membranes eliminate the need for post-treatment removal of the nanoparticles, one major limitation of immobilising nanoparticles onto membrane supports is the reduction in the available surface area of the nanoparticles due to coverage by the polymer phase material.

### 3.1.2.2. Biaxial stretching

Biaxial stretching is a physical method where membranes are stretched to modify their properties in an effort to improve overall membrane performance. This modification induces significant and permanent membrane pore deformation, which may result in improved porosity [20]. In a typical study, catalytic membranes were fabricated via biaxial stretching of a polytetrafluoroethylene (PTFE) extrusion containing 2 wt.% of anatase  $\text{TiO}_2$ . The catalyst particles were uniformly distributed throughout the membrane. The photocatalytic membrane could degrade organic solutes in ultra-pure water [21].

### 3.1.2.3. In-situ generated photocatalysts

The formation of mixed matrix membranes through in-situ generation of the desired nanomaterials is a relatively new innovation in membrane technology. The main advantages of in-situ generation of nanoparticles include control over nanoparticle–membrane matrix compatibility, nanomaterial loading capacity, water flux as well as selectivity [22].

Luisa Di Vona et al. successfully synthesised a sulfonated poly(ether ether ketone) (SPEEK) nanocomposite membrane via an in situ mixed sol–gel process in which titanium butoxide/2,4-pentanedione in DMAc was added to a SPEEK solution and the solvents allowed to evaporate at  $120^\circ\text{C}$ . The resulting composite membranes were flexible and transparent, and showed improved mechanical and thermal properties as well as hydrolytic stability [23]. In another study, a mixed matrix membrane was fabricated through in situ polymerisation of

titanium isopropoxide in polyvinyl acetate, PVAc. The titanium alkoxide can cross-link with PVAc through a transesterification reaction. The strong chemical interaction prevents phase separation and improves TiO<sub>2</sub> dispersion within the PVAc matrix. One major drawback is that the Ti-based clusters contain some residual isopropyl groups and the TiO<sub>2</sub> phase may show limited crystallinity [24].

### 3.2. TiO<sub>2</sub>-based ceramic membranes

Ceramic membranes are currently receiving significant attention as candidates for water decontamination because of their various properties, including sufficiently high mechanical strength, thermal stability, high flux, lower life cycle cost and resistance to corrosive environments. Depending on their pore diameters, they can be classified as MF, UF, NF, RO, pervaporation (PV), gas separation (GS) or ceramic membrane reactors (CMR). Oxides such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub> and combinations thereof are some of the common ceramic membrane fabrication materials [25].

Ceramic membranes are fabricated through methods such as dip-coating, where a photocatalyst is deposited on a porous ceramic support (e.g. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/ZrO<sub>2</sub>, SiN/SiC, Al<sub>2</sub>O<sub>3</sub>/SiC), and hydrothermal synthesis followed by filtration and calcination, where a suspension of hydrothermally synthesised TiO<sub>2</sub> is filtered through a glass fibre filter, dried and calcined at high temperature. Another method is grafting of TiO<sub>2</sub> onto ceramic membranes, where TiO<sub>2</sub> nanotubes are grafted onto channels of ceramic membranes such as alumina (Al<sub>2</sub>O<sub>3</sub>) [26]. Other methods such as chemical vapour deposition (CVD) and atmospheric plasma spraying (APS) have also been used to fabricate ceramic membranes [27,28].

### 3.3. Polymeric versus ceramic photocatalytic membranes

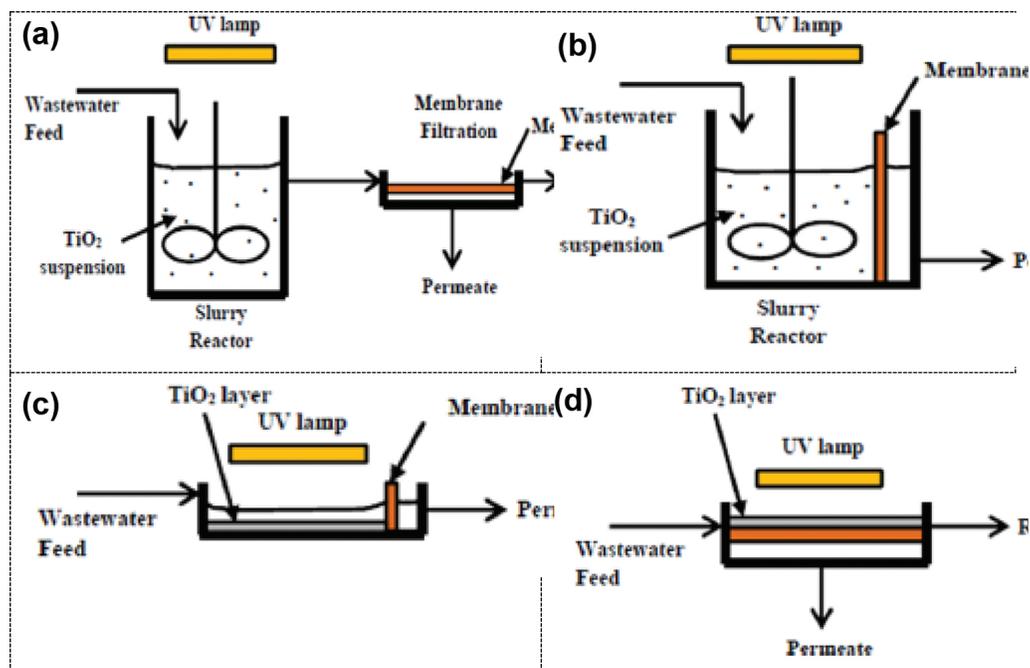
Ceramic membranes generally have many advantages compared to polymeric membranes from an application point of view, mainly because of their superior thermal properties and resistance to corrosion by harsh chemicals. With polymeric membranes, there are some risks associated with membrane degradation under extreme chemical conditions. Ceramic membranes are also less prone to membrane fouling because of their hydrophilic surfaces. Ceramic membranes generally have relatively uniform pore structures and thus significantly higher flux and lower membrane resistance compared to polymeric membranes. Unlike polymeric membranes which are soft and rather difficult to analyse by most physicochemical characterisation techniques, the composition of ceramic membranes can be well-characterised. Ceramic membranes have a lower membrane resistance and therefore require a lower pressure to produce the same volume of water as the polymeric ones. They also have a longer lifespan. However, the capital costs are huge [10].

Anchoring photocatalytic nanoparticles on commercially available ceramic membranes requires appropriate anchor sites on the membrane in order to form bonds between the nanoparticles and the ceramic support. This is currently a big hindrance to ceramic membrane modification attempts.

#### 4. Photocatalytic membrane reactor configurations

A number of engineering designs and configurations have been proposed for possible scaling up of the photocatalytic membrane technology. The photocatalytic membrane reactors can be classified into four different configurations based on the stage at which the membrane will be used in the water treatment train (**Figure 4**):

- Slurry photocatalytic reactor followed by a membrane filtration unit,
- Ceramic or polymeric membrane submerged in a slurry photocatalytic reactor,
- Membrane placed inside a photocatalyst-coated ( $\text{TiO}_2$ ) photoreactor,
- Photocatalytic membranes (pure  $\text{TiO}_2$  or  $\text{TiO}_2$ -mixed matrix membranes).



**Figure 4.** Photocatalytic membrane reactor configurations. (a) Slurry reactor followed by a membrane filtration unit; (b) Submerged membrane in a slurry reactor; (c) Submerged membrane in  $\text{TiO}_2$ -coated reactor; (d) Photocatalytic membrane. (Adapted from [9], with permission from Elsevier. Copyright © 2014 Elsevier B.V.).

While a number of these configurations have been put to test, the photocatalytic membrane is currently receiving immense research focus because of its potential advantages over the other configurations. Some of its advantages include the duality of physical separation during membrane filtration, and degradation of organics and bacteria, all achieved in a single unit. Generally, photocatalytic membranes tend to outperform conventional membranes in terms of reducing membrane fouling and improving permeate quality [6,18].

Despite the potential advantages using these different reactor configurations, the research on a combined use of photocatalysis and membranes is still not sufficiently developed.

## 5. Application of TiO<sub>2</sub> photocatalytic membranes

Photocatalytic membranes have evolved as promising innovations for providing sustainable quality water to end users. The use of multimembrane systems or coupling membrane separation with other biological, chemical or physical treatments is envisaged to have a huge positive impact on the provision of quality water at low cost and lower energy consumption. TiO<sub>2</sub>-based catalytic membranes have found applications in a wide range of wastewater and water treatment applications.

### 5.1. Disinfection

Membrane biofouling is the deposition of microorganisms and microbial products on the surface of a membrane. Incorporation of TiO<sub>2</sub> into polymeric or ceramic membranes has been reported to mitigate membrane biofouling. In a study on self-assembly of TiO<sub>2</sub> nanoparticles on hybrid thin-film composite (TFC) membrane, dramatic photoactivity for bactericidal degradation of *E. coli* under UV light illumination was observed [13]. Ma et al. prepared Ag-TiO<sub>2</sub>/hydroxyapatite bioceramic composite membrane for membrane separation and photocatalytic bacterial inactivation (*E. coli*) using a sol-gel method followed by calcination. *E. coli* inactivation was evaluated under UV illumination, and a higher inactivation performance was achieved compared to dark conditions. The permeate flux decline pattern of membrane however remained the same under UV irradiation and in the dark [29]. Liu et al. deposited Ag nanoparticles on electrospun TiO<sub>2</sub> nanofibers to form a membrane. The group reported irreversible bacterial cell damage under UV light irradiation. A 99.9% bacteria inactivation and 80.0% dye degradation under solar irradiation was reported within 30 min [30]. In another application study, Damodar et al. embedded TiO<sub>2</sub> on PVDF membranes through the phase inversion method and tested the membrane for its antibacterial property by using *E. coli*, photocatalytic activity using Reactive Black 5 (RB5) dye and antifouling properties using 1% BSA solution. The membrane showed enhanced flux and permeability properties. Almost 100% of *E. coli* was degraded by 4% TiO<sub>2</sub>/PVDF membrane after 1 min of UV irradiation. A faster RB5 colour removal rate was also reported, while the self-cleaning study showed a lower fouling resistance for the 2% TiO<sub>2</sub>/PVDF membrane [31]. Rahimpour et al. loaded 4% TiO<sub>2</sub> on PVDF/Sulfonated PES blend membrane through a phase inversion method and observed dramatic antibacterial (*E. coli*) effect under 1 h of UV irradiation, which the inhibition rings on the composite membrane as evidence of the antibacterial effect against *E. coli*. The photocatalytic bactericidal effect was attributed to the presence of reactive oxygen species like O<sub>2</sub> radicals, H<sub>2</sub>O<sub>2</sub> and OH radicals generated by the entrapped TiO<sub>2</sub> upon UV illumination [32].

### 5.2. Removal of pollutants

By and large, removal of pollutants in water is the widely used application of photocatalytic membranes. A number of studies have recently emerged on batch and reactor scale application of photocatalytic membranes for fouling mitigation through photodegradation of foulants. A PVDF/TiO<sub>2</sub> mixed matrix UF membrane was reported to show enhanced performance for the removal of methylene blue (MB) due to the extra adsorption sites provided by the

embedded TiO<sub>2</sub> nanoparticles [33]. In a similar study, Hua et al. fabricated a PVDF membrane with self-assembled TiO<sub>2</sub> nanoparticles, and the permeability and antifouling ability of self-assembled membranes were significantly improved [34]. A multifunctional polyurethane (PU)/TiO<sub>2</sub>/fly ash composite membrane fabricated through electrospinning showed enhanced adsorption of heavy metals (Pb, Hg), enhanced MB dye removal, superior water flux and antibacterial properties attributed to the photocatalytic properties of TiO<sub>2</sub> as well as the adsorptive property of fly ash [35]. Bae and Tak observed a positive effect of the presence of dip-coated and entrapped TiO<sub>2</sub> on membrane antifouling in a membrane bioreactor (MBR) [36]. Cao et al. observed remarkable improvement in the antifouling property of PVDF membrane with different sizes of nanosized TiO<sub>2</sub> particles, with smaller particles having greater effect than the larger ones [37]. Kim et al. self-assembled TiO<sub>2</sub> nanoparticles on carboxylic acid groups on the surface of a thin-film composite (TFC) polymer membrane. The membrane was observed to mitigate biofouling through photodegradation effect under UV radiation [13].

A ceramic TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composite membrane was prepared using a sol-gel technique and applied in a filtration/photodegradation membrane reactor under UV radiation. UV irradiation enhanced the wettability of the ceramic membrane, and a stable water flux was rapidly archived. 25% of Acid Orange dye was degraded within several milliseconds. The membrane could easily be cleaned by irradiating the membrane surface under static conditions [38]. Syafei et al. observed greater flux decline with TiO<sub>2</sub>-coated alumina/titania/zirconia (ATZ) ultrafiltration ceramic membrane disk under UV irradiation than with uncoated membrane in the treatment of natural organic matter (NOM). It was postulated that UV irradiation alters the molecular weight distribution of humic materials to below 1 kDa, which facilitates their attachment to TiO<sub>2</sub> nanoparticles [39]. In a similar approach, TiO<sub>2</sub> nanoparticles were coated on Al<sub>2</sub>O<sub>3</sub> nanoparticles through solid-state sintering method. The resulting membrane was reported to show enhanced photocatalytic properties and reduced membrane fouling in oil emulsion wastewater treatment [40]. The effect of UV irradiation on membrane performance was evaluated on TiO<sub>2</sub>-entrapped and self-assembled PES membranes. The TiO<sub>2</sub>-coated membranes showed a uniform distribution of the TiO<sub>2</sub> nanoparticles on the membrane surface. The non-irradiated membranes showed a flux decline while the irradiated membranes exhibited higher fluxes and superior antifouling properties. It was then concluded that dip-coating TiO<sub>2</sub> on PES membrane surface is a superior technique to minimise membrane fouling than entrapping the TiO<sub>2</sub> [41]. Similar observations were reported by other researchers on TiO<sub>2</sub>/PES, TiO<sub>2</sub>/poly(styrene-alt-maleic anhydride)/poly(vinylidene fluoride) (TiO<sub>2</sub>/SMA/PVDF) and TiO<sub>2</sub>/PES/polyimide (PI) composite membranes, using polyethylene glycol-5000 [42] and Bovine serum albumin (BSA) [34,43]. In a study by Lin et al., it was concluded that the effectiveness of photodegradation of 1,2-dichlorobenzene was higher with TiO<sub>2</sub> immobilised on low-density polyethylene (LDPE) support than on quartz support using four UV lamps of 15 W each [44].

Inasmuch as progress has been realised in the application of photocatalytic membranes for water decontamination, further research is needed to investigate the combined effects of water

chemistry, nature of nanoparticles, loading capacity and the photocatalyst incorporation conditions on membrane performance.

## 6. Conclusions and perspectives

As engineering technology innovation continues to grow, new opportunities and prospects to solve the ever-increasing environmental challenges continue to emerge. Innovative techniques for the integration of photocatalyst in both polymeric and ceramic membranes need to be continuously developed in order to open new insights into the development of functional membranes capable of mitigating fouling with minimal consequences on water flux. Polymer and ceramic membranes have both been used as TiO<sub>2</sub> supports, though the stability of polymeric membranes under UV irradiation still requires further investigation. Commercialisation of photocatalytic membranes will depend on the design of the membrane reactors as well as optimisation of the radiant flux on the membrane surface during the short time frame that the polluted water filters through the membrane. The use of solar light as an energy source instead of UV light could reduce the cost of the filtration process. This requires band-tuning of the TiO<sub>2</sub> through doping with non-metals or metals to shift the absorption edge to the visible region. Currently, the membrane fouling mechanisms are not fully understood. Another challenge is possible leaching of the entrapped photocatalyst particles into the permeate solution during the filtration process. Given the present knowledge gaps regarding possible health and ecological hazards of nanoparticles' aquatic environment, caution should be exercised to avoid discharge of the particles into the water stream.

## Author details

Alex T Kuvarega\* and Bhekie B Mamba

\*Address all correspondence to: [kuvarat@unisa.ac.za](mailto:kuvarat@unisa.ac.za)

University of South Africa, Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, Florida Science Campus, Johannesburg, South Africa

## References

- [1] Ahmed FE, Lalia BS, Hashaikeh R. A review on electrospinning for membrane fabrication: challenges and applications. *Desalination*. 2015; 356: 15–30. DOI:10.1016/j.desal.2014.09.033
- [2] Meng S, Greenlee LF, Shen YR, Wang EG. Basic science of water: challenges and current status, towards a molecular picture. *Nano Res*. DOI: 10.1007/s12274-015-0822-y

- [3] UnionEuropean. Membrane technologies for water applications: highlights from a selection of European research projects. European Union. 2010; DOI: 10.2777/25163
- [4] Bet-moushoul E, Mansourpanah Y, Farhadi KH, Tabatabaei M. TiO<sub>2</sub> nanocomposite based polymeric membranes: a review on performance improvement for various applications in chemical engineering processes. *Chem Eng J*. 2016; 283: 29–46. DOI: 10.1016/j.cej.2015.06.124
- [5] Sealy C. Cleaning up water on the nanoscale. *Nano Today*. 2013; 8: 337–338. DOI: 10.1016/j.nantod.2013.06.004
- [6] Romanos GE, Athanasekou CP, Likodimos V, Aloupogiannis P, Falaras P. Hybrid ultrafiltration/photocatalytic membranes for efficient water treatment. *Ind Eng Chem Res*. 2013; 52: 13938–13947. DOI: 10.1021/ie303475b
- [7] Shi F, Ma Y, Ma J, Wang P, Sun W. Preparation and characterization of PVDF/TiO<sub>2</sub> hybrid membranes with different dosage of nano-TiO<sub>2</sub>. *J Membr Sci*. 2012; 389: 522–531. DOI: 10.1016/j.memsci.2011.11.022
- [8] Yin J, Deng B. Polymer-matrix nanocomposite membranes for water treatment. *J Membr Sci*. 2015; 479: 256–275. DOI: 10.1016/j.memsci.2014.11.019
- [9] Leong S, Razmjou A, Wang K, Hapgood K, Zhang X, Wang H. TiO<sub>2</sub> based photocatalytic membranes: a review. *J Membr Sci*. 2014; 472: 167–184. DOI: 10.1016/j.memsci.2014.08.016
- [10] Kim J, Van der Bruggen B. The use of nanoparticles in polymeric and ceramic membrane structures: review. *Environ. Poll*. 2010; 158: 2335–2349. DOI: 10.1016/j.envpol.2010.03.024
- [11] Barni B, Cavicchioli A, Riva E, Zanoni L, Bignoli F, Bellobono IR, Gianturco F, De Giorgi A, Muntau H, Montanarella L, Facchetti S, Castellano L. Pilot-plant-scale photodegradation of phenol in aqueous solution by photocatalytic membranes immobilizing titanium dioxide (PHOTOPERM® process). *Chemosphere*. 1995; 30: 1861–1874. DOI: 10.1016/0045-6535(95)00067-I
- [12] Bai H, Liu Z, Sun DD. Hierarchically multifunctional TiO<sub>2</sub> nano-thorn membrane for water purification. *Chem Commun*. 2010; 46: 6542–6544. DOI: 10.1039/C0CC01143F
- [13] Kim SH, Kwak SY, Sohn BH, Park TH. Design of TiO<sub>2</sub> nanoparticle self-assembled aromatic polyamide thin-film-composition (TFC) membrane as an approach to solve biofouling problem. *J Membr Sci*. 2003; 211: 157–165. DOI: 10.1016/S0376-7388(02)00418-0
- [14] Kwak SY, Kim SH. Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling 1. Preparation and characterization of TiO<sub>2</sub> nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane. *Environ. Sci Technol*. 2001; 35: 2388–2394. DOI: 10.1021/es0017099

- [15] Bae TH, Tak TM. Preparation of the TiO<sub>2</sub> self-assembled polymeric nanocomposite membranes and examination of their fouling mitigation effects in a membrane bioreactor system. *J Membr Sci.* 2005; 266: 1–5. DOI: 10.1016/j.memsci.2005.08.014
- [16] Razmjou A, Holmes ARL, Li H, Mansouri J, Chen V. The effect of modified Ti O<sub>2</sub> nanoparticles on polyethersulfone ultrafiltration hollow fiber membranes. *Desalination.* 2012; 287: 271–280. DOI: 10.1016/j.desal.2011.11.025
- [17] Madaeni SS, Zinadini S, Vatanpour V. A new approach to improve antifouling property of PVDF membrane using in situ polymerization of PAA functionalized TiO<sub>2</sub> nanoparticles. *J Membr Sci.* 2011; 380: 155–162. DOI: 10.1016/j.memsci.2011.07.006
- [18] Molinari R, Palmisano L, Drioli E, Schiavello M. Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification. *J Membr Sci.* 2002; 206: 399–415. DOI: 10.1016/S0376-7388(01)00785-2
- [19] Chin SS, Chiang K, Fane AG. The stability of polymeric membranes in a TiO<sub>2</sub> photocatalysis process. *J Membr Sci.* 2006; 275: 202–211. DOI: 10.1016/j.memsci.2005.09.033
- [20] Morehouse JA, Taylor DL, Lloyd DR, Lawler DF, Freeman BD, Worrel LS. The effect of uni-axial stretching on the roughness of microfiltration membranes. *J Membr Sci.* 2006; 280: 712–719. DOI: 10.1016/j.memsci.2006.02.027
- [21] Morris RE, Krikanova E, Shadman F. Photocatalytic membrane for removal of organic contaminants during ultra-purification of water. *Clean Technol Environ Policy.* 2004; 6: 96–104. DOI: 10.1007/s10098-003-0198-7
- [22] Kotte MR, Choi M, Diallo MS. A facile route to the preparation of mixed matrix polyvinylidene fluoride membranes with in-situ generated polyethyleneimine particles. *J Membr Sci.* 2014; 450: 93–102. DOI: 10.1016/j.memsci.2013.08.025
- [23] Luisa Di Vona M, Ahmed Z, Bellitto S, Lenci A, Traversa E, Licocchia S. SPEEK-TiO<sub>2</sub> nanocomposite hybrid proton conductive membranes via in situ mixed sol–gel process. *J Membr Sci.* 2007; 296: 156–161. DOI: 10.1016/j.memsci.2007.03.037
- [24] Lantelme B, Dumon M, Mai C, Pascault JP. In situ polymerization of titanium alkoxides in polyvinylacetate. *J Non-Cryst Solids.* 1996; 194: 63–71. DOI: 10.1016/0022-3093(95)00498-X
- [25] Xing W, Fan Y, Jin W. Application of ceramic membranes in the treatment of water. In Duke M, Zhao D, Semiat R (eds), *Functional Nanostructured Materials and Membranes for Water Treatment.* Wiley-VCH Verlag GmbH & Co. KGaA, 2013. ISBN: 978-3-527-32987-8
- [26] Basile A. (Ed). *Handbook of membrane reactors: Volume 2 Reactor types and industrial applications.* Woodhead Publishing, Cambridge, 2013. ISBN: 978-0-85709-415-5
- [27] Athanasekou CP, Romanos GE, Katsaros FK, Kordatosb K, Likodimos V, Falaras P. Very efficient composite titania membranes in hybrid ultrafiltration/photocatalysis

- water treatment processes. *J Membr Sci.* 2012; 392–393: 192–203. DOI: 10.1016/j.memsci.2011.12.028
- [28] Lin Y-F, Tung K-L, Tzeng Y-S, Chen J-H, Chang K-S, Rapid atmospheric plasma spray coating preparation and photocatalytic activity of macroporous titania nanocrystalline membranes. *J Membr Sci.* 2012; 389: 83–90. DOI: 10.1016/j.memsci.2011.10.018
- [29] Ma N, Fan X, Quan X, Zhang Y. Ag-TiO<sub>2</sub>/HAP/Al<sub>2</sub>O<sub>3</sub> bioceramic composite membrane: fabrication, characterization and bactericidal activity. *J Membr Sci.* 2009; 336: 109–117. DOI: 10.1016/j.memsci.2009.03.018
- [30] Liu L, Liu Z, Bai H, Sun DD. Concurrent filtration and solar photocatalytic disinfection/degradation using high-performance Ag/TiO<sub>2</sub> nanofiber membrane. *Water Res.* 2012; 46: 1101–1112. DOI: 10.1016/j.watres.2011.12.009
- [31] Damodar RA, You SJ, Chou HH. Study the self-cleaning, antibacterial and photocatalytic properties of TiO<sub>2</sub> entrapped PVDF membranes. *J Hazard Mater.* 2009; 172: 1321–1328. DOI: 10.1016/j.jhazmat.2009.07.139
- [32] Rahimpour A, Jahanshahi M, Rajaeian B, Rahimnejad M. TiO<sub>2</sub> entrapped nanocomposite PVDF/SPES membranes: preparation, characterization, antifouling and antibacterial properties. *Desalination.* 2011; 278: 343–353. DOI: 10.1016/j.desal.2011.05.04
- [33] Ngang HP, Ooi BS, Ahmad AL, Lai SO. Preparation of PVDF-TiO<sub>2</sub> mixed-matrix membrane and its evaluation on dye adsorption and UV-cleaning properties. *Chem Eng J.* 2012; 197: 359–367. DOI: 10.1016/j.cej.2012.05.050
- [34] Li JH, Xu YY, Zhu LP, Wang JH, Du CH. Fabrication and characterization of a novel TiO<sub>2</sub> nanoparticle self-assembly membrane with improved fouling resistance. *J Membr Sci.* 2009; 326: 659–666. DOI: 10.1016/j.memsci.2008.10.049
- [35] Kim HJ, Pant HR, Kim JH, Choi NJ, Kim CS. Fabrication of multifunctional TiO<sub>2</sub>-fly ash/polyurethane nanocomposite membrane via electrospinning. *Ceram Int.* 2014; 40: 3023–3029. DOI: 10.1016/j.ceramint.2013.10.005
- [36] Bae TH, Tak TM. Effect of TiO<sub>2</sub> nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. *J Membr Sci.* 2005; 249: 1–8. DOI: 10.1016/j.memsci.2004.09.008
- [37] Cao XH, Ma J, Shi XH, Ren ZJ. Effect of TiO<sub>2</sub> nanoparticle size on the performance of PVDF membrane. *Appl Surf Sci.* 2006; 253: 2003–2010. DOI: 10.1016/j.apsusc.2006.03.090
- [38] Mendret J, Hatat-Fraile M, Rivallin M, Brosillon S. Hydrophilic composite membranes for simultaneous separation and photocatalytic degradation of organic pollutants. *Sep. Purif Technol.* 2013; 111: 9–19. DOI: 10.1016/j.seppur.2013.03.030

- [39] Syafei AD, Lin CF, Wu CF. Removal of natural organic matter by ultrafiltration with TiO<sub>2</sub>-coated membrane under UV irradiation. *J Colloid Interface Sci.* 2008; 323: 112–119. DOI: 10.1016/j.jcis.2008.03.037
- [40] Qi Z, Fan Y, Xu N. Effect of the surface properties on filtration performance of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> composite membrane. *Sep Purif Technol.* 2009; 66: 306–312. DOI: 10.1016/j.seppur.2008.12.010
- [41] Rahimpour A, Madaeni SS, Taheri AH, Mansourpanah Y. Coupling TiO<sub>2</sub> nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes. *J Membr Sci.* 2008; 313: 158–169. DOI: 10.1016/j.memsci.2007.12.075
- [42] Luo M-J, Zhao J-Q, Tang W, Pu CS. Hydrophilic modification of poly (ether sulfone) ultrafiltration membrane surface by self-assembly of TiO<sub>2</sub> nanoparticles. *Appl Surf Sci.* 2005; 249: 76–84. DOI: 10.1016/j.apsusc.2004.11.054
- [43] Mansourpanah Y, Madaeni SS, Rahimpour A, Farhadian A, Taheri AH. Formation of appropriate sites on nanofiltration membrane surface for binding TiO<sub>2</sub> photo-catalyst: performance, characterization and fouling-resistant capability. *J Membr Sci.* 2009; 330: 297–306. DOI: 10.1016/j.memsci.2009.01.001
- [44] Lin HF, Ravikrishna R, Valsaraj KT. Reusable adsorbents for dilute solution separation 6. Batch and continuous reactors for the adsorption and degradation of 1,2-dichlorobenzene from dilute wastewater streams using titania as a photocatalyst. *Sep Purif Technol.* 2002; 28: 87–102. DOI: 10.1016/S1383-5866(02)00017-5

