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High performance PVDF-TiO_2 membranes for water treatment

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HIGHLIGHTS

- TiO_2 nanoparticles improve membrane structure and permeability.
- TiO_2 addition and UV irradiation limit pure water flux decline and enable high fluxes.
- UV cleaning of fouled composite membrane enables total recovery of performances.

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ABSTRACT

In order to obtain low-fouling membranes, TiO_2 nanoparticles were entrapped in PVDF membranes prepared by the NIPS wet-process. Typical asymmetric membrane structure was obtained. Membrane structure, hydrophilic properties and permeability were improved in comparison with PVDF neat membrane when increasing TiO_2 concentration up to an optimum concentration of 25%wt. Maximum permeate flux of 150 L/h/m^2 was successfully obtained. For TiO_2 content beyond 25%wt, TiO_2 particles agglomeration prevents the improvement of hydrophilic properties and permeability. Under UV irradiation, phenomena of super-hydrophilicity due to presence of TiO_2 in the composite membrane permits to suppress pure water permeate flux decline and reach higher fluxes. Fouled composite membranes after BSA filtration were successfully cleaned using water and UV irradiation. Permeate flux was totally recovered after this cleaning.

1. Introduction

If membrane technologies have emerged as advanced separation processes in water treatment over the last decades as they can be operated with minimal chemical, low energy, easy automation and optimal quality of treated water, membrane fouling remains today as the main limitation of the process. In particular, the very little size of organic pollutants causes rapid and severe internal and surface fouling which results in a strong decrease of membrane permeate flux and separation performances. PVDF is a common ultrafiltration and microfiltration membrane material because of its good mechanical properties, thermal stability and chemical resistance but its hydrophobicity induces a high tendency of these membranes to fouling.

Recent studies have investigated the possibility of coupling membrane filtration and a photocatalyst, because of interesting property of these membranes to mitigate membrane fouling (Cao et al., 2006; Mozia 2010). Among photocatalysts, anatase-type titanium dioxide (TiO_2) presents several advantages: an important photocatalysis activity under UV irradiation, a high stability, a low environmental impact, a low cost and an important availability (Mills A. and Lee 2002). Two main approaches associate membranes and catalytic TiO_2 nanoparticles to form composite membranes are possible: blending nanoparticles in the membrane matrix or coating the nanoparticles on the surface of the membrane (Mozia 2010). Nonetheless, when using this second configuration, a release of catalyst nanoparticles could be observed (Bian et al., 2011; Alaoui et al., 2009; Reijnders 2009) due to the difficulty to immobilize them on membranes without using binding mediums to form covalent bonds between nanoparticles and membrane. Despite many attempts made to find appropriate organic binders, the residual release of nanoparticles from the membrane may still raise questions about the properties of the membrane during long filtration period. The first configuration where TiO_2 nanoparticles are entrapped inside the membrane matrix presents thus practical advantages: (i) the particles release should be limited, (ii) all advantages of membrane process such as easy scale-up and modularity are maintained. PVDF is a good candidate for such coupling because of its high resistance to UV degradation and photocatalytic activity.

Entrapped TiO_2 composite membranes can be prepared by the induced phase separation process (usually Non-solvent Induced Phase Separation wet-process, or NIPS wet-process) (Damodar et al., 2009),

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where nano-sized TiO_2 particles are added to the polymer-solvent solution, which is cast on an appropriate plate and then immersed in a coagulation bath of non-solvent (usually water) to induce phase separation. Different studies from literature have shown that entrapped TiO_2 / polymer membranes prepared by NIPS process could present higher permeabilities and self-cleaning capacities than neat polymer membranes.

As observed on Table 1, literature review shows that TiO_2 can have a beneficial effect on membrane properties (hydrophilicity for example) and performances (permeability for example). However, some contradictory results can be observed and the exact influence of the operating parameters of preparation on composite membrane properties may still be unclear. Some authors found a great improvement of membrane surface hydrophilicy with TiO_2 (Yang et al., 2006; Yu et al., 2009; Hamid et al., 2011; Yuliwati and Ismail 2011) while others observed only a slight increase (Alaoui et al., 2009; Damodar et al., 2009; Bae and Tak 2005; Oh et al., 2009). Few authors also pointed out a decrease of this hydrophilicity for TiO_2 concentration higher than 6–10 wt% TiO_2/PVDF (Damodar et al., 2009; Yu et al., 2009; Yuliwati and Ismail 2011). Same trends and contradictory results are observed concerning membrane permeability. Although authors seem to agree about the existence of an optimum TiO_2 concentration for the improvement of permeability, this value can change dramatically according to the studies: 3-4 wt% TiO_2/PVDF for Song et al. and Wu et al. Song et al., (2012; Wu et al., 2008); 6–11 wt% TiO_2/PVDF for Yang et al., Yu et al. and Yulliwati et al. Yang et al., (2006; Yu et al., 2009; Yuliwati and Ismail 2011); or 24–25 wt% TiO_2/PVDF for Li et al. Li et al., (2009).

Compared to neat polymer (PVDF, PES) membrane under UV light, a photocatalytic property due to the presence of TiO_2 was put in evidence despite this photocatalytic property was not enhanced significantly by an increase of TiO_2 content from 0 to 20 wt% TiO_2/PVDF. Ngang et al. observed a great improvement of self-cleaning capacity of the membrane during filtration of dye solution (Ngang et al., 2012). Song et al. did not observe any clear effect of TiO_2 on pure water flux (Song et al., 2012) but a self-cleaning ability was offered by UV irradiation prior filtration experiments (Vatanpour

Table 1
Review of composite polymer/TiO_2 membranes in literature (F: flatsheet membranes and H: hollow fiber membranes).

	Polymer (wt%)	Solvent	Additives (wt%)	Nanoparticles/ Polymer (wt%)	Contact angle (°C)	Permeability (L/h/m^2/bar)	References
F	PVDF (10)	NMP	–	0 10 to 40	89 82 to 88	~ 770 ~ 1430 to ~480	(Damodar et al., 2009)
F	PVDF (12)	NMP	–	0 17	73 68	~ 330 ~ 310	(Oh et al., 2009)
F	PVDF (12)	DMAc	PEG600 (2)	0 2 2 to 4 4 to 17	78 74	~ 300 ~ 290 ~ 290 to~340 ~340 to ~250	(Song et al., 2012)
F	PVDF (15)	DMF	–	0 50	78 81		(Alaoui et al., 2009)
F	PVDF (15)	NMP	–	0 30	87 81	303 331	(Bae and Tak 2005)
F	PSF (15)	NMP	–	0 10 to 50 30	88 73	243 ~ 240 to~205 230	(Bae and Tak 2005)
F	PES (15)	DegOH-DMAc (1:1)	–	0 7 to 24 24 to 29	~ 86 ~ 83 to 82 ~ 82 to~80	~ 2850 ~ 3160 to 3711 3711 to ~3650	(Li et al., 2009)
F	PES (15)	DMAc	PVP (5) H_2O (5)	0 2 to 3 3 to 5	77 72 to 70 70 to 66	340 411 to 596 596 to 365	(Wu et al., 2008)
F	PVDF (16)	DMF	–	0 < 12.5%	78 76	88.2 111.7	(Cao et al., 2006)
F	PES (16)	DMAc	PVP (2)	0 13 to 25 25 to 38	66 61 to 59 59 to 54	~ 67 ~ 35 to ~29 ~ 29 to ~55	(Rahimpour et al., 2008)
F	PES (16)	DMAc	PVP (?)	0 13	~ 70 ~ 60	~ 350 ~ 340	(Razmjou et al., 2011)
F	PVDF (8.8), SPES (7.2)	DMAc	PVP (4)	0 0.6 to 25 25 to 38	74 to 65 65 to 64	1068 ~ 800 to 616 616 to~670	(Rahimpour et al., 2011)
F	PVDF (18)	DMAc	–	0 8.3		~ 77 ~ 393	(Ngang et al., 2012)
HF	PVDF (18)	DMAc-NMP (4:1 vv)	PVP (5)	0 3 to 6 6 to 28	79 65 to 58 58 to 73	~ 110 ~ 120 to ~150 ~ 150 to~75	(Yu et al., 2009)
F	PS (18)	DMAc-NMP (4:1 vv)	PVP (4)	0 6 to 11 11 to 28	72 53 to 49 49 to 40	~ 30 ~ 41 to ~49 ~ 49 to~26	(Yang et al., 2006)
HF	PSF (18)	DMAc	PVP (5)	0 11	75 45	59 78	(Hamid et al., 2011)
HF	PVDF (19)	DMAc	LiCl (0.98)	0 5 to 10 10 to 20	81 61 to 47 47 to 58	~ 40 ~ 45 to ~90 ~ 90 to~75	(Yuliwati and Ismail 2011)
F	PES (21)	DMAc	PVP (1)	0 5 to 19	65 52 to 44	0.7 0.92 to 1.44	(Vatanpour et al., 2012)
F	PVDF (24)	NMP	PEG400 (5)	0 0.4 to 2	79 77 to 72	~ 75 ~ 100 to~250	(Bian et al., 2011)