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Comparing the antifouling effects of activated carbon and TiO_2 in ultrafiltration membrane development

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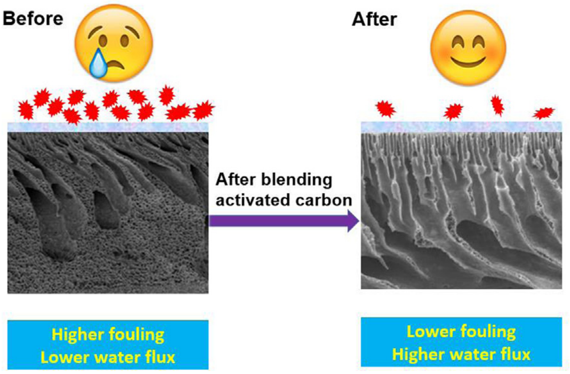
GRAPHICAL ABSTRACT



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ABSTRACT

We use activated carbon (AC) and titanium oxide (TiO_2) nanomaterials as the additives to prepare four polyvinylidene fluoride (PVDF) based ultrafiltration membranes by nonsolvent induced phase separation. The surface properties (pore size, porosity, hydrophilicity and roughness) of the membranes are characterized by scanning electron microscopy, water contact angle measurement, and atomic force microscopy. The chemical properties of the membranes are evaluated by Fourier transform infrared spectroscopy with attenuated total reflection and X-ray diffraction. All these additives can improve the surface hydrophilicity and water permeation flux of the membrane. However, the addition of TiO_2 nanoparticles (20–30 nm) results in larger surface porosities and pore sizes, which causes more severe membrane fouling compared with the neat PVDF membrane. The PVDF-AC membrane exhibits excellent fouling resistance. Particularly, the irreversible fouling after blending AC into PVDF reduces dramatically from 40% to 25%. The antifouling performance of the PVDF-AC membrane may result from the improved hydrophilicity and the favorable surface and structure properties of the membrane. To the best of our knowledge, this is the first demonstration of the antifouling function of AC in membrane preparation. This study suggests that AC could be a new type of nanomaterial for developing antifouling membranes.

1. Introduction

Water scarcity is one of the most severe problems of the world, particularly for arid regions. Membrane separation has been

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recognised as the new generation of desalination and water purification technology due to its high efficiency and reduced costs [1]. However, fouling has been the most critical challenge in almost all sorts of membrane processes since the birth of membrane technology [2,3]. Membrane fouling can reduce water flux, deteriorate product water quality, decrease membrane lifespans, and increase energy consumption [3].

Numerous strategies have been taken to minimise membrane fouling, such as feed pretreatment, optimization of operational conditions, antifouling membrane development, and physical/-chemical cleaning. Among them, developing antifouling membranes is a fundamental strategy to minimise the fouling problem. Antifouling membranes can be realised by hydrophilic polymer [4–7] or nanoparticle [8–11] blending, and surface modification [2,12–16]. Recently, many nanoparticles with high hydrophilicity or antimicrobial properties have been incorporated into membrane bulk or on the membrane surface to improve fouling resistance of the membrane. Table 1 summarises the early investigations of typical nanoparticles for antifouling membrane development.

These nanoparticles generally have versatile effects on membrane structures and properties. They often improve membrane fouling resistance by increasing the membrane surface hydrophilicity. Some researchers found that nanoparticles could enlarge the membrane pore sizes and thus increase membrane permeability but reduce selectivity [17,18]. Some reported reduced membrane pore sizes and membrane permeability [19]. It is also possible to achieve increased both membrane permeability and selectivity by selecting suitable content of nanoparticles [20,21]. Either rougher [13,22] or smoother [23] membrane surfaces after membrane modification with nanoparticles were also reported. Lower content of nanoparticles could cause smoother membrane surfaces, and vice visa [20].

Activated carbon (AC) is a well-known adsorption material due to its well-developed porous structures and large active surface area. The most studied two types in membrane separation are granular activated carbon (GAC) and powdered activated carbon (PAC). Compared with PAC, GAC has larger particle sizes (1.2–1.6 mm). Wang et al. selected fluidized GAC to minimise membrane surface fouling by mechanical scouring [33]. PAC has been used in pretreatment of membrane processes to mitigate membrane fouling via adsorption [34–38]. However, PAC may also deteriorate membrane fouling when PAC coupled with organic matters is deposited on the membrane surface [39].

Compared with other nanomaterials, AC has been less studied in developing new membranes. Mukherjee and De employed AC as the filler to prepare a mixed matrix membrane (MMM) with adsorptive properties for organic contaminant removal [40]. Torras et al. reported AC composite membranes for enzymatic membrane reactors where activated carbon acted as a support for the metal-enzyme complex [41]. Hwang et al. added AC and hydrophilic polyethylene glycol (PEG) into the casting solution to prepare composite membranes [42,43]. The prepared membranes showed improved hydrophilicity and permeation flux. However, the role of AC in membrane performance was unclear.

To summarize, AC has been used in membrane studies by four ways: (1) to mitigate membrane fouling by mechanical scouring, (2) to develop adsorptive membranes, (3) to act as the adsorbent in pretreatment of membrane processes, and (4) to prepare antifouling composite membranes with hydrophilic PEG. However, AC only has not been used to develop antifouling membranes.

In this study, we blend nanoparticles, including AC and TiO_2 into polyvinylidene fluoride (PVDF) to prepare new membranes. The original idea is to take advantage of the light absorption property of AC to enhance the photocatalytic performance of the TiO_2-blended PVDF membrane. However, we find that AC has superior performance than TiO_2 in improving the hydrophilicity and antifouling property of the membrane. The structures, surface properties (pore size, porosity, hydrophilicity and roughness) and antifouling performance of four membranes (PVDF, PVDF-TiO_2, PVDF-AC, and PVDF-TiO_2-AC) are evaluated and compared. This work demonstrates that AC can be a new type of nanomaterial for developing antifouling membranes.

2. Experimental

2.1. Experimental material

Palm shell activated carbon powders (pore sizes ~ 470 nm, particle size distribution is shown in Fig. 1) were supplied by Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Polyvinylidene fluoride (PVDF) was purchased from Dongguan plastic Co. Ltd. TiO_2 particles (P25) with nominal sizes of 20–30 nm were obtained from Degussa Corp. Bovine serum albumin

Table 1
Early investigations of typical nanoparticles for antifouling membrane development.

Nanoparticles & sizes		Membranes	Membrane characteristics after nanoparticle modification	Years & Refs.
Metals	Ag, ~50 nm	PAN hollow fiber	Improved anti-biofouling performance; Ag particles may be depleted during filtration	2003 [24]
	Cu	PSf	Reduced biofouling	2011 [25]
Metal oxides	SiO_2, 14 nm	CA UF	Increased pore size, water flux, and fouling resistance; decreased protein rejection	2008 [26]
	TiO_2, ~10 nm	TFC	Reduced water flux, improved salt rejection and anti-biofouling performance	2003 [19]
	ZnO, ~25 nm	PVDF	Increased hydrophilicity, water flux, mechanical strength and anti-irreversible fouling performance	2012 [9]
	Fe_3O_4, 80 μm	PSf UF	Improved antifouling performance	2008 [27]
	Al_2O_3, 10 nm	PVDF UF	Improved hydrophilicity, water flux, mechanical strength and antifouling performance	2005 [28]
	ZrO_2, ~250 nm	PES	Improved strength and antifouling performance	2010 [29]
	$Mg(OH)_2$, ~300 nm	PVDF MF	Improved hydrophilicity, and anti-biofouling performance	2012 [30]
Zeolite	NaA, 2 μm	PPESK UF	Increased rejection, hydrophilicity and fouling resistance; reduced water flux	2009 [31]
Boehmite	15 nm	PES	Improved hydrophilicity, water flux and antifouling property	2012 [23]
Carbon-based	CNTs	PSf	Increased hydrophilicity, and fouling resistance	2009 [32]
	GO	PVDF UF	Improved hydrophilicity, water flux, mechanical strength, and antifouling property	2012 [17]
	PAC, ~470 nm	PVDF	Increased surface hydrophilicity, roughness and antifouling property	This study

PAN: polyacrylonitrile, PSf: polysulfone, CA: cellulose acetate, UF: ultrafiltration, TFC: thin film composte, PVDF: polyvinylidene fluoride, PES: polyethersulfone, MF: microfiltration, PPESK: poly(phthalazinone ether sulfone ketone), CNTs: carbon nanotubes, GO: graphene oxide, PAC: powdered activated carbon.