Journal of Membrane Science 389 (2012) 532–543

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fouling mechanism of low-pressure hollow fiber membranes used in separating nanosized photocatalysts

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ARTICLE INFO

Article history:
Received 19 August 2011
Received in revised form 15 October 2011
Accepted 11 November 2011
Available online 22 November 2011

Keywords:
Membrane
Fouling mechanism
Nanosized photocatalyst
Cake layer
Force analysis

ABSTRACT

Low-pressure hollow fiber membranes were applied to separate and recover the nanosized TiO_2 photocatalysts in a photocatalysis and membrane separation coupling process, and the fouling mechanism of membranes with different material and pore structure was investigated in detail. The cross-flow filtration experiments were performed on polyacrylonitrile (PAN) ultrafiltration membrane with MWCO 60,000 Da, polyether sulfone (PES) ultrafiltration membrane with MWCO 65,000 Da, and other two kinds of polyether sulfone (PES) microfiltration membrane with pore size 0.2 μm and 0.4 μm. Rapid flux decline happened after TiO_2 particles entered into the membrane, blocked internal pores and formed cake layer on the top of membrane. The fouling behaviors of membranes were explored and associated with membrane pore size as well as the interaction between TiO_2 particles and membrane. The fundamental relationship was set up between various operating conditions and the characteristics of cake layer formed on membrane by analyzing the forces exerted on the TiO_2 particles. It was found that TiO_2 aggregates presented a stable diameter larger than 0.2 μm in nature aqueous media, and the porosity of TiO_2 cake increased along the height of the cake in the presence of flux decline. Hydrodynamic backflush was unable to completely recover TiO_2 catalysts and eliminate the filtration resistance due to the adhesion of nanosized TiO_2 catalysts in/on the membranes. The progresses in this research are of potential benefit to solve the membrane fouling problems caused by nanosized TiO_2 photocatalysts in the coming application of photocatalytic membrane reactor.

1. Introduction

With an exponential growth, nanocatalysts have played more and more important role in various fields, such as chemical synthesis, environmental protection and energy exploitation in the past decades [1–3]. As the size of the catalyst is becoming smaller and smaller, new physical and chemical properties including higher specific surface areas and lower mass transfer restrictions emerge, and facilitate the reactions and interactions among reactants [4]. Since the Honda–Fujishima effect was reported in 1972 [5], the research field of photocatalysis was extensively promoted and covered various discipline, including environmental protection of course. Titanium dioxide (TiO_2) seems to be the most suitable photocatalyst for industrial application in current research and also probably in the future [6–9]. By now, TiO_2 photocatalytic technology bears tremendous hope in helping solve many serious pollution challenges. The practical applications of nanosized TiO_2 catalysts in air purification and surface self-cleaning have been carried out [4]. However, a main drawback with the nanosized TiO_2 catalysts was their separation and recovery from the aqueous reaction system because nanosized TiO_2 particles were too fine to be removed by gravity setting, which still hindered the practical application of nanosized TiO_2 catalysts in water purification [10,11]. To break through this bottleneck, many useful attempts have been made, for example, attaching the nanosized catalysts on various substrates. In this way, the specific surface area and related photocatalytic efficiency of the nanosized catalysts inevitably decreased. To separate nanosized catalysts while keeping their good photoelectrochemical properties, membrane technology appears to be more practical and promising [10,12,13].

Several publications in recent years concerned with the combination of TiO_2 photocatalysis process and membrane process, and some valuable results, which can improve the understanding of this combination, i.e. the photocatalytic membrane reactor (PMR), were obtained [13–23]. Even so, only few investigations focused on membrane fouling caused by TiO_2 particles, which usually was the main limiting factor that hindered the implementation of membrane technologies during separation of fine particles in suspension. The TiO_2 caused membrane fouling in the pressure-driven membrane processes, which have more potential for industrial

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doi:10.1016/j.memsci.2011.11.027

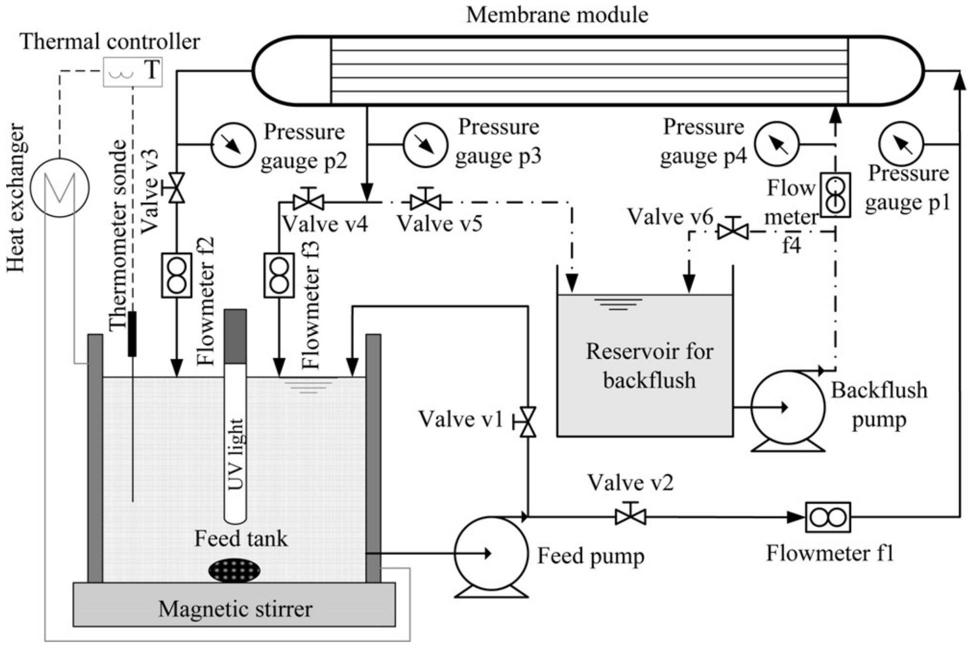

Fig. 1. Schematic diagram of the PMR experimental setup.

application than membrane dialysis [16] and distillation process [19] due to its higher permeate flux [10], was observed during the separation of TiO_2 catalysts. In the scanty investigations focusing on the membrane fouling which was caused by TiO_2 photocatalysts, the effects of operating parameters, such as trans-membrane pressure (TMP), cross-flow velocity (CFV), feed concentration, pH and electrolyte in solution, on the permeate flux were investigated [13,15,24], but there was no further discussion on the fouling mechanisms, for example, the cake layer formation or pore blocking. Researchers also tried to investigate the characteristics of TiO_2 cake layer on the top fleet sheet ultrafiltration (UF) membrane in drinking water treatment using photocatalysis coupled with membrane process [14], but the observed phenomena was only limited to one kind of specific membrane. Meanwhile, cake layer formation and pore blocking (include complete blocking, intermediate blocking and internal pore constriction) have been thought as the two main fouling mechanisms in the separation of other particles, and attracted many attentions in conventional low-pressure membrane process, such as microfiltration (MF) and ultrafiltration (UF) [25–27]. In this field, the forces exerted on other particles were investigated and used to describe the deposition and characterization of cake layer [26]. Correspondingly, so far there is still no reasonable interpretation of the discrepancy of flux behavior as well as the membrane fouling mechanism during the separation of TiO_2 particles with membrane. The unavoidable membrane fouling, apart from the origin from operating condition, also depends on the properties of membrane, such as morphology, pore size and hydrophilic affinity, etc. [28]. To provide a more comprehensive description of the fouling mechanisms of TiO_2 particles on membrane, the main objective of this study is to investigate the fouling of membranes with different types and pore sizes during separation of nanosized TiO_2 catalyst. A cross flow hollow fiber membrane system equipped with backflush device was applied in the experiments. The effect of membrane type and pore size on the rejection of TiO_2 catalysts, related fouling mechanism and filtration resistances were investigated in detail. Specific attention was drawn to the characteristics of the TiO_2 cake layer formed on the membrane surface. Further, the efficiency of the hydrodynamic backflush in the recovery of TiO_2 catalysts and the mitigation of filtration resistance was also estimated.

2. Materials and methods

2.1. Experimental setup

The experimental setup of catalyst separation system, which comprised a recirculation loop and a backflush arrangement, was presented schematically in Fig. 1. For the recirculation loop, a 2 L feed tank which was sealed with glass cap and jacketed for temperature control was used. During experiment, the temperature of feed tank was kept at 303 ± 2 K by the thermostat. A magnetic stir (IKA, German) operated continuously with a velocity set at $600\,\mathrm{r\,min^{-1}}$ to ensure the liquid to mix completely. A diaphragm pump (QIAN, China) with open flow $90\,\mathrm{L\,h^{-1}}$ and maximum pressure 0.90 MPa was used as feed pump. By adjusting the valves (v1, v2 and v3), the cross-flow velocity was controlled between 0.5 and $2.0\,\mathrm{m\,s^{-1}}$ and the trans-membrane pressure of membrane modules was set between 0.04 and 0.16 MPa. In this way, various operating conditions can be selected in accordance with different purposes of the respective experiments. All catalyst separation experiments were carried out in constant pressure filtration mode. TMP was the average pressure of the inlet pressure gauge p1 and the outlet pressure gauge p2 of membrane module. To investigate the flux decline mechanism in different experimental conditions, membrane flux was monitored in the whole process. The permeate water (except for samples to analysis) and concentrate were returned to the feed tank in order to keep the total volume constant. After each catalyst separation experiment, backflush for the membrane module was carried out. In the backflush system, a 1 L reservoir and a diaphragm pump (QIAN, China) with open flow $60\,\mathrm{L\,h^{-1}}$ and maximum pressure 0.88 MPa were utilized. The pressure of backflush was adjusted by v5 and v6 during operation. Each backflush experiment was performed at a low backflush pressure about 0.15 MPa for 30 s.

2.2. Membrane modules

Four types of self-made hollow fiber membrane modules were used in the photocatalytic membrane reactor (PMR) system, in which polyacrylonitrile (PAN) UF membrane (MOTIMO, China), polyether sulfone (PES) UF membrane (SENO, China) and polyether sulfone MF membrane (SENO, China) with different pore size were