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A novel photocatalytic self-cleaning PES nanofiltration membrane incorporating triple metal-nonmetal doped TiO_2 (K-B-N-TiO_2) for post treatment of biologically treated palm oil mill effluent

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ABSTRACT

Biologically treated palm oil mill effluent (POME) still has a dark-brown color and contains residual organic matter. In this paper, a novel self-cleaning mixed matrix K-B-N triple doped-TiO_2/PES nanofiltration membrane at three weight fractions (0.1, 0.5 and 1 wt%) was prepared by the phase inversion method. The performance of the prepared membranes was investigated in terms of permeability, fouling resistance and capability for post treatment of the biologically treated POME. The prepared membranes were characterized by contact angle measurement, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The obtained results indicated that the pure water flux of the modified membranes improved significantly by addition of K-B-N-TiO_2 nanoparticles up to 0.5 wt% which could be attributed to the hydrophilic nature of the nanoparticles and induced photocatalytic ability. Also, flux recovery ratio (FRR) of the optimized membrane was increased from 48 to 95.4% relative to unfilled membrane that confirmed antifouling and self-cleaning capability of the nanocomposite. This behavior was ascribed to the photocatalytic role of the nanoparticles resulting mineralization of organic matter from surface of the modified membrane that enhanced reusability of the prepared membranes. Maximum permeation flux, dye and COD removal efficiencies were obtained about 27 kg/m^2 h, 98% and 90%, respectively for treating the biologically treated POME.

1. Introduction

The palm oil mill generates a large amount of highly polluted wastewater. The palm oil mill effluent (POME) is a thick and brownish slurry waste that has water-soluble components of palm fruit, a variety of lipids and carbohydrates ranging from hemicellulose to simple sugars, phenol, phenolic compounds, nitrogenous compounds from proteins to amino acids, free organic acids and nutrients [1,2]. POME is a major source of pollution if it is discharged untreated into receiving waters, causing considerable environmental problems [3]. Among traditional technologies, biological treatments such as anaerobic and aerobic systems are widely used for POME treatment as its most of the organic contents are biodegradable. However, current methods are not efficient for complete treatment and biologically treated POME retains its dark-brown color due to presence the plant constituents such as lignin and phenolic compounds which are not degraded in the biological treatment processes [4–6].

Membrane separation, as a promising technology, is extensively used for different applications such as gas separation, protein concentration, and water and wastewater treatment [7] due to technical benefits, lack of phase change, high separation efficiency, compact design, reasonable operating costs [8], low energy consumption and simplicity of operation [9,10].

Nanofiltration (NF) membranes are normally made from polyethersulfone (PES) for water and wastewater treatment that shows a good thermal stability, a wide range of pH tolerance, ease of fabrication, well mechanical strength and chemical resistance [11]. However, the hydrophobic nature of PES and high tendency to fouling is an obstacle for wide application of pure NF PES membrane that lead to decline the permeation flux, rejection, membrane lifespan and increase the operation cost.

Recently, different modification methods on PES membranes have been conducted to overcome the fouling phenomenon that improved membrane surface hydrophilicity. Among various modification

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Nomenclature

POME	Palm oil mill effluent
SEM	Scanning electron microscopy
AFM	Atomic force analysis
FRR	Flux recovery ratio
PES	Polyethersulfone
NF	Nanofiltration
MWCNTs	Multiwalled carbon nanotubes
K-B-N-TiO_2	Potassium-boron-nitrogen triple doped dioxide titanium
XRD	X-ray diffraction
FT-IR	Fourier Transform Infra-red
NPs	Nanoparticles
PVP	Polyvinylpyrrolidone
PWF	Pure water flux
CF	Particular concentration in feed
Cp	Particular concentration in permeate
DMAc	*N*, *N*-dimethylacetamide
J_p	Powder milk solution flux
$j_{w,1}$	Pure water flux
$J_{w,2}$	Pure water flux after fouling
R_t	Total fouling resistance
R_r	Reversible fouling resistance
R_{ir}	Irreversible fouling resistance
M_1	Unfilled PES membrane
M_2	Membrane with 0.1 wt% nanoparticle
M_3	Membrane with 0.5 wt% nanoparticle
M_4	Membrane with 1 wt% nanoparticle
COD	Chemical oxygen demand

techniques, blending with inorganic compounds especially metal oxide nanoparticles and the polymeric hydrophilic additives has attracted considerable attention to improve membrane performance in recent studies [12]. The metal oxide nanoparticles have been extensively used to modify the NF polymeric membranes due to their exceptional performance characteristics [13]. Organic-inorganic nanocomposite membranes gain benefits such as high separation efficiency, low-cost and ease of working as well as unique optical, thermal and photochemical activities [14].

In the recent years, nano-sized titanium dioxide (TiO_2) has been widely used due to its high hydrophilicity, adsorption capacity, antibacterial property, good chemical property, low cost and safety toward both humans and the environment [15,16]. Furthermore, TiO_2 nanoparticles have a high photocatalytic activity that can decompose the organic foulants on the TiO_2/PES composite membrane surface. Since the band gap of titania is about ~3.2 eV, the irradiation of UV-light below 380 nm is necessary for the photocatalytic process [17]. However, the combination of polymeric membrane with UV irradiation may be challenging due to degradation of polymeric martial under UV irradiation in long time operation [12].

Numerous investigations also recommended intrinsic effects of TiO_2 nanoparticles on the membrane performance without UV irradiation at high concentrations of TiO_2 nanoparticles and a positive effect was reported [12]. Furthermore, some studies indicated the addition of excessive TiO_2 nanoparticles may lead to negative effects on the morphology and elasticity of the polymeric membranes instead of improvement [18]. Vatanpour et al., [19] reported that multiwalled carbon nanotubes (MWCNTs) coated with anatase titanium dioxide (TiO_2) nanoparticles/PES nanofiltration membrane had higher antibiofouling properties due to lower surface roughness and synergistic photocatalytic activity induced by incorporated nanoparticles [19]. Safarpour et al., [20] reported that graphene oxide/TiO_2 blended PES nanofiltration showed higher water permeation rate, antifouling ability and dye rejection due to its higher hydrophilicity in comparison with bare PES membranes [20].

Doping TiO_2 with metal or nonmetal ions has been considered as one of the most promising ways to develop TiO_2-based photocatalysts for reducing the recombination of photogenerated electrons and holes, and to extend its light absorption into the visible region [21]. Accordingly, a novel structure (triple doped-TiO_2 with metal and nonmetal) is prepared by doping metal and nonmetal in TiO_2 for enhancement of light harvesting and improvement of electron and hole pair separation and finally increasing photocatalytic activities. The triple doped TiO_2 nanoparticles, as a hydrophilic and active photocatalyst modifier at low concentration in polymer matrix, can degrade organic foulant on membrane surface under solar or visible light irradiation that decrease membrane fouling and finally improve permeation flux. In this work, the effect of the nanoparticle content on the permeation flux and antifouling properties of blended PES nanocomposite membranes were investigated. The characterization of the NPs and the prepared membranes were determined using XRD, SEM, FT-IR spectroscopy, AFM and water contact angle measurement. At the end, performance of the optimized self-cleaning synthetic membrane was evaluated for treatment of the biologically treated POME as a real sample in terms of permeate flux, dye rejection and COD removal efficiency.

2. Materials and methods

2.1. Materials

All the chemicals used were reagent grade without further purification. Potassium nitrate (KNO_3), boric acid (H_3BO_3), ammonia (NH_3, H_2O, 37 wt%), tetraisopropyltitanate ($C_{12}H_{28}O_4Ti$, 99 wt%) and ethanol (C_2H_5OH, 99 wt%) from Merck was used to synthesize K-B-N triple doped TiO_2 nanoparticles. Polyethersulfone (Ultrason E 6020P, MW = 58,000 g/mol and glass transition temperature Tg = 225 °C) as polymer and dimethyl acetamide (DMAc) as a solvent were purchased from BASF Co., Germany. Polyvinylpyrrolidone (PVP) with 25,000 g/mol molecular weight as a pore forming in the coagulation process was obtained from Merck Co., Germany. Distilled water was used as the non-solvent agent. Chemical substances which were used for COD experiments were supplied by Merck.

2.1.1. Preparation of K-B-N-triple doped TiO_2 nanoparticles

The desired amount of boric acid (H_3BO_3) (1 wt%: B/(B + Ti)) and potassium nitrate (KNO_3) (0.5 K/(K + Ti)) were dissolved in a mixture of 10 ml of anhydrous ethanol and 3 ml water in an ultrasonic bath for 60 min (solution A and B). Next, 12 ml of tetran-butylorthotitanate was dropped into 33 ml anhydrous ethanol under strong stirring (solution C). Subsequently, 1 ml HCl (12 M) was added dropwise into the solution C. The solution A and B were slowly added to the solution C. Afterward, a desired amount of ammonia ($NH_3 \cdot H_2O$) was added dropwise to the solution C (5 wt%: N/(N + Ti)). A white precipitate was observed immediately. After aging for 24 h at room temperature, the white precipitate was filtrated, dried at 100 °C for 10 h, and then calcined at 450 °C for 2.5 h.

2.1.2. Fabrication of K-B-N-TiO_2/PES membranes

The K-B-N-TiO_2 embedded PES membranes were prepared using the conventional phase inversion method according to pervious work [22]. First, the desired amount of K-B-N-TiO_2 nanoparticles (0.1, 0.5 and 1 wt %, related to the total solution weight) was dispersed into the DMAC and sonicated about 1 h using DT 102H Bandelin ultrasonic (Germany) and afterward, PES (20 wt%) and PVP (1 wt%) was dissolved in the solution by continuous stirring at 400 rpm for 24 h to provide casting solution. The compositions of the prepared membranes are presented in