Development of nanocomposite membranes for dairy wastewater treatment

Thesis booklet

by

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Contents

Abstract

A novel photocatalytic nanocomposite membrane was prepared successfully by blending polyvinylidene fluoride (PVDF) with TiO_2, and/or carbon nanotube (CNT), and/or $BiVO_4$ at various ratios in the membrane material via phase inversion method**.** The prepared membranes were evaluated for model or real dairy wastewater treatment. The membranes were characterized by several surface characterization methods as SEM, AFM, XRD, and EDX. XRD and SEM measurements revealed that the nanoparticles were present as 200–300 nm-sized aggregates in the membrane, which increased the roughness of composite blended membranes (AFM results). EDX measurements exhibited that he proteins have covered a relatively large area of the pristine PVDF membrane, resulting in a relatively high N/F ratio. Addition of TiO_2, and/or carbon nanotube (CNT), and/or $BiVO_4$ nanoparticles into the PVDF membrane material decreased the contact angle of membrane surface, thus increased the hydrophilicity of modified blended membranes. In dead end cell BSA filtration experiment, PVDF -TiO_2-CNT-$BiVO_4$ nanocomposite blended membrane exhibited a pure water flux up to 150.52 Lm^{-2} h^{-1} which is two-fold higher than virgin membrane and a higher bovine serum albumin (BSA) rejection of about 97 %. Based on flux recovery ratio and flux the optimal CNT ratio in the PVDF-TiO_2-CNT and $BiVO_4$ in PVDF-TiO_2-$BiVO_4$ nanocomposite membrane was 2 % and 50 % respectively. More importantly, the PVDF -TiO_2-CNT-$BiVO_4$-50 (PTCB50) (containing 0.48 wt % TiO_2, 0.02 wt % CNT and 0.5 wt % $BiVO_4$) and PVDF-TiO_2-$BiVO_4$-50 (PTB50) (containing 0.5 wt % TiO_2 and 0.5 wt % $BiVO_4$ in PVDF) membrane exhibited a smaller irreversible fouling and a higher flux recovery ratio, revealing that blending with TiO_2, and/or CNT, and/or $BiVO_4$ could improve the self-cleaning under visible irradiation and the antifouling properties of PVDF membrane. The application of B-PTB50 and B-PTCB50 membranes to treat real dairy wastewater were promising. They exhibited better antifouling and foulant degradation performance as compared to pristine membrane. However, the lower rejection performances of the membranes were due to ability of lactose to pass through the membranes which requires further treatment. Overall, the incorporation of nanoparticles in the polymer matrix enhanced the antifouling and foulant degradation performance of the photocatalytic nanocomposite membrane to a remarkable extent.

Keywords: PVDF, photocatalytic membranes, fouling control, antifouling, visible light, bismuth vanadate, carbon nanotube

Introduction

Food production requires large amount of water and large volumes of wastewater is generated, and dairy industry is among the food production industries that generates the largest volume of wastewater. In recent years, the application of **membrane filtration in dairy wastewater** treatment is growing, among them, ultrafilter membranes have received more attention due to their capability to efficiently reject macromolecules, colloids, bacteria, and particles. Recent publications have focused on fouling reduction by offering innovative cleaning processes, optimizing the existing techniques, or integrating devices to the membrane set-up.

Poly (vinylidene fluoride) (PVDF) is a widely applied **polymeric membrane material** commonly used in ultrafiltration. Despite their superior physical, chemical, and mechanical properties PVDF membranes are easily fouled by wastewaters containing proteins, oils, and natural organic matter due to their hydrophobic nature. This problem may be overcome by using the recently developed photocatalytic membranes, (e.g. polymeric membranes modified by **TiO_2**) which may be applied in the photodegradation of membrane foulants under UV light. However, TiO_2 has its limitations: the high recombination ratio of photocatalytically generated electron–hole pairs reduce photocatalytic activity, moreover its photocatalytic activity can only be efficiently activated under UV light (λ<390 nm). In recent years, **bismuth-based oxides** have gained attention in photo-catalytic technology because of its superior band gap and efficient visible light absorption performance, however, their relatively low surface area and activity hinders their broader application. **Carbon nanotubes (CNTs)** are semiconductor materials that also have received considerable attention due to their outstanding properties, moreover they are broadly used as electron acceptors and reduce the recombination rate. Taking advantage of their benefits, the aim of this work was to develop a novel photocatalytic composite PVDF membrane containing TiO_2-CNT-$BiVO_4$ nanoparticles and examine their applicability for the treatment of a model and real dairy wastewater, and to explain the improved antifouling properties of the developed membranes. Moreover, the visible-light driven photocatalytic cleanability of nanocomposite membranes also was investigated.

Materials and methods

Bovine serum albumin (BSA) solution (1g L^{-1}), synthetic dairy wastewater contains BSA and other chemical compounds (synthetic wastewater, SWW), were used as model dairy wastewaters as this protein concentration represents realistic dairy wastewater protein content. Real dairy wastewater was collected from nearby milk processing industry.

The concentration of BSA in the model dairy wastewater was measured before and after filtration by a spectrophotometric method. Chemical oxygen demand (COD) of the samples was determined via the potassium–dichromate oxidation method. Electrical conductivity (EC) and total dissolved solid (TDS) were analysed by multiparameter analyser, and pH was measured by pH meter.

$BiVO_4$ nanoparticles were synthetized by hydrothermal method. The $BiVO_4$ catalyst had a band gap of 2.35 eV. The photocatalytic activity of the synthesized $BiVO_4$ and other used photocatalysts were examined by1 gL^{-1} BSA and methylene blue (MB) (10^{-3} $molL^{-1}$) degradation under visible light irradiation. Moreover, commercial TiO_2 (Aeroxide P25) and carbon nanotubes (CNT) were used for membrane preparation.

Two types of **membranes were fabricated**, firstly, physically modified modification of commercial PVDF membranes by physical deposition method, secondly pristine and photocatalyst blended membranes were prepared by phase-inversion method, incorporating TiO_2, CNT and/or $BiVO_4$ nanoparticels into the membrane material. Membranes were characterized by using several up-to date surface characterization method as AFM (determining surface roughness), SEM, zeta potential measurements and surface contact angle measurements. Filtration experiments were carried out using a dead-end filtration cell (Millipore, XFUF04701, USA), flux, filtration resistanes (resistances-n-series model) and pollutant rejection were examined.

Membrane regeneration efficiency was examined by performing flux recovery experiments of the photocatalytic membrane reactors by means of UV or visible light irradiation of fouled photocatalytic membranes, and comparing their water permeability.

One-way analysis of variance (ANOVA) was performed using Stata17 statistical software program

New scientific results

1. New TiO_2 and CNT containing PVDF based photocatalytic composite UF membranes were produced. It was proved that despite its hydrophobic nature, addition of CNT enhanced the hydrophilicity of the membrane. I have determined the optimal CNT ratio in the membrane and it was 2%.
    - The enhanced hydrophilicity of the membrane was proved by reduced contact angle (from 75° pristine commercial PVDF to 0° of C-PTC2 and from 78° of fabricated pristine PVDF to 71° B-PTC2,)
    - It was proven that these membranes can be successfully regenerated by UV-irradiation. Best regeneration with 96.89 % flux recovery ratio (FRR) was achieved in case of coated membrane (C-PTC2, containing 11.37 gm^{-2} TiO_2 and 0.057 gm^{-2} CNT), while FRR=64.07% can be obtained by blended PVDF-TiO_2-CNT (B-PTC2, containing 0.98 % TiO_2 and 0.02 % CNT in the PVDF) after 2h UV light exposure.

2. $BiVO_4$ blended photocatalytic PVDF membranes were fabricated. It was proven, that $BiVO_4$ was successfully built to PVDF-base membranes resulting in new, visible light-active photocatalytic composite membranes.
    - Membrane performance can be further enhanced by addition of TiO_2 or CNT.
    - The highest and improved water flux (150.52 L m^{-2} h^{-1}) was obtained by PVDF-TiO_2-CNT- $BiVO_4$ blended hybrid UF membrane.
    - High (more than 97%) BSA rejection was obtained by PVDF-TiO_2-CNT-$BiVO_4$ blended hybrid UF membrane.
    - Lower irreversible and total resistances were gained by PVDFTiO_2/$BiVO_4$ and PVDF-TiO_2/CNT/ $BiVO_4$ blended hybrid UF membranes than pristine PVDF.
    - The lowest irreversible and total resistance were presented by PVDF-TiO_2/CNT/ $BiVO_4$ blended hybrid UF membrane
    - The best antifouling propriety which was proved by lowest irreversible and total resistance was exhibited by PVDF-TiO_2-CNT/-$BiVO_4$ blended hybrid UF membrane
    - Energy-dispersive X-ray spectroscopy (EDX) measurements revealed that the nitrogen to fluorine ratio (N/F) of BSA fouled PVDF membrane was 3-4 times higher than fouled PVDF-TiO_2-$BiVO_4$ and PVDF-TiO_2-CNT--$BiVO_4$ blended hybrid UF membranes, which imply that the antifouling propriety of the hybrid membranes is better than the pristine PVDF membrane.

- PVDF-TiO_2/$BiVO_4$ blended hybrid membrane showed best photocatalytic regeneration performance under visible light, provided the best, (70%) flux recovery ratio during BSA solution filtration.

3. The effect of salt content, pH and concentration of lactose on filtration performance were investigated in order to establish the application of composite membranes for treatment of dairy wastewaters
    - It was proved that the salinity affects the membrane performance as higher irreversible and total resistance, and slightly lower COD rejection was observed at higher EC level (>4) than lower EC level.
    - The presences of lactose increased the irreversible resistance and severely reduce COD rejection. In the presence of $1gL^{-1}$ of lactose during synthetic dairy waste water UF filtration, the COD rejection of pristine PVDF, B-PTB50 and B-PTCB50 membranes were reduced to about 50-60 %.
    - Lower resistances and slightly better COD rejection were observed at pH 7.5 and pH 9.5 as compared to pH 4. The lower resistance at higher pH was due to strong repulsion force between negative charge surface of the membranes and the negative charge of the protein (BSA).

4. It was proved PVDF-TiO_2-$BiVO_4$ and PVDF-TiO_2-CNT-$BiVO_4$ blended hybrid membranes performed better antifouling, flux, regeneration and COD rejection during real dairy waste water treatment as compared to pristine PVDF
    - During real dairy waste water UF, both the total and irreversible resistances of B-PTB50 (containing 0.5 wt % TiO_2 and 0.5 wt % $BiVO_4$ in PVDF) and B-PTCB50 (containing 0.48 wt % TiO_2, 0.02 wt % CNT and 0.5 wt % $BiVO_4$) hybrid blended membranes were lower than pristine membranes.
    - The highest COD rejection performance for unfiltered and prefiltered real dairy wastewater were 60 % by B-PTCB50 and 30 % by pristine PVDF membrane respectively
    - During real dairy waste water UF B-PTCB50 blended hybrid UF membrane performed the best regeneration, about 50% FRR under visible light.

List of Publications

Publications related to the topic of the PhD work

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Elias Jigar, Sisay; Ákos, Fazekas; Zsuzsanna, László. Investigation of inorganic nanoparticles containing photocatalytic PVDF membranes for model dairy wastewater treatment **(In progress)**

MTMT identification number: 10066623

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Co-author statement in connection with submission of PhD thesis

With reference to the Regulations of the Environmental Science Doctoral School of University of Szeged, statement from the Author in charge about the **Sisay Elias Jigar's** contribution in the shared work, which is already published and included in the PhD thesis of the applicant (Sisay, Elias Jigar, Szabolcs, **Ákos Fazekas**, Zoltán Jákói, Endre Zsolt Kedves, Tamás Gyulavári, Áron Ágoston, Gábor Veréb, and Zsuzsanna László. 2023. "Application of $BiVO_4/TiO_2$/CNT Composite Photocatalysts for Membrane Fouling Control and Photocatalytic Membrane Regeneration during Dairy Wastewater Treatment" *Catalysts* 13, no. 2: 315. https://doi.org/10.3390/catal13020315 (Q2, IF 4.5)), must be presented to the PhD Committee. The Author in charge states that the published work, or the indicated part of the work, has not been and will not be used in another Ph.D. thesis.

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Szeged, 2023. 03. 06.

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https://doi.org/10.1016%2Fj.chemosphere.2022.135589 (Q1, IF: 8.943), must be presented to the PhD Committee. The Author in charge states that the published work, or the indicated part of the work, has not been and will not be used in another Ph.D. thesis.

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Ákos Fazekas

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