

Journal of Environmental Informatics 41(1) 37-51 (2023)

Journal of Environmental Informatics

www.iseis.org/jei

## Multifunctional PVDF Membrane Coated with ZnO-Ag Nanocomposites for Wastewater Treatment and Fouling Mitigation: Factorial and Mechanism Analyses

X. J. Chen<sup>1\*</sup>, C. Z. Huang<sup>2\*</sup>, R. F. Feng<sup>3</sup>, P. Zhang<sup>4</sup>, Y. H. Wu<sup>4</sup>, and W. W. Huang<sup>5\*\*</sup>

<sup>1</sup> Department of Civil Engineering, University of Texas at Arlington, Arlington, Texas 76019, USA.

<sup>2</sup> Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada

<sup>4</sup> Environmental Systems Engineering, University of Regina, Regina, Saskatchewan S4S 0A2, Canada.

<sup>5</sup> Department of Civil Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada.

Received 12 June 2021; revised 20 December 2021; accepted 25 July 2022; published online 02 January 2023

**ABSTRACT.** In this study, a multifunctional poly(vinylidene fluoride) (PVDF) membrane was developed through chemical binding with ZnO-Ag nanocomposites to increase wastewater treatment efficiency. The unique characteristics of ZnO-Ag nanocomposites endowed the membrane with high surface hydrophilicity, organic/bio fouling resistance, and photocatalytic antibacterial activity. The significantly decreased water contact angle and increased under-water oil contact angle suggested improved surface hydrophilicity and organic fouling resistance. Through factorial analysis, it was found that the antibacterial activity of the multifunctional membrane could be significantly improved under visible light condition and with ZnO-Ag nanocomposites which obtained under higher Ag concentration and sintering temperature. The increase of Ag composition of ZnO-Ag nanocomposites on modified membrane surface significantly improved the membrane antibacterial activity but had little effect on membrane hydrophilicity. In addition, the photocatalytic antibacterial activity of ZnO-Ag nanocomposites could further improve the membrane biofouling resistance through simple exposure to visible light. The effects of different Ag chemical states on the performances of ZnO-Ag nanocomposites and the corresponding modified membranes were studied, and the relevant mechanism of antibacterial activity under both dark and light conditions was discussed. Filtration experiments with secondary wastewater effluent as feed solution indicated that the developed membrane exhibited one order of magnitude larger permeate flux compared to the pristine PVDF membrane, while maintaining comparable bacteria rejection rates during the filtration process.

Keywords: ZnO-Ag nanocomposites, multifunctional PVDF membrane, photocatalytic antibacterial activity, organic/bio fouling resistance

## 1. Introduction

Membrane-based filtration technology has been extensively applied in wastewater treatment due to its advantages in high compactness, reliability, and efficiency (Wang et al., 2022). Poly(vinylidene fluoride) (PVDF) membranes, one of the most robust membranes with excellent mechanical strength, thermal stability, and chemical resistance, are commonly used for wastewater treatment processes (Chen et al., 2020; Ali et al., 2021). However, due to low surface energy and high hydrophobicity, they usually suffer from membrane fouling, particularly organic and biological fouling (Zhu et al., 2018; Chen et al., 2022a). Organic fouling involves the formation of cake layer through the accumulation of organic matters, and biofouling is associated with the growth of biofilm due to the adhesion of microorganisms on the membrane surface (Li et al., 2013; Ramil et al., 2020; Liu and Huang, 2021). The problem of membrane fouling leads to dra-

ISSN: 1726-2135 print/1684-8799 online

matic decrease in permeate flux, thus increasing operation costs and shortening membrane lifetime (Chen et al., 2019; Sri Abirami Saraswathiet al., 2019). Therefore, developing a PVDF membrane with both properties of hydrophilicity and antimicrobial is desired for its practical application in wastewater treatment.

Membrane modification with nano materials has been extensively studied to mitigate membrane fouling and increase permeate flux (Li et al., 2013; Sri Abirami Saraswathiet et al., 2019; Li et al., 2022). Recently, loading hydrophilic nanocomposites decorated by silver nanoparticles (Ag NPs) was proposed to simultaneously improve membrane hydrophilicity and antibacterial performance, such as silver/multiwalled carbon nanotubes (MWNTs-Ag), silver/graphene oxide (GO-Ag), SiO<sub>2</sub>-Ag, TiO<sub>2</sub>-Ag, and ZnO-Ag nanocomposites (Ahsani et al., 2020; Huang et al., 2020a; Huang et al., 2020b; Abdel-Karim et al., 2021; Chen et al., 2022b). Among these nanocomposites, ZnO-Ag nanocomposites have been considered as a promising candidate since they not only have hydrophilic and antibacterial properties, but also exhibit photocatalytic activity under both UV and visible light (Wang et al., 2016). Ponnaiyan and Gopalakrishnan (2019) blended ZnO-Ag nanocomposites into the

<sup>&</sup>lt;sup>3</sup> Canadian Light Source, Saskatoon, Saskatchewan S7N 2V3, Canada.

<sup>\*</sup> Co-first authors.

<sup>\*\*</sup> Corresponding author. Tel.: +1-403-220-6234.

E-mail address: wendy.huang3@ucalgary.ca (W. Huang).

<sup>© 2023</sup> ISEIS All rights reserved. doi:10.3808/jei.202300486.

casting solution of polysulfone/polyvinyl pyrrolidone (PSF/PVP) membrane to enhance the performances of water permeability, antimicrobial activity, and sulphate rejection (Ponnaiyan and Gopalakrishnan, 2019). Huang et al. (2020) incorporated Ag-ZnO core-shell nanoparticles into the polyamide (PA) layer of thin film nanocomposite (TFN) membranes during interfacial polymerization. The resultant TFN membrane exhibited better membrane performance in terms of higher salt rejection, lower flux decline, and excellent antibacterial property, compared with the nanoparticle-free TFC membrane (Huang et al., 2020c). El-Samak et al. (2021) mixed ZnO-Ag nanocomposites into polystyrene (PS) fibers to improve antibiological fouling properties of oil-separating films (El-Samak et al., 2021).

However, previous studies mainly focused on fabrication of mixed-matrix membranes through incorporating ZnO-Ag nanocomposites into casting solutions, which may limit the improvements of membrane performances due to agglomeration of nanocomposites within polymer matrices (Dechnik et al., 2017). There have been few reports of research on immobilization of silver decorated zinc oxide (ZnO-Ag) nanocomposites on membrane surfaces for wastewater treatment. Through this strategy, membrane performances could be maximally improved since most of the ZnO-Ag nanocomposites can be dispersed on modified membrane surfaces. Moreover, the effects of different Ag chemical states on the performances of ZnO-Ag nanocomposites and its modified membranes have not been investigated.

Therefore, a multifunctional PVDF membrane was developed through chemical binding with ZnO-Ag nanocomposites on commercial membrane surface. A poly(acrylic acid) (PAA) layer was introduced onto membrane surface by cold plasmainduced graft-polymerization to immobilize ZnO-Ag nanocomposites. The obtained membrane was expected to have high surface hydrophilicity, organic/bio fouling resistance, and photocatalytic antibacterial activity. In detail, factorial analysis was employed to investigate the effects of Ag content and sintering temperature of ZnO-Ag nanocomposites, as well as light condition and their interactions on the antibacterial activity of the multifunctional membrane. Then, how the significant factors affected the surface property and antibacterial activity of multifunctional membrane was investigated detailedly. Moreover, the relevant mechanism of antibacterial activity on multifunctional membrane surface under both dark and light conditions was explored. Finally, the improvements in filtration performance and antifouling ability of the functionalized membrane were demonstrated through the treatment of secondary wastewater effluent. Implications of the results for the developed multifunctional PVDF membrane to improve wastewater treatment efficiency were evaluated and discussed.

## 2. Materials and Methods

## 2.1. Synthesis of ZnO-Ag Nanocomposites

A typical deposition-precipitation method was applied to synthesize ZnO-Ag nanocomposites. In detailed, 10 g of ZnO nanoparticles (NPs) was dispersed in 100 mL of AgNO<sub>3</sub> solution under sonication in a conical flask. The mixture was shaken with 400 rpm at 20° for 24 h to allow the deposition of  $Ag^+$  on ZnO NPs. Then 100 mL of NaBH<sub>4</sub> solution with same molar concentration of AgNO<sub>3</sub> was added to the mixture and stirred for 30 min. After reaction, the precipitates were separated by centrifugation and washed by deionized (DI) water three times, and then the collected particles were dried completely and then sintered for 2 h to obtain ZnO-Ag nanocomposites for further usage.

## 2.2. Functionalization of PVDF Membrane with ZnO-Ag Nanocomposites

The clean PVDF membrane was cut into pieces and fixed in the chamber of a gas plasma treatment system (IoN 40; PVA TePla) with the active surface layer facing up. After evacuation, 300 sccm of argon was injected into the chamber, following plasma generation under 100 W of power for 90 s. Then the chamber was evacuated again, and 450 sccm of oxygen was injected to generate oxyradicals on the membrane surface for 3 min. The membrane was then taken out and immediately dipped in 60% of acrylic acid (AA) solution for poly acrylic acid (PAA) graft polymerization at 50 °C for 1.25 h. The PAA-coated membrane was removed and rinsed in DI water three times. The PAAcoated membrane was in contact with fresh suspensions of ZnO-Ag nanocomposites for 1 h. This process was performed on a rocking platform with 300 rpm at 20 °C. The suspensions were prepared through dispersion of certain amounts of ZnO-Ag nanocomposites in 50 mL of DI water, followed by 20-min of sonication. Then, the membrane was removed and dried at room temperature for 1 h. The membrane was washed in DI water at 300 rpm for 30 min to remove weakly bounded nanocomposites. Finally, the membrane was dried at room temperature to obtain the final functionalized membrane. A description of membrane functionalization with ZnO-Ag nanocomposites was presented in Supporting Information (Figure S1).

# 2.3. Antibacterial Activity of Membrane and ZnO-Ag Nanocomposites

The antibacterial activity of the membrane and nanocomposites were evaluated through cfu enumeration assay. Briefly, E. coli suspension (108 cfu/mL) was exposed to membranes  $(0.5 \text{ cm} \times 0.5 \text{ cm})$  for 3 h at 20 °C under dark and light conditions (20 W). After removing the excess bacterial suspension, saline solution (5 mL, 0.9% NaCl) was used to rinse unattached bacteria from the membrane. The membrane was then transferred to saline solution (5 mL) and was sonicated for 5 min (26 W, FS60 Ultrasonic Cleaner) to detach cells from the membrane surface. After cell removal from the membrane surface, the supernatant was cultured on LB agar media and then incubated 24 h at 37 °C for cfu enumeration. The biofouling resistance of the membranes was assessed using the same approach, the number of live bacteria which attached on the used membrane surface was measured by cfu enumeration. For each membrane, two independent samples were tested and the average value was reported. To evaluate the toxicity of nanocomposites in suspension, E. coli suspension with concentration of 10<sup>7</sup> cfu/mL was exposed to nanocomposites (180 µg/mL) at 20 °C under 150 rpm for 3 h. At the end of exposure period, the bacterial suspension was sonicated for 5 min to break aggregates. The bacterial suspension was then cultured on LB agar media followed by 24 h of incubation at 37  $^{\circ}$ C for cfu enumeration.

## 2.4. Factorial Experiment Design

To investigate the effects of Ag content and sintering temperature of ZnO-Ag nanocomposites, as well as light condition and their interactions on the antibacterial activity of the functionalized membrane, a 23 factorial analysis was employed. The variable levels of these three factors are presented in Table 1. The design matrix was generated through Design-Expert v10 (Stat-Ease Inc., Minneapolis, USA) and shown in Table S1. The cfu (% of control) on membrane surface was used as the experimental response, and a lower cfu (% of control) number indicated a better antibacterial activity.

Table 1. Experimental Factors and Their Levels.

Factors	Low level (-1)	High level (+1)
A: Ag concentration (mM)	6	8
B: Sintering temperature (°C)	60	450
C: Light condition	0 (Dark)	1 (Visible light)

## 2.5. Intracellular Reactive Oxygen Species (ROS)

Intracellular ROS induced by nanocomposites was monitored using DCFH-DA as oxidation-sensitive fluorescent probe. After incubation of E. coli (108 cfu/mL) with nanocomposites (180 µg/mL) in solution at 37 °C for 3 h, bacterial suspension was incubated with DCFH-DA (20 µg/mL) at 37 °C for 25 min. The suspension was centrifuged and the bacteria were washed two times with saline solution. The fluorescence intensity was measured through a microplate reader (Synergy H1; BioTek) at excitation and emission of 488 and 525 nm, respectively. To further investigate the potential roles of oxidative stresses induced by nanocomposites, intracellular superoxide dismutase (SOD) and catalase (CAT) activities were measured using SOD and CAT assay kits, respectively, following the specifications provided by the manufacturer (Nanjing Jiancheng Bioengineering Institute). SOD activity was determined with hydroxylamine method by using a nitrite as the detector of superoxide radicals. The radicals were generated by xanthine and xanthine oxidase due to the presence of SOD. The absorbance was measured by the microplate reader at 550 nm. The SOD activity unit was defined as the amount of the enzymes which caused 50% inhibition of the color formation. Colorimetric method was applied to measure CAT activity based on the decrease of absorbance at 405 nm because of H2O2 consumption. The CAT activity unit was defined as the amount of enzymes that decomposed 1 µmol of H<sub>2</sub>O<sub>2</sub> per second under experimental conditions.

## 2.6. Filtration Experiments

The impacts of nanocomposite coating on membrane performances were assessed in a cross-flow filtration system with an effective membrane area of  $20.6 \text{ cm}^2$  (CF016 membrane test skid; Sterlitech Corporation). The water samples from seconddary wastewater effluent were pre-filtered through filter papers (pore size:  $80 \sim 120 \ \mu m$ ) to remove suspended and large particulate matters. Before filtration experiments, all membranes were submerged in DI water for one day. Membrane performances including pure-water flux, permeate flux, and removal rates of total organic carbon (TOC), total nitrogen (TN) and bacteria were investigated in recycling mode with 10 L of feed solution. The concentrations of TOC and TN in feed and permeate solutions were monitored using a TOC/TN analyzer (TOC-L; Shimadzu). The reusability and biofouling resistance of the pristine and modified PVDF membranes were evaluated in batch filtration mode. Four experimental cycles were tested, each cycle started with 10 L of feed solution and ended when 7 L of permeate water was collected. The fouled membrane was exposed to visible light (20 W) for 20 min in DI water after the filtration process in each cycle. All the filtration processes were performed under 1 bar of pressure at  $20 \pm 1$  °C. The permeate flux was monitored by an electronic weighing balance (Valor® 1000, OHAUS, Parsippany). The membrane permeation flux  $(J_w, L/m^2 \cdot min)$  was defined as (Li et al., 2021):

$$J_{w} = V / (A \times \Delta t) \tag{1}$$

where *V* denotes permeate water volume (L), *A* denotes effective membrane area (m<sup>2</sup>), and  $\Delta t$  denotes permeation time (min). The removal rate *R* (%) was defined as:

$$R(\%) = (1 - C_p / C_f) \times 100$$
<sup>(2)</sup>

where  $C_p$  denotes the concentration of bacteria in the permeate solution (cfu/mL), and  $C_f$  denotes the concentration of bacteria in the feed water (cfu/mL). The detailed information about materials, chemicals, membrane characterization, data analysis and QA/QC program were provided in Supporting Information.

## 3. Results and Discussion

#### 3.1. Membrane Surface Morphology

Surface morphology and structure of the pristine and modified PVDF membranes were investigated through SEM (Figure 1) and AFM imaging (Figure S3). According to Figures 1(a) ~ (b) and Figures S3(A) ~ (B), the pristine membrane surface had pores with average size of 0.1  $\mu$ m in diameter, and its average roughness (Ra) was 120 nm. After plasma-induced PAA polymerization, a PAA layer with net structure formed on the membrane surface, and the surface roughness decreased to 100 nm (Figures 1(c) ~ (d) and Figures S3(C) ~ (D)).

ZnO-Ag nanocomposites were immobilized to PAA-coated membrane surface through combining with carboxyl groups of PAA, forming a nanocomposite coating with some clusters and increasing the roughness to 191 nm (Figures 1(e) ~ (f) and Figure S3(E)). Previous studies reported that PAA coating could enable homogeneous surface functionalization with ZnO nanoparticles (Laohaprapanon et al., 2017). Results of SR-XRF spectra and mappings of ZnO-Ag nanocomposite distribution from



**Figure 1.** SEM images of membrane surfaces for (a) ~ (b) pristine PVDF membrane, (c) ~ (d) PAA-coated membrane, and (c) ~ (d) ZnO-Ag modified membrane. Scale bar: 1  $\mu$ m. SR-XRF mappings of Zn distributions on (g) pristine PVDF and (h) ZnO-Ag modified membrane surfaces, and Ag distributions on (i) pristine PVDF and (j) ZnO-Ag modified membrane surfaces.

membrane surfaces also proved the successful formation of nanocomposite coating. As shown in Figure S4, the SR-XRF spectrum from the pristine membrane surface had small peaks at about 2958 and 4512 eV. These two peaks were ascribed to characteristic X-ray emission K lines of argon (Ar) and titanium (Ti), respectively, which were caused by the existence of Ar in measurement environment and the occurrence of titanium in membrane substrate. As for the spectrum from modified membrane surface, there were two similar peaks, however, the first peak was also contributed to the characteristic X-ray emission L lines of silver (Ag) (Figure S4(c)). In addition, two large peaks at 8638 and 9570 eV from the characteristic X-ray emission lines of Zn  $K\alpha$  and Zn  $K\beta$  were newly detected in the spectrum. Moreover, no Zn and Ag could be measured on the pristine membrane surface from SR-XRF images (Figures 1(g) and 1(i)), whereas both Zn and Ag were observed to cover membrane surface after modification with the same distribution pattern (Figures 1(h) and (j)). These results indicated that ZnO-Ag nanocomposites were immobilized on membrane surface, and the Ag NPs would not split from nanocomposites during the modification process. Thus, the photocatalytic performance of ZnO-Ag nanocomposites under visible light would not be significantly affected after immobilized on membrane surface. This ZnO-Ag nanocomposite coating was expected to significantly improve the wettability, oleophobicity, and antibacterial activity of the PVDF membrane, which could improve the permeate flux and biofouling resistance of the membrane during wastewater treatment.

## 3.2. Factorial Analysis

Based on the obtained experimental data in Table S1, the analysis of variance (ANOVA) for the factorial design was calculated and the result was summarized in Table S2, and the assumptions for ANOVA were verified in Figure S5. Model terms with values of "Prob > F" less than 0.05 were identified to be significant. In this case, A, B, C, BC are significant model terms, and their effects are illustrated in Figure 2. These significant effects and their contributions on the antibacterial activity of the functionalized membrane were summarized in Figure S6. The '-' signage represented a negative effect on the response, which indicated that the increase of this factor level would lead to a decrease in cfu number on membrane surface (an improvement of antibacterial activity).

As shown in Figures  $2(a) \sim (c)$ , all three individual parameters had significant negative effects on the cfu number on membrane surface. This indicated that the antibacterial activity of the functionalized membrane could be significantly improved under visible light condition and with ZnO-Ag nanocomposites which obtained under higher Ag concentration and sintering temperature. Besides, the effect of factor B (Sintering temperature) is the most significant one, which contributed 78.56% to the decrease of cfu number (Figure S6). It was also found that the interaction effects of factor B (Sintering temperature) and factor C (Light condition) was significant (Figure 2(d)). Compared to under visible light condition, the cfu number on functionalized membrane surface decreased more significant with the increase of sintering temperature under dark condition, though the overall cfu number under visible light condition was smaller than that under dark condition. Based on such results of factorial analysis, how the three factors affected the membrane surface property and antibacterial activity was further investigated in the following chapters.

## 3.3. The Effects of Ag Concentration

To assess the impacts of nanocomposite coatings with different Ag depositions on the property of membrane surface, different Zn-Ag nanocomposites (1% m/v ZnO with 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mM Ag) were synthesized and immobilized on functionalized membranes. Water contact angle, under-water oil contact angle, and surface energy for the pristine and functionalized PVDF membranes were measured. As shown in Figures  $3(a) \sim (b)$ , the pristine PVDF membrane showed poor hydrophilicity and oleophobicity with a water contact angle of approximately 94.4° and under-water oil contact angle of 54.1°. After modification, the ZnO-Ag nanocomposite coating significantly improved the membrane hydrophilicity as expected, reflected by the reduced water contact angle ( $< 30^{\circ}$ ). Meanwhile, the coating remarkably increased the under-water oil contact angle (> 150°), indicating considerably improved oleophobicity on the modified membrane surface (Figure 3(b)). In addition, increasing the Ag content in ZnO-Ag nanocomposites neither continued to significantly improve the membrane hydrophilicity, nor contribute to oleophobicity enhancement. To understand the detailed changes of membrane hydrophilicity, surface energy corresponding to each membrane was calculated (Figure 3(c)). The pristine PVDF membrane had relatively small surface energy, which was mainly composed of dispersion force. After modification, the surface energy was doubled and mainly contributed by significantly increased polar force. These results indicated that the ZnO-Ag nanocomposite coating greatly reduce the dispersion force and strengthen the polar force for modified membrane surface. Besides, with the increase of Ag content, the dispersion force slightly increased from 8.85 to 13.09 mN/m, the polar force declined from 55.58 to 50.00 mN/m, and thus the total surface energy did not changed significantly.



Figure 2. Significant factor effects: (a)  $\sim$  (c) main effects of individual parameters, and (d) interaction effect of factors B and C.

However, the Ag content of ZnO-Ag nanocomposites had significant effects on the antibacterial activity of modified membrane under both visible light and dark conditions. Figure 3(d) compared the relative number of viable E. coli cells after 3 h of contact with membrane surfaces. After bacteria exposure, attached cells on the membrane surfaces were detached through moderate sonication in saline solution and incubated 24 h for cfu plate counting. The cfu data was then normalized to the data of the pristine PVDF membrane for analysis. It was found that the modified PVDF membranes showed lower cfu counts, indicating much higher antibacterial activities compared to the pristine membrane, and increasing Ag contents further improved the antibacterial activity. In addition, the antibacterial activity of modified PVDF membranes under the visible light condition was stronger than that under the dark condition. The numbers of viable E. coli cells attached on ZnO-3Ag modified membrane were only 35.7 and 46.2% of that on the pristine membrane under visible light and dark conditions, respectively. These numbers decreased to 16.2 and 27.7% for ZnO-7Ag modified membrane, 16.2 and 24.6% for ZnO-8Ag modified membrane. These results demonstrated that the ZnO-Ag nanocomposite coating led to the increase of membrane antibacterial activities under both visible light and dark conditions.

The cfu results could be influenced not only by the cytotoxicity of nanocomposites but also by the ability of bacteria to adhere to membrane surface. Compared to the pristine PVDF membrane, the much better hydrophilicity and oleophobicity of modified membrane could significantly mitigate the adhesion of bacteria to surface (Anselme et al., 2010; Lee et al., 2010), though the slightly higher roughness might enhance cell adhesion (Chang et al., 2016). Note that because of the small amount of immobilized nanocomposites on the membrane surface, the exploration of cytotoxicity and relevant mechanism required the use of free ZnO-Ag nanocomposites suspended in solution. Thus, the induced intracellular ROS after contacting with nanocomposites were measured, and the results were presented in Figure S7. It was evident that the intensities of intracellular ROS induced by ZnO-Ag nanocomposites were higher than that by ZnO NPs under both visible light and dark conditions. A similar relationship between Ag content and antibacterial activity was also observed, corresponding to modified membranes. This could be attributed to both non-photocatalytic and photocatalytic antibacterial activities of ZnO-Ag nanocomposites. On one hand, nanocomposites with higher Ag content would release more Ag+ ions into water, inducing more intracellular ROS. On the other hand, the photocatalytic antibacterial activity of ZnO-Ag nanocomposites could be triggered by visible light, and be increased with Ag content, thus resulting in stronger stress responses to bacteria (Ghosh et al., 2012). Nevertheless, the antibacterial activities could not be obviously enhanced for ZnO-7Ag and ZnO-8Ag nanocomposites and the corresponding modified membranes. This could be because that the surfaces of ZnO-7Ag and ZnO-8Ag nanocomposites were completely covered by Ag NPs, reaching their limit of photocatalytic antibacterial activity. Therefore, the modified membrane with ZnO-7Ag nanocomposites was selected for further research.

## 3.4. The Effects of Sintering Temperature

It was reported that, during deposition, most of  $Ag^+$  ions were reduced to metallic Ag (Ag(0)) on the ZnO NP surface

42

with a part of oxidized Ag (Ag(I)) remained unreacted or from reoxidation of Ag in air (Zhang et al., 2008). The Ag(I) and a portion of Ag(0) on ZnO-7Ag nanocomposites would become Ag<sub>2</sub>O after thermal treatment at 200 °C in air, and most of Ag(I) would decompose to Ag(0) during thermal treatment at 450 °C (Zhang et al., 2008). Thus, to study the effects of such difference on the surface property and antibacterial activity of nanocomposite coating for modified membrane and further optimize membrane performances, ZnO-7Ag nanocomposites were sintered at 60, 200 and 450 °C for 2 h before immobilization to PVDF membrane surface. All three types of ZnO-7Ag nanocomposites showed the same wurtzite structure of ZnO in Xray powder diffraction (XRD) patterns, and the diffraction peaks for Ag(0) were also observed (Figure S8) (Yıldırım et al., 2013). Besides, the peaks for Ag(0) in the spectrum of ZnO-7Ag 450 nanocomposites had relatively higher intensity, which indicated its higher degree of crystallinity for Ag after thermal treatment at 450 °C. Unexpectedly, no peak for Ag(I) or Ag<sub>2</sub>O could be found in all samples, which might be due to their low amounts. The membranes functionalized with corresponding nanocomposites were denoted as modified membrane ZnO-7Ag 60, modified membrane ZnO-7Ag 200, and modified membrane ZnO-7Ag 450, respectively.

The hydrophilicity, oleophobicity, surface charge, and antibacterial activity of the membranes were evaluated and compared in Figure 4. Among them, the modified membrane ZnO-7Ag 450 was the most hydrophilic with the smallest water contact angle  $(21.6^{\circ})$  (Figure 4(a)), which could be attributed to the strongest dispersive force on its surface due to Ag(0) (Figure 4(b)). The modified membrane ZnO-7Ag 200 showed relatively poor hydrophilicity with 29.8° water contact angle (Figure 4(a)), meanwhile, its surface dispersive force was the smallest and the polar force was the largest (Figure 4(b)). The largest polar force could be due to the higher polarity of Ag<sub>2</sub>O on ZnO-7Ag 200 NPs compared to that of metallic Ag on ZnO-7Ag 450 NPs (Kadam et al., 2016). However, all the three membranes had similar under-water oil contact angles, indicating that their oleophobicities were comparable (Figure 4(a)). As for the property of surface charge, zeta potentials of the pristine PVDF and modified membranes were measured and presented in Figure 4(c). After modification, the membrane surfaces exhibited lower zeta potentials at low pH levels (pH < 5), but slightly higher zeta potentials at high pH levels (pH > 9). At pH 7, compared with the pristine PVDF membrane, the modified membrane ZnO-7Ag 200 showed a similar surface charge, and the modified membranes with ZnO-7Ag 60 and ZnO-7Ag 450 NPs displayed much more negative charges. This could be reasonable, since the zeta potential of  $Ag_2O$  was higher than that of Ag(0)(Kim et al., 2004; Wang et al., 2020), leading to the relative positive charge of the modified membrane ZnO-7Ag 200.

Figure 4(d) summarized the relative numbers of viable *E. coli* cells after contacting with ZnO-7Ag membrane surfaces for 3 h. As expected, all the three ZnO-7Ag membrane surfaces showed higher antibacterial activities under light conditions than that under the dark condition. In addition, it was note-worthy that their antibacterial activities were comparable under the visible light and UV light conditions. Moreover, under all



**Figure 3.** Water contact angles in air (a), under-water oil contact angles (b), and surface energies (c) of the pristine and modified PVDF membranes under different Ag contents; (d) relative number of viable *E. coli* cells after contact with membrane surfaces for 3 h, determined through cfu plate counting and normalized to the result of the pristine PVDF membrane surface.

conditions, the numbers of viable E. coli cells attached on both modified membranes ZnO-7Ag 200 and 450 were smaller than that on modified membrane ZnO-7Ag 60, and the modified membrane ZnO-7Ag 450 had the smallest number. These results could be caused by a combination of membrane surface properties and cytotoxicity of nanocomposites. In addition to the hydrophilicity and oleophobicity mentioned above, surface charge could also affect the biofouling resistance of membranes (Hadi et al., 2019). It was reported that the surface charges of most bacterial cells (including E. coli) were negative (Soni et al., 2008), thus the electrostatic repulsion between the negatively charged membrane surface and the bacteria would not be conducive to cell adhesion. Hence, the most hydrophilic and negatively charge surface helped the modified membrane ZnO-7Ag 450 achieve the best antibacterial activity. Nevertheless, it was interesting that modified membrane ZnO-7Ag 200 with larger water contact angle and higher zeta potential showed lower viability of E. coli cells compared to the modified membrane ZnO-7Ag 60.

## 3.5. Mechanism of Antibacterial Activity

To further elucidate the contribution of cytotoxicity of nanocomposites to antibacterial activity of modified membranes and to explore the relevant mechanism, intracellular SOD and CAT activities were measured to reflect oxidative stresses from superoxide radicals ( $O_2^{-}$ ) and  $H_2O_2$ , respectively, the genera-

tion of hydroxyl radical ('OH) was also assessed through EPR measurement (He et al., 2020). As shown in Figure 5 and Figure S9, all the three indicators of nanocomposites demonstrated much higher oxidative stress in visible light condition than that in the dark. It was thus unsurprising to observe higher antibacterial activities of modified membranes under light conditions in Figure 4(d). Compared with ZnO NPs, the oxidative stresses induced by all ZnO-7Ag nanocomposites were more intense under the visible light condition (Figure 5); under the dark condition, the intracellular SOD activities of nanocomposites were stronger (Figure 5(a)), while the CAT activities and the generated EPR intensities of nanocomposites were similar (Figure 5(b) and Figure S9). These suggested that the deposited Ag contributed to the improvement of photocatalytic antibacterial activity for nanocomposites, due to the intensified chemical oxidation which stem from increased ROS generation under light condition. Increasing oxidative stress from O2<sup>--</sup> could be the main contribution of Ag to enhance the non-photocatalytic antibacterial activity of ZnO-Ag nanocomposites.

Additionally, all the three ZnO-7Ag nanocomposites caused comparable intracellular SOD activities in light and CAT activities in dark. The intracellular SOD activities induced by nano-composites in dark could be ordered as: ZnO-7Ag 60 > ZnO-7Ag 200 > ZnO-7Ag 450 (Figure 5(a)), while the ZnO-7Ag 450 nanocomposites lead to the most intensive intracellular SOD activity in light (Figure 5(b)). Meanwhile, the intensity of 'OH



**Figure 4.** Water contact angles in air and under-water oil contact angles (a), and surface energies (b) of ZnO-7Ag modified membranes; (c) surface zeta potentials of the pristine and ZnO-7Ag modified membranes; (d) relative number of viable *E. coli* cells after contact with ZnO-7Ag membrane surfaces for 3 h, determined by cfu plate counting and normalized to the result of the pristine PVDF membrane surface.

generated by ZnO-7Ag 200 nanocomposites in light was the highest (Figure 5(c)). This intensity was slightly higher than that by ZnO-7Ag 450 nanocomposites, and was considerably higher than that by ZnO-7Ag 60 nanocomposites. These could be ascribed to that the ZnO-7Ag 60 nanocomposite contained a small portion of Ag(I) which could easily release Ag<sup>+</sup> ions to water, leading to the highest intracellular SOD activity in dark and lowest 'OH intensity in light. After thermal treatment, this portion of Ag(I) and a part of Ag(0) would become  $Ag_2O$  on ZnO-7Ag 200 nanocomposite surface, and most of Ag(I) would decompose to Ag(0) on ZnO-7Ag 450 nanocomposite surface. It was reported that, the deposition of Ag(0) could be the main reason for the photoexcitation of nanocomposites in the visible light region because of plasma resonance, and could contribute to the stability of the photocatalysts; the Ag<sub>2</sub>O could act as active sites to enhance photocatalytic abilities (Zhang et al., 2008).

That could be the reason why the ZnO-7Ag 200 nanocomposites could result in the highest intensity of 'OH and the ZnO-7Ag 450 nanocomposites could stimulate the strongest intracellular SOD activity under the visible light condition. Thus, the generation of 'OH could be the main contributor of the lower viability of *E. coli* cells for modified membrane ZnO-7Ag 200 in light. Taken together, the results from surface property investigation, plate counting assay, and ROS generation analysis demonstrated that the modified membrane ZnO-7Ag 450 had the strongest antibacterial activity among the modified membranes under both light and dark conditions.

## 3.6. Membrane Surface Chemistry

The organic functionalities of the membrane surfaces were investigated with ATR-FTIR spectroscopy and mapping. The spectra obtained from membrane surfaces and NPs were summarized and compared in Figure 6(a) and Figure S10 within a wavenumber range of 400 ~ 4000 cm<sup>-1</sup>. Spatial distributions of peak intensity at wavenumbers of 1377, 1405, 1515, 1590, and 1650 cm<sup>-1</sup> on membrane surfaces obtained from synchrotron ATR-FTIR mapping were shown in Figure 6(b). According to Figures 6(a-5) to (a-8) and Figure S10(b), no significant difference could be observed from the spectra of ZnO NPs and ZnO-Ag nanocomposites. This could be due to the characteristic vibration band of Ag-O was approximately 500 cm<sup>-1</sup> (Kadam et al., 2016), which was hidden by the broad and intensified absorption in the range of  $400 \sim 600 \text{ cm}^{-1}$  because of the stretching mode of Zn-O (Azizi et al., 2016). All spectra of membrane surfaces showed strong absorbance at 1180 and 1405 cm<sup>-1</sup>, which were corresponded to vibrations of C-F and C-H from PVDF,



**Figure 5.** Relative intracellular (a) SOD and (b) CAT activities of *E. coli* (10<sup>8</sup> cfu/mL) induced by nanoparticles after 1 h of contact; (c) EPR spectra of ZnO NPs and ZnO-7Ag nanocomposites after the irradiation with xenon lamp for 30 min.

respectively (Pan et al., 2017). After surface modification, much more intensified absorptions at the wavenumber of 400 ~ 600 cm<sup>-1</sup> were observed in the spectra of modified membrane surfaces owing to the coverage of ZnO-Ag nanocomposites. Besides, absorption bands at about 1590 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> with identical spatial distributions were newly observed on modified membrane surfaces. Their appearances could be due to the formations of bidentate and monodentate species between carboxyl group and ZnO during the immobilization process of ZnO-Ag nanocomposites on PAA layer (Liu et al., 2020). More obvious absorbance at 1377 cm<sup>-1</sup> could be witnessed on the spectra of modified membrane surfaces with higher content of Ag (Figure S10(a)), which could be attributed to N-O bonds from unreacted AgNO<sub>3</sub> on ZnO-Ag nanocomposites (Gan et al., 2016). Thus, compared to the pristine membrane surface with same spatial distributions at 1405 and 1377 cm<sup>-1</sup>, modified membrane surfaces showed strengthened peak intensities at 1377 cm<sup>-1</sup>, and their distributions were significantly different with those at 1405 cm<sup>-1</sup> (Figure 6(b)). In addition, a small peak at 1515 cm<sup>-1</sup> was shown in the spectrum of modified membrane ZnO-7Ag 200, whereas it was not obvious in the spectra of modified membranes ZnO-7Ag 60 and ZnO-7Ag 450 ((Figure 6(a)) and Figure S11). The reason might be that carboxyl groups of PAA

complexed with the  $Ag_2O$  to form monodentate or bidentate species on the surface of modified membrane ZnO-7Ag 200 (Gan et al., 2016). However, modified membranes ZnO-7Ag 60 and ZnO-7Ag 450 also displayed similar spatial distributions at 1515 cm<sup>-1</sup> with the other three wavenumbers (Figure 6(b)). This was probably because that a small amount of Ag(I) existed in these two ZnO-7Ag nanocomposites and also combined with PAA.

XPS analyses were also performed to study the chemical compositions of membrane surfaces modified with ZnO-7Ag 60, ZnO-7Ag 200, and ZnO-7Ag 450 nanocomposites. As shown in Figure S12(b), evident peaks attributed to Zn 2p and small signals of Ag 3d were newly detected from all XPS wide-scan spectra of modified membranes, which was consistent with the SR-XRF results in Figure S4. Increased intensities of O 1s were also detected due to the ZnO-7Ag nanocomposite coatings on modified membrane surfaces. The C 1s XPS spectra from membrane surfaces before and after modification were showed in Figure S13. Besides three peaks at 284.7, 286.4, and 290.8 eV which were corresponding to binding energies of C-H, C-C, and C-F from PVDF, new energy peaks at 288.7 eV were noticed in the spectra of modified membranes. This peak could be attributed to O=C-O introduced by PAA polymerization (Wu



**Figure 6.** (a) Synchrotron ATR-FTIR spectra from membrane surfaces and NPs, (b) spatial distributions of peak intensity at wavenumbers of 1377, 1405, 1515, 1590, and 1650 cm<sup>-1</sup> on membrane surfaces obtained from synchrotron ATR-FTIR mapping. The mapping area is  $300 \ \mu m \times 300 \ \mu m$ .

et al., 2015). Figure 7 presented the XPS core-level spectra of Ag 3d, Zn 2p, and O 1s from the three ZnO-7Ag nanocomposites and modified membrane surfaces. For ZnO-7Ag nanocomposites, the Ag (3d5/2) and Ag (3d3/2) peaks for Ag(0) at ~367.6 and ~373.6 eV were observed (Corro et al., 2017), and no obvious shift or peak for Ag(I) or Ag<sub>2</sub>O could be measured due to their low contents (Figure 7(a)). Same binding energies of 1021.4 eV for Zn (2p3/2) and 1044.5 eV for Zn (2p1/2) were detected for nanocomposites (Figure 7(c)). Figure 7(e) also showed similar O 1s spectra from nanocomposites, which contained peaks at ~530.2, ~531.4, and ~533.0 eV for lattice oxygen (Zn-O, Ag-O), surface hydroxyl group, and adsorbed water, respectively (Lakshmi Prasanna and Vijayaraghavan, 2015). After immobilization of nanocomposites to membrane surfaces, all peak positions of Ag 3d and Zn 2p significantly shifted toward higher binding energies on the spectra of all modified membrane surfaces (Figures 7(c) and (d)). Previous studies and FTIR spectra analyses demonstrated that the carboxyl groups of PAA could act as complexing ligands to combine with ZnO (Isawi et al., 2016), which may cause the shifts of Zn 2p peak positions (~0.7 eV). Thus, the shifts of binding energies for Ag 3d (~0.6 eV) could be attributed to the complexation between PAA layer and Ag NPs. In addition, the energy peaks of lattice oxygen from ZnO-7Ag nanocomposites could not be found in Figure 7(f), while shifts of C-O peak at ~533.0 eV for the pristine PVDF membrane to ~532.2 eV for modified membranes were observed (Figure 7(f) and Figure S14), which might be

owing to the formation of C-O-M (M: Zn or Ag) (Song et al., 2015). Taken together, these results suggested that the PAA layer could help immobilize ZnO-7Ag nanocomposites by forming covalent bonds of C-O-M on nanocomposite surfaces, thus generating nanocomposite coatings on modified membrane surfaces.

## 3.7. Membrane Performances

The filtration performance and antibacterial behavior of the modified membranes with ZnO-7Ag nanocomposites were investigated and compared to that of the pristine PVDF membrane. The secondary wastewater effluent from municipal wastewater treatment plant was selected to be the feed solution, since it contained large number of bacteria and organic pollutants. Before application to wastewater treatment, the water permeability of membranes were evaluated through testing pure-water fluxes. According to Figure 8(a), the pure-water flux was significantly increased from 104.4 L/m<sup>2</sup> min for the pristine membrane to 802.2, 799.8, 823.2 L/m<sup>2</sup>·min after surface modification with ZnO-7Ag 60, ZnO-7Ag 200, and ZnO-7Ag 450 nanocomposites, respectively. Results demonstrated that all the modified membranes showed much larger water permeability due to their stronger surface hydrophilicity, which was a result of ZnO-7Ag nanocomposite coatings. The oleophobic properties and antibacterial activities of nanocomposite coatings also contributed to the improvement of biofouling resistance for wastewater treatment. As shown in Figure 8(b), the stable permeate



**Figure 7.** (a) ~ (b) Ag 3d, (c) ~ (d) Zn 2p, (e) ~ (f) O 1s XPS spectra of (1) ZnO-7Ag 60 nanocomposites and its modified membrane surface, (2) ZnO-7Ag 200 nanocomposites and its modified membrane surface, and (3) ZnO-7Ag 450 nanocomposites and its modified membrane surface.

flux of pristine membrane was less than 10 L/m<sup>2</sup>·min during a 100 min of filtration operation. In comparison, the modified membranes had notably high permeate fluxes, which were larger than 170, 200, and 250 L/m<sup>2</sup>·min for modified membranes ZnO-7Ag 60, ZnO-7Ag 200, and ZnO-7Ag 450, respectively.



**Figure 8.** Performances of the pristine and modified PVDF membranes: (a) pure-water flux, (b) permeated flux with time, and (c) relative number of viable *E. coli* cells on used membrane surfaces before and after irradiations.

Besides, the viabilities of bacteria attached on used membrane surfaces after filtration operation were shown in Figure 8(c). It could be found that much less viable bacteria could accumulate on modified membranes. The improved hydrophilicity and reduced bacteria adhesion combined with the remarkable antibacterial properties of ZnO-7Ag nanocomposites could explain the mechanism by which modified membranes could hinder the development of biofilm. For example, the best surface hydrophilicity, most negative charge, and strongest antibacterial activity of modified membrane ZnO-7Ag 450 were adverse to bacteria accumulation and survival, leading to its highest permeate flux and lowest bacteria viability among modified membranes. In addition, Figure 8(c) displayed the changes of bacteria viabilities on used modified membranes after exposure surfaces to visible and UV light irradiations for 20 min. The amounts of viable bacteria were obviously decreased for modified membranes after exposure, while the same observation was not noted for the pristine membrane. Moreover, the changes under visible and UV light irradiations for modified membranes could not be considered statistically different, further indicating the similar antibacterial activity of modified membranes under both light irradiations. Thus, the modification with ZnO-7Ag nanocomposites conferred the membrane surfaces great abilities to improve biofouling resistance during filtration process and enhanced photocatalytic antibacterial activity to mitigate biofouling under visible light.

The efficiencies of modified membranes for wastewater treatment were expected to be significantly improved due to their excellent hydrophilicity and antibacterial properties. To further verify this, the stabilities of the membrane performances were also evaluated through recycling tests, and the results were shown in Figure 9. Considering the photocatalytic antibacterial activity of modified membranes, the fouled membrane surfaces were exposed to visible light (20 W) in DI water for 20 min to alleviate biofouling after each cycle. Compared to modified membranes, the pristine PVDF membrane exhibited much lower stable permeate fluxes for all cycles (Figure 9(a)). As expected, modified membranes achieved super-high permeate fluxes and comparable removal rate of bacteria from wastewater during each cycle, and the removal rate kept steady among cycles (Figure 9(b)). However, bacteria accumulated on membrane surfaces could not be completely inactivated within 20 min of exposure (Figure 8(c)), which may result in the continuous growth of biofilms on membrane surfaces during recycling tests. Thus, the stable permeate fluxes decreased 39.4% for the pristine membrane, 30.8% for modified membrane ZnO-7Ag 60, 24.3% for modified membrane ZnO-7Ag 200, and 15.0% for modified membrane ZnO-7Ag 450, respectively (Figure 9(a)). It could be seen that the decreasing amplitudes of permeate fluxes for modified membranes were smaller than that of the pristine membrane under the same filtration condition. Particularly, the modified membrane ZnO-7Ag 450 showed the largest permeate flux, lowest decreasing amplitude, and highest bacteria removal rate among all the membranes in each cycle. According to the above analysis, three aspects could contribute to the best performance of the modified membrane ZnO-7Ag 450. (1) Its excellent hydrophilicity brought about the superhigh water recovery. (2) The oleophobic and negatively charged surface reduced bacteria adherence and organics accumulation, and the strong non-photocatalytic antibacterial activity could

deactivate some of the adhered bacteria. This could efficiently reduce the formation of biofilm and cake layer on membrane surfaces. (3) The photocatalytic antibacterial activity could further sterilize adhered bacteria under visible light, ensuring favourable biofouling resistance and stable separation performance.



**Figure 9.** Performances of the pristine and modified PVDF membranes under different cycles: (a) stable permeated flux, and (b) bacteria removal rate.

## 4. Conclusions

The strategy of PVDF membrane functionalization with ZnO-Ag nanocomposites was proposed to improve treatment efficiency and mitigate biofouling for membrane-based processes. ZnO-Ag nanocomposites could be attached onto the membrane surface through covalent bonding with bridging agent which was a PAA layer introduced by cold plasma-induced graft-polymerization. The formation of ZnO-Ag nanocomposite coating endowed properties of hydrophilicity, oleophobicity, and non-photocatalytic antibacterial activity to modified membrane. The modified membrane thus showed both strong antiadhesive and biofouling resistance, while maintaining superhigh water flux without sacrificing bacteria rejection rates during filtration process. The photocatalytic antibacterial activity of ZnO-Ag nanocomposites further improved the membrane biofouling resistance through simple exposure to visible light. It was found that the Ag content of ZnO-Ag nanocomposites could significantly affect the membrane antibacterial activity

rather than surface hydrophilicity. In addition, the membranes modified with ZnO-7Ag nanocomposites, which were obtained under 200 and 450 °C of sintering, had more improved performances; the modified membrane ZnO-7Ag 450 achieved the best performance due to the most Ag(0) composition. Overall, the ZnO-Ag nanocomposite modified membrane could be promising for the treatment of biological contaminated wastewater with high efficiency.

Acknowledgments. This research was supported by the Natural Science and Engineering Research Council of Canada. The authors are particularly thankful to the beamlines of Very Sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron (VESPERS) and Mid Infrared Spectromicroscopy (MID-IR) at Canadian Light Source for providing support in measurements and analysis. Research about XRF and FTIR described in this paper was performed at the Canadian Light Source.

## References

- Abdel-Karim, A., El-Naggar, M.E., Radwan, E.K., Mohamed, I.M., Azaam, M. and Kenawy, El-R. (2021). High-performance mixedmatrix membranes enabled by organically/inorganic modified montmorillonite for the treatment of hazardous textile wastewater. *Chem. Eng. J.* 405, 126964. https://doi.org/10.1016/j.cej.2020.126964
- Ahsani, M., Hazrati, H., Javadi, M., Ulbricht, M. and Yegani, R. (2020). Preparation of antibiofouling nanocomposite PVDF/Ag-SiO<sub>2</sub> membrane and long-term performance evaluation in the MBR system fed by real pharmaceutical wastewater. *Sep. Purif. Technol.* 249, 116938. https://doi.org/10.1016/j.seppur.2020.116938
- Ali, A., Quist-Jensen, C.A., Jørgensen, M.K., Siekierka, A., Christensen, M.L., Bryjak, M., Hélix-Nielsen, C. and Drioli, E. (2021). A review of membrane crystallization, forward osmosis and membrane capacitive deionization for liquid mining. *Resour. Conserv. Recycl.* 168, 105273. https://doi.org/10.1016/j.resconrec.2020.105273
- Anselme, K., Davidson, P., Popa, A.M., Giazzon, M., Liley, M. and Ploux, L. (2010). The interaction of cells and bacteria with surfaces structured at the nanometre scale. *Acta Biomater*. 6(10), 3824-3846. https://doi.org/10.1016/j.actbio.2010.04.001
- Azizi, S., Mohamad, R., Rahim, R.A., Moghaddam, A.B., Moniri, M., Ariff, A., Saad, W.Z. and Namvab, F. (2016). ZnO-Ag core shell nanocomposite formed by green method using essential oil of wild ginger and their bactericidal and cytotoxic effects. *Appl. Surf. Sci.* 384, 517-524. https://doi.org/10.1016/j.apsusc.2016.05.052
- Chang, C.C., Kolewe, K.W., Li, Y., Kosif, I., Freeman, B.D., Carter, K.R., Schiffman, J.D. and Emrick, T. (2016). Underwater superoleophobic surfaces prepared from polymer zwitterion/dopamine composite coatings. *Adv. Mater. Interfaces.* 3(6), 1500521. https:// doi.org/10.1002/admi.201500521
- Chen, X.J., Huang, G., An, C.J., Feng, R.F., Yao, Y., Zhao, S., Huang, C. and Wu, Y.H. (2019). Plasma-induced poly(acrylic acid)-TiO<sub>2</sub> coated polyvinylidene fluoride membrane for produced water treatment: Synchrotron X-Ray, optimization, and insight studies. *J. Clean. Prod.* 227, 772-783. https://doi.org/10.1016/j.jclepro.2019.04.226
- Chen, X.J., Huang, G., Li, Y.P., An, C.J., Feng, R.F., Wu, Y.H. and Shen, J. (2020). Functional PVDF ultrafiltration membrane for Tetrabromobisphenol-A (TBBPA) removal with high water recovery. *Water Res.* 181, 115952. https://doi.org/10.1016/j.watres.2020.115 952
- Chen, X.J., Huang, G.H., An, C.J., Feng, R.F., Wu, Y.H. and Huang, C. (2022a). Superwetting polyethersulfone membrane functionalized with ZrO<sub>2</sub> nanoparticles for polycyclic aromatic hydrocarbon removal. J. Mater. Sci. Technol. 98, 14-25. https://doi.org/10.1016/j.

jmst.2021.01.063

- Chen, X.J., Huang, W. and Zhang, B.Y. (2022b). Perspectives on surface functionalization of polymeric membranes with metal and metal-oxide nanoparticles for water/wastewater treatment. *J. Environ. Inform. Lett.* 7(2), 103-125. https://doi.org/10.3808/jeil.202200083
- Corro, G., Vidal, E., Cebada, S., Pal, U., Bañuelos, F., Vargas, D. and Guilleminot, E. (2017). Electronic state of silver in Ag/SiO<sub>2</sub> and Ag/ZnO catalysts and its effect on diesel particulate matter oxidetion: An XPS study. *Appl. Catal. B.* 216, 1-10. https://doi.org/10. 1016/j.apcatb.2017.05.059
- Dechnik, J., Gascon, J., Doonan, C.J., Janiak, C. and Sumby, C.J. (2017). Mixed-matrix membranes. *Angew. Chem. Int. Ed.* 56(32), 9292-9310. https://doi.org/10.1002/anie.201701109
- El-Samak, A.A., Ponnamma, D., Hassan, M.K., Adham, S., Karim, A., Ammar, A., Alser, M., Shurbaji, S., Eltai, N.O. and Al-Maadeed, M.A.A. (2021). Multifunctional oil absorption with macroporous polystyrene fibers incorporating silver-doped ZnO. ACS Omega. 6(12), 8081-8093. https://doi.org/10.1021/acsomega.0c05683
- Gan, Y., Bai, S.B., Hu, S.L., Zhao, X. and Li, Y.F. (2016). Reaction mechanism of thermally-induced electric conduction of poly(vinyl alcohol)–silver nitrate hybrid films. *RSC Adv.* 6(61), 56728-56737. https://doi.org/10.1039/C6RA08994A
- Ghosh, S., Goudar, V.S., Padmalekha, K.G., Bhat, S.V., Indi, S.S. and Vasan, H.N. (2012). ZnO/Ag nanohybrid: Synthesis, characterization, synergistic antibacterial activity and its mechanism. *RSC Adv.* 2(3), 930-940. https://doi.org/10.1039/C1 RA00815C
- Hadi, P., Yang, M.Y., Ma, H.Y., Huang, X.Y., Walker, H. and Hsiao, B.S. (2019). Biofouling-resistant nanocellulose layer in hierarchical polymeric membranes: Synthesis, characterization and performance. *J. Membr. Sci.* 579, 162-171. https://doi.org/10.1016/j.memsci.2019. 02.059
- He, L., Li, Y.P., Zhu, F., Sun, X., Herrmann, H., Schaefer, T., Zhang, Q.Z. and Wang, S.G. (2020). Insight into the mechanism of the OHinduced reaction of ketoprofen: A combined DFT simulation and experimental study. J. Environ. Inform. 35(2). 138-147. https:// doi.org/10.3808/JEI.201900408
- Huang, J., Huang, G.H., An, C.J., Xin, X.Y., Chen, X.J., Zhao, Y.Y., Feng, R.F. and Xiong, W.H. (2020a). Exploring the use of ceramic disk filter coated with Ag/ZnO nanocomposites as an innovative approach for removing *Escherichia coli* from household drinking water. *Chemosphere*. 245, 125545. https://doi.org/10.1016/j.chemo sphere.2019.125545
- Huang, W., Chen, X. J., Fan, Y.R. and Li, Y.P. (2020b). Management of contaminated drinking water source in rural communities under climate change. *J. Environ. Inform.* 39(2), 136-151. https://doi.org /10.3808/jei.202000431
- Huang, X.J., Chen, Y.B., Feng, X.S., Hu, X.Y., Zhang, Y.F. and Liu, L. (2020c). Incorporation of oleic acid-modified Ag@ZnO coreshell nanoparticles into thin film composite membranes for enhanced antifouling and antibacterial properties. J. Membr. Sci. 602, 117956. https://doi.org/10.1016/j.memsci.2020.117956
- Isawi, H., El-Sayed, M.H., Feng, X.S., Shawky, H. and Abdel Mottaleb, M.S.A. (2016). Surface nanostructuring of thin film composite membranes via grafting polymerization and incorporation of ZnO nanoparticles. *Appl. Surf. Sci.* 385, 268-281. https://doi.org/10.1016 /j.apsusc.2016.05.141
- Kadam, A., Dhabbe, R., Gophane, A., Sathe, T. and Garadkar, K. (2016). Template free synthesis of ZnO/Ag<sub>2</sub>O nanocomposites as a highly efficient visible active photocatalyst for detoxification of methyl orange. J. Photochem. Photobiol. B, Biol. 154, 24-33. https:// doi.org/10.1016/j.jphotobiol.2015.11.007.
- Kim, K.D., Han, D.N. and Kim, H.T. (2004). Optimization of experimental conditions based on the Taguchi robust design for the formation of nano-sized silver particles by chemical reduction method. *Chem. Eng. J.* 104(1), 55-61. https://doi.org/10.1016/j.cej.2004.08. 003

- Lakshmi Prasanna, V. and Vijayaraghavan, R. (2015). Insight into the mechanism of antibacterial activity of ZnO: Surface defects mediated reactive oxygen species even in the dark. *Langmuir*. 31(33), 9155-9162. https://doi.org/10.1021/acs.langmuir.5b02266
- Laohaprapanon, S., Vanderlipe, A.D., Doma Jr, B.T. and You, S.J. (2017). Self-cleaning and antifouling properties of plasma-grafted poly(vinylidene fluoride) membrane coated with ZnO for water treatment. J. Taiwan. Inst. Chem. Eng. 70, 15-22. https://doi.org/ 10.1016/j.jtice.2016.10.019
- Lee, W., Ahn, C.H., Hong, S., Kim, S., Lee, S., Baek, Y. and Yoon, J. (2010). Evaluation of surface properties of reverse osmosis membranes on the initial biofouling stages under no filtration condition. *J. Membr. Sci.* 351(1), 112-122. https://doi.org/10.1016/j.memsci. 2010.01.035
- Li, J.H., Shao, X.S., Zhou, Q., Li, M.Z. and Zhang, Q.Q. (2013). The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance. *Appl. Surf. Sci.* 265, 663-670. https://doi.org/10.1016/j.apsusc.2012.11.072
- Li, M.N., Chen, X.J., Wan, Z.H., Wang, S.G. and Sun, X.F. (2021). Forward osmosis membranes for high-efficiency desalination with Nano-MoS<sub>2</sub> composite substrates. *Chemosphere*. 278, 130341. https: //doi.org/10.1016/j.chemosphere.2021.130341
- Li, M.N., Huang, G., Chen, X.J., Yin, J.N., Zhang, P., Yao, Y., Shen, J., Wu, Y.W. and Huang, J. (2022). Perspectives on environmental applications of hexagonal boron nitride nanomaterials. *Nano Today*. 44, 101486. https://doi.org/10.1016/j.nantod.2022.101486
- Liu, H. and Huang, G.W. (2021). A Study of *E. coli* contamination in household drinking water: A case study in rural areas of Zhangye City, Northwest China. *J. Environ. Inform. Lett.* 5(2), 111-119. https: //doi.org/10.3808/jeil.202100064
- Liu, Y.Q., Huang, G., An, C.J., Chen, X.J., Zhang, P., Feng, R.F. and Xiong, W.H. (2020). Use of Nano-TiO<sub>2</sub> self-assembled flax fiber as a new initiative for immiscible oil/water separation. *J. Clean. Prod.* 249, 119352. https://doi.org/10.1016/j.jclepro.2019.119352
- Pan, Y., Yu, Z.X., Shi, H., Chen, Q., Zeng, G.Y., Di, H.H., Ren, X.Q. and He, Y. (2017). A novel antifouling and antibacterial surfacefunctionalized PVDF ultrafiltration membrane via binding Ag/SiO<sub>2</sub> nanocomposites. J. Chem. Technol. Biotechnol. 92(3), 562-572. https://doi.org/10.1002/jctb.5034
- Ponnaiyan, P. and Gopalakrishnan, N. (2019). Enhancement of the PSF/PVP membrane performance by Ag-ZnO incorporation. *Mater. Res. Express.* 6(11), 115006. https://doi.org/10.1088/2053-1591/ab 448a
- Ramil, A., Vázquez-Nion, D., Pozo-Antonio, J.S., Sanmartín, P. and Prieto, B. (2020). Using hyperspectral imaging to quantify phototrophic biofilms on granite. *J. Environ. Inform.* 35(1), 34-44. https:// doi.org/10.3808/jei.201800401
- Song, N., Fan, H.Q. and Tian, H.L. (2015). Reduced graphene oxide/ ZnO nanohybrids: Metallic Zn powder induced one-step synthesis for enhanced photocurrent and photocatalytic response. *Appl. Surf. Sci.* 353, 580-587. https://doi.org/10.1016/j.apsusc.20 15.06.062
- Soni, K.A., Balasubramanian, A.K., Beskok, A. and Pillai, S.D. (2008). Zeta potential of selected bacteria in drinking water when dead, starved, or exposed to minimal and rich culture media. *Curr. Microbiol.* 56(1), 93-97. https://doi.org/10.1007/s002 84-007-9046-z
- Sri Abirami Saraswathi, M.S., Nagendran, A. and Rana, D. (2019). Tailored polymer nanocomposite membranes based on carbon, metal oxide and silicon nanomaterials: A review. J. Mater. Chem. A. 7(15), 8723-8745. https://doi.org/10.1039/C8TA11460A
- Wang, H.F., Liu, X.Q. and Han, S. (2016). The synthesis of a Ag–ZnO nanohybrid with plasmonic photocatalytic activity under visiblelight irradiation: the relationship between tunable optical absorption, defect chemistry and photocatalytic activity. *CrystEngComm.* 18(11), 1933-1943. https://doi.org/10.1039/C5CE 02381E
- Wang, J.L., Tang, X.B., Liu, Y.Y., Xie, B.H., Li, G.B. and Liang, H.

(2022). Self-sustained ultrafiltration coupling vermifiltration for decentralized domestic wastewater treatment: Microbial community and mechanism. *Resour. Conserv. Recycl.* 177, 106008. https://doi.org/10.1016/j.re-sconrec.2021.106008

- Wang, Y., Bi, N., Zhang, H., Tian, W., Zhang, T., Wu, P. and Jiang, W. (2020). Visible-light-driven photocatalysis-assisted adsorption of azo dyes using Ag<sub>2</sub>O. *Colloids Surf. A Physicochem. Eng. Asp.* 585, 124105. https://doi.org/10.1016/j.colsurfa.2019.124105
- Wu, J.D., Jiang, Y.L., Jiang, D.J., He, J., Cai, G.Q. and Wang, J.P. (2015). The fabrication of pH-responsive polymeric layer with switchable surface wettability on cotton fabric for oil/water separation. *Mater. Lett.* 160, 384-387. https://doi.org/10.1016/j.matlet.2015.07. 146
- Yıldırım, Ö.A., Unalan, H.E. and Durucan, C. (2013). Highly efficient room temperature synthesis of silver-doped zinc oxide (ZnO:Ag) nanoparticles: Structural, optical, and photocatalytic properties. J. Am. Ceram. Soc. 96(3), 766-773. https://doi.org/10.1111/jace.12218
- Zhang, H., Wang, G., Chen, D., Lv, X.J. and Li, J.H. (2008). Tuning photoelectrochemical performances of Ag-TiO<sub>2</sub> nanocomposites via reduction/oxidation of Ag. *Chem. Mater.* 20(20), 6543-6549. https://doi.org/10.1021/cm801796q
- Zhu, Y.Z., Wang, J.L., Zhang, F., Gao, S.J., Wang, A.Q., Fang, W.X. and Jin, J. (2018). Zwitterionic nanohydrogel grafted PVDF membranes with comprehensive antifouling property and superior cycle stability for oil-in-water emulsion separation. *Adv. Funct. Mater.* 28(40), 1804121. https://doi.org/10.1 002/adfm.201804121