

Article

Photocatalytic Self-Cleaning PVDF Membrane Blended with MWCNT-ZnO Nanocomposites for RhB Removal

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Abstract: Polyvinylidene fluoride (PVDF) membranes blended with various amounts of MWCNT-ZnO (0.1%–3%) nanocomposites were prepared by the phase inversion method. The effect of nanocomposites blending on the membrane structural and morphological properties was investigated by XRD, FT-IR and SEM techniques. Contact angle measurement reveals that the hydrophilicity of the membrane increases with the increase of nanocomposite content; a reduction of the contact angle from 103° for PVDF to 49° for hybrid membrane was obtained. An optimum amount of 0.5% of MWCNT-ZnO blended in a PVDF hybrid membrane assured 85% removal rate of RhB under UV light irradiation. It was observed that the pollutant removal occurs through the simultaneous action of two processes: adsorption and photocatalysis. By blending with MWCNT-ZnO nanoparticles, the PVDF membrane acquires photocatalytic properties which assure a self-cleaning property in the membrane, increasing its lifetime.

Keywords: PVDF membrane; MWCNT-ZnO nanocomposites; photocatalysis; hydrophilicity



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1. Introduction

In recent years, overpopulation and industrial development drove a shortage of clean water. Different industries such as textile, leather, paper printing, paint, food, cosmetic, plastic, and pharmaceutical industries used commercial synthetic dyes. The textile industry utilizes different dyes and huge volumes of water during manufacture. In the course of the dyeing process, about 10%–15% of dye molecules remain unattached on textile fibre and consequently they are liberated as an unutilized dye in the effluent [1]. The majority of textile dyes are toxic chemicals and generate nausea, hemorrhage, skin and mucous membrane ulcers, dermatitis, perforation of the nasal septum, several irritations of the respiratory tract. Due to the complex structure, the dyes contain compounds which can be carcinogenic, mutagenic, and teratogenic in aquatic life. One of the most utilized dyes is Rhodamine B (RhB), an important hydrophilic xanthene dye known for its stability. It is soluble in water, methanol, and ethanol [2]. Rhodamine dye is accumulated especially in the mitochondria and blocks ATP production, driving cellular apoptosis [3].

Therefore, dye pollution is a significant problem that needs to be solved. Thus, the wastewater treatment becomes very important under the decreasing of natural water resources. One of the most effective methods used in water treatment is membrane filtration because it involves minimal chemical or thermal energy and does not induce harmful by-products [4]. In addition, modifying membrane structures and the pore sizes, membrane filtration selectively removes the contaminants [5]. Based on the pore sizes, the membranes are classified as microfiltration, ultrafiltration, and nanofiltration. Microfiltration is generally used to remove suspended solids, prokaryotes, yeasts, and fungi, while ultrafiltration is applied to remove virus, colloids, and macromolecules. Nanofiltration is specific to heavy metals, and dissolved organic matters [6].

Polyvinylidene fluoride (PVDF) membranes are universally used due to their good mechanical strength, high dielectric constant, and thermal stability [7]. As in the case of other polymer membranes, the use of PVDF membranes to filtration is restricted by membrane fouling, which occurs both on the surface and inside the pores and is a consequence of its hydrophobic property. The accumulation of foulants causes a water flow decline, decreasing the membrane life, leading to a more expensive membrane technology [8].

Therefore, the researchers have applied different strategies to improve PVDF membrane hydrophilicity such as physical blending, chemical grafting, and surface modification [9–12]. The blending method can be used on a wide variety of inorganic materials and their specific properties can improve the permeability, anti-contamination and solvent resistance of the PVDF membrane [13]. The most used inorganic nanomaterials are transitional metal oxides such as TiO_2 [14], ZnO [15], and carbon structure (MWCNT, GO) [16,17]. Carbon nanotubes can generate reactive oxygen species (ROS) upon direct contact with microorganisms and are antimicrobial, but their hydrophobicity does not recommend them as a membrane filler. A strategy to enhance their hydrophilicity consists in the treatment with a mixture of sulfuric acid and nitric acid by producing oxygen functional groups [18]. In addition, the decoration of functionalized MWCNT with semiconductor oxide nanoparticles increases the hydrophilicity even more. Thus, in addition to hydrophilicity, the membranes will also have self-cleaning capacity due to semiconductor oxide which is generally photoactive. Between semiconductor oxides, ZnO is quite popular in the field of photocatalysis due to its non-toxicity and low prices [19]. The photocatalytic process consists in the generation of ROS capable to degrade organic compound by photocatalyst, in this case, ZnO . These species result from interaction between electrons and holes generated by ZnO under UV or visible irradiation and adsorbed O_2 on ZnO surface and H_2O molecules. Unfortunately, the generated charges on the ZnO surface are easily recombined, resulting in diminished photocatalytic efficiency. In previous studies, it was proved that the combination between ZnO and MWCNT enhance photocatalytic activity by delaying the charge carrier recombination [20,21].

In this study, Polyvinylidene fluoride (PVDF) membranes blended with different amounts of MWCNT- ZnO (0.1%–3%) nanocomposites were fabricated by a phase inversion method. The influence of the nanocomposite materials amount on the hydrophilicity, pollutant removal capacity and photocatalytic self-cleaning performance of the membrane was studied. In addition, the reutilization studies were performed. The photocatalytic mechanism was explored based on the generated ROS evidenced from ESR coupled with spin-trapping method.

2. Materials and Methods

2.1. Materials

The materials used for the fabrication of membranes blended with different amounts of MWCNT- ZnO are as follows: Poly(vinylidene fluoride)-PVDF, Poly(ethylene glycol)-PEG400, N, N-demethyl formamide–DMF (Sigma-Aldrich, Merck, KGaA, Darmstadt, Germany), multi-walled carbon nanotubes (MWCNTs) with a 99% purity were purchased commercially (Sigma-Aldrich, Merck, KGaA, Darmstadt, Germany), zinc nitrate hexahydrate- $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alpha Aesar, Bio Aqua Group, Targu Mures, Romania), sodium hydroxide - NaOH (Alpha Aesar, Bio Aqua Group, Targu Mures, Romania) absolute ethanol- $\text{C}_2\text{H}_5\text{OH}$ - EtOH (Alpha Aesar, Bio Aqua Group, Targu Mures, Romania). All chemical reagents were used right away without any additional purification. The aqueous solutions were prepared with Milli-Q water obtained from the Direct-Q 3UV system (Millipore, Bedford, MA, USA). Dimethyl sulfoxide (DMSO; >99.9%) was purchased from VWR Chemicals (Lutterworth, Leicestershire, UK) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO; >97%), dimethylformamide (DMF), and Rhodamine B were purchased from Sigma-Aldrich, Merck, KGaA, Darmstadt, Germany.

2.2. Synthesis of MWCNT-ZnO

The decoration of MWCNT with ZnO nanoparticles was realized after MWCNT functionalization by acid treatment in a mixture of $\text{H}_2\text{SO}_4\text{:HNO}_3$ (3:1 vol ratio) under ultrasonic irradiation (Bandelin Sonorex ultrasonic bath RK 52H) used to reduce the reaction time from 24 h, necessary for the refluxing process, to 5 h [22]. This process ensures the generation of -COOH, -OH functional groups on MWCNT surface. The attaching of ZnO nanoparticles on the MWCNT surface were performed through sequential chemical precipitation on the functionalized MWCNT. For synthesis, 100 mL of 0.1 M zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ solution were added to water-dispersed functionalized MWCNT, under continuous stirring for 3 h. Subsequently, a solution of 1 M sodium hydroxide $\text{Na}(\text{OH})$ was dropwise added at a constant stirring rate until a white precipitate of zinc hydroxide was obtained. After the pH = 12 was reached, the mixture was transferred to the ultrasonic bath maintaining the sonication for 4 h at 60 °C to ensure a good attaching of ZnO on functionalized MWCNT [23]. The obtained MWCNT-ZnO was washed with ultrapure water and then dried at 70 °C for 12 h. After that, the samples were thermally treated at 400 °C, for 2 h. The molar ratio MWCNT-ZnO was 1:4.

2.3. Membrane Preparation

The phase inversion method was utilized to prepare the PVDF membrane. A given amount of MWCNT-ZnO is dispersed for 1 h in DMF using an ultrasonic bath. PVDF (15 wt%) and PEG (5 wt%) are added to the obtained solution and stirred on a magnetic stirrer (100 rpm) at 60 °C until a homogeneous solution is obtained (24 h). To remove air bubbles the solution is left for another 5 h at 60 °C without stirring. An MSK-AFA-III thin film applicator was used to coat the degassed solution on a substrate. The membrane thickness is 160 µm. To remove the membrane from the substrate, the obtained thin film was submerged in a coagulation bath containing DI water at 6 °C. The obtained membrane was rinsed and maintained in DI. A different amount of MWCNT-ZnO nanoparticles were inserted in the membrane: 0, 0.1, 0.5 and 3%, and the obtained membranes were labeled: PVDF, PVDF-CZ0.1, PVDF-CZ0.5 and PVDF-CZ3.

2.4. Methods

The structural characterization was carried out by X-ray diffraction using a Rigaku-SmartLab automated Multipurpose X-ray Diffractometer with $\text{Cu-K}\alpha$ radiation, operating at 45 kV, 200 mA and using a D/tex Ultra 250 detector monochromator with XRF reduction. The powder X-ray diffraction patterns were collected in a step-scanning mode with steps of $\Delta\theta = 0.02^\circ$, in the 2θ range 10–70°. The PDXL2: Integrated X-ray powder diffraction software was used for diffraction patterns processing. The Fourier transform infrared (FTIR) spectra were acquired in Attenuated Total Reflection Mode (ATR) in the 400–1500 cm^{-1} spectral range using a JASCO FTIR 4600LE spectrophotometer. To record the IR spectra, a 2 cm^{-1} spectral resolution was used. To evaluate the surface and cross section morphology, a scanning electron microscope (SEM) Hitachi SU-8230 with cold field emission electron beam accelerated at 30 kV was used. The UV–Vis characterization was performed using a JASCO V570 UV–Vis–NIR Spectrophotometer equipped with an absolute reflectivity measurement JASCO ARN-475 accessory. The obtained reflectance spectra were transformed in absorbance using the intern soft of spectrophotometer. To evaluate the hydrophilicity, the water contact angle was measured. To monitor the ROS generation, the ESR Bruker E-500 ELEXSYS X-band (9.52 GHz) spectrometer coupled with the spin trapping probe technique was used. As a spin-trapping reagent, 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was utilized. To record the EPR spectra, the following experimental parameters were employed: microwave power, 2 mW; modulation frequency, 100 kHz; magnetic field modulation amplitude; 1 G. For the EPR spectra simulation, the following software used Anisotropic SpinFit, Bruker.

2.4. Evaluation of photocatalytic activity

The photocatalytic activity was tested by evaluating the degradation of Rhodamine B (RhB) under UV light irradiation. A laboratory reactor consisting of two UV lamps (15 W)

emitting at 365 nm and a quartz reaction vessel was used for this purpose. The distance between the UV lamps and reaction vessel is 20 cm. The membrane having a surface area of 4 cm² was suspended in an aqueous solution of RhB (1.0×10^{-5} mol L⁻¹, 10 mL). The degradation experiment was carried out for 240 min. After each hour of irradiation, the absorption spectrum of the mixture was measured using a UV-VIS spectrometer (PG Instruments). Based on these spectra, the removal rate was calculated using the following formula:

$$\text{Removal rate (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where, A_0 and A_t represent the initial and the absorbance of RhB at time t , respectively (at 553 nm wavelength).

3. Results and Discussion

The crystalline structure of the hybrid membrane and the presence of MWCNT-ZnO nanoparticles into the membrane were investigated by X-ray diffraction. PVDF is a semi-crystalline polymer that, depending on the preparation conditions, can crystallize into different polymorphic forms: α , β and γ [11]. Each polymorphic form is characterized by distinctive diffraction peaks. The obtained diffraction patterns are shown in Figure 1.

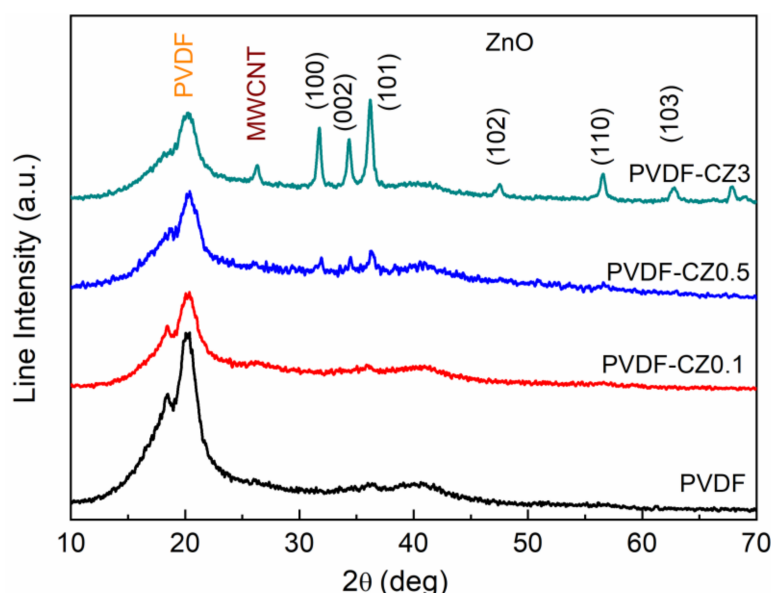


Figure 1. XRD patterns of PVDF and hybrid membranes.

The diffraction patterns of the prepared membrane show distinctive peaks located at 18.4°, 20.3°, 36.3° and 40.1° which are specific to PVDF. The peak located at 20° is specific for all polymorphic phases α , β and γ [18]. It may correspond to the diffraction at (110)/(200) planes in case of β phase, to (100)/(020) planes for α phase or to (110) crystalline plane if γ phase exist in the membrane [18,24]. If this peak is associated with the formation of α and γ phases usually another peak at about 18° appears. The presence of α phase is also supported by the existence of the diffraction peak at 41° associated with the diffraction at crystalline plane (111) [12]. The low intense peak at 36.3° is specific to (020) crystalline plane of β phase. Consequently, the obtained membranes are composed of a mixture of all three polymorphic phases.

The crystalline nature of PVDF was not influenced by the presence of MWCNT-ZnO composites. In addition, the following additional peaks appear at: 31.6°, 34.3°, 36.09°, 47.44°, 56.51° and 62.71° assigned to the (100), (002), (101), (102), (110) and (103) planes of ZnO, which can be observed in the diffraction patterns of PVDF-CZ0.1, PVDF-CZ0.5 and PVDF-CZ3 membranes. Supplementary to this, in the membrane with the highest

MWCNT-ZnO content, a well defined diffraction peak located at 26.3° assigned to MWCNT was evidenced. As the amount of composite material increases in the membranes, the intensity of MWCNT and ZnO specific peaks becomes higher. Therefore, the presence of MWCNT-ZnO nanocomposites was revealed in all prepared hybrid membranes.

For detailed information of the polymorphic phases stabilized in membranes during the synthesis, FTIR spectroscopy was conducted. The resulted spectra are presented in Figure 2. Analyzing the spectra, we can identify some bands specific to β phase (1273 cm^{-1} , 473 cm^{-1} and 443 cm^{-1}) and one band assigned to γ phase (1232 cm^{-1}). Among them, there are some low intense bands which can be attributed to α phase (979 cm^{-1} , 745 cm^{-1} and 412 cm^{-1}) [25]. The assignment of the 511 and 838 cm^{-1} band is still in dispute in the literature, and can be attributed to both γ and β phase [26]. The presence of these bands sustained the XRD results which showed that the membrane contains a mixture of all three polymorphic phases. No modification of polymorphic phases was observed after the nanoparticle's insertion into the membrane. By blending nanocomposites with PVDF, previous studies assumed that there is an interaction between the hydroxyl groups on the nanoparticles surface with the CH_2 groups of PVDF [27,28]. However, no important modifications in the spectra are detected, only a slight band shift can be observed in the case of the sample PVDF-CZ3 in $400\text{--}570\text{ cm}^{-1}$ range. This shift can be due to the appearance of the band situated at 460 cm^{-1} specific to Zn-O bond [29] or to the mentioned interactions.

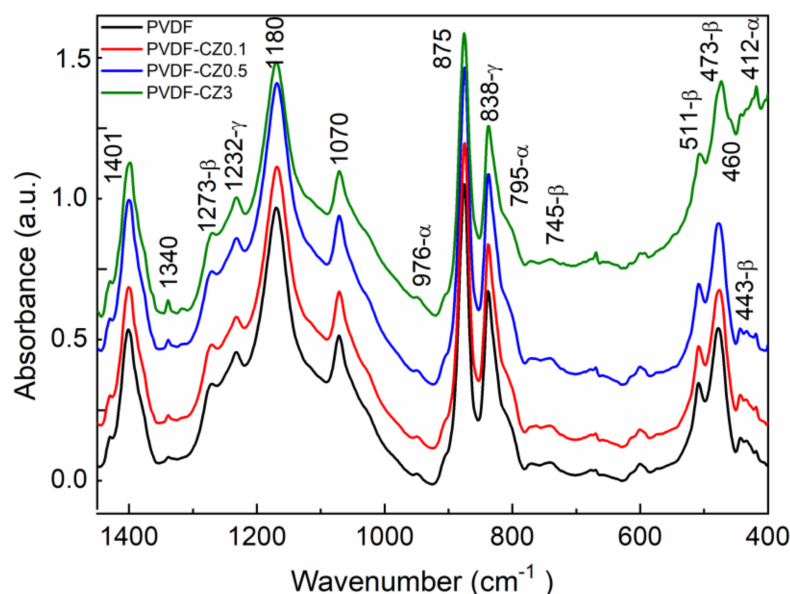


Figure 2. FT-IR spectra of PVDF and PVDF hybrid membrane.

The FT-IR spectra contain some supplementary strong bands situated at 1401 cm^{-1} , 1070 cm^{-1} and 875 cm^{-1} which are usually assigned to CF_2 group, and at 1180 cm^{-1} due to C-F stretching vibrations [30]. The low band observed at 1340 cm^{-1} is due to CH_2 group [31].

Scanning electron microscopy was performed to depict the membrane morphology. Images of top surface and cross section of PVDF membrane are presented in Figure 3. A relative uniform distribution of pores can be observed on the membrane surface. The mean size diameter of pores is $4\text{ }\mu\text{m}$. The cross-section image indicates the existence inside the membranes of parallel pores with a diameter of $120\text{ }\mu\text{m}$. Consequently, the membrane has an asymmetric structure composed by a globular structure in top which continues with a finger-like structure.

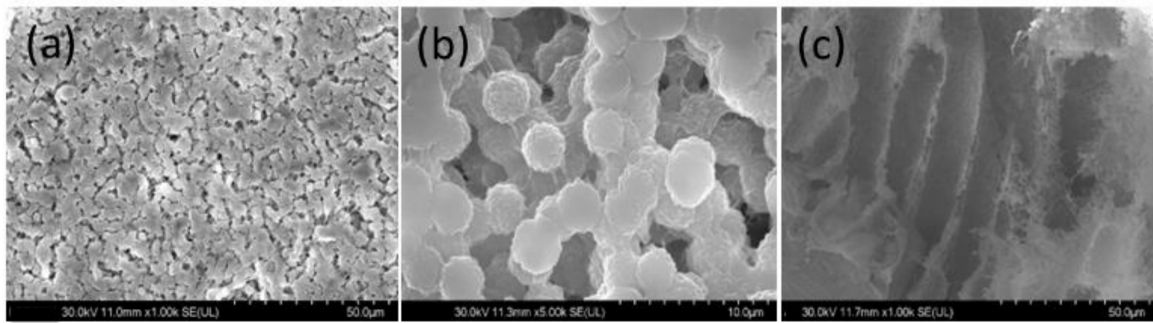


Figure 3. SEM image of PVDF membrane: (a,b) top side with different magnification and (c) cross section.

As can be seen in Figure 4a–f, the surface morphology was not changed by the insertion of the composite material. Some agglomeration of MWCNT-ZnO can be observed inside the membrane pores.

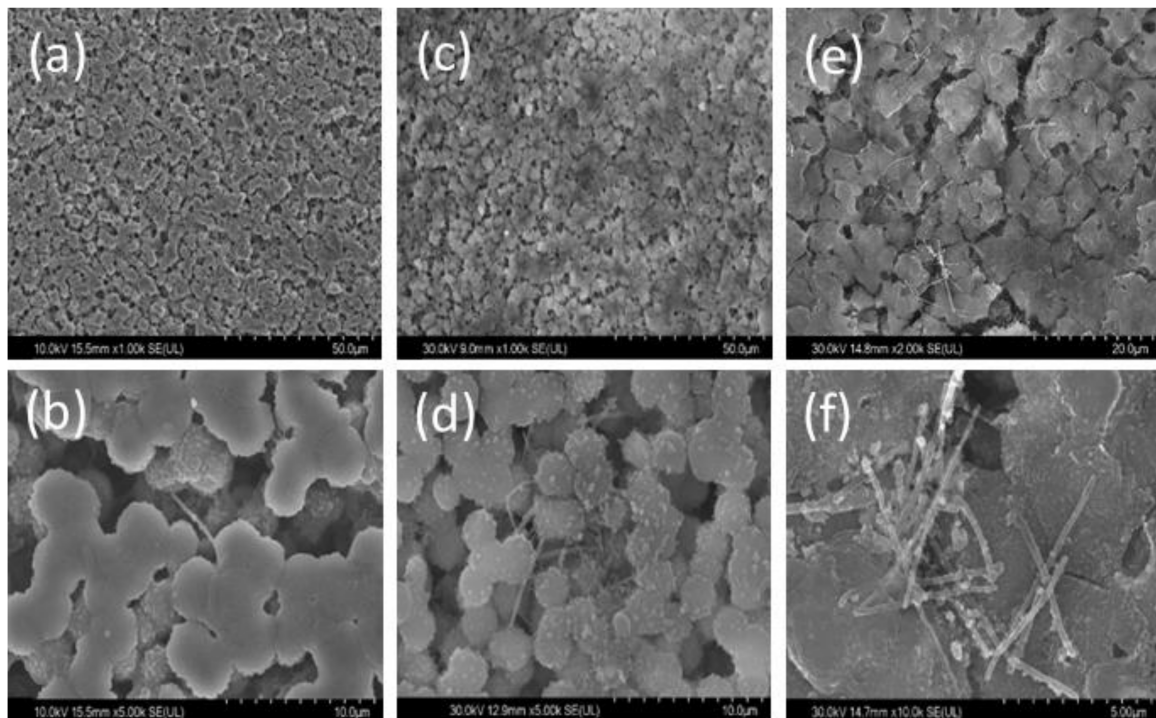


Figure 4. SEM image of: (a,b) PVDF-CZ0.1 membrane, (c,d) PVDF-CZ0.5 membrane and (e,f) PVDF-CZ3 membrane at different magnifications.

An elemental mapping analysis was performed to prove the insertion of MWCNT-ZnO nanocomposite inside the PVDF membrane. Figure 5 shows, as an example, the elemental mapping images corresponding to PVDF-CZ0.5 membrane. F and C were identified, elements which are the main components of the PVDF membrane. Moreover, Zn and O elements were also identified with similar results obtained for all samples.

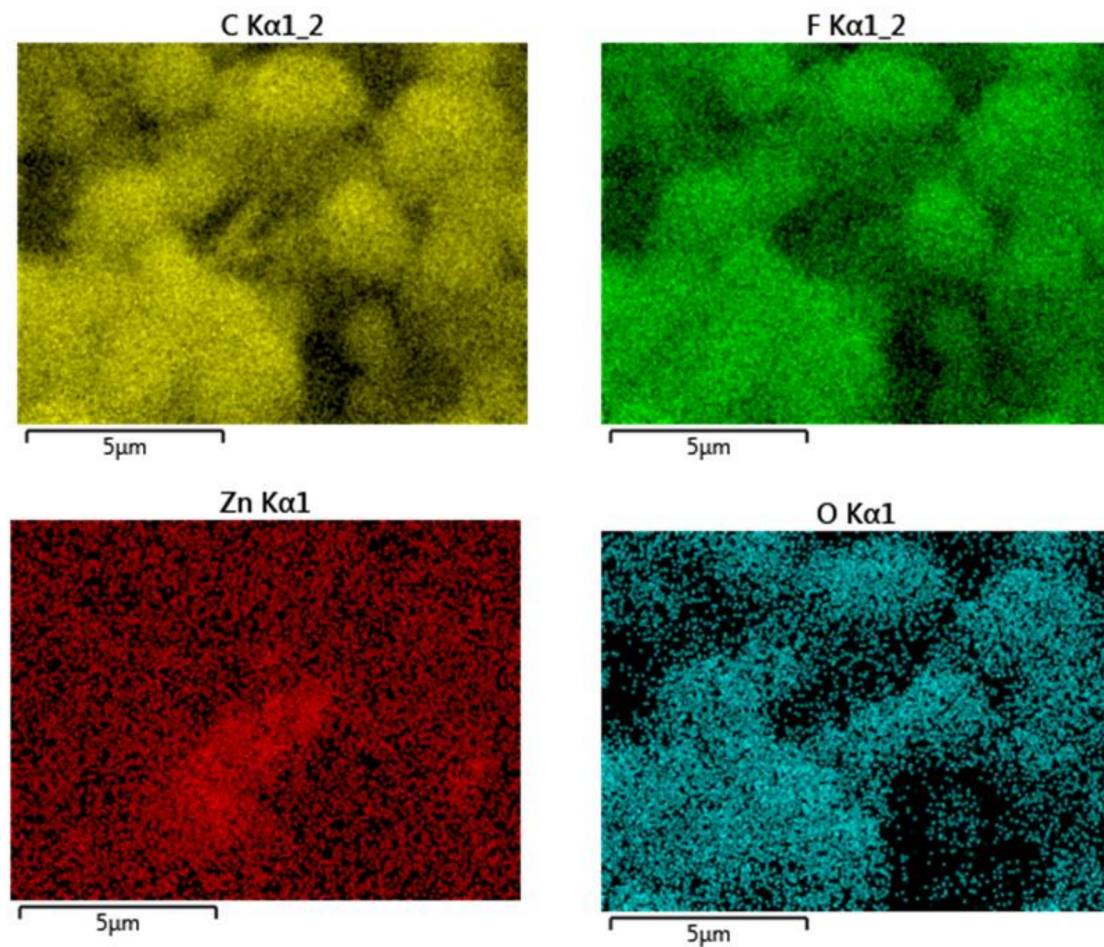


Figure 5. Elemental mapping image of PVDF-CZ0.5 membrane surface (corresponding to image presented in Figure 4d).

The optical properties were analyzed by UV–Vis spectroscopy and the spectra obtained are shown in Figure 6a. It can be seen that the PVDF membrane shows very weak absorption in the UV range.

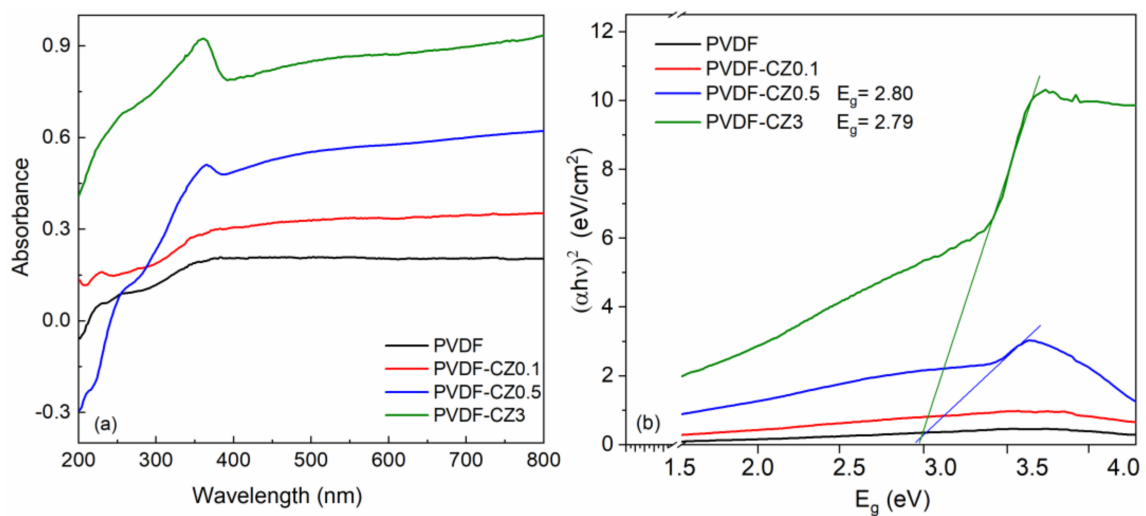


Figure 6. (a) UV–Vis absorption spectra of PVDF hybrid membranes and (b) evaluation of band gap energy from Tauc's plots.

By adding MWCNT-ZnO into the membrane, a broad absorption in UV range is observed, starting with 0.5% MWCNT-ZnO. A higher concentration of composite material provides a higher absorption of light in the UV range. To evaluate the energy of the band gap, the Tauc plot was used:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

where α is the optical absorption coefficient, $h\nu$ represent the photon energy, A is a constant specific to the material and n depends of the type of transition between bands. For direct allowed transitions $n = 2$ and $n = 1/2$ for indirect allowed transitions.

Since ZnO is a semiconductor with a direct band gap, the values of the bandgap energy (E_g) were calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ versus photon energy. The results are shown in the Figure 6b inset. As can be seen, the energy of the band gap is about 2.8 eV lower than that corresponding to ZnO bulk [32,33]. The decrease of the band gap energy is probably caused by the influence of MWCNT and PVDF.

A very important characteristic of membranes used in water decontamination processes is their hydrophilicity. Therefore, the influence of the incorporation of composite nanomaterial on the membrane hydrophilicity was analyzed. For this purpose, contact angle determinations were performed. In Figure 7 is illustrated the image of a contact angle for the PVDF and PVDF hybrid membrane. Initially, the PVDF membrane has a contact angle of 75° degrees. As the concentration of composite material increases, a decrease in contact angle is observed from 70° for PVDF-CZ0.1 to 49° for PVDF-CZ3. The decrease in water contact angle can be explained by utilizing MWCNT treated with a mixture of $H_2SO_4:HNO_3$ which provide -COOH, -OH functional groups on its surface [18]. Furthermore, the addition of ZnO nanoparticles is known as a useful strategy to enhance the membrane hydrophilicity [34]. Therefore, an improvement of the membrane hydrophilic character occurs which will avoid the pollutant molecules linking to the membrane surface, preventing the pore size reduction and membrane filling [35,36].

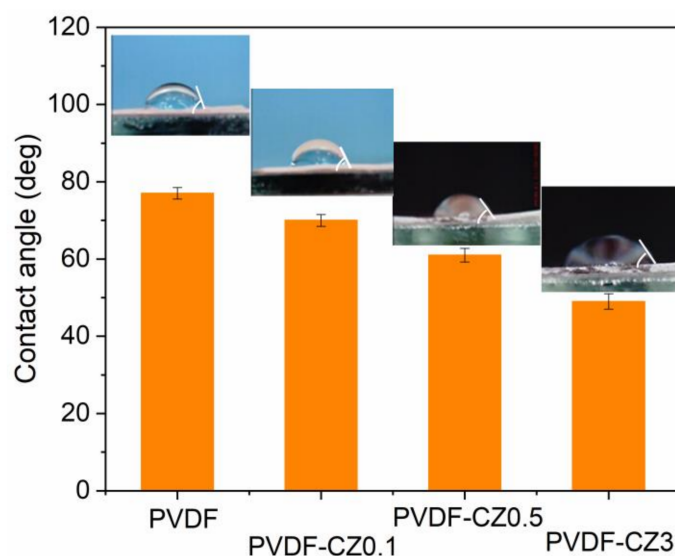


Figure 7. Contact angle for PVDF and PVDF hybrid membrane. Error bars refer to standard deviation of quadruplicate samples.

The membrane removal rate is shown in Figure 8. Before irradiation, the membrane adsorption capacity was assessed in dark. After 4 h, the PVDF membrane presents an adsorption of 69%. By inserting the composites material, the adsorption decreases. The high adsorption capacity of PVDF membrane is due to its hydrophobic character, which conducts to the pollutant attachment and agglomeration on the membrane surface. By blending PVDF with the composite material, the membranes became hydrophilic and consequently increase its anti-fouling capacity [37].

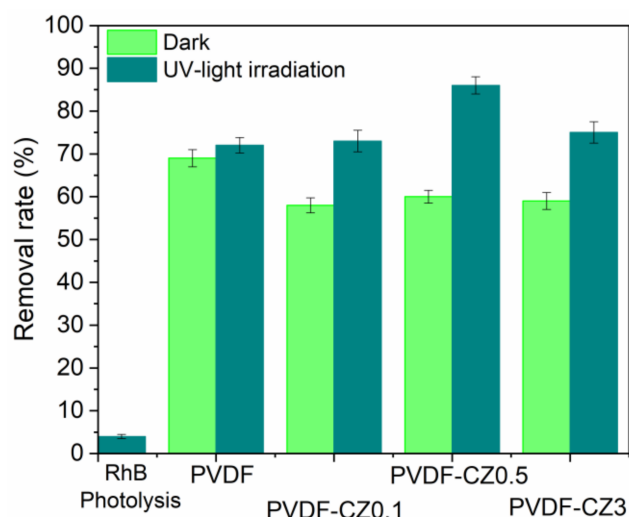


Figure 8. RhB removal rate in dark and under UV-light irradiation in the presence of PVDF hybrid membranes. Error bars refer to standard deviation of triplicate samples.

By UV irradiation, the percentage of pollutant removal increases for all analyzed samples compared with the rate observed when the experiments were performed in the dark. In the case of PVDF membranes, the low increase is probably due to the photolysis of the pollutant molecules adsorbed on the membrane surface. However, for hybrid membrane, an important enhancement of the removal rate was observed, indicating that the introduction of MWCNT-ZnO increases the removal activity of the membranes. The PVDF-CZ0.5 hybrid membrane shows the highest removal rate 85%. The increase of pollutant molecule removal is due to the photocatalytic process induced by the presence of MWCNT-ZnO. However, for higher concentration of MWCNT-ZnO content, a small decrease of the removal rate appears explained by the composite agglomeration into the membrane which has, as a consequence, low adsorption of UV light [38].

Therefore, the coexistence of two phenomena: adsorption and photocatalysis can be considered responsible for the pollutant molecules removal. The presence of MWCNT-ZnO into PVDF membranes surface and pores, generates the production of ROS under UV irradiation which are responsible for the photocatalytic activity. When the hybrid membrane is irradiated with energy higher than the energy of the ZnO bandgap, the electron jumps from the valence band to the conduction band, creating a gap in the valence band. Normally, a large proportion of the generated charge carriers recombine, and only a small proportion participate in photocatalysis reactions. By coupling ZnO to MWCNT, which are excellent electron acceptors, the photoexcited electrons are transferred from the conduction band of ZnO to the nanotubes, delaying the recombination process. Thus, the electron is transferred to oxygen where the superoxide anion is generated; this is a highly reactive radical that degrades the dye molecules adsorbed on the nanotube surface [30]. The holes react with water to form the hydroxyl radical, which also has the ability to degrade dye molecules.

To prove the generation of ROS, ESR coupled with the spin-trapping method was performed. DMPO was used as a spin-trapping agent. The obtained spectrum of PVDF-CZ0.5 hybrid membrane after 25 min UV irradiation is shown in Figure 9. The spectrum is a complex one containing many resonance lines. To identify the contribution of the generated species, a simulation of the spectrum was done. From the simulation, the presence of the following spin adducts resulted: $\bullet\text{DMPO-O}_2^-$ ($a_N = 12.8$ G, $a_H^\beta = 10.35$ G, $a_H^\gamma = 1.32$ G, relative concentration 41.5%), $\bullet\text{DMPO-OOH}$ ($a_N = 14.6$ G, $a_H^\beta = 21.7$, $a_H^\gamma = 0.8$ G, relative concentration 32.2%), and $\bullet\text{DMPO-OCH}_3$ ($a_N = 13.2$ G, $a_H^\beta = 8.5$ G, $a_H^\gamma = 1.3$ G, relative concentration 21.4%). Additionally, a nitroxide-like radical ($a_N = 14$ G, relative concentration 4.8%) due to the N–C bond break accompanied by the ring-opening of spin trapper (DMPO) appears. Superoxide radical $\bullet\text{O}_2^-$ is generated by reduction of molecular oxygen absorbed on the nanocomposites surface. $\bullet\text{OOH}$ radical is obtained by protonation of superoxide radical [39]. The $\bullet\text{DMPO-OCH}_3$ adduct spin arises through the interaction between the DMSO solvent and $\bullet\text{OH}$ radical [40]. Therefore, by ESR analysis the results were that $\bullet\text{O}_2^-$ is the majority species generated by membrane under UV irradiation.

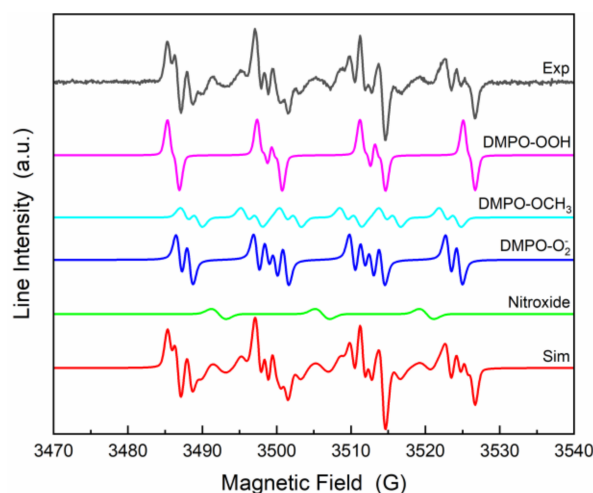


Figure 9. Experimental and simulated ESR spectra of DMPO spin adducts generated in PVDF–CZ0.5 hybrid membrane/DMSO/DMPO suspension after 25 min of irradiation.

The reusability of the membranes is very important, so, the hybrid membrane with the highest removal rate was selected to test the membrane reusability. The RhB removal was evaluated after 5 successive cycles of adsorption and UV light irradiation. The results corresponding to the PVDF- PVDF-CZ0.5 membrane are shown in Figure 9.

After each run, the membrane was cleaned using water and ethylic alcohol. The photo-stability of this type of membranes could be affected by photo-corrosion of ZnO and degradation of the membrane structure due to UV irradiation [41]. As shown in Figure 10, only a slight decrease of removal rate can be observed after 5 runs, indicating a good stability of the membrane and, consequently, this type of membrane can be considered a good candidate in membrane technology. The self-cleaning ability of the membrane is evidenced in the images presented in Figure 11. It can be observed that the membrane exposed to UV-light during the RhB removal experiment has a lighter color compared with the membrane held in dark.

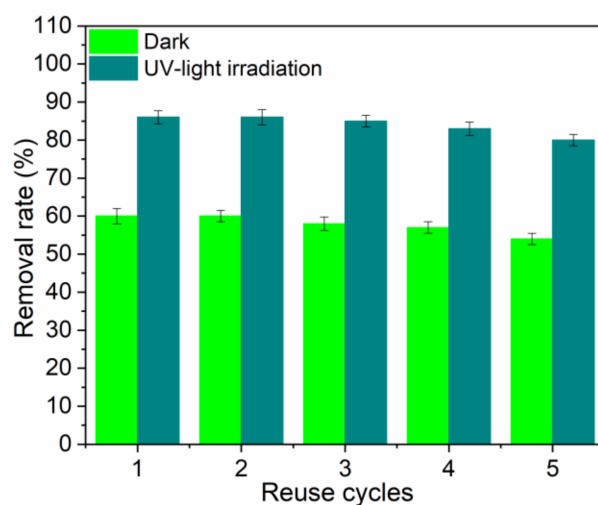


Figure 10. The reusability of PVDF-CZ0.5 membrane for removal of RhB dye for five cycles under UV irradiation. Error bars refer to standard deviation of triplicate samples.

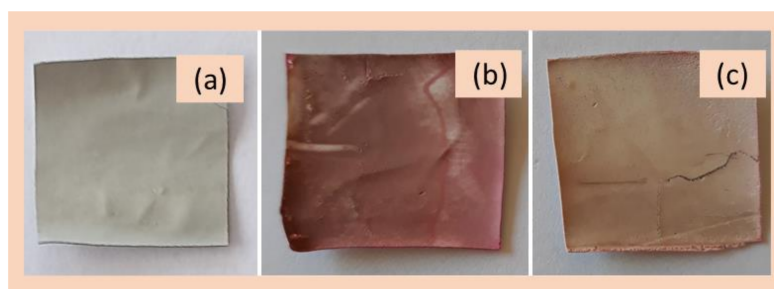


Figure 11. Pictures of the PVDF-CZ0.5 hybrid membranes (a) as prepared, (b) with adsorbed RhB molecules in dark and (c) after 4 h UV irradiation.

4. Conclusions

MWCNT-ZnO nanocomposites were used to fabricate hybrid PVDF blending membranes by phase inverted method. The successful incorporation of MWCNT-ZnO was proved by XRD characterization which evidences the presence of both ZnO and MWCNT specific diffraction peaks. Moreover, XRD correlated with FT-IR results shows that the PVDF membrane contains a mixture of α , β and γ polymorphic phases and its composition is not influenced by the presence of the composite material. SEM images reveal a uniform distribution of pores on the membrane surface with a mean size of 4 μm for all analyzed membranes. The presence of nanocomposite materials led to a broad absorption in the UV range and improved the hydrophilic character of the membranes. The RhB removal was tested in dark and under UV light irradiation. An optimum level of composite material was determined, which assured the best removal rate, 85% under UV light irradiation. It was proved that RhB removal takes place by the simultaneous action of photocatalysis and adsorption. The generation of ROS species was analyzed by ESR coupled with a spin-trapping technique using DMPO as spin trapper. The obtained results indicate $\bullet\text{O}_2^-$ as the majority species generated by membrane under UV irradiation. The photocatalytic properties of the hybrid membrane assure an anti-fouling/self-cleaning ability.

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Conflicts of Interest: The authors declare no conflict of interest.

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