Photocatalytic study of nanocomposite membrane modified by CeF₃ catalyst for pharmaceutical wastewater treatment

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Abstract

Cerium fluoride (CeF₃) nanoparticles (NPs) were synthesized and applied in polysulfone (PS) membrane fabricated by phase inversion method. The produced nanocomposite membranes (PS/CeF₃) with different contents of CeF₃ NPS (0.25%, 0.5%, 0.75% and 1% w/w) were used to treat pharmaceutical wastewaters. The membranes were characterized by FESEM, EDX, XRD, FTIR, porosity, and water contact angle analyses. Evaluation of the characteristics and performance of the nanocomposite membranes confirmed that utilizing photocatalytic CeF₃ NPs in membrane structure could effectively decompose organic contaminants in pharmaceutical wastewaters. It also improves the hydrophilicity and antifouling ability of membrane during filtration especially, in the presence of UV irradiation. The permeate flux of the PS membrane increased from 35.1 to 63.77 l/m²h by embedding 0.75% of CeF₃ NPs in membrane structure due to the porosity enhancement from 71.36–78.42% and the decrease in contact angle from 62.9° to 53.73°. Moreover, the flux decline of PS/CeF₃-0.75% membrane under UV irradiation was from 63.6 to 46.1 l/m²h that considerably lower than that of the neat PS membrane (from 34.7 to 4.9). On the other hand, the degradation efficiency of PS/CeF₃-0.75% membrane was more than 97%, and COD removed was more than 65% while they were 75% and 31%, respectively for the nascent PS membrane. Therefore, applying the appropriate amount of CeF₃ NPs in PS membranes not only greatly increased the permeate flux but also significantly enhanced the degradation efficiency and COD removal. This indicates that nanocomposite membranes can be confidently applied for pharmaceutical wastewater treatment UV irradiation.

Keywords Photocatalytic membrane · CeF₃ catalyst nanoparticles · Antifouling properties · Pharmaceutical wastewater

Introduction

In the last decades, the pollutant wastewaters produced in the pharmaceutical industry, have been converted to one of the significant emerging environmental problems [1]. Generally, pharmaceuticals is manufactured with high stability to be

effective in humans and animals [2]. They are classified into eight groups of anti-inflammatory drugs, beta-blockers, antibiotics, antiepileptic, hormones, lipid-lowering agents, antihistamines and anti-depressants based on their therapeutic applications [3, 4]. Among all the contaminant pharmaceutical products, antibiotics have a high consumption rate in both human and veterinary medicines [5]. Unfortunately, the abuse of antibiotics has made severe concerns because of their biological activity, high persistency and toxic effects on ecosystems [6]. Moreover, during the pharmaceuticals production process, a lot of water is used to sterilize and clean the related equipment (e.g. barrels, tanks, etc.) which would be discarded as wastewater. Consequently, regarding the high contamination potential of pharmaceutical wastewaters, it is necessary to completely remove the pharmaceuticals and their active compounds from aquatic systems [3, 7, 8].

Combining photocatalysis and membrane process, called photocatalytic membrane process, has attracted more attention and represents an emerging technology

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[9]. It can incorporate the advantages of membrane separation and photocatalytic degradation of pollutants [10, 11]. As a result, it can minimize environmental hazards and optimize economic aspects because of anti-fouling and self-cleaning ability, mineralization of organic contaminants to CO_2 and H_2O and high flexibility for industrial applications [12].

The use of semiconductors as the photocatalyst has been extensively investigated and emerged as a preferred method for the degradation of organic contaminants in wastewaters [13]. So far, many semiconductor nanoparticles have been reported to represent the photodegradation properties of organic contaminants. Among the rare-earth metal compounds, cerium fluoride (CeF_3) is regarded as an important nanoparticle with full practical applications in the photocatalytic process [14, 15], optical components [16] and sensors [17] due to its high ionic conductivity, fast response and optical properties. For example, some researchers have determined that the $\text{CeF}_3/\text{TiO}_2$ nanocomposite has an excellent photocatalytic activity for CO_2 reduction under visible light radiation than pure TiO_2 [15]. Miao et al. studied the influence of CeF_3 nanoparticles (NPs) on the degradation of methylene blue (MB) under UV radiation. It was reported that the CeF_3 NPs could effectively decompose and degrade organic matters in aqueous solutions and show higher photocatalytic activity than CeO_2 nanoparticles. Moreover, CeF_3 NPs represented high stability because of the bandgap energy of 3.32 (eV) and their photocatalytic behavior was much similar to that of commercial TiO_2 (P25) [14]. It is worth quoting that the studies on nanosized CeF_3 as photocatalytic semiconductors are limited. However, there is no study on the CeF_3 NPs entrapped in the structure of polysulfone (PS) membrane.

This work was mainly focused on a feasibility study of the PS induced membrane on photocatalytic degradation of the organic pollutants in pharmaceutical wastewater. To achieve a new photocatalytic PS membrane, CeF_3 NPs were firstly synthesized with favorite nanosized distribution and dispersed in the scaffold of PS membrane. Further, the influence of CeF_3 NPs on the membrane structural properties such as hydrophilicity, surface porosity and pharmaceutical wastewater permeability was investigated. The fabricated membranes were used to treat pharmaceutical wastewater for photocatalytic decomposition of the organic contaminants. Moreover, a comprehensive fouling investigation of the PS induced membrane was examined to find how the incorporation of CeF_3 nanocatalyst can influence on the photocatalytic degradation of the pharmaceutical pollutants on the membrane surface or inside the pores under UV light irradiation.

Experimental

Materials

Polysulfone (PS, p-3500, Udel, Germany) was used as a polymeric substrate for membrane fabrication. 1-methyl 2-pyrrolidone (NMP, > 99.8%) as the solvent and polyvinylpyrrolidone (PVP) as the pore former were obtained from Merck. Cerium (III) nitrate hexahydrate (99.9%) and sodium fluoride (ACS reagent, > 99%), were supplied by Sigma-Aldrich. Oleic acid (90%) was purchased from Merck. Pharmaceutical wastewater was collected from effluents of antibiotic manufacturers in Iran. The pH of effluents was 5.5–6, total dissolved solids (TDS) was 4740 mg/l, chemical oxygen demand (COD) was 17360 mg/l and conductivity was 4.63 μS .

Preparation of CeF_3 nanoparticles

CeF_3 nanoparticles were synthesized by precipitation reactions [18]. Typically, 30 mmol sodium fluoride (NaF) was dissolved in 80 mL distilled water. To this, a solution containing 1.5 mL oleic acid in 80 mL of ethanol was added and the solution was stirred and heated to 80°C with purging of argon gas. Then a solution of 10 mmol of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 60 mL DI water was dropwise added to the above solution. The mixture was continually stirred at 80°C for 4 hr. After cooling naturally, the resultant precipitates were separated by centrifugation and washed with ethanol for several times and dried at 50 °C for 12 h under vacuum.

Preparation of PS/ CeF_3 nanocomposite membrane

The phase inversion by immersion precipitation technique was applied for the fabrication of CeF_3 embedded dense asymmetric PS membranes [19]. Different concentrations of CeF_3 nanoparticles (0, 0.25, 0.5, 0.75 and 1 wt.%) in NMP were prepared to disperse by an ultrasonic bath for 30 min. After that, PS polymers (19 wt.%) and PVP (2 wt.%) were added into the casting solution under continuous stirring for 12 h. The PVP is known as a pore former and is soluble in NMP and DI water so that it can be leached out of the casting solution during the phase inversion. The homogeneous solutions were aged motionless for several hours to remove air bubbles. Then they were cast by self-made casting knife (75 μm thickness) on polyester non-woven fabrics and were promptly immersed into a non-solvent coagulation bath containing DI water. After the phase inversion process, the membranes were left in another water bath for about 24 h to complete removing the residual solvents. Finally, the membranes were stored and dried between two filter paper sheets at room temperature for at least one day. In this paper, the naming of each membrane was according to the weight percent of CeF_3 in its casting solution.

Characterization

Characterization of nanoparticles and membranes

The nanoparticle samples, PS and PS/CeF₃ composite membranes were analyzed by X-Ray diffraction applying a Philips X'pert X-ray diffractometer (XRD) with Cu K α radiation of wavelength 1.54056 Å for 2 θ angles between 0° and 80°. The chemical structure of CeF₃ nanoparticles was characterized by attenuated total reflection (ATR) technique using Bruker -IFS 48 FTIR spectrometer (FTIR model: TENSOR27, Germany) with the horizontal ATR device (Ge, 45°). The hydrophilicity of the neat and modified membranes was evaluated by contact angle measurements (KRUS BmbH, Germany). The morphology of CeF₃ nanoparticles, top surface and cross-section of the prepared membranes were studied by field emission scan electron microscope (FESEM:Mira3-XMU). The elemental composition of nanoparticles and membranes was assessed using Energy Dispersive X-ray (EDX) detector. The membranes overall porosity (ϵ) was determined by the gravimetric method. In this method, the membrane was immersed in the distilled water at room temperature for one day and the weight of dry and wet membranes in distilled water was measured. Then, the overall porosity (ϵ) was determined as follows:

$$\epsilon = \frac{(W_w - W_d)/\rho_w}{(W_w - W_d)/\rho_w + W_d/\rho_p} \times 100$$

where W_w and W_d are the wet and dry weight of the membrane, respectively. ρ_w and ρ_p are the water and polymer density, respectively.

Permeability

A photocatalytic membrane system was applied to determine the water permeation tests (Fig. S1). The system was conducted by applying a continuous cross-flow filtration system consists of a reservoir tank, a cross-flow membrane cell with an effective area of 39 cm², two pressure gauges, valves and a high-pressure pump. In this system UV lamp (Hitachi, Japan, 24watt, =365 nm) was placed at the top of the membrane cell. The distance between the membrane surface and the UV lamp was 15 cm. The feed suspension was kept at a constant amount by recycling the concentrate streams back into the reservoir tank. The pharmaceutical wastewater was pumped into the membrane cell at 5 bar pressure and the permeate flux of the wastewater was recorded every 10 minutes in each cycle of filtration by measuring the volume of collected permeate.

The permeate flux of pharmaceutical wastewater was calculated by the following equation:

$$J = \frac{V}{A \cdot \Delta t}$$

where V is the volume of permeate (l), Δt is the filtration time (hr) and A is the membrane surface area (m²).

Antifouling ability

In order to determine the antifouling ability of modified membranes, flux recovery ratio (*FRR*) of membranes were measured. After pure water flux calculations (J_0), the cross-flow cell was subjected to a pharmaceutical wastewater solution, and the permeate flux of pharmaceutical solution (J_p) was measured for 10 min. After that, the membranes were washed with DI water for 20 min. Then the pure water permeability of cleaned membranes (J_1) was measured again. The *FRR* was determined as follow:

$$FRR(\%) = \left(\frac{J_1}{J_0} \right) \times 100$$

In general, higher *FRR* shows the better antifouling ability of the membrane. Fouling is a phenomenon whereby the flux declines due to the formation of cake or gel layer on the membrane surface and/or plugging of membrane pores. Reversible (R_r) and irreversible (R_{ir}) fouling and the total fouling resistance (R_t), were calculated by the following statements:

$$\begin{aligned} R_r &= \left(\frac{J_1 - J_p}{J_0} \right) R_{ir} = 1 - \left(\frac{J_1}{J_0} \right) R_t = R_r + R_{ir} \\ &= \left(1 - \frac{J_p}{J_0} \right) \end{aligned}$$

Photodegradation property

For measuring the COD, at first, the samples were pipetted into vials consisting of digestion solutions and were shaken for 30 sec [20]. Then, they were placed into the COD reactor (Model Aqua Lytic ET 108) and heated at 150 °C for 120 min. Every 10 min, the vials were shaken to mix the precipitated compounds and homogenize the solution. After 120 min, the reactor was turned off and the vials were aged in dark condition and ambient temperature. The Aqua Lytic spectrometer (Germany) at 600 nm was used to determine the absorbance of the compounds [21]. The COD removal rate was calculated by the following equation:

$$CODRemoval\% = \left(1 - \frac{COD_p}{COD_f} \right) \times 100$$

where the COD_p and COD_f are the COD of permeate and feed

solution, respectively.

The concentration of pharmaceuticals in wastewater was calculated by UV-visible spectrophotometer (Unico 2800UV/Vis spectrophotometer) at the highest absorption peak of pharmaceutical compounds ($\lambda_{\max}$ = 364 nm). Rejection percent (R%) was calculated from the pharmaceutical concentrations in permeate (C_p) and feed (C_f) as the equation:

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

In order to investigate the effect only of UV irradiation on pharmaceutical wastewater degradation, the wastewater was exposed under UV light for 30 min. Then the sample was measured by UV- spectrophotometer. As a result, the degradation efficiency was reported to be 3.4%. It shows that the only UV light was not significantly degraded the wastewater over time.

Result and discussion

Characterization of nanoparticles and membranes

CeF₃ nanoparticles

The crystalline structure of the synthesized CeF₃ NPs was confirmed by XRD patterns (Fig. 1a). The sharp peaks depicted at 2θ = 24.80, 28.32, 35.58, 44.80, 45.30, 52.10, 53.72 and 65 were expressive of the hexagonal structure of CeF₃ [18]. The microstructure, size, and morphology of the synthesized CeF₃ were characterized by FESEM as shown in Fig. 1b. The uniform particle size distribution for CeF₃ NPs can be observed and the CeF₃ NPs exhibit a microsphere structure with an average diameter of ~20 nm. In addition, the EDX spectra of CeF₃ nanoparticles in Fig. 1c demonstrates only three elements of Ce, O, and F which confirms that CeF₃ nanoparticles are well synthesized.

Figure 1d demonstrates the result of the IR spectroscopy of the CeF₃ NPs. The weak absorption peak at 1639 cm⁻¹ and the strong peak at 1386 cm⁻¹ can be ascribed to C=O and C–O stretching vibrations in oleic acid, respectively [22]. Absorption bands for symmetric and asymmetric stretching vibration of C–H groups were presented at 2854 and 2925 cm⁻¹, respectively [23]. IR peaks at 3433 cm⁻¹ can be assigned to the –OH stretching vibration mode of oleic acid or the water molecules which bounded with CeF₃ molecules by hydrogen bonds [24, 25].

Membrane characterization

The XRD patterns of the PS membrane and PS/CeF₃ composite membrane were depicted in Fig. S2. It can be observed that the XRD spectra of neat PS membrane are characterized by only one peak at 16.80° [26], while, The pattern of PS/CeF₃ composite membrane has four sharp crystalline peaks at 2θ of 24.80°, 28.32°, 44.80° and 45.30° that corresponds to the characteristic peaks of CeF₃ hexagonal crystalline particles in PS polymer matrix [18].

To investigate the surface morphology of the neat and modified membranes, FESEM analyses were carried out. Figure 2 shows the top view images of neat and nanocomposite membranes. According to Fig. 2a, a relatively homogeneous and smooth skin without any defect was formed as a dense layer. Figure 2b reveals that the NPs were uniformly distributed within the PS matrix. The white spots with spherical shapes in PS structure are related to CeF₃ nanoparticles. On the other hand, because of the proper adhesion between CeF₃ domains and polymer matrix, NPs agglomeration is negligible (Fig. 2c, d). The EDX analysis in Fig. S3 confirms the presence of CeF₃ NPs in membrane structure.

Figure S4 shows the FESEM cross-section micrographs of neat and PS/CeF₃ (0.75% CeF₃) membranes. The membrane structures are in agree with usual characteristics of asymmetric membranes composed of a dense top surface layer and finger-like and porous sublayer full of macropores. However, comparing to the neat PS membrane, the membrane prepared by 0.75 wt.% CeF₃ (Figure S4 (b)) reveals higher porosity with a prolonged finger-like structure along with the thickness of the membrane. Adding hydrophilic CeF₃ NPs to the organic phase resulted in the faster interchange between the solvent (NMP) and non-solvent (DI water) during the phase inversion process that caused the formation of the wider finger-like structure with more macro void pores than the neat PS membrane [27–29].

The surface porosity of the produced membranes is shown in Table 1. The results revealed that all membranes presented a high porosity in the range of 71–78%, which could be attributed to the PVP additive. As PVP is water-soluble, it would be leached out of the membrane matrix during the phase inversion process [30]. Moreover, the PS/CeF₃ membranes have higher porosity than the neat membrane. Up to 0.75% w/w of CeF₃ NPs, increasing the CeF₃ content enhanced the membrane porosity that principally due to the diffusion of CeF₃ NPs into the coagulation bath during phase inversion. The hydrophilicity of CeF₃ accelerates the water transformation from the aqueous phase into the solvent-rich liquid phase which results in the formation of liquid-filled membrane pores, so the porosity of the nanocomposite membranes will enhance. On the other hand, the porosity of CeF₃-1% membrane decreased, which can be ascribed to the

Fig. 1 Characterization of CeF_3 nanoparticles; (a) XRD pattern (b) FESEM images (c) EDX and (d) FTIR spectra

nanoparticle aggregation and pore plugging in the high concentration of CeF_3 NPs [31].

To study the hydrophilicity of neat PS, PS/ CeF_3 and UV irradiated membranes, the water contact angle measurement was applied. In general, hydrophilic membranes exhibit smaller surface contact angles [32]. Fig. S5 depicts the water contact angle of neat PS and nanocomposite membranes. Results show that, the neat PS membrane presents the largest contact angle of 62.9° in dark condition. In contrast, The contact angle of nanocomposite membranes decreased with increasing the content of CeF_3 NPs. This confirms the enhancement in hydrophilicity of the nanocomposite membrane in aqueous media. This is due to the considerable increase in the number of hydrogen bonds between $-\text{OH}$ of water molecules and $-\text{F}$ of the NPs [30]. Besides, UV irradiation practically decreases the contact angle of PS/ CeF_3 modified membranes. The results showed a decrease in the contact angle of neat PS membrane from 62.3° to 53.73° for the PS/ CeF_3 -1% membrane after UV irradiation, while the contact angle of neat PS membrane didn't change significantly. CeF_3 is known as a semiconductor with a conduction band and a valence band. When the

nanoparticle is irradiated by UV irradiation with energy equal or higher than the bandgap energy of nanoparticles, the photoexcited electron (e^-) transfers the valence band (VB) to conduction band (CB). It results in the generation of holes (h^+) in the valence band of the semiconductor. The pairs e^-/h^+ would be separated and transfer to the CeF_3 surface and participate in oxidation and reduction processes. The valence band holes react with the H_2O molecules in the environment and hydroxyl radicals would be generated. Finally, The generated OH radicals react with the air humidity to create OH group. This increases the surface energy that leads to the increase in membrane surface hydrophilicity and the decrease of contact angles [33].

Performance of PS/ CeF_3 nanocomposite membranes

Figure 3 reveals the pharmaceutical wastewater flux of neat and nanocomposite membranes with and without UV radiation. The permeate flux of the neat PS membrane was $34.69 \text{ l/m}^2\text{h}$. The permeate flux increased with the CeF_3 concentration up to 0.75 wt.%, which can be confirmed by the enhanced porosity (Table 1) and improved hydrophilicity (Fig. S5) of

Fig. 2 FESEM images of membranes surface: **(a)** neat PS membrane, **(b)** PS/CeF₃_0.75% nanocomposite membrane, **(c,d)** Higher magnification of modified membrane (PS/CeF₃_0.75%)

the nanocomposite membranes. Moreover, the permeate flux of nanocomposite membranes is higher in the presence of UV radiation than in UV absence condition due to the photoactivity and higher hydrophilicity. The PS membrane containing 0.75 wt% CeF₃ (PS/CeF₃) exhibited permeate flux of 63.77 L/m² h under UV radiation, which was more than 80% higher than that of neat PS membrane. However, the higher CeF₃ concentration (more than 0.75 wt.%) in the synthesized membranes led to a flux decline, which can be related to the pore blocking and reducing in porosity [34]. When the content of CeF₃ was increased from 0.75 wt.% to 1 wt.% at UV irradiation condition, the rejection efficiency decreased, which might be attributed to the large pores generated on the membrane surface due to the CeF₃ NPs agglomeration.

The photocatalytic behavior of PS/CeF₃ membranes

In order to precisely investigate the photocatalytic performance of PS/CeF₃ membrane, pharmaceuticals degradation and COD removal were evaluated. Figure 4a depicts the

degradation rates (R%) of organic contaminants in pharmaceutical wastewater for produced membranes in the absence and presence of UV irradiation. As can be seen, the degradation of pharmaceuticals was greater for PS/CeF₃ membranes than that of neat PS membrane. In addition, the UV irradiation considerably enhanced the R% for nanocomposite membranes and increasing the CeF₃ content, improved the ratio of R% between the absence and presence of UV. In dark conditions, all membranes represented less than 85% removal of pharmaceuticals in wastewater while under UV light more than 97% of contaminants were rejected by PS/CeF₃-0.75% [14]. However, the neat PS membrane almost had no change

Table 1 The overall porosity of the PS/CeF₃ nanocomposite membranes at different concentration of CeF₃

Membranes	Overall Porosity%
PS	71.36
PS/CeF ₃ -0.25%	75.08
PS/CeF ₃ -0.5%	76.91
PS/CeF ₃ -0.75%	78.42
PS/CeF ₃ -1%	77.31

Fig. 3 Pharmaceutical wastewater flux of neat and modified membranes (0.25, 0.5, 0.75 and 1 wt.% CeF₃) in the absence and presence of UV radiation

in degradation rates of pharmaceuticals under UV light, thus neat PS membrane didn't have any photocatalytic potency itself.

As shown in Fig. 4b, COD removal of membranes process was influenced by photocatalytic NPs. It increased sharply under UV radiation with CeF₃ content compared with the dark condition. This can be related to the photocatalytic degradation of organic contaminants in pharmaceutical wastewater. The PS/CeF₃-1% membrane exhibited the highest COD removal from pharmaceutical wastewater. Higher CeF₃ concentration is favorable to produce more OH[•] radicals and also accelerate the photocatalytic decomposition reaction [14].

Table 2 summarizes the degradation efficiency of organic contaminants in pharmaceuticals wastewater by the applied photocatalytic membranes produced via different methods. These results show that the use of photocatalytic NPs was significantly effective in the degradation efficiency of the

hybrid photocatalytic membranes for pharmaceutical wastewater treatment.

The antifouling behavior of PS/CeF₃ modified membranes

Fouling is the main problem in the case of PS membranes due to the hydrophobic behavior between the foulant and the surface of the membrane [35]. Membrane fouling results in flux decline and decreases the lifetime of the membrane [33]. The antifouling behavior of the neat PS and the modified PS nanocomposite membranes were analyzed in the absence and presence of UV radiation for 150 min (Fig. 5). As can be seen, all membranes exhibited a similar trend of flux decline due to the attachment of some drug molecules and organic matters on the surface of membranes. The neat PS membrane showed the highest flux decline. The flux of the neat PS membrane decreased to 86% during 150 min operating time. However, the flux decline of nanocomposite membranes was 60%, 37% and 34% for PS/CeF₃-0.5%, PS/CeF₃-0.75% and PS/CeF₃-1% membranes, respectively in dark conditions. These results can be clarified by the improved hydrophilicity of the CeF₃ NPs in PS membranes that can reduce the membrane fouling. The hydrophilic nature of CeF₃ NPs causes a layer of water molecules layer to form on the membrane surface. It could prevent the attachment of hydrophobic contaminants on the membrane surface [32]. Moreover, the presence of UV radiation lessened the flux decline of nanocomposite membranes and as the NPs contents increased the flux decline decreased. This is because of the photocatalytic behavior of CeF₃ NPs that increase the hydrophilicity and reduce the membrane fouling [36].

The flux recovery ratios (*FRR*) are depicted in Fig. 6. A higher *FRR* is indicative of higher antifouling ability for the membrane. *FRR* for neat PS membrane (45%) was lower than

Fig. 4 Degradation rate (a) and COD removal (b) of pharmaceutical wastewater for neat and modified membranes in the absence and presence of UV radiation

Table 2 Comparison between nanoparticles at different photocatalytic membrane reactors

Adsorbents	Pharmaceutical wastewater	Photocatalytic conditions	Degradation efficiency	references
TiO ₂ in polymeric hollow fiber UF membrane	Chlorhexidine Digluconate (CHD)	1500W solar simulator, 0.2 m/s velocity	> 40% degraded	[39]
TiO ₂ /UVC in UF ceramic membrane	Oxytetracycline	UVC lamp each (16 W), TMP of 0.1 MPa velocity of 6 m/s ⁻¹	~ 52% DOC removal	[40]
TiO ₂ /PES and TiO ₂ /PVDF polymeric membrane	diclofenac	7.6 mW/cm ² UVA lamp 0.5 bar pressure, Up to 120 min	For PES, 68% degraded For PVDF, 55% degraded	[41]
Polycrystalline TiO ₂ and a NF membrane reactor	Furosemide Ranitidine	(MP 120 W) UV/ TMP = 4–8 bar UP To 120 min	> 80% furosemide degraded > 50% ranitidine degraded	[42]
TiO ₂ in UF membrane reactor	diclofenac	24 W UV lamp flow rate:1.17 l/h	TOC removal: 40–70%	[43]
TiO ₂ in NF membrane reactor	Six pharmaceuticals	150 W UV medium pressure mercury lamp during 6 h irradiation	About 90%	[11]
PS/CeF ₃ polymeric membrane system	Pharmaceutical industry wastewater	24W UV lamp Pressure = 5 bar	97% degraded	The present work

the modified membranes. The maximum *FRR* of 78.5% is related to PS/CeF₃-0.75% membrane under UV irradiation related to the hydrophilicity of CeF₃ and its photocatalytic properties [37]. In other words, the presence of CeF₃ NPs in membrane structure caused the decomposition of drug molecules under UV radiation, so the flux recovery ratio was enhanced significantly after UV irradiation. All the membranes showed better *FRR* values under UV irradiation compared to the neat PS membrane.

The reversible (R_r), irreversible (R_{ir}) and total fouling ratios (R_t) were calculated for the synthesized membranes and presented in Fig. S6. As shown, the highest R_{ir} (54.7%) and R_t and also the lowest R_r are attributed to the neat PS membrane because of the lower hydrophilicity. The R_{ir} of PS membrane was about 89% R_t . However, applying CeF₃ NPs in membrane structure could remarkably decrease the R_{ir} under UV radiation due to the improvement of antifouling characteristics

while the R_r increased. The PS/CeF₃-0.75 wt% membrane had the highest R_r value of 29.36% and the lowest R_{ir} value of 21.7%. under UV light radiation.

The possibility of the recovery for neat PS and PS/CeF₃ membrane was determined by using the long term fouling experiment under UV irradiation for three cycles by cleaning the fouled membrane periodically with 0.1% SDS and deionized water. Figure 7 shows the results of the three-cycle separation processes with pharmaceutical wastewater as a foulant. As shown in Fig. 7, the extent of permeate flux recovery after washing is directly due to the antifouling efficacy of the membrane. Moreover, By comparing the permeate flux of the neat and PS/CeF₃-1% membranes with each other, it shows that prior to each cycle, the PS/CeF₃ membrane has a higher flux recovery rate rather than neat membrane. It can be related to the antifouling behavior of the PS/CeF₃ membrane at UV radiation condition.”

Fig. 5 Pharmaceutical wastewater permeate flux for neat and modified membranes during 150 min in the absence and presence of UV radiation

Fig. 6 Flux recovery ratio (FRR%) for PS and PS/CeF₃ membranes in the absence and presence of UV radiation

Toxicity analysis

In order to assay the quality of the treated pharmaceutical effluent via photocatalytic membrane filtration, a toxicity test was carried out through a zone of inhibition method called Kirby-Bauer test using E-Coli. E-Coli is known as a sensitive strain to toxic contaminants. The broth media used for the test was Luria agar [38]. 0.4 cm culture media was punched in Luria agar plates. Subsequently, the culture of E. coli was spread on the agar plates. Thereafter, 40 μ L of samples were poured in well. After the preparation of culture media, it was kept in an incubator at 37°C for 24 hr.

The toxicity evaluation of the samples was determined based on the zone of inhibition. If the zone of inhibition was too low, it means that the photocatalytic membrane could degrade the treated effluent to non-toxic compounds. As shown in Fig. 8, after incubation, the bigger zone of inhibition

Fig. 7 Fouling behavior of the neat (blue dots) and modified (PS/CeF₃-1%) (red dots) membranes in three sequential cross flow filtration cycles at UV irradiation condition

Fig. 8 Inhibition zone areas for toxicity assay of different samples (Control (a), untreated (b) and treated pharmaceutical wastewater (c))

was observed at the untreated effluent sample (Fig. 8b). On the other hand, it was observed that there was the lower zone of inhibition for treated sample (Fig. 8c) than untreated, where the toxic compounds of the pharmaceutical effluent could be degraded by the photocatalytic membrane process.

Conclusion

CeF₃ nanoparticles were synthesized by precipitation method and applied for the fabrication of PS/CeF₃ nanocomposite membranes by phase inversion method. XRD and EDX analyses confirmed the presence of CeF₃ NPs in membranes matrix. The FESEM micrographs displayed that the synthesized nanocomposite membranes possessed a finger-like structure. The hydrophilicity of PS/CeF₃ nanocomposite membranes was higher than the neat PS membrane because of the presence of hydroxyl groups on the surface of CeF₃ NPs. By irradiation of UV light the hydrophilicity of nanocomposite membranes was improved due to the generation of OH radical group. The permeate flux of pharmaceutical wastewater under UV radiation was higher than the neat PS membrane due to the increment of membranes hydrophilicity and porosity. Results showed that in low concentrations of NPs (up to 0.75%) the permeate flux increased with NPs content but more increasing the NPs content declined the flux due to the pore blocking on the membrane surface. The investigation of photocatalytic performance by measuring the degradation of organic contaminants revealed a greater rejection of the PS/CeF₃ membranes under UV radiation than the neat PS membrane. Antifouling properties were evaluated which showed that the FRR of PS/CeF₃ nanocomposite membranes under UV radiation is much higher compared to the neat PS membrane due to improving the hydrophilicity. This study

confirmed the improved permeate flux, rejection rate and antifouling properties of PS/CeF₃ membranes for pharmaceutical wastewater treatment.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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