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Research Article

Monitoring of Estrone from Hospital Wastewater and its Removal by Photocatalytic Membrane Reactor

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Abstract

Steroid hormones, classified as endocrine-disrupting compounds (EDCs), pose significant environmental and health concerns due to their persistence and potential adverse effects. This study investigates the presence of estrone (E1) in hospital wastewater and the efficiency of E1 removal through a photocatalytic membrane reactor (PMR). Wastewater samples were collected from two hospitals with different wastewater treatment processes. The concentration of E1 was analyzed using a combination of solid phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (LC-MS/MS). The PMR experimental setup involved a polyvinylidene fluoride (PVDF) membrane incorporated with 1 wt% titanium dioxide (PVDF/TiO_2). The PMR performance was evaluated with and without UVC radiation. The membranes were characterized for their water contact angle (WCA) and surface morphology. The maximum concentration of E1 in the hospital wastewater was 2.46 ± 1.90 ng L^{-1}. The PMR, operated for 180 min, demonstrated that PVDF/TiO_2 (UV) exhibited the highest E1 removal efficiency (96.7 ± 1.4%). This superior performance was attributed to the synergistic effect of PVDF/TiO_2 membrane filtration combined with UV irradiation, enhancing the removal capacity. The removal of E1 in the PVDF/TiO_2 membrane (36.5 ± 2.7%) surpassed that of the PVDF membrane (32.6 ± 7.8%). The kinetics analysis indicated that the degradation of E1 followed pseudo first-order kinetics. These findings underscore the potential of PMR technology, specifically employing PVDF/TiO_2 membranes with UV irradiation, for efficient removal of E1 from hospital wastewater, offering insights for future applications in mitigating micropollutant release into the environment.

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Introduction

Steroid hormones (SH) are a category of endocrine-disrupting compounds (EDCs) that have the potential to accumulate in the environment, often detected at low concentrations ranging from nano-grams per liter (ng L^{-1}) to micrograms per liter (μg L^{-1}) [1]. These substances, including Estrone (E1), 17β-estradiol (E2), and 17 -ethinyl estradiol, are classified as natural steroid hormones. Environmental exposure to E1 primarily occurs through the consumption of food and water or medications containing estrone as an ingredient [2]. Once ingested, these hormones are excreted via feces and urine, contributing to environmental contamination. Such pollutants have been implicated in health-related issues, affecting growth, fertility, and reproduction. Importantly, conventional wastewater treatment technologies have shown inefficiency in removing hormones [3–4]. As a result, E1 has been detected in various

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environmental matrices, including surface water (not detected (ND) - 52.3 ng L^{-1}) [5] and groundwater (ND – 166 ng L^{-1}) [6]. Furthermore, wastewater treatment plants (WWTPs) handling domestic and hospital wastewater in Canada have reported E1 concentrations to be as high as 270 ng L^{-1} [7]. In hospital settings, E1 is widely used in pharmaceuticals for disease treatment and prevention. The discharge of pollutants directly into the environment from hospital wastewater poses a significant risk to both ecosystems and water quality [4, 8–9]. While various contaminants have been identified in the environment at low concentrations, the long-term consequences of exposure to one or more low-level pollutants remain largely unknown.

In the European Union, the established environmental quality standard for E1 is 3.6 ng L^{-1}, as outlined in the Commission Implementing Decision (EU) 2018/840 (2018) [10]. Conversely, Australia sets a limit of 30 ng L^{-1} for E1 in reused water for water supply, according to the regulations set by the Environment Protection and Heritage Council (Australia) and Natural Resource Management Ministerial Council (Australia) in 2008 [11]. The US Food and Drug Administration (FDA) has initiated monitoring efforts to assess the harmful effects of EDC occurrence [12]. However, it is noteworthy that there are currently no specific regulations or guidelines in place for E1 in hospital wastewater, underscoring a gap in measures to safeguard human health and the environment from these contaminants.

To address the challenge of removing E1 and other micropollutants from wastewater, innovative technologies such as photocatalytic degradation using TiO_2 have shown great promise. A study by Pan et al. [13] has demonstrated that UV+TiO_2 can degrade 17β-estradiol (EE2) more efficiently than UV alone. The use of advanced technologies like the photocatalytic membrane reactor (PMR) is essential for the efficient removal of micropollutants in wastewater treatment plants [4]. PMR combines photocatalysis and membrane filtration, offering a comprehensive approach to water and wastewater treatment, especially with micropollutant removal. Furthermore, numerous studies have utilized titanium dioxide (TiO_2) as a catalyst due to its high photocatalytic activity when exposed to UV irradiation, which generates hydroxyl radicals capable of breaking down pollutants into smaller, less toxic compounds [14–16]. TiO_2 is valued for its stability, cost-effectiveness, and eco-friendly properties [17] making it a promising candidate for addressing micropollutants in wastewater treatment processes.

In recent years, various studies have utilized TiO_2 in photocatalytic degradation. Doping TiO_2 with nitrogen can lead to the removal of ciprofloxacin by 66 percent within 4 h [18] and paraquat by 85.79 percent within 2 h [19]. When co-modified with iron and nitrogen (Fe-N-TiO_2), the presence of the nitrogen dopant hinders the function of iron as a recombination site for the electrons and holes created by light [20]. Notably, the performance of PMR with immobilized TiO_2 (PVDF-TiO_2) under UV (365 nm) showed an 84 ± 6 percent removal efficiency for E1 and E2. However, it is important to consider that hormone degradation is influenced by catalysts and light transmission [21]. Furthermore, PMR was put to the test using a microfiltration membrane with UVA (UVA-MF) and TiO_2-P25 photocatalysis (UVA/TiO_2-MF) for the removal of oxytetracycline. The study demonstrated an oxytetracycline removal efficiency of over 90 percent after 30 min, with the highest TiO_2-P25 loading (0.4 g L^{-1}) resulting in the highest removal efficiency but a decline in permeate flux of the membrane [22]. While studies have detected E1 at low concentrations in aquatic environments, Zhang et al. (2021) [23] have shown that high E1 concentrations (>10 mg L^{-1}) can significantly reduce productivity and metabolic activity. These findings highlight the im-portance of effective wastewater treatment strategies, such as PMRs, in addressing the challenges posed by hormone pollutants in diverse environmental settings.

Expanding on the literature review outlined above, this study aims to address two primary objectives. Firstly, it seeks to monitor E1 levels in wastewater samples obtained from two hospitals with different types of wastewater treatment plants. Through a comparative analysis, the study aims to uncover variations in E1 concentrations and provide insights into the effectiveness of wastewater treatment processes in different healthcare facilities. Secondly, the study investigates the E1 removal efficiency of a PMR, using E1 initial concentration of 5 mg L^{-1}. The investigation aims to assess the PMR technology's capability to reduce E1 concentrations in hospital wastewater, contributing to a better understanding of its potential applications in mitigating the release of micropollutants into the environment. The outcomes of this study are expected to provide valuable insights into hormones monitoring in hospital wastewater and enhance understanding of the effectiveness of PMR technology in micropollutant removal. These findings will not only advance scientific knowledge in the field but also provide practical implications for enhancing wastewater treatment strategies in hospital settings, ultimately contributing to environmental protection and public health.

Materials and methods

1) Reagents and chemicals

The materials used in the study were sourced from reputable suppliers. Polyvinylidene fluoride (PVDF, molecular weight 20 kDa), polyvinylpyrrolidone (PVP, molecular weight 40 kDa), titanium (IV) butoxide ($Ti[OC(CH_3)_3]_4$), and estrone hormone (E1) were all provided by Sigma-Aldrich® (Germany). N-methyl-2-pyrrolidone (NMP) was acquired from Loba Chemie (India). For the extraction and purification of samples, acetonitrile of HPLC-grade (Sigma-Aldrich®) and Ultrapure water (Merck, Germany) were utilized. The choice of high-quality solvents and materials from reputable suppliers ensures the reliability and accuracy of the experimental procedures, thereby enhancing the robustness of the study.

2) Sampling and preparation of sample

The study collected samples from two hospital wastewater treatment plants located in Songkhla, Thailand, as illustrated in Figure 1. Hospital A, a regional hospital, employs an activated sludge (AS) system in their wastewater treatment plant. Hospital B employs two distinct treatment plants. Hospital B (AL) utilizes an aerated lagoon treatment plant, responsible for wastewater collection from dormitories and hospital facilities. Meanwhile, Hospital B (AS) operates an activated sludge treatment plant specifically designed for wastewater within the hospital premises. To capture variations over time, water samplings were collected on two separate occasions, aiming to represent the years 2022 and 2023. This systematic approach ensures a comprehensive understanding of the dynamics of estrone (E1) residues in hospital wastewater, considering different treatment plant configurations and temporal variations.

To ensure the integrity of the samples, initially the samples were filtered through a Whatman membrane filter (pore size 0.45 m) to remove particulate matter and subsequently stored at -4 °C until analysis. Extraction of estrone (E1) was conducted using the solid-phase extraction (SPE) technique, employing polypyrrole magnetic microspheres, as detailed in previous literature [24]. Following extraction, the water underwent evaporation using a rotary evaporator, followed by re-dissolution with 0.50 mL of acetonitrile. After that, the solutions were filtered through a nylon syringe filter (0.45 μm). The samples volume of 20 L was injected into LC-MS/MS (LCMS-8060, Shimadzu, Japan) [25]. The limit of detection (LOD) for E1 was 0.94 ± 0.05 ng L^{-1} and the limit of quantitation (LOQ) was 3.13 ± 0.17 ng L^{-1}. Additionally, wastewater characteristics, including chemical oxygen demand (COD), dissolved organic carbon (DOC), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), and pH, were analyzed following standardized methods [26].

3) Synthesis of TiO_2 composite photocatalytic membrane

The synthesis of TiO_2 followed a reflux technique, as outlined by Bootluck et al. [27]. The procedure involved the sequential addition and mixing of 3 mL of titanium (IV) butoxide with 30 mL of ethylene glycol until a homogeneous solution was achieved. The solution underwent refluxing at 180°C for 120 minutes, yielding precipitates that were subsequently washed with ethanol via centrifugation and air-dried at room temperature. The dried powder underwent calcination in a furnace at 450 °C for 180 min, utilizing a heating rate of 5 °C min^{-1}. The final product obtained through this process was the TiO_2 powder.

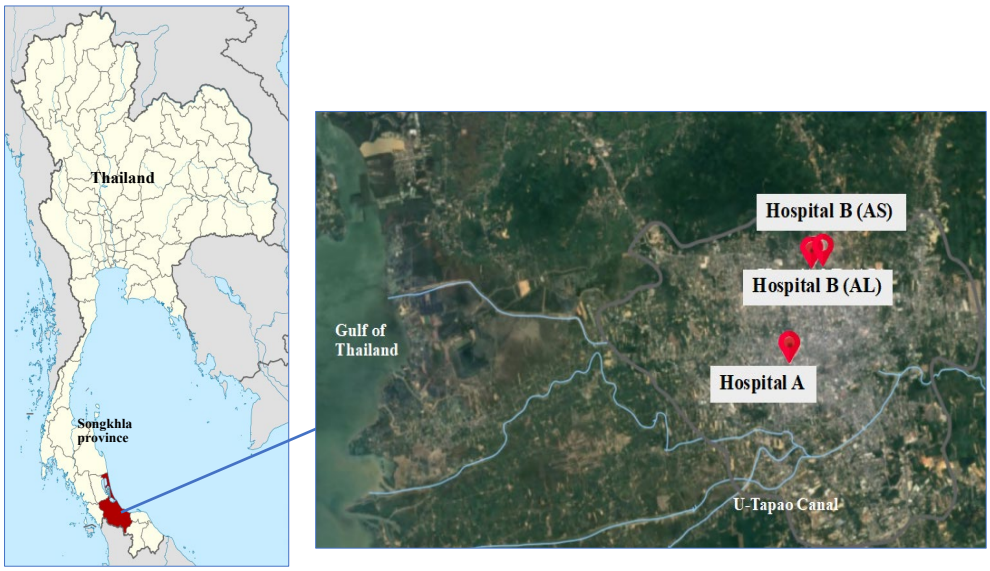

Figure 1 The study area and sampling sites in Songkhla, Thailand.

4) Membrane preparation and characterization

The mixed matrix membranes (MMM) were fabricated using the phase inversion method. The PVDF membrane formulation consisted of PVDF powder (17 wt%), with the addition of PVP (0.1 wt%) to the mixture in NMP solvents (82.90 wt%). After dissolution and homogenization at 60°C for 24 h, residual air bubbles were eliminated through ultrasonic treatment (VGT-1620T, GT sonic, China) for 30 min. The casting membrane was then applied onto a glass substrate at room temperature. Subsequently, the membranes were immersed in a water bath followed by multiple washes with reverse osmosis (RO) water to remove residual solvent. The same procedure was followed for the PVDF/TiO_2 membrane, with the addition of 1 wt% TiO_2 powder to the PVDF solvent. The membranes were then stored in RO water at room temperature until analysis.

All membrane samples underwent comprehensive characterization of their physical properties, including the examination of surface morphology using a scanning electron microscope (SEM, Quanta 400, Thermo Fisher Scientific, Czech Republic) and the observation of diffraction peaks via XRD (Empyrean, PANalytical, Netherlands). The water hydrophilicity of the membranes was assessed through water contact angle (WCA) measurement using the Data Physics Optical Contact Angle (OCA15, GmbH, Filderstadt, Germany). The rectangular membrane samples were affixed to glass slides, and water was dropped at a rate of 1 µL s^{-1} and the WCA was determined a minimum of ten times to ensure accuracy and reliability of the measurements.

5) Photocatalytic degradation experiments

A schematic representation of the batch experimental setup for the PMR is depicted in Figure 2. The crossflow reactor, covering a membrane area of 416.5 cm^2 (24.5 cm. x 17 cm.), was employed with an initial E1 concentration of 5 mg L^{-1}. The E1 stock solution was prepared using acetonitrile and subsequently diluted with ultrapure water. The synthetic wastewater (1.5 L) was introduced to the membrane cell through a peristaltic pump (Model 77200-50, Masterflex, Germany) at a flow rate of 60 mL h^{-1}. For the irradiation experimental, UVC lamps (PL-L 2G11, Philips) delivering 27 W of UV-C radiation were utilized. The lamps were positioned at a distance of 5 cm from the reactor. The UF membrane performance under UV irradiation is denoted as PVDF/TiO_2 (UV), while the UF membrane with TiO_2 but without UV irradiation is referred to as PVDF/TiO_2. The pristine PVDF membrane without catalyst and irradiation, is called PVDF. All experiments were conducted over a period of 180 minutes, with the permeate collected in amber glass vials for subsequent analysis of E1 concentration through High-Performance Liquid Chromatography with Diode Array Detection (HPLC-DAD) using equipment from Hitachi, Japan [24].

The water flux of the membrane was calculated following Eq. 1 [28].

$$J_w = \frac{V}{A \times t} \qquad \text{(Eq. 1)}$$

where J_w is the membrane flux (L $m^{-2}h^{-1}$), V is permeate volume (L) and t is time (min). A is the effective membrane area (m^2), respectively.

The photocatalytic performance of the membrane was calculated by using Eq. 2 [29].

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{(Eq. 2)}$$

where C_i and C_f are the initial and final concentrations of E1 (mg L^{-1}).

Statistical analyses were performed using analysis of variance (ANOVA) to scrutinize the experimental data, significant variance was achieved at $p < 0.05$, ensuring a robust assessment of the results.

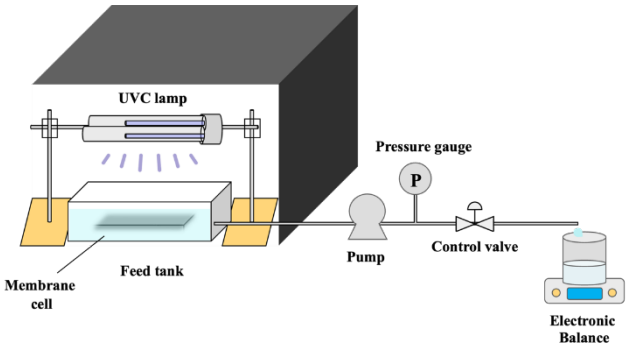

Figure 2 Schematic diagram of photocatalytic membrane reactor.

Results and discussion

1) The monitoring of Estrone (E1) in hospital wastewater

The wastewater samples from the two hospital WTPs were comprehensively characterized with several key parameters as summarized in Table 1. The pH values across all sampling sites ranged from 7.0 to 7.9. The strength of the raw sewage was found to be the highest at Hospital B (AL) influent, in which COD concentrations were 371.9 to 600 mg L^{-1}.

Table 1 Characteristics of collected water samples including influent (raw sewage) and treated effluent from the two hospitals

Sampling 1				
Parameter	**Sample**	**Hospital A (AS)**	**Hospital B (AL)**	**Hospital B (AS)**
pH	Influent	7.2 ± 0.1	7.9 ± 0.1	7.5 ± 0.2
	Effluent	7.0 ± 0.2	7.5 ± 0.1	7.7 ± 0.21
TSS (mg L^{-1})	Influent	86.0 ± 5.9	48.7 ± 5.2	58.0 ± 1.6
	Effluent	10.7 ± 2.5	32.7 ± 3.8	15.3 ± 2.5
COD (mg L^{-1})	Influent	176.2 ± 31.1	371.9 ± 33.9	264.2 ± 0.0
	Effluent	95.4 ± 0.0	161.5 ± 83.0	132.1 ± 0.0
DOC (mg L^{-1})	Influent	21.9 ± 0.7	29.2 ± 1.1	41.0 ± 1.4
	Effluent	8.3 ± 0.0	7.8 ± 0.1	21.4 ± 0.0
TKN (mg L^{-1})	Influent	35.6 ± 0.8	32.2 ± 0.8	46.5 ± 0.4
	Effluent	7.3 ± 2.0	2.5 ± 0.8	31.4 ± 5.2
Sampling 2				
Parameter		**Hospital A (AS)**	**Hospital B (AL)**	**Hospital B (AS)**
pH	Influent	7.1 ± 0.1	7.4 ± 0.1	7.4 ± 0.1
	Effluent	7.0 ± 0.2	7.4 ± 0.1	7.0 ± 0.4
TSS (mg L^{-1})	Influent	82.7 ± 0.9	87.3 ± 3.4	51.3 ±2.5
	Effluent	26.7 ± 0.9	22.7 ± 0.9	10.0 ± 0.0
COD (mg L^{-1})	Influent	305.9 ± 11.1	600.0 ± 29.3	337.3 ± 55.5
	Effluent	117.7 ± 11.1	41.4 ± 19.5	31.4 ± 0.0
DOC (mg L^{-1})	Influent	35.0 ± 1.4	35.8 ± 1.5	69.3 ± 2.1
	Effluent	31.5 ± 1.0	7.5 ± 0.1	17.8 ± 0.7
TKN (mg L^{-1})	Influent	45.4 ± 0.8	28.4 ± 0.3	60.5 ± 2.4
	Effluent	38.1 ± 1.6	1.1 ± 0.0	20.7 ± 0.0

The Pollution Control Department (BE.2010) mandates effluent discharge limits, stipulating that the COD, TKN, and TSS of the effluent must not exceed 120 mg L^{-1}, 35 mg L^{-1}, and 30 mg L^{-1}, respectively. During the first sampling occasion, COD of the effluent at Hospital B (AL) and Hospital B (AS) and TSS of the effluent at Hospital B (AL) were found to be higher than the effluent discharge standard, indicating that improvement of the existing wastewater treatment facilities are needed.

To assess performance of the WTPs at the two hospitals, removal efficiency for each wastewater treatment facility was compared. For COD removal, the Hospital B (AL) achieved the highest removal efficiency of 56.6 and 93.1 percent for the Sampling 1 and Sampling 2, respectively. However, the removal efficiency for TSS by Hospital B (AL) was comparatively lower at than the other AS systems. For the Sampling 1 and Sampling 2, the TSS removal by Hospital B (AL) was at 32.9 and 74.0 percent while the two AS systems achieved 67.7–87.6 percent TSS removal. Thus, the lack of a sedimentation tank in AL wastewater treatment has led to lower TSS removal. It is important to note that these variations may be attributed to factors such as treatment system efficiency, wastewater management practices, influent volume, and daily population served, as suggested by Wiafe et al. [30]. These results underscore the imperative for implementing effective wastewater treatment strategies to comply with regulatory standards and ensure environmental protection.

In these two hospital wastewaters, the E1 concentrations were detected in the range of ND–2.46 ng L^{-1}. The LOD for E1 was 0.94 ± 0.05 ng L^{-1} while the LOQ for E1 was 3.13 ± 0.17 ng L^{-1}. The very low concentration or the absence of E1 were previously reported in surface water in Malaysia [31] and wastewater treatment plants in Portugal [32]. Hydrophobic properties and low solubility in water of E1 could attributed to the absence of E1 in the aquatic environment. The Kow of 3.43 indicates that E1 tends to accumulate in sludge or organic colloids rather than dissolve in water. Possible explanations for the absence of E1 in

hospital wastewaters, or its presence at levels below the LOD of the method employed, should be explored. Long-term monitoring is essential to comprehensively assess the effects and risks associated with E1, thereby safeguarding ecosystems from potential contaminants.

2) Membrane characterization

2.1) Physical properties

The hydrophilic property of the membrane was assessed through WCA) measurements (Figure 3). The WCA for the PVDF membrane and PVDF/TiO_2 membrane was 84.07° and 78.14°, respectively. Notably, the PVDF membrane exhibited a higher contact angle compared to the PVDF/TiO_2 membrane, indicating lower hydrophilicity. This finding aligns with previous research by Zhao et al. [33], which reported a decrease in water contact angle with an increase in TiO_2 content (in the range of 1–5 wt%). TiO_2 nanoparticles exhibit hydrophilicity, indicating a strong attraction towards water. When integrated into a PVDF membrane, it enhances the hydrophilicity of the membrane surface, rendering it more conducive to wetting by water [34]. Additionally, the presence of TiO_2 nanoparticles can enhance the surface roughness of the PVDF membrane, facilitating greater interaction between the surface and liquid molecules [35]. This elucidates the greater hydrophilic nature of the PVDF/ TiO_2 membrane in comparison to the PVDF membrane. The addition of TiO_2 catalysts has been associated with heightened hydrophilicity, increased water permeate flux, and enhanced anti-fouling properties of membranes [36–37].

2.2) Surface morphology properties

The morphological structure of the membrane was examined using scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX). Figure 4 illustrates SEM images depicting the outer surface and cross-section of the membranes. SEM analysis was carried out at 10000x magnification for the outer surface and 500x magnification for the cross-section. Figures 4(a) and Figures 4(b) present the outer surface membranes at 10000x magnification, revealing that TiO_2 was not prominently visible on the surface of membranes prepared using the mixed matrix membrane (MMM) method. The morphology exhibited an asymmetric nature, characterized by a finger-like structure on the top and a sponge-like structure on the bottom, as depicted in Figures 4(c) and 4(d). Notably, the pores in the bottom cross-section of the PVDF membrane appeared large. This observation is consistent with findings by Gayatri et al. [36], who reported that the addition of TiO_2 contributes to an improved membrane morphology. Consequently, the incorporation of TiO_2 is seen to enhance mass transfer and increase water flux in the membrane structure.

Figure 5 shows the elemental distribution within the cross-section of the PVDF/TiO_2 membrane, as analyzed by SEM-EDX. The EDX images confirm the substantial presence of fluorine (F) at 47.8 0.9 wt%, carbon (C) 44.7 0.9 wt%, oxygen (O) 7.1 0.9 wt%, and titanium (Ti) 0.4 0.2 wt% respectively. Furthermore, the result indicates that Ti was dispersed both on top surface and throughout the cross section of membrane as shown in Figure 5(b). The ultrasonic process effectively prevented precipitation of substances during membrane casting [28]. Moreover, XRD patterns of TiO_2, PVDF membrane and PVDF/TiO_2 membrane are shown in Figure 6. The PVDF membrane exhibits various crystalline forms, with a diffraction angle of 18.5° corresponding to the α-phase peak and 20.5° corresponding to the β-phase peak [38]. The diffraction peaks of TiO_2 became evident in the XRD curves with increasing TiO_2 dosage. The diffraction curve of the PVDF/TiO_2 membrane closely resembled that of the TiO_2 powder. The presence of an anatase structure of TiO_2 was indicated by diffraction peaks at 25.5°, 37.9°, and 48.2°, corresponding to the (101), (004), and (200) planes, respectively [39]. The results highlight the presence of TiO2 particles in a powder form and their distribution within the PVDF/TiO_2 membrane.

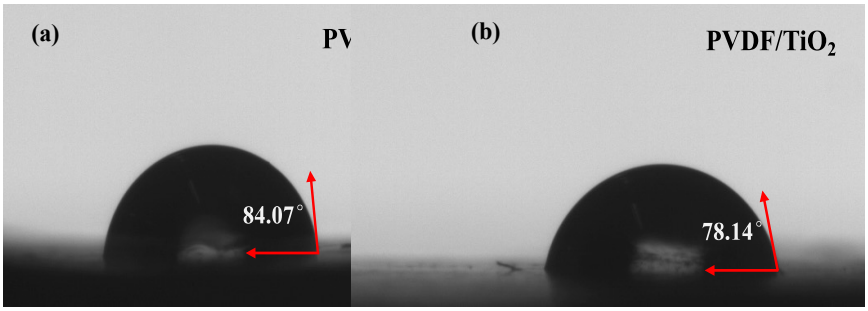

Figure 3 The water contact angle of the UF membrane.

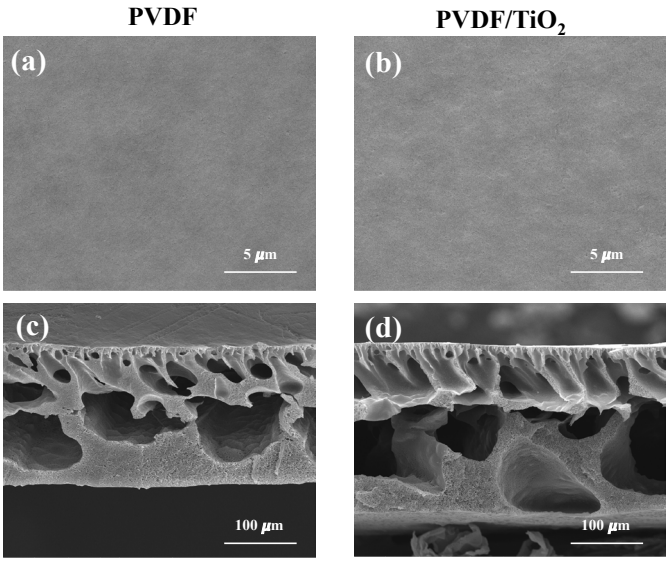

Figure 4 Scanning electron microscope images of membrane outer surface (a) PVDF, (b) PVDF/TiO_2 membranes and cross-section of (c) PVDF and (d) PVDF/TiO_2 membranes.

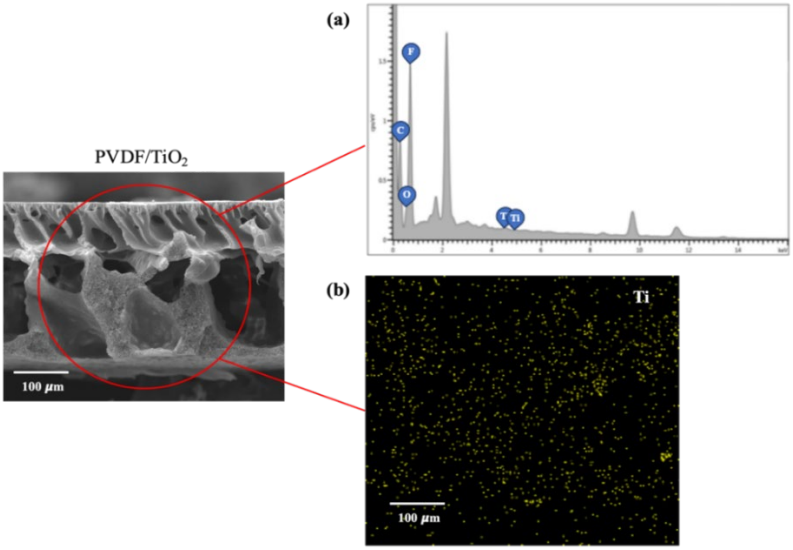

Figure 5 Elemental composition in cross-section of PVDF/TiO_2 membrane (a) EDX spectrum and (b) EDX mapping.

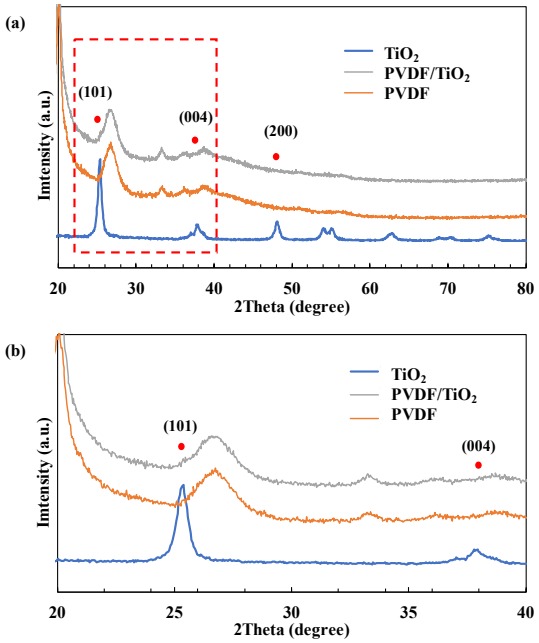

Figure 6 The XRD patterns of TiO_2, PVDF membrane, and PVDF/TiO_2 membrane in different 2Theta (a) 20-80 and (b) enlarged between 20-40 degrees.

3) The performance of PMR degradation

The performance of the PMR in E1 degradation over a 180-minute duration is depicted in Figure 7. The permeate flux values varied among the different membranes: the PVDF membrane exhibited the lowest permeate flux at 402 L m^{-2} h^{-1}, followed by 495 L m^{-2} h^{-1} for the PVDF/TiO_2 membrane, and 562 L $m^{-2}h^{-1}$ for the PVDF/TiO_2 with UV irradiation. Notably, there was a 23.15 percent increase in permeate flux for the PVDF/TiO_2 membrane compared to the PVDF membrane. The combination of UV irradiation with membrane filtration (PVDF/TiO_2 with UV) successfully improved anti-fouling capabilities and water permeability, resulting in a 39.62 percent increase in permeate flux. Statistical analysis revealed significant differences ($p < 0.05$) in water flux over 180 min among all membranes (PVDF, PVDF/TiO_2, and PVDF/TiO_2 with UV). The enhanced water flux under UV light is attributed to photoinduced hydrophilicity activated by UV light on TiO_2, as supported by previous studies. [40-41].

In terms of E1 removal efficiency, the filtration mechanism without UV irradiation achieved a removal of 36.5 ± 2.7 percent for the PVDF/TiO_2 membrane, surpassing the PVDF membrane which attained 32.6 ± 7.8 percent. Throughout the 180-min E1 removal experiment, the PVDF membrane exhibited significantly lower removal compared to the PVDF/TiO_2 membrane ($p = 0.01$). The photocatalytic membrane reactor PVDF/TiO_2 with UV achieved the highest removal efficiency at 96.7 ± 1.4 percent. Comparable studies by Padovan et al. [42] on solar TiO_2-photocatalytic degradation of hormones in tap water achieved 85 percent removal after 3 h. Additionally, Yang et al. [43] reported higher degradation of bisphenol A (BPA) using the Fe-TiO_2/PVDF membrane (69.9%) compared to the PVDF membrane (45.1%) over 180 min.

The mechanism of E1 removal by PVDF/TiO_2 with UV irradiation can be elucidated through the following steps:

Firstly, the filtration mechanism efficiently separates particles and pollutants in water. The incorporation of TiO_2 into the PVDF membrane enhances hydrophilicity, as evidenced by a decrease in water contact angle from 84.07° to 78.14°.

Secondly, under UV irradiation, TiO_2 absorbs photons and generates electron-hole pairs (e^- and h^+). These electron-hole pairs can subsequently react with water or oxygen to generate reactive oxygen species (ROS), including hydroxyl radicals (•OH) and superoxide ions ($•O_2$). These ROS play a pivotal role in breaking down pollutants on the surface of the membrane [43].

The pseudo first-order kinetic model demonstrates a superior correlation coefficient, effectively describing all E1 degradation processes. The rate of E1 degradation is contingent upon its initial concentration, with an increase in light intensifying the degradation rate. Photocatalytic membranes employing TiO_2 catalysts exhibit high efficacy in degradation due to the rapid transfer of photogenerated hole electrons in the reaction [44].

Figure 8 illustrates the performance of the E1 removal in various water matrices, specifically comparing the influent of the Hospital A in the experiment using real wastewater. A noteworthy observation from the comparison of percent removal by the PMR in synthetic wastewater and real wastewater reveals a significant decrease in percent removal ($p = 0.01$). The PVDF/TiO_2 membrane with UV demonstrated the most effective removal, surpassing 96.7 percent removal in synthetic wastewater. However, when the real wastewater was used in the experiment, the removal efficiency experienced a slight decrease of 7.96 percent. This difference can be attributed to the presence of particulate and organic matter in the real wastewater, which may hinder the removal process within the system.

The degradation of E1 and its transformation to a new product was explained by Escudeiro Oliveira et al. [14]. There are two major steps in the degradation routes in a hydroxyl radical-containing medium of E1. First, the addition of the hydroxyl radical to the molecule in the degradation, results in by-products with a m z-1 for each of the hormones. The second step involves the removal of a water molecule, which is followed by new hydroxyl radical additions. The process occurred until the rings ruptured, producing new chemicals. The major ion peaks with m z^{-1} of 268, 269, and 285 were observed in the photodegradation product of E1. It can be identified as lumiestrone, has the same molecular weight as E1 and also activated human estrogen receptor [42, 45].

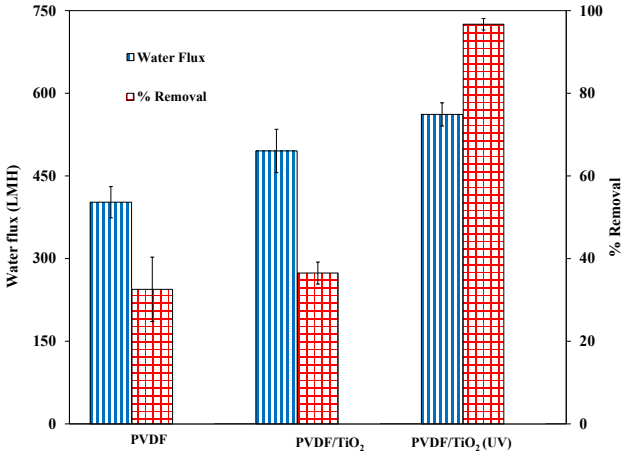

Figure 7 The E1 degradation performance of PMR at 180 min.

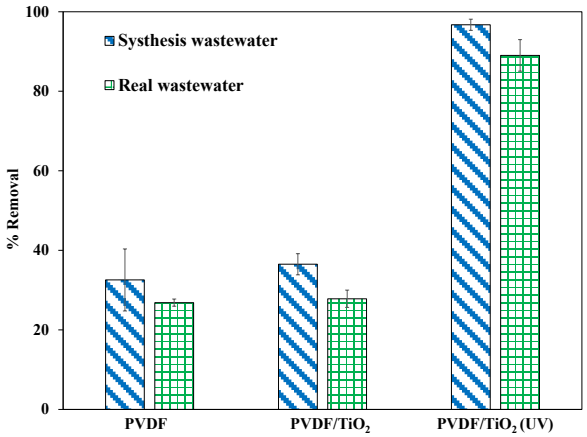

Figure 8 Comparative assessment of E1 removal from synthetic wastewater versus real hospital wastewater (operation time of 180 min).

Conclusion

This study comprehensively investigated the presence of estrone (E1) in hospital wastewater and the removal of E1 using a photocatalytic membrane reactor (PMR). Despite being detected at low concentrations, the presence of E1 in hospital wastewater underscores the importance of effective wastewater treatment strategies to mitigate environmental contamination. The synthesis and characterization of TiO_2 composite photocatalytic membranes demonstrated enhanced hydrophilicity and surface morphology, contributing to improved membrane performance and water permeability. The integration of TiO_2 nanoparticles into PVDF membranes exhibited promising results in terms of E1 removal efficiency, especially when coupled with UV irradiation, up to 96.7 percent removal was achieved for synthetic wastewater in 180 mins. The challenges posed by the presence of complex matrices in real wastewater may affect treatment efficiency. Understanding these challenges is crucial for the optimization of wastewater treatment technologies to address the diverse composition of real-world wastewater streams. By elucidating the effectiveness of PMR technology in removing micropollutants like E1 from hospital wastewater, the study provides valuable insights for enhancing wastewater treatment strategies.

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