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Hybrid membrane system with electrochemical oxidation process for removal of Diclofenac sodium from Aqueous Solution

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ABSTRACT

This study presents an innovative approach to eliminating the pharmaceutical pollutant diclofenac sodium (DFS) by combining nanofiltration membrane technology with an electrochemical oxidation process. The nanofiltration membrane was prepared by phase inversion, and modified with cetyltrimethylammonium chloride (CTAC) to improve surface properties and pore structure. The concentrate from the nanofiltration treatment has been utilized as the input feed for the electrochemical section, employing Ti/SnO₂- α -Fe₂O₃ electrodes. The PES/CTAC membrane exhibits a more uniform and stable pore structure, leading to increased permeability and antifouling properties. Additionally, the inclusion of CTAC through the surface adsorption mechanism improved the DFS rejection performance, achieving a maximum rejection rate of 65.2% for the membrane with a composition of 0.1 wt% CTAC. The obtained results show that the titanium electrode coated with SnO₂ and α -Fe₂O₃ nanoparticles removed the DFS pollutant by 56%. In total, both membrane and electrochemical process removed 80.5% of the primary Diclofenac pollutant. According to the low energy consumption of this process (EEC=0.014144 US\$/m³) and other results, the combination of the PES/CTAC membrane and Ti/SnO₂- α -Fe₂O₃ electrode is an efficient method for diclofenac sodium pollutant removal.

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1. Introduction

The presence of emerging organic pollutants (EOPs) in wastewater, particularly in hospital wastewater, poses a significant threat to our environment. These pollutants are not removed by traditional wastewater treatment processes, and they can harm aquatic ecosystems [1]. EOPs consist of a variety of substances, including pharmaceuticals, persistent organic pollutants, endocrine-disrupting chemicals, and personal care products [2]. Diclofenac is a nonsteroidal anti-inflammatory drug (NSAID) that is excreted unchanged in the urine and has raised concerns about its potentially harmful effects. Studies have shown that diclofenac even at low concentrations can cause physiological disturbances, biochemical changes, and behavioral changes in aquatic organisms [3]. Polyether sulfone (PES) membranes are a type of polymeric membrane widely utilized in water and wastewater treatment applications because of their high hydrophilicity, chemical stability, mechanical strength, and relatively low cost, making them easy to fabricate [4]. However, PES membranes are susceptible to fouling, which can diminish their performance and lifespan [5]. There are several ways to overcome the limitations and disadvantages of using PES membranes in treating organic and pharmaceutical pollutants. These include membrane modification methods such as blending with other polymers [6], incorporating nanoparticles [7], surface coating [8], plasma treatment, and grafting [9]. Modifying PES membranes with surfactants can enhance their hydrophilicity, porosity, and antifouling properties [10]. Surfactants are molecules that have both hydrophilic and hydrophobic parts [11]. Cetyltrimethylammonium chloride (CTAC) is a cationic surfactant that is relatively inexpensive and easy to use [12]. It can interact with the PES polymer chains through both electrostatic and hydrophobic interactions, forming

a layer on the surface of the membrane. This layer enhances the hydrophilicity, porosity, and antifouling properties of the PES membrane [13]. Another approach to enhancing the performance of modified membranes is by integrating them with electrochemical process. PES membranes can be combined with other membrane technologies or electrochemical oxidation process to enhance their removal efficiency for organic and pharmaceutical pollutants [14]. Electrochemical oxidation process removes pollutants by generating hydroxyl radicals ($^{\circ}\text{OH}$). The significant advantages of electrochemical technologies include their environmental compatibility, versatility, high efficiency, selectivity, low cost, ease of use due to minimal equipment requirements, and safety [15]. Hydroxyl radicals ($^{\circ}\text{OH}$) are highly reactive and can oxidize a wide range of organic pollutants [16]. Titanium was chosen to make the electrode due to its corrosion resistance, biocompatibility, mechanical strength, relatively low cost, and high electrocatalytic activity. However, due to the tendency of titanium to oxidize and form an oxide layer (TiO_2) on the surface of titanium, its electrical conductivity decreases. To solve this issue, its catalytic performance can be improved by modifying its surface by applying a coating [17]. Electrophoretic deposition (EPD) is an effective method for coating electrodes to increase the ability of electro-catalytic oxidation and the stability of electrodes [18]. In EPD, charged particles in a suspension are deposited on the surface of an electrode by applying an electric field. The orientation of the electric field determines whether the particles are deposited on the anode or the cathode. The thickness and morphology of the deposited film can be controlled by adjusting the voltage, time, and composition of the suspension [19]. A variety of different materials can be used to coat electrodes for electrochemical oxidation

process, including noble metals, metal oxides, and carbon materials [18]. SnO_2 and Fe_2O_3 , metal oxides with high electrocatalytic activity, enhance titanium performance by improving removal efficiency, reducing fouling, and enhancing corrosion resistance. These coatings are non-toxic, biocompatible, and suitable for water and wastewater treatment [20]. To overcome the limitations of nanofiltration technology and electrochemical oxidation process in wastewater treatment, these two technologies can be combined. Combining these technologies can enhance the efficiency of the electrochemical method and bring the membrane concentrate to a safe level before environmental discharge. The high concentration of micropollutants in the concentrate provides suitable conditions for the effective operation of the electrochemical oxidation process [21]. Below are two examples of studies that have integrated membrane and electrochemical technologies for water treatment. Valentina Buscio et al. conducted a study on treating Yellow S-3R textile wastewater using a combination of nanofiltration membrane and electrochemical processes. The study found that the use of Nanofiltration membranes Hydracore10 and Hydracore50 resulted in up to 98% removal of synthetic dyeing effluents. Following the membrane filtration, an electrochemical process was used to treat the concentrate with a high dye concentration, resulting in a 70% reduction of pollutants from the nanofiltration concentrate [22]. Álvaro Soriano et al. developed a mathematical model to simulate the integrated NF-ELOX process. The results indicate that the integrated NF-ELOX process can significantly decrease the energy consumption for PFHxA removal compared to EO alone. The NF90 membrane, which exhibited high rejection of PFHxA and ions, enabled a 59.2% reduction in energy consumption while achieving a 99% PFHxA removal ratio [23].

This study investigates the hybrid of nanofiltration membrane technology with an electrochemical oxidation process, specifically using Ti/SnO_2 - α - Fe_2O_3 electrode, for removal of diclofenac sodium pharmaceutical pollutant.

2. Experimental

2.1. Materials and methods

Polyether sulfone (Ultrason® PESU, BASF-Germany) was procured from the esteemed BASF/Germany Company. Polyvinylpyrrolidone with a purity of 99% (PVP, 25,000 g/mol) and Dimethyl acetamide (DMAc) with a minimum purity of 98.0% were also added to the solution. Sodium sulfate (Na_2SO_4), Nickel (II) chloride (NiCl_2), and Diclofenac sodium (DFS) was provided by Merck Millipore Corporation (Germany). Bovine serum albumin (BSA), a lyophilized powder with 96% electrophoresis and a pH of 7 was purchased from Sigma Aldrich. The cationic surfactant Cetyltrimethylammonium chloride (CTAC), nanoparticles SnO_2 , and α - Fe_2O_3 (purity > 99%) were purchased from Neutrino Company, Iran.

2.2 Preparation of Nanofiltration Membrane

PES-NF membranes were fabricated using the phase inversion separation technique [24]. The casting solution was prepared using PES polymer (18% w/w), DMAc solvent, PVP polymer (0.5% w/w), CTAC surfactant (concentrations of 0.01%, 0.02%, and 0.1% w/w), and non-solvent [25]. The polymer solution was stirred for 3-4 hours at room temperature to ensure uniformity and homogeneity. The casting solution was then spread onto a flat glass plate using a hand-made film applicator and immersed in a coagulation bath of non-solvent to initiate the phase inversion process. The membrane was then immersed in distilled water and ethanol for 24 hours to ensure complete phase inversion and then dried. The membrane thickness and pore diameter were measured to be approximately 150 μm and 148 nm [26].

2.3 NF membrane performance assessment experiments

The surface morphology and properties of the bare PES and modified CTAC/PES membranes were investigated using various techniques, including Field Emission Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM), and porosity measurements. The Guerout-Elford-Ferry equation was used to calculate the mean pore radius (r_m) of the membrane based on porosity data. The permeability, antifouling properties, and performance of nanofiltration membranes were evaluated using a dead-end system. All filtration tests associated with the flux of purified water were evaluated at room temperature (25 °C) under various nitrogen gas pressures (1, 2, 3, and 4 bar). This was followed by a one-hour water flux test and a protein rejection test using a bovine serum albumin (BSA) solution. BSA concentration was determined using the UV-Vis spectrophotometric method at λ_{max} of 260 and 280 nm. To evaluate the efficiency of NF membranes in DFS removal, the solution container was emptied after the second stage of pure water filtration and filled with a diclofenac sodium solution of 10 ppm. The concentration of DFS was measured at λ_{max} of 271 nm.

2.4 Electrochemical setup, electrode preparation, and performance experiment

The Ti/SnO₂- α -Fe₂O₃ electrode was fabricated according to the method described by (Abdolyousefi et al., 2020). Additionally, the morphology of the electrode surface was analyzed using a Field Emission Scanning Electron Microscope (FE-SEM). Linear Sweep Voltammetry (LSV) was conducted to assess the oxygen evolution potential (OEP), Chronopotentiometry (CP) was utilized to evaluate the electrochemical stability of the anodes, and Cyclic Voltammetry (CV) was performed to determine whether the electrode was

active or inactive, as reported by (Abdolyousefi et al., 2020) [20].

The electrochemical oxidation process was carried out with a pharmaceutical concentrate of nanofiltration along with the electrolyte Na₂SO₄ under an anodic current density of 0.1 A/cm². The amount of DFS removal was observed by the absorption spectrum of the sample using a UV-Vis spectrophotometer, and the percentage of pollutant removal at different times was calculated using the following equation.

$$X = \frac{A - A_0}{A_0} \times 100 \quad (1)$$

In this equation, A_0 is equal to initial absorption, and A is equal to absorption at a certain time.

Also, to measure the economic efficiency of the electrochemical oxidation process, the Electrical Energy Consumption (EEC) was calculated.

3. Results and discussion

3.1. Characterization of prepared nanofiltration membrane

This study investigates the use of CTAC as a hydrophilic additive in the casting solution for PES nanofiltration membranes. The addition of CTAC resulted in the formation of finger-like voids extending almost to the bottom of the membrane, and a decrease in the number of spongy pores. As the concentration of CTAC increased, wider and longer parallel columnar voids were observed, leading to an increase in porosity. The presence of hydrophilic additives, specifically CTAC, enhances the infiltration of the non-solvent (water) into the casting solution, expediting the rate of exchange between the solvent and non-solvent during membrane formation. This rapid exchange increases the precipitation rate, facilitating instantaneous demixing and enabling the production of highly porous membranes.

3.2. SEM analysis

The SEM images in Fig. 1 depict the CTAC/PES membranes. The unmodified membrane exhibits an irregular skin layer with finger-like structures. This irregularity is due to the less organized PES molecules in the non-modified membrane compared to the CTAC-modified membranes. The presence of CTAC surfactant helps to organize the PES molecules, resulting in a more uniform membrane surface. All the modified membranes show more finger-like pores compared to the bare PES membrane, which increases the permeation rate of these modified membranes [27]. The largest pore size is observed in the PES/CTAC 0.1 wt% blended membrane, where the addition of CTAC surfactant creates a more hydrophilic environment, promoting the formation of larger pores [28].

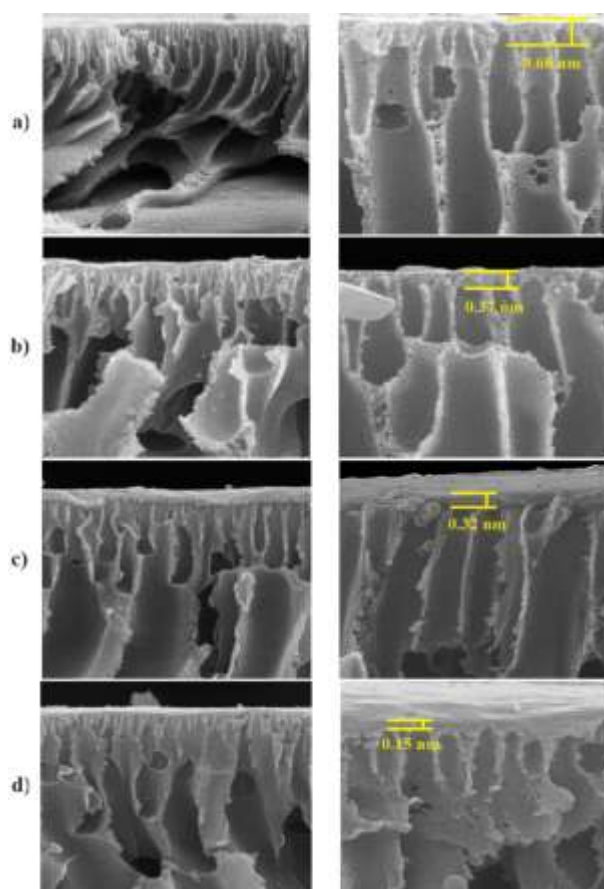


Fig. 1. SEM images of cross-sections of a) Pure PES b) PES/CTAC 0.01 wt% c) PES/CTAC 0.02 wt% d) PES/CTAC 0.1 wt%

3.3. AFM test

Fouling behavior in membranes is governed by the surface's degree of roughness, affecting the binding and unbinding of fouling agents. A smoother surface on the membrane demonstrates enhanced anti-fouling properties. Fig. 2 displays the AFM images captured from both the pure membrane and the membranes modified with CTAC ($5 \mu\text{m} \times 5 \mu\text{m}$). The AFM images illustrate that the addition of CTAC can modify the surface properties of the membrane. These images provide insight into the hydrophilic and hydrophobic characteristics of the sample surface, which are indicated by varying levels of elevation. The DME/SPM software (version 2.1.1.2) was used to compute various roughness parameters of the membrane surface, including roughness (S_a), root mean square of the Z data (S_q), and deviation between the maximum peak and minimum valley (S_z). The values of these parameters are compiled in Table 1.

Table 1. Roughness parameters, overall porosity and mean pore radius of the surfactant blended PES membranes.

Membrane	Porosity (%)	Mean pore radius (nm)	Roughness parameters		
			S_z (nm)	S_q (nm)	S_a (nm)
M ₀	30.5±1.6	1.30±0.4	24	33	208
M ₁	37.2±2.1	5.16±0.3	11	14	142
M ₂	44.2±1.3	4.89±0.4	10	12	83
M ₃	59.64±1.5	13.44±1.3	5	8	78

An analysis of Table 1 and Fig. 2 reveals that the pure membrane exhibits a higher degree of roughness compared to the PES/CTAC membranes. Conversely, among the blended membranes, the PES/CTAC 0.1 wt% membrane has the smoothest surface. The integration of the CTAC surfactant with the membrane surface can reduce surface roughness and increase porosity. The S_a , S_q , and S_z values decrease with increasing CTAC surfactant content up to 0.1 wt% [29].

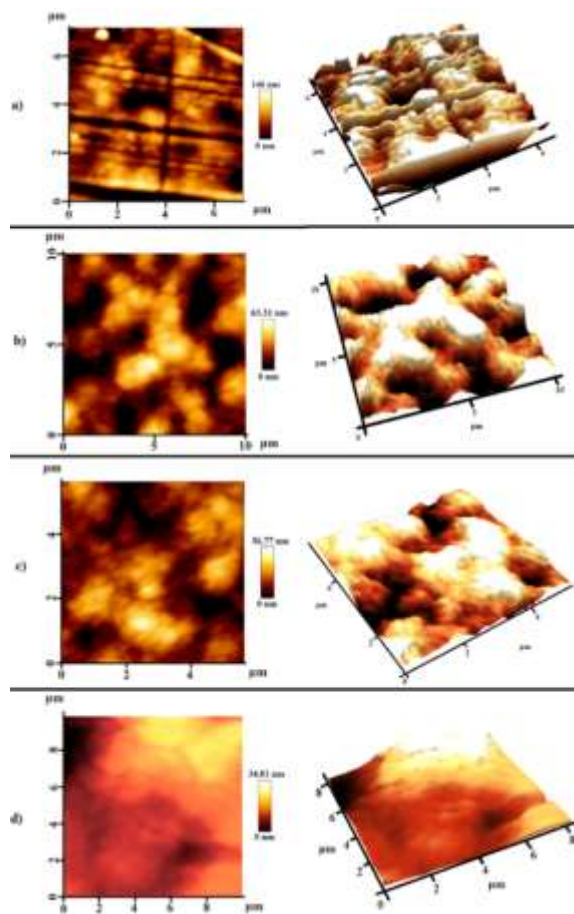


Fig. 2. Surface AFM images of a) Pure PES b) PES/CTAC 0.01 wt% c) PES/CTAC 0.02 wt% d) PES/CTAC 0.1 wt%

3.4. Antifouling behavior

As filtration proceeds, particles, and solutes accumulate and penetrate the membrane surface, leading to fouling and a decrease in flux. To simulate fouling, BSA was used, and the relative permeate water flux before and after BSA filtration was compared to calculate the flux recovery ratio [30]. The antifouling performance of CTAC/PES blended membranes by testing their rejection of a 200 mg/L BSA feed solution. As shown in Fig. 3, all modified membranes had higher BSA rejection rates than unmodified PES membranes, and membranes containing 0.1 wt% PES/CTAC showed the highest BSA rejection (98.65%). This study confirmed that the addition of CTAC improved the antifouling and rejection of BSA [31].

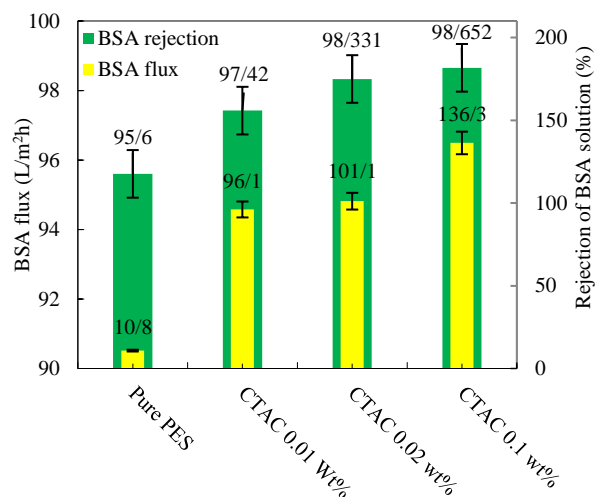


Fig. 3. Rejection and flux of BSA solution through the NF membranes at 3 bar

The effectiveness of the CTAC additive in enhancing the hydrophilicity and permeability of PES/CTAC membranes at varying CMC concentrations was demonstrated in Fig. 4. All PES/CTAC membranes had higher BSA and water fluxes compared to the unmodified PES membrane. The blended PES membranes containing 0.1 wt% CTAC had the highest reported fluxes of pure water permeation, which were assessed before and subsequent to BSA filtration [32].

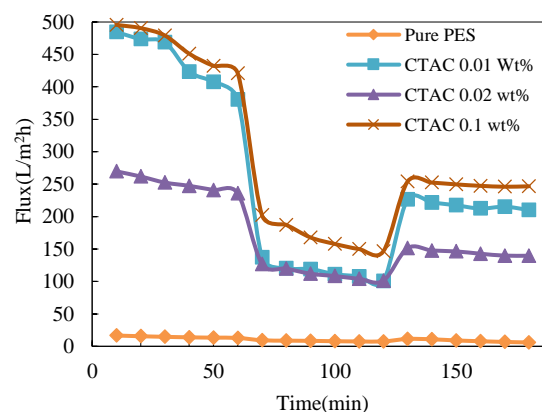


Fig. 4. The temporal evolution of membrane flux across three distinct stages: initial pure water, filtration of BSA solution, and second pure water filtration stage after membrane washing at a pressure of 3 bar

3.5. DFS removal by NF membrane

The study employed a dead-end cell operating at a pressure of 4 bar and a pH of 7.1, with a concentration of 10 ppm of Diclofenac sodium, to

investigate the effect of CTAC additive on DFS rejection by PES nanofiltration membranes. The DFS rejection rate was 35.6% for the bare PES membrane and increased to 65.2% for a membrane with 0.1 wt% CTAC (Fig. 5). The inclusion of CTAC and PVP additives in the membrane solution augmented pharmaceutical retention in modified membranes due to the pore-forming characteristics of PVP and the hydrophilic properties of CTAC. Decreasing the membrane roughness increases the hydrophilicity and reduces the contact angle, causing significant changes in rejection up to 65.17% [33]. The primary mechanism of separation in the constructed membranes is predominantly surface adsorption. The modified membranes exhibit increased hydrophilicity and decreased surface roughness due to the incorporation of CTAC. Surfaces like these are generally less conducive to the adsorption of hydrophobic molecules such as DFS. Notwithstanding, the interaction between the cationic heads of CTAC in the membrane surface and the anionic particles of DFS results in a surface adsorption effect. This phenomenon attracts and retains DFS molecules on the membrane surface, preventing DFS particles from passing through the membrane pores [34].

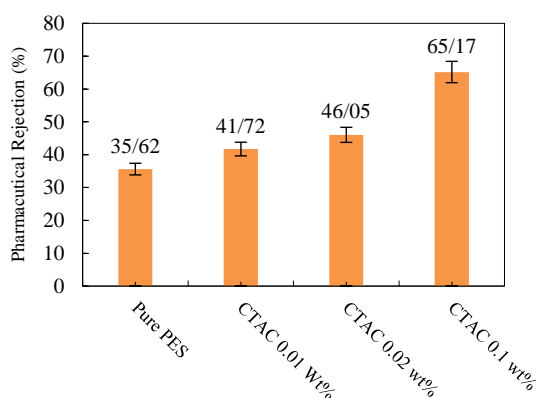


Fig. 5. DFS rejection rate of a) Pure PES b) PES/CTAC 0.01 wt% c) PES/CTAC 0.02 wt% d) PES/CTAC 0.1 wt%

A comparison of the pure water flux results obtained in this study with the results of previous findings that use other modifiers is presented in Table 2. The Pure water flux of the nanofiltration membrane modified

with CTAC surfactant in this study was higher than that of the membranes modified with surfactants in studies [35], [36], and [37]. Additionally, compared to modifiers in studies [38], [39], [40], [41], and [42] which did not use surfactants, the CTAC-modified membrane exhibited higher flux, indicating the efficacy of CTAC in improving the morphological characteristics of the nanofiltration membrane.

Table 2. The effect of different surfactants on the rejection of polymeric membranes

Modifier	Pure water flux (L/m ² h)	Ref.
CTAC	461	This work
Triton X-100	10	[35]
Brij 58	68	[36]
CTAB	67	[37]
Eutectic solvent (L-M/CSA)	111	[38]
Spirocyclic quaternary ammonium diamine monomer (SBI)	33	[39]
Methacrylic acid	41	[40]
Polydopamine	9	[41]
Chitosan	22	[42]

3.7. DFS removal by electrochemical oxidation

The DFS removal experiment was conducted using an undivided cylindrical glass container containing a pharmaceutical concentrate with a concentration of 6 ppm and using Na₂SO₄ salt as a supporting electrolyte. An anode made of Ti/SnO₂- α -Fe₂O₃, in combination with a stainless-steel plate cathode, was used with a 1 cm distance between them. Voltage and current control were applied using the MEGATEK M 3005 power supply model and the VICTOR 86 D digital multimeter model, respectively. Samples of pharmaceutical pollutants were analyzed at 15-minute intervals to show changes in pharmaceutical concentration removal using a UV-Vis spectrophotometer by measuring DFS absorbance at λ_{max} of 271 nm. The results showed that the Ti/SnO₂- α -Fe₂O₃ electrode removed 56% of DFS.

In total, the combination of nanofiltration membranes with electrochemical oxidation process, considering the removal of 65.2% of the initial

concentration of 10 ppm of pollutant by NF and the 56% efficiency of electrochemical oxidation process in removing the nanofiltration concentrate, removes 80.5% of pollutant.

3.8. Electrical Energy Consumption (EEC)

When the electro-oxidation process is applied, the process must be technically and economically feasible, finding the best performance and most cost-effective design and operational options for the process, as the economic yield has a direct impact on the cost-effectiveness of the treatment method. Here, the Electrical Energy Consumption (EEC) refers to the amount of electrical energy required to treat 1 m³ of polluted water by reducing and removing the concentration of the soluble pollutant by at least 90% [43]. This value can be computed using the following equation:

$$EEC = \frac{P * t * s}{V * X} \quad (2)$$

where EEC is the Electrical Energy Consumption (in US\$/m³), P is the consumed electrical power by the applied shaker (in kWh), t is the time of the process (in h), S is the industrial price of the electricity, V is the total volume of the treated solution (in m³; four solutions were placed on the shaker at a time), and X is the mineralization efficiency of the process. According to the recorded data, the amount $P=V*I=3.9*0.01=0.000039$ kW, $t=3$ h, $s=0.0727$ US\$/kWh in the year 2021, $V=0.00025$ m³ and $X=0.9$ was chosen as the desired point for treatment. The EEC value was calculated as 0.014144 US\$/m³. which according to the consumption of Ozone 0.1-0.3 US\$/m³ [44], UV 0.05-0.15 US\$/m³ [45], and Fenton 0.05-0.2 US\$/m³ [46], indicates the optimal use of electrochemical oxidation process in removing Diclofenac pollutant.

4. Conclusion

This research examines the hybrid of membrane technology and electrochemical oxidation process, by nanofiltration membrane CTAC-modified and

Ti/SnO₂-α-Fe₂O₃ electrode for the removal of diclofenac sodium pharmaceutical pollutant. The incorporation of CTAC resulted in a more uniform and durable pore structure in the PES/CTAC membrane, leading to enhanced permeability and resistance to fouling. Moreover, the addition of CTAC through the surface adsorption mechanism improved DFS rejection capabilities, with a rejection rate of 65.2% observed for the membrane containing 0.1 wt% CTAC. The Ti/SnO₂-α-Fe₂O₃ electrode had an electrical energy consumption (EEC) of 0.014144 US\$/m³ for the removal of 56% of the diclofenac sodium pollutant, which required less energy consumption compared to other advanced oxidation processes. Overall, the hybrid approach of nanofiltration membrane with electrochemical oxidation process holds considerable potential for achieving a total pollutant removal rate of up to 80.5%. This combination not only enhances electrochemical activity but also plays an important role in reducing both energy demand and the environmental impact of DFS.

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Declarations

Ethical approval: Not applicable.

Competing interests: The authors declare no competing interests.

Authors' contributions:

A. R.: Methodology, Software, Investigation, Writing-Original draft preparation.

A. B.: Supervision, Conceptualization, Writing-Reviewing and Editing

F. N. C.: Supervision, Conceptualization, Visualization, Investigation, Writing- Reviewing and Editing.

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References

- [1] Mashile, G. P., Selahle, S. K., Mpupa, A., Nqombolo, A., & Nomngongo, P. N. (2022). Chapter 8 - Remediation of emerging pollutants through various wastewater treatment processes. In T. Dalu & N. T. Tavengwa (Eds.), *Emerging Freshwater Pollutants* (pp. 137-150). Elsevier.
- [2] Zhong, M., Wang, T., Zhao, W., Huang, J., Wang, B., Blaney, L., Bu, Q., & Yu, G. (2022). Emerging Organic Contaminants in Chinese Surface Water: Identification of Priority Pollutants. *Engineering*, *11*, 111-125.
- [3] Elizalde-Velázquez, A., Subbiah, S., Anderson, T. A., Green, M. J., Zhao, X., & Cañas-Carrell, J. E. (2020). Sorption of three common nonsteroidal anti-inflammatory drugs (NSAIDs) to microplastics. *Science of The Total Environment*, *715*, 136974.
- [4] Kanwal, A., Yaqoob, A. A., Siddique, A., Ibrahim, M. N. M., & Ahmad, A. (2023). Chapter 13 - Polyethersulfone (PES) nanofiltration membrane for treatment of toxic metal contaminated water. In A. Ahmad, R. Kumar, & M. Jawaid (Eds.), *Emerging Techniques for Treatment of Toxic Metals from Wastewater* (pp. 319-341). Elsevier.
- [5] Nthunya, L. N., Bopape, M. F., Mahlangu, O. T., Mamba, B. B., Van der Bruggen, B., Quist-Jensen, C. A., & Richards, H. (2022). Fouling, performance and cost analysis of membrane-based water desalination technologies: A critical review. *Journal of Environmental Management*, *301*, 113922.
- [6] Yin, J., & Zhang, H.-f. (2021). A combined physical blending and surface grafting strategy for hydrophilic modification of polyethersulfone membrane toward oil/water separation. *Polymer*, *233*, 124177.
- [7] Hosseini, S. M., Afshari, M., Fazlali, A. R., Farahani, S. K., Bandehali, S., Van der Bruggen, B., & Bagheripour, E. (2019). Mixed matrix PES-based nanofiltration membrane decorated by (Fe₃O₄-polyvinylpyrrolidone) composite nanoparticles with intensified antifouling and separation characteristics. *Chemical Engineering Research and Design*, *147*, 390-398.
- [8] Elyasi Kojabad, m., & Momeni, M. (2020). Fabrication of PEBA Polymeric Membrane Layers on Nanostructure PSF Supports to Separation of CO₂ from N₂ and CH₄. *Applied Chemistry*, *15*(54), 101-112.
- [9] Saffarimiandoab, F., Gul, B. Y., Tasdemir, R. S., Iltter, S. E., Unal, S., Tunaboylu, B., Menciloglu, Y. Z., & Koyuncu, İ. (2021). A review on membrane fouling: Membrane modification. *Desalin. Water Treat*, *216*, 47-70.
- [10] Vatanpour, V., Dehqan, A., & Harifi-Mood, A. R. (2020). Ethaline deep eutectic solvent as a hydrophilic additive in modification of polyethersulfone membrane for antifouling and separation improvement. *Journal of Membrane Science*, *614*, 118528.
- [11] Bagheri, A. (2020). Interfacial and micellization properties of pure surfactants with similar hydrocarbon chain length (C₁₆H₃₃) and different polar head in aqueous medium. *Applied Chemistry*, *15*(57), 55-64.
- [12] Ly, N. H., Nguyen, T. H., Nghi, N. Đ., Kim, Y.-H., & Joo, S.-W. (2019). Surface-Enhanced Raman Scattering Detection of Fipronil Pesticide Adsorbed on Silver Nanoparticles. *Sensors*, *19*(6).
- [13] Zhang, X., Cui, H.-M., Gao, Y., Yan, Z.-W., Yan, X., Chen, Y., Guo, X.-J., & Lang, W.-Z.

- (2023). Surfactant-induced intervention in interfacial polymerization to develop highly-selective thin-film composite membrane for forward osmosis process. *Desalination*, 558, 116617.
- [14] Khan, N. A., Singh, S., López-Maldonado, E. A., N. P., Méndez-Herrera, P. F., López-López, J. R., Baig, U., Ramamurthy, P. C., Mubarak, N. M., Karri, R. R., & Aljundi, I. H. (2023). Emerging membrane technology and hybrid treatment systems for the removal of micropollutants from wastewater. *Desalination*, 565, 116873.
- [15] Zamora-Ledezma, C., Negrete-Bolagay, D., Figueroa, F., Zamora-Ledezma, E., Ni, M., Alexis, F., & Guerrero, V. H. (2021). Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods. *Environmental Technology & Innovation*, 22, 101504.
- [16] Vahid, B. (2018). Mineralization of reactive green 19 in recirculating system by combined O₃/UV process. *Applied Chemistry*, 13(46), 139-156.
- [17] Moradi, M., Vasseghian, Y., Khataee, A., Kobya, M., Arabzade, H., & Dragoi, E.-N. (2020). Service life and stability of electrodes applied in electrochemical advanced oxidation processes: A comprehensive review. *Journal of Industrial and Engineering Chemistry*, 87, 18-39.
- [18] Akbari, N., & Nabizadeh Chianeh, F. (2022). Optimization of reactive dye removal by electrochemical oxidation with Ti/nanoZnO (Experimental study). *Applied Chemistry*, 17(63), 67-86.
- [19] Wang, H., Shao, Y., Yin, Z., Yu, D., Zhang, J., Yin, Z., & Li, J. (2023). Construction of MXene/Ti membrane electrode with Ti₃C₂TX via electrophoretic deposition for high-efficient electrochemical degradation of antibiotic wastewater. *Journal of Water Process Engineering*, 54, 103893.
- [20] Abdoulyousefi, F. M., Chianeh, F. N., & Asghari, A. (2020). Application of a novel Ti/nanoSnO₂- α -Fe₂O₃ anode for the electro-catalytic degradation of dye pollutant: optimization of operational parameters by central composite design. *Journal of The Electrochemical Society*, 167(10), 103507.
- [21] El Kateb, M., Trelu, C., Darwich, A., Rivallin, M., Bechelany, M., Nagarajan, S., Lacour, S., Bellakhal, N., Lesage, G., Héran, M., & Cretin, M. (2019). Electrochemical advanced oxidation processes using novel electrode materials for mineralization and biodegradability enhancement of nanofiltration concentrate of landfill leachates. *Water research*, 162, 446-455.
- [22] Buscio, V., García-Jiménez, M., Vilaseca, M., López-Grimau, V., Crespi, M., & Gutiérrez-Bouzán, C. (2016). Reuse of Textile Dyeing Effluents Treated with Coupled Nanofiltration and Electrochemical Processes. *Materials*, 9(6).
- [23] Soriano, Á., Gorri, D., & Urtiaga, A. (2019). Membrane preconcentration as an efficient tool to reduce the energy consumption of perfluorohexanoic acid electrochemical treatment. *Separation and Purification Technology*, 208, 160-168.
- [24] Gholami, N., & Mahdavi, H. (2023). Synthesis and application of graphene oxide and sulfonated graphene oxide nanoparticles for using in nanofiltration membranes polyether sulfone. *Applied Chemistry*, 18(66), 241-260.
- [25] Dickhout, J. M., Virga, E., Lammertink, R. G. H., & de Vos, W. M. (2019). Surfactant specific ionic strength effects on membrane

- fouling during produced water treatment. *Journal of colloid and interface science*, 556, 12-23.
- [26] Khorram, M., Chianeh, F. N., & Shamsodin, M. (2022). Preparation and characterization of a novel polyethersulfone nanofiltration membrane modified with Bi₂O₃ nanoparticles for enhanced separation performance and antifouling properties. *Journal of Industrial and Engineering Chemistry*, 114, 456-474.
- [27] Bera, A., Trivedi, J. S., Kumar, S. B., Chandel, A. K. S., Haldar, S., & Jewrajka, S. K. (2018). Anti-organic fouling and anti-biofouling poly(piperazineamide) thin film nanocomposite membranes for low pressure removal of heavy metal ions. *Journal of Hazardous Materials*, 343, 86-97.
- [28] Yahya, A. A., Rashid, K. T., Ghadhban, M. Y., Mousa, N. E., Majdi, H. S., Salih, I. K., & Alsalhy, Q. F. (2021). Removal of 4-nitrophenol from aqueous solution by using polyphenylsulfone-based blend membranes: Characterization and performance. *Membranes*, 11(3), 171.
- [29] Rajakumaran, R., Kumar, M., & Chetty, R. (2020). Morphological effect of ZnO nanostructures on desalination performance and antibacterial activity of thin-film nanocomposite (TFN) membrane. *Desalination*, 495, 114673.
- [30] Esmaeili, M., Madaeni, S. S., & Barzin, J. (2010). The dependence of morphology of solid polymer electrolyte membranes on transient salt type: effect of cation type. *Polymer international*, 59(7), 1006-1013.
- [31] Zinadini, S., Rostami, S., Vatanpour, V., & Jalilian, E. (2017). Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite. *Journal of Membrane Science*, 529, 133-141.
- [32] Vatanpour, V., Esmaeili, M., & Farahani, M. H. D. A. (2014). Fouling reduction and retention increment of polyethersulfone nanofiltration membranes embedded by amine-functionalized multi-walled carbon nanotubes. *Journal of Membrane Science*, 466, 70-81.
- [33] Su, P., Jia, M., Huang, J., Li, W., & Tang, C. Y. (2021). Multilayer assembly of thin-film nanocomposite membranes with enhanced NaCl and antibiotic rejection. *Desalination*, 517, 115261.
- [34] Sloutskin, E., Tamam, L., Sapir, Z., Ocko, B. M., Bain, C. D., Kuzmenko, I., Gog, T., & Deutsch, M. (2022). Counterions under a Surface-Adsorbed Cationic Surfactant Monolayer: Structure and Thermodynamics. *Langmuir*, 38(40), 12356-12366.
- [35] Mansourpanah, Y., Alizadeh, K., Madaeni, S., Rahimpour, A., & Afarani, H. S. (2011). Using different surfactants for changing the properties of poly (piperazineamide) TFC nanofiltration membranes. *Desalination*, 271(1-3), 169-177.
- [36] Omidvar, M., Soltanieh, M., Mousavi, S. M., Saljoughi, E., Moarefian, A., & Saffaran, H. (2015). Preparation of hydrophilic nanofiltration membranes for removal of pharmaceuticals from water. *Journal of Environmental Health Science and Engineering*, 13(1), 42.
- [37] Sadeghi, M., & Emadzadeh, D. (2019). Investigation of the Effect of Anionic and Cationic Surfactants on the Performance of Polyamide Membrane Nanofiltration. *Journal of Water and Wastewater; Ab va Fazilab (in persian)*, 30(4), 122-129.
- [38] Moradi, G., Rahimi, M., Zinadini, S., Shamsipur, M., & Babajani, N. (2022). Natural

deep eutectic solvent modified nanofiltration membranes with superior antifouling properties for pharmaceutical wastewater treatment.

Chemical Engineering Journal, 448, 137704.

[39] Guo, X., Zhao, B., Wang, L., Zhang, Z., Li, J., & Gao, Z. (2023). High flux nanofiltration membrane via surface modification using spirocyclic quaternary ammonium diamine for efficient antibiotics/salt separation. *Separation and Purification Technology*, 325, 124736.

[40] Kim, J.-H., Park, P.-K., Lee, C.-H., & Kwon, H.-H. (2008). Surface modification of nanofiltration membranes to improve the removal of organic micro-pollutants (EDCs and PhACs) in drinking water treatment: Graft polymerization and cross-linking followed by functional group substitution. *Journal of Membrane Science*, 321(2), 190-198.

[41] Huang, S., McDonald, J. A., Kuchel, R. P., Khan, S. J., Leslie, G., Tang, C. Y., Mansouri, J., & Fane, A. G. (2021). Surface modification of nanofiltration membranes to improve the removal of organic micropollutants: Linking membrane characteristics to solute transmission. *Water research*, 203, 117520.

[42] Kamrani, M., Akbari, A., & Yunessnia lehi, A. (2018). Chitosan-modified acrylic nanofiltration membrane for efficient removal of

pharmaceutical compounds. *Journal of Environmental Chemical Engineering*, 6(1), 583-587.

[43] Feng, H., Mao, W., Li, Y., Wang, X., & Chen, S. (2021). Characterization of dissolved organic matter during the O₃-based advanced oxidation of mature landfill leachate with and without biological pre-treatment and operating cost analysis. *Chemosphere*, 271, 129810.

[44] Yadav, A. K., Yadav, H. K., Naz, A., Koul, M., Chowdhury, A., & Shekhar, S. (2022). Arsenic removal technologies for middle- and low-income countries to achieve the SDG-3 and SDG-6 targets: A review. *Environmental Advances*, 9, 100262.

[45] Dires, T. T., & Saroha, A. K. (2022). Electrocoagulation: operational parameters, sludge & economic analysis. *International Journal of Environmental Analytical Chemistry*, 1-16.

[46] Gasmia, A., Elboughdirib, N., Ghernaoutb, D., Hannachia, A., Halimb, K. A., & Khanf, M. I. (2022). Electrocoagulation process for removing dyes and chemical oxygen demand from wastewater: Operational conditions and economic assessment—A review. *Desalination Water Treat*, 271, 74-107.