RESEARCH ARTICLE

Removal of endocrine disrupting chemicals from water through urethane functionalization of microfiltration membranes via electron beam irradiation

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HIGHLIGHTS

- Urethane functionalities created on PES membranes via electron beam irradiation.
- Water contact angle decreased from 58° to 52°, higher hydrophilicity.
- 13% increase in water permeability via functionalization.
- 17β-estradiol adsorption enhanced by five times.
- Functionalized membranes reused for three cycles without a loss of adsorption capacity.

GRAPHIC ABSTRACT
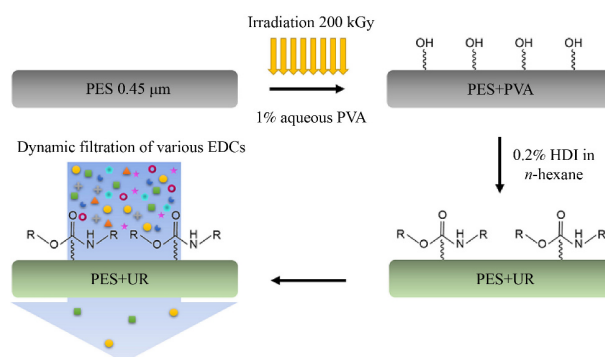
ARTICLE INFO

ABSTRACT

Polyethersulphone (PES) membranes modified with urethane functional groups were prepared through an interfacial reaction using electron beam irradiation. The removal of eight endocrine disrupting chemicals (EDCs) was studied using both pristine and functionalized PES membranes. The prepared membranes underwent characterization using several techniques, including attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy, contact angle analysis, and measurements of pure water flux. Furthermore, dynamic adsorption experiments were conducted to evaluate the adsorption mechanism of the prepared membrane toward the eight EDCs. The urethane functionalized membranes were hydrophilic (52° contact angle) and maintained a high permeate flux (26000 L/h m^2 bar) throughout the filtration process. Dynamic adsorption results demonstrated that the introduction of urethane functional groups on the membranes significantly enhanced the removal efficiency of 17β-estradiol, estriol, bisphenol A, estrone, ethinylestradiol, and equilin. The adsorption loading of 17β-estradiol on the functionalized PES membrane was 6.7 ± 0.7 mg/m^2, exhibiting a 5-fold increase compared to the unmodified PES membrane. The membranes were successfully regenerated and reused for three adsorption cycles without experiencing any loss of adsorption capacity.

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1   Introduction

Endocrine disrupting chemicals (EDCs) are increasingly being detected in natural water sources. This has become a matter of global concern. EDCs are a class of hazardous emerging organic micropollutants that have the ability to

interfere with the endocrine system of humans, mammals, and aquatic life. Among the various types of EDCs, estrogenic EDCs are particularly potent in their endocrine-disrupting abilities. Exposure to trace concentrations (ranging from ng/L to μg/L) of estrogenic EDCs has the potential to induce obesity, infertility, and various types of cancer in humans (Yilmaz et al., 2020). Despite ongoing efforts to eliminate EDCs from water through conventional water and wastewater treatment methods, their effective removal continues to pose a challenge. Hence, elevated levels of EDCs are increasingly being detected in drinking water and natural water sources in various regions worldwide (Zhang et al., 2022).

Various techniques have been extensively studied to evaluate their effectiveness in removing EDCs from water. One such method is photocatalytic oxidation, which utilizes light energy to initiate chemical reactions that break down and degrade EDCs present in water. The efficiency of this process relies on factors such as temperature, the characteristics of the photocatalyst's surface, and the source of light utilized (Belgiorno et al., 2007). In addition to photocatalytic oxidation, other commonly employed techniques in water and wastewater treatment include chlorination and ozonation, which use specific disinfectants to eliminate contaminants from the water (Azizi et al., 2022). On the other hand, biological treatments harness the capabilities of microorganisms to biodegrade EDCs, converting them into simpler and less harmful compounds (Wang et al., 2017). These microorganisms can effectively metabolize and break down EDCs, reducing their overall toxicity. Although some studies have demonstrated the degradation of EDCs into by-products or intermediate compounds with endocrine-disrupting properties during these treatments, there is a concern that certain by-products might persist in the environment, potentially leading to environmental and health challenges (Mansor and Tay, 2020).

Physical treatment methods, such as activated carbon (AC) adsorption and membrane filtration, have been extensively researched as alternatives to chemical techniques. Among these methods, AC adsorption has garnered significant attention due to its ease of operation and suitability for both batch and continuous processes (Rao et al., 2021). However, the efficiency of AC adsorption in removing EDCs relies on various factors, including the dose of the adsorbent, contact time, and the physical and chemical properties of the targeted compounds. One limitation of using activated carbon is its finite adsorption capacity. As AC adsorbs EDCs from the water, it becomes saturated over time, leading to reduced effectiveness. To maintain its efficiency, regular replacement or regeneration of the carbon is necessary. Another concern with AC adsorption is the management of spent activated carbon. Once saturated with adsorbed EDCs, it becomes hazardous waste that requires proper disposal, which can be both challenging and costly.

Though some activated carbon can be regenerated and reused, this process may not always be practical or cost-effective, especially when dealing with complex mixtures of EDCs. Additionally, in real-world scenarios, water often contains a mixture of pollutants, including substances that may compete with EDCs for adsorption sites on the activated carbon. This competition can diminish the overall effectiveness of AC adsorption in removing EDCs (Cecen and Aktaş, 2011; Trellu et al., 2018).

Membrane technologies are regarded as another highly promising physical approach for removing EDCs in advanced water and wastewater treatment processes. These technologies offer numerous advantages, making them an excellent alternative for water and wastewater treatment. One key advantage is their broad spectrum of selectivity, enabling them to efficiently target and remove a wide range of EDCs from water sources. Additionally, membrane processes operate continuously, ensuring a consistent and reliable removal of pollutants. Another benefit is that membrane technologies do not produce any harmful by-products or metabolites during the treatment process. This is crucial in preventing the introduction of new pollutants into the environment. Furthermore, membrane technologies can seamlessly integrate with conventional water treatment methods, making them highly adaptable and compatible with existing systems. One of the most significant advantages is the high quality of the treated water they produce. The effluent generated through these membrane processes exhibits an extremely low organic concentration, effectively eliminating microbes and viruses without the need for additional chemical disinfection (Comerton et al., 2007; Hao et al., 2021).

Extensive research has been conducted to assess the performance and efficacy of reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF) membranes for the purpose of removing EDCs from water (Kim et al., 2018; Khoo et al., 2022). According to previous research, the predominant mechanism for removing EDCs using NF and RO membranes in the initial stages involves the adsorption of EDCs onto the membrane surfaces. This adsorption process occurs to a much greater extent than what could be anticipated solely based on size exclusion (Nghiem and Schäfer, 2002). The adsorption of EDCs onto membranes primarily occur through specific interactions. These interactions entail the formation of hydrogen bonds between the hydroxyl and carbonyl functional groups present in the EDC molecules and the functional groups located on the surfaces of the membranes. Moreover, it has been suggested that hydrophobic interactions with the membrane backbone also play a role in contributing to the adsorption process (Shin et al., 2022). It was demonstrated that the level of EDCs removal by NF membranes is significantly related to the hydrophobicity

(log K_{ow}) of the molecule (Jin et al., 2007). Molecules with a higher log K_{ow} value are more hydrophobic and exhibit a grater affinity to the hydrophobic membranes. After surpassing the initial adsorption phase, the membrane becomes saturated, and the system enters a state of steady-state rejection. At this state the rejection of hormones has been linked to their molecular weight, implying that the process is controlled by size exclusion (McCallum et al., 2008). The ultimate conclusion based on these studies is that adsorption in NF and RO membranes plays a crucial role in achieving a significantly high rate of hormone removal. In a study conducted by Liu et al. (2018), the researchers examined the adsorption of various pharmaceuticals by isolating the polyamide (PA) active layer from the polysulfone (PS) support layer. The findings revealed significant differences between the PA layer and the PA + PS layer in terms of pharmaceutical adsorption capacity and the time required to reach adsorption equilibrium. These results strongly indicated that the presence of the PS layer significantly influenced the adsorption process and its rate for pharmaceuticals. Moreover, the study demonstrated that PA alone does not solely contribute to the adsorption process; rather, it heavily relies on the support provided by the PS layer. One drawback associated with NF/RO membranes is their reliance on high pressure for operation, making them energy-intensive processes. Additionally, these membranes are susceptible to fouling. Fouling can negatively affect their efficiency by reducing permeate flux and increasing the need for frequent cleaning and maintenance, leading to higher operational costs (Wu et al., 2022). Therefore, exploring MF membranes as an alternative to NF/RO membranes shows great promise, particularly due to their potential to operate at lower pressures while maintaining effective adsorption-based removal. MF membranes have limited capability to remove EDCs effectively. However, membrane modifications can significantly improve their adsorption capacity, leading to better removal of EDCs and other contaminants. Several techniques for enhancing the adsorption capacity of membranes have been developed, including surface coating, surface chemical modification, and blending with additives (Miller et al., 2017).

This study introduces a technique to modify MF PES membranes by employing electron beam irradiation to generate urethane functional groups on the membrane surface. The modified PES membranes with urethane functional groups (PES + UR) can be employed for the removal of various types of EDCs from water (Yasir et al., 2022). The modification was carried out by employing the concept of interfacial polymerization between polyols and isocyanates. The surface of the membranes was immobilized with polyols through the use of electron beam irradiation. Exposing polymer membranes to electron beam irradiation generates various

activated species, such as radicals, which have the potential to engage in recombination reactions and form covalent bonds. In contrast to the UV light treatment that has limited penetration depth, electron beam irradiation can penetrate the entire cross-section of the membrane, enabling more extensive and comprehensive modifications (Das et al., 2019). Furthermore, electron beam irradiation eliminates the need for hazardous polymerization initiators or other toxic reagents, making it an environmentally friendly choice. Additionally, electron beam irradiation is a rapid and targeted technique, allowing for swift modifications, making it highly desirable for industrial applications (Breite et al., 2020). Subsequently, an interaction occurred between the immobilized polyols and diisocyanates on the membrane surface, resulting in the creation of urethane groups. The modified and pristine PES membranes were subjected to various characterizations, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), water contact angle measurement, and water permeability. The primary objective of this study was to assess the removal capabilities of both modified and unmodified PES membranes concerning a range of EDCs with diverse properties, including log K_{ow}, molecular weight, water solubility, and chemical structures. Dynamic adsorption experiments were performed to study the removal capacities of the membranes. Furthermore, the membranes' adsorption performance was assessed using real water samples that also contained additional organic matter. Ultimately, a successful regeneration protocol was proposed to facilitate the reutilization of the modified membranes.

2 Materials and methods

2.1 Chemicals

Microporous polyethersulfone (PES) (0.45 μm, Express Plus, Merck Millipore) membranes were purchased from Merck (Darmstadt, Germany). Estrone (E1), 17β-estradiol (E2), ethinyl estradiol (EE2), estriole (E3), equilin (EQ), bisphenol A (BPA), androst-4-ene-3,17-dione (A4), testosterone (TST), polyvinyl alcohol (PVA, 2,000 g/mol), and hexamethylene diisocyanate (HDI) were obtained from Sigma Aldrich (St. Louis, MO, USA). Absolute ethanol was purchased from VWR (Radnor, PA, USA). Deionized water in Millipore® quality was used for experiments. All materials were used as they were received from suppliers.

2.2 Membrane modification

Polyurethanes can be synthesized using various methods, but the most effective approach involves the reaction

between a polyol and a diisocyanate. In this reaction, the hydroxyl groups of the polyol molecules react with the isocyanate groups of the diisocyanate molecules, resulting in the formation of urethane functional groups (Akindoyo et al., 2016). In this work, the polyurethane functional groups were formed on the outer surface and inner pores of the PES membrane through an interfacial reaction (Mahdavi et al., 2016). Pristine PES membrane disks (47 mm) were soaked in a 1 wt.% aqueous solution of polyvinyl alcohol (PVA), the selected polyol, for 30 min. After the immersion, the membranes were exposed to electron beam irradiation while in a wet state. This process aimed to immobilize the PVA on the surface and within the pores of the membrane through grafting (Schmidt et al., 2021). The irradiation process was conducted using a dose of 200 kGy, employing a custom-made electron accelerator (20 mA, 160 kV) in an N_2 atmosphere with O_2 levels kept below 10 mg/L. Afterwards, the membranes immobilized with PVA were rinsed with deionized water three times for 30 min to remove the non-grafted PVA and left to dry overnight at room temperature. Next, a 0.2 wt.% solution of Hexamethylene diisocyanate (HDI) in *n*-hexane was prepared. The PVA immobilized membranes were soaked in the HDI solution for 2 min to enable the interfacial reaction between the hydroxyl group of the immobilized PVA and the isocyanate group of the HDI. Subsequently, the modified membranes were dried for 1 h to remove the *n*-hexane. Finally, all the membranes were rinsed with deionized water three times for 30 min and dried at room temperature. Figure 1 illustrates the modification process.

2.3   Membrane characterization

2.3.1   Water permeance

The permeation experiments were conducted employing a stainless-steel filtration cell (16249, Sartorius Stedim Biotech, Göttingen, Germany). The permeance was calculated using the results from the filtration tests. The duration of filtration of 100 mL of deionized water was measured at a constant pressure of 0.5 bar. Each experiment was repeated three times, and the average value was calculated. Eq. (1) is used to calculate the water permeation J (L/h m^2 bar).

$$J = \frac{V}{t \cdot A \cdot p}, \qquad (1)$$

where V (L) signifies the volume of filtrated water, t (h) denotes the time taken for the filtration experiment, A (m^2) represents the active surface area of the membrane. p (bar) indicates the constant pressure applied for the filtration.

2.3.2   Water contact angle (WCA)

The surface wettability of the unmodified and modified PES membranes was investigated using a static contact angle measurement system (DSA 30E, Krüss, Hamburg, Germany) through the sessile drop method. In brief a 5 μL drop of deionized water was deposited on the top surface of each membrane and the water contact angle was measured. Each experiment was repeated three times, and the average value was calculated.

2.3.3   Chemical composition

The chemical composition of the top surface area of the pristine and modified PES membranes was analyzed using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra, Kratos Analytical Ltd., Manchester, UK).

2.3.4   Membrane morphology

The membrane top surface was investigated by scanning electron microscopy (SEM, Ultra 55 SEM, Carl Zeiss Ltd., Goettingen, Germany) under magnifications ranging from 10,000 to 25,000-fold. A chromium coating (30 nm, Z400 Sputter System, Leybold, Hanau, Germany) was used to prevent charging of the samples.

2.3.5   Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) measurements were taken in attenuated total reflection (ATR) mode with the vector 22 FTIR spectrometer (Bruker Corporation, Billerica) and a diamond cell (Golden Gate Specac). The spectra were recorded in the range of 4000–500 cm^{-1} at a spectral resolution of 2 cm^{-1}.

2.3.6   Dynamic adsorption experiments

To investigate the dynamic adsorption capacities of modified and unmodified PES membranes, a bench scale stainless-steel dead-end filtration unit (16249, Sartorius Stedim Biotech, Göttingen, Germany) was employed. One, two, or three layers of 47 mm membrane disks were stacked in the filter holder. The membranes were pre-wetted before the adsorption experiments by filtering 25 mL of an aqueous water/ethanol (9:1, v/v) solution.
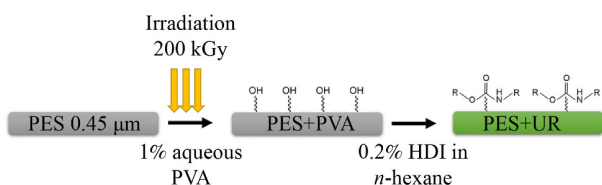

Fig. 1 Schematic illustration of the modification route. The membrane is soaked in PVA aqueous solution followed by exposure to electron beam irradiation. Ultimately, the PVA-immobilized membranes are immersed in an HDI solution to facilitate the interfacial reaction.

EDC solutions were prepared according to the procedure reported in our previous work (Niavarani et al., 2021), In brief, individual EDC solutions with an initial concentration of 5 mg/L were prepared using a 10 wt.% ethanol water solution. 60 mL of each EDC solution was filtered through one, two, or three layers of modified or unmodified membranes at a constant pressure of 10, 20, or 30 mbar. Permeate samples were collected at every 1–5 mL intervals to measure the EDC concentration in the permeate (C_p). Fluorescent detection or UV absorption of each of the EDCs were detected to quantify the EDCs concentrations (Infinite M200, Tecan, Germany). The dynamic adsorption loading (Q_{dyn}) was calculated at breakthrough (BT) points (defined at a C_p of 10% relative to the initial concentration (C_0)) according to Eq. (2).
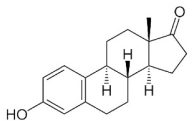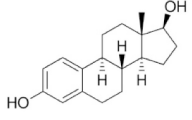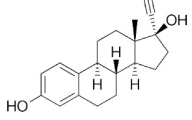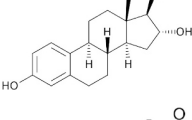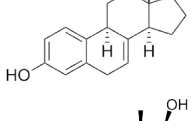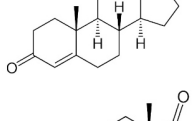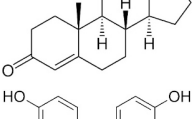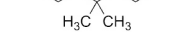
$$Q_{dyn} = \frac{m_{ads}}{A_{membrane}}. \tag{2}$$

The adsorbed amount of each EDC molecule, denoted as m_{ads} (mg), was determined by numerically integrating the BT curve data points between V_0 and V_{BT} using OriginPro 2019b (OriginLab). A (m^2) represents the active surface area of the membranes.

Eight endocrine disrupting compounds were selected to be representative of organic micropollutants found in wastewater and drinking water sources (Pironti et al., 2021). These compounds also represent a wide range of properties (e.g., solubility, hydrophobicity/hydrophilicity, molecular weight, and functional groups) that are expected to influence the removal performance of membranes. Table 1 provides information about the tested EDCs, including their chemical structure, octanol-water partition coefficient (log K_{ow}), water solubility, and detection mode.

To assess the increases in the adsorption loadings of the modified membranes, enhancement factor was calculated

Table 1 EDCs and their properties

	Chemical structure	Molecular weight (g/mol)	Water solubility[a,b,c] (mg/L)	log K_{ow}[a,b,c]	Detection mode (fluorescence excitation-emission (nm) or UV absorption (nm))
Estrone (E1) (metabolite of E2)		270.4	30	3.13	273–305
17ß-Estradiol (E2) (natural hormone)		272.4	3.6	4.01	273–305
Ethinylestradiol (EE2) (ovulation inhibitor)		296.4	10	3.67	273–305
Estriol (E3) (natural hormone)		288.4	30	2.45	262–290
Equilin (EQ) (estrogen replacement)		268.3	1.4	3.35	280–310
Testosterone (TST) (natural hormone)		288.4	23	3.32	246
Androst-4-ene-3,17-dione (A4) (natural hormone)		286.4	57	2.72	246
Bisphenol A (BPA) (plasticizer)		228.3	300	3.32	276–306

[a,b,c] (Comerton et al., 2007; Kim et al., 2007; Yoon et al., 2007).

according to Eq. (3) (Schmitt et al., 2020).

$$Enhancement\ factor = \frac{Q_{dyn-PES+UR}}{Q_{dyn-PES}}, \qquad (3)$$

where $Q_{dyn-PES+UR}$ (mg/m^2) refers to the adsorption loading on the modified membrane and $Q_{dyn-PES}$ (mg/m^2) refers to the adsorption loading on the unmodified PES membrane.

2.3.7 Regeneration and reuse

Regeneration of the modified and unmodified PES membranes were performed in two steps. After each adsorption cycle, the used membrane was first flushed with 25 mL of water/ethanol (1:1, v:v) solution. Next, the membrane was flushed again with a diluted solution of water/ethanol (9:1, v:v). After the regeneration procedure, the washed membrane was exposed to another cycle of adsorption. Fresh EDC solution was reintroduced to the filtration cell to test the reusability of the membranes. The dynamic adsorption loadings of the membranes under the same condition as the first adsorption cycle was monitored. The regeneration procedure was repeated three times.

3 Results and discussion

3.1 Membrane characterization

To confirm the successful functionalization of the PES membranes, SEM, FTIR, WCA, XPS, and permeability tests were carried out. Figure 2 shows SEM images of both unmodified PES membranes (a, b) and PES membranes modified with the urethane functionalities (c, d). The unmodified PES membrane shows an appearance of porous structure. The modified and unmodified PES membranes show a similar surface morphology, and the modification has not adversely affected the membranes. The images show no pore blockage or defects on the modified membranes.

Measurements of the WCA is regarded as a convenient quantitative index of membrane hydrophobicity and hydrophilicity. The WCA values for the unmodified and functionalized PES membranes are presented in Table 2. The unmodified PES membrane has a hydrophilic surface with a WCA of 58° ± 2°. The modification with urethane functional groups increases the hydrophilicity with a WCA of 52° ± 3° for the modified membranes. The decrease in the WCA value indicates that the modification enhances the wettability of the membranes. The reason for this finding can be attributed to the creation of hydrophilic urethane functional groups on the surface of the modified membranes (Król and Król, 2020).

Pure water flux was measured to investigate the membrane performance in terms of permeability. The modification with the urethane functional groups resulted in a significant increase in the water permeance of the modified membranes. The results are reported in Table 2. While the unmodified PES membrane had a water permeation flux of 23,100 L/h m^2 bar, the creation of urethane functional groups on the membrane surface resulted in an increase of 13% in the permeability of the modified membranes. The increase in permeability is consistent with the decrease in the WCA value of the modified membranes, suggesting that the enhanced hydrophilicity of the membrane surface helps to prevent hydrophobic interactions, resulting in a significant
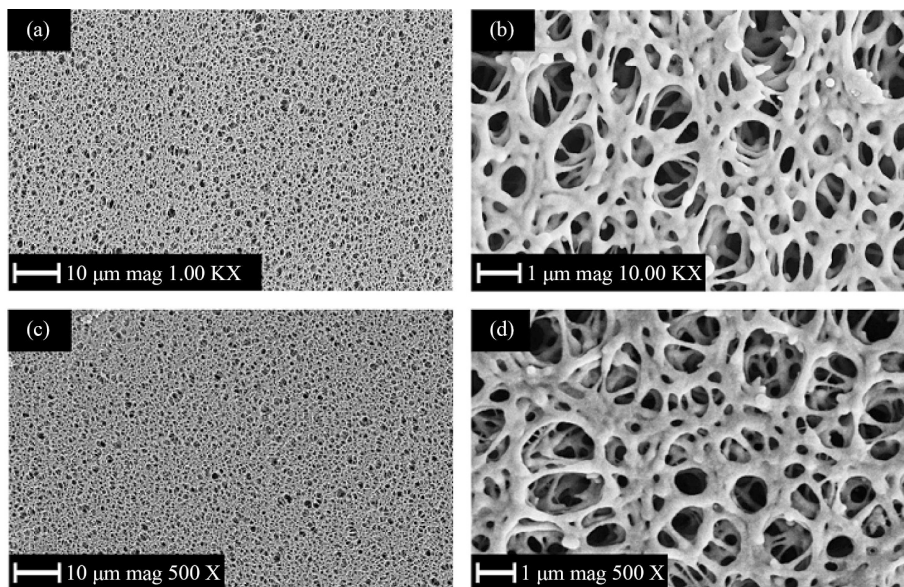

Fig. 2   SEM image (top side) of (a, b) unmodified PES and (c, d) of functionalized PES membranes.

Table 2 Water contact angle, permeance, and XPS analysis of pristine and modified PES membranes

	Water contact angle (°)	Permeance (L/h m² bar)	Chemical composition			
			O	N	C	S
PES	58 ± 2	23100 ± 1000	24.3	0	71.5	3.8
PES+UR	52 ± 3	26200 ± 1200	25.5	0.6	72.4	0.7

increase in water permeability.

The chemical composition of the unmodified and modified PES membranes was investigated by XPS. Table 2 summarizes the XPS results of the unmodified and modified PES membranes. The unmodified PES membrane is composed of 71.5% carbon, 24.3% oxygen, and 3.8% sulfur. The formation of the urethane functional groups changes the chemical composition of the top surface of the modified membranes. A significant increase in the nitrogen and oxygen content on the surface of the modified membranes is observed. The reference unmodified PES membrane does not contain any nitrogen, whereas the detection of nitrogen in the functionalized membranes suggests the successful formation of the urethane functional groups, confirming the success of the modification. The XPS data reveals a decrease in sulfur content in the functionalized membranes. The urethane functional groups exclusively consist of carbon, oxygen, and nitrogen elements. When the urethane functionalities are formed on the surface of the membrane, they act as a barrier, preventing the detection of sulfur from the backbone of the PES membrane. This results in a decrease in the sulfur content observed in the XPS data. Similar findings have been reported when modifying membranes with different functional groups (Schulze et al., 2017; Breite et al., 2020).

Figure 3 contains the ATR-FTIR spectra of both the unmodified and modified PES membranes. The spectra of both membranes show mostly similarities. The similarity observed in the spectra indicates that both the modified and unmodified membranes have a comparable backbone structure. Within the range of 1000 to 1160 cm^{-1} (Fig. 3 (b)), we observe SO_2 stretches. The weaker SO_2 peaks in the modified membrane's FTIR spectra suggest that the sulfur present in the original membrane has been shielded by the formation of urethane groups on its surface. This observation aligns perfectly with the XPS data, which indicated that sulfur was covered by the newly formed urethane groups on the modified membrane's surface. The appearance of a new peak at 1670 cm^{-1} (Fig. 3 (c)) is attributed to the presence of an amide functional group (forming part of the urethane structural motif) on the surface of the modified membranes (−CONH) (Ameri et al., 2015). The enhanced peak at 1730 cm^{-1} (Fig. 3 (d)) is attributed to the carbonyl group (Tirouni et al., 2015). The presence of this peak in the pristine membrane suggests the presence of hydrophilizing agents (possibly carboxylic acid, or similar compounds) that were already part of the pristine commercial membrane. Between the range of 1280 to 1330 cm^{-1} (Fig. 3 (e)), two peaks corresponding to C−S bonds are detected. Notably, the intensity of these peaks is lower for the modified membrane, suggesting that the sulfur content in the modified membrane has been masked or concealed by the newly formed urethane groups. The presence of the characteristic peak at 2270 cm^{-1} (Fig. 3 (f)), corresponds to the presence of isocyanate that was probably not removed during washing (Zia et al., 2014). The new peak at 2940 cm^{-1} (Fig. 3 (g)), is attributed to CH_2 groups which are present in PVA. Another characteristic peak can be seen at 3420 cm^{-1} (Fig. 3 (h)), which is attributed to the NH group in urethane (Bandyopadhyay et al., 2016; Mahdavi et al., 2016).

3.2 EDC adsorption studies

3.2.1 Dynamic adsorption optimization

The optimum number of layers of membranes for the highest EDC adsorption without a major loss in permeation was investigated. One, two, or three layers of membranes were employed, and the adsorption loadings and permeation was monitored. The active surface area of each membrane was 0.0017 m². The adsorption loadings of one, two, or three layers of modified and unmodified PES membranes and the corresponding permeation are reported in the supplementary information (Table S1). A 5 mg/L solution of E2 was used as a test solution. It was observed that increasing the numbers of layers of the membranes increases the adsorption loading as expected. Increasing the number of layers results in an increase in the surface area of the membranes, which in turn leads to an increase in the adsorption area. Based on the findings, it was determined that utilizing three layers of membranes yielded optimal adsorption performance for a 5 mg/L solution without negatively impacting permeation. This configuration was subsequently employed for further dynamic adsorption experiments.

3.2.2 EDC dynamic adsorption

Few studies have addressed the removal of various EDCs using microfiltration polymer membranes. In this study, the dynamic adsorption loadings of different EDCs were tested using reference microfiltration PES membrane and the PES membrane functionalized with urethane groups. Three layers of the functionalized or unmodified PES
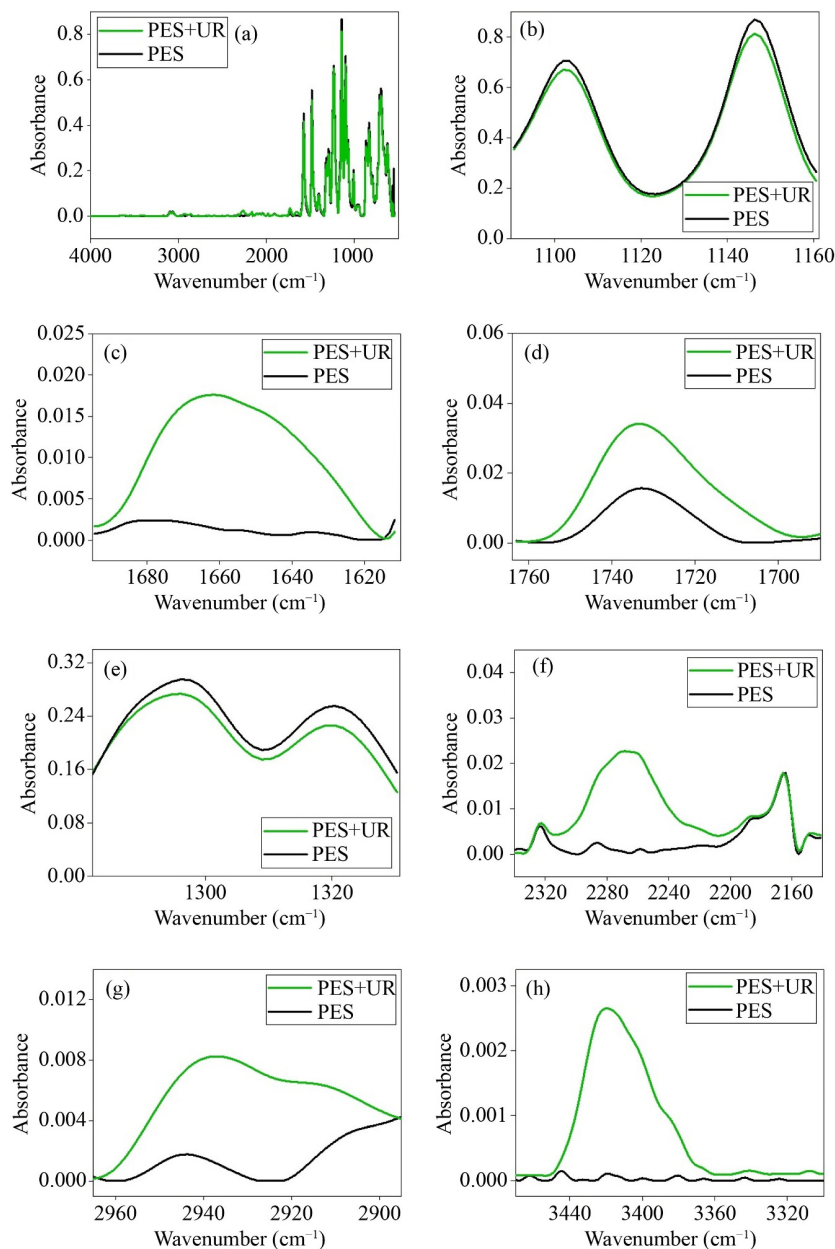
Fig. 3 ATR-FTIR spectra of pristine and modified PES membranes. (a) the full spectra at 4000–500 cm^{-1}, (b) spectra at 1160–1100 cm^{-1}, (c) spectra at 1964–1611 cm^{-1}, (d) spectra at 1762–1690 cm^{-1}, (e) spectra at 1330–1280 cm^{-1}, (f) spectra at 2341–2141 cm^{-1}, (g) spectra at 2964–2894 cm^{-1}; and (h) spectra at 3470–3300 cm^{-1}.

membranes were placed on the filter holder. The membranes were initially wetted by flushing with 25 mL of water/ethanol solution (1:1, v:v). Afterwards, 60 mL of the respective EDC solution with an initial concentration of 5 mg/L was passed through the membranes under a constant pressure of 30 mbar. Permeation concentrations were monitored by sampling at 1–2 mL intervals. Figure 4 illustrates the BT curves and adsorption loadings obtained for each EDC using the functionalized and unmodified PES membranes.

The results demonstrate that the permeate concentration gradually increased as the filtration progressed for all the eight EDCs until the membranes were completely saturated and no more adsorption took place. It was observed that the adsorption capacity of E1 is initially similar for both functionalized and unmodified PES membranes within the first 10 mL. However, as the filtration volume increased, the functionalized PES membrane exhibited a higher adsorption capacity compared to the unmodified membrane. At the end of 60 mL of filtration, both the reference and modified PES membranes were completely saturated. For E2, a different adsorption behavior was observed. The concentration of the first permeate sample at 2 mL for the unmodified PES
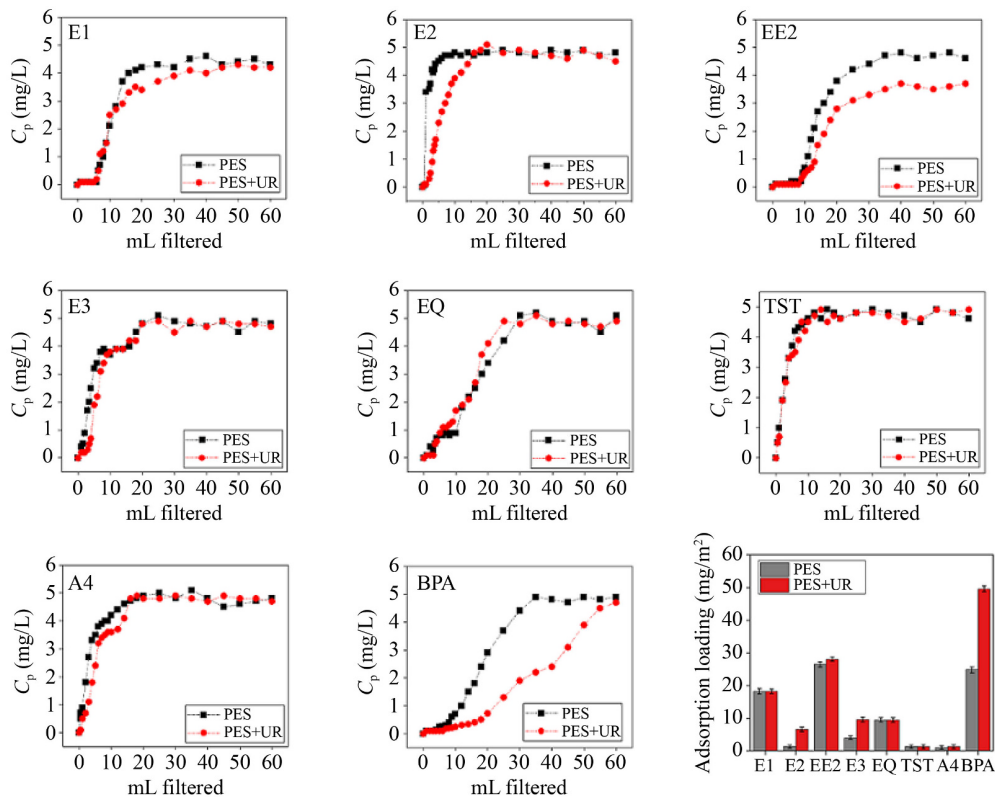
Fig. 4   Breakthrough curves and adsorption loading of different EDCs adsorbed to the pristine and functionalized PES membranes.

membrane was already more than 3 mg/L and the saturation plateau was reached after filtering 8 mL of E2 solution. In contrast, the functionalized PES membrane reached saturation at 20 mL. For EE2, both the functionalized and unmodified PES membranes adsorbed more than 90% of the initial EE2 in the first 10 mL. In addition, the functionalized PES membranes showed a better performance in the next 50 mL and exhibited a higher adsorption capacity. The PES + UR membrane reached saturation after filtering 40 mL of the EE2 solution, whereas the unmodified PES membrane reached saturation at 20 mL. The adsorption performance of functionalized and unmodified PES membranes was similar for hormones E3 and EQ, with no significant differences observed. The adsorption performance of both unmodified and functionalized PES membranes is similar for the hormones TST and A4 and no improvement in the adsorption by PES + UR membranes was observed. On the other hand, BPA was adsorbed by both PES and PES + UR significantly. The pristine PES membrane adsorbed more than 90% of the initial BPA in the first 10 mL and reached its saturation at 30 mL. While the PES + UR membrane adsorbed more than 90% of the initial BPA in the first 20 mL and reached the adsorption plateau at 60 mL.

Figure 4 also demonstrates the dynamic adsorption loadings of both modified and unmodified PES membranes for the tested EDCs at the breakthrough point.

The dynamic adsorption loadings for both types of membranes were calculated using Eq. (2). By comparing the adsorption loading of the unmodified membranes, the highest adsorption loading is for EE2, followed by BPA, E1, EQ, E3, E2, TST, and A4. The highest adsorption loading on the modified membranes belongs to BPA, with a value of 49.6 mg/m^2 followed by EE2 with an adsorption loading of 28 mg/m^2.

Different mechanisms can account for the retention or removal of EDCs by membranes, including size exclusion, electrostatic interaction, and the EDCs being adsorbed to the surface of the membranes. The eight EDCs that were investigated in this study remained in an undissociated state at experimental pH (pH ~7). Consequently, ionic interactions was not anticipated to occur between the EDCs and the membranes. Given that the size of the tested EDCs in the study was considerably smaller than the pore size of the membrane, it was also highly improbable that size exclusion played a significant role in their interactions with the membrane. Therefore, it was expected that adsorption would be the predominant removal mechanism, likely influenced by hydrophobic interactions or hydrogen bonding. (Schäfer et al., 2011). As indicated in Table 1, the eight EDCs studied in this research possess varying octanol-water partition coefficients (log K_{ow}) and different levels of water solubility. These log K_{ow} values suggest that the EDCs would exhibit different patterns of adsorption to hydrophilic

materials. Specifically, molecules with higher log K_{ow} values and lower water solubility are expected to be more easily removed from the water phase during the adsorption process (Yoon et al., 2006; Comerton et al., 2007).

Based on the comparison of adsorption loadings and the different log K_{ow} and water solubility values presented in Table 1, it can be inferred that the removal of EDCs through the unmodified PES membrane can be partly influenced by hydrophobic interactions. It can be assumed that the removal efficiencies of the tested EDCs are positively correlated with their hydrophobicity. EDCs with higher log K_{ow} values and lower water solubility are more likely to demonstrate higher removal rates when passing through the unmodified membrane. However, relying solely on hydrophobic interactions is not adequate, as demonstrated by the example of E2. Despite being more hydrophobic, E2 is adsorbed to the unmodified membrane in a lower amount when compared to BPA. It should be noted that the eight EDCs investigated in this study possessed distinct chemical structures, as outlined in Table 1. A significant difference among them is the presence of phenolic groups which have strong electron donating hydroxyl functionalities. Only the EDCs containing such phenolic groups demonstrated adsorption to either the modified or unmodified membrane. The assumption can be made that the presence of phenolic groups is responsible for the removal of molecules through the formation of π–π bonds (Dolar et al., 2017). It has been reported that as the number of phenolic groups increases in the adsorbate molecule the strength and occurrence of π–π interactions with the adsorbents also increase (Star et al., 2003). It can be inferred that due to its possession of two phenolic groups, BPA likely exhibits a higher affinity toward the unmodified membrane when compared to E2 (Lin and Xing, 2008). This hypothesis gains further support from the fact that A4 and TST, which lack phenolic groups, were not removed by either the unmodified or modified membrane. The absence of phenolic groups in these EDCs might hinder their ability to have any interactions with the membranes, consequently leading to their minimal removal. Nguyen et al. (2021), also reported a similar finding in their study. They observed that humic compounds containing phenolic groups hindered the adsorption of E2 onto single-walled carbon nanotubes. This inhibition might be attributed to these compounds adsorbing to the same sites as E2, thereby competing for adsorption on the nanotubes.

The enhancement factor, which indicates the improvement in adsorption resulting from the functionalization of the PES membrane, was computed using Eq. (3). Figure 5 displays the enhancement factor for each hormone.

The highest measured enhancement factor was observed for E2. The adsorption of E2 on the functionalized membrane was increased nearly five times
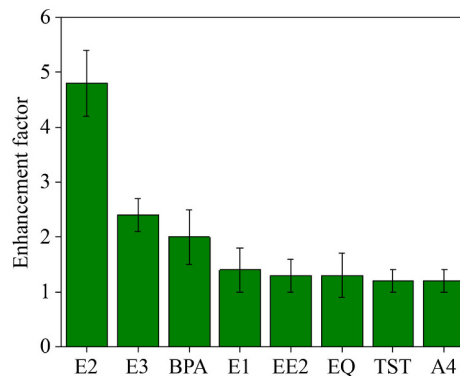

Fig. 5 Enhancement factors measured for each EDC.

compared to the unmodified PES membrane. The measured adsorption loading of E2 on PES + UR was 6.7 ± 0.7 mg/m^2, whereas on the unmodified PES, the adsorption loading for E2 was 1.4 ± 0.5 mg/m^2. In our previous study (Niavarani et al., 2021), we modified the surface of the same PES microfiltration membranes by introducing amide functional groups. The adsorption loading of the amide-modified membranes was 5.8 mg/m^2. However, in the current study, the modification with the urethane functional group resulted in an even greater enhancement in adsorption compared to the amide modification. The increase in adsorption loadings followed the order of E3, BPA, E1, and EE2. The measured adsorption loading values on the modified membranes were 9.7 ± 0.9 mg/m^2 for E3, 49.6 ± 3.2 mg/m^2 for BPA, 18.3 ± 1.2 mg/m^2 for E1, and 28.1 ± 2.3 mg/m^2 for EE2. The enhanced adsorption loadings can further prove that the modification was successful and a highly efficient adsorptive coating consisting of urethane groups was formed on the surface and pore walls of the membranes.

Han et al. (2013) reported an adsorption loading of 4.4 mg/m^2 for E1, 12.3 mg/m^2 for EE2, and 3.2 mg/m^2 for BPA on their polyamide microfiltration membrane. Niedergall et al. (2014) reported an adsorption loading of 1.1 mg/m^2 for BPA on their nanocomposite membranes. Muhamad et al. (2016) prepared hollow fiber PES membranes incorporated with different SiO$_2$ loadings and achieved a BPA adsorption capacity as high as 53 μg/g. By normalizing the adsorption loadings of the PES + UR membranes to the weight of the membranes, a 20 times higher adsorption capacity was achieved with our modification process. Rana et al. (2014) conducted a study involving the development of charged surface PES membranes. These ultrafiltration (UF) PES membranes were enriched with macromolecules to enhance the removal of EDCs and PCPs (Personal Care Products) from water. The study findings indicated that adsorption to the membrane was the primary mechanism responsible for removing EDCs and PCPs from the water. In the most favorable scenario, the researchers achieved a 50% removal of initial BPA from water using a modified PES

membrane blended with 3 wt.% charged macromolecules. The observed enhancement was considerable, indicating an approximately threefold increase in the adsorption capacity compared to the 17% removal achieved with an unmodified membrane. Our own research yielded comparable results, providing us with a clear advantage due to the use of a microfiltration membrane with lower operational pressure in the process. Koloti et al. (2018) worked on hyperbranched polyethyleneimine/polyether-sulfone (HPEI/PES) electrospun nanofibrous membranes and modified them by covalently binding Laccase enzymes to the membranes. According to their findings, the unmodified HPEI/PES membrane removed BPA with an efficiency of 67%. However, after modifying the membrane with Laccase, they achieved a remarkable 89% removal of the initial BPA from water. The adsorption loading for their modified membranes in regard to BPA was measured at 0.7 mg/m^2, which is notably lower than the adsorption capacity demonstrated by our membranes. Elakkiya et al. (2021) conducted modifications on PES membranes by embedding them with 1D and 2D iron pillared nanoclay to improve the removal of BPA from water. Under operational conditions similar to ours (pH 7), their modified membranes achieved an approximate 50% removal of BPA, while the unmodified pristine PES membrane only removed 30% of the initial BPA from water. Despite this enhancement, the reported permeation of their modified membrane was 50 L/h m^2 bar, which is still lower than the permeation of PES + UR membranes utilized in our study.

3.3 Application in real water and regeneration

The present study aimed to investigate the efficacy of both functionalized and unmodified PES membranes in removing E2 from real water samples. To assess their performance, a solution of E2 with an initial concentration of 5 mg/L in tap water/ethanol (9:1, v:v) was prepared. A volume of 60 mL of this solution was passed through the membranes, and the dynamic adsorption loading was determined by analyzing the breakthrough curves (refer to Fig. S2 in the supplementary information). The dynamic adsorption loading of the functionalized PES membrane containing urethane functional groups (PES + UR) was found to be 5.1 mg/m^2, which is slightly lower than the dynamic adsorption loading observed when pure water samples were used (6.7 ± 0.7 mg/m^2). The unmodified membrane also exhibited a lower dynamic adsorption loading (0.7 ± 0.2 mg/m^2). These results suggest that the presence of the various salts and organic matter in the tap water can also slightly affect the adsorption loading of the modified membrane, with its incorporated urethane functional groups. Table S2 in the supplementary information presents the composition of the tap water utilized in this experiment.

To evaluate the capacity of the membranes to be regenerated and reused repeatedly, the adsorption loadings after repeated cycles were investigated. Adsorption cycles with 60 mL of each EDC solution with an initial concentration of 5 mg/L were performed. The adsorption cycle was followed by flushing the used membranes with an active surface area of 0.005 m^2, with 25 mL of water ethanol solution (1:1, v:v) and another 25 mL of diluted water ethanol solution (9:1, v:v). The washed membranes were exposed to another adsorption cycle. This procedure was repeated two times for all the membranes and all eight EDCs. The results are illustrated in Fig. 6. It is observed that due to the regeneration procedure, PES + UR membranes can be used repeatedly for most of the EDCs as in almost all cases the modified membranes preserved their original adsorption loadings. For the hormones E2, EE2, EQ, TST, and BPA, the adsorption loadings increased after the washing procedure. This can be due to the swelling of the membrane because of using ethanol. Swelling of the membrane can increase the active surface area and the adsorption capacity can increase. The presence of used ethanol in the membrane could also attribute to the increase in the adsorption since most of the hormones have a higher solubility in ethanol. In case of E1, EE2 and E3, a decline in the adsorption capacity in the regenerated cycles is observed for the unmodified PES membranes. This might suggest that the washing procedure is not working for the unmodified PES membranes and the adsorption sites cannot be regenerated without the urethane functional groups. It is worth mentioning that if the regeneration procedure does not take place, after the first cycle, no more removal of the EDCs takes place for all membranes. This was expected as reported in the dynamic adsorption studies, all the membranes reached the adsorption plateau after filtering 60 mL of the EDC solution. Without a regeneration procedure, no more adsorption takes place. The proved reusability is a key factor for scaling up the system.

4 Conclusions

Microfiltration PES membranes were modified with urethane functional groups to enhance the adsorption capacity toward EDCs. Results from dynamic adsorption proved that this modification significantly increases the adsorption capacity of the membrane especially for the EDCs with phenolic groups. This increased adsorption is attributed to hydrogen bonds between the hydroxyl groups in the EDC molecules and the urethane functional groups generated on the surface of the membranes during modification. The enhancement in the adsorption capacity revealed that the adsorption is also controlled by the log K_{ow} of the respective EDCs. The adsorption loading of E2 was increased from 1.4 mg/m^2 for the unmodified
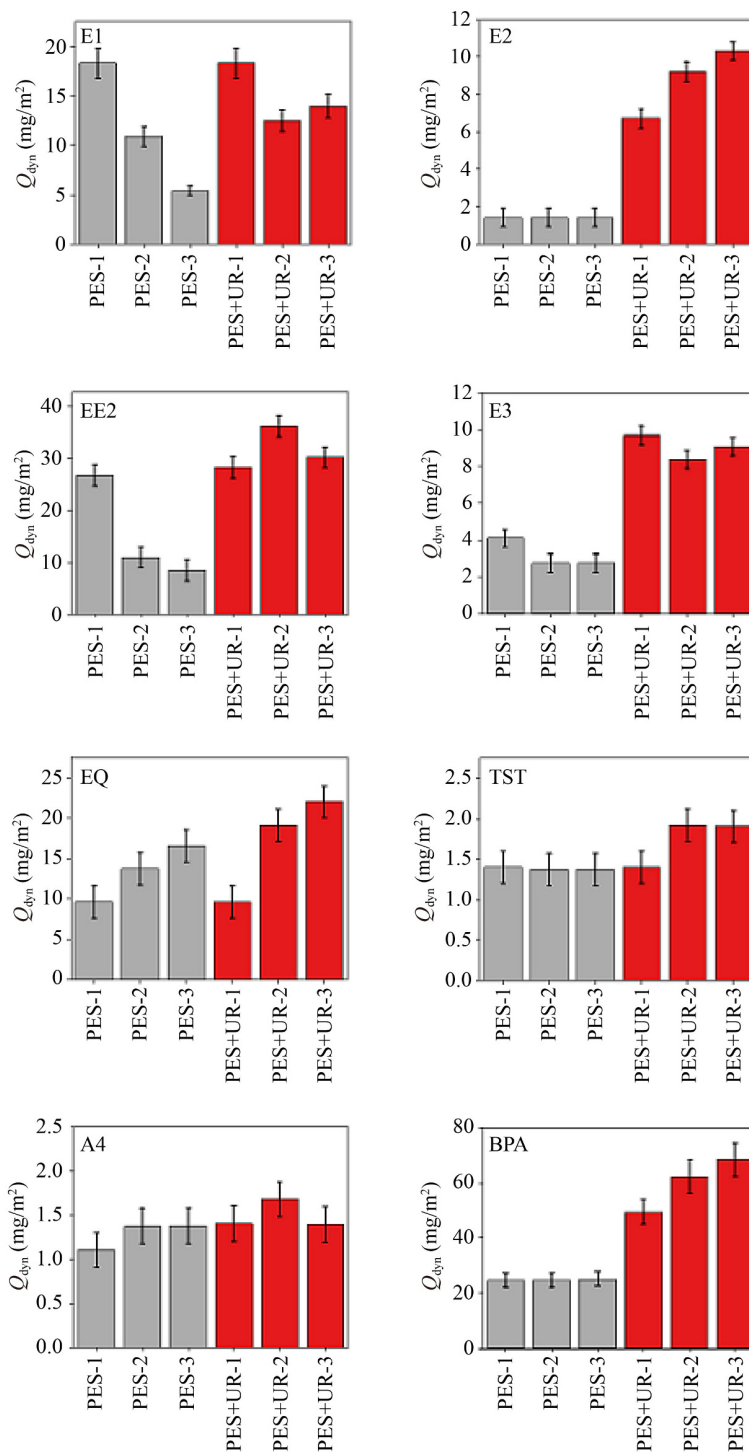
Fig. 6 Regeneration and subsequent adsorption cycles of pristine and functionalized PES membranes.

membrane to 6.7 mg/m^2 for the PES membrane containing urethane functional groups. This is two orders of magnitude more than the adsorption loading of commercial NF membranes. This work therefore shows that the concept of microfiltration can be used at a much lower pressure compared to RO and NF membranes, while the adsorption of EDCs is even higher. The

efficiency of functionalized and unmodified PES membranes in removing E2 from real water samples was investigated, with the functionalized membrane showing a dynamic adsorption loading of 5.1 mg/m^2. The identified adsorption loading is slightly lower than the experiments carried out with that of pure water samples, indicating the functionalized membranes are still effective

in E2 removal from real water samples. However, the presence of other salts and organic matter can adversely affect the removal capacity. The membranes can be regenerated and reused for three subsequent cycles without a loss in adsorption capacity. The present study proves that the surface modification by urethane functionalities is an efficient and cost-effective method to generate stable and high-performance membranes with improved adsorption capacity. This study provides a better understanding of the adsorption mechanisms of different endocrine disrupting chemicals onto polyether-sulfone membranes which can be helpful for upscaling and optimizing the adsorption process.

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