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EFFECTIVE WASTE MANAGEMENT WITH EMPHASIS ON CIRCULAR ECONOMY

Removal of pesticides from secondary treated urban wastewater by reverse osmosis

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Abstract

The residues of pesticides that reach water resources from agricultural activities in several ways contaminate drinking water resources and threaten aquatic life. This study aimed to investigate the performance of three reverse osmosis (RO) membranes (BW30-LE, SW30-XLE, and GE-AD) in rejecting four different pesticides (tributyl phosphate, flutriafol, dicofol, and irgarol) from secondary treated urban wastewater and also to elucidate the mechanisms underlying the rejection of these pesticides. RO experiments were conducted using pesticide-spiked wastewater samples under 10 and 20 bar transmembrane pressures (TMP) and membrane performances were evaluated. Overall, all the membranes tested exhibited over 95% rejection performances for all pesticides at both TMPs. The highest rejections for tributyl phosphate (99.0%) and irgarol (98.3%) were obtained with the BW30-LE membrane, while for flutriafol (99.9%) and dicofol (99.1%) with the GE-AD membrane. The increase in TMP from 10 to 20 bar did not significantly affect the rejections of all pesticides. The rejection performances of RO membranes were found to be governed by projection area as well as molecular weight and hydrophobicity/hydrophilicity of pesticides. Among the membranes tested, the SW30-XLE membrane was the most prone to fouling due to the higher roughness.

Keywords Dicofol · Irgarol · Tributyl phosphate · Flutriafol · Reverse osmosis

Introduction

Pollution in aquatic environments due to various micropollutants has become a significant issue, especially in the last 20 years. Even though they occur at nanograms per liter and micrograms per liter levels in aquatic environments (Cho et al. 2014; Barbosa et al. 2016), the threat and hazard imposed by these pollutants are serious. These pollutants include pesticides of natural or anthropogenic origin, industry compounds, pharmaceuticals, personal care products, steroid hormones, drugs, and heavy metals (Ribeiro et al. 2015).

It is estimated that approximately annually 3.5 million tons of various pesticides are consumed worldwide (Steingrimsdottir et al. 2018; Huang et al. 2019). Pesticides are classified as herbicides, insecticides, rodenticides, fungicides, and of the total pesticide consumption, approximately 45% is herbicides and 30% is insecticides (Vagi and Petsas 2020; Syafrudin et al. 2021). Due to the widespread use of pesticides in modern agriculture, the entry of these pollutants into rivers and streams as a source of agriculturally dispersed pollutants threaten the drinking water resources and aquatic ecosystem (Kimbrough and Litke 1996; Kreuger 1998; Leu et al. 2004; Schulz 2004; Jergentz et al. 2005; Probst et al. 2005; Zhang and Zhang 2011). The pesticide concentration in surface waters is associated with crop and soil management practices in the basin (Dabrowski et al.

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2002; Zablotowicz et al. 2006; Anderson et al. 2013). Although pesticides enter water bodies through infiltration and discharge from point sources, the infiltration of pesticides into the water sources is the major pathway. Surface runoff is the primary diffuse source of pesticides in surface waters and depends on the application and physicochemical properties of the pesticide and basin variables (Cole et al. 1997).

Pesticides that pose serious risks to the environment and human health can pass through from single cells to higher organisms by bioaccumulation, bioconcentration, and biomagnification in the food chain and can remain in the water and soil environment for a very long time (Ansari et al. 2014). The first legal regulation on pesticides was passed under the name of Federal Insecticide, Fungicide, and Rodenticide Act in 1947 in the USA (USDA 1947). USEPA included 43 pesticides as well as some of their metabolites to the Contaminate Candidate List 3 published in 2009 (USEPA 2009). The European Union (EU) has set a limit of 0.1 µg/L for a single active ingredient and 0.5 µg/L for the sum of all individuals of pesticides detected and measured through monitoring in the Drinking Water Directive (98/83/EC). The EU Environmental Quality Standards (EQSs) Directive (2013/39/EC) lists various pesticides as priority pollutants, including aldrin, dieldrin, endrin, endosulfan, dichlorvos, atrazine, alachlor, dicofol, and irgarol, and defines EQSs for these pollutants (EU 2013; Vagi and Petsas 2020). In line with this directive, Turkey's Regulation on Surface Water Quality Management also defines EQSs for these pesticides that must be met in inland and other surface waters (MoFWW 2015).

Depending on their physical and chemical properties, most micropollutants can remain in the environment for years without degradation. Since conventional urban wastewater treatment plants are not specifically designed for the removal of micropollutants, these pollutants cannot be fully removed and can reach into the receiving water bodies (Liu et al. 2009; Tijani et al. 2013; Margot et al. 2015). Better removal of micropollutants requires advanced treatment processes after conventional wastewater treatment processes (Siegrist and Joss 2012). Activated carbon adsorption, ozonation, advanced oxidation processes, and membrane processes are advanced treatment processes recommended for the further removal of micropollutants (Luo et al. 2014). Among these processes, membrane filtration, especially reverse osmosis (RO), is a more promising process as it provides higher efficiency in removing micropollutants (Van der Bruggen et al. 1998; Van der Bruggen and Vandecasteele 2003; Sahar et al. 2011). It is reported that the micropollutant removal performance of the membrane processes depends on the compound characteristics such as molecular weight and size, acid dissociation constant, hydrophobicity, diffusion coefficient as well as membrane and water characteristics (Bellona et al. 2004; Heo et al. 2020; Wu et al. 2021).

Typical micropollutants have a molecular weight of 100–400 Da (Rizzo et al. 2019) and RO membranes can successfully reject these contaminants (Bellona et al. 2004) as the rejection mechanism of micropollutants in RO membranes is mainly size/steric exclusion. It is reported that over 95% rejection can be achieved for most of the toxic contaminants regardless of water quality and operating conditions (Kim et al. 2018; Khanzada et al. 2020). Yangali-Quintanilla et al. (2011) reported that RO membranes can effectively reject both neutral and ionic emerging contaminants with an average rejection rate of 85% and 99%, respectively. RO has also proven to be an effective barrier against the majority of polar micropollutants (Albergamo et al. 2019). Wang et al. (2018) reported over 99.3% removal of most of 943 organic micropollutants, including tributyl phosphate by RO membranes from the secondary treated wastewater. In the study of Fini et al. (2020), optimized RO membranes by dopamine and m-phenylendiamine in interfacial polymerization were reported to provide over 92% rejection of three pesticides. Hydrophobic membrane fabricated using polyamide-polydimethylsiloxane increased pesticides rejection from 67 to 86.5% with respect to commercial membranes (Khairkar et al. 2020). On the other hand, the rejection performance of RO membrane for bisphenol-A with a maximum 87% (Khazaali et al. 2014), for cyclophosphamide (Wang et al. 2009) and ciprofloxacin (Alonso et al. 2018) up to 90%. However, rejection performance of RO membrane was much lower for N-nitrosodimethylamine up to ~50–65% (Plumlee et al. 2008), even as low as with 0.5% for smaller size antibiotics (Kosutic et al. 2007; Dharupaneedi et al. 2019).

Tributyl phosphate, which is used as a flame retardant in hydraulic fluids, a plasticizer for cellulose esters, plasticizers for plastic and vinyl resins, a defoamer, herbicide, and fungicide, is very stable and persistent in the natural environment. Flutriafol, a broad-spectrum chiral triazole fungicide, is commonly used for the production of corn, wheat, soybean, apple, cucumber, tomato, grape, pear, strawberries, cotton, etc. to control pests (Zhang et al. 2014; Bielska et al. 2021). Dicofol, a broad spectrum acaricide, is mostly applied to prevent and control insects of tea, cotton, vegetables, citrus, and other crops. Dicofol has acute and chronic toxicity and has serious impacts on living organisms such as carcinogenic, teratogenic, and mutagenic and endocrine disruptive (Lu et al. 2019). Since irgarol (cybutryne) in s-triazines structure is used as the algaecidal active agent in antifouling paints, it is one of the most commonly detected pesticides with 3 and 30 ng/L average concentrations in surface water and wastewater, respectively (Goswami et al. 2018). Hence, these pesticides are hardly affected by natural photolysis and hydrolysis and are resistant to biodegradability (Chaudhari et al.

2012; Nancharaiah et al. 2015; Pinto et al. 2018). In line with these characteristics, quite stringent EQSs are defined for these pesticides by the relevant national and EU legislation that necessitates research on removing these four pesticides from secondary treated urban wastewaters.

Although membrane separation-based wastewater treatment plants for wastewater reclamation are common all over the world (Ordonez et al. 2014; Tang et al. 2018), the pesticide rejection performance and the related fouling behavior of RO membranes in wastewater reclamation have not been fully addressed (Mehta et al. 2017). Particularly, the rejection of small molecular weight pesticides by the RO treatment of secondary treated urban wastewater remained relatively unexplored and researchers did not study the effects on permeate flux during this treatment. Fouling is the most significant issue in membrane filtration that membrane-based reclamation operations must tackle (Ordonez et al. 2014; Tang et al. 2018).

In the present study, these four pesticides, tributyl phosphate, flutriafol, irgarol, and dicofol, were chosen to study their tertiary treatment by RO process. RO tests were run using three different commercial RO membranes (BW30-LE, SW30-XLE, GE-AD) and their rejection performances were assessed at two different transmembrane pressures (TMP) (10 and 20 bar). The flux development and fouling behavior of the membranes were also investigated to improve the knowledge on the RO treatment applied to reduce the pesticide content of secondary treated urban wastewater to the EQS level.

Material and methods

Wastewater and chemicals

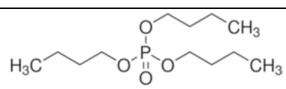
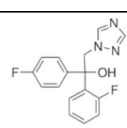
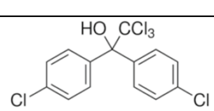
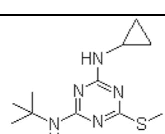
The wastewater samples used in this study were collected from the effluent of the secondary sedimentation tank of a biological urban wastewater treatment plant located in Turkey. The samples were firstly filtered using 1 μm filter paper to remove suspended solids and then kept in the dark at + 4 °C in the refrigerator until the analysis. The electrical conductivity (EC) of the filtered samples varied between 1063 and 1414 *μS/cm*, and the pH values varied between 6.31 and 8.64. The average COD and BOD_5 of the filtered samples were 45 mg/L and 6 mg/L, respectively. The mean total nitrogen and total phosphorus contents were measured as 7.9 mg/L and 25 mg/L, respectively.

Tributyl phosphate, flutriafol, dicofol, and irgarol standards of 99.9% purity were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Table 1 presents the typical characteristics of these pesticides. The chemicals of chloroform, acetone, methanol, and acetonitrile used in the pesticides analysis were of Merck grade purity (Merck, Darmstadt, Germany).

Membrane rejection tests

RO experiments were designed to evaluate the removal of tributyl phosphate, flutriafol, dicofol, and irgarol by RO membranes of SW30-XLE (Dow Filmtec), BW30-LE

Table 1 Properties of the pesticides[a]

Pesticide	Molecular Structure	Linear Formula	CAS Number	Molecular Weight (g/mol)	Projection Area, Å^2	Reference
Tributyl phosphate		$(CH_3(CH_2)_3O)_3PO$	126-73-8	266.31	44.8	Belles et al. (2018)
Flutriafol		$C_{16}H_{13}F_2N_3O$	76674-21-0	301.29	49.3	Fujioka et al. (2020)
Dicofol		$C_{14}H_9Cl_5O$	115-32-2	370.49	20.0	Tang et al. (2021)
Irgarol		$C_{11}H_{19}N_5S$	28159-98-0	253.37	62.7	Belles et al. (2018)

[a]The properties of pesticides were provided from https://pubchem.ncbi.nlm.nih.gov/. The projection area values of pesticides were obtained from related references

Table 2 Properties of the RO membranes used in the study[1]

Designation	Polymer structure	Rejection (% NaCl)	Pure water flux/TMP (LMH/bar)	Contact angle (°)[2]
GE-AD	Polyamide	99.75	20–32/55	62
BW30-LE	Polyamide	99.0	63–78/17	49
SW30-XLE	Polyamide	99.6	30–40/55	48

[1]https://www.sterlitech.com/flat-sheet-membranes.html. [2]Contact angle values were measured in this study

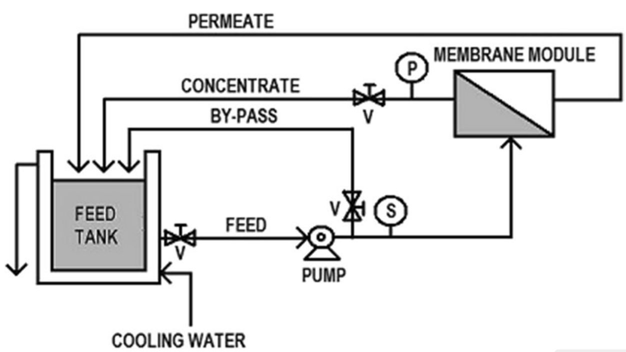


Fig. 1 Total-recycle mode flow diagram of lab-scale cross-flow high-pressure membrane filtration system (V: valve, P: pressure gauge, S: suction gauge) (Ates et al. 2009)

(Dow Filmtech), and GE-AD (GE) under two different operating TMPs of 10 and 20 bar. The properties provided by the manufacturers of the membranes used in this study are given in Table 2.

A lab-scale cross-flow high-pressure membrane filtration system (SEPA CF II, Sterlitech, USA) was used to perform RO tests (Fig. 1). The effective filtration area of the filtration cell was 140 cm^2. Prior to each RO test, each membrane coupon to be used in experiments was kept in ultra-pure water overnight to remove the impurities from the membrane surfaces. Then, they were placed in the filtration cell, which was then fed by distilled and deionized water until steady-state clean water flux was observed. Permeate samples were collected to calculate flux using the following equation: Eq. 1

$$J = \frac{dV/dt}{A} \quad (1)$$

where J is the permeate flux (LMH, L/m^2.h), dV/dt is the permeate flow (L/h), and A is the effective membrane area (m^2).

Feed samples for the RO process were prepared by spiking the desired amount of the standard pesticide solutions to the secondary treated municipal wastewater. The feed pesticides concentrations were adjusted as 100 µg/L for tributyl phosphate and flutriafol, and 1000 µg/L for dicofol and irgarol. The membrane experiments were conducted in total recycle mode in which both concentrate and permeate were diverted to the feed tank to keep the feed concentration constant (Fig. 1). Feed and permeate samples were collected at 60, 120, and 180 min during the operation to monitor the flux development and the pesticide rejection. The conductivity of the permeates was also monitored during the experiments as a further indicator of treatment efficiency. The pHs of the feed and permeate samples were measured as well. All RO tests were performed at the feedwater temperature of 25 ± 5 °C and repeated twice and the averages of all the measurements were taken and used in the data analysis. The tests were repeated at the TMP of 10 and 20 bar to investigate the effect of TMP.

Before their use, membranes were chemically cleaned with the use of a clean-in-place method. The membranes were placed into the membrane module and then subjected to HNO_3 at pH 3 for a duration of 30 min, followed by NaOH at pH 9–10 for 30 min. After acid–base application, double distilled water (DDW) was passed through the system for the measurement of initial clean water flux (J_{icw}). Following the RO test with the wastewater sample spiked with pesticide, DDW was applied again for the measurement of final clean water flux (J_{fcw}). The flux decline and fouling behavior of the membranes were assessed calculating percentage total flux decline and percentage flux recovery, respectively, using the equations given below: Eq. 2,3, and 4.

$$\%\text{Totalfluxdecline} = \frac{J_{icw} - J_{ww}}{J_{icw}} * 100 \quad (2)$$

$$\%\text{Fluxrecovery} = \frac{J_{fcw}}{J_{icw}} * 100 \quad (3)$$

where;

J_{icw}: initial clean water flux, which is the clean (pure) water flux determined with the clean membrane, which was subjected to the initial cleaning.

J_{ww}: wastewater flux stabilized with respect to time during wastewater filtration.

J_{fcw}: clean water flux measured with the fouled membrane after the wastewater filtration.

TMP is defined as:

$$TMP(\text{bar}) = \frac{(P_f + P_c)}{2} - P_p \quad (4)$$

where, P_f is the feed pressure, P_c is the concentrate pressure, and P_p is the permeate pressure.

Analytical methods

Tributyl phosphate and flutriafol were analyzed by Shimadzu QP2010 Ultra GC/MS equipped with Restek 5-MS column (30 m × 0.25 mm (i.d.) × 25 µm). The samples and calibration standards were extracted according to the dispersive liquid–liquid microextraction procedure. The sample was transferred to a 15 mL centrifuge tube containing 0.50 g of potassium iodide. The dispersed solution was prepared by adding 1 mL of chloroform to 2.0 ml of methanol in a separate centrifuge tube, and the sample and the dispersed solution were mixed in an ultrasonic bath for 10 min. Then, the tube was shaken for 30 s and centrifuged at 3500 g for 2 min. Approximately 300 µL volume was taken from the chloroform phase precipitated at the bottom of the tube and placed in insert vials for automatic injection and analyzed in the GC–MS device. Calibration curves based on at least 8 data points were obtained by preparing standard tributyl phosphate and flutriafol solutions at concentrations ranging from 5 to 100 µg/L. The limit of detection (LoD) and limit of quantification (LoQ) levels were 0.35 and 1.17 µg/L for tributyl phosphate and 0.50 and 1.67 µg/L for flutriafol, respectively.

Dicofol and Irgarol analyses were performed with an HPLC device (Shimadzu Prominence-i) equipped with a C18 column (Shim-pack Velox SP-C18) and UV detector. An isocratic elution method was employed using mobile phase, a mixture of acetonitrile and ultrapure water 4:1 v/v for dicofol and 7:3 v/v for irgarol. The mobile phase flow rate was 1.8 mL/min for dicofol analysis and 1.4 mL/min for irgarol analysis. The injection volume was 20 µL, and the column temperature was 40 °C. Dicofol and irgarol were detected at 225 nm and 223 nm wavelength, respectively. The R^2 values for the various linearized calibration curves were > 0.99 for all pesticides. Dicofol and irgarol concentration calibration curves were also based on at least 8 data points obtained by preparing standard solutions at concentrations ranging from 5 to 100 µg/L. The LoD and LoQ levels were 8.63 µg/L and 28.77 µg/L for dicofol and 7.42 µg/L and 24.73 µg/L for irgarol, respectively. The permeate samples were preconcentrated ten-fold in 1,2 dichloroethane before HPLC analysis.

The conductivity and pH measurements were performed using Hach HQ40D pH/Conductivity/DO meter. Standard methods were applied in measuring COD, BOD_5, total nitrogen, and total phosphorus measurements (APHA 2012).

Scanning electron microscope (SEM), atomic force microscopy (AFM), and surface contact angle analyses were performed for the characterization of the virgin and fouled membranes. SEM analyses were performed to determine the morphological structure of the membranes. SEM analyses of the membranes were performed with Zeiss Leo 440, Randburg analyzer. Membranes were cut approximately 3 mm long and 0.5 mm wide and coated with platinum before measurement. Analyses were carried out under 3 kV. Membrane surfaces of 5 × 5 µm in size were scanned with a MultiMode, Veeco brand AFM device to determine the surface roughness. The root mean squared roughness (R_{rms}) of each membrane was reported by taking roughness measurements at three different points on the membrane samples. The hydrophilic property of the membrane surface is directly proportional to the water permeability of the membrane. The contact angle value of the microliter (µL) water droplet dropped on the material surface with the surface was determined by the sessile drop method. In the contact angle measurement, first, the membranes were fixed to the slides using double-sided adhesive tape, and then approximately 3 µL of ultrapure water was dropped on the slide placed at the bottom of the syringe. Measurements were performed from three different points for each piece of membrane, and the average results were reported.

Results and discussion

Flux development and fouling

The highest and lowest clean water fluxes of all pesticides were obtained by BW30-LE and SW30-XLE membranes are shown in Table 3, respectively. As expected, there was an increase in both clean water and wastewater steady-state permeate fluxes as TMP increased from 10 to 20 bar. The ranges of clean water fluxes were observed between 6.37–11.58 and 15.05–37.27 LMH for GE-AD membrane, between 16.88–46.75 and 43.20–98.90 LMH for BW30-LE membrane, and between 2.00–15.49 and 7.19–36.70 LMH for SW30-XLE membranes at 10 and 20 bar pressures, respectively. The clean water fluxes of the membranes showed compatibility with the contact angles of the membranes, and the highest flux was obtained with the BW30-LE membrane, which had the lower contact angle (49°) and was more hydrophilic. Although BW30-LE and SW30-XLE membranes have similar contact angles, SW30-XLE provided the lowest water fluxes among RO membranes, even though the GE membrane is more hydrophobic (62°). Moreover, the flux values provided by manufacture for SW30-XLE are significantly lower than flux for BW30-LE even at higher applied pressure (Table 2). The water permeability and flux behaviors of the membrane depend on several parameters, including intrinsic membrane properties (contact angle, surface roughness, porosity, and liquid entry pressure) as well as hydraulic conditions (Damtie et al. 2018). The hydrophilicity of polyamide membranes is directly related to the roughness of the surface of the membranes. It is reported that the hydrophobicity of the membranes increases as the surface roughness increases (Lin et al. 2016). On the

Table 3 Flux development for GE-AD, BW30-LE, and SW30-XLE membranes at two different TMPs

Membrane	TMP (bar)	Flux (LMH)			Total flux decline (%)	Flux recovery (%)	Permeance (LMH/bar)		
		J_{icw}*	J_{ww}**	J_{fcw}***			J_{icw}/TMP	J_{ww}/TMP	J_{fcw}/TMP
Tributyl phosphate									
GE-AD	10	6.37	4.91	5.65	23	89	0.49	0.64	0.57
	20	18.31	15.53	18.51	15	101	0.78	0.92	0.93
BW30-LE	10	32.47	20.21	24.68	38	76	2.02	3.25	2.47
	20	72.18	41.65	52.25	42	72	2.08	3.61	2.61
SW30-XLE	10	3.9	3.25	4.15	17	106	0.33	0.39	0.42
	20	13.48	12.82	12.39	5	92	0.64	0.67	0.62
Flutriafol									
GE-AD	10	11.58	10.37	14.12	0	106	1.04	1.16	1.41
	20	37.27	33.83	31.36	0	130	1.69	1.86	1.57
BW30-LE	10	46.75	48.51	49.45	10	122	4.85	4.68	4.95
	20	98.9	107.14	128.57	9	84	5.36	4.95	6.43
SW30-XLE	10	15.49	16.69	16.07	0	104	1.67	1.55	1.61
	20	36.7	35.22	40.81	4	111	1.76	1.84	2.04
Irgarol									
GE-AD	10	7.04	6.93	6.52	7	93	0.69	0.70	0.65
	20	15.05	14.43	13.71	9	91	0.72	0.75	0.69
BW30-LE	10	16.88	16.31	16.55	2	98	1.63	1.69	1.66
	20	43.2	40.89	37.35	14	86	2.04	2.16	1.87
SW30-XLE	10	2.2	2.11	2.02	8	92	0.21	0.22	0.20
	20	7.19	7.04	6.19	14	86	0.35	0.36	0.31
Dicofol									
GE-AD	10	6.66	6.11	5.94	11	89	0.61	0.67	0.59
	20	16.03	12.84	13.16	18	82	0.64	0.80	0.66
BW30-LE	10	23.89	22.13	17.97	25	75	2.21	2.39	1.80
	20	53.35	52.22	50.24	6	94	2.61	2.67	2.51
SW30-XLE	10	2	1.82	1.42	29	71	0.18	0.20	0.14
	20	7.95	6.48	6.85	14	86	0.32	0.40	0.34

*clean water flux (LMH), **wastewater flux (LMH), ***cleaned water flux after treatment (LMH)

contrary to this generalization, the hydrophilicity of the membranes increased as the surface roughness increased in this study as shown in Table 4. Tang et al. (2009) reported that no apparent relation between surface roughness and hydrophilicity for fully aromatic RO membranes such as SW30-XLE membrane as it was in this study.

As shown in Fig. 2, the wastewater fluxes of the BW30-LE membrane increased to considerably high levels with an increase in TMP from the earlier already high fluxes. The highest wastewater permeates fluxes were obtained with the BW30-LE membrane at the 20 bar TMP for tributyl phosphate, flutriafol, irgarol, and dicofol. The other two membranes, the GE-AD and SW30-XLE, presented similar wastewater fluxes for all pesticides at both TMPs, although the surface of the GE-AD membrane was smoother and more hydrophobic than the SW30-XLE membrane. For the SW30-XLE membrane, the wastewater fluxes at 10 bar TMP were all the lowest (except for flutriafol), although the percentage increases in the flux with an increase in TMP from 10 to 20 bar appeared to be higher than those with the other two membranes.

Flux decline for each membrane was determined based on the differences between clean water and wastewater fluxes under steady-state conditions. As can be seen from Table 3, in general, the highest flux decline was observed for tributyl phosphate followed by dicofol, and the lowest flux decline was for flutriafol. In the rejection of tributyl phosphate, the highest flux decline of about 38–42% was exhibited by the BW30-LE membrane, which, in fact, provided the highest permeate flux in filtering tributyl phosphate and all the other three pesticides from the wastewater. On the other hand, flutriafol caused the lowest flux declines when using the GE-AD membrane. The flux decline was measured as 0% at both 10 and 20 bar TMPs. In line with this, the flux decline for flutriafol with the SW30-XLE membrane was also at the level of 0 to 4%. For irgarol, the highest flux decline of

Table 4 The contact angles, the root-mean-squared roughness, and roughness ratio of virgin membranes*

	GE-AD	BW30-LE	SW30-XLE
Contact angle (°)	62	49	48
R_{rms} (nm)	57.86 [6.20]	88.20 [9.60]	118.01 [12.50]
Roughness ratio (%)	21.21 [2.15]	45.00 [1.70]	95.30 [11.40]

*The numbers in square brackets indicate the standard deviation

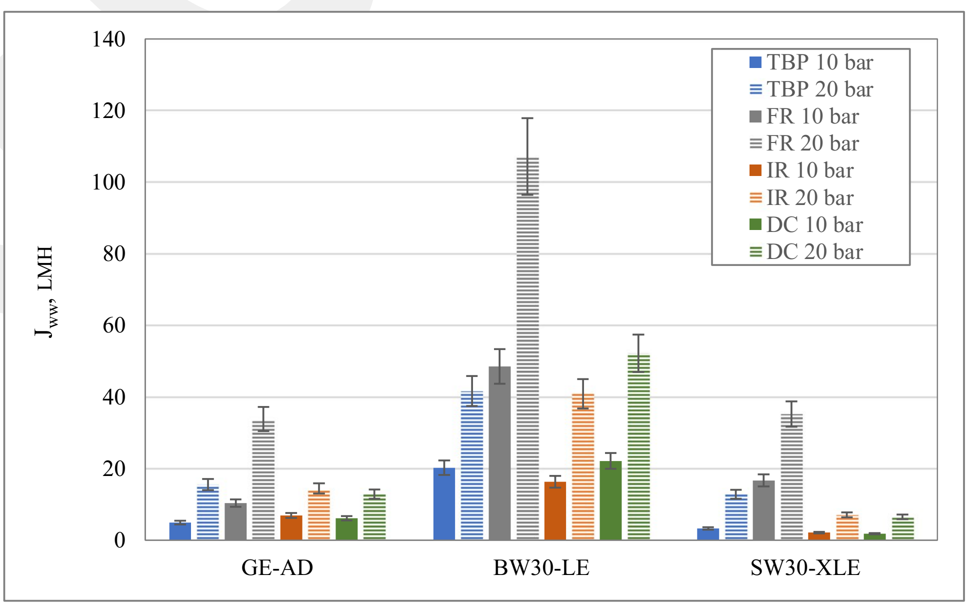
14% was observed with both the SW30-XLE and BW30-LE membranes, whereas the lowest decline was with the GE-AD membrane.

As shown in Table 3, there was an increase in flux decline with an increase in TMP except for TBP with the GE-AD and SW30-XLE membranes and for dicofol with the BW30-LE membrane. Indeed, flux decline is expected to increase with an increase in TMP (Tu et al. 2005; Alventosa de Lara et al. 2012). To provide a better insight into flux decline behavior, water and wastewater permeance values of the membranes were calculated (Table 3). As presented, there was an increase in the permeances of all membranes in all experiments with an increase in TMP. This finding indicated that the flux decline decreases observed (for TBP with the GE-AD and SW30-XLE membranes and for dicofol with the BW30-LE membrane) with an increase in TMP was not significant at all.

The calculated flux recoveries (%) based on the initial and final clean water fluxes were relatively high for all the pesticides rejections by all three membranes with an approximate average value of 93% (Table 3). The most severe membrane fouling with 71% and 72% recovery rates were observed dicofol and tributyl phosphate rejection using SW30-XLE and BW30-LE membranes at 10 bar pressure, respectively. On the other hand, the highest recovery rates were (82–130%) obtained with the GE-AD membrane. Basically, the flux decline is known to result from the increase in the membrane resistance by cake formation and membrane pore blockage (Harouna et al. 2019; Fujioka et al. 2020; Chen et al. 2021). The fact that the fluxes were not fully recovered indicates that pore-blocking has developed, which requires backwashing with a chemical agent (Ang et al. 2011). The trends of flux decrease in RO membranes were also confirmed by SEM and AFM images that cake formations are obvious in Fig. 3.

It is known that the hydrophobic nature of a membrane is well correlated with membrane fouling (Nabe et al. 1997; Kim et al. 2006; Yin et al. 2017), and the contact angle with water provides a good measure of fouling tendency. Previous research has shown that hydrophilic membranes tend to foul less rapidly than hydrophobic membranes (Fan et al. 2001; Zularisam et al. 2006). On the contrary to previous studies, the lowest flux decline was observed for the GE-AD membrane, which was more hydrophobic, having the highest contact angle (Table 4). This observation was attributed to the possible effects of surface roughness and porosity of the membranes on fouling behavior. The less porous and smooth membranes are likely to provide lower flux decline than the more porous and rough membranes. Additionally, membranes with high surface roughness are more prone to clogging due to their valleyed structure and, in turn, increased flux decline (Lin et al. 2016; Chen et al. 2021).

Fig. 2 Effect of TMP on wastewater fluxes (TBP: tributyl phosphate, FR: flutriafol, IR: irgarol, DC: dicofol)



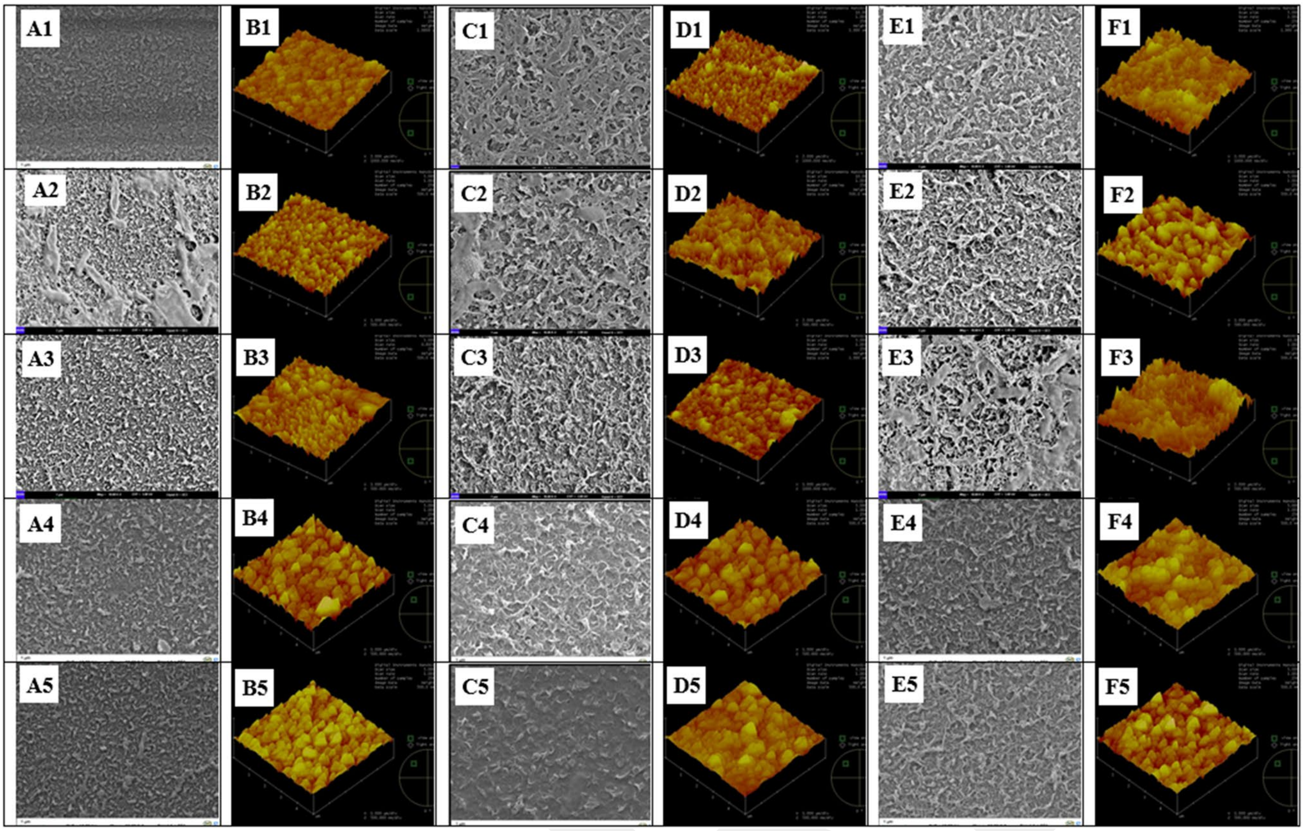


Fig. 3 The SEM and AFM images for membranes (GE-AD, BW30-LE, SW30-XLE) of virgin (A1-F1) and used membranes for removal of tributyl phosphate (A2-F2), flutriafol (A3-F3), irgarol (A4-F4), and dicofol (A5-F5) at 10 bar pressure, respectively

Removal of tributyl phosphate

Table 5 presents the time course of tributyl phosphate removal efficiency with three RO membranes tested under two different TMPs. As seen, tributyl phosphate removal was very rapid and the lowest removal attained in 60 min was 96% with the SW30-XLE membrane at both 10 and 20 bar TMPs and with the GE-AD membrane at 10 bar TMP. Yet, the BW30-LE membrane provided a higher rejection of 99% in 60 min at both TMPs. All three tested membranes provided 99% tributyl phosphate removal in 180 min, indicating a very effective RO removal.

The transport of pesticides through RO membranes is driven by three interactions, including size exclusion, electrostatic repulsion, and aromaticity/hydrophobicity. The exclusion of pesticides by polyamide-based membranes is primarily governed by size exclusion and charge interaction (Schafer et al. 2003; Plakas and Karabelas 2012; Fujioka et al. 2020; Shin et al. 2022). Fujioka et al. (2020) investigated the rejection of 158 pesticides by polyamide-based RO membrane and reported high variations for rejection of uncharged pesticides with 180–300 g/mol molecular weights. On the other hand, they observed strong relation between the rejection of uncharged pesticides and minimum rejection area and proposed that minimum rejection area is a better indicator to evaluate rejection of uncharged pesticides. As can be seen from Table 1, tributyl phosphate has an MW of 266.31 g/mol, and a projection area of 44.8 Å^2, the rejections of tributyl phosphate for all three RO membranes at steady-state (98–99%) are in agreement with the study of Fujioka et al. (2020) even its molecular weight is smaller than other pesticides. On the other, no apparent effect was observed on the removal of tributyl phosphate.

Similar to this study, Martinez et al. (2015) reported 99% rejection for tributyl phosphate using BW30-LE RO membrane from a UF pretreated secondary effluent. Besides, Agenson and Urase (2007) observed 96% and 95% of tributyl phosphate removal from a synthetic solution of 50 µg/L by hydrophilic NF (UTC20) and hydrophobic RO (LES90) flat sheet membranes, respectively. On the other hand, Krzeminski et al. (2017) reported lower tributyl phosphate removal efficiencies; 44% and 57% for UF membranes (10,000 and 1000 Da), 91% and 89% for NF membranes (200–400 and 150 Da), and 95% for RO membranes with a lab-scale pressured membrane filtration system fed by a pretreated secondary effluent.

Table 5 The effect of pressure on time-dependent removal of tributyl phosphate by RO membranes

Pressure (bar)	Time (min)	BW30-LE			SW30-XLE			GE-AD		
		EC[1] (*µS/cm*)	*pH*	TBP[2] rejection (%)	*EC (µS/cm)*	*pH*	TBP rejection (%)	EC (*µS/cm*)	pH	TBP rejection (%)
10	0	1308	8.35	-	1194	8.62	-	1167	8.64	-
	60	53	8.03	99.0	77	8.19	96.0	45	8.02	96.0
	120	50	8.21	98.0	68	8.01	97.0	39	7.79	97.0
	180	50	8.07	99.0	60	8.00	98.0	26	8.17	99.0
20	0	1234	8.56	-	1203	8.70	-	1270	8.45	-
	60	24	7.80	99.0	33	8.29	96.0	24	8.14	99.0
	120	25	8.03	99.0	33	8.06	98.0	21	8.32	99.0
	180	19	8.15	99.0	31	8.11	98.0	21	8.34	99.0

[1]*EC* electrical conductivity, [2]*TBP* tributyl phosphate

While this pesticide was rejected very effectively with all three membranes in the first 60 min, surprisingly, the electrical conductivity rejection was relatively slower. Even after 120 min, there observed a further decrease in the electrical conductivity of the permeates from all three membranes and the conductivity rejection reached to the levels of 95–98%. The remarkable, very rapid initial decrease observed in the conductivity of the wastewater spiked with pesticides verified the effective removal of all the dissolved solids of the secondary effluent as well. The wastewater pH values did not change significantly; they just varied between 8 and 8.7 for all the experimental conditions. On the other side, there was no visible effect of TMP on the removals of both tributyl phosphate and electrical conductivity. The removals achieved at the TMP of 10 bar were comparable to those at the TMP of 20 bar.

Removal of flutriafol

The results of RO experiments performed for the treatment of flutriafol containing wastewater are summarized in Table 6. The SW30-XLE and GE-AD membranes provided 98–99% of flutriafol rejection performances at 10 and 20 bar pressures. The lowest flutriafol removal was obtained for the BW 30-LE membrane as 92% at 20 bar TMP. It is known that the rejection of compounds increases with an increase in their molecular weight, hydrophobicity, and minimum projection area (Plakas and Karabelas 2012; Fujioka et al. 2020). The higher rejection of flutriafol by SW30-XLE and GE-AD membranes was related to the higher solute rejection capacity of seawater membranes. Besides, the higher rejection of flutriafol by SW30-XLE and GE-AD membranes was affected by the minimum projection area of flutriafol, which is similar to that of tributyl phosphate. It is reported in the literature that hydrophilic micropollutants (e.g., *Log* $K_{ow} \leq 2$) could exhibit higher rejection than hydrophobic

Table 6 The impact of TMP on time-dependent removal of flutriafol by the RO membranes

Pressure (bar)	Time (min)	BW30-LE			SW30-XLE			GE-AD		
		EC (µS/cm)*	pH	Flutriafol rejection (%)	*EC* (µS/cm)*	pH	Flutriafol rejection (%)	*EC* (µS/cm)*	pH	Flutriafol rejection (%)
10	0	1102	7.80	-	1066	7.60	-	1063	7.91	-
	60	144	7.80	86.1	37	6.99	96.5	15	7.23	98.6
	120	51	7.50	95.4	28	7.05	97.4	15	7.30	98.6
	180	26	7.26	97.6	16	7.80	98.5	22	7.19	99.9
20	0	1079	7.55	-	1082	7.54	-	1066	8.09	-
	60	77	7.78	92.9	19	7.28	98.2	19	7.13	98.2
	120	109	7.56	89.9	31	7.20	97.1	7	7.18	99.4
	180	86	7.62	92.1	12	7.10	98.9	10	7.24	99.0

[*]*EC* electrical conductivity

micropollutants (e.g., $Log\ K_{ow} \geq 2$) (Verliefde et al. 2009; Albergamo et al. 2019; Fujioka et al. 2020). Flutriafol is a moderately lipophilic compound ($Log\ K_{ow} = 2.3$) (Noble 1993), and its hydrophobicity is lower than tributyl phosphate ($Log\ K_{ow} \cong 4.0$) (Nakamura 1991), dicofol ($Log\ K_{ow} = 4.28$) (Thiel et al. 2011), and irgarol ($Log\ K_{ow} = 3.95$) (Biselli et al. 2000). Besides the effect of the minimum projection area, aromaticity/hydrophobicity interactions between flutriafol and membranes also might affect the rejection of flutriafol. However, the projection area and molecular weight of flutriafol is slightly higher than those of tributyl phosphate (Table 1), the rejection of flutriafol by BW30-LE was much lower than that of tributyl phosphate. As previously mentioned, the removal of pesticides by RO membranes is governed by size exclusion, electrostatic repulsion, and aromaticity/hydrophobicity.

With this membrane, the removal achieved at the TMP of 10 bar was 97.6%, indicating no positive effect of TMP on flutriafol removal. In this set of experiments, in line with the results for tributyl phosphate experiments, the electrical conductivity of the wastewater samples was reduced to below 100 *µS/cm* for all TMPs tested. Liu et al. (2018) investigated the influence of operating parameters, including current density, flow rate, and initial concentration, on electrooxidation of flutriafol wastewater using a novel 3DOM-PbO_2 filter and reported that the acute toxicity of flutriafol wastewater significantly decreased after the treatment using the 3DOM-PbO_2 filter. Although electrochemical oxidation adsorption is a promising technique for effective degradation of toxic and recalcitrant aqueous contaminants, our results showed that RO membranes are more efficient than these processes due to complete removal performances achieved in pesticide removals.

Removal of dicofol

The RO tests were performed for 3 h of operation with BW30-LE, SW30-XLE, and GE-AD membranes at two different pressures (10 and 20 bar), and electrical conductivity, pH, and dicofol removal values were monitored. The results obtained through the RO experiments performed for the treatment of dicofol-containing wastewater is summarized in Table 7. The highest removal performances were obtained for BW30-LE and GE-AD membranes with 98–99% at 10 and 20 bar pressures. Although dicofol had the lowest projection area (20.0), all three membranes exhibited very high removal performances for dicofol removal. Dicofol, on the other hand, has the highest molecular weight of 370.49 g/mol among pesticides, indicating that size exclusion is the major governing mechanism in the highly efficient removal of dicofol by membranes. Ahamad et al. (2020) produced a nanocomposite photocatalyst containing MoS_2/ZnS nanoparticles and tested for the degradation of dicofol under sunlight irradiation and reported approximately 85% degradation of dicofol. In the study of Mukherjee et al. (2020), removal efficiencies greater than 80% were reported for 33 of 43 pesticides with low-pressure thin-film composite membrane with 95% NaCl rejection. While the average removal efficiency of 72% was observed for dicofol spiked into the water at 20, 50, and 100 mg/L, the rejection performance decreased by about 15% as the initial dicofol concentration increased.

The pH values do not change significantly, just varying between 7 and 8 for all membranes and for two different pressures. Conductivity values were decreased from 1223 to 19 *µS/cm*, from 1248 to 60 *µS/cm*, and from 1298 to 15 *µS/cm* for the BW30-LE, SW30-XLE, and GE-AD membranes for 10 bar pressure, respectively. Besides, conductivity values were decreased from around 1300–1400 to 13 *µS/cm*

Table 7 The impact of TMP on the time-dependent removal of dicofol by RO membranes

Pressure (bar)	Time (min)	BW30-LE			SW30-XLE			GE-AD		
		*EC** (*µS/cm*)	*pH*	Dicofol rejection (%)	*EC** (*µS/cm*)	*pH*	Dicofol rejection (%)	*EC** (*µS/cm*)	*pH*	Dicofol rejection (%)
10	0	1223	7.11	-	1248	7.48	-	1298	7.63	-
	60	14	8.02	98.8	69	8.43	94.5	31	7.25	97.6
	120	15	7.69	98.8	63	6.98	94.9	25	6.87	98.1
	180	19	7.96	98.4	60	7.22	95.2	15	6.46	98.8
20	0	1303	7.52	-	1316	7.01	-	1414	6.31	-
	60	13	8.33	99.0	34	7.49	97.4	23	7.31	98.4
	120	15	8.05	98.8	34	6.89	97.4	14	7.08	99.0
	180	13	7.78	99.0	31	6.91	97.7	13	7.06	99.1

**EC* electrical conductivity

for the BW30-LE membrane, to 31 *μS/cm* for the SW30-XLE membrane, and 13 *μS/cm* for the GE-AD membrane. As the TMP increased, removal of dissolved ions (e.g., conductivity) increased for all membrane types, especially for SW30 that conductivity removal was increased from 94 to 98%. The effect of TMP was more pronounced for the SW30 membrane, where the removal performance increased from 95 to 98% when the pressure was increased from 10 to 20 bar.

Removal of irgarol

The irgarol rejections for the SW30-XLE, BW30-LE, and GE-AD membranes at the 10 bar TMP after 180 min RO tests were calculated as 98.2%, 98.0%, and 97.9%, respectively (Table 8). The rejections at the 20 bar TMP were 98.3%, 98.1%, and 95.3% with the BW30-LE, SW30-XLE, and GE-AD membranes, respectively. These slightly lower rejections of irgarol in comparison with the rejection of the other pesticides correlate with its lower MW. Although its projection area (62.7 $Å^2$) is significantly higher than other ones of pesticides, slightly lower rejections of irgarol (2–3%) compared to the other pesticides were recorded. Despite its higher projection area, the relatively lower irgarol rejections show that the hydrophobicity/hydrophilicity interactions between the irgarol and polyamide membranes, as well as the size exclusion also are effective based on its low molecular weight (253.37 g/mol) and hydrophobicity (*Log Kow* = 3.95).

Bester et al. (2011) tested the performance of activated soil-biofilters that contain organic materials such as peat have a high potential for removing irgarol from contaminated waters during high hydraulic loads and reported over 80% removal. While the removal efficiency of irgarol was 34% in the conventional activated sludge treatment, 32% and 0–60% removal efficiencies were observed in pilot-scale ozonation and PAC-UF process following biological process, respectively (Margot et al. 2013). Our results showed that the GE-AD membrane is more efficient for the irgarol rejection at about 95%.

When irgarol-containing wastewater was filtered using the SW30-XLE, BW30-LE, and GE-AD membranes at 10 and 20 bar TMPs, the results presented in Table 8 were obtained. As shown, the irgarol rejection did not change at all when the TMP was increased from 10 to 20 bar. Similar to dicofol-containing wastewater experiments, electrical conductivity reduced from ~ 1300 *μS/cm* to lower than 100 *μS/cm* at 10 bar pressure. The increase in the pressure slightly enhanced the electrical conductivity removal. BW30-LE exhibited superior performance for the removal of dissolved solids in irgarol-containing wastewater compared to the other membranes. All three membranes (SW30-XLE, BW30-LE, and GE-AD) rejected irgarol in both TMPs with about 98% performance, except at 20 bar with the GE-AD membrane. When the GE-AS membrane was used at 20 bar TMP, the irgarol rejection was about 95%.

Conclusions

In this work, the removal of tributyl phosphate, flutriafol, dicofol, and irgarol pesticides from a secondary treated wastewater using three different RO membranes (GE-AD, BW30-LE, and SW30-XLE) was investigated and flux development was assessed at the TMP of 10 and 20 bar. Based on our findings, it is concluded that although RO process, in general, is effective in the removal of these pesticides, the pesticide rejection varies with the membrane and pesticide characteristics. The following conclusions were also drawn:

Table 8 The impact of TMP on time-dependent removal of irgarol by RO membranes

Pressure (bar)	Time (min)	BW30-LE			SW30-XLE			GE-AD		
		EC* (*μS/cm*)	pH	Irgarol rejection (%)	EC* (*μS/cm*)	pH	Irgarol rejection (%)	EC* (*μS/cm*)	pH	Irgarol rejection (%)
10	0	1232	7.11	-	1355	7.48	-	1265	7.63	-
	60	26	8.02	98.3	62	8.43	97.7	84	7.25	98.6
	120	36	7.69	98.5	68	6.68	97.9	83	6.87	98.1
	180	29	7.96	98.2	64	7.22	98.0	86	6.46	97.9
20	0	1190	7.52	-	1532	7.01	-	1318	6.31	-
	60	21	8.33	97.7	54	7.49	97.7	98	7.31	94.9
	120	23	8.05	98.2	51	6.89	98.2	86	7.08	95.3
	180	17	7.78	98.3	54	6.61	98.1	74	7.06	95.3

[*] *EC* electrical conductivity

- All the membranes tested exhibited 95–99% rejection for all the pesticides tested. Yet, the BW30-LE membrane outperformed in the overall.
- The increase in TMP from 10 to 20 bar did not significantly affect the rejections of all pesticides.
- The highest permeate fluxes were obtained with the BW30-LE membrane which is more hydrophilic. More hydrophobic but with a smoother surface GE membrane exhibited a higher flux recovery than the other tested hydrophobic SW30-XLE membrane.
- Pesticides having higher projection area were rejected better. Tributyl phosphate with a moderate projection area bot a low molecular weight rejected at a level of 98–99% by all the membranes tested.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Declarations

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