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Lindane removal by membrane nanofiltration

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ABSTRACT

Lindane is the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (HCH) and it has been widely used in the pesticide industry due to its insecticide properties. In the production of lindane, significant quantities of other HCH isomers are generated as byproducts. All these compounds are typically stored in landfills, often with poor management practices. Polyamide membranes, two commercial membranes from Alfa Laval (NF99HF and NF99) and homemade thin film composite membranes prepared by interfacial polymerization on a porous polyimide support, were evaluated for water nanofiltration (NF) of HCH isomers, including lindane. Homemade membranes, with a lindane rejection of 91.3 % and a permeance of 2.7 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$, offered the highest performance in terms of both permeance and rejection. NF99 and homemade membranes were proven to be equally effective in removing α-HCH and β-HCH, showing similar results. Homemade membranes achieved 99.5 and 99.8 % rejections for α-HCH and β-HCH, respectively. Long-term experiments were carried out with NF99 and homemade membranes to assess their stability during filtrations with lindane solutions for up to 214 h. Homemade TFC membrane maintained its initial rejection (ca. 93.5 %) after 214 h, although its permeance decreased over time, ending in 2.5 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$.

1. Introduction

Currently, agricultural industry consumes around 70 % of the extracted water [1]. Major concerns have arisen from water contamination by pesticides during agricultural activities since polluted water is discharged to rivers and lakes. Pesticides are known as toxics for human beings and then the majority of them are eliminated in treatment plants. However, some of them are still harmful for the environment and large discharge of these pollutants to rivers and lakes must be prevented to preserve the environment. An example of these contaminants is the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (HCH), commonly known as lindane. This pesticide can be found as “technical lindane”, which contains all five major isomers of HCH at different concentrations: 55–80 % α-HCH, 5–14 % β-HCH, 5–15 % γ-HCH, 2–16 % δ-HCH and 3–5 % ε-HCH [2]. Among the five spatial arrangements of HCH, only γ-HCH presents pesticide activity [3]. Industrially, pure lindane is obtained from “technical lindane” by distillation [4]. In the production of “technical lindane”, only around 5–15 % of the γ-isomer is generated, while at least 85 % of the produced compounds are unusable and are disposed, on many occasions in landfills under non-controlled conditions.

Apart from pest control applications, lindane is also of industrial interest for numerous purposes, including health care (treatment against ectoparasites), treatment for wood or plastics, and for military use [5]. The most relevant physical-chemical properties are collected in Table 1.

Regarding the toxicity of lindane to human health, it is particularly worrying the fact that lindane is highly persistent in the environment. It has been found in soil [12], water [13] and air [14] at relevant concentrations, evidencing its ability of surviving at ambient conditions and spreading throughout the ecosystem. Its low degradability with light and low microbial activity account for its persistency in rivers and landfills [3]. The result is the bioaccumulation of lindane in living beings as reported in several studies [15,16]. Due to its facility to attach to organic matter, it causes a series of deleterious effects for all kinds of living beings, such as plants [17], animals [18,19] and humans [20,21].

Thousands of tons of lindane were used between 1950 and 2000, even for non-agricultural purposes. Lindane was banned in 2008 by the European Union (EU) and considered as a persistent organic pollutant (POP) after 2009. In Spanish territory, several cases of contamination of

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Abbreviations

NF	nanofiltration
TFC	thin film composite
PA	polyamide
TMC	trimesoyl chloride
MPD	phenylenediamine
HDA	hexanediamine
HCH	1,2,3,4,5,6-hexachlorocyclohexane
AC	activated carbon
IPA	isopropanol
DMSO	dimethyl sulfoxide
PI	polyimide
SEM	scanning electron microscopy
WCA	water contact angle
EDX	energy dispersive X-ray
STe	short-term experiments
LTe	long-term experiments

the population by lindane were detected. In Sabiñánigo (Spain) [14], unlined landfills stored 30,000–80,000 tons of lindane, resulting in the contamination of 0.5 km^2 of land and an aquifer. Similarly, the Bailín landfill in Aragón, known for contaminating nearby rivers, still holds 64,000 tons of HCH [22]. Other geographical points in Spain deal with similar issues: O Porriño (region of Galicia), where 1 km^2 of surface area was contaminated [3], and País Vasco, where up to 100,000 tons of lindane waste were dumped uncontrolled nearby [23]. Many European countries face similar problems of contamination due to leakage or inadequate lindane storage. For instance, Bitterfeld-Wolfen (Germany), where 40 km^2 of soil was contaminated, or in Twente (Netherlands), where 400,000 tons of contaminated soil had to be isolated due to this issue. In Spolana Neratovice (Czech Republic), 60,000 tons of this pesticide is currently stored implying a potential risk for the local population and environment [3]. In addition, large amounts of lindane and other HCH isomers have been found and stored in other parts of the world such as Mexico [24], Canada [25] and different parts of Asia [26,27].

Several removal methodologies have been studied to remove lindane from aquatic environments. These include the use of zero valent iron NZVI/Cu nanoparticles supported on activated carbon (AC) [28], electrochemical oxidation [29], adsorption [31,32], use of Pd nanoparticles on a high-density polyethylene in supercritical CO_2 [33], catalytic dechlorination [34,35] or photocatalysis using CeO_2-TiO_2 coatings [36]. The discovery of new materials has the potential to revolutionize certain technologies. For instance, 2D materials such as graphene and its derivatives have opened new opportunities for achieving higher removal rates through lindane adsorption [30]. Bioremediation techniques hold particular interest as they are recognized as safer and equally efficient for eliminating pollutants from the environment [34]. Among these methods, the adsorption of lindane using granular AC is currently the chosen technique in large scale installations due to its high separation ability (separation factor of AC are typically above 90 %) [28,37]. This approach has been successfully implemented in the water treatment plant that dealt with the lindane-contaminated water from the Bailín dumpsite previously discussed [22]. Nevertheless, AC is quite an expensive material (with prices reaching ca. $3000 per ton in the USA markets [38]) and large amounts are required to achieve high lindane removal rates and meet legal lindane concentration requirements. In addition, in most cases, the use of AC does not guarantee a total removal of lindane from the polluted medium and a further separation step is required [3]. It is then necessary to explore more cost-effective alternatives capable of substituting, or minimizing, the use of AC.

Despite many of the alternative methodologies having shown excellent results at laboratory scale for lindane removal, a series of factors must be considered when implementing such procedures in water treatment plants. Apart from the yield and efficacy of the separation process, the overall economic cost of the process must be also considered due to the uneconomical nature of such plants. Thus, it is necessary to explore economically affordable separation processes that do not involve the use of expensive catalysts, large amounts of chemicals or other high-cost operating conditions or components such as supercritical fluids, nanoparticles [34] or magnetic separations [39]. Removing lindane up to the required concentration level by legislation (0.1 ppb), as well as ensuring short residence times in the treatment plant, are also aspects to be considered when evaluating different separation techniques. Membranes have been demonstrated as an alternative to the state-of-the-art separation technologies. Membrane-based operations are well-known for being lower energy intensive processes, and therefore more economically attractive, as compared to most available separation technologies. In addition, membranes are highly flexible and can be tailored to address a specific separation, such as lindane removal [40,41]. A wide range of membrane-based technologies have been developed for water treatment applications, including ultrafiltration (UF), nanofiltration (NF) [42], reverse osmosis (RO) [43] and membrane distillation [44].

NF is a pressure-driven membrane separation capable of removing low molecular weight (in the ca. 200–1000 Da range) molecules and divalent salts from water at moderate transmembrane pressure (between 3 and 20 bar) [45]. Some studies have reported the use of NF and RO membranes to achieve physical separation of lindane, but pollutant removal at acceptable rates have not been achieved [46,47]. In contrast, other studies proved that is possible to remove organic pesticides such as bentazon and atrazin by NF [48,49]. In this work commercial NF99HF and NF99 (supplied by Alfa Laval) and homemade polyamide TFC membranes have been used for the removal of the three primary HCH isomers (α, β and γ), which represent the predominant isomers in technical lindane [2]. Long-term performance of both homemade and commercial membranes for up to 214 h were investigated to study the stability and robustness of the NF separation process. In addition, a preliminary economic perspective has been included to unveil the beneficial effects of implementing NF technology for lindane removal.

2. Experimental

2.1. Materials

The stock solution of lindane was prepared using milliQ water (Gilca Productos Químicos) and n-hexane (Sigma-Aldrich, 98.5 %). A mixture of α-HCH and β-HCH used in our experiments was obtained from the Bailín landfill site. γ-HCH was purchased from Sigma-Aldrich (98.0 %). P84® polyimide (PI) was obtained from HP polymer GmbH. Dimethyl sulfoxide (DMSO, 99.8 %), and isopropanol (IPA, 99.9 %) were purchased from Analisis Vinicos. Polypropylene nonwoven backing material was acquired at Freudenberg Performance Materials. Hexanediamine (HDA), phenylenediamine (MPD, 99 %) and trimesoyl chloride (TMC, 98 %) were bought from Merck. All materials were used as received.

All NF membranes tested consist of a polyamide (PA) layer on top of a porous support, which is known as thin film composite (TFC) membranes, and these include: NF99 and NF99HF membranes commercialized by Alfa Laval, and homemade TFC membranes. The commercial membranes NF99 and NF99HF are polyester supported, while homemade NF membranes used PI (P84®) as a support and the PA layer has been prepared following an optimized interfacial polymerization method [50]. The operational parameters of commercial membranes are shown in the supporting information (Table S1).

2.2. Preparation of polyimide (PI) supports

PI supports were prepared by dissolving P84® in DMSO (24 wt%) with the aid of magnetic stirring at room temperature (RT.). The polymer solution was then cast on a polypropylene nonwoven backing material and the thickness of the membrane was controlled using a doctor blade that removed the excess solution. A casting knife set (Elcometer 4340 automatic film applicator) was used, and the casting speed and the thickness were set at 0.04 $m \cdot s^{-1}$ and 250 μm, respectively. The polymer-solution film on polypropylene was immersed in a coagulation bath containing deionized (DI) water right after casting for 10 min leading to polymer precipitation and formation of the PI membrane. The PI membrane was moved into another DI water bath for 10 min to remove excess of solvent and then washed with IPA (four times, 1 h each) under stirring. The P84® membranes were crosslinked by immersing them in a 120 $g \cdot L^{-1}$ HDA solution in IPA for 16 h under stirring. Afterwards, PI membranes were washed twice (1 h each) with IPA to remove excess HDA and finally immersed in a polyethyleneglycol/IPA solution (3:2 volume ratio) to fill the membrane pores to guarantee their structural stability upon storing.

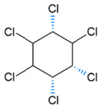
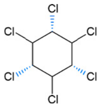
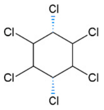
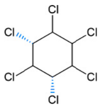
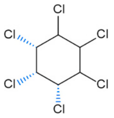
2.3. Preparation of TFC membranes

The PA layer of the homemade TFC membranes was synthesized on the P84® supports by interfacial polymerization (IP) at RT. A 60 cm^2 support was set in a glass filtration funnel and then 20 mL of an aqueous MPD solution (2 % *w/v*) was added and left for 2 min to impregnate the pores of the support. After this time, the excess of the aqueous solution was removed from the membrane surface using dry tissue paper. 20 mL of the TMC solution (0.2 % w/v) was then added and after 1 min the reaction was stopped by addition of 40 mL of fresh n-hexane. Excess of unreacted TMC was removed by washing twice with 10 mL of fresh n-hexane. The obtained membrane was heated up to 80 °C for 30 min to promote fully crosslinking of the PA layer. Finally, TFC membranes were stored in DI water in the fridge and tested within 72 h after preparation.

2.4. Characterization of membranes

Commercial PA membranes NF99 and NF99HF from Alfa Laval, and the homemade prepared PA TFC membranes were characterized using scanning electron microscopy (SEM), water contact angle (WCA). SEM images and energy dispersive X-ray (EDX) analysis were obtained using

Table 1
Physical-chemical properties of the primary HCH isomers.

Properties							
Isomers, [6]	Molecular weight	Density, [7]	Boiling point (°C), [8,9]	Melting point (°C), [10]	Vapor pressure (kPa), [11]	Henry's constant ($Pa \cdot m^3 \cdot mol^{-1}$), [12]	Water solubility ($mg \cdot L^{-1}$), [13]
 α-HCH	290.83	1.6	288	157–160	$6.0 \cdot 10^{-6}$ (25 °C)	0.870	10
 β-HCH	290.83	1.6	288	309–310	$4.8 \cdot 10^{-8}$ (20 °C)	0.120	5
 γ-HCH	290.83	1.6	323	112.5	$5.6 \cdot 10^{-6}$ (20 °C)	0.130	7.3
 δ-HCH	290.83	1.6	288	138–139	$4.7 \cdot 10^{-6}$ (25 °C)	0.073	10
 ε-HCH	290.83	1.59	288	141.5	$3.6 \cdot 10^{-5}$ (25 °C)	n. f.	n. f.

n. f.: not reference found.

a FEI-Inspect F20 microscope operating at 10 kW and at working distance of 10 mm equipped with a EDX detector. The SEM specimens were coated with Palladium (Pd) to endow electron conductivity to the membrane samples. WCA was measured using the sessile drop method by a Krüss Drop Shape Analyzer 10 MK2 at 25 °C. Average WCA values were obtained from measurements of three independent specimens for each membrane.

2.5. *Preparation of HCH solutions*

To prepare an aqueous solution of lindane, 12 mg of high purity lindane (98.0 %) was dispersed in 2 L of water, heated at 60 °C and stirred (1100 rpm) for 2 h. Stirring continued for 24 h at R.T. conditions. The prepared solutions had an estimated concentration of 6 ppm of lindane, higher concentrated solutions cannot be prepared due to the low solubility of the pesticide in water. For the evaluation of the membrane performance, a 600 ppb lindane solution was prepared from the concentrated solution. This concentration was selected since it has been reported to be the highest concentrations of lindane found in Spanish continental waters [51]. The same procedure was followed to prepare the solutions of both α-HCH and β-HCH isomers but using the sample from the Bailín landfill site as the HCH source.

2.6. *Membrane performance*

The membranes were evaluated for removal of lindane (γ-), and α- and β-HCH isomers, using a dead-end filtration module (Sterlitech HP4750) at RT and at 15–20 bar of pressure achieved by supply of N_2. A flow diagram of the NF rig can be seen in Fig. 1. The feed solution (250 mL) of lindane had a concentration of 600 ppb. Alfa Laval membranes were compacted by filtration of water for 2 h at 20 bar, whereas the homemade TFC membranes were compacted for 1 h at 20 bar with water. The rejection (%) and permeance ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$) were calculated by the Eqs. (1) and (2):

$$\text{Permeance} = \frac{V}{A \times t \times \Delta P} \left[\frac{L}{m^2\ h\ bar}\right] \tag{1}$$

$$\text{Rejection}(\%) = \left(1 - \frac{C_{permeate}}{C_{retentate}}\right) \times 100 \tag{2}$$

where V is the volume (L), A is the NF membrane area (m^2), t is the time for volume collection (h), and ΔP is the pressure gradient used (bar). The volume, measured from the mass collected (±0.0001 g), together with the density of the solution ($\rho_{solution} = 1\ kg \cdot L^{-1}$), determines the volume of permeate. The rejection, $C_{permeate}$ is the concentration of lindane in the permeate ($\mu g \cdot mL^{-1}$), while $C_{retentate}$ is the concentration of lindane in the dead-end filtration module ($\mu g \cdot mL^{-1}$).

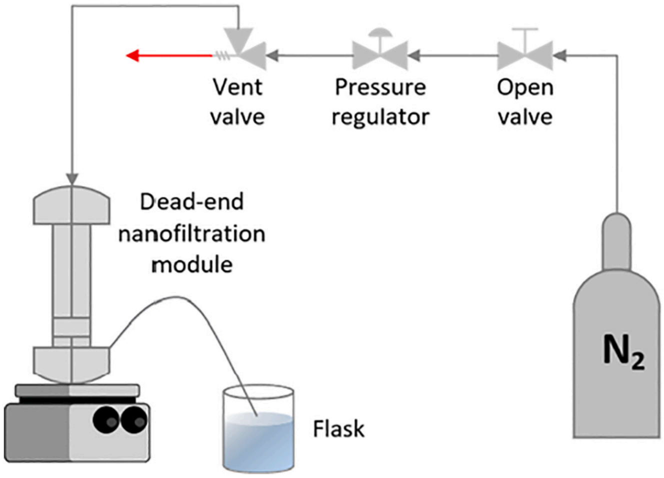


Fig. 1. Diagram of the dead-end NF set-up.

Permeate samples were collected at intervals determined by the total volume of liquid obtained. To increase the concentration of lindane and to ensure an amplified signal in GC–MS analysis, a liquid-liquid double extraction with n-hexane was conducted at R.T. When the sample volume was <50 mL, 5 mL of n-hexane was used in the first extraction. Then, another 5 mL of n-hexane was added to the aqueous portion of the first extraction to ensure complete extraction of lindane. Subsequently, the organic phases from both extractions were combined for analysis. If the volume exceeded 50 mL, the first extraction was carried out with 10 mL of n-hexane to prevent lindane saturation, and the process continued as in the previous case with a second extraction using 5 mL of hexane.

To quantify the lindane concentration a gas chromatograph-mass spectrometer (GC–MS) with a capillary column (TRB-50.2PONA 100 % dimethylpolysiloxane, 50 m × 0.20 mm and 0.50 μm internal width, Shimadzu GCMS-QP2010, Canby, OR, USA) was used. The analysis conditions were OV-210 temperature 180 °C, the injection and detector temperature were set-pointed at 275 and 220 °C, respectively.

Two kinds of experiments were carried out, short-time experiments (Ste) and long-time ones (Lte). Ste. for NF99HF, NF99 and TFC membranes were carried out for 1, 2 and 1 h, respectively, after a membrane compaction of 2 h. Permeance and rejection values presented in this manuscript corresponding to Ste. came from averaging of three individual experiments. Lte lasted for 214 h and only one membrane of each, NF99 and TFC, was tested. In the Lte of the TFC membrane, 40 mL of the permeate sample was used for rejection analysis and several permeance readings were taken every 3 h throughout the day. At certain time (24 h for TFCs and 72 h for NF99), the feed solution was changed to avoid oversaturation of the retentate. The discrepancy in time intervals is due to the higher permeance of TFC membranes in comparison to NF99 membranes. The low permeance of NF99 also implied that only one permeate for rejection analysis was collected per day, whereas in the case of the homemade TFC between 3 and 4 permeate samples were collected per day. In all the experiments, a minimum of 20 mL is collected in order to perform liquid extractions without difficulties.

2.7. *Economical estimation*

With the aim of demonstrating the savings in AC produced by implementing NF to the lindane removal plant, a series of material balances were carried out. The volume of water to be treated was assumed to be 9000 m^3, which is the full capacity of the plant as described on the website of the Government of Aragón [52]. The lindane concentration in the stream was set at the highest value recorded in Spanish hydrological data (600 ppm) [50].

For the calculations, the average rejection in LTe method with TFC membranes (93.5 %) was considered. The following Eq. (3) shows the amount AC saved:

$$AC_{saved} = \frac{AC_{ads} - AC_{TFC}}{AC_{ads}} \cdot 100 \tag{3}$$

where AC_{ads} is the mass of activated carbon (kg) required in the conventional procedure (solely based on AC technology) and AC_{TFC} is the required AC mass (kg) to retain the lindane present in the nanofiltration permeate.

3. Results and discussions

3.1. *Membrane characterization*

Fig. 2 depicts the water contact angle (WCA) values measured for all tested membranes before NF experiments (red column bars), showing that the commercial membranes have much lower values as compared to the homemade TFC membranes. According to the membrane

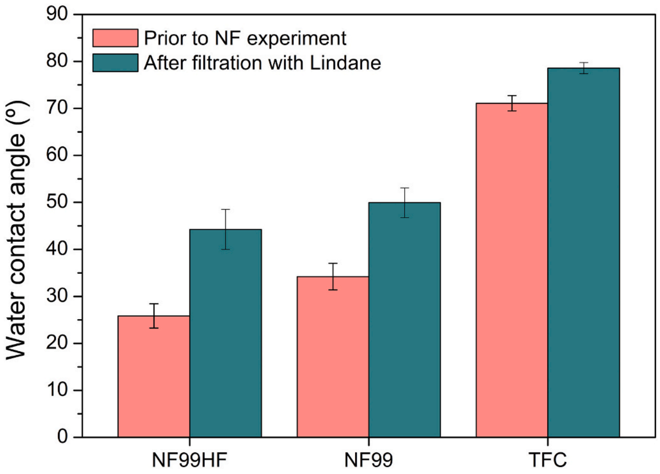


Fig. 2. Water contact angles of commercial NF99HF and NF99, and homemade TFC membranes before (red column bars) and after (green column bars) NF experiments with lindane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

specifications of the commercial materials [50], both NF99HF and NF99 consist of a polyester support and a thin PA layer on top. In turn, homemade membranes are composed of a thin PA layer on top of PI supports. Therefore, it is hypothesized that the different chemistry and roughness of the support layer accounts for the higher hydrophilicity of commercial membranes in comparison with that of the homemade TFC membranes. WCAs were also measured after filtration with lindane (green column bars). All membranes show higher WCAs compared to those before the NF experiments, which suggests the presence of lindane, a highly hydrophobic molecule, on the membrane surface after the NF experiments. The WCA of a control membrane (homemade TFC subjected to pure water filtration) was also measured. The WCA of the control membrane (72.3°) was similar to that observed for homemade TFC before the lindane experiment (71.1°) but significantly lower than the value after filtration with lindane (78.6°). This further suggests that the increase in WCA is due to the presence of lindane on the membrane surface.

The morphology of the membrane surface was characterized using SEM (Fig. 3). Commercial NF99HF and NF99 membranes show a smooth surface with a few earlike wrinkles which are characteristic of polyamide membranes. Homemade TFC membranes possess a rougher surface, as compared to the commercial membranes, having abundant wrinkles and leading to what is typically known as “ridge and valley” morphology. After conducting the NF experiments with lindane, the membrane surface was examined under SEM (Fig. 3d–f). The surface morphology of the commercial membranes did not exhibit any significant difference compared to that observed before the experiments. However, the number of wrinkles and protuberances in homemade TFC membranes were slightly diminished. This could be attributed to the deposition of lindane on the surface. As lindane molecules fill the gaps between the wrinkles, it creates the appearance of a flatter surface when observed with SEM, or at the very least, it reduces the contrast of the imaged features. Another reason for this observation is the compaction the membrane undergoes when subjected to a pressure of 20 bar, which may slightly affect the surface morphology.

Top-view SEM images at lower magnification can be found in the supporting information (Fig. S1). When comparing NF99HF to NF99, the latter shows more distinct features. Homemade membranes exhibit different morphologies before and after lindane treatment, also when observed at lower magnification.

EDX analysis was carried out on the surface of the membranes after NF experiments (Fig. 4). The presence of Cl atoms was not identified during the EDX analysis for any of the membranes. However, as said above, WCA revealed a significant change in the wetting properties of the membrane surface, which is consistent with the impregnation of the membrane with lindane. The absence of Cl in the EDX could be due to limitations of the EDX technique. If lindane is distributed throughout the whole surface and no agglomerates were formed (as suggested by SEM images), the amount of Cl on the surface could be below the detection limit of the technique.

To further investigate the presence of lindane on the membrane surface, after undergoing filtration with lindane, a homemade TFC membrane was soaked in n-hexane to extract lindane physically adhered

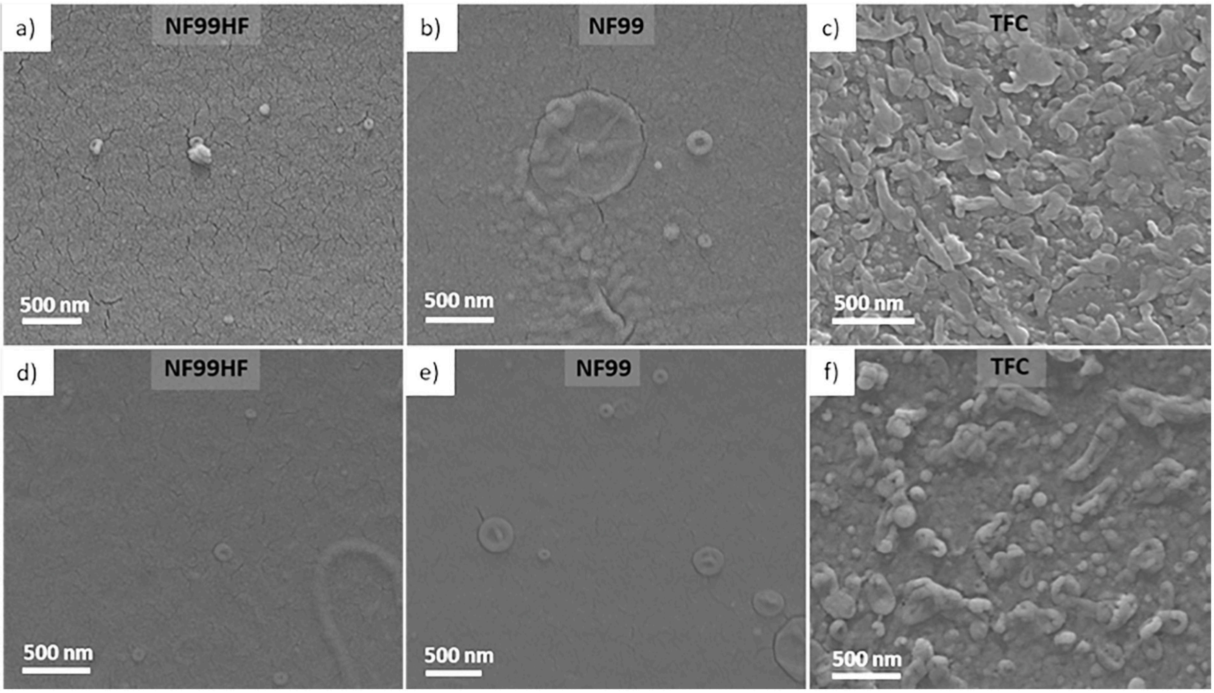


Fig. 3. Top-view SEM images of NF99HF, NF99 and homemade TFC membranes before (a, b, and c) and after (d, e, and f) lindane NF experiments.

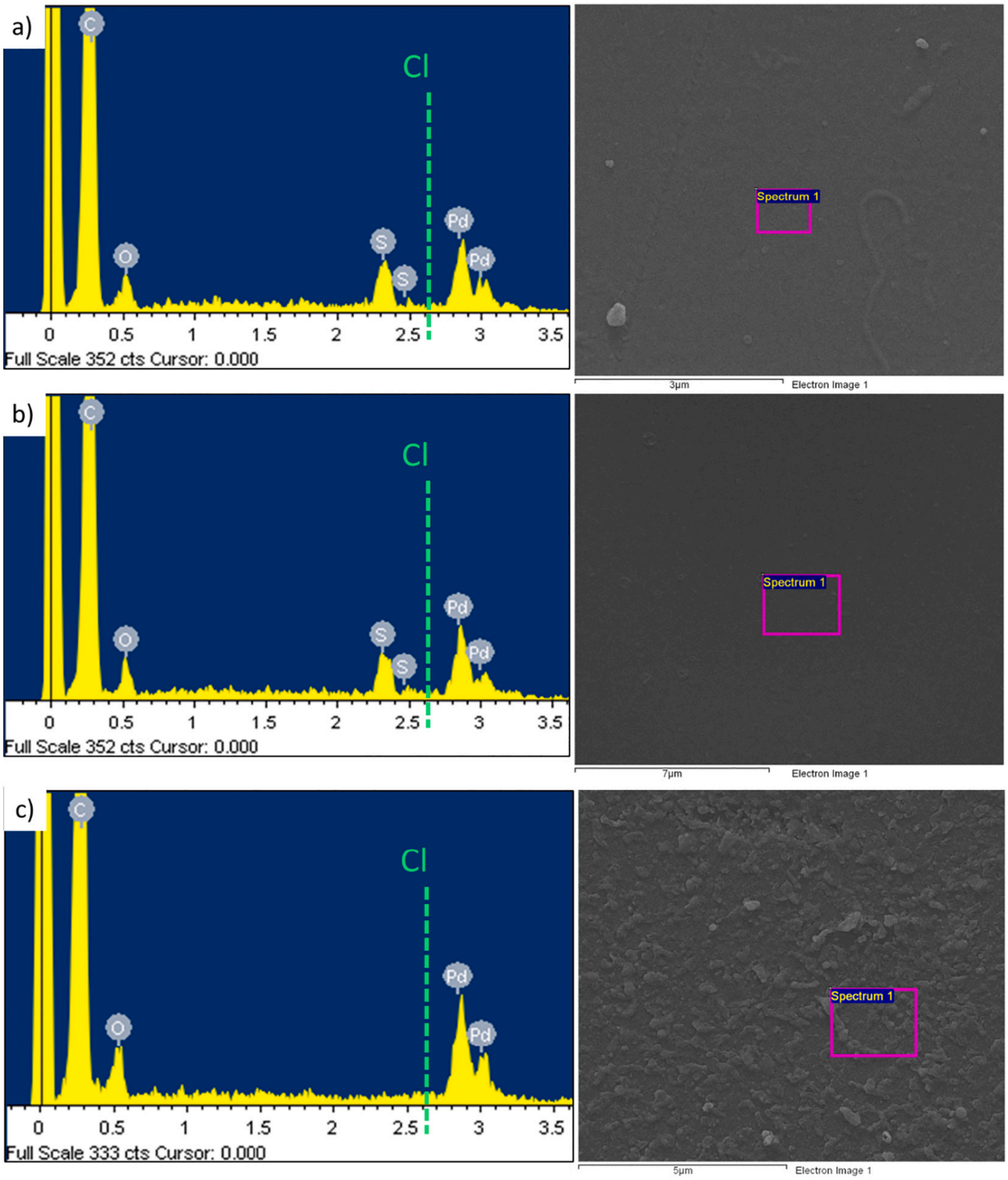


Fig. 4. EDX analysis of NF99HF (a), NF99 (b) and TFC (c) membranes and their corresponding SEM images where the analyzed area is shown by a pink rectangle. The green dashed line corresponds to where the Cl peak is expected. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to the membrane surface. Analysis of the extraction liquid confirmed the presence of lindane. The amount of lindane detected was 23.8 pg (over 19.6 cm^2 of membrane surface). The confirmation of the presence of lindane on the membrane surface is consistent with the abovementioned increase of the WCA.

Cross-sectional SEM images were acquired to study the morphology of both the polymer support and the selective PA film (Fig. 5). The polymer support in commercial NF99HF and NF99 membranes (Fig. 5a and c, respectively) displays a markedly porous structure with a consistent morphology through its thickness. In contrast, the P84® support layer of homemade membranes exhibits a characteristic integrally skinned asymmetric structure (Fig. 5e). This comprises large finger-like macrovoids in the intermediate layer and a thin skin layer on top with pores in the approximate ultrafiltration range. The presence of these elongated cavities in the intermediate layer of the P84® support results in meaningful differences in thickness. The homemade TFC support has a total thickness of ~200 μm, whereas that of the commercial membranes is around 30–50 μm. Higher magnification images were acquired to depict the presence of the thin PA selective layer (Fig. 5b, d, and f). The PA layer in the homemade membranes is notably rougher compared to that of commercial membranes, which agrees with that shown in the top-view SEM images (Fig. 3).

In both commercial and homemade membranes, the pore size of the skin layer of the polymeric support is predicted to fall within the ultrafiltration range. The dense layer atop the support is a continuous polymer without discrete pores. These dense layers are often characterized by their molecular weight cut-off (MWCO). According to Alfa Laval's specifications (Tables S1 and S2 in the supporting information), NF99 membranes exhibit a 99 % rejection rate for $MgSO_4$ salts (120 Da). It is important to note that this rejection rate for charged molecules is largely influenced by other factors, such as diameter of solvated ions, dielectric repulsions and the Donnan effect. Thus, the actual MWCO

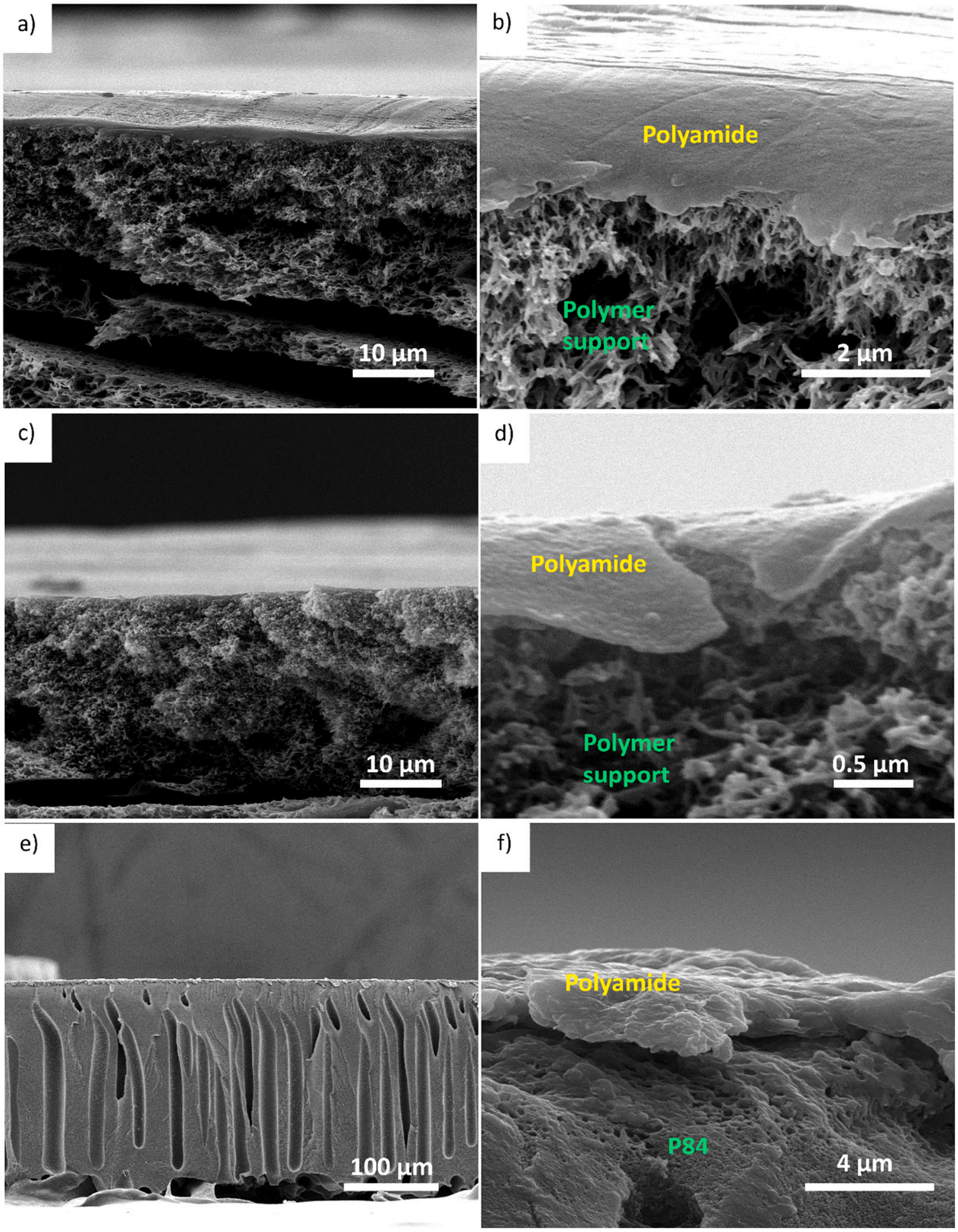


Fig. 5. Cross-sectional SEM images of NF99HF (a and b), NF99 (c and d), and homemade TFC membranes (e and f).

might be higher than the one the salt rejection indicates. The homemade TFC is estimated to have an MWCO ranging between 200 and 400 Da [54].

3.2. Membrane performance

Fig. 6 shows the water permeance and rejection of lindane in Ste. for all membranes tested under NF conditions. NF99HF exhibits the highest water permeance of 15 L·m^{-2}·h^{-1}·bar^{-1}, although the rejection of lindane is compromised and does not exceed 70 %. This is consistent with the specifications of the membrane, where the range of water permeance specified is between 9 and 18 L·m^{-2}·h^{-1} bar^{-1} with a rejection of 72 % in NaCl [55]. NF99 and homemade TFC membranes can reach 91.1 % and 91.3 % lindane rejections, respectively, at expense of lower water permeance as compared to NF99HF. Homemade TFC membrane showed a water permeance of 2.7 L·m^{-2}·h^{-1}·bar^{-1}, which was >20-fold that of NF99, 0.086 L·m^{-2}·h^{-1}·bar^{-1}. Homemade TFC membranes have been synthesized following a previously reported method [50] with the aim of maximizing the permeance while maintaining rejection of organic dyes above 99 %. However, commercial NF99 membranes are designed for a wide range of applications, including rejection of low-molecular weight organic molecules. The rejection performance of homemade TFC membranes is in good agreement with other studies which show that PA TFC membranes are capable of removing low-molecular weight pollutants such as pesticides [49,55]. The water permeance and rejection of the NF99 membranes are

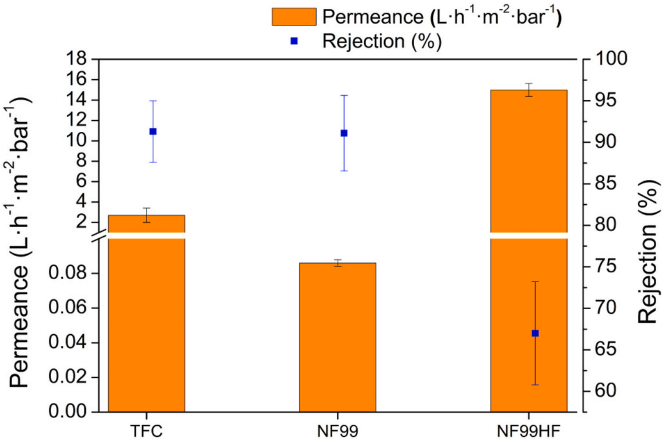


Fig. 6. Permeance and rejection for three membranes of TFC, NF99 and NF99HF using a lindane feed concentration of 600 ppb. The error bars come from the averaging of at least three different experiments carried out in the same conditions and with different membrane samples.

consistent with the 0.6 L·m^{-2}·h^{-1}·bar^{-1} and 99 %, respectively, found in the literature [57].

The two best-performing membranes (NF99 and TFC) were evaluated using a real sample from the Bailín landfill site containing the β-HCH and α-HCH isomers. Their performance was then compared to the results obtained for lindane (Fig. 7). NF99HF was excluded since this membrane showed poor rejection ability of γ-HCH (lindane). When using homemade TFCs, higher rejections for β-HCH (99.8 %) and α-HCH (99.5 %) were achieved as compared to lindane (91.3 %), as seen in Fig. 7. Commercial NF99 membranes used in our study achieved lower rejections of all HCH isomers than the homemade ones. Regarding the behavior of the NF99 membranes when using different HCH isomers solutions (Fig. 7), lindane is retained in a lower proportion (91.1 %) than α-HCH (99.0 %) and β-HCH (95.2 %). Therefore, it can be deduced that the spatial arrangement of the molecule has a significant influence on the water permeance mechanism through the membrane. Table 1 lists all the isomers and their respective spatial arrangements. These distinct arrangements lead to distinct properties, such as variations in water solubility. This difference in solubility suggests that each isomer exhibits unique intermolecular interactions. As a result, these interactions can influence the affinity of each isomer to the membrane surface, leading to different permeation rates. The rejection values show that cooperative effects from HCH isomers do not enhance the permeation of these isomers through the membrane. In fact, the interactions between these molecules might cause them to agglomerate into larger entities that are more likely to be rejected. This could potentially explain the higher rejection rates observed for α-HCH and β-HCH isomers. Interestingly, the rejection has a similar behavior between the different types of membranes for the α- and γ-isomers but differs to that of the β-isomer. Membranes are known to exhibit a trade-off between permeance and selectivity. In our observations with commercial NF99 membranes for the different isomers, the permeance increased when pesticide rejection decreased. In contrast, homemade TFC membranes behaved differently; a drop in rejection did not correspond to an increase in permeance but rather a decrease. The deposition of lindane, which reduces membrane roughness and increases its hydrophobicity, could be the cause of this reduced permeance in the homemade membranes. Moreover, this effect is more pronounced in homemade TFC membranes compared to commercial NF99 membranes, attributed to the much higher initial flux of the former.

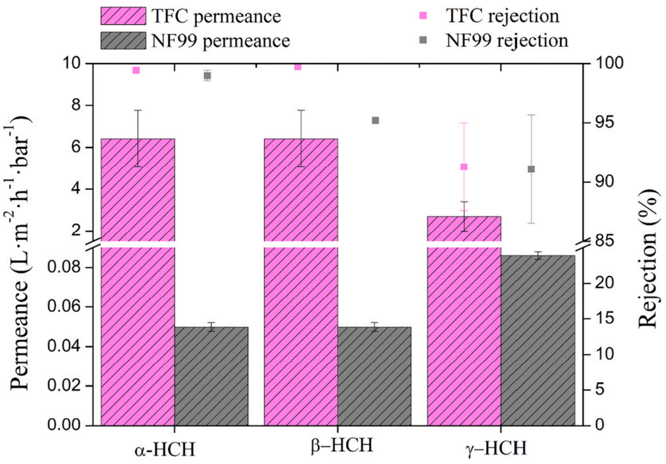


Fig. 7. Water permeance and rejection of NF99 and TFC membranes under filtrations with solutions of α-, β- and γ-HCH isomers in water (concentration of 600 ppb in each isomer solution). The error bars come from the averaging of at least three different experiments carried out in the same conditions and with different membrane samples. Error bars are included for all membranes, but in certain cases, they may be too small to be visually perceptible.

The presence of other substances at the landfill site could potentially affect the performance of the membrane. However, in this case, it does not seem to be an issue. The rejection rates of the homemade TFC membranes for α-HCH and β-HCH isomers exceed 99 %.

3.3. Long-term experiments with NF99 and TFC membranes

Long-term experiments were conducted with TFC and NF99 membranes. The NF99 membrane (Fig. 8a) showed a low initial water permeance (0.036 L·m^{-2}·h^{-1}·bar^{-1}) and became less permeable over time. The initial permeance was maintained at an average of 0.038 L·m^{-2}·h^{-1}·bar^{-1} for about 150 h, but then declined drastically until the membrane permeance was reduced up to 0.004 L·m^{-2}·h^{-1}·bar^{-1}. Lindane rejection is highly unstable over time ranging from 96.9 to 71.5 %. Fig. 8b shows the time-evolution of the permeance for the homemade TFC membrane over 214 h where a similar water permeance decay was observed over time. However, both the initial and final water permeance of the homemade TFC were significantly higher than that observed for commercial NF99. At the very beginning (first 24 h), the permeance rapidly dropped, probably due to compaction effects of the polymer layers. Then, the permeance decay continued for 120 h but seemed to reach a pseudo-stationary state where the permeance decreased very slowly over time, ending in a permeance of 2.5 L·m^{-2}·h^{-1}·bar^{-1}. The drop in permeance over time may be attributed to pore plugging by lindane molecules. Consequently, as fewer pores remain unclogged over time, the membrane permeance decline is slower and eventually reaches a pseudo-stationary state. The rejection of the homemade TFC was also higher (93.5 %) and more stable as compared to that of NF99.

3.4. Economical prospective

From the previous results, it can be estimated that the separation process based on the use of NF membranes can achieve a lindane concentration in the permeate stream of 1.5 ppm when using the best performing membrane, the homemade TFC. This means that NF does not reach the standards established by national e international authorities that consider water safe for human consumption at 0.1 ppb (0.1 μg·L^{-1}) for all HCH isomers, in line with the directive 2000/60/CE of the European parliament. However, due to the high rejection rates achieved, this technology has a strong potential to decrease the cost of the separation process. The combination of NF membranes with AC could be used to reduce the amount of AC needed. Due to the current high cost of AC, the incorporation of a pre-treatment capable of largely reducing the use of AC is expected to lead to significant cost savings in the wastewater treatment plant. The savings in AC are equivalent to the capacity of the membrane to retain lindane (93.5 %). In other words, as explained in

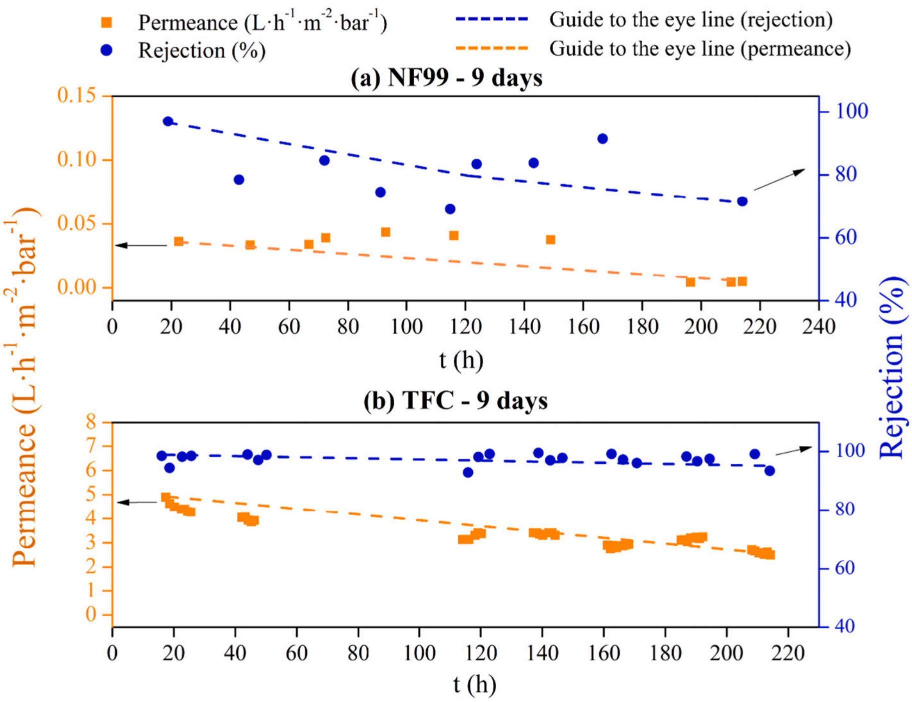


Fig. 8. Long-term experiments with NF99 (a) homemade TFC (b) membranes. Blue circles represent lindane rejection and orange squares correspond to permeance values. Solid lines are used to guide the eye and indicate the trend of rejection (blue) and permeance (orange) data in each experiment. Lindane feed concentration was 600 ppb. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Section 2.7. "Economical estimation", assuming 9000 m^3 of polluted water (full capacity of the Bailín plant [52]) with a concentration of 600 ppb, 5.4 kg of lindane need to be treated (Table 2). Implementing NF leads to a 10-fold reduction in AC usage compared to the conventional approach, as only 0.4 kg would remain in the effluent after the NF filtration (Table 2).

Table 3 provides a comparison of the estimated costs for lindane removal using NF and AC technologies. According to data from a governmental body responsible for the wastewater treatment in the Murcia region of Spain [58], 18 m^3 of AC is required to refill the adsorption zone of the treatment plant. This amount is sufficient to treat an overall volume of 350,000 m^3 over a 6-month period, which is the expected lifetime of the AC in that study. Given the current price of AC [38], this leads to a normalized cost of 0.263 $€\cdot m^{-3}$. It is important to note that the calculated cost is strongly influenced by the price of AC and its effective lifespan. In comparison, NF technology is more cost-efficient, with reported normalized costs ranging from 0.17 to 0.214 $€\cdot m^{-3}$ [59,60]. Moreover, NF is less reliant on fluctuations in the costs of raw materials, and the membrane lifespan typically extends to roughly 5 years [60]. Therefore, implementing NF offers substantial potential for cost savings for both immediate and extended operational periods.

Table 3
Economic analysis comparing AC and NF technology for lindane removal.

Parameters	NF plant	AC-based plant
Amount of AC used (m^3)	–	18[a]
AC cost ($€\cdot ton^{-1}$)	–	2549[b]
Normalized technology cost ($€\cdot m^{-3}$)	0.17–0.214[c,d]	0.263[a]
Functional material lifetime	5 years[d]	6–12 months[a]

[a] For a 6-month operational period, with a total treated volume of 350,000 m^3. Obtained from Pedro et al. [58].

[b] The cost value of AC was obtained from the latest available report [38].

[c] Obtained from Rita et al. [59].

[d] Obtained from Van der Bruggen et al. [60].

4. Conclusions

The results presented in this work evidenced that NF membranes can remove lindane and other HCH isomers from water. Among all the membranes studied, the commercial NF99HF membrane was found to be the most permeable and the least selective. Commercial NF99 and homemade TFC membranes exhibited lindane rejections of 91.1 % and 91.3 %, respectively. NF99 and homemade TFC membranes were also evaluated for the removal of other isomers, such as α-HCH and β-HCH. Homemade TFC membranes showed rejections of 99.5 % and 99.8 % to α- and β-isomers, respectively. Regarding long-term NF performance, NF99 and homemade TFC membranes showed a decrease in water permeance over time. After 214 h of cumulative NF operation, homemade TFC membranes depicted a water permeance of 2.5 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$, which represents a 49 % drop as compared to the fresh membrane. Concerning NF99 commercial membrane, this showed a lower initial water permeance with a higher decrease in water permeance over time, giving rise to a very low water permeance of 0.004 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$ after 214 h. Finally, despite the high rejection obtained, above 90 % in all cases, the concentrations of contaminants that are required to be achieved to meet the actual regulations were not reached at any time. Nevertheless, the implementation of NF is estimated to yield a significant reduction in the overall process cost, as it has the potential to decrease the amount of AC required by a factor of ten.

Table 2
Summary of parameters used for estimating the percentage of AC saved by incorporation of NF technology.

Parameters	With TFC membrane	Only AC adsorbing
Total lindane, kg	5.4	5.4
Membrane retention, kg	5.0	–
AC adsorption, kg	0.4	5.4

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2023.104649.

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