Understanding of phenolic compound retention mechanisms on PES-UF membrane

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Abstract: Ultrafiltration (UF) is investigated as a possible alternative to remove organic compounds from aqueous synthetic solution. This paper presents a comprehensive study towards a better understanding of phenolic compound retention mechanisms during UF processes. Thus, removal of phenol and resorcinol was studied using a polyethersulfone ultrafiltration (PES-UF) membrane. The influence of main operating conditions (feed concentration, transmembrane pressure, and pH) on the retention was evaluated. Membrane–solute interactions were found to play an important role during the process, suggesting the adsorption of the target compounds on the PES-UF membrane. The level of adsorption was consequently evaluated by measuring the quantity of each compound per surface unit of membrane. According to the kinetic study, the pseudo-first order model was found to fit better the experimental values. The adsorption equilibrium data fit the Langmuir model. In addition, the adsorption mechanism was evaluated by the intraparticle diffusion model and appeared to be a complex mechanism.

Key words: Water treatment, ultrafiltration, phenol, resorcinol, adsorption mechanism, equilibrium isotherm

1. Introduction

The industrial effluents discharged by some industries often have a high pollution load hardly biodegradable and highly detrimental for the environment. One of the most significant issues related to water contamination is the multiplicity and the discrepancy of industrial sewage containing organic compounds. These components are extremely toxic and are released in huge quantities by several industries.[1,2] They are included in the priority pollutant list of the US Agency for Environmental Protection and the European Union.[3,4]

Among these constituents, one can mention the phenolic compounds that have alarming and threatening repercussions for the environment since they are present in natural waters and are characterized by their high toxicity at low levels. Phenolic compounds are most frequently ejected into the environment by several processes such as those for pesticides, textiles, and medical industries.[5] In addition to environmental problems, all of the phenolic compounds are poisonous and some are known to be carcinogenic to humans. They can easily be incorporated into the food chain, where they generate significant problems.[6,7] For these reasons and with the standards of increasingly restrictive legislation for the protection of the environment, the search for alternatives to develop highly selective systems for the treatment of these complex aqueous media is required.

There are currently several standard methods for treating effluents containing phenolic compounds, which can be divided into two main categories:[8] destructive methods, namely biological degradation, incineration,

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ozonation[9] in the presence of UV radiation, and electrochemical oxidation;[10] and recovery methods, including liquid–liquid extraction,[11] adsorption[12] and electroadsorption on activated carbon,[13] ion exchange resins,[14] and membrane processes.[15,16] The latter techniques (membrane processes) such as reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF), are considered as methods with positive environmental impact, without phase change and with little energy consumption.

A number of studies[5] have been reported on the application of RO and NF for the removal of phenolic compounds. The results obtained show a low removal yield depending on different parameters such as molecular size, the degree of hydration of the molecules, and electrostatic interactions. It was also found that the rejection is mainly affected by the feed concentration, ionic strength, and hydrophobicity of both the membrane and the target compound.

The UF process is a separation technique that is increasingly considered for retaining organic molecules from industrial effluents. It operates at low pressures and generates high output with low power consumption and easy use. However, several studies dealing with the removal of organic compounds by UF membranes[17] reported a flux decline during the process. This was partially attributed to the adsorption phenomenon at the membrane surface.

In previous work,[18,19] we reported on the use of RO membranes for removing phenolic components. It was essentially found that the poor rejection for these compounds and the use of high pressure constituted the main disadvantages in our system. As a next step, it would be interesting to investigate the removal of phenolic compounds by UF membranes instead of RO, since the former method was developed in wastewater treatment mainly for organic micropollutants' removal.[20] For this sake, effects of operational conditions (feed pressure, concentration, and pH) on the removal of two phenolic compounds, phenol and resorcinol, are studied in detail. In addition, an evaluation of the adsorbed amount as well as kinetic and isotherm models will be fully discussed.

2. Results and discussion

2.1. Retention of phenol and resorcinol from model water

### 2.1.1. Effect of initial concentration and transmembrane pressure on the retention rate

The experiments were carried out separately on phenol and resorcinol solutions with concentrations ranging between 30 and 100 mg L^{-1}, at pH 6.5 and at various transmembrane pressures (Figures 1a and 1b).

Retention of phenol and resorcinol changes with the variation of feed concentration as well as transmembrane pressure.

The obtained results for both compounds revealed that the retention rate decreases while increasing either the transmembrane pressure or the feed concentration. The retention rate for feed concentration of 30 and 100 mg L^{-1} at 1 bar decreases from 61% to 36% for phenol and from 53% to 30% for resorcinol, respectively.

Increase in pressure results in a reduction in the retention rates. For a feed concentration of 100 mg L^{-1}, the retention rate varies from 36% to 28% for phenol and from 30% to 20% for resorcinol at 1 bar and 7 bar, respectively. Other authors[20] found similar results in case of the elimination of pesticides by UF. They explained the decline in retention rates by hydrophobic interactions between the surface of the membrane and the organic components, suggesting the effect of the adsorption of the organic compounds on polyethersulfone membranes. In addition, it was shown that UF membranes are generally hydrophobic.

López-Muñoz et al.[21] reported a partition coefficient of 1.482 and 0.761 for phenol and resorcinol, respectively, indicating their hydrophobic nature. Since both the UF membrane and phenolic compounds
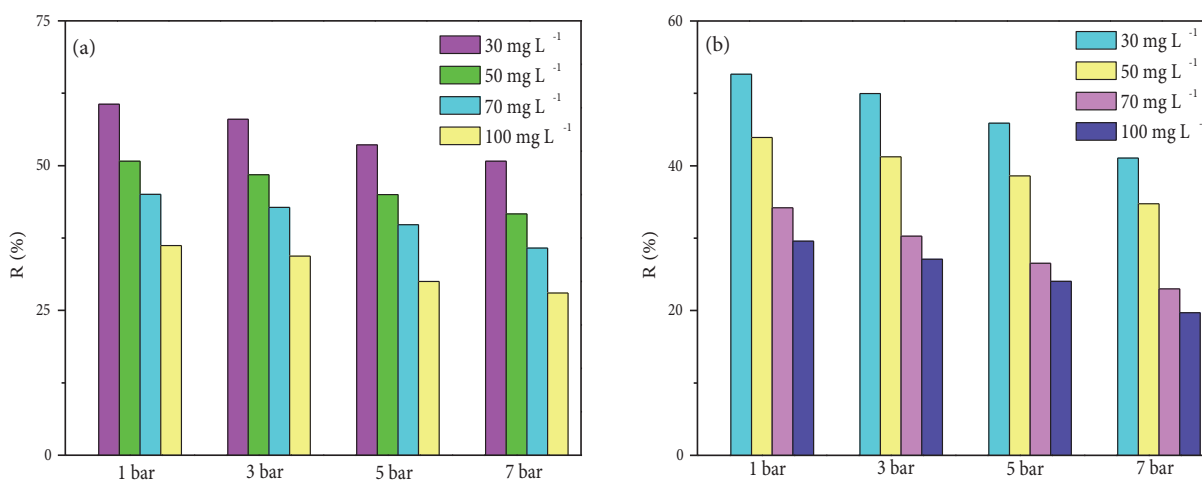
Figure 1. Evolution of retention rate as a function of feed concentration at different transmembrane pressures for (a) phenol and (b) resorcinol.

are hydrophobic, the declines in retention rates with the increase in feed concentration are probably due to hydrophobic interactions and consequently to the adsorption of phenolic components on the surface and in the pores of the membrane.

Indeed, when the concentration of phenolic compounds increases, all the membrane sites will be occupied by the adsorbed phenolic components, and when the partition of phenol between the feed solution and the membrane reaches equilibrium, the contribution of the adsorption decreases and consequently leads to an increase of the phenolic compound concentration in the permeate.[21]

Similarly, the pressure increase is also accompanied by a decrease in the retention rate, which is probably due to the convective transfer mechanism through the UF membrane.[22] In fact, the increase in pressure leads to an increase in the permeate flow and therefore the solute passes easily through the membrane pores. It was also shown that the driving forces increased with increasing pressure, causing the push of the particles through the membrane pores.[23] Thus, the cake formation on the membrane surface would be minimized and the percentage of phenol rejection would be lowered.

Figures 2a and 2b represent the percentage of adsorption of phenol and resorcinol respectively as a function of pressure for different feed concentrations and at pH 6.5.

It is observed that the adsorption percentage decreases with increasing pressure and concentration. The adsorption percentage decreases from 56% to 30% for phenol and from 48% to 25% for resorcinol at 1 bar for a feed concentration ranging from 30 to 100 mg L^{-1}.

The results show that the adsorption percentage for phenol is greater than that of resorcinol. This is probably due to the difference in the hydrophobic nature of the two phenolic compounds. It was shown that the hydrophobic membrane–solute interactions are related to the partition coefficient, which is proportional to the adsorption percentage.[20]

2.1.2. Effect of pH

In order to study the influence of pH in the removal of phenol and resorcinol by UF, stock solutions of 100 mg L^{-1} for each component were prepared. The pH was adjusted using dilute HCl and NaOH solutions. Solutions were filtered using an UF membrane with a constant recovery rate of 50%.
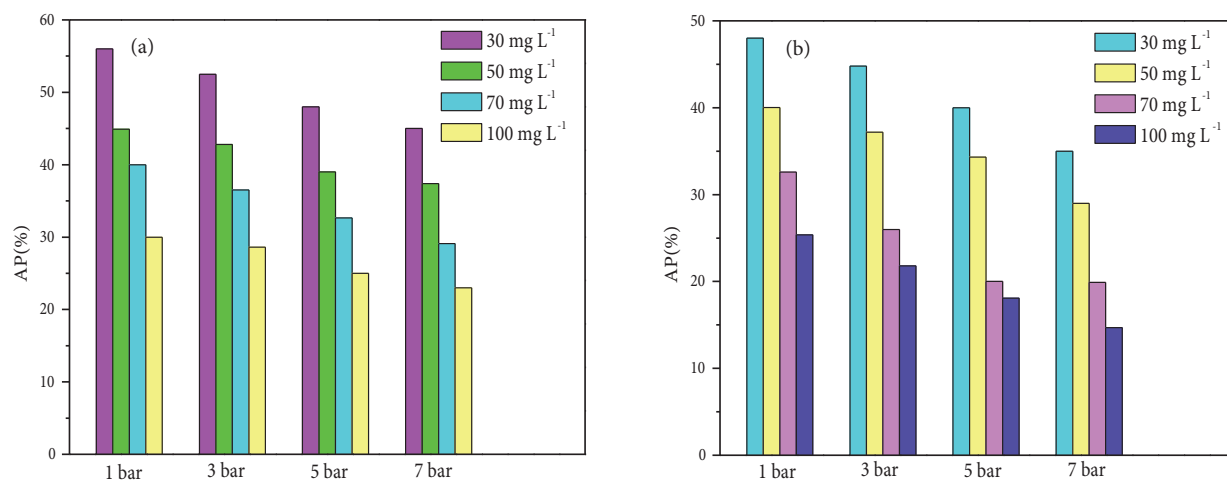
Figure 2. Adsorption percentage as a function of pressure for different concentrations for (a) phenol and (b) resorcinol.

The variation of phenol and resorcinol retention versus transmembrane pressure at various pH values is presented respectively in Figures 3a and 3b.
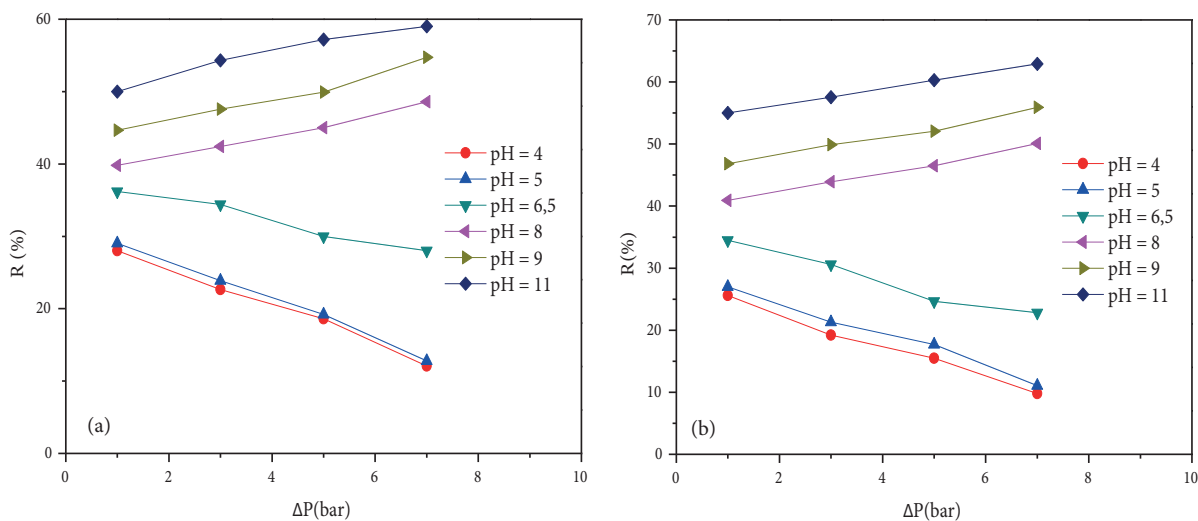
Figure 3. Evolution of retention as a function of pH for (a) phenol and (b) resorcinol.

It was observed that the elimination of phenol and resorcinol depends strongly on the pH of the feed solution. An increase in the pressure causes a decrease in the retention rate at acidic pH values, while an increase is observed for basic pH. This can be attributed to the effect of pH on the membrane charge, which changes from both sides of the isoelectric point (pHi). Indeed, above the pHi, the polyethersulfone active layer of the UF membrane is negatively charged. Its negative charge decreases monotonically as the pH comes closer to the pHi to became positively charged below the pHi. According to the literature, the pHi of the PES-UF membrane was found to be close to 5.5.[24]

Figure 3 shows that, at acidic pH levels, a decrease in the retention occurs with the increase in the pressure. This was previously attributed to hydrophobic membrane–solute interactions. However, the increase in pressure is accompanied by an increase in the retention at basic pH, which can be explained by the pH effect on both the membrane charge and the dissociation equilibrium of each compound.

Since phenol is a weak monoacid (pKa = 9.98) and resorcinol is a weak diacid (pKa$_1$ = 9.45 and pKa$_2$ =11.06), higher pH values cause an increase in the ionic form of each compound and therefore increase the electrostatic repulsions between the surface of the membrane and the anionic species.

At basic pH, the increase in pressure is accompanied by an increase in the level of retention.

Several authors[22] have shown that for pH values greater than 5, the membrane is negatively charged and the origin of these charges is mainly due to preferential adsorption of hydroxide ions on the PES membrane surface.

The variation of adsorption percentage has also been studied as a function of pressure for different pH values and the results are shown in Figure 4.
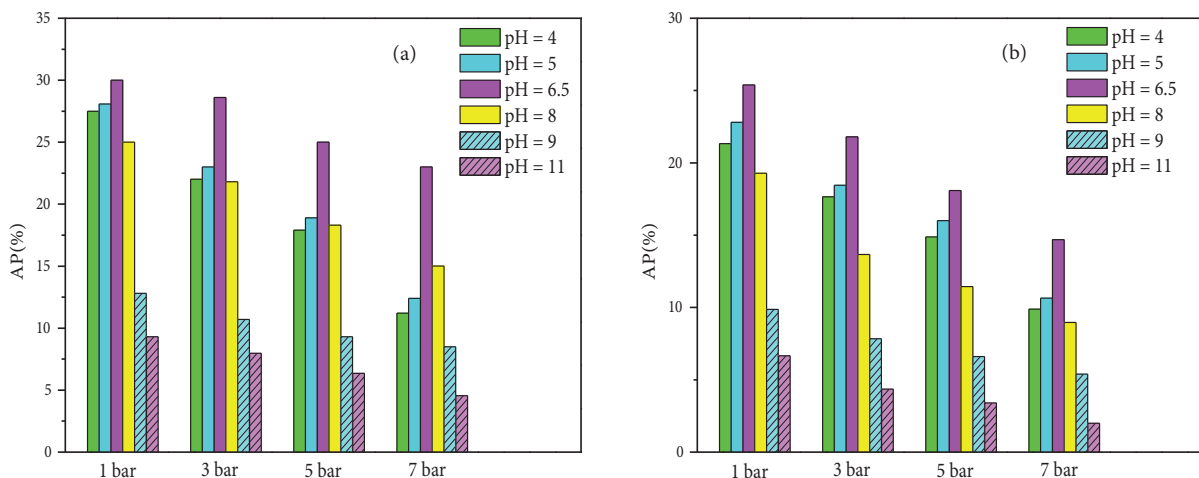
Figure 4. Adsorption percentage for phenol (a) and resorcinol (b) as a function of pressure for different pH values.

Figures 4a and 4b show the significant effect of pH on the adsorption phenomena at the water–membrane interface. For instance, the ability of a PES membrane to adsorb organic compounds essentially depends on the pH at the isoelectric point and the pH of the solution. The pH of the solution determines the charge on the surface of the membrane and the predominant phenolic species in the solution.

The results of this study suggest that the highest percentage of adsorption was found at pH 6.5 for both compounds at different applied pressures. For acidic pH, it was found that the pH increase is accompanied by an increase in adsorption percentages. However, for basic pH, higher pH values cause a reduction of the adsorption percentages of the two compounds. This is probably due to the electrostatic attractions between the negative surface of the membrane and the phenolic compounds in their anionic form,

likely due to the fact that each phenolic compound is in anionic form, leading to electrostatic attraction with the negative surface of the membrane.

2.2. Adsorption of phenol and resorcinol on PES-UF membrane

2.2.1. Equilibrium isotherm

Analysis of isotherm data is important for predicting the adsorption capacity of the membrane, which is one of the main parameters required for the design of an adsorption system.

For this purpose, the two most commonly used isotherm expressions, namely the Langmuir and Freundlich models, were used for representing the equilibrium adsorption data.[25]

The Langmuir adsorption isotherm is valid for monolayer sorption onto a surface with a finite number of identical sites while the Freundlich model is indicative of the surface heterogeneity of the sorbent. The corresponding equilibrium adsorption data are summarized in Table 1.

Table 1. Isotherms fitting parameters of phenol and resorcinol adsorption onto PES-UF membrane.

	Freundlich			Langmuir		
	K_F	1/n	R^2	K_L (L mg^{-1})	Q_m (g m^{-2})	R^2
Phenol	1.205	0.5671	0.9166	0.034	16.835	0.9424
Resorcinol	1.248	0.5872	0.9455	0.033	18.983	0.9642

Based on R^2 values, it was found that the Langmuir model gave a better fit to the experimental results. Similar results were obtained by Arsuaga et al.,[26] whereby the Langmuir model was found to better describe the adsorption performance of a nanofiltration membrane (NF90) in phenol removal. However, it was found that, for the phenol removal, the adsorption capacity of the PES-UF membrane ($Q_m = 16.83$ g m^{-2}) used in this work was much greater than that for the NF90 ($Q_m = 0.64$ g m^{-2}), suggesting that adsorption phenomena are more important in the case of ultrafiltration membranes.

Another dimensionless equilibrium parameter, R_L, giving by Eq. (1), can be used to indicate the type of isotherm.

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{1}$$

R_L values calculated from the present system are presented in Table 2. R_L values were within 0–1, indicating a favorable adsorption process. It also observed that the R_L values decrease with increasing feed concentrations, suggesting that the adsorption is less favorable at higher concentrations.[27]

Table 2. R_L values for phenol and resorcinol at different concentrations.

| C_0 (mg L^{-1})	30	50	70	100
$R_{Lphenol}$	0.4936	0.3690	0.2946	0.2262
$R_{LResorcinol}$	0.5006	0.3755	0.3005	0.2312

2.2.2. Adsorption kinetic studies

The kinetic parameters were investigated in order to predict the adsorption rate for phenol and resorcinol. Figures 5a and 5b show the PES-UF membrane adsorption kinetic curves of both phenol and resorcinol.

It has been observed that the adsorbed amount Q_{ads} increased as a function of time and adsorption equilibrium was reached at 90 min for phenol and at 120 min for resorcinol.

The adsorption mechanism of the PES-UF membrane was investigated using both pseudo-first and pseudo-second order kinetic models.

According to the R^2 values it was found that the kinetic data fit better with the pseudo-first order model for phenol as well as resorcinol. The corresponding results are summarized in Table 3.
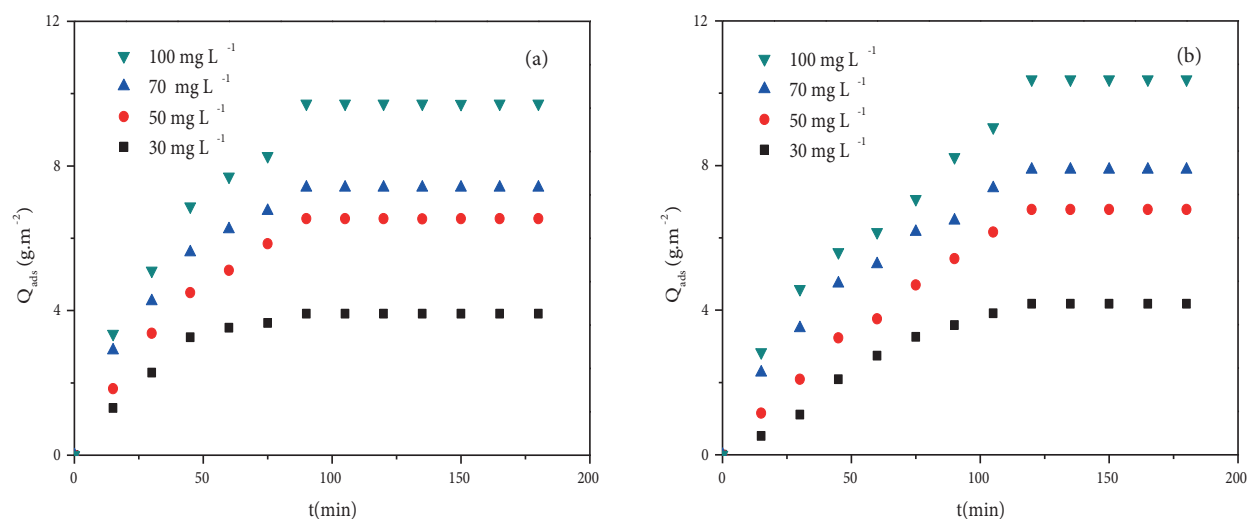
Figure 5. Kinetic adsorption at different concentrations of (a) phenol and (b) resorcinol.

Table 3. Kinetic parameters of phenol and resorcinol adsorption onto PES-UF membrane.

		Pseudo-first order		Pseudo-second order	
		K_1 (min^{-1})	R^2	K_2 (g m^2 min^{-1})	R^2
Phenol	30 mg L^{-1}	0.038	0.9852	2.9290	0.9844
	50 mg L^{-1}	0.029	0.9835	9.169	0.9765
	70 mg L^{-1}	0.032	0.9966	19.432	0.9913
	100 mg L^{-1}	0.026	0.9970	34.211	0.9864
Resorcinol	30 mg L^{-1}	0.025	0.9525	1.1644	0.9046
	50 mg L^{-1}	0.021	0.9305	4.243	0.9063
	70 mg L^{-1}	0.023	0.9442	11.7013	0.9857
	100 mg L^{-1}	0.017	0.9813	22.127	0.9685

2.2.3. Intraparticle diffusion

To better understand the diffusion mechanism that occurred in the PES-UF membrane, the intraparticle diffusion model given by the Weber–Morris equation (Eq. (2)) was used.[28]

$$Q_{ads} = K_p t^{1/2} \tag{2}$$

Here, K_p is the rate constant of the intraparticle diffusion model (mg g^{-1} $min^{-1/2}$).

Figures 6a and 6b respectively plot the amount of phenol and resorcinol adsorbed versus the square root of time.

By the plots of Q_{ads} versus $t^{1/2}$, multilinearities were observed in Figure 6 indicating the complexity of the adsorption process of both phenol and resorcinol.

It seems that three steps occurred during the adsorption process:[29] (i) an initial linear portion generally attributed to the diffusion of the compound through the solution to the external surface of membrane, (ii) an intermediate linear portion corresponding to a gradual adsorption stage where intraparticle diffusion was rate-limiting, and then (iii) a plateau attributed to the final equilibrium stage, for which the intraparticle diffusion started to slow down due to the extremely low component concentration left in the solution.
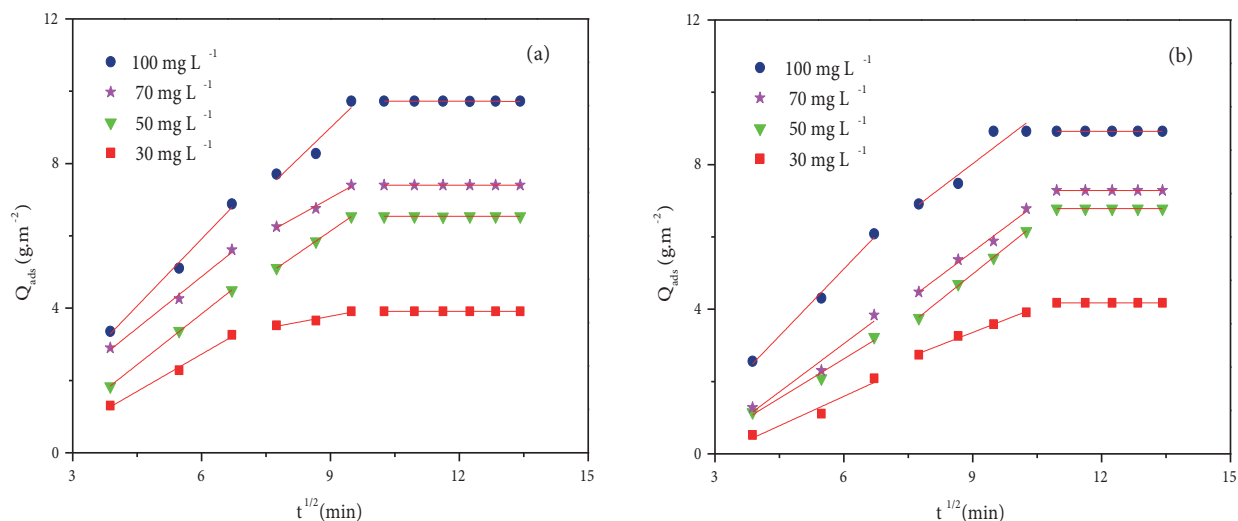
Figure 6. Intraparticle diffusion plots for the adsorption of phenol (a) and resorcinol (b) at various initial concentrations.

Several studies dealing with phenolic compounds' removal onto low-cost adsorbents reported that the phenol adsorption usually follows the first order kinetics and that the adsorption is pore diffusion-controlled.[30−32]

2.2.4. Possible mechanisms of interaction between the PES-UF membrane and phenolic compound

The retention process of organic compounds on an UF membrane is generally affected by three possible mechanisms: (i) pore blockage that occurs due to the full or partial closure of membrane pores by particles, (ii) cake formation that occurs when the particles build up layer by layer on the external surface of the membrane, and (iii) adsorption that occurs when specific interactions between solute particles and the membrane exist.[33]

In the studied system, the selected phenolic compounds (phenol and resorcinol), having molecular weights significantly smaller than the molecular weight cut-off (MWCO) of the PES-UF membrane (20 kDa), cannot block the pore entrance but could penetrate deeper into the pores of the active layer.[34,35]

In addition, and as reported previously, the cake formation in the membrane surface would be minimized, confirming the adsorption of phenolic compounds on the surface of the membrane.

To better elucidate the possible adsorptive mechanism, one can mention the interactions between the membrane surface and the selected compounds. Indeed, the PES-UF membrane has a functionalized polymeric surface that adsorbs organic compounds in aqueous solution because of the existence of a surface force field. The so-called surface force field includes van der Waals force, hydrogen bonding, and hydrophobic interactions.[36]

In addition, the benzene rings of the PES membrane may interact with the benzene ring of the phenolic compounds via $\pi-\pi$ stacking.[37] Consequently, the primary driving forces in the adsorption mechanism of the studied phenolic compounds on the PES-UF membrane may be a combination of multiple hydrogen bonding, hydrophobic interactions, and $\pi-\pi$ stacking.

A detailed surface analysis of the membrane could give more information on the retention mechanism. Indeed, Fourier transform infrared spectroscopy in conjunction with the attenuated total reflectance could be used to analyze the surface chemical composition of the membrane and detect the changes in functional groups of the PES membrane.

2.3. Conclusions

The present study focused on the removal of two phenolic compounds using a commercial polyethersulfone ultrafiltration membrane. Phenol and resorcinol were used as model solute.

The effect of transmembrane pressure, feed concentration, and pH on the adsorption percentage for target compounds was investigated. It was found that retention of both compounds decreases with increasing transmembrane pressure and feed concentration due to the presence of membrane–solute hydrophobic interactions. It was also observed that the retention depends strongly on the pH of the feed solution. An increase in the pressure causes an increase in retention at basic pH. This may be attributed to the electrostatic repulsion between the phenolic compounds and the membrane. Furthermore, adsorption was found to play an important role in the retention mechanism. The adsorption equilibrium data recorded at different concentrations best fit the Langmuir isotherm model, suggesting the formation of a monolayer adsorbate containing a finite number of identical sites on the membrane surface. In addition, two kinetic models were used to describe the adsorption process. It was found that in the adsorption system both phenol and resorcinol can be better represented by the pseudo-first order model. Moreover, the intraparticle diffusion was described by the Weber–Morris equation and appeared to be a complex mechanism.

3. Experimental

The present work was carried out at a pilot plant equipped with commercial spiral-wound UF membrane PW 2540 supplied by Osmonics.

Figure 7 shows the schematic diagram of the experimental set-up used in this study. Permeate and retentate water was recycled to the feed tank (80 L) in order to keep the concentration of the feed solution stable.
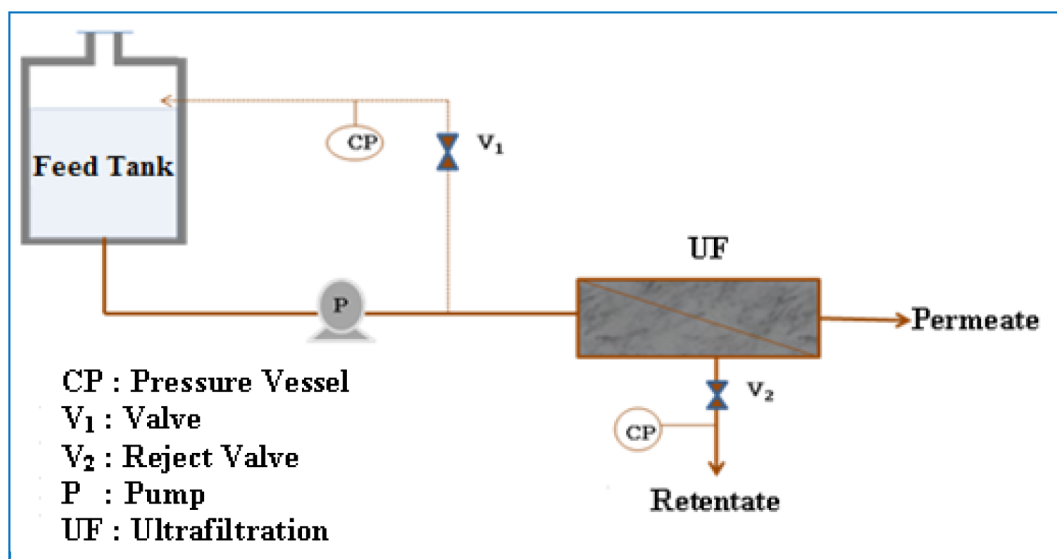

Figure 7. Schematic diagram of test system.

The specifications of the membrane in the pilot scale system are given in Table 4.

Before all experiments, the membranes were cleaned and rinsed with ultrapure water (0.05 μS cm^{-1}) at P = 1 bar for at least 30 min. The permeate flux (J_v) was determined by measuring the volume of permeate collected in a given time interval per unit membrane area.

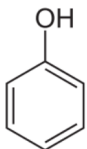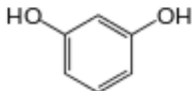**Table 4.** Specifications of UF-PW-2540 membrane.

	UF-PW-2540
Membrane type	Polyethersulfone (PES)
Maximum operating temperature	50 °C
Maximum operating pressure	14 bar
pH tolerance	4–11
Membrane area	4.6 m^2
Pure water permeability	121.02 L h^{-1} m^{-2} bar^{-1}
MWCO	20,000 Da

Pure water permeability (Lp) was measured to characterize the membrane by using the ultrapure water. The solvent flux (Jv) was determined by measuring the permeate flow rate per unit membrane area. The plot of (Jv) versus transmembrane pressure (ΔP) should give a linear shape characterized by a slope known as (Lp). According to Figure 8, the Lp value was found to be 121.02 L h^{-1} m^{-2} bar^{-1}. This value was used as a reference to evaluate the effectiveness of the cleaning procedure. For the same UF membrane, a value of 117.5 L h^{-1} m^{-2} bar^{-1} was obtained by Noeon et al.[38]
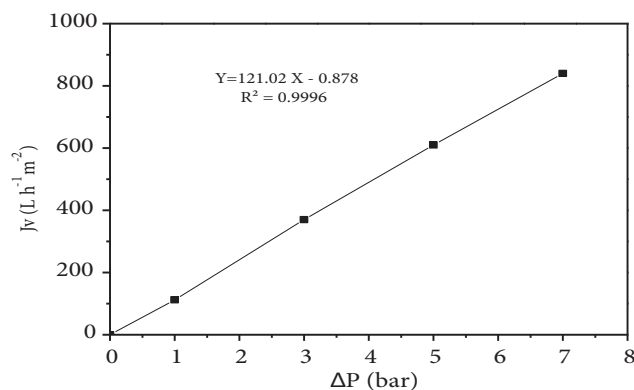
Figure 8. Permeate flux of water as a function of transmembrane pressure.

Among the organic compounds present in natural water, phenol and resorcinol were used in this study as model solutes. The properties of the high purity (99%) phenolic compounds purchased from Sigma-Aldrich are summarized in the Table 5.

Table 5. Properties of the phenolic compounds used in this work.[5]

Model compound	Molecular structure	Chemical formula	Molecular weight	Log K$_{ow}$
Phenol		C_6H_6O	94.1 g mol^{-1}	1.482
Resorcinol		$C_6H_6O_2$	110.1 g mol^{-1}	0.761

All reagents used were of analytical grade. Water was obtained from a Milli-Q water purification system. NaOH (99.8%, Merck) and HCl (37%, Merck) solutions were used for pH adjustments.

To determine the capacity of removing phenolic compounds in the production of treated water, a method based on the detection of a contamination of the permeate is often used. It consists of doping the feed with the compound selected and controlling the phenolic compound concentration on both sides of the membrane. The effectiveness of the method is evaluated by determining the retention rate R.

Observed rejection was calculated by Eq. (3):

$$R = (1 - \frac{C_p}{C_0}) \times 100 \tag{3}$$

Here, C_p (mg L^{-1}) and C_0 (mg L^{-1}) are permeate and feed concentrations, respectively.

The concentration of phenolic compounds was determined using a TOMOS V-1100 spectrophotometer model at 270 nm and 273.1 nm wavelengths for phenol and resorcinol, respectively.

The amount of phenolic compounds adsorbed to the surface of the membrane was measured by determining the adsorbed amount (Q_{ads}, (g m^{-2})) and the adsorption percentage (AP%) following Eqs. (4) and (5):

$$Q_{ads} = \left(\frac{C_0 V_0 - [(C_p V_p) + (C_r V_r)]}{S} \right) \tag{4}$$

$$AP\% = \left(\frac{C_0 V_0 - [(C_p V_p) + (C_r V_r)]}{C_0 V_0} \times 100 \right) \tag{5}$$

Here:

C_0 : Feed phenol concentration (mol L^{-1})
C_p : Permeate phenol concentration (mol L^{-1})
C_r : Retentate phenol concentration (mol L^{-1})
V_0 : Feed volume (L)
V_p : Permeate volume (L)
V_r : Retentate volume (L)
S   : Effective membrane area (m^2)

The Langmuir adsorption isotherm given by Eq. (6):

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{C_e Q_m K_L} \tag{6}$$

Here, Q_m is the maximum amount adsorbed per unit surface of membrane and K_L is the Langmuir constant related to the affinity of the binding sites.

The linear plot of $1/C_e$ versus $1/Q_e$ indicates the applicability of the Langmuir adsorption isotherm.

The Freundlich model is giving by Eq. (7):

$$LogQ_e = LogK_F + \frac{1}{n} LogC_e \tag{7}$$

The pseudo-first order model known also as the Lagergren equation [39] can be written as follows:

$$\log(Q_{ads}\text{-}Q_t) = \log Q_{ads}\text{-}\frac{K_1}{2.303}t \tag{8}$$

Here:

Q_t :   The adsorbed amount at time t ($g\ m^{-2}$);

Q_{ads} :   The adsorbed amount at equilibrium ($g\ m^{-2}$);

K_1 :   The rate constant of pseudo-first order adsorption (min^{-1}).

t   :   Time (min)

The pseudo-first order constant K_1 can be determined from the slope of $\log(Q_{ads}\text{-}Q_t)$ versus t.

The second kinetic model used is the pseudo-second order [40] represented by Eq. (9):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_{ads}^2} + \frac{1}{Q_{ads}}t \tag{9}$$

Here:

K_2 : The pseudo-second order constant ($g\ m^2\ min^{-1}$).

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