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Micellar Enhanced Ultrafiltration of Phenol with Dodecylpyridinium Chloride and Sodium Dodecylbenzene Sulfonate

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Graphical Abstract

Abstract

Micellar enhanced ultrafiltration is a surfactant-based separation process for wastewater treatment. The ultrafiltration of dodecyl pyridinium chloride (DPC) and sodium dodecyl benzene sulfonate (SDBS) solutions was realized with 5 kDa and 15 kDa molecular weight cut-off ceramic membranes. Surfactant concentrations under and over the micellar critical concentration at three different pressures were studied, and their effects on permeate flux and retention are reported. It was found that an increase in pressure operation, in 0.8-1.8 bar range, causes a lower surfactant concentration in permeate by the presence of a polarization layer. These systems were studied for phenol removal. DPC/phenol system (73.5mM/0.53mM) reaches a 61% removal of organic solute. SDBS/phenol system (14.7mM/0.58mM) reaches a 25% removal, both with 5 kDa membrane at 1.8 bar. In the case of the cationic surfactant the micelle's positive charge plays a preponderant role in attracting the phenol molecules, while the SDBS does not present this electrostatic interaction.

Keywords: *Micellar Ultrafiltration, MEUF, Phenol, Dodecyl Benzene Sulfonate, Dodecyl Pyridinium Chloride.*

INTRODUCTION

Phenol is a toxic compound that must be reduced or eliminated from effluents that contain it. Many industrial effluents have phenol, like oil produced waters, waters from oil refineries and plastic production effluents (Al Zarooni & Elshorbagy, 2006; Bodalo *et al.*, 2008; Eiroa *et al.*, 2008). In order to reduce the environmental risk of phenolic compounds in wastewaters, different techniques have been applied and studied, like catalytic oxidation (Santos *et al.*, 2002), Fenton and photo-Fenton reactions (Kavitha & Palanivelu, 2004; Maciel, Sant'Anna Jr & Dezotti, 2004; Pontes *et al.*, 2010), biological treatment (Gonzalez *et al.*, 2001; Annadurai, Juang & Lee, 2002; Margesin, Fonteyne & Redl, 2005; Nuhoglu & Yalcin, 2005), phenol extraction (Jiang *et al.*, 2003), membrane separation with liquid membranes (Correia

& de Carvalho, 2003) and micellar enhanced ultrafiltration (MEUF) (Christian & Scamehorn, 1989; Syamal, De & Bhattacharya, 1997; Jadhav *et al.*, 2001; Sabaté, Pujolà & Llorens, 2002; Zeng *et al.*, 2008).

In MEUF the objective is to use ultrafiltration to separate small solutes, like phenol, using micelles that can be retained by the membrane (Scamehorn & Christian, 1994; Scamehorn & Harwell, 1996). In this case, phenol is trapped by micelles and retained by ultrafiltration membranes. The advantage of this technique is that the membrane used has a pore size much bigger than the compound to separate and high permeate flux is obtained at low pressures. This means energy savings and small area if compared to smaller pore membranes. Moreover, a compound like phenol has relatively high diffusion coefficients and can pass polymeric nanofiltration and reverse osmosis membranes quite well. For MEUF phenol separation several studies have used cationic surfactants that form micelles and trap the phenol (Syamal *et al.*, 1997; Zeng *et al.*, 2008) and fewer have used anionic or nonionic surfactants (Talens-Alesson, Adamczak & Szymanowski, 2001). Other compounds like naphthenic acids (Deriszadeh, Harding & Husein, 2009), benzene and toluene (Sabatini *et al.*, 1998) , different cations such as copper (Li, Liu & Yen, 2006), palladium (Ghezzi *et al.*, 2008), chromium, nickel, magnesium (Yang, Baek & Yang, 2005) and anions such as chromate (Gzara & Dhahbi, 2001) have been separated using MEUF. In addition, this technique has also been studied with other processes in subsurface remediation (Sabatini *et al.*, 1998) applied not only in laboratory but also in field pilot tests with real wastewaters.

Several surfactants have been studied depending on the targeted solutes. For ionic removal the surfactant with opposed charge is the primary option but for organics compounds the solubilization occurs in the hydrophobic heart of the micelle (Schwarze, 2017). The most common surfactant used in phenol removal is by far the cetyl (hexadecyl) pyridinium chloride (Jadhav *et al.*, 2001; Sabaté *et al.*, 2002; Huang *et al.*, 2015), a cationic surfactant. Anionic surfactants like sodium dodecyl sulfate have been reported in simultaneous removal of phenol and Zn^{+2}/Ni^{+2} (Dunn Jr, Scamehorn & Christian, 1989). Apart from the surfactant, the type of membrane, its cut-off, and the operating conditions are important factors in solute removal using MEUF (Schwarze, 2017).

The aim of this work is to describe the ultrafiltration of dodecyl pyridinium chloride (cationic surfactant) and sodium dodecyl benzene sulfonate (anionic surfactant) solutions at different operating conditions using ceramic membranes. Then, the feasibility of phenol removal by MEUF using these surfactants is studied, comparing the flux and the retention with other systems described in the literature. This article is presented in the special issue of Journal of Surfactants and Detergents celebrating the retirement of Professor Jeffrey Harvell and David Sabatini, who definitely contribute to the use of surfactants in complex separation process with their work in the Institute for Applied Surfactant Research in Oklahoma.

MATERIAL AND METHODS

Materials

All the reagents and chemicals were used without any further purification. Sodium dodecyl benzene sulfonate (Aldrich Chemicals, analytical grade), dodecyl pyridinium chloride (Merck, 98 %) and phenol (Riedel de Haen, 98 %) were used as received without further purification. Distilled water was used in all the experiments.

Equipment

The equipment used for the micellar enhanced ultrafiltration was a TIA (Techniques Industrielles Appliquées, France) that had a membrane module with a capacity for one ceramic membrane of 25 cm long and 1 cm diameter. This module has a positive displacement pump, a heat exchanger, two manometers, one feed tank of 3,5 L capacity. The whole assembly is in stainless steel. The flow is controlled by means of an ABB frequency controller and the pressure is controlled by an outlet valve. The filtration unit diagram is shown in figure 1.

Figure 1

Ultrafiltration membranes are generally characterized by the molecular cutoff expressed in Dalton, which is the molecular weight of the globular protein that is 90% separated by the membrane. The membranes used were two ceramic tubular membranes manufactured by TAMI industries (TAMI, Nyons, France) with a cut off of 5 kDa and 15 kDa, an external diameter of 0.01m and length of 0.25m. Other characteristics of the membranes are shown in the Supporting Information.

The critical micelle concentration (CMC) was measured using a surface tensiometer 21 (Fisher Scientific) with a Pt/Ir ring of 5.935 cm diameter. Surface tension profiles are shown in the supplementary information section. The concentration of phenol and dodecyl pyridinium chloride was determined with an HPLC by Agilent Technologies, 1200 series, with a reverse Zorbax Eclipse XDB-C18 column. The mobile phase was methanol/water/0.1 M solution of NaCl in a volumetric proportion of 75:15:10 and 80:10:10, with a flow rate of 0.6 mL/min and 1.3mL/min respectively. pH was measured with a PHM210 Meter Lab by Radiometer Analytical.

Membrane characterization

Membranes were characterized by measuring the distilled water flow before and after the experiments with surfactants and phenol. In this case 3 L of distilled water were introduced in the feed tank, then the pump was adjusted to deliver a flow that gave a lineal velocity of 1.5 m/s and the pressure was adjusted with a valve. Permeate flow was taken until it became constant, at that point, the pressure was changed and the measures repeated. The pressures used for both membranes were 0.8, 1.3 and 1.8 bar. The permeability (k) of the membrane was calculated as the slope of volumetric flux (J_v) vs. transmembrane pressure (P) experimental data:

$$J_v = k\Delta P \qquad \text{Eq. 1}$$

Surfactant ultrafiltration

The experiments were carried out at three different pressures: 0.8, 1.3 and 1.8 bar and at five different concentrations of the two surfactants used. Table 1 shows all the experiments made with both membranes and surfactants.

Table 1

3 L of each solution were poured in the feed tank. The flow was adjusted with the pump control to achieve 1.5 m/s lineal velocity and the pressure was adjusted to the desired value (0.8, 1.3 or 1.8 bar). The permeate

flow was measured every five minutes during 30 minutes and at the same time, samples were taken for surfactant concentration analysis. After the 30 minutes period, the pressure was adjusted to another set point. Once the experiment is finished, the solution is discarded and the equipment was washed with distilled water four times.

Phenol separation

The same procedure as in the surfactant case was used, but in this case the solution was a mixture of surfactant and phenol. Different concentrations were used for the experiments as is shown in table 2.

Table 2

The separation efficiency of surfactant and phenol is quantified by the retention, defined as:

$$R = \left(1 - \frac{C_p}{C_r}\right) \qquad \text{Eq. 2}$$

Where C_p is the permeate concentration and C_r is the feed solution concentration.

Membrane cleaning

Membranes were washed five times with distilled water in the filtration equipment. Since the initial flows were not achieved, further washing was done, taking out the membrane from the ultrafiltration module. Membranes were placed in an ultrasonic bath (Parmer Cleaner, 8845-50 model) with a solution of sodium hydroxide (0.4M) and sodium hypochlorite (1.5mM) for 30 minutes.

RESULTS AND DISCUSSION

Surfactants ultrafiltration

Experiments were made filtrating pure solutions of both surfactants: n-dodecyl pyridinium chloride (CMC = 10.6mM) and sodium dodecyl benzene sulfonate (CMC = 1.6mM), with two ceramic membranes of 5 kDa and 15 kDa cut off. The permeability of both membranes obtained by pure water filtration was 108.1 L/h.m^2.bar for the 5 kDa and 142.8 L/h.m^2.bar for the 15 kDa membrane.

Dodecyl Pyridinium Chloride (DPC)

The permeate flow at two different concentrations of n-dodecyl pyridinium chloride DPC (lower and higher than CMC) through the 15 kDa membrane is shown in figure 2.

Figure 2

When the concentration of surfactant is lower than the CMC there is no permeate flow reduction in time (Figure 2A). Most of surfactant molecules are free to pass through the membrane. As expected, the permeate flow increases as the trans-membrane pressure increases and the values are similar to those of pure water. As the surfactant concentration is very low, no micelles are formed and neither a polarization layer. The permeate flow behavior changes when the same experiment is made with a surfactant concentration over the CMC of the DPC, as shown in figure 2B. In this case, the flow is slightly reduced continuously in time at 1.3 and 1.8 bar and they are much smaller than in figure 2A. Indeed, the deposition of colloids or macromolecules, sometimes in the form of a gel layer, on the membrane surface produces a lower permeate flow. This phenomenon is called concentration polarization and in our case the accumulation of micelles in the vicinity of the membrane generates an additional flow resistance. The experiments show that there was not plateau reached with a constant permeate flow except for the lower pressure experiment. For the 5 kDa membrane the flow behavior, before and after the CMC, was similar to the one observed for the 15 kDa membrane. In this case, the permeate flows were slightly lower than those of pure water and were lower (as expected) than with the 15 kDa membrane. An important parameter in MEUF process is the permeate surfactant concentration. Figure 3A shows the DPC concentration in the permeate for both membranes.

Figure 3

The permeate surfactant concentration below the CMC is slightly lower than the feed concentration (retentate concentration Co). This means that, at these conditions, even if the surfactant is free to transverse the membrane, there is a separation phenomenon. On the other hand, above the CMC, the permeate concentration is always smaller than in the feed, and this is because micelles are retained by the membrane. Indeed, when Co>CMC, the permeate concentration decreases as the trans-membrane pressure increases, probably due to compaction of polarization layer that creates an additional resistance to the flow and increases the separation.

The retention of the surfactant is shown in figure 3B. The 5 kDa membrane has higher retention than the 15 kDa membrane above the CMC, but is similar below it because no micelles are formed and the molecules of surfactant are free to pass through both membranes. Indeed, at these conditions the retention is almost independent of pressure and the separation only can be attributed to adsorption in the membrane. As pointed out in the experimental part, most of ultrafiltration membranes are characterized by the molecular cutoff and not by the exact pore size. As a reference point, Calvo *et al.* indicate that the mean pore size radius for ceramic membranes of the same manufacturer that ours are 5.4-6.5 nm for 50kDa and 5.5-8.0 nm for 150kDa (Calvo *et al.*, 2008). The membranes used in this work (5kDa and 15kDa) must have diameter pore sizes lower than 10.8 nm. DPC micelles have aggregation numbers around 18.6 (Fujio & Ikeda, 1992) and 20 (Ford, Ottewill & Parreira, 1966) and MW of 5.2-5.6kDa at the CMC. The micelle's size is responsible for retention increase after the CMC. However, over the CMC, the influence of the pressure is higher due to the formation of a polarization layer sensitive to this variable: more pressure, more resistance and thus higher retention of the surfactant. When the feed concentration increases, the DPC retention also increases. When using the 5 kDa membrane at 1.8 bar, the highest retention is 0.59 with a flux of 115.5 L/hm^2.

Sodium dodecyl benzene sulfonate (SDBS)

Similar experiments as those carried out with the DPC were made with SDBS, and results above and below the CMC are shown in figure 4.

Figure 4

Figure 4A shows that the flows are all constant in time for different pressures. When the surfactant concentration is higher than CMC (figure 4B) there is a constant permeate flow at higher pressures, and it seems that a polarization layer has already formed and reached a steady state. At 0.8 bar, there is a flow decrease that seems to reach a plateau in 15 minutes.

If compared to pure water flow or those obtained with DPC, these flows are smaller especially for the concentrations lower than CMC, indicating a certain change in the surfactant / membrane interaction, such as probably the formation of a concentration polarization layer. In order to compare both surfactants, table 3 indicates the different dimensionless flows J* (J/J_w) at 1.8 bar for all surfactants concentrations.

Table 3

For a similar C/CMC ratio, the dimensionless flow is lower for SDBS. The viscosity values of aqueous solutions for both surfactants are quite similar (at the same C/CMC ratio): at a shear rate of $200s^{-1}$ the viscosity of the 20.2mM DPC is 1.84 mPa·s and the viscosity of the 3mM SDBS solution is 1.86 m·Pas (Ontiveros, 2010). As the influence of viscosity is negligible, the main difference between them is the interaction with the membrane and its charge. De la Casa *et al.* (de la Casa *et al.*, 2007, 2008) quantify experimentally the point of zero charge of the ceramic membrane Céram Inside 25 from Tami Industries (with a pore size higher than our membrane) and it is 6.9. When the pH is lower than 6.9, the hydroxyl groups at the membrane surface became positively charged. The pH of DPC and SDBS solutions are 5.6 and 6.4 (Ontiveros, 2010), respectively. Even if the difference between their pH is small, our hypothesis is that negative SDBS micelles and monomers are probably electrostatically attracted to the membrane surface. The polarization layer and the adsorption into the pores are more easily reached with SDBS than with DPC, explaining the lower flows and probably the higher retentions obtained with the anionic surfactant.

The behavior of the 5 kDa membrane is similar to the 15 kDa membrane already shown, but with a lower permeate flow because of the smaller pore diameter. The concentration profile of SDBS for both membranes is shown in figure 5A. There is always certain retention of SDBS in both membranes, even at concentration lower than CMC as observed with DCP. The lower permeate concentrations are obtained, as expected, with the 5 kDa membrane. In order to compare permeate and feed concentrations of surfactant, figure 5B shows the retention of SDBS

Figure 5

In general the lowest rejection is below the CMC as the monomers are free to pass the membranes, nevertheless, there is always some retention that can be attributed to the adsorption of surfactants on the membrane (Jönsson & Jönsson, 1991), a modification of the pore structure and to concentration polarization phenomena, that can promote micelle formation in the vicinity of the membrane and surfactant retention. This behavior is shown by the 15 kDa membrane above the CMC, where the retention increases slightly at the highest concentrations; the micelles are not retained by the membrane. On the other hand, a much higher retention is observed by the 5 kDa membrane. The highest value being 75 % at 1.8 bar with a flux of 53.3 L/hm^2. At similar concentration, values of 95% retention with an acetate cellulose membrane have been reported (Yang *et al.*, 2005). Except for the 3.2 mM concentration, at higher values the retention is important and this is due to the formation of micelles. At the CMC, the aggregation number can be as low as N=11 and MW=3.8 kDa (Hait *et al.*, 2003). This low MW easily explains the low retention at C<CMC and in the vicinity of the CMC. At higher concentrations, we expected an increase in the aggregation number that enhances the separation. Gong *et al.* reported a value of 3.2 nm or 3.5 nm (depending on the measuring technique) for 5.7mM SDBS at 40 °C and an aggregation number of N=41 (Gong *et al.*, 2020). Sood and Aggarwal reported a value of 2.9 nm and an aggregation number of 57 at 25 °C. Based on the aggregation number, the MW of the micelle at this condition is 19.8kDa. (Sood & Aggarwal, 2018)

In general, higher retentions can be achieved with the 5 kDa membrane with the SDBS than with DPC. The pressure seems to have less influence over the retention and permeate surfactant concentration than the initial feed surfactant concentration. This does not mean that the best membrane is always the 5 kDa, since this depends on the application.

Phenol Separation by MEUF

Phenol Separation using n-dodecyl pyridinium chloride (DPC)

A 50 ppm phenol solution (0.53 mM) was treated using DPC as surfactant at different molar surfactant/phenol ratios with two ceramic membranes: 5 kDa and 15 kDa. Thakur *et al.* indicate that CMC slightly diminished and micellar growth is accelerated when adding phenol to DPC solutions due to its solubilization into the micelles. For the surfactant without phenol the transition between spherical and cylindrical micelles or CMC$_2$ is quite higher (352 mM at 20°C). When the ratio surfactant : phenol is 1.33, CMC$_2$ diminishes to 289mM but CMC$_1$ is approximately the same (Thakur, Dar & Rather, 2007). Our highest DPC concentration in MEUF experiments is 73.5mM and the surfactant: phenol ratio is 138, so the shape of micelles in the bulk solution must be spherical. The phenol and surfactant retentions are shown in figure 6.

Figure 6

Comparing figures 6A and 6B, the relation between the phenol and DPC retention is evident. When the micelles are retained, the phenol is also retained as expected. The higher phenol and surfactant retention are always obtained with the 5 kDa membrane. The membrane with the smaller pore size retains better the micelles (figure 6B). It is also shown that the 15kDa membrane retention is much lower and at very low surfactant concentration (19.6 mM or a surfactant/phenol relation of 33.4) the phenol retention reduces to 0.02. This extremely low phenol retention is produced when the surfactant concentration is approximately twice the CMC.

The phenol retention passes for the 5 kDa membrane from 0.59 to 0.69 at 1.8 bar when the DPC concentration increased from 41.5mM to 73.6 mM. This is due to the formation of more micelles that can trap phenol and thus increase retention. The retention achieved by the DPC under the studied conditions is lower than those obtained with cetyl pyridinium chloride, and this is certainly due to the lower CMC of the cetyl pyridinium chloride (0.83mM (Moulik *et al.*, 1996) vs. 14.6mM (Ford *et al.*, 1966)) and bigger micelle sizes (the aggregation numbers are 56 (Bhat *et al.*, 2007) and 18-20 (Ford *et al.*, 1966; Fujio & Ikeda, 1992) for CPC and DPC, respectively). Table 4 shows the comparison between studies with cetyl pyridinium chloride and this work.

The molar surfactant/phenol ratio is always much lower with the cetyl pyridinium chloride, compared to this study and this is a consequence of the CMC values of the two surfactants. In the case of the DPC, a higher concentration of monomers is required to have micelles and a higher concentration of free monomers is normally in the solution, and this reduces its effectivity. If the phenol retention of this work is compared with the retention reported by Sabaté *et al.* (only work using also a ceramic membrane), the retention is slightly lower but our permeate flux is much higher, even when the pore size of the membrane used in this work is much smaller (5 kDa vs 50 kDa). Compared with other membranes the retention is lower, except to the work of Huang *et al.*(Huang *et al.*, 2015), however their Surfactant/Phenol ratio is very low. It is important to note that although our retention is lower the permeate flux is much higher, except when compared to the 10 kDa polysulfone membrane.

Phenol Separation with SDBS

In this section, concentrations of surfactant of 12.6 and 15.7 mM (higher than its CMC) were used to retain phenol. The phenol concentration was changed in the range of 50 ppm to 160 ppm. There is no information about the phenol's effect in the micelles of SDBS in literature but Gong et al. study the effect of aniline and 1-hexene in SDBS solutions (Gong *et al.*, 2020). When adding aniline to SDBS solution, the diameter of spherical micelles increases and at some concentration the shape became rod-like. At 40 °C the aniline concentration was changed from 0 to 215mM in solutions with 5.7mM SDBS, and the micelle evolves from spherical to rod like at 54mM of aniline. In our case, phenol concentration was always lower than SDBS and we can make the hypothesis than micelles are spherical in the bulk of the solution. Phenol retention using SDBS is shown in figure 7 with both membranes at different pressures.

Figure 7

The retention observed is very low and this can be due to the negative charge of the surfactant monomers and micelles, that does not attract phenol molecules, that have a cloud of π electrons that makes them partially negative charged and therefore they tend not to approach the anionic micelles. This leaves the phenol free to pass through the membrane without much interference. A slight increase in retention to 0.25 is obtained when the surfactant/phenol relation is of 25.3. In any case, the charge effect seems to be more important than the hydrophobic effect inside the micelle and this determines the behavior of the system. Huang *et al.* (Huang *et al.*, 2015) reported a phenol retention of 0.35 using a polyether sulfone membrane and a surfactant/phenol molar ratio of 4. Compared to the DPC, the SDBS is not a good surfactant for phenol separation. In the case of the DPC the positive charge plays an important role in attracting the phenol molecules, while the SDBS tends to reject them. The use of this anionic surfactant could be considered in the case of simultaneous separation of cations and phenol. In the case of cationic surfactant, the efficiency is higher but there is still a non-negligible quantity of surfactant that is discharged into the water phase. Combining MEUF and activated carbon fiber (ACF) process is one of the proposed solutions in literature in order to remove the remaining surfactant in the permeate.

Conclusions.

Two ceramic membranes (15 kDa and 5 kDa) were studied for the retention of Dodecyl pyridinium chloride and sodium docecyl sulfate solutions. Retention of surfactants increase when feed concentration is higher than CMC as expected. Using the 5 kDa membrane at 1.8 bar, the highest retentions are 0.59 with a flux of 115.5 L/hm^2 for cationic and 0.75 with a flux of 53.3 L/hm^2 for the anionic surfactant, when concentration are 41.5 mM and 31.1 mM, respectively. When C>CMC, the permeate surfactant concentration diminishes when the pressure increases indicating the presence of polarization layer.

DPC and SDBS allow the separation of phenol using micellar enhanced ultrafiltration. The DPC is much better for retaining phenol (R=0.61 when the surfactant/phenol molar ratio is 73.5mM/0.53mM) than the SDBS (R=0.25 when the surfactant/phenol molar ratio is 14.7mM/0.58mM) using the same ceramic membrane (5 kDa). The difference in retention is due mostly to the charge of the surfactant, the DPC micelles have a positive charge that tends to attracts phenol while the SDBS has a negative charge that is less favorable to achieve an effective separation. As SDS, the SDBS could be studied in the separation of phenol when the target separation includes also some undesired cations. In order to diminish the remaining quantity of ionic surfactant in the permeate, mixtures of cationic/ nonionic surfactants with much lower CMC than pure cationic must be studied to optimize the phenol separation.

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Author contribution statement

Antonio Cárdenas and Johnny Bullón conceived and designed the study. Antonio Cárdenas wrote the first draft of the manuscript. Jesús F. Ontiveros carried out the research and analyzed the data. All authors contributed to and approved the final draft of the manuscript.

Ethics Statement

No human or animal subjects were used in this research

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Table 1. Experimental conditions (Surfactant concentration in the top and pressure in the bottom) for surfactant filtration.

Membrane	n-Dodecyl pyridinium chloride			Sodium dodecyl benzenesulfonate		
	1	2	3	1	2	3

5 kDa	A	41.5 mM 0.8bar	41.5 mM 1.3bar	41.5 mM 1.8bar	31.1mM 0.8bar	31.1mM 1.3bar	31.1mM 1.8bar
	B	20.2mM 0.8bar	20.2mM 1.3bar	20.2mM 1.8bar	15.1mM 0.8bar	15.1mM 1.3bar	15.1mM 1.8bar
	C	4.7mM 0.8bar	4.7mM 1.3bar	4.7mM 1.8bar	3.0mM 0.8bar	3.0mM 1.3bar	3.0mM 1.8bar
	D	1.6mM 0.8bar	1.6mM 1.3bar	1.6mM 1.8bar	1.3mM 0.8bar	1.3mM 1.3bar	1.3mM 1.8bar
	E	0.8mM 0.8bar	0.8mM 1.3bar	0.8mM 1.8bar	0.5mM 0.8bar	0.5mM 1.3bar	0.5mM 1.8bar
15 kDa	F	38.3 mM 0.8bar	38.3 mM 1.3bar	38.3 mM 1.8bar	32.1mM 0.8bar	32.1mM 1.3bar	32.1mM 1.8bar
	G	20.2mM 0.8bar	20.2mM 1.3bar	20.2mM 1.8bar	15.8mM 0.8bar	15.8mM 1.3bar	15.8 mM 1.8bar
	H	4.6mM 0.8bar	4.6mM 1.3bar	4.6mM 1.8bar	3.0mM 0.8bar	3.0mM 1.3bar	3.0mM 1.8bar
	I	1.6mM 0.8bar	1.6mM 1.3bar	1.6mM 1.8bar	1.3mM 0.8bar	1.3mM 1.3bar	1.3mM 1.8bar
	J	-------	-------	---------	0.5mM 0.8bar	0.5mM 1.3bar	0.5mM 1.8bar

Table 2. Experimental conditions (surfactant concentration, phenol concentration, surfactant/phenol molar ratio and pressure) for MEUF of phenol.

Membrane		N Dodecyl pyridinium chloride			Sodium dodecyl benzene sulfonate		
		1	2	3	1	2	3
5 kDa	A	-	-	-	14.7 mM Surf. 0.58 mM Phenol (25.3) 0.8bar	14.7 mM Surf. 0.58 mM Phenol (25.3) 1.3bar	14.7 mM Surf. 0.58 mM Phenol (25.3) 1.8bar
	B	57.9 mM Surf. 0.52 mM Phenol (111.3) 0.8bar	57.9 mM Surf. 0.52 mM Phenol (111.3) 1.3bar	57.9 mM Surf. 0.52 mM Phenol (111.3) 1.8bar	13.4 mM Surf. 0.86 mM Phenol (15.6) 0.8bar	13.4 mM Surf. 0.86 mM Phenol (15.6) 0.8bar	13.4 mM Surf. 0.86 mM Phenol (15.6) 0.8bar
	C	73.5 mM Surf. 0.53 mM Phenol (138) 0.8bar	73.5 mM Surf. 0.53 mM Phenol (138) 1.3bar	73.5 mM Surf. 0.53 mM Phenol (138) 1.8bar	11.5 mM Surf. 1.24 mM Phenol (9.3) 0.8bar	11.5 mM Surf. 1.24 mM Phenol (9.3) 1.3bar	11.5 mM Surf. 1.24 mM Phenol (9.3) 1.8bar
15 kDa	E	19.6 mM Surf. 0.59 mM Phenol (33.2) 0.8bar	19.6 mM Surf. 0.59 mM Phenol (33.2) 1.3bar	19.6 mM Surf. 0.59 mM Phenol (33.2) 1.8bar	12.6 mM Surf. 0.67 mM Phenol (18.8) 0.8bar	12.6 mM Surf. 0.67 mM Phenol (18.8) 1.3bar	12.6 mM Surf. 0.67 mM Phenol (18.8) 1.8bar
	F	57.9 mM Surf.	57.9 mM Surf.	57.9 mM Surf.	14.4 mM Surf.	14.4 mM Surf.	14.4 mM Surf.

		0.52 mM Phenol (111.3) 0.8bar	0.52 mM Phenol (111.3) 1.3bar	0.52 mM Phenol (111.3) 1.8bar	0.95 mM Phenol (15.2) 0.8bar	0.95 mM Phenol (15.2) 1.3bar	0.95 mM Phenol (15.2) 1.8bar
	G	73.5 mM Surf. 0.53 mM Phenol (138) 0.8bar	73.5 mM Surf. 0.53 mM Phenol (138) 1.3bar	73.5 mM Surf. 0.53 mM Phenol (138) 1.8bar	14.3 mM Surf. 1.16 mM Phenol (12.3) 0.8bar	14.3 mM Surf. 1.16 mM Phenol (12.3) 1.3bar	14.3 mM Surf. 1.16 mM Phenol (12.3) 1.8bar

Table 3. Dimensionless Flows and concentrations for 15kDa membrane at 1.8 bar

Surfactant	Concentration (mM)	C/CMC ratio	J/J_w ratio
DPC	1.6 mM	0.15	0.94
	4.6 mM	0.43	0.94
	20.2 mM	1.9	0.68
	38.3 mM	3.6	0.54
SDBS	0.5 mM	0.31	0.81
	1.3 mM	0.81	0.71
	3.0 mM	1.8	0.53
	15.8 mM	9.88	0.42

Table 4. Comparison for different retentions with cetyl pyridinium chloride and DPC (this study)

Author	Molar Ratio Surfactant:Phenol	Phenol retention	Conditions	Permeate flow
Syamal et al. (Syamal *et al.*, 1997) (1997)	38 (30mM/0.86mM)	0.86	Cellulose acetate membrane 1 kDa, not stirred batch module, P=2.07 bar	14.68 L/m^{2}h
Jadhav y et al. (Jadhav *et al.*, 2001) (2001)	50 (150mM/3mM)	0.92	Cellulose acetate membrane, 1 kDa, P=3.8 bar	Not reported
Sabaté et al. (Sabaté *et al.*, 2002) (2002)	10 (50mM/5mM)	0.71[1]	Ceramic membrane, 50 kDa, P=1.6 bar	19 L/m^{2}h
Purkait et al. (Purkait, Dasgupta & De, 2005) (2005)	30 (28.6mM/0.96mM)	0.67	Polyamide membrane, 1 kDa, P=3.45 bar	28.8 L/m^{2}h
Zeng et al. (Zeng *et al.*, 2008) (2008)	30 (30mM/1mM)	0.79 [1]	Polisulfone membrane, 10 kDa, P=1.5 bar	150 L/m^{2}h
Huang et al. (Huang *et al.*, 2015) (2015)	4 (4mM/1mM)	0.53	Polyether sulfone membrane, 10kDa, P=1.5 bar	Not reported
This study	138.5(73.5mM/0.53mM)	0.61	Ceramic membrane, 5 kDa, P= 1.8 bar	105.5 L/m^{2}h

Retention calculated from the data of the paper, not given directly by the authors.

Figure 1. Diagram of the filtration unit: 1 pump, 2 tubular filtration module, 3 heat exchanger, 4 feed tank, 5 manometers, 6 valve, 7 pump controller.

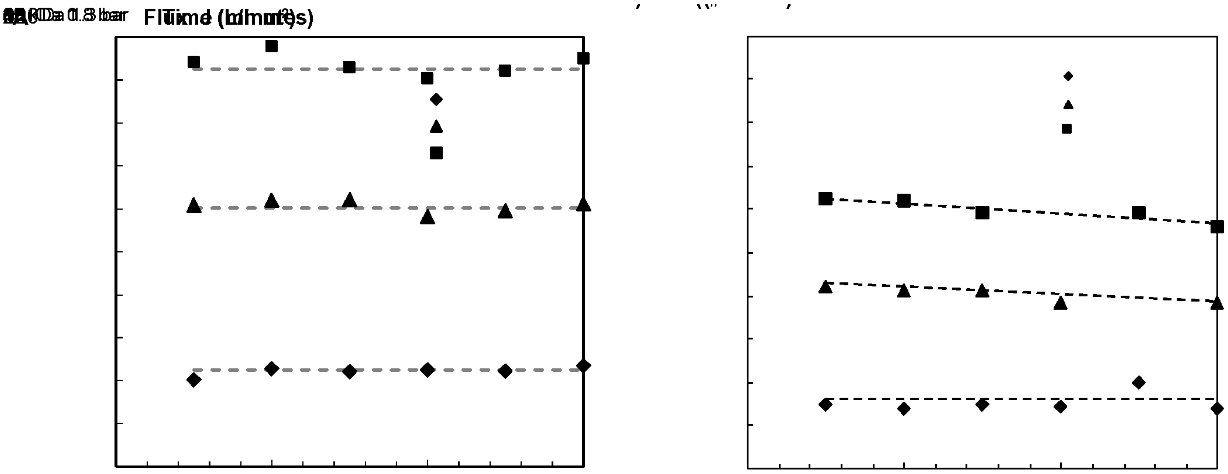

Figure 2. Flow of DPC at different pressures for the 15 kDa membrane. A) Surfactant concentration of 1.6 mM, below the CMC. B) Surfactant concentration of 20.2 mM, over the CMC

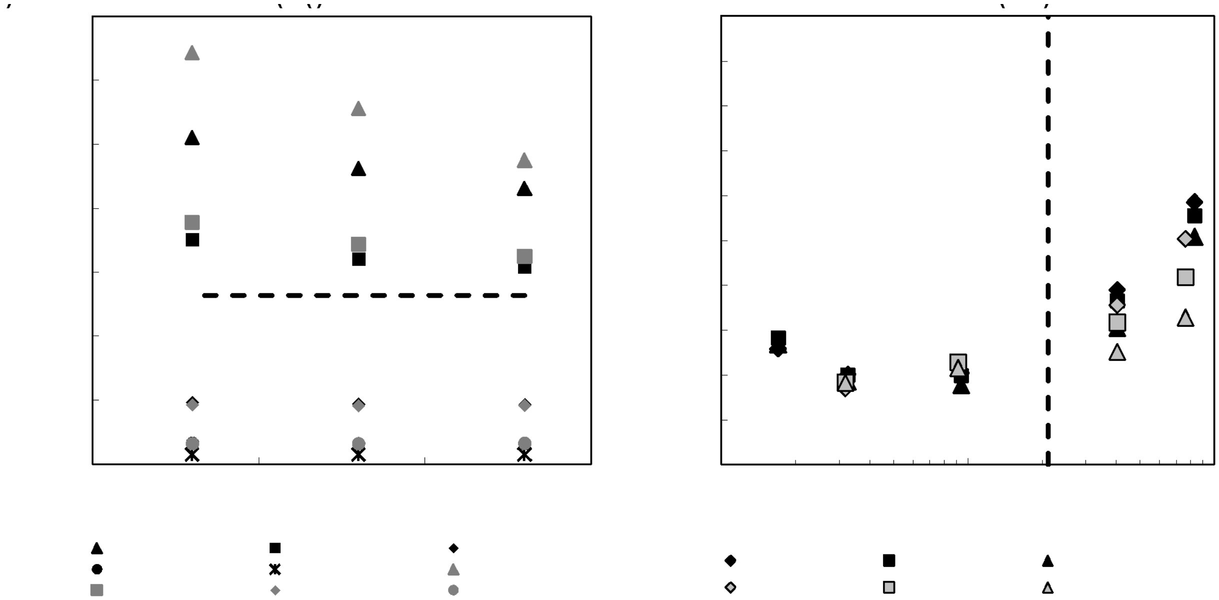

Figure 3. A) Permeate DPC concentration vs. trans-membrane pressure, at different retentate concentrations “Co”. Gray and Black symbols represent 15 kDa membrane and 5 kDa, respectively. B) DPC retention at different DPC retentate concentrations Co. Dotted line represents the CMC

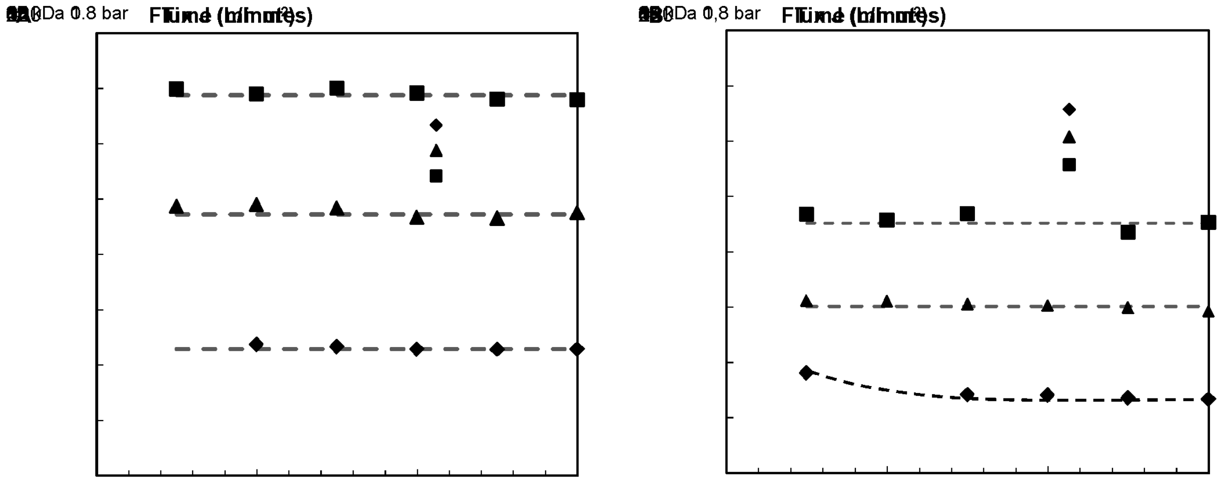

Figure 4. Flow of SDBS at different pressures for the 15 kDa membrane. A) Surfactant concentration of 0.5 mM, below the CMC. B) Surfactant concentration of 3 mM, over the CMC

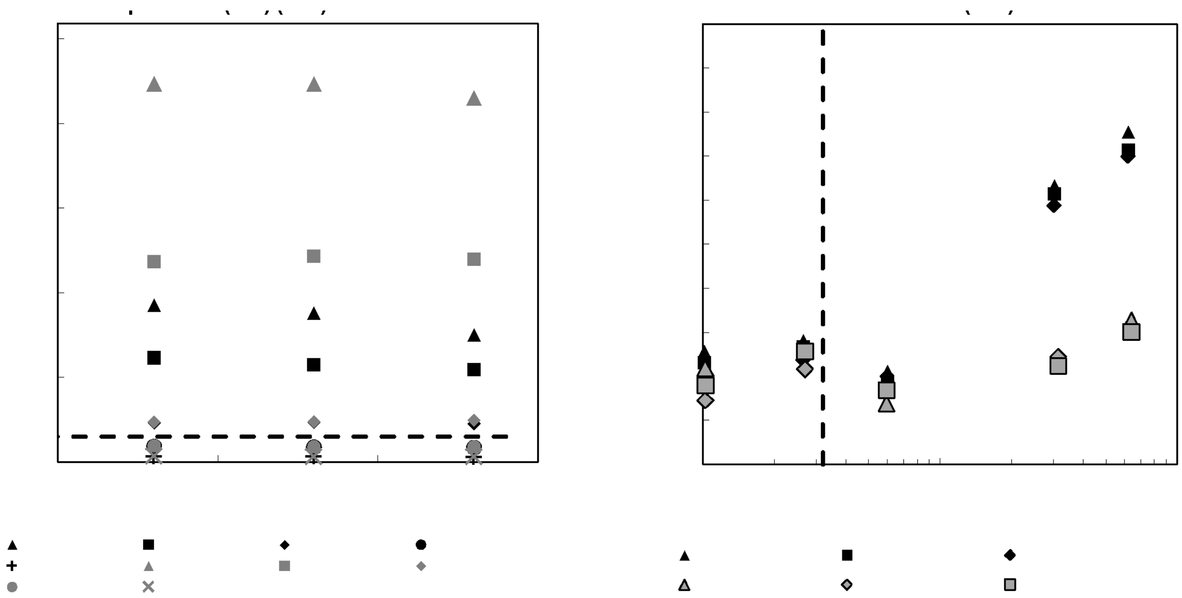

Figure 5. A) Permeate SDBS concentration vs. trans-membrane pressure, at different retentate concentrations “Co”. Gray and Black symbols represent 15 kDa membrane and 5 kDa, respectively. B) Rejection of SDBS in the 5 kDa and 15 kDa membranes. Dotted line represents the CMC

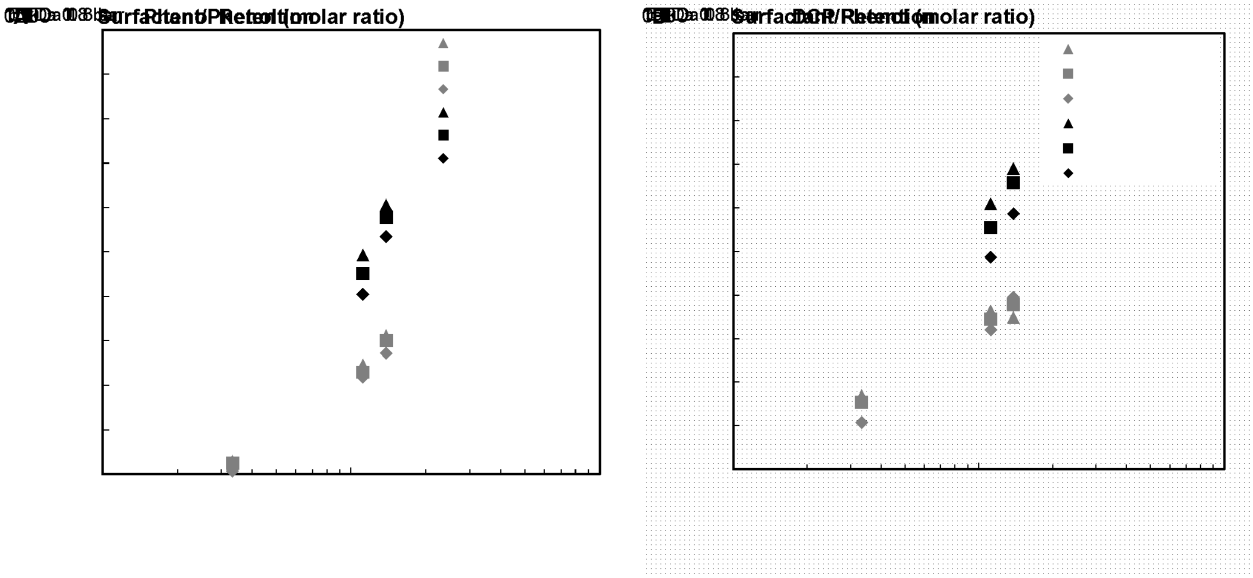

Figure 6. Solutes retention vs. Surfactant/Phenol ratio at different pressures for two ceramic membranes. A) Phenol Retention. B) Surfactant DPC retention.

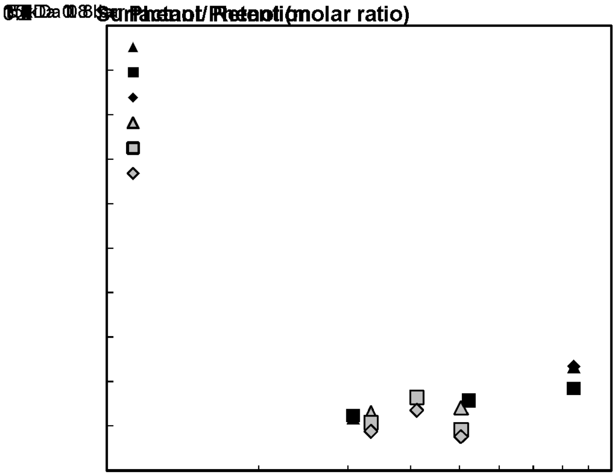

Figure 7. Phenol retention with SDBS at different molar surfactant/phenol ratios for two ceramic membranes.