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SEPARATION OF NATURAL MONOCYCLIC PHENOLICS USING MICELLAR ENHANCED ULTRAFILTRATION WITH A CATIONIC SURFACTANT

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Abstract

Phenolic compounds are known as recalcitrant pollutants in many industrial wastewaters, e.g. olive mill wastewater. An efficient treatment is therefore needed before the discharge of phenol-containing wastewaters into the environment. The possibility of removing some natural occurring phenolics, namely tyrosol, *p*-coumaric acid and vanillic acid, by micellar-enhanced ultrafiltration (MEUF) using a cationic surfactant, cetylpyridinium chloride (CPC), and polyethersulfone membranes of 20 and 50 kDa molecular weight cut-off (MWCO), was investigated. The effect of the surfactant and the solute concentrations on the retention and the permeate fluxes were studied. The elimination and recovery of the surfactant from the retentate stream under its Krafft point was also investigated. The rejection of vanillic acid and *p*-coumaric acid was higher than the rejection of tyrosol. The CPC was found to contribute significantly to the fouling phenomenon causing about 63% of flux reduction when using 2 CMC (1.8 mM) of the CPC. The increase of the feed concentration from 0.3 to 0.9 g/L (phenolic mixture) decreases the rejection rates from the range of 51-54% to 31-33%. The precipitation of CPC under its Krafft temperature allowed the recovery of about 92% of the initial concentration of CPC from retentate streams. The obtained results showed that the MEUF process can be used efficiently for the recovery of phenolic compounds from wastewaters and that the surfactant can be recovered from the retentate stream and reused.

Key words: cationic surfactant, Krafft temperature, micellar-enhanced ultrafiltration, phenol-containing wastewaters, surfactant recovery

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1. Introduction

Wastewaters containing dissolved organics are a common problem in many industries. These organics are often toxic and must be removed or degraded before the water can be discharged into the environment or reused in the process. However, these organics could be of a high added value such as in the case of polyphenols in some agro-industrial wastewater streams, e.g. olive mill wastewater. Phenolic derivatives are a common class of organic pollutants and are (more or less) toxic. Biological treatments are not suitable for these compounds due to their toxicity. Furthermore, common ultrafiltration is ineffective for most of these substances, especially those with low molecular weights which are generally known to be the most toxic. Several physical and chemical processes were proposed for the treatment of phenols, such as photocatalytic degradation (Feng et al., 2014; Karthikeyan and Gopalakrishnan, 2017), electrochemical oxidation (Ma et al., 2014) and supported liquid membrane (Diaconu et al., 2015; Peydayesh et al., 2014) among others. Micellar-enhanced ultrafiltration (MEUF) could be a good alternative for the removal and recovery of low molecular weight phenolics (El Abbassi et al., 2014).

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A survey of literature related to MEUF reveals that a number of studies have been carried out looking at the mechanisms of separation and solubilization of the solute in micelles. MEUF was first introduced by Scamehorn and co-workers in the 1980s for the removal of dissolved organic compounds and metal ions from aqueous streams (Dunn et al., 1985; Scamehom and Harwell, 1989). Few years later, the MEUF process was widely used. However, limited works on MEUF dealt with phenols and their derivatives (Chaudhari and Marathe, 2010; Purkait et al., 2005; Sabaté et al., 2002; Tung et al., 2002), the great majority of works focused on the MEUF separation of metal ions and heavy metals (Fu and Wang, 2011; Huang et al., 2014; Rahmanian et al., 2011; Tanhaei et al., 2014). Sabaté et al. (2002) studied a micellar-enhanced ultrafiltration (MEUF) separation of the phenol using a cationic surfactant, cetylpyridinium chloride (CPC), and two polysulfone membranes of 5 and 50 kDa molecular weight cut-off (MWCO) and two ceramic membranes of 15 and 50 kDa MWCO. They reported that the type of membrane material may affect the optimized parameters in a MEUF process. Purkait et al. (2005) studied the removal of four phenolic derivatives (catechol, meta-nitrophenol, para-nitrophenol and beta-napthol) from their mixtures using the CPC as a surfactant and an organic polyamide membrane with molecular weight cutoff of 1000 Da. This revealed a maximum retention of solute at a concentration ratio of surfactant-to-solute around 110 (Purkait et al., 2005).

To make the MEUF system more economical, it may be necessary to recycle the surfactant molecules that are present in permeate and retentate streams before final disposal. For example, foam fractionation to recover valuable surfactant (SDS) in the permeate of micellar-enhanced ultrafiltration was proposed by Qu et al. (2008). Free CPC surfactants molecules can be recovered from the permeate by a two-step chemical treatment, procedure studied by Purkait et al. (2005).

The works interested in the removal of natural phenolic compounds by MEUF process remain very scarce. In our previous work, we applied the MEUF for the rejection of phenolic compounds from OMW using SDS at pH2 (El-Abbassi et al., 2011). The rejection rate reached 70% when using a surfactant concentration 10 times the CMC. In this study, we investigated the possibility of removing some natural phenolics, namely tyrosol, *p*-coumaric acid and vanillic acid, using a cationic surfactant, cetylpyridinium chloride (CPC), and two polyethersulfone membranes of different. The ultrafiltring behavior of the studied natural phenolics and CPC was also studied for MEUF of individual phenolics and their mixture in view of reaching maximum retention since it has been never studied previously. The concentrations of the studied phenolic compounds in the model solutions were chosen to be more or less equivalent to the concentrations found in some phenolic wastewaters mainly olive mill wastewaters and table olive wastewaters. The effect of the surfactant and the solutes concentrations on the retention and the permeate fluxes were studied. The elimination and recovery of the surfactant from the retentate stream under its Krafft point was also investigated.

2. Experimental

2.1. Chemicals

Cetylpyridinium chloride (CPC), 4-Hydroxy-3-methoxybenzoic acid (vanillic acid, VA), trans-4-Hydroxycinnamic acid (*p*-coumaric acid, CA) and 4-Hydroxyphenylethanol (tyrosol, TY) were supplied by Sigma-Aldrich (Germany). Isopropyl alcohol was purchased from Merck (Germany). Deionized water was produced by a water purification system DI4000 (TKA, Germany).

2.2. Apparatus, membranes and solutions

The ultrafiltration experiments were conducted in a 500 mL capacity stirred filtration cell. Inside the cell, a circular membrane is placed over a base support (Fig.1). The effective membrane area is 50 cm². The permeate is collected from the outlet of the cell at the bottom. The cell is pressurized by nitrogen. Two polyethersulfone membranes (Microdyn-Nadir, Germany) with different molecular weight cut-offs (Table 1) were used.

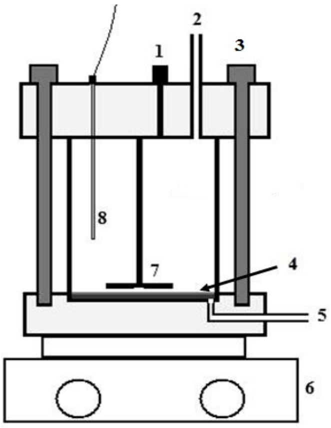


Fig. 1. Scheme of ultrafiltration experimental set-up: 1. Feed inlet, 2. Connection to the nitrogen cylinder, 3. Screw, 4. Membrane, 5. Permeate outlet, 6. Magnetic stirrer, 7. Magnetic bar, 8. Temperature sensor

Feed solution for each experiment was prepared using specific amounts (0.1, 0.2 and 0.3 g, individually or mixed) of the different phenolic compounds (Fig. 2) and the CPC as a surfactant, dissolving them in 1000 mL of deionized water. After removing the feed solution, the membrane surface was externally rinsed twice by filling the cell with isopropanol alcohol / pure water (20:80 *v*/*v*, 200 mL) and leaving it under high stirring rate (800 rpm) for 10 min. The membrane was reused as the water flux reduction after use of membrane did not exceed 5%. Otherwise, the membrane was replaced by new one.

Table 1. Main characteristics of the tested membranes

Membrane	*Membrane material*	*MWCO (kDa)*	*Water flux (L.h^{-1}.m^{-2})*	*pH range*	*Processing temperature (°C)*
UP020	PES	20	600*	0-14	5-95
UH050	PESH	50	1500*	0-14	5-95

**Test conditions: 3 bar, 25°C, stirring rate 200 rpm, membranes were treated by isopropanol alcohol before use, Abbreviations: PES, polyethersulfone; PESH, permanently hydrophilic polyethersulfone; MWCO, molecular weight cut-off*

2.3. Procedures

The experiments were conducted under ambient temperature (25°C ± 2°C), and were carried out in triplicate to confirm a good stability and reproducibility of results. The membranes were left overnight in Isopropyl alcohol solution (50%) and then treated by filtering distilled water under high transmembrane pressure (10 bar). The feed volume was 200 mL and the cell were stirred at 200 rpm using a magnetic stirrer. The CPC surfactant, which is an ammonium salt containing a long aliphatic chain (Fig. 2), has a critical micellar concentration (CMC) equal to 0.91 mM (Zeng et al., 2008). It is not considered to be affected by adding the phenolics. The MEUF experiments of model solutions were carried out under transmembrane pressure at 3 bars. Permeate fluxes were determined continuously using a graduated cylinder connected to the permeate outlet. Before and after each run, deionized water was filtered to determine and compare the permeability of the membrane.

The MEUF experiments were stopped on reaching a volume concentration (*VCF*) factor equal to 2 (Eq. 2):

$$VCF = \frac{V_o}{V_r} \tag{1}$$

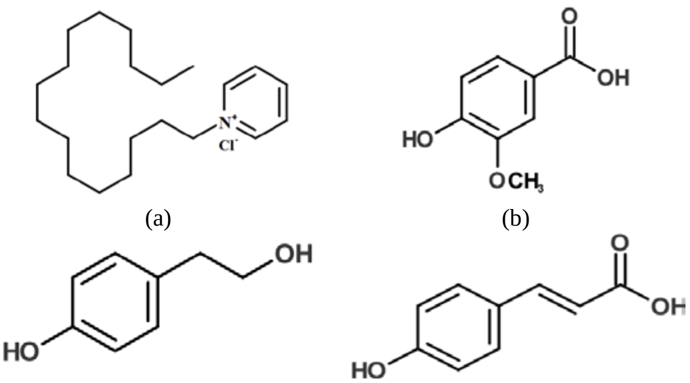
Rejection of phenols was calculated using the coefficient of rejection *R* according to Eq. (2):

$$R = \left(1 - \frac{C_p}{C_r}\right) \times 100 \tag{2}$$

The removal of surfactant from the retentate stream was performed by its precipitation below its Krafft temperature at 9°C and 5°C. 50 mL of the retentate stream in a graduate cylinder was placed in a bath with the temperature adjusted to the desired value. Samples of 100 µl were taken against time at the same height (30 mL) and were diluted adequately prior to analysis.

2.3. Analysis

Feed and permeate concentrations of surfactant and solute were measured by UV-VIS spectrophotometer (550S PERKIN-ELMER). The wavelengths at which maximum absorption occurs and the molar extinction coefficients of different species were obtained from the measurements of the pure components and shown in Table 2. The concentrations of different solutes and surfactant in the mixture were calculated from the absorbance at different wavelengths using the molar extinction coefficients.



(a) (b)

(c) (d)

Fig. 2. Chemical structures of the studied phenolic compounds and surfactant:
(a) Cetylpyridinium chloride; (b) Vanillic acid; (c) Tyrosol; (d) p-Coumaric acid

Table 2. Molar extinction coefficient of surfactant and the studied phenolic compounds at different wave lengths

	Molar Extinction Coefficient, ε (L/mol/cm)			
wave length (nm)	*tyrosol*	*p-coumaric acid*	*vanillic acid*	*CPC*
258	621 ± 18	5 156 ± 69	9 111 ± 105	4 131 ± 49
275	1 554 ± 24	13 209 ± 184	4 309 ± 79	46 ± 3
285	673 ± 16	17 254 ± 175	4 678 ± 57	0
288	234 ± 13	17 053 ± 142	4 819 ± 68	0

3. Results and discussion

3.1. Ultrafiltration of surfactant solution

3.1.1. Hydraulic permeability and resistances

Ultrafiltration experiments were conducted under different transmembrane pressure (2 to 6 bar) using deionized water. The permeate flux was plotted against the operating pressure and fitted with a straight line through the origin (Fig. 3). The slope of this straight line is the membrane permeability (L_p, L.h^{-1}.m^{-2}.MPa^{-1}) and can be calculated using Eq. (3):

$$L_p = \frac{J_w}{\Delta P} \qquad (3)$$

where: J_w is the volumetric permeate flux of deionized water in L.h^{-1}.m^{-2}, and ΔP is the transmembrane pressure in MPa. The membrane hydraulic resistance was calculated from the permeability as given by Eq. (4):

$$R_m = \frac{1}{\mu L_p} \qquad (4)$$

In the case of surfactant solution, the CPC molecules create an additional resistance called the secondary membrane resistance (R_s) which reduces the permeability of the membrane. The R_s (in m^{-1}) was calculated as Eq. (5):

$$R_s = \frac{\Delta P}{\mu J_{CPC}} - R_m \qquad (5)$$

The secondary membrane resistance average was found to be about 219.6 ± 2.06 10^{10} m^{-1} which is considerably higher than the intrinsic membrane resistance, 90.8 ± 0.53 10^{10} m^{-1} (Table 3). The membrane resistance created by CPC molecules contributes to about 71% of the total resistance. When considering the resistance-in-series model (Kim et al., 1998) the total resistance can be written as Eq. (6):

$$R_{tot} = R_{mem} + R_{cp} + R_f = R_{mem} + R_s \qquad (6)$$

where: the total membrane resistance R_{tot} is composed of the resistances caused by: the membrane itself (R_{mem}), concentration polarization (R_{cp}) and fouling (R_f).

The most important parameter for flux decline is fouling resistance (R_f), which contributes to a great part of the secondary resistance. Nevertheless, R_f can be reduced by appropriate methods such as cross-flow ultrafiltration. Talens-Alesson et al. (2001) studied the effect of secondary resistance on membrane permeability when rejecting two synthetic phenolics namely phenol and 4-nitrophenol by mean of MEUF process using different surfactants.

The results showed that some adaptation of the forming gelation layer to gain permeability (Talens-Alesson et al., 2001). It was found also that the presence of salt reduces the membrane resistant in presence of cationic (CTAB) and nonionic (APG) surfactant (Talens-Alesson et al., 2001).

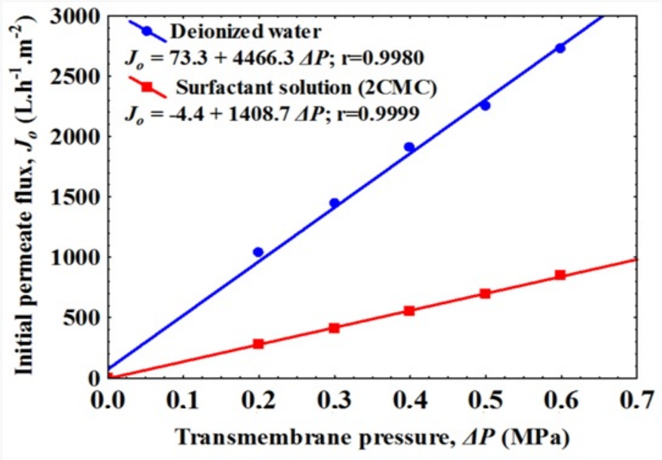


Fig. 3. Initial permeate fluxes of deionized water and CPC solution (1.82 mM) on UH050 membrane against transmembrane pressure

Table 3. Permeate fluxes and resistances of the membrane UH050 under different transmembrane pressure conditions

ΔP (MPa)	J_W (L.h^{-1}.m^{-2})	J_{CPC} (L.h^{-1}.m^{-2})	L_P (L.h^{-1}.m^{-2}.MPa^{-1})	R_{mem} (10^{10} m^{-1})	R_s (10^{10} m^{-1})
0.2	1038 ± 46	276 ± 15	5190 ± 230	83 ± 0.51	230 ± 2.3
0.3	1451 ± 51	413 ± 13	4836 ± 170	89 ± 0.53	224 ± 2.9
0.4	1909 ± 69	556 ± 24	4772 ± 172	91 ± 0.60	220 ± 1.8
0.5	2250 ± 68	699 ± 23	4500 ± 136	96 ± 0.52	213 ± 1.6
0.6	2725 ± 73	847 ± 36	4542 ± 122	95 ± 0.49	211 ± 1.7

The membrane fouling can be divided into reversible and irreversible fouling depending on the attachment strength of solutes to the membrane material. In the case of CPC solution ultrafiltration, a great part of the membrane fouling was reversible because the flux reduction after external cleaning of the membrane did not exceed 5%. Thus, the membrane was reused for several times.

3.1.2. Surfactant retention

It can be observed from the Fig. 4 that the permeate concentration of CPC increases with the progressing MEUF. The increase of CPC concentration in the feed increases the permeate CPC concentration but remains under its CMC in all cases in the studied range of concentrations (2 to 10 CMC) (Fig. 4). This increase in permeate concentration may be due to the concentration polarization over the membrane surface, which promotes the convective transport of CPC molecules through the membrane along with smaller size micelles to the permeate side. The retention of micelles by the membrane results in the concentration polarization and the deposition of micelles on the membrane surface (Zeng et al., 2008). Consequently, the concentration of CPC adjacent to the membrane surface is higher than the bulk concentration of CPC. An aggregation of micelles and rearrangement of molecules may occur resulting in a deformation and change of micelle dimension and shape. This rearrangement can produce more free monomers that pass through the membrane, so the permeate CPC concentration increases. Some authors reported that micelles can pass through the membrane after changing shape due to the fact that membranes have a distribution of pore sizes and micelles have a distribution of sizes (Markels et al., 1994).

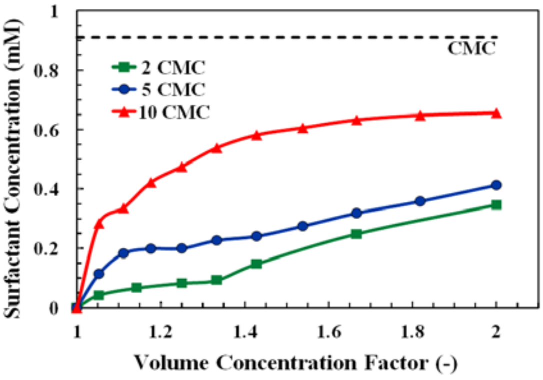


Fig. 4. The CPC concentration in the permeate against the volume concentration factor for ultrafiltration (on UP020 membrane) of surfactant solutions of different feed concentrations

3.2. Micellar-enhanced ultrafiltration using UH050 PES membrane

The effect of surfactant concentration in the feed on the permeate flux and retention of *p*-coumaric acid is shown in Fig. 5. In this case, *p*-coumaric acid concentration was kept constant at 0.1 g/L while different CPC concentrations were tested. The results depicted in Fig. 5 show that the initial fluxes in the permeate decrease considerably with the increase of CPC surfactant. The permeate flux exceeds 1400 ± 45 L.h^{-1}.m^{-2} for the ultrafiltration of the phenolic solution without surfactant but the permeate flux (520 ± 23 L.h^{-1}.m^{-2}) decreases by 63% when using 2 CMC (1.8 mM) of the CPC. Further increases in the surfactant concentration significantly ($p<0.001$) affect the permeate flux, which reaches values as low as 66 ± 3.6 L.h^{-1}.m^{-2} when using CPC concentrations as high as 80 CMC (72 mM). It can also be observed from Fig. 5 that the retention did not exceed 7% for the solution of *p*-coumaric without any surfactant. This retention may result from adsorption on the membrane surface.

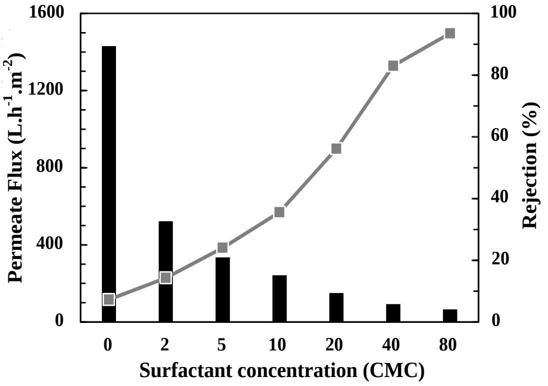


Fig. 5. Permeate initial fluxes (column) and rejection rates (strait line) for the micellar-enhanced ultrafiltration of *p*-coumaric solution (0.1 g/L) against surfactant concentration on the membrane UH050

Susanto et al. (2009) reported that phenolic compounds can be adsorbed on the surface of polyethersulfone membranes. When surfactant is used (2 to 80 CMC) the retentions increased significantly ($p<0.001$) and reached 93% at the highest used surfactant concentration (80 CMC). This clearly indicates that *p*-coumaric acid is solubilized on/in the surfactant micelles, which are subsequently retained by the ultrafiltration membrane. Syamal et al. (1997) studied the solubilization of phenol on CPC micelles and reported that a maximum solute solubilization within micelles was controlled by an optimum surfactant/solute ratio. Theoretical development of the concentration profile within micelle suggested that there is a uniform distribution of the solute throughout the micelle (Syamal et al., 1997).

In aqueous solutions exempt from electrolytes, the reported micelle aggregation number for CPC is 95 at a concentration close to 1 CMC (Attwood and Florence, 1983; Paradies, 1985). This gives the micelle an equivalent molecular weight of about 32 kDa. However, the high *p*-coumaric acid retention values indicate that CPC micelles were rejected by the membrane even if its nominal molecular weight cut-off is 50 kDa. At higher CPC concentrations, aggregation of micelles and/or formation of bigger micelles can occur. As a result, the rejection of CPC micelles is improved and consequently higher retention of *p*-coumaric compound is observed (Fig. 5).

3.3. Micellar-enhanced ultrafiltration of phenolics using the UP020 membrane

3.3.1. Micellar-enhanced ultrafiltration of individual phenolic compounds

Fig. 6 demonstrates that the three phenolic compounds showed similar behavior during ultrafiltration at different CPC concentrations. The increase of the surfactant concentration increased significantly the rejection of the phenolics (p<0.01).

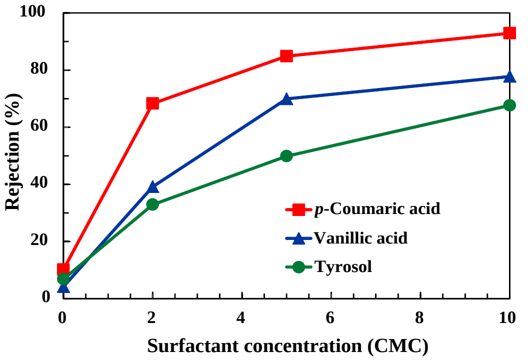


Fig. 6. Rejection rates of single phenolic compounds (0.1 g/L) by MEUF on UP020 membrane under different surfactant concentrations

p-Coumaric acid exhibits the highest rejection coefficient followed by vanillic acid and tyrosol. This finding indicates clearly that the three phenolics are solubilized into the CPC micelles but with different partition coefficients between the water phase and micelles pseudo-phase most likely in respect to the hydrophobicity degree of these phenolics.

The hydrophobicity of a chemical can be estimated by the octanol-water partition coefficient (K_{ow}) expressed in log units. The log K_{ow} of *p*-coumaric acid, vanillic acid and tyrosol are 1.6 (Eastwood, 1999), 1.42 and 0.69 (Noubigh et al., 2009), respectively. From these values we can notice that the rejection coefficients of each phenolic compound are correlated positively to their octanol-water partition coefficients (K_{ow}).

It should also be noted that the retention of solutes decreases during the MEUF processing of phenolic solution. During the ultrafiltration of *p*-coumaric acid solution (0.1 g/L) on UP020 using 10 CMC of CPC, the retention decreased from 92% at the start of the MEUF separation to 78%, which is reached at a VCF of 2 (data not shown), most likely as a result of the increase of phenolics concentration in the retentate with operating time. This increase of the permeate phenolics concentration is related to the increase of the concentration of micelles-unsolubilized phenolics in the feed which pass through the membrane.

The phenolics are involved to the same extent as the surfactant. Thus, when a change is introduced, the equilibrium between phenolics in bulk water and in micelles is reestablished as fast as the equilibrium between monomers and micellar CPC. Sabaté et al. (1999) developed a mathematical model to predict the permeate composition in continuous MEUF of phenol using different surfactants and membranes with different MWCO.

The micelle rejections for different surfactants were correlated with the equivalent molecular weight of the micelles and they are not affected by the addition of phenol (Sabaté et al., 1999). However, the effect of the membrane MWCO on the micelle rejection could not be quantitatively explained because of the lack of knowledge about the concentration polarization layer (Sabaté et al., 1999).

3.3.2. Micellar-enhanced ultrafiltration of a phenolics mixture

A phenolic mixture was filtered through UP020 using different concentrations of the CPC and a final concentration of each phenolic compound of 0.1 g/L. As revealed by the results depicted in Fig.7, rejections for the different compounds are more or less identical. When mixed, these phenolic compounds behave differently to single phenolics. The rejections of tyrosol and vanillic acid were enhanced in the presence of *p*-coumaric acid compared to their rejections when processed separately. A rejection up to 35% of phenolics was observed in absence of any surfactant (Fig.7).

Most likely some adsorptions of phenolic compounds occur on the membrane material. When the surfactant is used, the retentions of phenolics are increased significantly (p<0.01), depending on the surfactant concentration and show similar rejection rates. This clearly evidences that the solutes are somehow linked to the surfactant micelles, which are subsequently retained by the ultrafiltration membrane. Fig.8 shows the MEUF of different total concentrations of phenolic mixture using 2 CMC of the surfactant. The retention decreases from the range of 51-54% to the range of 31-33% with the increase of the total phenolics concentration from 0.3 to 0.9 g/L.

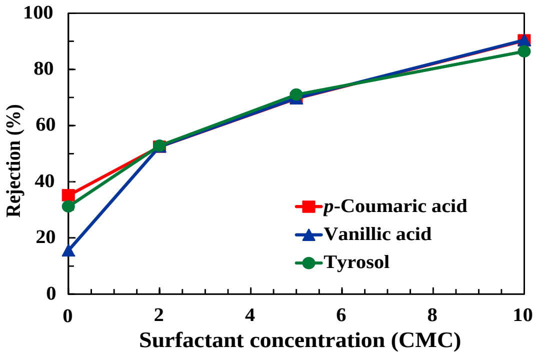


Fig. 7. Rejection rates of phenolic compounds from their mixture (0.1g/L each) by MEUF on UP020 membrane under different surfactant concentrations

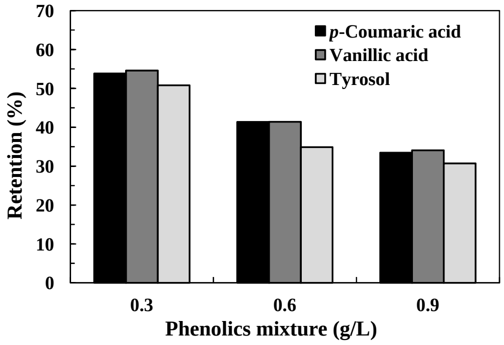


Fig. 8. Rejection of phenolics by MEUF on UP020 membrane using 2 CMC surfactant concentration and different concentrations of a phenolic mixture (the different phenolic compounds concentrations were equivalent, wt. 1:1:1)

The increase of the solute concentration affects negatively the individual rejection of phenolic compounds (Fig. 8). The rejection rates of *p*-coumaric acid and vanillic acid were found to be similar ($p<0.05$) but higher than the rejection of tyrosol ($p<0.05$). This finding indicates clearly that the three phenolics are solubilized into the CPC micelles in respect to their hydrophobicity degree as shown previously (Fig. 6).

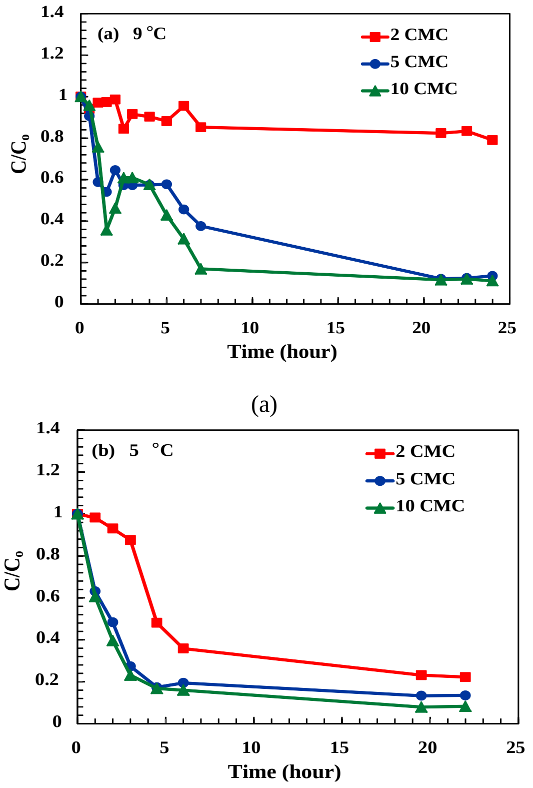
The increase in the concentration of phenolic compounds did not affect the permeate flux which remains more or less unchanged (140 ± 8 $L.h^{-1}.m^{-2}$) (data not shown). This is due to the fact that the major contribution of resistance against the solvent flux comes from the deposited layer of CPC micelles, which are quite large, compared to the phenolics molecules. Since CPC concentration remains constant and the total phenolics concentration varies over a range between 0.3 and 0.9 g/L, the permeate flux remains almost unchanged. Previous study (El Abbassi et al., 2014) showed also that the permeate fluxes remain almost unchanged when increasing the phenolics concentration within the range of 0.1-0.9 g/L. However, the increase of the surfactant concentration caused a drastic decrease in the fluxes.

3.4. Surfactant recovery

An important characteristic feature of ionic surfactants is their tendency to precipitate from aqueous solutions as solid hydrates. The temperature at which the solubility of the surfactant falls below its critical micellar concentration is termed its Krafft temperature. The Krafft temperature of CPC is about 10°C (Sasaki, 2009). At 9°C, the CPC molecules of the retentate streams of the phenolics MEUF using 5 and 10 CMC precipitate to about 50% of the initial concentration within two hours of low temperature treatment (Fig. 9a).

The CPC removal reached about 90% after 20 hours. However, the CPC concentration in the retentate stream of MEUF with 2 CMC was still more or less unchanged (Fig.9a). Furthermore, the surfactant concentration decreased in the three retentate streams at 5°C (Fig. 9b). The crystal formation was rapid within the first hours and the removal exceeded 80% after 6 hours.

The treatment for longer durations (up to 24 hours) did not significantly enhance the removal rate ($p>0.05$). This removal is about 80%, 90% and 95% for the 2 CMC, 5 CMC and 10 CMC retentate streams, respectively. The precipitate can easily be recovered by filtration at low temperature or centrifugation. After filtration on a 2 µm pore size cellulose membrane, the solid phase was dried at 105°C for 6 hours and the residue was weighted. The recovered surfactant was up to 92% of the initial concentration of CPC in the retentate stream.



(a)

(b)

Fig. 9. Removal of surfactant from different retentate streams by precipitation at: 9°C (a), 5°C (b)

4. Conclusions

The CPC molecules were found to reduce the permeate flux considerably and contribute to the membrane fouling phenomenon. However, a great part of the membrane fouling caused by CPC was reversible since the flux reduction after external cleaning of the membrane did not exceed 5%. The rejection of phenolics by micellar-enhanced ultrafiltration using CPC was positively correlated to their hydrophobicity, estimated by the octanol-water partition coefficient.

The relatively more hydrophobic compounds (vanillic acid and *p*-coumaric acid) were rejected more by MEUF using CPC than tyrosol. The membrane of 20 kDa (MWCO) exhibits higher rejection than the membrane of 50 kDa. The CPC was removed and recovered efficiently from the retentate streams by precipitation under its Krafft temperature, especially at 5°C. The surfactant recovery makes the MEUF process more economic. Further investigations are needed to enhance the permeate fluxes and the rejection of phenolics.

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Nomenclature

Symbols

V: volume (mL)
C: concentration of phenolic compounds (g/L)
R: rejection (%)
J: permeate flux ($L.h^{-1}\cdot m^{-2}$).
L_p: membrane permeability ($L.h^{-1}.m^{-2}.MPa^{-1}$)
R_m: membrane hydraulic resistance (m^{-1})
R_s: membrane secondary resistance (m^{-1})
Δ: transmembrane pressure (bar and MPa)
μ: dynamic water viscosity (Pa·s)
K_{ow}: octanol-water partition coefficient

Subscripts

0: initial value
p: permeate
r: retentate
w: water
f: feed

References

Attwood D., Florence A.T., (1983), *Surfactants Systems, Their Chemistry, Pharmacy and Biology*, Chapman & Hall, London, U.K.

Chaudhari R.R., Marathe K.V., (2010), Separation of dissolved phenolics from aqueous waste stream using micellar enhanced ultrafiltration, *Separation Science and Technology*, **45**, 1033-1041.

Diaconu I., Mirea C.M., Ruse E., Nechifor G., (2015), Selective recovery of phenolic derivatives through the technique of liquid membranes, *Environmental Engineering and Management Journal*, **14**, 625-630.

Dunn R.O.-Jr., Scamehorn J.F., Christian S.D., (1985), Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous streams, *Separation Science and Technology*, **20**, 257-284.

Eastwood M.A., (1999), Interaction of dietary antioxidants in vivo: how fruit and vegetables prevent disease?, *International Journal of Medicine*, **92**, 527-530.

El-Abbassi A., Khayet M., Hafidi A., (2011), Micellar enhanced ultrafiltration process for the treatment of olive mill wastewater, *Water Research*, **45**, 4522-4530.

El-Abbassi A., Kiai H., Hoinkis J., Hafidi A., (2014), Removal of phenolic compounds by micellar enhanced ultrafiltration using an anionic surfactant. *Journal of Materials and Environmental Science*, **5**, 57-66.

Feng X.H., Guo H.J., Patel K., Zhou H., Lou X., (2014), High performance, recoverable $Fe_3O^{4-}ZnO$ nanoparticles for enhanced photocatalytic degradation of phenol, *Chemical Engineering Journal*, **244**, 327-334.

Fu F., Wang Q., (2011), Removal of heavy metal ions from wastewaters: A review, *Journal of Environmental Management*, **92**, 407-418.

Huang J., Peng L., Zeng G., Li X., Zhao Y., Liu L., Li F., Chai Q., (2014), Evaluation of micellar enhanced ultrafiltration for removing methylene blue and cadmium ion simultaneously with mixed surfactants, *Separation and Purification Technology*, **125**, 83-89.

Karthikeyan S., Gopalakrishnan A.N., (2017), Effect of microwaves on photocatalytic degradation of phenol and cresols in a microwave-ultraviolet reactor, *Environmental Engineering and Management Journal*, **16**, 285-292.

Kim C.K., Kim S.S., Kim D.W., (1998), Removal of aromatic compounds in the aqueous solution via micellar enhanced ultrafiltration: Part 1. Behavior of nonionic surfactants, *Journal of Membrane Science*, **147**, 13-22.

Ma W., Cheng Z., Gao Z., Wang R., Wang B., Sun Q., (2014), Study of hydrogen gas production coupled with phenol electrochemical oxidation degradation at different stages, *Chemical Engineering Journal*, **241**, 167-174.

Markels J.H., Lynn S., Radke C.J., (1994), Micellar ultrafiltration in an unstirred batch cell at constant flux, *Journal of Membrane Science*, **86**, 241-261.

Noubigh A., Abderrabba M., Provost E., (2009), Salt addition effect on partition coefficient of some phenolic compounds constituents of olive mill wastewater in 1-octanol-water system at 298.15 K, *Journal of the Iranian Chemical Society*, **6**, 168-176.

Paradies H.H., (1985), *The Structure of Triton X 100 and Hexadecylpyridinium Chloride in Aqueous Solutions: Fluorescence and Small-Angle X-Ray Scattering Studies in the Presence of $Hg(CN)_2$*, In: *Surfactants in Solution*, Mittal K.L. (Ed.), Plenum, New York, U.S.A., 159-180.

Peydayesh M., Kazemi P., Nabavi M.S., Mohammadi T., (2014), Phenolic wastewater treatment by supported liquid membrane using different cooking oils as liquid membrane, *Chemical Engineering Communications*, **201**, 1593-1605.

Purkait M.K., DasGuptaand S., De S., (2005), Separation of aromatic alcohols using micellar enhanced ultrafiltration and recovery of surfactant, *Journal of Membrane Science*, **250**, 47-59.

Qu Y.H., Zeng G.M., Huang J.H., Xu K., Fang Y.Y., Li X., Liu H.L., (2008), Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionator, *Journal of Hazardous Materials*, **155**, 32-38.

Rahmanian B., Pakizeh M., Esfandyari M., Maskooki A., (2011), Fuzzy inference system for modeling of zinc removal using micellar-enhanced ultrafiltration, *Separation Science and Technology*, **46**, 1571-1581.

Sabaté J., Pujolà M., Centelles E., Galan M., Llorens J., (1999), Determination of equilibrium distribution constants of phenol between surfactant micelles and water using ultrafiltering centrifuge tubes, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **150**, 229-245.

Sabaté J., Pujola M., Llorens J., (2002), Comparison of polysulfone and ceramic membranes for the separation of phenol in micellar-enhanced ultrafiltration, *Journal of Colloid and Interface Science*, **246**, 157-163.

Sasaki S., (2009), Kinetic studies on hydrated solid transform of cetylpyridinium chloride in aqueous solution, *Journal of Physical Chemistry*, **B113**, 8545-8551.

Scamehorn J.F., Harwell J.H., (1989), *Surfactant-Based Separation Processes*, Marcel Dekker, New York, USA.

Susanto H., Feng Y., Ulbricht M., (2009), Fouling behavior of aqueous solutions of polyphenolic compounds during ultrafiltration, *Journal of Food Engineering*, **91**, 333-340.

Syamal M., De S., Bhattacharya R.K., (1997), Phenol solubilization by cetyl pyridinium chloride micelles in micellar enhanced ultrafiltration, *Journal of Membrane Science*, **137**, 99-107.

Talens-Alesson F.I., Urbanski R., Szymanowski J., (2001), Evolution of resistance to permeation during micellar enhanced ultrafiltration of phenol and 4-nitrophenol, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **178**, 71-77.

Tanhaei B., Chenar M.P., Saghatoleslami N., Hesampour M., Laakso T., Kallioinen M., Sillanpaa M., Mänttäri M., (2014), Simultaneous removal of aniline and nickel from water by micellar-enhanced ultrafiltration with different molecular weight cut-off membranes, *Separation and Purification Technology*, **124**, 26-35.

Tung C.C., Yang Y.M., Chang C.H., Maa J.R., (2002), Removal of copper ions and dissolved phenol from water using micellar-enhanced ultrafiltration with mixed surfactants, *Waste Management*, **22**, 695-701.

Zeng G.M., Xu K., Huang J.H., Li X., Fang Y.Y., Qu Y.H., (2008), Micellar enhanced ultrafiltration of phenol in synthetic wastewater using polysulfone spiral membrane, *Journal of Membrane Science*, **310**, 149-160.