Mixed micelles-mediated dephenolisation of table olive processing's wastewaters

Jihane Raiti and Abdellatif Hafidi

ABSTRACT

Olive processing wastewaters account for highly pollutant agro-industrial effluents. Their phenolic compounds are responsible for their toxicity. Those natural compounds have to be degraded or recovered before any discharge into the environment. This investigation deals with the extraction and concentration of the phenolic compounds into an aqueous phase using a mixture of nonionic/anionic surfactants. A synergistic effect for the extraction of the natural phenolic compounds was observed when Genapol X-80 was combined with sodium dodecyl sulphate (SDS). For the tested Genapol X-80 concentration (1–5%), a minimum concentration of 2.5 mM SDS was demonstrated to be necessary to reach maximum extraction rates. The extraction efficiencies were only slightly affected by temperatures between 20 and 50 °C. However, the recovery rate of the phenolic compounds increased with the augmentation of the contact time. The pH has also been found to greatly influence the extraction of the phenolic compounds and the coacervate volume fraction. At optimal conditions, the coacervate phase was enriched up to four times whereas the maximum reduction of the phenolic content in the diluted phase reached more than 40% in one step extraction.

Key words | mixed micelles, olive processing, phenolic compounds, wastewaters

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INTRODUCTION

Olive processing effluents (preparation wastewaters of olive oil and table olives) are among the most polluting agro-industrial activities mainly because of high concentration of polyphenols. Most of these compounds are recognised as phytotoxic and poorly biodegradable (Justino *et al.* 2012). According to most national legislations, these effluents require adequate treatments before their discharge.

A variety of approaches have been developed to remove the phenolic compounds (PhC) from olive mill wastewaters, including liquid-liquid extraction, chemical oxidation, adsorption, coagulation flocculation, membrane separation and biological degradation (Paraskeva & Diamadopoulos 2006). Many of the proposed methods showed inherent disadvantages, which hampered their industrial application (expensive, toxic and inflammable organic solvents, stringent running conditions, secondary pollution, etc.).

Furthermore, these natural polyphenols are claimed to have a wide spectrum of interesting health promoting effects (prevention of some cancers and cardiovascular diseases, tissue ageing, etc.). Radical scavenging, interaction with specific enzymes, and with transcription factors, are among the most cited mechanisms involved (Fraga *et al.* 2010). Polyphenol-rich wastes such as those from olive and grape processing can be regarded as cheap sources of these interesting bio-products. Their recovery may be very beneficial not only from an environmental point of view but it could be very useful for pharmaceutical, food and cosmetic applications.

In spite of the largely recognised health promoting properties of the olive PhC, treatment studies of olive processing wastewaters still focus on biological, chemical and physico-chemical degradation methods (El-Gohary *et al.* 2009; Chiavola *et al.* 2014; Gursoy-Haksevenler & Arslan-Alaton 2014). Investigations on recuperative processes remain relatively scarce: adsorption (Ena *et al.* 2012), liquid-liquid extraction (Jiang *et al.* 2003) and membrane separation techniques (El-Abbassi *et al.* 2009, 2011).

Surfactant-based methods are gaining interest as promising alternatives and environmentally friendly extraction techniques (Liang *et al.* 2009). It is well known that

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surfactants are amphiphilic molecules, which associate to form molecular aggregates called micelles. These organised structures show excellent capacities to solubilise different mineral and organic compounds by electrostatic or hydrophobic interactions or a combination of both effects (Hinze & Pramauro 1993).

When a nonionic micellar solution is heated over a certain temperature, the solution becomes turbid. This temperature is called cloud point temperature (CPT). Above the CPT the micellar solution separates into a surfactant-rich phase of a small volume and thus a high enrichment factor can be obtained, and a diluted aqueous phase in which the surfactant concentration is close to the critical micellar concentration (CMC). This cloud point extraction (CPE) was firstly reported for preconcentration of trace-metal ions in the form of their hydrophobic complexes (Watanabe & Tanaka 1978). Nowadays, preconcentration prior to the analysis of metal ions remains the most reported. The abundant related literature has been reviewed in many papers (Bezerra *et al.* 2005; Pytlakowska *et al.* 2013; Samaddar & Sen 2014). Comparatively little work has been devoted to the extraction of organic solutes. Preconcentration prior to analysis of polycyclic aromatic hydrocarbons and polychlorinated biphenyls are the most reported studies (Ferrera *et al.* 2004; Pan *et al.* 2010). However, most studies remain focused on preconcentration prior to analysis of different organic compounds from different matrices (food, water, biological): dyes from water (An *et al.* 2010), antibiotics residues and colorants from foods (Kukusamude *et al.* 2010; Pourreza *et al.* 2011), aflatoxins from peanut and peanut oil (Jinling & Yaling 2013), saponins from *Ziziphus joazeiro* bark (Dias *et al.* 2014), and PhC from wines (Vichapong *et al.* 2014).

A combination of different surfactants can be used simultaneously, aiming for some advantages like greater efficiency and lower energy costs. The so-called mixed micelles-mediated extraction has been reported for preconcentration of organic compounds and metal cations (Kang *et al.* 2001; Paleologos *et al.* 2003). A combination of ionic with nonionic surfactant is reported to increase the extraction efficiency of polar organic compounds (Zhou & Zhu 2005).

The aim of this work is the development of a mixed micelles-based extraction method for dephenolisation of table olive processing wastewaters (TOPW). A mixture of a nonionic surfactant (Genapol X-80) and an anionic surfactant sodium dodecyl sulphate (SDS) was tested. The parameters affecting the natural PhC extraction, such as concentration of the surfactants, the pH, and the contact time and temperature, were investigated.

MATERIAL AND METHODS

Reagents

Polyethylene glycol monoalkyl ether (Genapol X-80), SDS, Folin–Ciocalteu reagent and anhydrous sodium carbonate were purchased from Sigma-Aldrich (Germany). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Merck (France). All chemicals used were of analytical-reagent grade and were prepared using distilled water.

Sample characterisation

Effluent samples were obtained from a table olive industrial unit at Marrakesh (Morocco). Conductivity (EC) and pH of TOPW samples were determined by a digital calibrated pH and conductivity meter MultiLab P5 (WTW, Germany). Total solids were determined by weight difference before and after drying samples overnight at 105 °C. The chemical oxygen demand (COD) was determined by the dichromate method as described by LaPara *et al.* (2000). The total phenolic content (TPC) was determined colorimetrically using the Folin–Ciocalteu method (Singleton & Rossi 1965) and expressed as tyrosol equivalents (TYE). The main physicochemical characteristics of the samples are summarised in Table 1.

Mixed-micelles cloud point extraction

TOPW were mixed with SDS to get a concentration of 10 mM and homogenised by magnetic stirring (300 rpm) at room temperature for 120 min. This solution was diluted by TOPW to have a series of SDS concentrations. Different amounts of Genapol X-80 (w/v) were added to each SDS concentration. The final volume of each tube was 20 ml. The tested concentrations of surfactant varied from 0.006 to 10 mM SDS and from 1 to 5% w/v Genapol X-80. Effects of the Genapol X-80 and SDS concentrations, process

Table 1 | Main physicochemical characteristics of TOPW

Parameters	TOPW
pH	4.45 ± 0.06
EC (mS/cm)	88.5 ± 1.09
Dry residue (g/l)	78.5 ± 1.12
COD (g of O_2/l)	18.6 ± 0.95
TPC (g of TYE/l)	5.2 ± 0.42

Values are the average of three measurements ± standard deviation.

temperature, mixing duration, and pH on extraction efficiency, coacervate volume fraction and partition coefficients were investigated.

Extraction efficiency estimation

Complete separation of the two phases was obtained after centrifugation of the tubes at 1,500 rpm for 5 min. After a careful separation of both phases, the volume of each phase was accurately determined and their ratio calculated.

The partitions of the PhC among the two phases were approached by determination of their partition coefficient (K) and their elimination rates (E), which were calculated according to the following equations:

$$K = \frac{C_c}{C_d}$$

$$E = 100 \times \left(1 - \left(\frac{C_c}{C_d}\right)\right)$$

where C_c and C_d are equilibrium concentrations of the PhC in the coacervate and in the diluted phases, respectively.

RESULTS AND DISCUSSION

Effects of surfactant concentration

In aqueous solutions, micelles offer hydrophobic micro domains inside their cores. Solutes can partition between the bulk aqueous phase and the hydrophobic pseudo phase. The recovery of such micelles results in the isolation of the solubilised solutes. As illustrated in Table 1, TOPW showed a very high conductivity (89 mS/cm) because of the high NaCl concentration used in the brining solution. In the TOPW, Genapol X-80 showed a CPT of 24 °C, whereas its CPT in water is often reported in the range 75–80 °C (Eiguren *et al.* 1997). It is well established that salts contribute to greatly lowering the interactions between water and surfactant molecules leading to lower CPT, while having no effect on the CMC values of nonionic surfactants.

Results depicted in Figure 1 show the PhC recovery rates obtained with different Genapol X-80 concentrations (1, 3 and 5%) combined with SDS concentrations. PhC compounds extraction increased both with the increase of Genapol X-80 and SDS. A synergistic effect for PhC extraction was observed when Genapol X-80 was combined with SDS. When Genapol X-80 was tested without any SDS addition only low extraction rates of the PhC were obtained

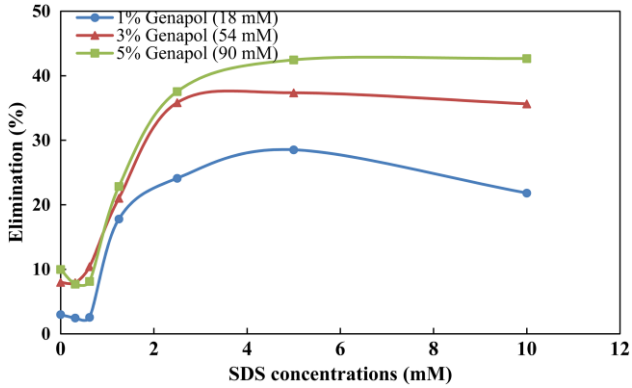

Figure 1 | Effect of anionic surfactant concentrations on the polyphenol elimination efficiency at different Genapol X-80 concentrations. Contact time: 120 min, process temperature: 25 °C.

(<10%). At SDS concentrations between 0.6 and 2.5 mM, PhC partition in the surfactant-rich phase seems to be linearly dependent on SDS concentration. Above 2.5 mM SDS concentration, only the increase of the Genapol X-80 concentration leads to better solubilisations of the PhC in the coacervate. 2.5 mM SDS was found to be the smallest SDS concentration that allows good PhC eliminations. When SDS is added to 3% Genapol X-80, the PhC elimination rates increased from the 8% obtained without SDS addition to 36% at 2.5 mM SDS. In the range of the tested surfactant concentrations, the most efficient PhC extraction (42.5%) was reached with a mixture of 5% Genapol X-80 and 10 mM SDS.

With the assumption that Tyrosol is one of the typical PhC in TOPW and that after separation, the quasi totality of the surfactants are found in the coacervate, our results show that the molar ratios of the eliminated PhC to SDS and Genapol X-80 are 1:2:0.3 when using 2.5 mM SDS and 1% (18 mM) Genapol X-80, 1:3:0.14 in the case of 2.5 mM SDS and 3% (54 mM) Genapol X-80, and 1:3:0.08 for the mixture of surfactants 2.5 mM SDS and 5% (90 mM) Genapol X-80.

Effects of process temperature

Optimisation of a CPE implies the determination of the shortest possible contact time and the lowest process temperature allowing the best extraction efficiency. In general, CPE methodology is achieved at an optimum equilibrium temperature where it is 15–20 °C higher than the CPT of the surfactant (Santalad *et al.* 2009). As mentioned in the previous section the CPT of the tested surfactant is greatly lowered in the brine solution in comparison to pure water (24 °C vs 75 °C). In fact, TOPW are salt rich (electrical

conductivity 88.5 ± 1.09 mS/cm, Table 1). In our study, the effect of the process temperature was investigated over the range 20–50 °C. Our results (Figure 2) demonstrate that the extraction efficiencies were only slightly affected by temperatures between 20 and 50 °C. Owing to energy and product preservation considerations, it is more suitable to process at a low temperature. So, 25 °C was selected for the subsequent experiments.

According to many authors, the cloud point of nonionic surfactants was dramatically increased with the addition of small amounts of cationic or anionic surfactant (Gu & Galera-Gomez 1995; Nascentes & Arruda 2003). In parallel, electrolytes greatly affect the cloud point in mixed nonionic/ionic surfactant systems. A significant decrease in the cloud point is noted when small amounts of inorganic salts are added to the system (Hinze & Pramauro 1993; Pino *et al.* 2002; Ferrera *et al.* 2004). The interactions of the PhC with water molecules and with surfactant micelles and their partition between the micellar phase and the bulk water may also be influenced by temperature.

Influence of contact time

To evaluate the effect of the contact time on the extraction of the PhC from the TOPW, different durations ranging from 0 to 120 minutes were tested (Figure 3). The recovery rate of the phenolics increased with the augmentation of the contact time from 0 to 20 min and remained almost unchanged beyond this. The maximum reduction rates

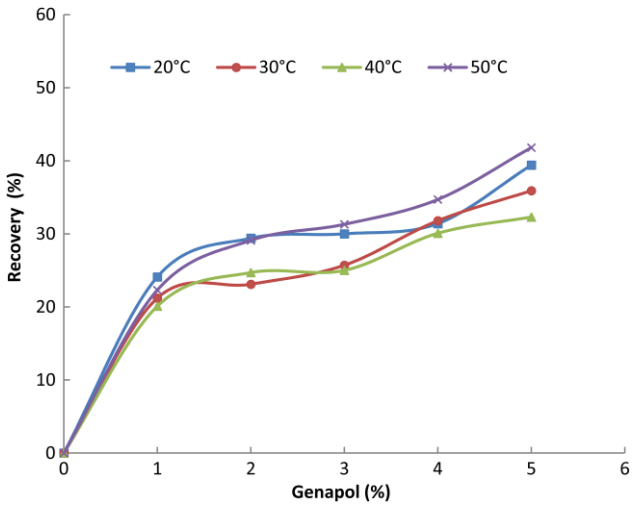

Figure 2 | Effect of Genapol X-80 concentration on PhC recovery at different temperatures. 2.5 mM SDS, Genapol X-80 concentrations from 1–5%, process temperature 25 °C, contact time: 120 min.

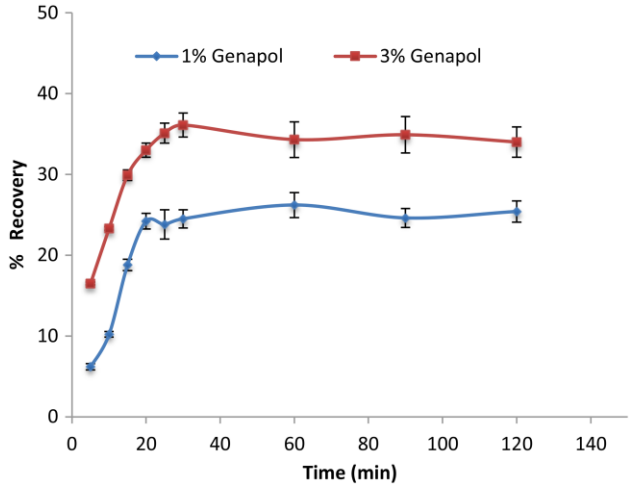

Figure 3 | Effect of equilibration duration on phenolic compound recovery (2.5 mM SDS, equilibration temperature 25 °C).

obtained are in the range 23.8 ± 1.8% to 26.2 ± 1.5% with 1% of Genapol X-80 and 33.0 ± 0.9% to 35.1 ± 1.5% with 3% of Genapol X-80.

Influence of pH

The simple PhC are known to be weakly acidic with pK_a values from 2.5 to 4.9. These phenolic acids are greatly dissociated at pH values above 5, while under pH 2.7 they remain mostly undissociated and may present less interactions with water molecules. The effect of pH on the CPE of the natural PhC was studied in the range pH 2–10. The results demonstrate that the pH had greatly influenced the extraction of phenols (Figure 4). The highest reduction rate was obtained at acidic pH values. The elimination of phenol from TOPW remained low at alkali pH (8–10). Because of their predominant undissociated state at acidic pH the simple PhC are more prone to interact with the more hydrophobic micellar phase inducing a micellar swelling as recently reported by Dharaiya & Bahadur (2012) which demonstrated a Triton X-100 micelles growth promoted by an increase p-cresol concentration, a decrease in pH and an increase of temperature.

Effect of the surfactant dose on the coacervate volume fraction

The coacervate volume fraction is a key parameter for the appreciation of the efficiency of the CPE. For maximum elimination, the coacervate volume should be the smallest and its PhC concentration the highest. The results showed that the coacervate volume fraction depends mainly on the

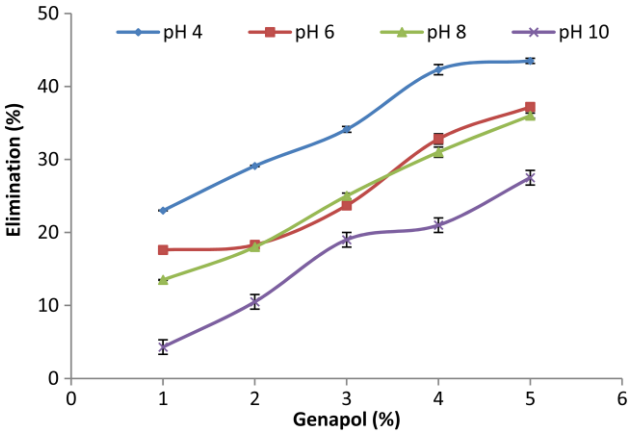

Figure 4 | Effect of Genapol X-80 concentration on PhC elimination from TOPW at different pH. 2.5 mM SDS, process temperature 25 °C, contact time: 1 h.

surfactant concentration (Figure 5). A slight effect of the pH is noticed at high surfactant dose. The coacervate volume fraction increases with the increase of surfactant concentration and slightly decreases with the decrease of pH mainly at high concentrations of surfactant. As shown in Figure 5, at pH 8 and a Genapol X-80 concentration of 5% (v/v), the coacervate volume fraction was 0.44 ± 0.20. The lowest volume fraction (0.10 ± 0.05) was obtained at pH 2, when using 1% Genapol X-80. Linear positive correlations ($R^2 > 0.90$) were obtained between the volume fraction and the PhC elimination.

Partition coefficients

Partition coefficients of the natural PhC of TOPW as a function of pH and Genapol X-80 concentrations are depicted in

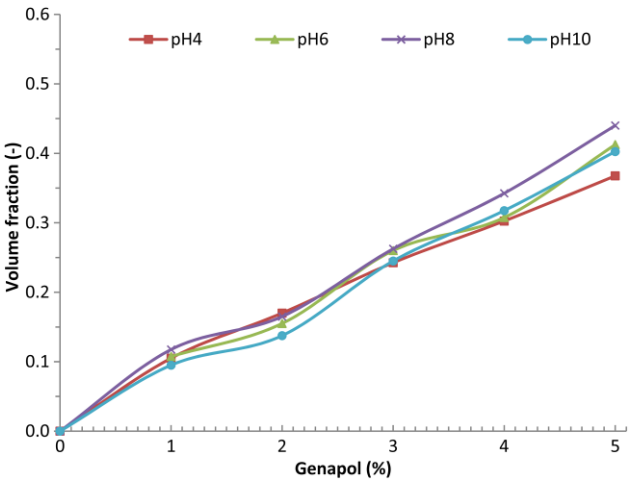

Figure 5 | Coacervate volume fractions obtained with different Genapol X-80 concentrations and pH. 2.5 mM SDS, process temperature 25 °C, contact time: 1 h.

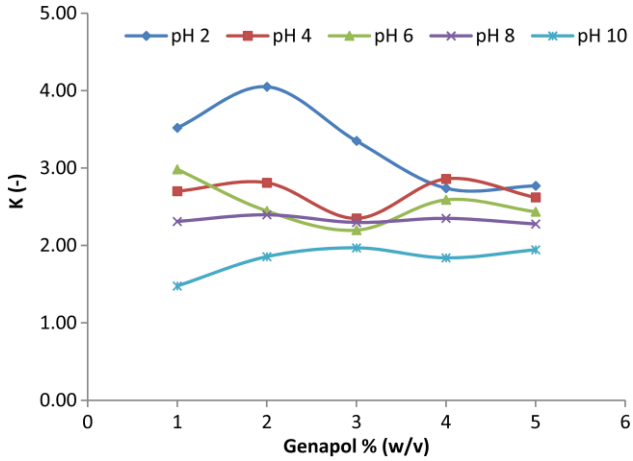

Figure 6 | Partition coefficients obtained with different Genapol X-80 concentrations and pH. 2.5 mM SDS, process temperature 25 °C, contact time: 1 h.

Figure 6. The partition coefficients were higher under acidic or near neutral conditions than in basic solution. The highest partition coefficients obtained (3.5–4.0) were at pH 2 for 1–3% Genapol X-80. At pH 4–8 almost similar partition coefficients were obtained for all the tested surfactant concentrations. The partition coefficients were the lowest (1.5–2) at pH 10. Most likely, such behaviour is linked to the magnitude of ionisation of the different phenolic molecules that are known to have very low pK_a. Consequently, undissociated forms predominate at lower pH enhancing their partition in favour of the nonionic micelles of the Genapol X-80.

CONCLUSION

Mixed micelle-CPE using Genapol X-80 and SDS anionic surfactants has been proven to be an effective dephenolisation method that is simple, rapid and provides good efficient separation. This method, which has shown excellent potential for the dephenolisation of TOPW, can be used as depollution treatment. In fact, the biological oxygen demand (BOD)/COD ratios (0.4 for the treated TOPW vs 0.18 for the untreated) demonstrate an improvement in the biodegradability of these recalcitrant wastewaters. However, more studies are needed to evaluate the impact of the direct disposal of these treated wastewaters on the environment (soil and water streams).

The recovery of concentrates of natural PhC using the mixed micelle is a very interesting valorisation of these agro-industrial wastewaters. The extent of extraction is influenced by the surfactant concentrations, the pH of the

medium, and the equilibrium temperature. Our results demonstrate that an optimal recovery of the PhC can be obtained with 2.5 mM SDS mixed with Genapol X-80. A minimum of 30 min contact time at 25 °C is necessary to reach a maximum recovery of the PhC in the coacervate. Increasing the temperature above 25 °C is not found to be accompanied by an amelioration of the PhC partition in the coacervate; acidic conditions are more suitable for this. It is worth noting that these PhC elimination rates can be further increased by repeated sequential extractions. In comparison to solvent extraction methods, this method is much safer since only small amounts of a surfactant which has a low toxicity is used. This fact is particularly attractive, because the green chemistry concept can be employed here.

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