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Towards a high yield recovery of polyphenols from olive mill wastewater on activated carbon coated with milk proteins: Experimental design and antioxidant activity

Asma Yangui[a,b,*], Manef Abderrabba[a]

[a] Preparatory Institute for Scientific and Technical Studies (IPEST), Laboratory of Materials, Molecules and Applications (LMMA), BP 51 La Marsa 2070, Tunis, Tunisia
[b] University of Tunis El Manar, Faculty of Sciences of Tunis, Campus University 2092, El Manar, Tunis, Tunisia

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ABSTRACT

Activated carbon coated with milk proteins was used for the removal and recovery of phenolic compounds from actual olive mill wastewater (OMW). The extraction of polyphenols using the new adsorbent based on natural coating agent has significant potential compared with traditional extraction methods, as it significantly increases the extraction yield (80%) and overall efficiencies of the process for total phenols (75.4%) and hydroxytyrosol (90.6%) which is the most valuable compound. Complete discussions on the adsorption isotherms, kinetic and thermodynamic were performed and the optimum adsorption variables were investigated using the response surface methodology and the central composite experimental design. The extracted polyphenols exhibited a high antioxidant activity and a fast scavenging effect on DPPH free radical. The strategy devised in this work for polyphenol extraction using modified activated carbon with biological coating agent is of simple design, very effective and ensure the recovery of highly antioxidant extract.

1. Introduction

In the recent years, the olive oil production has increased considerably. The consumption of olive oil is growing concern over the world due to its health benefits and its great nutritional properties (Dermeche, Nadour, Larroche, Moulti-Mati, & Michaud, 2013). Unfortunately, the Mediterranean countries are seriously damaged by the problem of the treatment and the disposal of olive mill wastewater (OMW) owing to its high content in organic load. Essentially, OMW is composed of water (83–96%), organic matters (3.5–15%) and mineral salts (0.5–2%) (Asses, Ayed, Bouallagui, Sayadi, & Hamdi, 2009).

During the extraction of olive oil, olive polyphenols are partitioned between the water phase and the oil phase; however, the major fraction is missing in the wastewater from the fact that they are water soluble substrates of high polarity. The concentration of polyphenols in OMW is ranging between 5 and 25 g L^{-1} (McNamara, Anastasiou, O'Flaherty, & Mitchell, 2008). Then, their extraction is very promising since they are potent natural antioxidants, which have raised enormous interest in cosmetic, food and pharmaceutical industries (Dermeche et al., 2013). More than fifty different phenolic compounds have been quantified previously in OMW (Rahmanian, Jafari, & Galanakis, 2014). Indeed, the region of olive cultivation, the storage conditions and the type of the processing system could justify this variance. The main challenge in the treatment of OMW is the removal and the recovery of polyphenols before it discharges into the environment. This procedure offers a great economic interest and makes these wastewaters less hazardous and easier to treat. Without purification, polyphenols are progressively oxidized and polymerized which give OMW the toxicity and the recalcitrant character (Chatzisymeon, Xekoukoulotakis, & Mantzavinos, 2009). Therefore, extensive research effort has been directed towards the recovery of polyphenols from OMW, i.e. the enzymatic treatment (Olivieri et al., 2012; Ergül, Sargin, Öngen, & Sukan, 2011), the solvent extraction (Azaizeh et al., 2012; El-Abbassi, Kiai, & Hafidi, 2012), the membrane separation (Shadabi, Ghiasvand, & Hashemi, 2013), the use of silica–alginate–fungi biocomposites (Duarte et al., 2014), the solar distillation (Sklavos, Gatidou, Stasinakis, & Haralambopoulos, 2015) and the supercritical carbon dioxide (SCO_2) coupled with a polar co-solvent (Schievano et al., 2015). Nevertheless, there is a serious necessity for more feasible and ecological friendly tools.

Due to its highly beneficial importance, green procedures have been established either to recover natural products such as polyphenols or to decontaminate wastewater. These technologies include green liquid extraction using a deep eutectic solvent (Wang et al., 2017), deionized water or aqueous solutions of cyclodextrins using a semiautomatic

* Corresponding author at: Preparatory Institute for Scientific and Technical Studies (IPEST), Laboratory of Materials, Molecules and Applications (LMMA), BP 51 La Marsa 2070, Tunis, Tunisia.
E-mail address: yangui.asma@gmail.com (A. Yangui).

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extractor (Diamanti, Igoumenidis, Mourtzinos, Yannakopoulou, & Karathanos, 2017) and multielemental mixed micelle cloud point extraction procedure (Meeravali, Manjusha, Madhavi, & Kumar, 2016).

The adsorption system pathway is now considered as useful method and among the most existing economic methods. Compared to other technologies, it has several figures of merit for its simplicity, reversibility, its easy regeneration and low cost. Additionally, it avoids the use of toxic solvents, and minimizes the degradation of the adsorbate (Soto, Moure, Domingues, & Pajaro, 2011). Extensive research efforts have been focused on the discovery and development of new green adsorbents. For example, apple seeds waste and lanthanum-impregnated green sand were used as efficient green adsorbents for dye and fluoride from aqueous medium, respectively (Suteu, Coseri, Badeanu, & Zaharia, 2015; Vivek Vardhan, & Srimurali, 2016).

Activated carbon (AC) is known for its high adsorption performance, surface area and commercial availability. These characteristics make it a potential material as support for many grafting agents. The unmodified AC from various sources were previously investigated for the adsorption of phenolic compounds (Kumar, & Jena, 2016; Thue et al., 2016,2017). Another approach was to use a coating agent for the development of a new adsorbent with new active sites. Furthermore, the surface modification technique of AC using a varied range of novel functional groups offers better interaction of target species with the sorbent. For instance, methylene blue adsorption was assessed on palygorskite coated AC (Zhang, Cheng, Wu, Tang, & Wu, 2015). In addition, AC coated with Mn_30_4 was also employed for the adsorption of Pb and Cu from aqueous solution (Lee, Park, Chung, Lee, & Kang, 2015). Nitrate removal from water using AC coated with nanoparticles of Fe_2O_3 was also conducted (Nguyen et al., 2016).

In the present study, milk protein (MP) was selected as coating biopolymer on the surface of AC, the adsorbent is denoted MP-AC. This material was used for the extraction of polyphenols from OMW. Polyphenols are chemically arranged as a hydroxyl group bonded to an aromatic ring. In addition, protein molecules are polymers consisting of carbons attached to hydrogen atoms, amino and carboxyl groups. The chemical structure of polyphenols offers it the property to be excellent hydrogen donors that interact via hydrogen bonding with the carboxyl and the amine groups in protein biomolecules (Poncet-Legrand et al., 2006).

The preparation of MP-AC was used as a new, simple, low cost, and rapid adsorbent followed by UV detection for polyphenols. Detailed discussions on the adsorption isotherms, kinetic and thermodynamic were performed to explore the interaction adsorbent/adsorbate mechanism. To achieve the best performance for polyphenols adsorption, a set of the optimal variables, i.e. the adsorbent concentration, the pH, the temperature and the contact time were met using the central composite experimental design (CCD) linked to the response surface methodology (RSM). The features desorption were also achieved and the antioxidant activity of OMW polyphenols obtained with this method was performed. As Butylated hydroxytoluene (BHT) is largely used to minimize the oxidation of lipids in nutriments during food storage, its scavenging activity was investigated for comparative purpose.

2. Experimental

2.1. Materials

OMW sample was obtained from an olive oil mill located Sfax (the South of Tunisia). It was conducted to purification via Buchner filtration apparatus to remove any residual solid wastes and stored in plastic containers at 4 °C. AC was supplied by Strem Chemicals. All solvents and reagents were provided by Sigma Aldrich and were used without additional purification.

2.2. Preparation of the coating agent

25 mL of nonfat milk was added to 50 mL of ethanol and left stirring on medium speed to precipitate MP (2 min). The precipitated fraction was transferred to centrifuge bottles and maintained at 5000 rpm for 5 min at room temperature. Subsequently, the protein pellets were suspended in 50 mL of distilled water and adjusted to a pH 9.0 with 0.1 M NaOH.

2.3. Preparation of the adsorbent (MP-AC)

The preparation of MP-AC was realized according to a modified reported protocol (Opet, & Levin, 2014). The AC was powdered to increase the surface contact with the MP, washed and dried at 55 °C. Then, it was treated with hydrochloric acid (HCl) 2 N for 12 h. The material was after that filtered, washed several times with distilled water and dried at 100 °C. The solution containing milk protein pellets was transferred to 500 mL beaker and was stirred with the treated AC on a rotary shaker (150 rpm) at 37 °C for 120 min. Subsequently, the liquid was poured off and the resulting solid was then rinsed gently with bi-distilled water several times to remove unbound proteins. MP-AC was finally transferred to an incubator at 55 °C until complete drying. The protocol was optimized several times until no protein pellets were precipitated in the medium and the maximum amount of milk proteins coating 10*g* of activated carbon was 0.125 g.

BET surface area, pore volumes and diameters were derived from the nitrogen adsorption–desorption isotherm at 77 K on a Micromeritics ASAP 2010 apparatus.

2.4. Polyphenols determination

The polyphenols concentration in OMW was determined using the method reported by Singleton, Orthofer, & Lamuela-Raventos (1999). The calibration curve was realized by preparing a series of gallic acid solutions in the range between (60–300 mg L^{-1}). Aliquots of 100 μL were mixed with 500 μL of Folin & Ciocalteu's reagent, 6 mL of distilled water and 1.5 mL of Na_2CO_3 (20% in water). The solution was then adjusted to 10 mL with distilled water and stirred vigorously. Two hours of incubation latter, the absorbance was measured at 760 nm. The same procedure was used to determine total polyphenols in OMW.

The identification of polyphenols in the extract after desorption was achieved using HPLC-DAD apparatus set at 280 nm. The separation was made in gradient mode using two mobile phases, namely an aqueous solution of 0.01% acetic acid and acetonitrile. The separation was performed on a C18 column over 30 min. The flow rate was 0.1 mL min^{-1} and the injection volume was 20 μL.

2.5. Adsorption experiments

Adsorption experiments were performed under static conditions at 298 K in a 250 mL batch stirred Pyrex bottles (200 rpm). The equilibrium adsorption isotherms were obtained by varying MP-AC concentration between 0 and 70 g L^{-1} in OMW. Additionally, an internal standard was used to evaluate the adsorption efficiency of MP-AC for a mixture of commercial phenolic compounds occurring in OMW (hydroxytyrosol, tyrosol, gallic acid, 3,4-Dihydroxybenzoic Acid, caffeic Acid and p-coumaric Acid). Weights of 5 mg of each phenolic compound were mixed together and dissolved in one liter of distilled water and then 0.3 g of MP-AC was added to the solution under agitation. All experiments were performed over 24 h. After filtration, the resulting liquid phase was analyzed by Folin & Ciocalteu's test and HPLC measurement. A negative control was also conducted in the washed liquid of MP-AC with both considered analyzing methods and no trace of phenolic compound has been quantified.

The adsorption efficiency A (%) and capacity q_e (mg g^{-1}) were calculated as follows.