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REVIEW

Recovery and Removal of Phenolic Compounds from Olive Mill Wastewater

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Abstract Food wastes are today considered as a cheap source of valuable components since the existent technologies allow the recovery of target compounds and their recycling inside the food chain as functional additives in different products. Olive mill wastewater (OMW) is generated from olive oil extraction systems. It has high added-value compounds namely phenolics, recalcitrants, pectin, and some important enzymes. It causes a certain amount of toxicity/phytotoxicity because of its phenolic compounds. OMW also has significant impacts when discharged directly into surface waters. Therefore, the treatment of olive mill wastewater is very much needed. Several types of techniques have been investigated for OMW treatment along with recovery and removal of its phenolic compounds. Among these techniques, physical ones are utilized for extraction purposes, while chemical and biological methods are applied in order to diminish organic load. In this review, current status and recent developments in the recovery and removal of phenolic compounds from OMW have been critically examined.

Keywords Olive mill wastewater · Treatment · Recovery · Phenols

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Introduction

Olive oil production is typically conducted with the following extraction processes: (1) a traditional discontinuous press process [1], (2) three-phase centrifugal or (3) two-phase centrifugal extraction systems (Fig. 1). Olive mill wastewater (OMW) is the main liquid effluent of the olive oil production process. This waste stream is generated in several forms and compositions following the particular characteristics of the used extraction equipment, olive variety, season and maturity of the fruit [2]. Pressure and three phase centrifugation systems produce considerably more liquid effluent than two phase centrifugation process [3]. The discontinuous process produces less but more concentrated wastewater (0.5–1 m^3 per 1,000 kg) than the centrifugation process (1–1.5 m^3 per 1,000 kg) [4]. Although the liquid waste is reduced in the two-phase centrifugation system, large amounts of semi-solid or slurry waste-commonly referred to as two-phase pomace are discharged [3]. The annual world OMW production is estimated from 10 to over 30 million m^3 [5]. OMW is claimed to be one of the most polluting effluents produced by the agro-food industries because of its high polluting load [6]. The high concentration of darkly colored polyphenols in OMW can discolor streams and rivers and can inhibit plant seed germination. In addition, the high concentration of reduced sugars can stimulate microbial respiration, lowering dissolved oxygen concentrations [7]. Therefore, it is widely accepted that OMW treatment is highly necessary. A literature review shows that the currently employed systems for OMW treatment can be classified as biological, physicochemical, and combined processes [8] aiming at either the recovery or the removal of phenolic compounds from the discharging effluents.

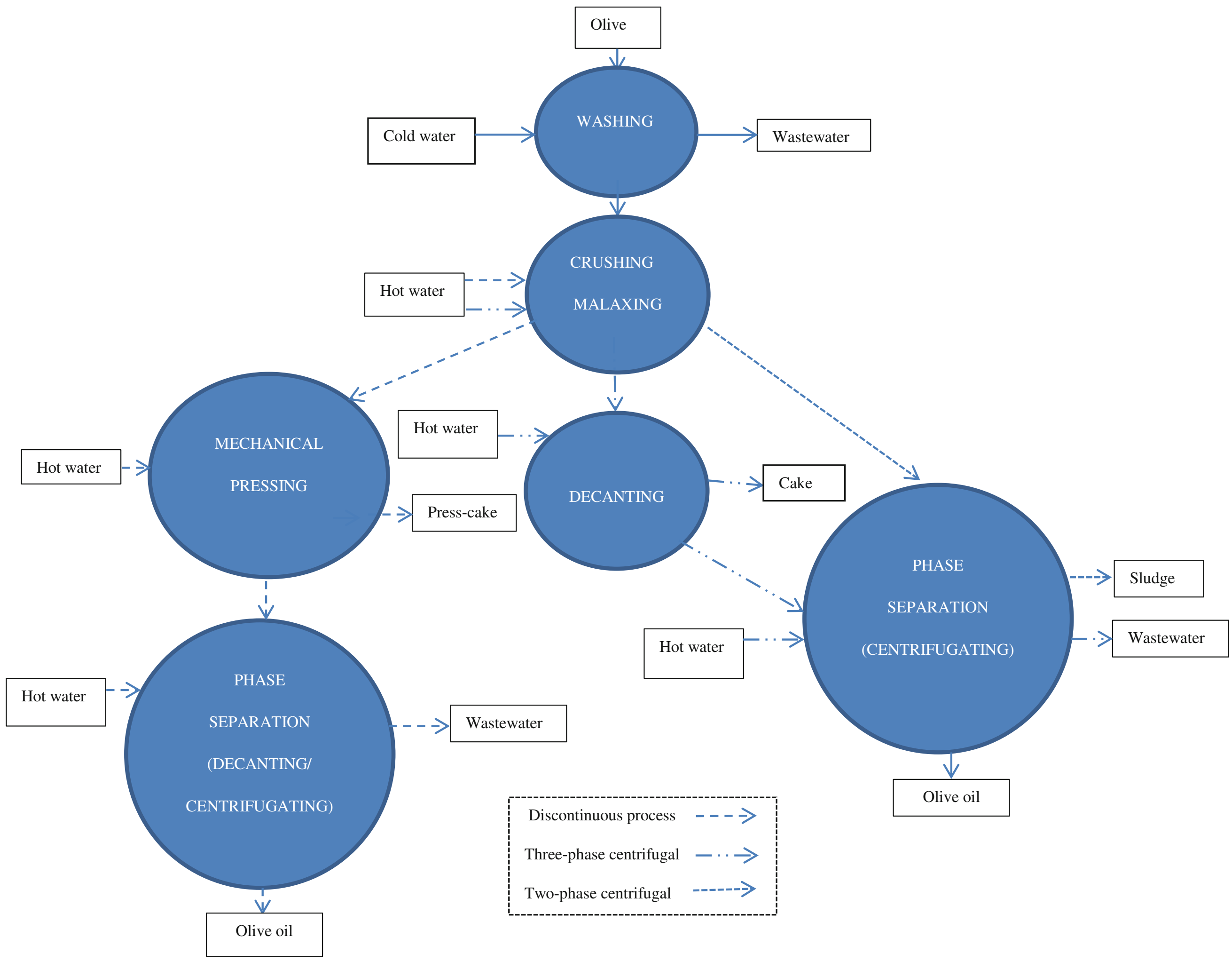

Fig. 1 Olive oil extraction processes

Physicochemical Characterization and Phenolic Composition of OMW

The characteristics of OMW are variable, depending on many factors such as method of extraction, type and maturity of olives, region of origin, climatic conditions and associated cultivation/processing methods [4]. OMW is a dark, acidic matrix made up of water (83–94 %), organic substances (4–18 g/100 g) including carbohydrates (2–8 g/100 g), pectins, mucilage, lignin and tannins (which give it a characteristic dark color [4]) (1.0–1.5 %), lipids (0.03–1.1 %) and inorganic substances[1] (0.4–2.5 %) with physicochemical characteristics which are listed in Table 1. Free sugars account for 1–4.5 g/100 g and comprise glucose, fructose, galactose, mannose and saccharose traces [9–11]. Some of the above compounds have been said to possess advanced functional properties, i.e.. pectin from OMW showed gelling properties that allow their re-utilization as a fat replacement in meat products [12, 13]. However, most importantly, OMW contains phenolic compounds and long-chain fatty acids which are toxic to microorganisms and plants.

Phenolic compounds (that vary from 0.5 to 24 g/L OMW) [4] contain typically about 98 % of the phenols present in olive fruit [14] since only 2 % of them is in the oil phase during extraction process [15, 16]. Phenolics could exist inherently in olive fruit or have been generated during the olive oil production process [17]. Particularly, olive fruit contains phenolic acids and alcohols, secoiridoids and flavonoids, whereas today more than 50 and 40 phenolic compounds have been isolated in OMW and olive oil, respectively [18, 19]. Phenolic acids include *o*- and *p*-coumaric, cinnamic, caffeic, ferulic, gallic, sinapic, chlorogenic,

[1] The range of some important metals in OMW are: Pb (6.7–10 μg/L), Cd (0.03–10 μg/L), Fe (0.45–20 mg/L), Zn (1.7–4.98 mg/L), Cu (0.49–2.96 mg/L), Mn (0.46–20 mg/L), Mg (0.03–0.17 g/L), Ca (0.03–0.29 g/L), K (0.73–6.1 g/L), Cl (0.76–1 g/L), Na (0.03–0.13 g/L).

Table 1 Bibliographic data for the content of olive mill wastewater

Parameter	Unit	Value	References
pH	–	4.7–5.7	[16]
Conductivity	mS/cm	5–41	[16]
COD	g/L	16.5–190	[16]
BOD_5	g/L	41.3–46	[16]
Water	g/100 g	83–94	[121, 126]
Organic compounds	g/100 g	4–18	[121, 122]
Inorganic compounds	g/100 g	0.4–2.5	[121–123]
Total solids	g/100 g	3.2–30	[124]
	g/100 mL[a]		[125]
Fats and oils	g/100 g	0.03–1.1	[126, 127]
	g/100 mL[a]	0.03–2.3	[128, 129]
	g/100 mL[a]	0.02–1.0	[123]
Sugars	g/100 g	1–4.7	[124, 130]
Carbohydrates	g/100 g	2–8	[128]
Pectin	g/100 g	1–1.5	[126, 128]
Total phenols	g/100 mL[a]	0.0002–8	[124, 131]
	g/100 g	0.6–4.0	[127, 132]
	g/100 g	0.5–24	[4]
Nitrogen (N)	g/100 mL[a]	0.03–0.15	[124, 129]
	g/100 g	0.58–2	[127, 128]
Potassium (K^+)	g/100 mL[a]	0.3–0.8	[129, 131]
Phosphorus (P)	g/100 g	0.06–0.32	[127]
	g/100 mL[a]	0.3–1.1	[129]
Calcium (Ca^{2+})	g/100 g	0.32–0.53	[127]
	g/100 mL[a]	0.01–0.08	[129, 131]
Sodium (Na^+)	g/100 g	0.04–0.48	[127]
	g/100 mL[a]	0.01–0.09	[127, 129]
Magnesium (Mg^{2+})	g/100 g	0.06–0.22	[127]
	g/100 mL[a]	0.01–0.04	[129, 131]

[a] The density of olive mill wastewater ranges from 1.01 up to 1.10 g/mL [122]

protocatechuic, syringic, vanillic and elenolic acids [20–23]. The most typical phenolic alcohols are tyrosol and hydroxytyrosol [24, 25]. The qualitative and quantitative HPLC analysis of raw OMW have shown that hydroxytyrosol and tyrosol are the most abundant phenolic compounds [26]. In fact, one liter of crude OMW provides 4 g of dry extract and 1 g of pure hydroxytyrosol [27].

Other phenolic compounds of OMW comprise oleuropein, demethyloleuropein, verbascoside, catechol, 4-methylcatechol, *p*-cresol and resorcinol [28–30]. OMW contain also important amounts of secoiridoid derivatives like di-aldehyde of 3,4-dihydroxyphenyl-elenolic acid, which is bound to hydroxytyrosol. The two latest compounds are generated by the hydrolysis of oleuropein and demethyloleuropein during olive fruit malaxation [31, 32]. More recently, two more secoiridoids have been identified: hydroxytyrosyl acyclodihydroelenolate (HT-ACDE) and comselogoside [33, 34]. Finally, the most important isolated flavonoids are apigenin, hesperidin, cyanidin flavone, anthocyanin and quercetin [15, 17, 35, 36].

Bioactivities of OMW Phenolic Compounds

OMW phenols are well known for their unique antioxidant properties for human health which strongly suggests their re-utilization as additives in foodstuffs and cosmetics [37]. In particular, one of the most established antioxidant activities of OMW phenols is their ability to capture free radicals. This ability has been studied using various radical-generator compounds like reagent DPPH˙ (1,1-diphenyl-2-picrylhydrazyl) [38, 39] or $ABTS^+$ [2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt] [15] or hyperoxide anion [36, 40]. Another antioxidant activity is the scavenging ability against hypochlorous acid (HClO) [41, 42] and the reducing ability of Fe^{3+} or Ferric Reducing/Antioxidant Power-FRAP) [43, 44]. The antioxidant action of phenols has been studied in biological systems (*in vivo*), too. For instance, phenols can inhibit the oxidation of human lipoproteins of low density (low density lipoproteins-LDL) that is associated with atherosclerosis [36, 45–47]. In addition, they can limit the oxidation-destruction of DNA [48–50].

The most bioactive OMW phenols are *o*-diphenols such as hydroxytyrosol, oleuropein and tyrosol [51] since they exert an *in vitro* protective effect against low-density lipoprotein (LDL) oxidation [15, 52] as well as being effective at low concentrations to protect human erythrocytes and DNA against oxidative damages [52]. For instance, several authors have reported studies dealing with rat heart [53, 54] and have shown the cardio-protective effect of oleuropein.

On the other hand, hydroxytyrosol is one of the few nutraceuticals approved by the European Food Safety Authority for its ability to maintain healthy LDL cholesterol levels and lipid antioxidation [55]. The antioxidant ability of hydroxytyrosol has been proven in the plasma and liver of rats [56, 57], while its cardio-protective effect has been successfully assayed in human cells [40]. Besides, Hamden, Allouche, et al. (2009) demonstrated its beneficial effect as a hypoglycemic and antioxidant agent in alleviating oxidative stress and free radicals as well as in enhancing enzymatic defenses in diabetic rats. Indeed, the antioxidant activity of hydroxytyrosol was higher than that of antioxidants such as ascorbic acid and BHT. Moreover, the good solubility of hydroxytyrosol in oil and aqueous media allows its useful application in multi-component foods [52]. For example, lard with olive phenol can be considered as a ''novel food'' that satisfies the modern consumer's demand for natural, safe and healthy food.

Moreover by this application, a significant utilisation of the olive-mill wastewater is proposed [58].

Finally, hydroxytyrosol can be used as a biological fungicides against *B. cinerea*, an ubiquitous plant–pathogen generating grey mold on several economically important vegetable and fruit crops [59].

Olive Mill Waste Water Treatment

Many different processes have been proposed to treat the OMW: lagooning or direct watering on fields, co-composting, physicochemical methods (flotation and settling, coagulation, oxidation using O_3 and Fenton reagent, flocculation, filtration, sedimentation, dilution, open evaporating ponds, and incineration), ultrafiltration/reverse osmosis, chemical and electrochemical treatments and manufacturing into animal food [4, 60, 61].

In an attempt to categorize the proposed methodologies of OMW treatment or processing, three categories can be given:

1. Waste reduction via olive production systems conversion (i.e. 2-phase instead of 3-phase continuous systems).
2. Detoxification methods aiming at the reduction of impact of the pollution load to the recipient.
3. Recovery or recycling of components from OMW.

Table 2 presents a summary of detoxification technologies and their characteristics. Physical processes are typically applied as pre-treatment steps for the removal of solids. Thermal processes target the condensation or destruction of the waste material, but they are ineffective due to the very high operating costs. Although physicochemical methods (neutralization, precipitation, etc.) are relatively cheap, they require further treatment of the waste. On the other hand, the advanced oxidation methods are very effective, but they also have high costs. Besides, the treatment of OMW by a combination of chemical or physical processes and a biological process has not been completely successful, and a longer lag phase has been found to be necessary for biological treatment [62, 63]. In addition, reuse of the OMW by spreading onto agricultural soil as an organic fertilizer has been considered [60].

Conclusively, none of the proposed processes has found a widely accepted application. More recently, researchers have directed their interests to the recovery of valuable compounds and recycling of OMW in order to recapture the treatment cost and find an economically feasible solution. More specifically, OMW are utilized either as a substrate for the growth of microorganisms and the production of fertilizers, bio-products and animal feed, or as a cheap source for the recovery of components that provide high added-value nutrients.

Table 3 summarizes some of the relative processes. The productive of fertilizers is accomplished using biological processes like composting, with or without mixing with other household or agro-industrial wastes. Besides, bio-products generated from OMW include biopolymers, bio-gas, ethanol, microbial polysaccharides (e.g. xanthans) and bio-detergents. These are produced upon the growth of suitable microorganism populations on the waste material, which is usually applied as a substrate. The products are recaptured with several techniques, i.e. ethanol is recovered using distillation.

Recovery and Removal of Phenols from OMW

The most popular high added-value ingredients of OMW are phenols (e.g. simple phenolic compounds, tannins, flavonols, anthocyanins, etc.), while recently, dietary fiber (pectin) has also been investigated (Table 3). Processes of phenols recovery involve typically a condensing step (i.e. thermal concentration, ultrafiltration or lyophilization) prior to the carrying out of sequential extraction steps with organic solvents (e.g. methanol, ethanol or hydro-alcoholic solutions). Other practices include the application of resin chromatography, selective concentration by liquid membranes or supercritical fluid extraction [58]. These processes aim either to recover a particular phenol (i.e. hydroxytyrosol) in pure form or in the recovery of a phenols mixture as a crude product.

Bioactivity-guided fractionation combines the use of bioassay and chromatographic separation for isolation of potent bioactive compounds from highly complex plant extracts, such as OMW [64]. Among different extraction methods, each one with different efficiency and complexity, the liquid–liquid extraction process was preferred for its simplicity and convenience. In order to develop an effective (both qualitatively and quantitatively) extraction, different parameters are optimized: solvent nature, pH of OMW, volumetric ratio between solvent and OMW, number of extraction stages [15]. Direct contact membrane distillation (DCMD), microporous hydrophobic membranes, polyvinylidene fluoride and polytetrafluoroethylene has also been used for OMW treatment, while OMW concentrate may represent a source of high added-value compounds [65].

On the other hand, commercial hydroxytyrosol production from OMW is conducted using the following steps: (1) acid treatment, (2) an incubation process that converts oleuropein to hydroxytyrosol and then (3), a supercritical fluid extraction process and (4) finally freeze-drying [66]. Besides, pure hydroxytyrosol (99.5 %) is produced from OMW using chromatographic columns filled with two resins [67]. The corresponding product is used as a preservative in bakery products. Finally, a more recent commercial methodology reports the recovery of a phenols

Table 2 Treatment technologies of olive mill wastewater

Category	Methodology	Description	Results	Notes	References
Physical	Sedimentation, filtration, flotation, centrifugation	Total solids removal	Total or partial removal of solids, 70 % COD removal, 30 % oil recovery	Common pre-treatment methodology	[133, 134]
	Micro-, ultra-, nano-filtration, reverse osmosis	Separation of compounds (existing in the same phase) according to their molecular weight	99 % COD removal, but membrane fouling	They are applied in series, but the cost is high due to membrane fouling	[135–139]
	Dilution				[4]
	Evaporation				[4]
	Sedimentation (settling)				[140]
	Filtration				[72, 141]
	Centrifugation				[58]
	Adsorption/desorption				[142]
	Solar distillation				[4]
	Combined				[4]
Thermal	Evaporation, distillation	Water removal and waste reduction	20–80 % COD removal, needing additional treatment	High energy demands	[143, 144]
	Combustion, pyrolysis	Decomposition, waste elimination	Toxic gases production and high cost	Very high energy demands	[132, 143]
Physicochemical	Neutralization, precipitation, adsorption	Addition of $FeCl_3$, $Ca(OH)_2$/MgO, Na_2SiO_3, adsorption on activated carbon	30–50 % COD removal	80–95 % COD removal by combining precipitation with adsorption	[93, 104, 145–147]
	Oxidation and advanced oxidation processes	Ozonolysis, wet oxidation, O_3/H_2O_2 photolysis, photocatalysis	40–60 % COD removal using simple oxidation practices	85 % COD removal by combining methods	[118, 148–152]
	Oxidation				[92]
	Wet hydrogen peroxide photocatalytic oxidation				[98]
	Electro-Fenton				[96]
	Ozonation				[101]
	Lime treatment				[130]
	Electrocoagulation				[86, 104, 145]
	Cloud point extraction (CPE)				[90]
	Combined				[15]
Biological	Anaerobic processes	Dilution, nutrients addition and alkalinity regulation	60–80 % COD removal for 2–5 digestion days	90 % COD removal for 25 digestion days	[108, 153–156]
	Aerobic processes	Composting			[4]

Table 2 continued

Category	Methodology	Description	Results	Notes	References
	Aerobic processes	Biofilm, activated sludge	55–75 % COD removal for few days of digestion	80 % COD for longer period	[157–159]
	Mixing and digestion				[4]
	Mixing and digestion	Together with other agricultural wastes	75–90 % COD removal	Nutrients and pH adjustment by combining wastes	[160–162]
	Enzymatic				[1, 97]
Combined	Oxidation and biological processes	2–3 sequential methods	75 % phenols 80–99 % COD removal	High cost due to processes combination	[63, 99, 163, 164]

mixture. In this case, OMW is defatted and concentrated prior to the extraction of phenols using ethanol in combination with an organic acid. Thereafter, separation of phenols and dietary fibers is conducted by precipitation of the latter in condensed ethanol [68]. The phenolic extract is already being used as a healthy additive in chocolates.

Physicochemical Techniques

Membrane (Filtration)

Membrane operations (Table 4) can be considered a valid approach for the selective removal of polyphenols from OMW. Many studies indicate that the future direction of the processes for the recovery of antioxidants from OMW is presumably towards the utilization of membranes in a sequential design [3]. Russo used several microfiltration (MF) and ultrafiltration (UF) membranes to concentrate the recovered polyphenols from vegetation waters (VW), using a final reverse osmosis (RO) consisting of a polymeric hydranautics membrane (composite polyamide). By direct contact membrane distillation (DCMD) process with polytetrafluoroethylene (PTFE) membranes, El-Abbassi et al. [186] were able to separate polyphenols from OMW by ~100 % after operating DCMD for 8 h. Cassano et al. [69] have used UF membranes with regenerated cellulose membranes and an enhancement of the polyphenols in the permeate stream was observed in comparison with the feed solution. Fluoropolymer membranes are also known to separate successfully hydroxycinnamic acid derivatives from anthocyanins and flavonols in both streams [70]. Nanofiltration (NF) and reverse osmosis (RO) processes have been proposed alternatively to concentrate specific phenol classes [71], although corresponding separation of phenolic classes was not so successful as in the case of UF membranes. Besides, a 25-kDa polysulfone UF membrane has been applied to partially remove the heavier fragments of hydroxycinnamic acid derivatives and flavonols, and simultaneously to sustain the antioxidant properties of a phenol containing beverage derived from OMW [72]. Garcia-Castello et al. [189] used a system including MF and NF, osmotic distillation [73] and vacuum membrane distillation (VMD) to recover, purify and concentrate polyphenols from OMW. In this case, 78 % of the initial content of polyphenols was recovered in the permeate stream. El-Abbassi et al. [188] was able to achieve a less dark (88 %) permeate by rejecting 74 % of polyphenols using (as) Micellar Enhanced Ultrafiltration (MEUF) in the presence of an anionic surfactant [sodium dodecyl sulfate salt (pH < 2)] and (b) a hydrophobic polyvinylidene fluoride (PVDF) membrane. According to their study, MEUF process can be efficiently applied for the treatment of

Table 3 Processes for the generation of products and the recovery of valuable compounds from olive mill wastewater

Product type	Process	Description	Notes	References
Fertilizers	Bio-fertilization	Bacteria (Azotobacter) degrade phenols, sugars and organic acids generating nitrogen compounds and N_2	A prerequisite for the fertilizer is that it contains nutrients and lower amounts of phyto-toxic compounds (phenols)	[165, 166]
	Composting	Controlled aerobic degradation along with other agro-industrial wastes	At least 2 months are necessary	[167–169]
Bio-products	Bio-polymer production	Production of exo-polysaccharide and polyhydroxy alkanides (PHA) of specific microbial cultures	Polysaccharides (pullulan, xanthan) possess advanced rheological properties and PHA are appropriate for bio-degraded plastics	[165, 170–172]
	Bio-detergent production	*Pseudomonas* sp. cultures are used in order to produce Raman-lipids	Sequentially, waste is diluted and $NaNO_3$ is added	[173, 174]
	Biogas production	Gas of CH_3OH/CH_4 is produced by anaerobic fermentation of organic compounds (up to 80 %). Theoretical yield equal to 37 m^3 CH_3OH/m^3 of waste	The real yield is much lower due to the toxicity of the phenols	[175–177]
	Ethanol production	Conversion of polysaccharides to simple sugars and ethanol	Recovery of generated ethanol is achieved via distillation	[178, 179]
Animal feed	Components processing	Drying and chemical treatment with $NaOH–NH_3$ targeting the conversion to a digestible substrate	Potassium and phenols concentration reduction is demanded	[180]
High added-value compounds	Pectin recovery	Insoluble residue to ethanol is recovered prior pectin separation from rest polymers	Recovery of pectin with advanced gelling properties that can be applied as fat replacement in meat products	[12, 13, 68, 72, 181, 182]
	Antioxidants recovery (phenols, tannins, flavones, flavonoids, anthocyanins, etc.)	Pre-treatment with membrane technology prior to sequential extraction steps with organic solvents or resin/activated carbon adsorption or liquid membranes	Important parameters include pH adjustment, solvent type, solvent/waste ratio and number of stages for the recovery and the clarification of antioxidants	[36, 87, 90, 128, 183–185]

OMW and the recovery of polyphenols in the concentrate stream. On the other hand, Reis et al. [74] used hydrophobic polypropylene membrane contactors with Cyanex 923 for the recovery of phenol from aqueous solutions. Thus, the use of 2 % Cyanex 923 allowed the almost quantitative recovery of phenols (97–99 %) in 5–6 min (contact time) from single solute solutions as well as their mixtures.

Conventional physicochemical technologies like MF, UF, NF and RO are generally assumed as being safe and cheap since most of them have been widely applied in different food industry and potable water sectors [37, 75, 76]. However, the cost of the process is governed directly by fouling and restrictions in the cleaning procedure. Thus, MF has been proposed as the critical step of the process [32]. MF and UF permeates or RO concentrate can be used as functional integrators or in pharmacologic compositions.

Adsorption

A physical adsorption method (Table 5) is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic compounds [77]. For instance, 95 % removal of phenolic compounds was achieved using sand filtration and subsequent treatment with powdered activated carbon in a batch system [78]. On the other hand, the recovery yield was lower (60 %) using a solid phase extraction, by employing Amberlite XAD16 resin as the adsorbent and ethanol as the biocompatible desorbing phase [79]. Bertin et al. [190] suggested that Amberlite XAD7, XAD16, IRA96 and Isolute ENV+ are the four most promising adsorption resins. Considering the integrated adsorption–desorption processes, ENV+ achieved the highest recovery of total phenols from OMW when elution was performed with acidified ethanol. Indeed, the highest recovery of hydroxytyrosol (77 %) was achieved when non-acidified ethanol was used as the desorbing phase. Nevertheless, when the recovery of phenols is carried out with ENV+, the protocol has to be adjusted from time to time. Considering the study conducted by Ferri et al. [191], the highest phenol adsorption (76 %) was achieved using IRA96 polar resin. Conversely, non-polar adsorbents allowed higher desorption ratios. A purified olive extract rich in phenolic and oleosidic compounds was prepared from OMW by adsorption onto an amphoteric polymer resin. The corresponding yield was 2.2 % (w/v).

Table 4 Summary of membrane techniques for OMW treatment

Membrane technique	Results	References
Direct contact membrane distillation/polytetrafluoroethylene membranes	100 % phenol separation	[186]
Ultrafiltration membranes with regenerated cellulose membranes/nanofiltration/reverse osmosis	0.5 and 30 g/L total polyphenols concentrated	[71]
Liquid membrane with 2 % Cyanex 923	90–97 % phenol was extracted	[187]
Micellar enhanced ultrafiltration/anionic surfactant (sodium dodecyl sulfate salt, SDS)/hydrophobic polyvinylidene fluoride membrane	74 % polyphenols was rejected	[188]
Nanofiltration/microfiltration/osmotic distillation osmotic distillation/vacuum membrane distillation	Recovery of 78 % the initial content of polyphenols	[189]
Filtration/lime treatment	For 1 % lime concentration 60 % phenol reduction and for 2 % lime concentration 63 %	[26]
Microfiltration/ultrafiltration/reverse osmosis consisting of a polymeric hydranautics membrane	Retentate containing 464.870 mg/L free low MW polyphenols	[137]

Table 5 Summary of adsorption technique for OMW treatment

Adsorbent	Results	References
Granular activated carbon (GAC)	Polyphenols 3.23 % matrix	[142]
Amphoteric polymer resin	99 % hydroxytyrosol was absorbed	[14]
Amberlite XAD16 resin/ethanol	Recovery of 60 % polyphenols	[79]
Amberlite XAD7, XAD16, IRA96/Isolute ENV+	Recovery of 77 % hydroxytyrosol	[190]
IRA96 polar resin	76 % phenol was adsorbed/60 % phenols recovered	[191]
Banana peel	Increased the phenolic compounds adsorption rates from 60 to 88 %	[77]
Powdered activated carbon	Removal of 95 % of the phenolic compounds	[78]
Liquid chromatography	Recovery of phenolic compounds 90–100 %	[192]

Ena et al. [142] stated that granular activated carbon can be more efficient than Azolla (vegetable matrices) in terms of phenols adsorption and desorption. The recaptured powder contained hydroxytyrosol in concentrations 3.5-fold higher than those of Azolla (3.23/1.51 % matrix). Singh et al. [80] investigated the adsorption of both phenol and 2,4-dichlorophenol through the acid treatment of coconut shells (ATSAC) and the results show higher monolayer adsorption capacity for both compounds. Achak et al. [77] used banana peel as a low-cost solution biosorbent for removing phenolic compounds from OMW. According to the results, by increasing banana peel dosage from 10 to 30 g/L, phenolic compounds adsorption was significantly increased from 60 to 88 %. Desorption studies showed that a low pH value was efficient for the desorption of phenolic compounds.

Zeolite, compared to other substrates (clay soil and bentonite), appeared to be a useful mineral in reducing the organic load of OMW. In addition, the regeneration of zeolite was easy after treatment either by simple settling or light centrifugation procedures. Besides, the low temperature ashing-procedure appears to be a very interesting eco-friendly technique since it is capable of reducing polyphenols and COD from OMW [81].

Extraction

Conventional solvent extraction conditions (i.e., pH value, time, solvent type, and concentration) can be very critical for the activity of phenolic extracts obtained from OMW [73]. Phenols include one or more hydroxyl groups (polar part) attached directly to an aromatic ring (non-polar part) and are often found in plants as esters or glycosides, rather than as free molecules [82]. This stereochemistry distinguishes them according to their polarity variance. For example, phenols are generally solubilized easier in polar protic media like alcohols (ethanol and methanol), but gallic, cinnamic and coumaric acids prefer water, dichloromethane and acetone, respectively. For this reason, recovery of phenols is proposed to be carried out initially with a polar protic solvent (hydro-ethanolic mixture) prior to progressing sequentially extraction steps with solvents of reducing polarity, with a final purpose of separating the target compounds in each case [83, 84]. Indeed, hydro-ethanolic mixtures have been selected as the most appropriate solvents for the extraction of phenolic compounds from OMW due to their food grade nature. Besides, a hydroethanolic mixture of 85 % ethanol has been shown to preserve phenol compounds and antioxidant activities for 18 weeks [85]. Takaç and Karakaya [3] used ethanol up to 70 % and an organic acid in the range of 0.5 % to 3 % to extract polyphenols from OMW. Other

Table 6 Summary of extraction, oxidation, and coagulation techniques for OMW treatment

Technique	Classification	Results	References
Extraction	Liquid–liquid extraction/ethyl acetate	Recovery of over 90 % phenolic molecules	[15, 27, 58]
		Recovery of 85.46 % hydroxytyrosol	[193]
	Cloud Point Extraction (CPE)/Genapol X-080	Total phenol recovery was 89.5 %	[90]
	Cloud Point Extraction (CPE)/Triton X-114	Phenol recovery rates (from the water phase) was higher than 96 %	[89]
Oxidation	Fenton-like reaction using FeCl3 as catalyst	Removal of 99.8 % of total phenols	[194]
	AOPs (O_3/UV, H_2O_2/UV)	Over 99 % phenol removal	[93, 94]
	Photo-Fenton	100 % phenols reduction	[99]
	Photo-Fenton	Removal of 97.44 % total phenolic compounds	[95]
	Wet hydrogen peroxide photocatalytic oxidation (WHPCO)	Reduction of 86 % caffeic acid and 70 % hydroxytyrosol	[98]
	Ozonation process	80 % phenol removal	[195]
Coagulation	Electrocoagulation/NaCl	Removal of 97 % phenol	[103]
	Electrocoagulation/aluminium electrodes	Removal of 91 % polyphenols	[104]

studies [15, 27, 58] reported that ethyl acetate is the most convenient solvent for the extraction of low and medium molecular weight phenolic monomers, as a corresponding recovery percentage of up to 90 % [86]. High yield (85.46 %) recovery of hydroxytyrosol from OMW has been achieved using a three-stage continuous counter-current liquid–liquid extraction unit. In this case, hydroxytyrosol was extracted at 1.225 g/L of OMW [87]. More studies showed that super critical-CO_2 extraction can be an efficient technology for the recovery of phenolic compounds from OMW with relatively high antioxidant activity [73]. For instance, it has been deduced that OMW storage facilitates the continuous extraction procedure and improves the extraction yield of hydroxytyrosol from 85.5 to 96.8 % [88].

Cloud point extraction methodology is a clean technology since it only requires 4–12 % surfactant volumes of the liquid sample. This procedure is a useful tool for the pre-concentration of phenolic compounds [89]. Total phenol recovery by simple and successive cloud point extraction of OMW with Genapol X-080 was up to 89.5 %. The complete recovery of tocopherols has also been shown to be possible with this technology [90]. Katsoyannos et al. [89] was able to achieve individual phenol recovery rates (from the water phase) higher than 96 % with one or more successive cloud point extraction steps using a total of 4–6 % Triton X-114 (Table 6). Other emerging technologies (i.e. laser ablation, high voltage electrical discharge and pulsed electric field) applied to the extraction of nutraceuticals from agricultural wastes [91] have not been studied for the case of OMW yet.

Oxidation

The advanced oxidation processes (AOPs) (Table 6), which promote the formation of highly oxidizing species such as hydroxyl radical ($OH^{\cdot}$), have been successfully investigated for the removal of a wide variety of recalcitrant or toxic compounds and the improvement of biodegradability. Moreover, iron-based coagulation coupled with H_2O_2 (thus simulating a Fenton[2] reaction) was investigated as a pre-treatment step of OMW with a final aim of enhancing organic matter degradation. Due to the acidic pH value of OMW and the satisfying efficiency in phenols removal, Fenton and Photo-Fenton processes have been considered as proper technologies for OMW treatment. Photocatalysis is an AOP that has been applied in water and wastewater treatment to remove organic and inorganic pollutants as well as for system disinfection [92]. AOPs (O_3/UV, H_2O_2/UV) remove over 99 % of both COD and total phenols, while a sludge without color is generated [93, 94]. The technique entitled "photo-Fenton" is a homogeneous photocatalytic oxidation or a heterogeneous photocatalytic oxidation using a UV/semi-conductor catalyst (such as TiO_2, ZrO_2 and FAZA). Under the optimum conditions, the photo-Fenton process can achieve COD, TOC, lignin (total phenolic compounds) and total suspended solids (TSSs) removal values of 87, 84, 97.44 and 98.31 %, respectively [95]. The electro-Fenton [96–98] approach is conducted either by adding ferrous iron or by reducing ferric iron electrochemically with a simultaneous

[2] Fenton oxidation is achieved from the reaction between H_2O_2 and a ferrous salts under acidic conditions according to the following reaction:

$Fe_2^{+} + H_2O_2 \rightarrow Fe3^{+} + OH^{-} + OH^{\cdot}$ [1]

The UV radiation can improve the Fenton reaction, according to the reaction [2]:

$H_2O_2 + h\_ \rightarrow 2OH^{\cdot}$ [2].

Table 7 Biological techniques for OMW treatment

Technique	Classification	Results	References
Anaerobic and aerobic	*Rhodotorula mucilaginosa* CH4 and *Aspergillus niger* P6	Removal of 83.45 % and 94.58 % polyphenolic compounds respectively	[196]
	Two-phase anaerobic digester reactors	Phenol removal 70–78 %	[109]
	Aerobic treatment/ cheese whey's (CW), *Lactobacillus paracasei*	22.7 % phenol reduction	[111]
	Aerobic treatment/ pre-treatment by *Candida tropicalis*	Biodegradation of 54 % phenol	[110]
Enzymatic	Laccase of *Trametes versicolor*	Reduction of 89 % polyphenols	[197]
	Laccase of several *Pleurotus* spp. strains	Removal of 69-70 % phenolic compounds	[115]
	Laccase from the white-rot fungus *Lentinula edodes*	Reduction of 90 % polyphenols	[113]
	Phenol oxidase produced by the white-rot basidiomycete *Pleurotus ostreatus*	Reduction of 90 % polyphenols	[112]

production of H_2O_2 upon the reduction of O_2 on several electrodes.

It has been reported that phenols are removed more efficiently by photo-Fenton treatment than by biological or enzymatic treatments. For instance, treatment by laccase was able to reduce 4–70 % of phenols whereas treatment by photo-Fenton oxidation was responsible for 100 % phenols reduction [99].

Important percentages of phenol abatement after the wet hydrogen peroxide photocatalytic oxidation (86 % for *o*-diphenols and 70 % for caffeic acid and hydroxytyrosol) have been achieved in 24 h [98]. A complete abatement of the toxicity was achieved when the catalytic treatment effectively reduced the concentration of monomeric phenols [100].

Phenolic compounds present in OMW react strongly with ozone. Ozonation is more selective than advanced oxidation processes [101]. Karageorgos et al. [199] were able to achieve phenol and color removal of more than 80 % in OMW treatment. Moreover, a fast and selective degradation of phenols was described due to the direct electrophilic attack by molecular ozone (ozonolysis).

Coagulation

Electrocoagulation (Table 6) is based on the *in-situ* formation of the coagulant as the sacrificial anode corrodes due to an applied current. Simultaneously, hydrogen evolution at the cathode allows the pollutant removal by flotation [102], while several parameters like pH, operating time, current density, initial phenol concentration and NaCl addition play a significant role. Phenol removal during electrocoagulation has been achieved due to the combined effect of sweep coagulation and adsorption [103]. Consequently, electrocoagulation is considered as a suitable alternative technology to existing methods or it can be applied as a pre-treatment step of a biological process for OMW treatment. Besides, the application of electrocoagulation with aluminium electrodes permitted higher removal of pollutants (76 % COD [102], 91 % polyphenols and 95 % of dark color) by assaying either fresh or stored OMW, just after 25 min treatment [104]. Nevertheless, optimum removal was obtained after 15 min treatment after the addition of 2 g/L NaCl to the wastewater and the application of 250 A/m^2 as current density [102]. Results showed that a remarkable phenols' removal (97 %) can be reached after 2 h of treatment at high current density and solution pH 7. Indeed, the maximum removal rate was attained at 30 mg/L phenol concentration [103].

Biological Techniques

Since phenol removal (particularly the low biodegradable lignin-like polymer) meets several problems with conventional treatment methods (chemical coagulants, hydrogen peroxide and filtration), biological processes (Table 7) have been alternatively suggested to be more appropriate [1, 105]. Thereby, a number of different microorganisms (Archaea, Bacteria and fungi) and processes (aerobic or anaerobic bioreactors, composting) have been tested to treat OMW. Aerobic bacteria have been primarily assayed as an approach for the removal of phytotoxic compounds. On the other hand, fungi have proved to be effective for COD and toxicity elimination [7]. Nevertheless, yeasts strains show higher concentrations than fungi and bacteria in OMW. For example, among the 105 yeast strains isolated from OMW, around 20 are able to grow on all kinds of OMW [106]. Selectivity of microorganisms can be obtained following the consumption of total phenols and total organic load. Thereby, the most effective yeast strains have been shown to be in the following sequence: *Phanerochaete chrysosporium* > *Aspergillus niger* > *Aspergillus terreus* [107].

Anaerobic and Aerobic

Anaerobic digestion [108] is a complex process consisting of a series of microbial transformation of organic materials into methane and volatile fatty acids such as acetate, propionate, butyrate, isobutyrate, valerate and isovalerate [86]. Generally, it can reduce COD, but it is sensitive to phenolics. Thereby, anaerobic digestion cannot deal with the high organic load of OMW yet and it needs to be diluted several times prior to treatment. The latest parameter increases the cost dramatically and has environmental implications. Besides, the presence of some inhibitors and toxic compounds (i.e. polyphenols and lipids) makes OMW inappropriate for direct biological treatment. Thus, pretreatment methods aimed at decreasing the concentration of phenolics have been developed in an effort to make OMW more amenable to anaerobic digestion [60, 96].

For instance, OMW pretreatment with sand filtration and activated carbon can partially remove phenols [78]. Alternatively, by using two-phase anaerobic digester reactors operated at mesophilic temperature, phenol and color removal efficiencies accounted for 70–78 % and in 24–55 %, respectively [109]. On the other hand, aerobic digestion can degrade phenols by 45 and 23 %, when whey is used as a co-substrate, yeast *Candida tropicalis* [110] or *Lactobacillus paracasei* [111] is selected, respectively.

Enzymatic

As is well known, white rot basidiomycetes are the most efficient lignin degraders by means of oxidative reactions catalyzed by phenol oxidases and peroxidases [1, 112]. The treatment of OMW with immobilized laccase from the white-rot fungus *Lentinula edodes* led to a partial decolorization as well as to significant polyphenols reduction (90 %) [113]. Another white-rot fungus *Panus tigrinus* CBS 577.79 was used to remove organic load, color and phenols from OMW and the results showed that 4-hydroxy-substituted monophenols were completely removed [114]. Treatment of OMW with purified phenol oxidase produced by the "white-rot" basidiomycete *Pleurotus ostreatus* showed a significant reduction in phenolic content (90 %), too, but no decrease in its toxicity was observed by applying *Bacillus cereus*. Otherwise, OMW processing with the entire microorganism resulted in a noticeable detoxification with concomitant abatement of the phenol content [112]. High laccase activity of several *Pleurotus* spp. strains caused ~70 % phenols reduction, while the color changed from black to yellow. However, the remaining phenols and some of the laccase oxidation products were more toxic than the original phenolic compounds [115]. The use of *Trametes trogii* broth culture showed an oxidation of phenolic compounds due to its high laccase activity. Contrarily, *Funalia trogii* demonstrated the best production of laccase (27,000 U/g), whereas *Trametes versicolor* appeared to be a good pollutant degrader by reducing phenols by up to 87 %. Finally, Bouzid et al. [52] performed an enzymatic treatment (Table 7) [107, 113, 116] (culture broths of *Aspergillus niger* enriched in cinnamoyl esterases) in order to release large amounts of free hydroxytyrosol from OMW. Particularly, they recovered hydroxytyrosol (1.4 g/kg dry OMW) with a purity of 85 % using a two-step chromatographic treatment with HP-20 resin and Sephadex LH-20.

Table 8 Summary of combined techniques for OMW treatment

Technique	Results	References
Pleurotus sajor caju and *Trametes versicolor,* adsorption, biodegradation, diffusion	Reduction of total phenolic content from 85.3 to 88.7 %	[198]
Photocatalytic degradation (TiO_2) and adsorption processes (powdered activated carbon sorbent)	Removal of 87 % of total polyphenols	[120]
Electro-Fenton, anaerobic digestion, ultrafiltration	Removal of 95 % monophenolic compounds	[96]
Filtration, adsorbent resins (XAD16 and XAD7HP), evaporation	Reduction of 99.99 % polyphenols	[199]
Settling, centrifugation, filtration and activated carbon adsorption	94 % phenol removal	[4]
Electro-Fenton process, anaerobic digestion	Reduction of 100 % total polyphenolic compounds	[200]
Lime treatment, coagulation/flocculation/ sedimentation/filtration	62–73 % phenol removal	[4]
Phanerochaete chrysosporium, ultrafiltration	Depolymerization	[201]
Anaerobic digestion, ozonation	Reduction of total phenolic compounds	[202, 203]
Ozone-UV radiation	Disappearance of total phenolics	[119]

Combined Techniques

Combined techniques are applied in order to maximize phenols removal, but on the other hand the increasing number of steps can dramatically increase the total cost of the applied process. Thereby, the combination of settling, centrifugation, filtration and activated carbon adsorption (Table 8) leads to a maximum phenol (94 %) and organic matter (83 %) removal [4]. Combination of biological and

UV/O_3 oxidation process (advanced) has also been applied to reduce COD [8]. Catalytic wet oxidation and microbial technologies [(Al–Fe) PILC/H_2O_2], the system operating at 50 °C reduced considerably the COD, color and total phenolic contents in another approach [117]. Besides, oxidizing agents such as monosulfuric acid and MnO_2 have been proposed as enhancing phenol removal from OMW [104].

Khoufi et al. [200] demonstrated that the electro-Fenton process removed total phenols by ~ 66 % and subsequently decreased OMW toxicity by up to 100 %. The latest process improved the performance of anaerobic digestion. Later, Khoufi et al. [96] developed a process on a pilot scale for the treatment of OMW by combining electro-Fenton, anaerobic digestion and ultrafiltration. Application of the electro-Fenton procedure in semi-continuous mode permitted high removal monophenolic compounds (95 %). The use of ultrafiltration technology as a post-treatment can completely detoxify the anaerobic effluent and subsequently remove phenols of high molecular mass. An economic calculation of this treatment revealed that a surplus of energy of 73.5 kWh can be recaptured after the treatment of 1 m^3.

In another study, the combination of ozonation and aerobic degradation for the treatment of OMW was investigated, and an improvement in the removal of the organic material was obtained [118]. Treatments with UV in combination with ozone–UV radiation [119] caused the destruction of OMW-organic material, which was followed by the disappearance of the COD and total phenols. Duarte et al. [198] suggested a three-step process (adsorption, fungal biodegradation, and diffusion of the biodegraded products. *Pleurotus sajor caju* and *Trametes versicolor* were applied, while the second biocomposite was the most effective and responsible for the reduction in color (up to 45 %), COD (up to 64 %), and total phenols (up to 89 %) after 29 days of treatment. Lime treatment on various OMW after a classic coagulation/flocculation/sedimentation/filtration process, resulted in 62–73 % phenol removal depending on the process used for olive oil extraction. More than 40 % COD and 95 % oil removal were also observed [4]. Agalias et al. [199] has investigated the treatment system of OMW consisting of three main successive sections: filtration, adsorbent resins (XAD16 and XAD7HP) and thermal evaporation. The results of these procedures was an odorless yellowish OMW with a quantitative removal of phenols and COD, an extract rich in polyphenols and lactones with high antioxidant activity. The latter contained coloring substances of the olive fruit, and pure hydroxytyrosol. The synergetic effect between photocatalytic degradation (TiO_2) and adsorption processes (powdered activated carbon sorbent) at a medium phenolic concentration caused the removal of the latter compounds by 87 %, compared to 58 % COD removal after 24 h exposure to 365 nm UV light [120]. Finally, Ceccon et al. [192] acidified OMW to pH 2 in order to precipitate proteins. Thereafter, acetone and hexane were added to eliminate the colloidal fraction and lipidic substances, respectively. Finally, filtering and injection through a liquid chromatography system led to the recovery of 9 individual phenolic compounds ranging from 20 to 2,000 mg/L.

Conclusion

OMW represents a relevant source of biophenols having a wide range of biological activities. This literature review shows that the recovery of important phenols is possible by physicochemical processes such as membrane techniques and resin adsorption. Biosorbents such as banana peel and coconut shell can be used for this purpose, too, since they are available as a cheap source along with extraction processes. The combination of different physicochemical techniques (especially the physical ones) can cause a high level of phenol recovery. Biological processes are useful for the removal of phenols although they are typically applied as a pretreatment method. Oxidation and coagulation methods can remove phenols, too. Following the high importance of phenolic compounds which are abundant in OMW, researchers should pay more attention to recovering them from OMW using economically feasible and environmental friendly techniques.

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