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Recovery and Concentration of Antioxidants from Industrial Effluents and from Processing Streams of Underutilized Vegetal Biomass

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Abstract The research on alternative sources of natural food antioxidants has been incentivized by the contradictory information available on the safety of synthetic antioxidants and the biological properties of the natural ones. In this field, the utilization of abundant, biorenewable and low cost sources (for example, waste fractions from agricultural and industrial activities and the underutilized forestal and marine algal biomass) has attracted a special interest. The efficient utilization of these raw materials by methods involving environmentally friendly technologies has become a major target. In this study, the role of separation methods based on membranes and/or resins for the concentration and recovery of different fractions with antioxidant properties (ascribed to phenolics, soluble proteins and/or oligosaccharides) from liquid effluents obtained by processing residual and underutilized vegetal biomass is reviewed.

Keywords Vegetal biomass, Antioxidant, Membranes, Resins

1. Introduction

The increasing consumer demand for natural food additives and ingredients has incentivated the search for different sources of bioactive compounds. Antioxidants are one of the additives which have attracted more attention in last decades. A vast number of plants, food and food wastes have been screened for potential antioxidant activity. Most studies have been focused on the identification of bioactive components, with special emphasis on those of phenolic nature. Lignocellulosic materials (for example, agricultural and forestal wastes) and seaweeds are renewable and cheap sources of bioactive compounds, and their fractionation could be a valuable approach to the sustainable development principle. For this purpose, the development of environmentally friendly extraction and purification processes, using non toxic and food grade solvents, is necessary.

Pressurized solvents can be seen as a potential tool to extract bioactive natural components from biomass selectively. Autohydrolysis is an environmentally friendly method for lignocellulose fractionation, and leads to liquid phases containing valuable components which can be concentrated and/or recovered using separation technologies based on the utilization of membranes and/or resins. Related processing schemes can be used to recover phenolic, proteic and saccharidic fractions from industrial waste effluents.

This review provides an overview on the literature dealing with the extraction, concentration and purification of bioactive components with antioxidant properties, using wastes or underutilized biomass as feedstocks. Some extraction stages are performed using hot, compressed water, and special interest is paid to concentration and refining stages based on the utilization of membranes and food-grade resins.

2. Interest of Natural Antioxidants from Low Cost Sources and from Underutilized Biomass

2.1. Reactive Species and Antioxidants

Several reactive oxygen species (ROS), including both free radicals (such as superoxide radical and hydroxyl radical) and non-free radical species (such as hydrogen peroxide), are known to cause oxidative damage[1]. ROS not only induce lipid peroxidation causing rancidity and shelf-life reduction of foods, but also cause oxidative damage by oxidizing biomolecules (DNA, proteins and small cellular molecules).

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Because of this, ROS are believed to play a significant role in the occurrence of diseases such as atherosclerosis, diabetes, cancer, cirrhosis and Alzheimer's disease[2, 3].

Even though synthetic antioxidants are widely used in the food, cosmetic and pharmacy industries, the concern about their safety has boosted the interest in natural antioxidants, which are presumed to be safer and may offer a simpler and effective way to scavenge free radicals and reactive species, thereby reducing oxidative stress and associated damage. Various health claims have been made regarding the use of natural antioxidants[4], which can act at different levels in an oxidative sequence, protecting foods against lipid oxidative damage during processing, storage and cooking[5], and exerting beneficial health effects that may make them suitable for therapeutic use[6,7].

2.2. Low Cost Sources of Natural Antioxidants

Waste streams or vegetal byproducts from the food, agricultural and forestry sectors could be regarded as biorenewable sources of valuable components, which can be used in the food, cosmetic and pharmaceutical sectors. These feedstocks have the additional advantages of being widely distributed, largely available and inexpensive, particularly when they are geographically concentrated and their uncontrolled disposal would create environmental problems. A number of cheap and widely distributed sources of antioxidants, particularly those of phenolic nature and residual origin, are under research[8, 9]. Some oligosaccharides, peptides and protein hydrolysates also exhibit antioxidant activity.

Phenolic compounds have been identified in a number of agroindustrial by-products, including, barley husks[10], coconut husks[11], potato peel[12], sunflower shells[13] and litchi seeds[14]. By-products from the olive industry such as mill wastes[15] and olive leaves[16] have been considered as a source of phenolics. Residues from grape juice and winemaking[17] also present antioxidant activity; whereas fruit wastes and byproducts such as apple pomace[18], banana peel and pulp[19], peach and pears peels[20] and mango peels[21] contain valuable phenolics. Seaweeds, and particularly their phlorotannin fraction, have been proposed as a source of highly active antioxidants[22]. Wheat bran [23-25], corn fiber[25], and marine red algae[26] are natural sources of antioxidant oligosaccharides. Antioxidant activity has been detected in hydrolysates of plants containing proteins or protein hydrolysates, as it has been reported for zein protein[27], whey protein[28], and hydrolysates of peanut[29] and rapeseed[30].

2.3. Antioxidant properties of Phenolics, Peptides, Proteins and Oligosaccharides

In recent years, the activities of natural antioxidants in different oxidative systems have been identified and characterized, including abilities as inhibitors of lipid peroxidation, scavengers of free radicals and chelating agents for transition metal catalysing the generation of radical species[31, 32].

In general, antioxidants can act by mixed mechanisms, and their activity depends on the assay considered[31, 33]. The antioxidant activity depends on the type of substrate, the medium, initiators, oxidation conditions, the partitioning properties of the antioxidant between lipid and aqueous phases, and on the specific method used. The need of simple and reliable tests to evaluate the in vitro antioxidant capacity is generally recognized, and also keep in mind that the antioxidant capacities obtained in individual tests can be contradictory. Several classifications of antioxidants assays have been proposed, based on mechanisms such as ability to quench free radicals by hydrogen donation, ability to transfer one electron, or a combination of both[31]. Measurement of the reducing capacity and a test based on radical scavenging are recommended, whereas the protection of oil oxidation (in bulk phase and in emulsions) also provides valuable information, particularly for food and cosmetic applications. *In vitro* experiments are very useful for preliminary assessment of various extraction and purification conditions, but the results can be hardly extrapolated to the complex *in vivo* systems, where absorption, distribution, metabolism and excretion have also to be considered.

The structure of phenolic compounds is a key factor determining their abilities to scavenge free radicals, to donate hydrogen atoms or electrons, or to chelate metal cations. The reducing power and radical scavenging capacities of extracts from olive tree pruning[34] and wood[35] were concentration dependent.

Olive mill wastewaters have been identified as a promising source of antioxidants to retard lipid oxidation in fish oil-enriched food products[36]. Pereira de Abreu et al.[37] evaluated the effectiveness of a new active packaging film containing natural antioxidants from barley husks that retard lipid damage in frozen Atlantic salmon. Phenolic extracts from natural sources exhibit a wide range of physiological properties, including anti-allergenic, anti-artherogenic, anti-inflammatory, anti-microbial, anti-thrombotic, cardioprotective and vasodilatory effects [9].

Proteins and peptides show an excellent potential as antioxidant food additives, and are known to possess a wide range of biological properties, including antihypertensive, immunomodulatory, antithrombotic, anti-cancer, and antimicrobial activities[32]. The antioxidant activity of native proteins depends on the processing conditions employed in isolation[38]. The oxidative stability of protein - based emulsions depends on the emulsion characteristics, whereas the chelating and radical scavenging properties of peptides also depend on their structure, composition and hydrophobicity[39]. The peptide size and the amino acid sequence affect the antioxidant properties of protein hydrolysates, as it has been reported for whey protein hydrolysates, for which 0.1-2.8 kDa peptides have been reported to show the strongest radical scavenging activities

against DPPH, hydroxyl and superoxide radicals[28]. Soy peptides with 5-16 amino acid residues (500-2000 Da) display high ability to protect linoleic acid from oxidation [39], whereas a 717.37 Da antioxidant peptide from chickpea protein hydrolysates presented a comparatively high activity[40]. The amino acids Tyr, Met, His, Lys and Trp have been reported to play an important role in antioxidant activity[39, 40]. Rapeseed peptides showed reducing power and ability for scavenging free radicals and inhibiting lipid peroxidation, but presented low ferrous ion-chelating capacity[30]. The effects of protein concentration on the reducing power have been reported for soy protein fractions[38] and for recombinant thioredoxin h protein from sweet potato[41]. The results obtained for three types of free radicals (DPPH, superoxide and hydroxyl) indicated that the antioxidant activity of whey protein isolates[28, 42] was related to their radical quenching capability.

Oligosaccharides are also gaining importance as functional food ingredients, in the pharmaceutical industry, and as feed ingredients, but there is scarce information on their antioxidant activity, which is usually ascribed to the presence of certain functional groups. Chen et al.[43] studied the effect of different functional groups (sulphate, amine and hydroxyl and/or their ionized groups) on the antioxidant capacities of low-molecular weight polysaccharides from starch. Several studies have been reported on the antioxidant behaviour of feruloylated oligosaccharides. Allerdings[44] isolated two oligosaccharides containing feruloyl and p-coumaric arabinosyl esters from maize bran insoluble fibre hydrolysates after purification by GPC and semi-preparative RP-HPLC. The production of feruloylated oligosaccharides from insoluble wheat flour arabinoxylan by enzymatic hydrolysis and their subsequent purification by ion-exchange and SEC has also been reported[45]. This method led to a feruloyl arabinoxylotrisaccharide with high DPPH radical scavenging activity and ability to inhibit the copper - mediated oxidation of human low density lipoprotein. Rose and Inglett[46] employed two autohydrolysis steps to obtain feruloylated arabinoxyloligosaccharides from wheat bran. The liquid phase was purified with ethyl acetate extraction, vacuum concentration and ion exchange to yield a concentrate (containing 32.0% arabinoxylooligosaccharides, 4.8% esterified ferulate and 36% of other oligosaccharides and free sugars) with an antioxidant activity equivalent to 29.7 μmol Trolox/g. Feruloylated arabinooligosaccharides from wheat bran obtained with *Bacillus subtilis* xylanases were active DPPH scavengers[23, 47] and inhibited the *in vitro* hemolysis of erythrocytes induced by peroxyl free radicals (generated from 2.2'-azobis-2-amidinopropane dihydrochloride, AAPH) by 91.7%[23]. Acid hydrolysis of corn fiber released feruloylated oligosaccharides with higher antioxidant potential than ferulic acid[25]. The *in vivo* protective effects of feruloyl oligosaccharides were confirmed by feeding rats with a standard diet supplemented with this type of compounds, after assessing the levels of oxidative stress markers and the activities of antioxidant enzymes[24].

Other hemicellulosic poly- and oligo-saccharides also present antioxidant activity. Galactoglucomannan and its acetylated form from Norway spruce showed DPPH radical scavenging activity[48], as well as the water-soluble components of almond shells[49] and the products of wheat bran autohydrolysis and/or alkaline hydrolysis[50]. Alkaline hydrolysis of corn cobs led to soluble products (containing xylose, arabinose, galactose and glucose in relative proportions 5.0:1.5:2.0:1.2) showing an antioxidant activity equivalent to 48.4 mg of ascorbic acid/g and a high ferric chelating activity[51]. Pristov[52] found that cellulose, pectin, galactomannan, arabinogalactan and xylan exhibit antioxidative activities against the hydroxyl and superoxide radicals, which were was ascribed to the presence of phenolic acids. A mixture of xylooligosaccharides from ragi showed higher DPPH radical scavenging activity and reducing capacity that samples of the same products obtained from rice, maize and wheat; whereas rice xylooligosaccharides presented a better activity in emulsion[53].

The antioxidant activity of commercial acidic and neutral oligosaccharides has been assessed on a comparative basis [54], whereas soybean oligosaccharides reduced the oxidative stress and improved the abnormal blood lipid levels induced by high fat diets[55]. Agarooligosaccharides can permeate across the cell membrane and act as an efficient antioxidant in liver cell, confirming a remarkable potential as antioxidant agents[56]. Carrageenan oligosaccharides from marine red algae and their derivatives showed remarkable antioxidant activity both *in vitro* and in a cell system[26].

2.4. Commercial Applications

Natural antioxidants can be used in food systems to prevent the oxidation of fats, oils and lipid-based foods through several reactions upon both heating and long term storage. Incorporation of bioactive compounds, such as phenolics, peptides, proteins and oligosaccharides, into food systems provide a simple way to develop novel functional foods or nutraceuticals that may provide medical or health benefits, including the prevention and treatment of diseases. Alternatively, active packaging systems can be used for adding antioxidants to foodstuffs. Public health authorities consider the prevention and treatment with nutraceuticals as a powerful instrument for maintaining health and for acting against nutritionally induced acute and chronic diseases, thereby promoting optimal health, longevity and quality of life.

Antioxidant compounds have been found as suitable prophylactic and therapeutic agents for several diseases, but their bioavailability through dietary supplementation depends on the assimilation mechanisms. Skin aging and skin care are target fields for the pharmaceutical and cosmeceutical industries, in which plant-derived antioxidants can play a significant role.

3. Membrane and Resin Technologies

3.1. Membrane Technologies

The concentration of extracts from natural feedstocks containing bioactive compounds is traditionally carried out by high temperature processes involving high energy consumption. In this field, membrane separation processes stand out owing to their advantages, including operation at low temperature, absence of phase transition and low energy consumption[57-59].

Membranes can be defined as semipermeable barriers that separate two phases and restrict the transport of defined components in a selective manner[60]. Membranes allow the passage of certain components while retaining others, enabling the enrichment of the permeate and the retentate in certain components[61]. The transport of components through the membrane is achieved by applying a driving force (concentration gradient, pressure, temperature or electric potential). Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) employ hydraulic pressure as a driving force. MF membranes operate at pressures below 2 bar and separate suspended particles (in the size range 0.025 - 10 μm). UF is carried at 2-10 bar, although in some cases up to 30 bar have been used [75]; and is employed to retain macromolecules and colloids with molar masses between 1 and 300 kDa, while allowing water and small molecules to pass through. NF membranes operate at 10 - 40 bar and can separate particles with molar masses between 0.35 and 1 kDa. RO, performed at 40-100 bar, can retain essentially all solutes in concentrate, including small ions such as sodium[59],[61].

3.1.1. Membrane Characteristics

The efficiency of a membrane is determined by the flux and the selectivity[60]. The flux or permeation rate (J) is defined as the volume flowing through the membrane per unit of area and time. Fluxes in liquid filtration are typically reported in $L/m^2 \cdot h$.

The selectivity is generally expressed in terms of the coefficient of retention. The retention of component i (R_i) measures its degree of separation between streams, and is defined as:

$$R_i = \left(1 - \frac{C_{i,permeate}}{C_{i,feed}}\right) \quad (1)$$

where $C_{i,\text{permeate}}$ is the concentration of component i in permeate, and $C_{i,\text{feed}}$ is the concentration in feed.

Permeation rate and selectivity are strongly related to the morphology, structure and chemical nature of the membranes. Concerning membrane morphology, membranes can be classified as symmetrical or asymmetrical. Symmetrical membranes show uniform pore sizes in their cross-section, whereas the pore distributions of asymmetrical membranes are usually larger[62]. From the morphological point of view, membranes can be divided in porous and dense. In porous membranes the separation of solutes is mainly a function of molecular size and pore size distribution. The membranes employed in MF, UF and NF are porous. In dense membranes, solutes are transported by diffusion under the driving force[63]. Membranes are generally made from polymers or ceramics. Common polymeric materials include polyethersulfone (PES), polysufone (PS), polypropylene (PP), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and cellulose acetate (CA). PES, PS, PP and PVDF have excellent structural integrity, but their hydrophobic nature results in a marked tendency to fouling, causing an exponential flux decline. PAN is relatively hydrophilic, but it is still sensitive to fouling. Cellulosic membranes resist fouling better, but are subjected to degradation by microorganisms. Ceramic membranes are based on zirconium or alumina oxides, and show high thermal and chemical resistances, but they are expensive and fragile.

3.1.2. Effect of Operating Conditions Affecting Membrane Operation

The greatest problem in membrane separation is the reduction of the permeate flux caused by concentration polarization and fouling, which in turn increase the costs associated with routine cleaning and shorten membrane life[58].

The initial rapid decline in the first few minutes of processing is attributed to the arrival of rejected molecules to the membrane surface by convective transport. These particles distribute in a concentrated layer at the membrane surface, forming a concentration gradient termed concentration polarization[62]. After the initial drop in flux due to concentration polarization, the flux continues to decline due to membrane fouling, resulting from the deposition of macromolecules within the membrane pores and by adsorption of the solute onto the membrane walls. Membrane fouling depends on several factors, including the properties of membranes and feed (including molecular size of solutes, interaction with solute-membrane and operating conditions)[64]. The decay of permeate flux caused by concentration polarization can be reversed by modifying operational conditions such as flow velocity, feed concentration and transmembrane pressure. When the decay of flux caused by fouling is irreversible, the membrane has to be cleaned using chemicals or by back-flushing[58].

In addition to the membrane characteristics, the separation performance is influenced by operational parameters (such as crossflow velocity and transmembrane pressure), as well as by the feed characteristics (such as concentration or temperature). An increase in crossflow velocity increases the permeation flow rate, since the thickness of the polarized layer decreases due to the higher turbulence[61, 65]. The flux increases with increasing driving pressure (TMP, transmembrane pressure) until it becomes limited by the formation of a gel layer on the membrane surface. Once gel polarisation occurs, the permeation flux cannot be increased, and it may eventually decrease upon further pressure increase due to compaction of the gel layer. The flux increases with temperature due to the drop in viscosity and to

the increased diffusivity. Usually, the permeation flux increases by 3-4% *per* degree of temperature rise.

The membrane performance is also affected by its configuration. Typical module configurations are flat sheet, tubular, spiral wound, plate units and hollow fibers. Design efforts are focused in decreasing the transport resistance associated to the concentration polarization by increasing turbulence near the membrane surface. The flux can be improved by hydrodynamic modifications to enhance mixing at the membrane surface (increasing cross flow velocity, or using static turbulence promoters, pulsatile flow, corrugated membranes, vortex generators, periodic back flushing, or injection of gas bubbles).

3.1.3. Recovery of Antioxidant Compounds by Membrane Technologies

Membrane technologies can be used to concentrate and/or fractionate bioactive compounds with antioxidant activity from aqueous and alcoholic processing streams of products, by-products and wastes from biomass processing, particularly phenolic compounds, soluble proteins and peptides, and oligosaccharides. This section reviews the information available on the recovery, fractionation and concentration of these fractions. Some examples dealing with the recovery of antioxidant compounds by membrane technologies are summarized in **Tables 1** and **2**.

3.1.3.1. Phenolic Compounds

The utilization of membranes for concentrating and purifying bioactive phenolic compounds from aqueous streams is a topic of growing interest. For example, concentration of phenolics was reported for conventional crude extracts from mate leaves and bark[59, 66], *Geranium robertianum* and *Salvia officinalis*[67], licorice root[68], *Castanea sativa* leaves[69], *Ginkgo biloba* leaves[57], raspberry marc[70], propolis[71, 72], *Sideritis* ssp. L.[73], rosemary[74], grape seeds[75] and distilled grape pomace[76].

Membranes allow an easy and fast separation of phenolics from plant extracts according to their molecular weight (MW). Fractionation of phenolics into low- and high- MW was reported for conventional solvent crude extracts from edible mushrooms[77] and mulberry root cortices[78]. Phenolic compounds from persimmon pulp were fractionated in to tannin fractions of different MW using a polysulfone ultrafiltration membrane[79]. Kalbasi and Cisneros - Zevallos[80] found that membrane separation was suitable used for tailoring monomer and polymer anthocyanin fractions from Concord grape (*Vitis labrusca* L.) juice. The membrane (<100 kDa) separated polymers in the retentates, whereas permeates contained low-MW compounds. Santamaría *et al*.[81] developed a filtration sequence with four different membranes to recover proanthocyanic fractions with different degrees of polymerization. At the analytical scale, almond skin phenolics were fractionated into low MW compounds (recovered in permeate) and proanthocyanidin oligomers (which were kept in retentate)[82].

Membranes and adsorption-desorption processing were employed (alone or in combination) for obtaining isolates of high antioxidant activity from distilled grape pomace pressing liquors[83]. González-López *et al*.[84] processed non-isothermal hydrolysis extracts of chestnut husks using membranes, to obtain a final product with increased concentration of phenolics and an antioxidant activity comparable to the ones of synthetic antioxidants. Sarmento *et al*.[85] used NF and RO membranes to concentrate phenolic compounds obtained by conventional and supercritical CO_2 extraction from cocoa seeds.

The recovery of different fractions from the same raw material by consecutive processing stages was successfully addressed. Todisco *et al*.[86] concentrated catechins from black tea after a preliminary UF stage carried out to retain proteins. In a related study, ultrafiltration of green tea water extracts was suitable for retaining small particles, proteins, polysaccharides and tannic acid, leading to permeate containing more than 40% of tea polyphenols[87].

The separation selectivity can be improved using membranes able to interact with some compounds in solution. For example, a modified PVDF membrane favouring the formation of hydrogen bonds with flavonoids improved their separation from a *Ginkgo biloba* extract[88].

Membranes technologies enable an environmentally friendly approach to the concentration and/or fractionation of waste liquid effluents. Studies have been reported on the use of membranes to process wastewaters with high content of hardly biodegradable organic compounds, containing significant amounts of phenolics. In this field, UF in a flat-sheet module allowed the reduction of chemical oxygen demand (COD) of olive mill wastewaters, as well as the recovery of valuable compounds such as fats, sugars or polyphenols[64]. Several techniques have been employed to separate low molecular weight phenolics from olive mill wastewaters at the pilot scale[89], including combinations of MF, UF, NF, and RO[90-92]. Bernardo *et al*.[93] studied the processing of cork wastewaters by UF and NF, in order to establish the most convenient MWCO to obtain biodegradable permeates and concentrates enabling the recovery of tannins. Processing of soymilk making plant by UF performed in diafiltration (DF) mode and further RO concentration of isoflavones from the permeate has been reported[94].

3.1.3.2. Polysaccharide Fraction

Table 1. Examples of Recovery antioxidant compounds using membrane technology from by-products and agro-food industrial wastes

Raw material	Type of separation	Configuration	Material	Area (m^2)	Cut off (kDa)	Flow velocity Feed flow	TMP (bar)	T (ºC)	VRF	Ref.
Phenolic										
Almond skin extracts	Centrifugal UF	-	-	-	10, 30, 50	-	-	-	-	[82]
Bark Mate tree extracts	NF	Spiral	-	0.9	0.15-0.30	-	60	22	1.5-6	[66]
Castanea sativa leaves extracts	UF	Flat sheet	PES	0.077	5, 10	-	2	20	3	[69]
Chestnut husk extracts	NF	-	-	-	-	-	4	20	3	[84]
	UF				1		-	20	3	
Cork processing wastewater	UF	Flat Sheet	CA	0.147	0.125-91	-	-	-	-	[93]
	NF	Spiral	PS/PA	2.09	0.125					
Grape seed extracts	UF	-	-	-	0.22, 0.45 µm		5	23	-	[75]
Grape seed extracts	UF	-	PS, PVDF		8, 20, 200	-	0.2, 2, 5	-	-	[81]
	NF	-	PA		60% $CaCl_2$ rejection		6			
Distilled Grape Pomace liquors	NF	Spiral	PA/PS		0.250, 0.35		8	20	3	[83]
	UF	Tubular	Ceramic		1		6		3	
Pressed distilled Grape Pomace extract	NF	Spiral	PA/PS, TF		0.25, 0.35, 0.15-0.30	2- 3 m/s	-	20	5.5-6.5	[76]
	UF	Spiral, tubular	Titania, TF		1	2- 3 m/s		20	5.5-6.5	
Mulberry root cortice extracts	MF	-	-	-	0.45 µm		5	25	4	[78]
	UF	-	PS, PA	-	200 , 50, 20, 10					
Olive mil wastewater	UF	Flat sheet	PS	-	17	-	0.5-3	30	-	[64]
Olive mill wastewater	MF	Tubular	Al_2O^5	0.0048	200 nm	760 L/h	0.72	22	-	[91]
	NF	Spiral	PES	1.6	0.578	-	8	20	-	
Olive mill wastewater	MF	Tubular, spiral	Ceramic, PES	0.35, 3.8	0.8 µm, 0.35 µm, 500	4, 3.4 m^3/h	1.5, 2	20-25	3, 3.4	[89]
	UF	Spiral, tubular	PS, PES, Zirconium oxide	5, 8.36, 0.35	80, 20, 6, 1	3-5, 4 m^3/h	2.5-4.5, 1.5	20-25	3, 2.5	
	RO	Spiral	PA	7	99.5 % salt rejection	1.2 m^3/h	10-15	20-25	2.5	
Olive mill wastewater	MF	Tubular	PP	0.036	0.2 µm	-	0.5	25	-	[92]
	UF	Flat Sheet	PES Regenerated cellulose	0.00038465	4, 5, 10		5, 2	25	3	
Olive mill wastewater	UF	Filter sheets	PS, PES	-	100, 25, 10, 2	-	2, 3, 5, 8	-	-	[90]
	NF	Filter sheets	PA	-	120*	-	12			
Olive mill wastewater	MF		Ceramic	0.35	0.1-1.4 µm	-	-	-	-	[99]
	UF	Spiral	Polymeric		1-20					
	NF	Spiral	Polymeric		0.15-0.250					
	RO	Spiral	PA							
Olive mill wastewater	MF			0.24	120	-	-	-	-	[100]
	UF	-	-	1.6	120-20, 20-1					
	NF			2.5	1-0.35					
	RO			2.5	0.35					
Olive mill wastewater	MF	Tubular	PP	8	0.1-0.3 µm	-	-	-	-	[101]
	UF	Spiral	PA/PS	16	7					
	RO	Spiral	PS	9	0.10					
Olive cake extract	NF	-	-	-	0.25	-	10	-	-	[102]
	RO				-		25			
Persimmon pulp extract	UF	Hollow fiber	PS	-	-	10 L/h	0.5	-	-	[79]
Waste stream of a soymilk making plant	RO	Plate and frame	-	-	98% salt rejection	3.2 L/min	14	20	-	[94]

*) The manufacturer measured retentate of 2000 mg/L MgSO4 is ≥ 99% at 9 bar and 25ºC

Table 2. Examples of recovery antioxidant compounds using membrane technology from by-products and agro-food industrial wastes

Raw material	Type of separation	Material	Area (m2)	Cut off (kDa)	TMP (bar)	T (ºC)	Reference
Carbohydrates							
Ornithogalum Caudatum Ait extract	UF	-	-	20, 60	0.8	35	[96]
Tea leaves extract	UF	-	-	10, 100	-	-	[95]
Sargassum pallidum extract	UF	-	0.1	3, 10, 50, 100	-	-	[97]
Peptides and protein							
Alfalfa leaf hydrolysates	UF	PS	-	3	3	20	[106]
Barley hydrolysates	UF	-	-	1, 10	-	-	[109]
Bean protein hydrolysates	UF	-	-	1	-	-	[103]
Phaseolin hydrolysates	UF	-	-	1	-	-	[103]
Potato hydrolysates	UF	-	-	3, 5, 10	-	-	[105]
Rapeseed protein isolates	UF	PS	-	10	-	40	[107]
Soy protein hydolysates	UF	PES	0.07	5, 10, 30, 50	-	-	[104]
Wheat gluten hydrolysates	UF	-	-	5	-	20	[98]
Wheat gluten hydrolysates	UF	-	-	3, 5, 10	-	-	[108]

Recent studies show that polysaccharides can scavenge multiple ROS derived from a series of physical and chemical reactions in organisms[95]. Therefore, the extraction and isolation of bioactive polysaccharides from plants has become a hot research topic[96]. Nevertheless, scarce information has been reported on the separation of polysaccharides with antioxidant activity using membranes. Polysaccharides from the brown seaweed *Sargassum pallidum* obtained by supercritical and ultrasonic-aided extraction were fractionated by UF to obtain antioxidant fractions[97]. Wang *et al*.[95] obtained three polysaccharide fractions of different MW and antioxidant activity by UF of crude tea polysaccharides extracted from lower grade tea leaves. Membrane separation and gel filtration chromatography were used to separate polysaccharides from *Ornithogalum caudatum Ait* into fractions with remarkable antioxidant activity[96].

3.1.3.3. Protein and Peptides

Some protein hydrolysates exhibit antioxidant activity against the peroxidation of lipids and/or fatty acids[98]. Protein recovery followed by membrane fractionation is a well-known technology for producing isolates from defatted soy flour and for the processing of soy protein isolates and hydrolysates.

Rapeseed protein isolates are suitable for food applications due to their functional properties and health benefits, such as ACE inhibition, bile acid-binding and free radical scavenging activity. Two protein isolates were prepared, one by precipitation at controlled pH and the other by ultrafiltration. The ultrafiltered protein isolate had good functional properties, whereas the precipitated protein isolate showed ACE inhibition ability, bile acid-binding capacity and DPPH radical-scavenging capacity[107].

Alfalfa leaf protein was hydrolyzed with protease, and the reaction products were fractionated by UF and purified by adsorption, showing high nutritive value, chelating ability, reducing power, and radical scavenging activity[106]. Protein hydrolysates from potato tubers and by-products from the potato industry were ultrafiltrated with 3-10 kDa membranes to separate the ACE-inhibitory compounds in permeate[105]. Protein hydrolysates of wheat gluten were fractionated by molecular weight using a 5 kDa membrane, yielding a permeate and a retentate with strong antioxidative activities (measured by the linoleic acid oxidation and the DPPH radical scavenging tests). The antioxidative activity of the permeate was almost the same as that of vitamin E at pH 7.0[98].

Enzymatic hydrolysates of wheat gluten were subjected to UF to obtain selected fractions suitable for both protecting against linoleic acid oxidation and scavenging radicals[108]. Hydrolysates from barley glutelin were fractionated by UF and reverse-phase chromatography to separate large-size peptides (MW > 10 kDa) with enhanced DPPH scavenging activity and reducing power, and small-size peptides (MW < 1 kDa) effective for chelating Fe^{2+} and for scavenging OH•[109]. Bean protein and phaseolin were hydrolysed with pepsin and pancreatin, and the resulting hydrolysates were filtered through a 1 kDa MWCO membrane and fractionated by size exclusion chromatography, to obtain concentrates behaving as active metal chelators[103].

3.2. Resin Technologies

3.2.1. Resin Characteristics

Resin technologies are suitable for the selective removal / recovery and concentration of antioxidant compounds from industrial effluents and from processing streams of vegetal wastes generated in the food, agricultural and forestry sectors[110, 111]. Conventional processes involve a saturation, adsorption or loading steps, followed by desorption, elution or regeneration stages. Compared to alternative technologies, adsorption is a cost-efficient and non-toxic separation technique, applicable to units at the industrial scale, offering advantages derived from its high adsorption capacities, possible recovery of the adsorbed

molecules and easy regeneration[110].

Adsorption consists on the selective retention of compounds from fluids onto surfaces of solid bodies. The surface of the solid (adsorbent) presents sites with defined electronic and sterical characteristics enabling interactions with the solutes of the fluid phase (adsorbates)[111]. The adsorption driving force is the concentration gradient of the solute molecules between the adsorbent and the aqueous phase. The type of interaction may be chemical or physical, depending on the functional groups present in the solid and on the ones belonging to the surfactant. The adsorption / desorption capacities of an adsorbate/adsorbent system cannot be easily predicted, because a number of interactions occur at the solid-liquid interface. The following types of interactions have been identified: (i) chemisorption, (ii) hydrogen bonding, (iii) hydrophobic bonding, and (iv) van der Waals forces. When the interactions are weak, the adsorbed solutes can be easily desorbed and recovered for re-use[112].

The theoretical and practical principles of adsorption - desorption are well known, and aspects related to adsorption fundamentals, models and equations have been revised[111]. The adsorption kinetics describes the evolution of the system until the equilibrium is reached. In general, the process involves: (*i*) transport of the solute from the bulk phase to the boundary layer of the adsorbent; (*ii*) transport of solute across the boundary layer; (*iii*) intra-particle diffusion of the solute to the pores of the adsorbent; and (*iv*) adsorption.

Knowledge on the interactions between adsorbent and adsorbate, as well as on the regeneration and recycling of exhausted adsorbents, is needed for design. The adsorption capacity of an adsorbent for a given solute can be calculated from the adsorption isotherm, defined by the distribution of the solute between adsorbent/adsorbate under defined conditions. Adsorption isotherms can be studied in batch experiments to predict the behaviour of the resins in dynamic systems like fixed-bed chromatography. The different classes of adsorption isotherms have been defined according to the configuration of the initial part. The two-parameter isotherm equations of Langmuir and Freundlich are commonly used to model the adsorption process[111]. Even though most adsorption studies have been performed in batch systems, pilot-plant scale data are needed to check aspects such as optimization and industrial feasibility. Adsorption in fixed-bed columns offers high yields and valuable data for scaling-up. The breakthrough curves provide information on the adsorption dynamics and equilibrium, enabling a successful design and operation.

In recent years, polymeric or macroporous non ionic resins have been employed to recover antioxidant compounds from vegetal byproducts[113-115], becoming more and more common in industrial applications[116, 117]. Polymeric resins are classified not only on the basis of their matrix composition, polarity, and chemical and physical resistance; but also considering properties such as particle size distribution, inner and specific surface areas, density, porosity and pore radius distribution[118].

Polymeric resins within a range of polarities can be produced by copolymerization of a monomer (such as styrene, acrylate or vinylpyridine) and a crosslinking agent, mainly divinylbenzene (DVB). Polystyrene-divinylbenzene (PS-DVB) and polyacrylate-divinylbenzene (PA-DVB) resins, with hydrophobic and hydrophilic character, respectively, are the most common ones used for the recovery and separation of pharmaceuticals or their intermediates, foods, and nutraceuticals[119]. These resins are approved for food contact by the U.S. Food and Drug Administration (FDA) and the Council of Europe, which provide limitations and general requirements for use:

- Council of Europe, Resolution AP(2004) 3 on ion exchange and adsorbent resins in the processing of foodstuffs, adopted by the Committee of Ministers on 1 December 2004 at the 907th meeting of the Ministers `Deputies (replacing Resolution AP(97) 1).
- U.S. Food and Drug Administration, Code of Federal Regulation Title 21-Food and Drugs-Revised as of April 1, 2010. Part 173, secondary direct food additives permitted in food for human consumption.

Ion exchange resins are cross-linked polymer matrices with relatively uniform distributions of ion-active sites, able to exchange ions with a solution. Ion exchange resins are insoluble acids or bases having insoluble salts, able to exchange positively charged ions (cation exchangers) or negatively charged ions (anion exchangers). Anionic resins are classified according to the functional group. Weak base anionic resins are made up of a matrix of polystyrene or polyacrylic ester with amines (primary, secondary or ternary) as major functional groups; whereas strong base anionic resins also have a polystyrene matrix, but the active group is a quaternary ammonium. Weak acid cationic resins contain a matrix of polyacrylic or polymethacrylic acid, and carboxylic acids as functional groups; whereas strong acid cationic resins have a polystyrene matrix and functional sulfonic acid groups.

3.2.2. Effect of Operating Conditions Affecting Resin Operation

In adsorption/desorption studies, the influence of the major operational variables on the whole process should be known in order to achieve high recovery rates and economical production. The physical properties of the adsorbent, such as surface area, functionality, porosity, polarity, irregularities, strongly bound impurities, internal porous structure and particle size of adsorbents are influential on adsorption[119]. Also, solubility, pKa, polarity, molecular weight, molar volume, shape and size of the adsorbate lead to differences in affinity for the adsorbent [120]. The adsorption capacity of and the adsorption kinetics depend on the operational conditions, such as pH, flow rate, solvent, temperature, oxygen availability and presence of competing compounds. Temperature and pH are two of the most important factors affecting the adsorption/desorption of target compounds onto non ionic polymeric resins[121-123].

Non ionic polymeric resins are highly porous, and a

variety of compounds can be adsorbed and desorbed, depending on the polarity of the solvent. The economical feasibility of a given adsorption process is strongly affected by the costs derived from the regeneration of exhausted adsorbents. Saturated resins may be regenerated on site at ambient temperature by solvent elution, or by other means such as pH adjustment, microwave, or steam treatments. Non-thermal regeneration cuts the energy costs, enabling applications in the food and pharmaceutical sectors[110]. Detailed studies concerning the effects of various process parameters on the adsorption and desorption efficiency have been reported recently[110, 111].

Resins can be regenerated by contacting with solutions containing an excess of the appropriate ion (a strong acid as a source of protons to regenerate cationic resins, or a strong base as a source of hydroxyl groups to regenerate anionic resins). Ion exchange is used in water treatment and other applications such as chemical synthesis, medical research, food processing, mining, and agriculture. The chemical, physical, and mechanical stability and the ion-exchange behaviour of resins depend on the structure of the matrix and on the nature and number of functional groups. The degree of cross-linking controls the swelling ability of the resin and the intraparticle mobility of the counter ions, which in turn determines the rates of ion-exchange in the resin. Highly cross linked resins are harder and more resistant to mechanical breakdown. The capacity of the resin (measuring the number of counter-ion equivalent in the resin available for exchange *per* unit weight or unit volume) is one of the major parameters to be considered in ion exchange. The selectivity is another parameter to take into account when the objective is the separation of several ionic compounds. The selectivity for two ions A and B is defined as:

$$K_A^B = \frac{m_B^*/m_B}{m_A^*/m_A} \quad (2)$$

where m and m* are the concentrations of ions in solution and resin phases, respectively.

3.2.3. Recovery and Concentration of Antioxidant Compounds by Resin Technologies

The versatility, simplicity, low cost, high efficiency and easy upscaling of adsorption make it an attractive possibility for the selective removal and/or recovery of antioxidant components (including phenolic compounds, small proteins and peptides and oligosaccharides) from industrial effluents and from streams of biomass processing[117, 124, 125].

3.2.3.1. Phenolic Compounds

Phenolic compounds are present in wastewaters from a number of industries. They have a strong and unpleasant smell and are extremely toxic, causing environmental problems. Industrial effluents containing phenolics include olive mill wastewaters[126], vinasses or spent wash molasses[127] and grape and wine byproducts[17, 83]. A pulp wash stream from plant processing pigmented oranges was utilized as a source of anthocyanins and hydroxycinnamates, which were concentrated onto resins[116]. The richest fractions collected from resins contained about 95% of the total anthocyanins in a volume about 2% of the initial one[128]. Yields of 5-60 g total pomegranate tannins/kg husk have been reached in column operation[124, 129]. Resins are widely used for purification of crude extracts from vegetal biomass, yielding either concentrates of enhanced purity and antioxidant activity suitable for specific food applications, or refined products free from undesired components. Resins have been employed in the adsorption of phenolic compounds from crude extracts, such as spinacetin and patuletin from spinach leaves[130], anthocyanins from Roselle[131], narirutin from *Citrus unshiu* peels[132], flavonoids and glycyrrhicid acid from licorice roots[133], genistein and apigenin[115] and vitexin and isovitexin from pigeonpea extracts[134], and flavonoids from leaves of *Ginkgo biloba* L.[135]. Resins have also been used for the adsorption and separation of hesperidin[136] and cyanidin 3-glucoside from aqueous solutions[121]. After adsorption/desorption onto polymers, an enriched licorice flavonoid extract with 22% purity and an enriched glycyrrhizic acid extract with 66% purity were separated from crude licorice extract[133]. Purity degrees above 50% have been obtained for phenolic compounds from extracts of vegetal biomass[137], fruits and vegetables[138]. Adsorption/desorption onto polymeric resins improves the antioxidant activity of extracts from orange peel[139], spinach[130], apple pulp[140], mango peel[23] and tree barks[141]. Adsorption from a multicomponent solution is a complex problem and requires the knowledge of each single component system[112, 122, 142, 143]. The study of plant extracts is complex due to the interactions of other plant constituents, which could have an impact on phenolic binding[144, 145].

A process for the combined recovery of pectin and phenolic compounds from apple pomace, the primary by-product of apple juice production, has been reported[146]. The polyphenols recovered from apple pomace may be used as natural antioxidants or as functional food ingredients, whereas refined pectins are suitable for a number of applications. Enrichment in polyphenols may increase the shelf life of processed foods, causing additional health benefits, as it has been reported for pomegranate husk ellagitannins (which show potent antioxidant, antiatherosclerotic and anticancer activities)[124].

3.2.3.2. Polysaccharide Fraction

Adsorption has been used in combination with other treatments for the refining of oligosaccharides, intending the separation of oligo- from mono-saccharides[147] and/or the removal of non-saccharide compounds. Free galacturonic acid and pectic fragments resulting from enzymatic hydrolysis of olive by-products were retained onto an adsorbent resin, and further elution with deionized water allowed the complete recovery of low molecular pectic

oligosaccharides[148]. Undesired colouring compounds from crude soybean oligosaccharides were removed by adsorption onto polymeric resins, allowing their further utilisation in industries[123].

3.2.3.3. Protein and Peptides

Proteins are of particular interest for the food and pharmaceutical industries due to their biofunctional properties. Resin adsorption is also a valuable tool for the recovery of protein isolates from byproducts of sunflower oil processing. Selected resins undergo minimal interactions with the proteins, and may bind the phenolic compounds from crude protein extracts selectively, resulting in protein-containing concentrates of high nutritional and sensory quality. On the other hand, the phenolics bound to the resin may be recovered and used as natural antioxidants in foods or in other technical applications[149]. Resins have also been employed for isolating functional food-grade proteins from industrial potato juice, enabling the simultaneous removal of salts and phenolics[117, 150]. The capture efficiency of the total crude protein was moderate (20–25%) owing to diffusion limitations and aggregated protein[117].

Data on the utilization of ionic exchange resins for the recovery and purification of components with antioxidant activity have been summarized in **Table 3**. Most applications are based on the selective removal of undesired components, as it happens in the refining oligosaccharides or fermentable sugars from lignocellulosic hydrolysates.

Table 3. Studies reported on the use of ionic resins for the recovery and/or purification of components with antioxidant activity from agricultural and industrial waste streams

Product	Resin	Type	Matrix	Functional group	Ref.
Oligosaccharides/lactic acid	Amberlite IRA 96	WBAE		Tertiary amine	[151]
	Amberlite IRA 400	SBAE	Styrene-divinybencene	Quaternary amine	
Catechin, caffeic acid, Chlorogenic acid, Phloridzin, rutin	Lewatit S 2528	SACE	Crosslinked polystyrene	Sulfonic acid	[112]
	Lewatit S 2328	SACE	Crosslinked polystyrene	Sulfonic acid	
	Lewatit S 8227	WACE	Crosslinked polyacrylate	Carboxylic acid	
	Lewatit S 8528	WACE	Crosslinked polyacrylate	Carboxylic acid	
	Lewatit OC 1072	WBAE	Crosslinked polyacrylamide-divinylbencene	Tertiary amine	
	Lewatit S 4528	WBAE	Crosslinked polystyrene	Tertiary and quaternary amino groups	
	Lewatit S 6328A	SBAE	Crosslinked polystyrene	Quaternary amine	
	Lewatit S 5428	SBAE	Crosslinked polyacrilamide	Quaternary amine	
Fructose, glucose, sucrose	Dowex Monosphere 88	SACE	Polystyrene-divinilbencene	Sulfonate	[152]
	Dowex Monosphere 99K/320	SACE	Polystyrene-divinylbencene	Sulfonate	
	Lewatit MDS 1368	SACE	Crosslinked styrene-divinylbencene	Sulfonic acid	[153]
Arabinose, fructose, Galactose, glucose, Mannose, rhamnose, Sucrose, xylose	Finex CS 11 GC	SACE	Styrene-divinylbencene	Sulfonate	[154]
	Finex CA 12 GC	WACE	Acryl-divinylbencene	Carboxylate	
	Finex AS 510 GC	SBAE	Styrene-divinylbencene	Trimethylamine	
	Finex AA 12 GC FB	WBAE	Methacrylate-divinylbencene	Dimethylamino-propylamine	
Glucose, fructose, sucrose, fructooligosaccharides	Amberlite CR1320Ca	SACE	Crosslinked polystyrene	Sulfonate	[155]
Corn stover hydrolysates	Amberlyst A21	WBAE	Polystyrene		[156]
Rice straw hydrolysates purification for xylitol production	Amberlite IRA 400	SBAE	Styrene-divinybencene	Quaternary amine	[157]
Sugarcane bagasse hydrolysate purification for ethanol production	Purolite A-860S	SBAE	Crosslinked polyacrylyc-divinilbencene	Quaternary amine	[158]
	Purolite A-500PS	SBAE	Crosslinked polystyrene-divinilbencene	Quaternary amine	
	Purolite C-150	SACE	Crosslinked polystyrene-divinilbencene	Sulfonic acid	
	Diaion HPA 25	SBAE	Polystyrene	Quaternary amine	[159]

WBAE: Weakly basic anion exchanger; SBAE: Strongly basic anion exchanger
WACE: Weakly basic cation exchanger; SACE: Strongly basic cation exchange

4. Examples of Valuable Components Recovery

4.1. Recovery of Protein from Soy Concentrates Effluent

Soy protein concentrates (SPC) are produced from defatted soy flour by removing both low molecular weight oligosaccharides and minerals. The production of SPC in acidic media generates a waste stream containing suspended solid particles, acid-soluble proteins, oligosaccharides and minerals. The separation and valorisation of individual components with nutritional and functional properties from this effluent provide an alternative to the conventional wastewater treatment.

UF has been proposed as a first stage for the sequential fractionation of proteins present in the effluents from a soy plant[160]. Soy oligosaccharides were recovered by coupling UF and NF stages (**Figure 1**).

Concentration polarization and irreversible fouling result in flux decline and low productivity[104]. Proteins have been considered as the major contributors to the fouling observed in the filtration of soy processing streams, whereas the sugars did not play a significant role in concentration polarization and/or fouling. A correlation between protein rejection and the MWCO of the membrane was observed.

Centrifugation of the feed stream before membrane processing increased the permeate flux[104].

Operation with a sloping membrane may improve the operation respect to horizontal membranes, as confirmed by data obtained with the soy plant effluent. **Figure 2** displays information concerning the permeate flux and protein concentration in permeate when using the 10 kDa membrane placed horizontally or inclined. A slope of + 45° (the retentate outlet is elevated respect to the feed inlet) resulted in additional turbulence and increased the flux. The opposite arrangement also increased turbulence respect to the horizontal configuration, causing a significant effect on the permeate flux.

Operation along several cycles was possible, despite the progressive flux reduction from the 10th cycle onwards (**Figure 3**). Flux was completely recovered operating at a TMP (transmembrane pressure) below 10 kPa. Operating in successive cycles, the hysteresis effects disappeared progressively, suggesting irreversible fouling, probably caused by protein denaturation. A NaOH solution and a commercial protease were evaluated as cleaning agents to recover the membrane permeability (**Figure 4**).

The cleaning efficiency was measured by flux recovery and on protein removal, which followed the same trends. Chemical cleaning enabled higher flux recovery than enzymatic cleaning. Recycling decreased the permeate flux, owing to protein hydrolysis, which resulted in the deposition of protein fragments.

The protein recovered by UF was subjected to enzymatic hydrolysis with a commercial protease, yielding hydrolyzates with higher reducing power, higher antioxidant potency in emulsion and higher radical scavenging capacity than the original fractions; whereas their ability for inhibiting the β-carotene bleaching was comparable to those of synthetic antioxidants[38].

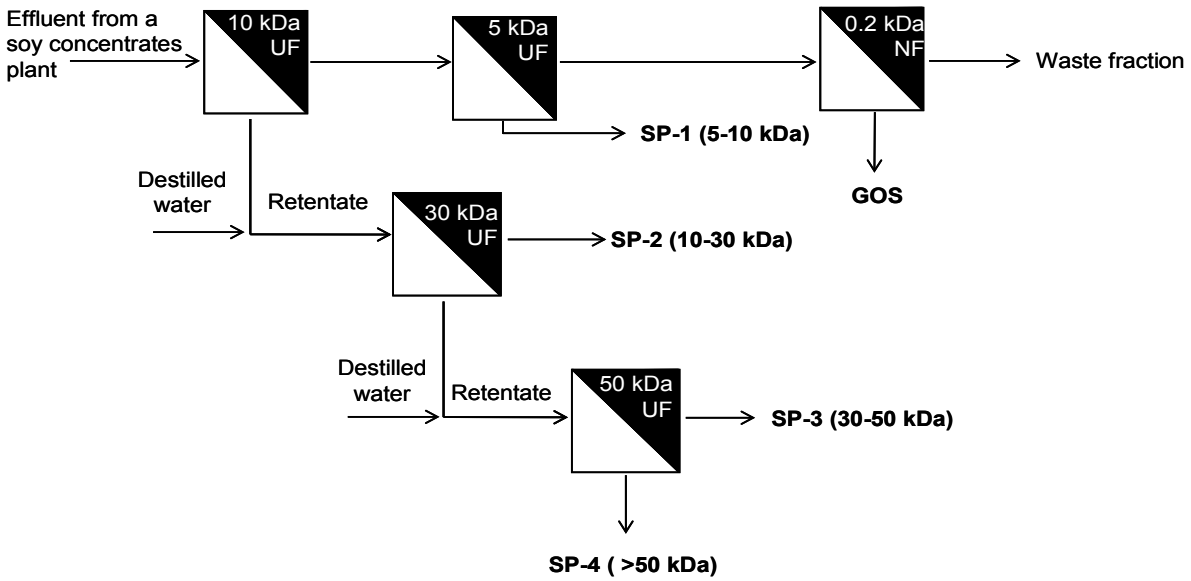

Figure 1. Flow diagram of a combined process for processing a centrifuged effluent from a plant manufacturing soy protein concentrates

4.2. Recovery of Oligosaccharides

4.2.1. Recovery of Oligosaccharides from Soy Industrial Effluents

The permeate stream obtained when processing the soy plant effluent with a 10 kDa membrane (**Figure 1**) contained the mono and oligosaccharide fractions removed from the defatted soy meal during the extraction step. This stream contained monosaccharides (fructose, rhamnose and arabinose), sucrose and galactooligosaccharides (denoted GOS), with the general formula $(Ga)_n$–Glu–Fr, where Ga stands for galactose, Glu for glucose and Fr for fructose, and include raffinose (n = 1), stachyose (n = 2) and verbascose (n = 3). The recovery of GOS from this residual stream is of interest owing to their nutritional and prebiotic properties. Additionally, the antioxidant ability of these components in plant cells has been reported[161].

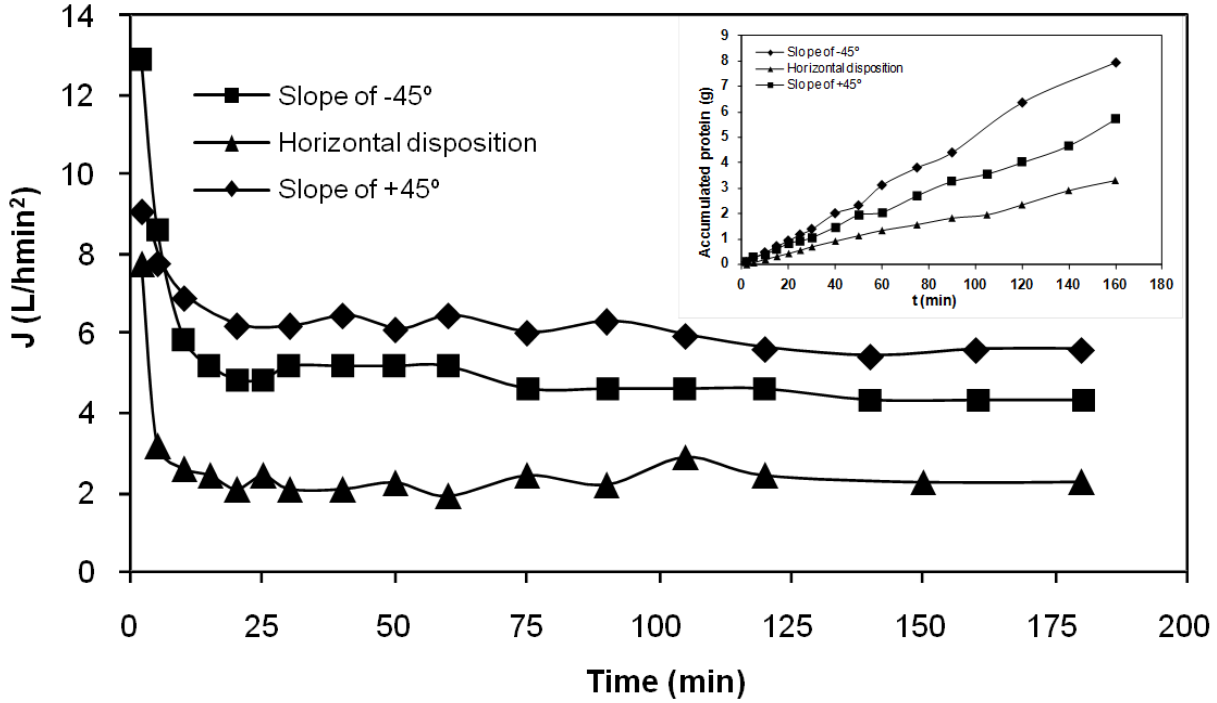

Figure 2. Effect of the inclination of the 10 kDa MWCO membrane on the permeate flux: (a) accumulated protein in the permeate; (b) accumulated protein in retentate. Symbols (■) slope of + 45°, (◆) slope of - 45°. (▲) horizontal

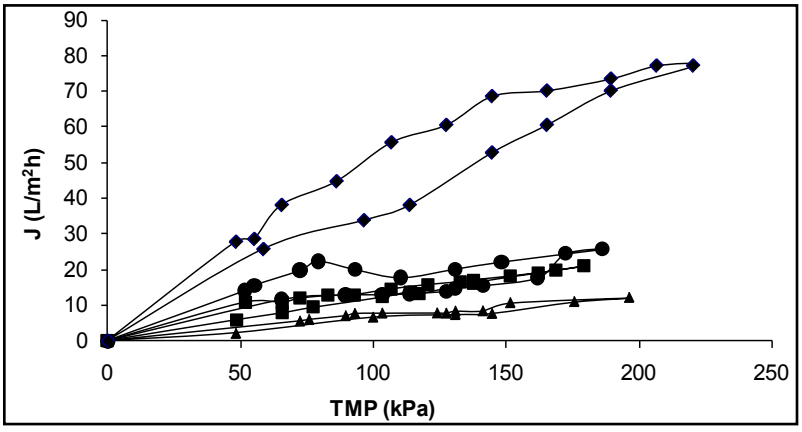

Figure 3. Effects of membrane aging on flux along successive filtration cycles. (◆) 1-14 cycles, (●) 15-20 cycles, (■) 21-27 cycles, (▲) 28 cycles

The permeate obtained with the 10 kDa membrane was further processed in a 5 kDa MWCO unit, yielding a concentrate containing a low molecular protein (SP-1) with excellent functional properties, whereas the permeate was subjected to NF for GOS recovery (**Figure 1**). Operating under selected conditions, the 5 kDa MWCO membrane enabled the fractionation of low molecular weight protein (71% rejection) from GOS, galactose (18% rejection), raffinose (13% rejection), stachyose (13% rejection) and fructose (56% rejection). NF allowed the recovery of 57% of the GOS contained in the effluent permeate from the 5 kDa membrane. These rejection values were in the range reported for the nanofiltration of sugar mixtures (raffinose, sucrose, fructose)[162] and for a commercial mixture of oligosaccharides, lactose and glucose.

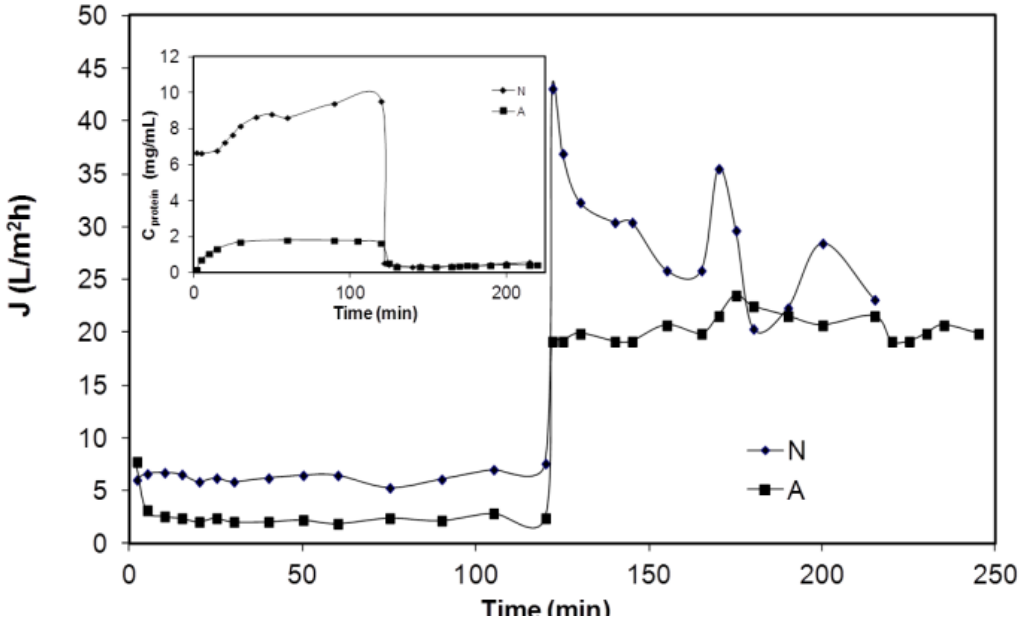

Figure 4. Time profiles of permeate flux and protein concentration in the retentate upon cleaning with NaOH solutions (N) and with Alcalase (A)

4.2.2. Recovery of Oligosaccharides Resulting from Hydrothermal Processing of Lignocellulosic Biomass

Although the manufacture and purification ofoligosaccharides from several sources has been extensively studied, there is little information dealing with theconcentration/purification of oligosaccharides with antioxidant properties.

Depending on the severity of treatments, autohydrolysis of xylan-containing lignocellulosic substrates (such as hardwoods, seeds, straws and agricultural wastes) may lead to the formation of xylooligomers (XOS) as the major products[163, 164]. Alternatively, the hydrothermal processing of softwoods (rich in glucomannan) may result in the formation of glucooligosaccharides. Other compounds present in autohydrolysis liquors include sugar degradation products and phenolics (from extractives, acid-soluble lignin and aromatic acids esterified to hemicelluloses). In order to obtain concentrates enriched in XOS, autohydrolysis liquors must be subjected to a sequence of physico-chemical stages. The waste fractions resulting from these separation stages contain phenolic compounds, which could be valorized as antioxidants[163].

Along the past few years, a number of lignocellulosic materials have been processed by autohydrolysis to produce xylooligomers, which were further concentrated using membranes **(Table 4)**. The antioxidant properties of hemicellulose-derived saccharides have been confirmed for the products from rice husks, *Eucalyptus globulus* wood and *Pinus pinaster* wood. After physicochemical refining of the liquid phases (performed to reduce their contents of monosaccharides and non-saccharide compounds), the major components were oligosaccharides and low molecular polymers. The reducing power and radical scavenging capacity of the non-refined fractions were comparable to that of butylhydroxytoluene (BHT). Membrane processing of autohydrolysis liquors resulted in 40–65% phenolics removal, and further purification was achieves using ion exchange resins. Rice husk hydrolyzates contained saccharides with esterified ferulic and *p*-coumaric acids, which are major contributors to the antioxidant activity. The FRAP (ferric reducing antioxidant power) values determined for the raw hydrolyzates were higher than the ones observed for the fractions treated with membranes or subjected to full refining, according to the phenolic content of the streams. Oppositely, the TEAC values determined for raw and membrane-processed samples did not differ, probably due to the acetyl and uronyl groups content of oligomeric and polymeric saccharides and to their degrees of polymerization, which are major parameters affecting activity[53].

4.3. Recovery of Phenolic Compounds

4.3.1. Recovery of Phenolic Compounds from Industrial Wastes

Grape and wine byproducts have been widely studied as sources of antioxidant phenolics. The selective recovery and concentration of the phenolic compounds from sources such as a diluted stream from winery[17], liquors obtained by pressing distilled grape pomace[83] and aqueous extracts from pressed distilled grape pomace[76] have been reported. Some studies have been focused on the development of new strategies based on aqueous extraction, membrane filtration, resin adsorption and combined processes. **Figure 5** summarizes a possible approach to fractionate and concentrate the antioxidant compounds from present in distilled grape pomace.

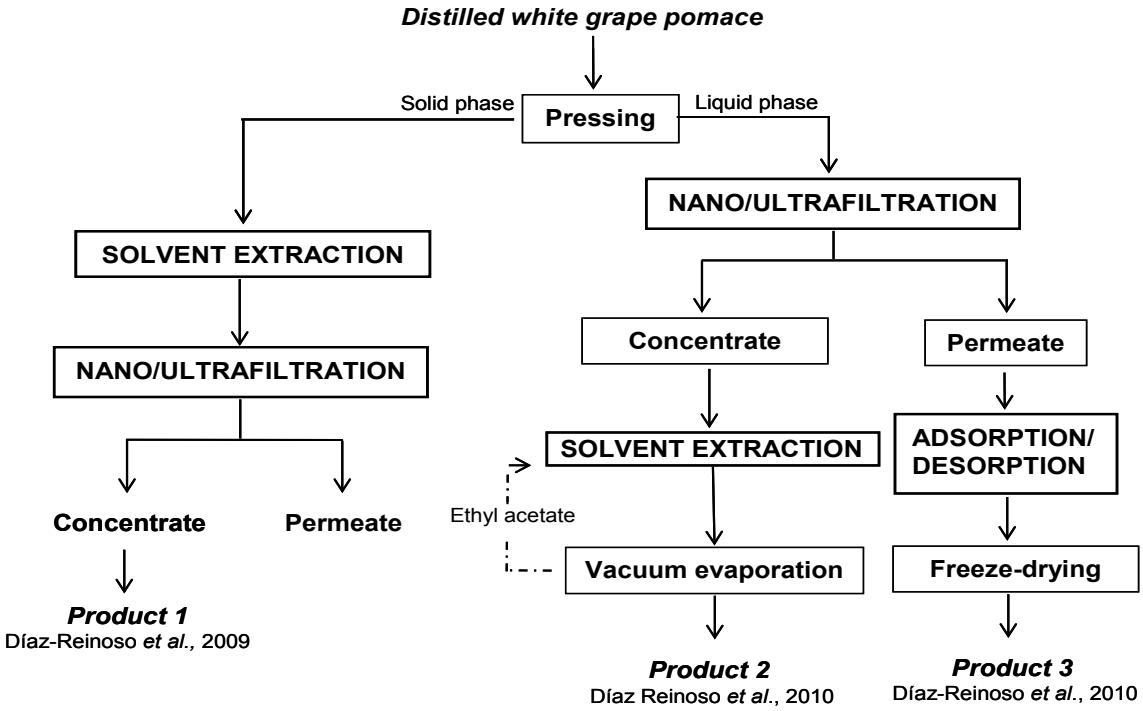

Figure 5. Recovery and concentration of phenolic components from wine byproducts

Table 4. Studies dealing with combined processing involving autohydrolysis and membrane technologies for the recovery, fractionation and concentration of oligosaccharides

Raw Material	Membrane operation	Component of interest	Ref.
Barley husks	Polymeric spiral membrane DF + NF	Xylooligosaccharides	[125]
Eucalyptus globulus	Polymeric spiral membrane DF + NF	Xylooligosaccharides	[125]
Eucalyptus globulus	Tubular ceramic membranes UF	Xylooligosaccharides	[166]
Pinus pinaster	Regenerated cellulose membrane DF	Galactomannooligosaccharides	[167]
Rice husks	Enzymatic membrane reactor, Hydrosart cassette membrane UF	Xylooligosaccharides	[165]

Polymeric and ceramic UF membranes have been tested for this objective. The permeate flux depended on the MWCO and the nature of the building material. TMP caused different effects on the rejection coefficient of solids and phenols for different membranes: increased retentions were observed for the ceramic membrane, almost constant values were determined for Nanomax-95, and decreasing retentions were found for DL2540 and GE2540 membranes. The ceramic membrane had the worst fouling behaviour, whereas the GE2540 membrane presented the best performance.

As a general trend, the tested membranes did not show a preferential rejection of phenolics over sugars, the most selective being the Osmonics and Nanomax 50 membranes.

The adsorption of antioxidant phenolic compounds present in diluted liquid waste streams from wineries was performed with non ionic polymeric resins, and the further desorption was achieved with ethanolic solutions. Adsorption yields in the range 75-90% were reported, whereas the maximum desorption yields (51-67%) and the optimal conditions for phenolic content of the desorbed products (30-51%) and ABTS (2,2-azino-bis-(3-ethylbenzthiazoline -6-sulfonic acid) radical scavenging capacity (7.6-14.0 mM Trolox) were determined using an experimental design[17] . A combined method enabled the manufacture of a richer phenolic concentrate, showing high radical scavenging and FRAP activities[69].

4.3.2. Recovery of Phenolic Compounds from Liquids Obtained by Hydrothermal Processing of Lignocellulosic Biomass

The effects of the operational conditions of autohydrolysis or steam explosion on the recovery of phenolics have been assessed for several agroindustrial wastes, forest residues and brown seaweeds. A generic flow diagram is shown in **Figure 6**. The phenolic content of crude extracts from autohydrolysis of different substrates was in the range 25-35% (weight basis). The extraction yield and DPPH radical scavenging activity are shown in **Table 5**. The ethyl

acetate fraction of hydrolyzates is a complex mixture of different active compounds and impurities. Removal of impurities is required for food applications, and different technologies (including membranes, solvent fractionation and adsorption onto different matrices) have been used for this purpose.

Extraction with a sequence of solvents of increasing polarity and further fractionation of the selected extracts in Sephadex LH-20 gels was applied to the ethyl acetate soluble fraction of barley husks extracts. A correlation between the phenolic content of the extract and the antioxidant activity was found. Only one fraction from the ethyl acetate extract, eluted with methanol/acetone, showed both high content of phenolic compounds (up to 90%) and antioxidant potency ($IC_{50, DPPH}$= 0.22 g/L).

However, the low recovery yield (less than 8%) and the type of solvents employed limited the potential of this process for food-related applications[10].

Activated charcoal was suitable for adsorbing the antioxidants present in autohydrolysis liquors of grape pomace. Fixed-bed adsorption onto granulated activated charcoal presented a favourable adsorption capacity and could be reused for several operation cycles. However, the fractions eluted with 96% ethanol showed activity comparable to the crude extract and the recovery of the adsorbed compounds was limited (21% of the adsorbed phenolics)[168].

Crude extracts from nonisothermal autohydrolysis of barley husks (containing benzoic and cinnamic acids as major compounds) were refined using food grade resins and biorenewable eluting solvents, yielding a concentrate with 48% phenolic content and high antioxidant activity, at a yield of 18 g/kg of barley husks. Processing resulted in significant improvement of both purity and concentration of the active compounds (3,4-dihydroxybenzaldehyde, 4-hydroxybenzaldehyde, vanillin, syringaldehyde and benzoic acid)[11].

The phenolic fractions released upon hydrothermal processing of feedstocks such as corn cobs, eucalypt wood chips, almond shells, chestnut burs, and white grape pomace, could be selectively recovered by extraction with ethyl acetate.

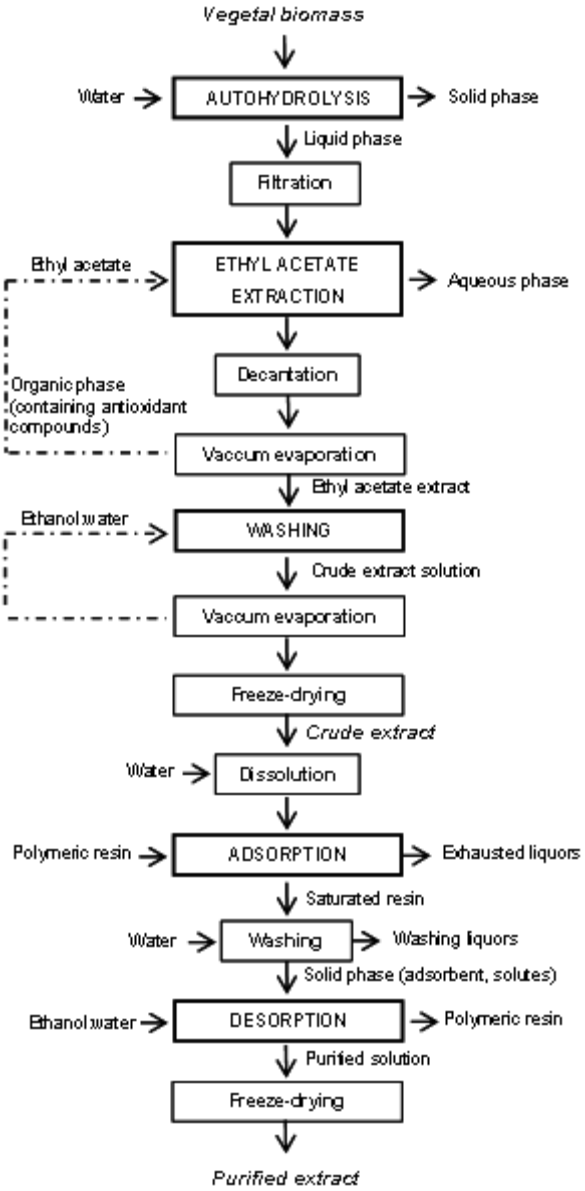

Figure 6. Flow diagram of the autohydrolysis of lignocellulosic materials combined with solvent extraction and adsorption-desorption for phenolics recovery

Table 5. Ethyl acetate solubles yield (EAS) and DPPH radical scavenging capacity of extracts from mild acid fractionation of underutilized materials

Residual material	Extraction yield (g EAS/100 g raw material)	DPPH radical scavenging (IC50, g/L)	Reference in relation to production of the crude extract
Almond shells	6.24	0.63	[137]
Barley husks	8.99	0.68	[164]
Brown algae	11.52	0.72	[84]
Corn cob	6.47	0.55	[163]
Chestnut burs	5.46	0.17	[137]
Eucalyptus globulus wood	8.72	0.48	[163]
Grape pomace	2.42	0.21	[137]
Olive tree pruning	6.51	0.56	[34]
Olive wood	2.35	0.56	[35]
Pinus pinaster wood	3.50	0.07	[160]

Synthetic antioxidants: $IC_{50,BHA}$= 0.24 g/L; $IC_{50,BHT}$= 2.79 g/L

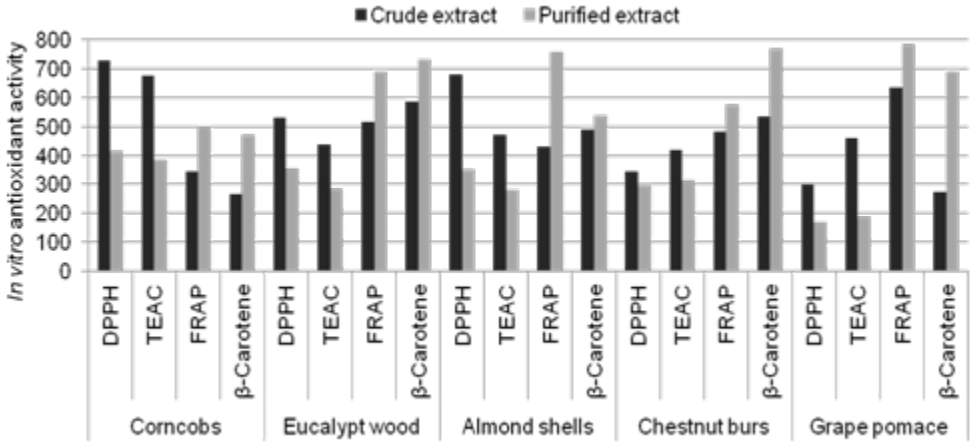

Figure 7. Comparison of the in vitro antioxidant properties of the crude and refined extracts from lignocellulosic materials processed by autohydrolysis

Adsorption of the ethanol/water soluble and further elution with 96% ethanol resulted in 47.0-72.6% phenolic recovery.

The refined products contained 49-60% w/w phenolics (with a significant enrichment with respect to the crude extracts, which contained 32-43% phenolics)[137]. Comparative data on the antioxidant properties of the crude and the refined extracts are shown in **Figure 7.**

A different concentration pattern was observed for the phenolic compounds. The proportions of 4-hydroxybenzoic acid, chlorogenic acid, and vanillic acid decreased upon purification, whereas the aldehydes showed higher concentrations in the refined products. Compared to the respective crude extracts, the concentrations of phenolic acids (p-coumaric and ferulic acids) increased upon refining in samples from corn cobs, but remained similar or even decreased for other raw materials. Other components were selectively enriched in some extracts, as it was found for 3,4-dihydroxybenzaldehyde and vanillin in the purified extract from grape pomace (which increased by 4-5 times), and syringaldehyde in the purified extracts from eucalypt wood and almond shell (which were 5 and 6-fold higher than in the respective crude extracts). During hydrothermal processing, sugar degradation resulted in the formation of furfural and 5-hydroxymethylfurfural (from dehydration of pentoses and hexoses, respectively). Upon adsorption-desorption, these components were removed by 40-87% [137].

Potential food applications of refined extracts were confirmed, for example based on their suitability for protecting bulk oil and oil-in-water and water-in-oil emulsions[169] and polymer stabilization[170].

5. Conclusions

Many wastes and byproducts from the food, agricultural and forestry sectors contain bioactive compounds. Following the worldwide tendency of recovering, recycling and upgrading wastes, these residues can be used as feedstocks for producing high-value substances. Membrane and resin technologies have a huge potential for refining antioxidant-containing solutions resulting from vegetal biomass processing. These technologies are of practical interest for industrial applications, and could provide a way for the benefit of currently underutilized food by-products, particularly through the manufacture of phytoceuticals with potential health benefits for the pharmaceutical, cosmetic and food industries. Combinations of adsorption stages with

other conventional and/or emerging technologies provide opportunities to develop effective and environmentally friendly processes enabling the manufacture of concentrates enriched in defined target compounds, suitable for commercial exploitation.

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