Critical Reviews in Biotechnology

http://informahealthcare.com/bty ISSN: 0738-8551 (print), 1549-7801 (electronic)

Crit Rev Biotechnol, Early Online: 1–7 © 2013 Informa Healthcare USA, Inc. DOI: 10.3109/07388551.2013.803020

REVIEW ARTICLE

Biotransformation and bioconversion of phenolic compounds obtainment: an overview

Jose Valdo Madeira Junior, Camilo Barroso Teixeira and Gabriela Alves Macedo

Food Science Department, College of Food Engineering, Campinas State University, Sao Paulo, Brazil

Abstract

Phenolic compounds have recently been recognized for their influence on human metabolism, acting in the prevention of some chronic diseases as well as proving to be important antioxidants in food. Nevertheless, the extraction and concentration processes are usually carried out by organic solvent extraction from natural sources and can generate some drawbacks like phenolic compound degradation, lengthy process times and low yields. As a solution, some eco-friendly technologies, including solid-state fermentation (SSF) or enzymatic-assisted reaction, have been proposed as alternative processes. This article reviews the extraction of phenolic compounds from agro-industrial co-products by solid-state fermentation, even as friendly enzyme-assisted extractions. It also discusses the characteristics of each bioprocess system and the variables that affect product formation, as well as the range of substrates, microorganisms and enzymes that can be useful for the production of bioactive phenolic compounds.

Introduction

In recent years, attention has turned to phenolic compounds with biological activity due to their ability to promote benefits for human health, such as reduction in the incidence of some neurodegenerative diseases, reduction in the occurrence of factors linked to cardiovascular disease and antioxidant, antimutagenic, anti-allergenic, anti-inflammatory and anti-microbial activities (Martins et al., 2011; Tripoli et al., 2007). Some phenolic compounds may have an important technological role in the prevention of lipid oxidation and other substances, thereby increasing their shelf life (Pokorný, 2007). Research has been intensified in order to find plants and agricultural co-products that produce bioactive phenolic compounds. Agricultural co-products, as well as any plant species, have a unique profile that will produce phenolics according to specific needs and the characteristics provided by the environment. Thus, each co-product has a concentration of a specific pronounced phenolic compound, enabling the production and extraction of a variety of bioactive compounds for use (Aliakbarian et al., 2011; Harrison et al., 2012; Martins et al., 2011; Pingret et al., 2012; Saad et al., 2012; Wu et al., 2012).

Phenolic compounds are derived mainly from the secondary metabolites of plants from phenylalanine (Treutter, 2001). Numerous compounds of different chemical structure are grouped together, including: hydroxybenzoic acids,

Keywords

Agro-industrial co-products, bioprocess, enzymatic reactions, phenolic compounds, solid-state fermentation

informa

healthcare

History

Received 5 July 2012 Revised 17 April 2013 Accepted 2 May 2013 Published online 15 July 2013

hydroxycinnamic acids, flavanols, flavonols, anthocyanins and tannins (Martins et al., 2011). These compounds are considered important to the plants, both structurally and physiologically. In plants, they can attract pollinating insects, contribute to the pigmentation (flowers and fruits), act as antioxidant agents, protect against UV light, and finally, play a role in plant growth and development, preventing the action of pathogens and predators (Martins et al., 2011; Soto et al., 2011).

Currently, phenolic compounds are obtained by chemical synthesis or extraction. Phenolic compounds are recovered from natural sources by solid-liquid or liquid-liquid extraction employing organic solvents in systems of heat. However, other techniques have been used to obtain these compounds, including the use of supercritical fluids, high pressure processes, and extraction by microwave or ultrasound. Over the past 5 years, more than 1700 articles on extraction of phenolic compounds have been published, demonstrating that this type of process is already well studied. So far, most studies published discuss obtaining phenolic compounds using chemical and physical processes. As an example, commercial ellagic acid is obtained by chemical extraction of ellagitannin-rich materials, such as plants, using acidified methanol. Such a process results in high cost and high contamination of the product and is aggressive with a low income (Aguilera-Carbó et al., 2009; Lei et al., 2001; Wilson & Hagerman, 1990).

Some of these processes are not feasible for the food and/or pharmaceutical industries, in both cases because of cost, use of organic solvents and low rate of productivity (Capote et al., 2007; Hayat et al., 2010; Setianto et al., 2009).

Address for correspondence: Jose Valdo Madeira Junior, Food Science Department, College of Food Engineering, Campinas State University, P.O. Box 6121, 13083-862, Sao Paulo, Brazil. Tel.: +55 19 3521 2175. Fax +55 19 3521 1513. E-mail: madeira_jr@hotmail.com

2 J. V. Madeira Jr et al.

The biotransformation of bioactive compounds is also an interesting alternative that deserves attention, since it precludes the use of toxic compounds such as organic solvents in the extraction. In these processes, bioactive compounds are obtained from natural sources by microorganisms through their secondary metabolism or by exogenous enzymatic action (Martins et al., 2011; Puri et al., 2012).

The purpose of this article is to provide an overview of the study of production and obtainment of phenolic compounds by biotransformation using agro-industrial co-products.

Obtaining phenolic compounds by biotransformation

Biotransformation can be defined as chemical transformations that are catalyzed by biological systems through their effective enzyme activity or by microorganisms through solid-state fermentation (SSF) (Banerjee et al., 2012; Martins et al., 2011). In addition, this bioprocess has received great attention due to the potential conversion of inexpensive agroindustrial co-products, as well as plants, in a great variety of valuable compounds.

In this review, processes were shown using the technique of solid-state fermentation and enzymatic reaction as alternative processes for obtaining different phenolic compounds.

Solid-state fermentation in phenolic obtainment

Solid-state fermentation has many advantages, such as high biotechnological productivity, high concentration, product stability and growth of microorganisms in non-water soluble substrates. It also has some disadvantages, such as formation of a temperature gradient throughout the fermented substrate and difficulty in controlling the pH and the amount of water. These problems result in reduced mobility of nutrients derived from reduced movement of the water in the substrate. Changes in temperature and water content in the substrate can be caused by heating resulting from fermentation, which makes it difficult to control the substrate under uniform conditions. However, there is great interest in the SSF process among researchers and industries, particularly due to the fact that the process is usually cheaper with higher productivity than submerged fermentations (Barrios-González, 2012; Singhania et al., 2009).

Solid-state fermentation emerged as an attractive alternative for obtaining phenolic compounds. However, they are expensive compounds using current methods of extraction (Martins et al., 2011; Sepúlveda et al., 2011).

The first report of the production of phenolic compounds is from Betts et al. (1974), which describes a screening of over 40 microorganisms for the production of compounds with antitumor activity. According to the results, there was a 30% increase in the production of phenolic 9-hydroxyacronycine by the microorganism *Cunninghamella echinulata* NRRL 3655 in a stirred fermentor.

There are patents reported for the production of polyphenol using microbial fermentation. Kanji (1991) reported the production of O-methylated phenolic compounds from the hydroxyl grouping by the microorganism *Aspergillus repens* in a liquid medium. Another process for the production of gallic acid was created using a mixed culture of *Aspergillus foetidus* and *Rhizopus oryzae* residues, rich in tannins (Banerjee & Mukherjee, 2003).

Table 1 presents the process used for the production of phenolic compounds by solid-state fermentation. Below, some works are cited regarding solid-state fermentation used in the process of obtaining phenolic compounds.

The choice of residue interferes deeply in obtaining the phenolic compound of interest. Machado et al. (2012) studied the selection of fungal strains with potential growth and release of phenolic compounds in two coffee residues, coffee silverskin (CS) and spent coffee ground (SCG), by solid-state fermentation. The strains GH2 Penicillium purpurogenum, Neurospora crassa and Mucor sp. 3 P showed higher growth conditions in the SCG and increased the release of phenolics by approximately 40%. The increasing availability of phenolic compounds varies according to the type of residue. Regarding the silverskin, the spent coffee ground has a higher content of phenolic compounds, such as catechin, epicatechin, chlorogenic acid, protocatechuic acid and ferulic acid, amongst others. Thus, the choice of residue as the substrate for fermentation is important for achieving different phenolic compounds.

Besides the residue, the microorganism interferes in the fermentation and obtainment of phenolic compounds. Cai et al. (2012) reported the effect of three different microorganisms in the fermentation of oat bran as a source of

Table 1. Phenolic compounds production by microbial fermentation of agroindustrial residues.

Substrate	Microorganism	Incubation ^a	Phenolic compounds	Increased (%) ^b	References
Cranberry residue	Lentinus edodes	120 h/28 °C	Ellagic acid	37.5	Vattem et al. (2004)
Cheonggukjang	Bacillus pumilus	60 h/37 °C	Gallic acid	233.3	Cho et al. (2009)
Pistachio hulls	Phanerochaete chrysosporium	16 d/30 °C	Caffeic acid	12.5	Abbasi et al. (2007)
Tar bush	Aspergillus niger	5 d/30 °C	Pyrocatechol	150	Ventura et al. (2009)
Creosote bush	Aspergillus niger	4 d/30 °C	Gallic acid	1700	Ventura et al. (2009)
Soybeans residue	Lentinus edodes	30 d/25 °C	Catechin	83.3	McCue et al. (2004)
Soybeans residue	Kluyveromyces marxianus	72 h/30 °C	Gallic acid	542.9	Rashad et al. (2011)
Black soybeans	Bacillus subtilis	18 h/40 °C	Catechin	30.5	Juan & Chou (2010)
Soybean seed	Trichoderma harzianum	7 d/25 °C	Genistin	200	Singh et. al. (2010)
Wheat bran	S. cerevisiae	48 h/32 °C	Ferulic acid	75	Moore et. al. (2007)
Cranberry pomace	Letinus edodes	60 d/25 °C	Gallic acid	35.1	Zheng & Shetty (2000)
Maize kernel	Thamnidium elegans	4 d/28 °C	Gallic acid	18.2	Salar et. al. (2012)
Lupinus angustifolious seed	Bacillus subtilis	$48 \text{ h}/30 ^{\circ}\text{C}$	Catechin	489.5	Fernandez-Orozco et al. (2008)

^aTemperature and time of incubation.

^b[(FC–IC)/IC] \times 100; IC: initial concentration, FC: final concentration.

DOI: 10.3109/07388551.2013.803020

phenolic compounds. After the solid-state fermentation, the phenolics, caffeic and ferulic acids, respectively, presented: 230 and 790% increase for *Aspergillus oryzae* var. effuses, 170 and 450% for *Aspergillus niger*, 37 and 0% increase for *Aspergillus oryzae*. According to the analyses, the phenolic compounds in larger quantities are caffeic and ferulic acids, which are in esterified form. With hydrolysis by microorganisms, these compounds increased solubility and facilitated their extraction, showing great advantage over other processes that use high temperatures and therefore generate high energy costs. This difference in clearance of phenolic compounds is due to the metabolic activity of each microorganism. This case is related to various types of microbial enzymes and their activities.

After selecting the microorganism, fermentation kinetics should be performed in order to evaluate the obtainment of the product during the process. Georgetti et al. (2009) evaluated the bioconversion of polyphenol glycosides from soybeans to form non-glycosides through solid-state fermentation by Aspergillus awamori. The conversion of the glycoside to the form of phenolic non-glycoside was accompanied by production of the enzyme β -glucosidase. The non-glycoside form presents a greater number of free hydroxyl groups in regard to glycoside, thus increasing their biological activity. According to the results, the concentration of genistein increased by 1880% in fermented soy. The production of β -glucosidase increased with fungal growth during 48 h of incubation at 30 °C, showing values of $1000 \,\mathrm{UmL}^{-1}$, leading to the conclusion that the enzyme was responsible for the release of phenolic compounds in the soybean during the fermentation. After 48 h, enzyme activity dropped approximately 20%. In this case, studies have indicated that high concentrations of genistein inhibited the activity of β -glucosidase, which in turn inhibits the hydrolysis of phenolic glycosides. Therefore, one should evaluate the kinetics of the release of phenolic compounds so that no interference inhibits its extraction.

Another important factor for obtaining phenolic compounds is the addition of water to the substrate for microbial growth. A strain of Aspergillus was subjected to fermentation in grape residue to increase phenolic antioxidants. Fermentation kinetics were performed to evaluate the time when gallic acid is present in higher concentration. The results showed that after 6h of incubation, the concentration of gallic acid increased 100%. After 15h of incubation, the concentration of gallic acid decreased abruptly, probably indicating that the phenolic compounds were present during the metabolism of the microorganisms. During the process, it was noted that in solid-state fermentation, adding water to the substrate is extremely important, especially if the substrate has hemicellulose and pectin, which can absorb more water, potentially leading to an increase in microbial growth in the substrate. The most commonly used materials for SSF are those with high water absorption levels, since the moisture content of these materials can be modified during the bioprocess (Martínez-Ávila et al., 2012).

In addition to the presence of water in the substrate, the relative humidity also affects the product of interest. Bhanja et al. (2008) compared a new solid-state reactor to the conventional process, for the enrichment of the phenolic in

rice by Aspergillus oryzae for 72 h at 30 °C. The results showed that the reactor increased the concentration of phenolics to 330 mg g^{-1} as compared to the conventional process, the increase of which was 270 mg g^{-1} . This result is explained because in the first case, supplemental oxygen, heat transfer and water activity were monitored in the reactor, which increased the fungal growth and production of the phenolic compounds. Probably, with circulation of humidified air, the heat produced by the fermentation was dissipated and also facilitated the oxygen permeability into the substrate. At the same time, this maintenance of humidified air maintains the water percentage in the substrate during fermentation, which increases fungal growth and, consequently, the release of aglycon phenolics.

Several other factors also influence the production of phenolic compounds, such as pH. The fermentation by fungus *Chaetomium globosum* was assessed in cottonseed and sugarcane bagasse, under alkaline conditions for the production of phenolic compounds. The alkaline stress is an important factor in the production and/or release of these compounds. According to the results, there was an increase of 620 and 500% of gallic acid in the sugarcane bagasse and cottonseed, respectively. The results showed a linear correlation between increasing pH and the amount of gallic acid. Probably at a pH level between 10 and 12, the enzymes β -endoglucanase, β -glucosidase and β -exoglucanase were produced, which have higher enzymatic activity and thus their respective substrates was hydrolyzed, finally releasing the phenolic compounds (Ravindran et al., 2011).

Therefore, several studies have been carried out in order to optimize the production of phenolic compounds, reducing the costs of the process, as well as evaluating the effects that influence the yield of the final product. The properties of the agro-industrial co-products used, such as particle size, biodegradability, water absorption and water activity, in addition to their chemical composition, should be evaluated for obtainoffing a high yield phenolic compounds (Martínez-Avila et al., 2012). Most papers showed that the main factors affecting the fermentation are temperature, pH, aeration, water activity, microorganisms, moisture and substrate. According to studies, the latter three factors have further interference in the final product, in this case, the production of phenolic compounds (Cai et al., 2012; Georgetti et al., 2009; Machado et al., 2012; Martínez-Avila et al., 2012; Martins et al., 2011; Ravindran et al., 2011).

Enzymatic processing in phenolic obtainment

Enzyme production is an important field in biotechnology, having worldwide sales near five billion dollars annually, with a growth rate of approximately 6.5 to 10%, while the number of patents and research papers is listed (Panke et al., 2004). The use of enzymes, especially in biocatalysis in agroindustrial residues, has been introduced for the hydrolysis of plant cell walls, which is complexed with polyphenols. In this scenario, it should be concluded that enzymes can act on this substrate in plant cells.

Table 2 presents some published procedures for the extraction of phenolic compounds by the action of microbial enzymes from agro-industrial wastes. The main enzymes used

Table 2. Phenolic compounds production by microbial enzyme of agroindustrial residues.

Substrate	Enzyme(s)	Enzymatic activity	Incubation ^a	Phenolic compounds	Increased (%) ^b	References
Corn cobs	Esterase	$0.367 \mathrm{nkat g^{-1}}$	4 5 h/pH 5.0/50 °C	Coumaric acid	1100	Topakas et al. (2004)
Red dragon pomace	Xylanase Pectinase	$1.483 \text{ nkat g}^{-1}$ 10,292 PGU mL ⁻¹	6 h/30 °C	Gallic acid	87.5	Kunnika & Pranee (2011)
Hizikin fusiformis	Protease Carboidrase	$2.4 \mathrm{Ug}^{-1}$ $45 \mathrm{Ug}^{-1}$	24 h/pH 8.0/56 °C	Gallic acid	295.3	Siriwardhana et al. (2008)
Olive Wastewater	B-glucosidase Esterase	3000 U mL^{-1} 100 U mL^{-1}	2 h/pH 4.8/50 °C	Hydroxytyrosol	610	Khoufi et al. (2011)
Grape pomace	Pectinase Cellulase	- -	2 h/pH 4.0/40 °C	Phenolic acids	550	Maier et al. (2008)
Goldenberry Pomace oil	Cellulase Pectinase	$\frac{1}{300}$ U mL ⁻¹	2 h/pH 4.3/50 °C	Caffeic acid	102	Ramadan et al. (2008)
Bilberry	Polygalacturonase	100 nakt g^{-1}				Puupponen-Pimiä et al. (2008)
pointace	Endoglucanase Xylanase	38 nakt g^{-1} 39 nakt g ⁻¹	2 h/pH 3.5/45 °C	Gallic acid	37	
Wheat straw	Xylanase Esterase	$\frac{1 \text{ Ug}^{-1}}{20 \text{ Ug}^{-1}}$	2 h/pH 5.0/40 °C	Coumaric acid	133.3	Tapin et al. (2006)
Rice flour	α-Amilase β-Glucosidase	$100 \mathrm{UmL}^{-1}$ $6 \mathrm{UmL}^{-1}$	15 min/50 °C	Free phenolics	139	Bhanja et al. (2008)

^aTime, pH and temperature of incubation.

^b[(FC-IC)/IC] × 100; IC: initial concentration, FC: final concentration.

in the process of obtaining phenolic compounds are reported below, as well as the studies performed.

Cellulases, xylanases and ligninases are enzymes that are capable of breaking the structure of the hemicellulose, cellulose and lignin of a plant cell wall. They usually have three important complex enzymes, endo-1,4- β -glucanase, cellobiohydrolase and cellobiase. These enzymes work cooperatively to catalyze the hydrolysis of cellulose. The effect of these enzymes' activity is the release of cellobiose and glucose. Cellulases have numerous applications and biotechnological potential for chemicals, fuel, alcoholic beverages, animal feed, textile, and pulp and paper (Gnana Soundari & Sashi, 2009; Khandeparker & Numan, 2008; Kirby, 2005; Lin et al., 2011; Paës et al., 2012; Verma et al., 2011).

Min et al. (2006) studied the conditions of dry and humidified stems of sweet potatoes for release of ferulic acid primarily using commercial β -glucanase. The reaction was performed with enzyme mixtures, degrading plant cell walls, Ultraflo-L Viscozyme (Novozymes A/S) and the α -amylase (Sigma-Aldrich) in a buffer solution with pH 6.0 at 37 °C spinning at 12 rpm for 12 h. The results showed a concentration of 0.5% of Viscozyme-Ultraflo L, 50 mU of released α -amylase and 6 mg of ferulic acid/g of substrate humidified, which is 3 times higher compared to the dry substrate. The ferulic acid increase in the humidified substrate must have been due to the fact that the enzymes were easily adsorbed into the substrate, which facilitated and enhanced the catalytic action.

Moore et al. (2006) evaluated commercial enzymes and their action regarding the release of phenolics in wheat bran. The reaction was conducted in the dark with 10% humidity at room temperature for 72 h. The results indicated that extracts of multi-enzyme complexes (e.g. Ultraflo-L- Novozymes A/S) had a greater effect than the addition of various purified enzymes. However, each enzyme complex responds differently to each type of substrate. As previously mentioned in this article, the effects of moisture in the reaction can influence the release of phenolics. However, this condition should be evaluated together with the catalytic activity of the enzyme.

The pectinases are a heterogeneous group of enzymes that degrade pectin. These enzymes are especially important in the industrial sector and are used in various segments, such as clarification of fruit juice and wine, and product manufacturing of pectin hydrolysate extract oil from seeds and pigments. Degradation of the pectin molecule occurs through a coordinated action of multiple synergistic and pectinolytic enzymes, including pectin-lyase (EC 4.2.2.10) and polygalacturonase (EC 3.2.1.15) are of great relevance to the process of depolymerization of pectin, acting in the cleavage of glycosidic bonds α -1,4, polygalacturonic acid and pectin, respectively (Alimardani-Theuil et al., 2011; Kashyap et al., 2001; Pedrolli & Carmona, 2009).

Oszmianski et al. (2011) studied the action of pectinase on apple pomace to increase the availability of phenolic compounds for the enrichment of apple juice. According to the results, pectinase increased the concentration of phenolic compounds by 245%, especially procyanidins, flavan-3-ols and flavonols. Apple peels always had tangibly higher concentrations of proanthocyanidins than whole apples. Procyanidins have been shown to bind readily to cell-wall polysaccharides through hydrogen-bonding and/or hydrophobic interactions.

The β -glucosidase (β -D-glucoside glucohydrolase, EC 3.2.1.21) catalyzes the hydrolysis of disaccharide glycosides and conjugates from the non-reducing end. The β -glucosidase enzyme has numerous applications in the food and pharmaceutical industries, working in the hydrolysis of cellobiose to glucose, the process of conversion of cellulose to glucose in combination with other cellulolytic

enzymes, and the release of aroma compounds in fruit juices and wine. This enzyme is also used in the hydrolysis of cyanogenic compounds present in plants for hormone replacement therapy (Puri et al., 2012; van den Brink & de Vries, 2011).

Hamza et al. (2012) studied the action of the multienzymatic complex β -glucosidase (4600 UmL⁻¹), esterase (200 UmL⁻¹), α -amylase (92 UmL⁻¹), xylanase (5.4 Uml⁻¹) and carboxymethyl-cellulase (0.6 UmL⁻¹) in waste water from olives for the production of hydroxytyrosol. According to the results, the oleuropein could be hydrolyzed and hydroxytyrosol obtained. The reaction probably occurred during the breakdown of the glycosidic bond and resulted in the formation of hydroxytyrosol and elenolic acid (Figure 1).

According to the results, the highest concentration of hydroxytyrosol were between pH 4 and 5 and coincided with the highest activity of β -glucosidase, leading to the conclusion that the release of phenolics is directly related to the aforesaid action of the enzyme. Also, it was observed that within 30 min of stirring, the hydroxytyrosol concentration tripled, and after that time these values decreased. On the other hand, the static extraction was doubled after 250 min, compared to the values before the enzymatic extraction. Thus, prolonged exposure of the phenolic compounds to O₂, changed their structure and bioactive function.

Tannin acyl hydrolase, commonly referred to as tannase (EC 3.1.1.20), is an inducible enzyme produced by fungi, yeasts and bacteria. This enzyme is mostly characterized by its activity in the polyphenol complexes and is capable of hydrolyzing ester bonds (between gallic acid and glucose) and depside linkage (between two gallic acids) substrates, such as tannic acid, epicatechin-gallate, epigallocatechin-gallate and chlorogenic acid, among others. This enzyme has wide

industrial applications, in juices, beer, cosmetics, pharmaceutics and chemicals. It is primarily used in the stabilization of the color of wine, in the leather treatment process, and for wastewater treatment and production of gallic acid and other phenolics (Banerjee et al., 2001; Battestin & Macedo, 2007; Lekha & Lonsane, 1997; Madeira et al., 2012).

Chamorro et al. (2012) studied the release of phenolic grape residue after its reaction to the carbohydrase enzyme (cellulase and pectinase) and tannase. The reaction medium was performed at pH 5.5 at 35 °C under agitation for 24 h, with the addition of pectinase (135 Ug^{-1}) , cellulase (3150 Ug^{-1}) and tannase (200 U m g⁻¹). The results showed that both cellulase and pectinase used alone had no change in the concentration of phenolics. However, with the action of tannase, the concentration of phenolic acids increased, especially gallic acid. The concentration of epigallocatechingallate, gallocatechin and epicatechin-gallate decreased simultaneously. Therefore, it is possible to conclude that the tannase hydrolyzed the ester linkages of phenolic compounds, proving that it has become an important factor in the release of phenolic compounds in grape residue.

Dueñas et al. (2007) evaluated the effect of different enzymes in the quantification of free phenolics in lentil flour. The residue was incubated in acetate buffer with pH 5.5 at 37 °C in four reactors, each of which received a different enzyme, α -galactosidase, viscozyme, tannase and phytase. According to the results, both the phytase and the tannase released the greatest amount of gallic acid, 1–0.8 µg g⁻¹ lentil flour. Despite the considerable increase of gallic acid, phytase decreased the antioxidant activity of the matrix due to the release of phosphate groups of phytic acid chelates and other cations in them. Phytic acid is considered to be a potent iron chelator, which in turn prevents the formation of hydroxyl



Figure 1. Enzymatic reaction to hydroxytyrosol from oleuropein (Khoufi et al., 2011).

radicals. At the same time, there is an increase in oxidation cations released in the medium that is present. However, the use of tannase for the release of phenolic antioxidants has become interesting for various types of agro-industrial waste. This is because most of these residues can release the phenolic compounds without requiring a pre-treatment such as the action of the pectinase or cellulase, or variation in temperature or pH.

Briefly, the majority of published studies investigated the best conditions for enzyme activity added to the residue to release the phenolic compounds. The main variables are the enzyme concentration, reaction time, pH, and particularly the class of enzymes used, ranging in accordance with the type of residue (Chamorro et al., 2012; Dueñas et al., 2007; Hamza et al., 2012; Min et al., 2006; Moore et al., 2006). Thus, process modeling studies should be performed in order to increase the yield of a phenolic compound of interest, wherein the class(es) of enzyme(s) and substrate are the major interferences in the final product.

Conclusion

The microbial and enzyme biotransformation of phenolic compounds seems to be a promising way to increase the concentration of free phenolics. These bioprocesses are clean technologies with great potential for obtaining biologically active compounds from natural sources. In this case, the use of residues is of particular interest because of its availability, low cost and features that allow obtaining different bioactive phenolic compounds, as well as being an environmentally friendly alternative for their removal. For better obtainment of these compounds, factors such as type of substrate, microorganism, class of enzyme(s), moisture in the substrate, time and temperature of incubation can be assessed through bioprocesses. In most cases, it was noted that between the biological processes reviewed, the yield obtained with the enzymatic process was greater than that obtained with the microbial process. Therefore, modeling the bioprocess can increase the product yield and consequently lower the cost of the process.

Declaration of interest

The authors acknowledge the financial support received from CAPES (*Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil*) and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo).

References

- Abbasi S, Vahabzadeh F, Mehranian M. (2007). Profiles of phenolics and antioxidant activity of pistachio hulls during solid-state fermentation by *Phanerochaete chrysosporium* – involvement of lignin peroxidase and manganese peroxidase. Sci Iran, 14, 373–8.
- Aguilera-Carbó A, Hernández-Rivera JS, Augur C, et al. (2009). Ellagic acid production from biodegradation of creosote bush ellagitannins by *Aspergillus niger* in solid state culture. Food Bioprocess Technol, 2, 208–12.
- Aliakbarian B, Casazza AA, Perego P. (2011). Valorization of olive oil solid waste using high pressure-high temperature reactor. Food Chem, 128, 704–10.
- Alimardani-Theuli P, Gainvors-Claisse A, Duchiron F. (2011). Yeasts: an attractive source of pectinases – from gene expression to potential applications: a review. Process Biochem, 46, 1525–37.

- Banerjee D, Mondal KC, Pati BR. (2001). Production and characterization of extracellular and intracellular tannase from newly isolated *Aspergillus aculeatus* DBF 9. J Basic Microbiol, 41, 313–18.
- Banerjee R, Mukherjee G. (2003). Process for the preparation of gallic acid by co-culture. United State of American. US7118882 (B2).
- Banerjee S, Singh S, Rahman LU. (2012). Biotransformation studies using hairy root cultures – a review. Biotechnol Adv, 30, 461–8.
- Barrios-González J. (2012). Solid-state fermentation: physiology of solid medium, its molecular basis and applications. Process Biochem, 47, 175–85.
- Battestin V, Macedo GA. (2007). Tannase production by *Paecilomyces variotii*. Biores Technol, 98, 1832–7.
- Betts RE, Walters DE, Rosazza JP. (1974). Microbial transformations of antitumor compounds. 1. Conversion of acronycine to 9-hydroxyacronycine by *Cunninghamella echinulata*. J Med Chem, 17, 599–602.
- Bhanja T, Rout S, Banerjee R, Bhattacharyya BC. (2008). Studies on the performance of a new bioreactor for improving antioxidant potential of rice. LWT – Food Sci Technol, 41, 1459–65.
- Cai S, Wang O, Wu W, et al. (2012). Comparative study of the effects of solid-state fermentation with three filamentous fungi on the total phenolics content (TPC), flavonoids, and antioxidants activities of subfractions from oats (*Avena sativa L*.). J Agric Food Chem, 60, 507–13.
- Capote FP, Jiménez JR, De Castro MDL. (2007). Sequential (step-bystep) detection, identification and quantitation of extra virgin olive oil adulteration by chemometric treatment of chromatographic profiles. Anal Bioanal Chem, 388, 1859–65.
- Chamorro S, Viveros A, Alvarez I, et al. (2012). Changes in polyphenol and polysaccharide content of grape seed extract and grape pomace after enzymatic treatment. Food Chem, 133, 308–14.
- Cho KM, Hong SY, Math RK, et al. (2009). Biotransformation of phenolics (isoflavones, flavanols and phenolic acids) during the fermentation of cheonggukjang by *Bacillus pumilus* HY1. Food Chem, 114, 413–19.
- Dueñas M, Hernández T, Estrella I. (2007). Changes in the content of bioactive polyphenolic compounds of lentils by the action of exogenous enzymes. Effect on their antioxidant activity. Food Chem, 101, 90–7.
- Fernendez-Orozco R, Frias J, Muñoz R, et al. (2008). Effect of fermentation conditions on the antioxidant compounds and antioxidant capacity of *Lupinus angustifolius* cv. zapaton. Eur Food Res Technol, 227, 979–88.
- Georgetti SR, Vicentini FTMC, Yokoyama CY, et al. (2009). Enhanced in vitro and in vivo antioxidant activity and mobilization of free phenolic compounds of soybean flour fermented with different β -glucosidase-producing fungi. J Appl Microbiol, 106, 459–66.
- Gnana Soundari S, Sashi V. (2009). Bacterial xylanases. Asian J Microbiol Biotechnol Environ Sci, 11, 677–82.
- Hamza M, Khoufi S, Sayadi S. (2012). Fungal enzymes as a powerful tool to release antioxidants from olive mill wastewater. Food Chem, 131, 1430–6.
- Harrison JE, Oomah BD, Diarra MS, Ibarra-Alvarado C. (2012). Bioactivities of pilot-scale extracted cranberry juice and pomace. J Food Process Preserv, DOI:10.1111/j.1745-4549.2011.00655.x.
- Hayat K, Zhang X, Farooq U, et al. (2010). Effect of microwave treatment on phenolic content and antioxidant activity of citrus mandarin pomace. Food Chem, 123, 423–9.
- Juan M-Y, Chou C-C. (2010). Enhancement of antioxidant activity, total phenolic and flavonoid content of black soybeans by solid state fermentation with *Bacillus subtilis* BCRC 14715. Food Microbiol, 27, 586–91.
- Kanji D. (1991). O-Methylation of phenolic hydroxyl group by fermentation. Japan. JP3232495 (A).
- Kashyap DR, Vohra PK, Chopra S, Tewari R. (2001). Applications of pectinases in the commercial sector: A review. Biores Technol, 77, 215–27.
- Khandeparker R, Numan MTh. (2008). Bifunctional xylanases and their potential use in biotechnology. J Ind Microb Biotech, 35, 635–44.
- Khoufi S, Hamza M, Sayadi S. (2011). Enzymatic hydrolysis of olive wastewater for hydroxytyrosol enrichment. Biores Technol, 102, 9050–8.
- Kirby R. (2005). Actinomycetes and lignin degradation. Adv Appl Microbiol, 58, 125–68.
- Kunnika S, Pranee A. (2011). Influence of enzyme treatment on bioactive compounds and colour stability of betacyanin in flesh and

peel of red dragon fruit *Hylocereus polyrhizus* (Weber) Britton and Rose. Int Food Res J, 18, 1437–48.

- Lei Z, Jervis J, Helm RF. (2001). Use of methanolysis for the determination of total ellagic and gallic acid contents of wood and food products. J Agric Food Chem, 49, 1165–8.
- Lekha PK, Lonsane BK. (1997). Production and application of tannin acyl hydrolase: State of the art. Adv Appl Microbiol, 44, 215–60.
- Lin H, Li W, Guo C, Qu S, Ren N. (2011). Advances in the study of directed evolution for cellulases. Front Environ Sci Eng China, 5, 519–25.
- Machado EMS, Rodriguez-Jasso RM, Teixeira JÁ, Mussatto SI. (2012). Growth of fungal strains on coffee industry residues with removal of polyphenolic compounds. Biochem Eng J, 60, 87–90.
- Madeira Jr JV, Macedo JA, Macedo GA. (2012). A new process for simultaneous production of tannase and phytase by *Paecilomyces variotii* in solid-state fermentation of orange pomace. Bioprocess Biosyst Eng, 35, 477–82.
- Maier T, Göppert A, Kammerer DR, et al. (2008). Optimization of a process for enzyme-assisted pigment extraction from grape (*Vitis vinifera L.*) pomace. Eur Food Res Technol, 227, 267–75.
- Martínez-Ávila GC, Aguilera-Carbó AF, Rodríguez-Herrera R, Aguilar CN. (2012). Fungal enhancement of the antioxidant properties of grape waste. Ann Microbiol, 62, 923–930.
- Martins S, Mussatto SI, Martínez-Avila G, et al. (2011). Bioactive phenolic compounds: production and extraction by solid-state fermentation. A review. Biotechnol Adv, 29, 365–73.
- McCue P, Horii A, Shetty K. (2004). Mobilization of phenolic antioxidants from defatted soybean powders by *Lentinus edodes* during solid-state bioprocessing is associated with enhanced production of laccase. Innov Food Sci Emerg, 5, 385–92.
- Min J-Y, Kang S-M, Park D-J, et al. (2006). Enzymatic release of ferulic acid from *Ipomoeba batatas L*. (sweet potato) stem. Biotechnol Bioprocess Eng, 11, 372–6.
- Moore J, Cheng Z, Hao J, et al. (2007). Effects of solid-state yeast treatment on the antioxidant properties and protein and fiber compositions of common hard wheat bran. J Agric Food Chem, 55, 10173–82.
- Moore J, Cheng Z, Su L, Yu L. (2006). Effects of solid-state enzymatic treatments on the antioxidant properties of wheat bran. J Agric Food Chem, 54, 9032–45.
- Oszmianski J, Wojdylo A, Kolniak J. (2011). Effect of pectinase treatment on extraction of antioxidant phenols from pomace, for the production of puree-enriched cloudy apple juices. Food Chem, 127, 623–31.
- Paës G, Berrin J-G, Beaugrand J. (2012). GH11 xylanases: Structure/ function/properties relationships and applications. Biotechnol Adv, 30, 564–92.
- Panke S, Held M, Wubbolts M. (2004). Trends and innovations in industrial biocatalysis for the production of fine chemicals. Curr Opin Biotechnol, 15, 272–9.
- Pedrolli DB, Carmona EC. (2009). Pectin lyase from Aspergillus giganteus: comparative study of productivity of submerged fermentation on citrus pectin and orange waste. Appl Biochem Microbiol, 45, 610–16.
- Pingret D, Fabiano-Tixier AS, Le Bourvellec C, et al. (2012). Lab and pilot-scale ultrasound-assisted water extraction of polyphenols from apple pomace. J Food Eng, 111, 73–81.
- Pokorný J. (2007). Are natural antioxidants better and safer than synthetic antioxidants? Eur J Lipid Sci Technol, 109, 629–42.
- Puri M, Sharma D, Barrow CJ. (2012). Enzyme-assisted extraction of bioactives from plants. Trends Biotechnol, 30, 37–44.
- Puupponen-Pimiä R, Nohynek L, Ammann S, et al. (2008). Enzymeassisted processing increases antimicrobial and antioxidant activity of bilberry. J Agric Food Chem, 56, 681–8.
- Ramadan MF, Sitohy MZ. (2008). Solvent and enzyme-aided aqueous extraction of goldenberry (*Physalis peruviana L.*) pomace oil: impact

of processing on composition and quality of oil and meal. Eur Food Res Technol, 226, 1445-8.

- Rashad MM, Mahmoud EA, Abdou MH, Nooman UM. (2011). Improvement of nutritional quality and antioxidant activities of yeast fermented soybean curd residue. Afr J Biotechnol, 10, 5750–9.
- Ravindran C, Varatharajan GR, Azagesan K. (2011). Role of alkalinetolerant fungal cellulases in release of total antioxidants from agrowastes under solid state fermentation. Biores, 6, 3142–54.
- Saad H, Bouhtoury FC, Pizzi A, et al. (2012). Characterization of pomegranate peels tannin extractives. Ind Crop Prod, 40, 239–46.
- Salar RK, Certik M, Brezova V. (2012). Modulation of phenolic content and antioxidant activity of maize by solid state fermentation with *Thamnidium elegans* CCF 1456. Biotechnol Bioproc Eng, 17, 109–16.
- Sepúlveda L, Ascacio A, Rodríguez-Herrera R, et al. (2011). Ellagic acid: Biological properties and biotechnological development for production processes. Afr J Biotechnol, 10, 4518–23.
- Setianto WB, Yoshikawa S, Smith Jr RL, et al. (2009). Pressure profile separation of phenolic liquid compounds from cashew (*Anacardium* occidentale) shell with supercritical carbon dioxide and aspects of its phase equilibria. J Supercrit Fluids, 48, 203–10.
- Singh HB, Singh BN, Singh SP, Nautiyal CS. (2010). Solid-state cultivation of *Trichoderma harzianum* NBRI-1055 for modulating natural antioxidants in soybean seed matrix. Biores Technol, 101, 6444–53.
- Singhania RR, Patel AK, Soccol CR, Pandey A. (2009). Recent advances in solid-state fermentation. Biochem Eng J, 44, 13–18.
- Siriwardhana N, Kim K-N, Lee K-W, et al. (2008). Optimisation of hydrophilic antioxidant extraction from Hizikiafusiformis by integrating treatments of enzymes, heat and pH control. Int J Food Sci Technol, 43, 587–96.
- Soto ML, Moure A, Domínguez H, Parajó JC. (2011). Recovery, concentration and purification of phenolic compounds by adsorption: A review. J Food Eng, 105, 1–27.
- Tapin S, Sigoillot J-C, Asther M, Petit-Conil M. (2006). Feruloyl esterase utilization for simultaneous processing of nonwood plants into phenolic compounds and pulp fibers. J Agric Food Chem, 54, 3697–703.
- Topakas E, Kalogeris E, Kekos D, et al. (2004). Production of phenolic from corn cobs by coupling enzymic treatment and solid state fermentation. Eng Life Sci, 4, 283–6.
- Treutter D. (2001). Biosynthesis of phenolic compounds and its regulation in apple. Plant Growth Regul, 34, 71–89.
- Tripoli E, La Guardia M, Giammanco S, et al. (2007). Citrus flavonoids: molecular structure, biological activity and nutritional properties: a review. Food Chem, 104, 466–79.
- Van Den Brink R, De Vries RP. (2011). Fungal enzyme sets for plant polysaccharide degradation. Appl Microbiol Biotechnol, 91, 1477–92.
- Vattem DA, Lin Y-T, Labbe RG, Shetty K. (2004). Phenolic antioxidant mobilization in cranberry pomace by solid-state bioprocessing using food grade fungus *Lentinus edodes* and effect on antimicrobial activity against select food borne pathogens. Innov Food Sci Emerg Technol, 5, 81–91.
- Ventura J, Gutiérrez-Sanchez G, Rodríguez-Herrera R, Aguilar CN. (2009). Fungal cultures of tar bush and creosote bush for production of two phenolic antioxidants (pyrocatechol and gallic acid). Folia Microbiol, 54, 199–203.
- Verma N, Bansal MC, Kumar V. (2011). Enzymatic deinking with cellulases: A review. J Solid Waste Technol Manage, 37, 297–306.
- Wilson TC, Hagerman AE. (1990). Quantitative determination of ellagic acid. J Agric Food Chem, 38, 1678–83.
- Wu T, Yan J, Liu R, Marcone MF, Aisa HA, Tsao R. (2012). Optimization of microwave-assisted extraction of phenolics from potato and its downstream waste using orthogonal array design. Food Chem, 133, 1292–8.
- Zheng Z, Shetty K. (2000). Solid-state bioconversion of phenolics from cranberry pomace and role of *Lentinus edodes* β-glucosidase. J Agric Food Chem, 48, 895–900.