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Functional foods based on the recovery of bioactive ingredients from food and algae by-products by emerging extraction technologies and 3D printing

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A B S T R A C T

3D food printing is an emerging technology developed to facilitate the life of consumers and food enterprises. This technology allows to obtain any type of new foods according to our wishes. It is possible to develop a food with the exact nutritive value necessary for our body, with the most benefiting nutrients we want, or without any ingredients that we have an allergy, and even predict or personalize the taste, the color, the shape, and the size of a food. Therefore, 3D food printing is considered a promising strategy for developing healthy foods. On the other hand, many foods enterprises release high amounts of waste from their processing activities. These wastes contain many bioactive ingredients such as polyphenols, carotenoids, vitamins, minerals, fibers, unsaturated fatty acids, among others, which have physiological and health benefits. Similarly, several bioactive compounds have been identified in algae. They can be extracted by conventional methods with solvents such as water, ethanol, methanol, chloroform, acetone, and many others, but with some limits like environmental contamination, human toxicity, and low extraction rate. For these reasons, it will be interesting to use emerging extraction technologies to recover bioactive compounds and use them in a 3D food printer to make functional foods that can bring a targeted health benefit to consumers.

1. Introduction

Nowadays, consumers are more aware of their well-being, and are increasingly interested in functional foods. There has been growing awareness of the importance of promoting healthy and sustainable diets as one of the key strategies to safeguard human and environmental health. In this context, food processing industries have been increasingly criticized for the unhealthy quality and in some cases the poor taste and flavor of the foods produced. In addition, consumers are more concerned about the negative ecological impact of these industries, due to the large amount of food processing waste that is disposed into the environment. Numerous scientific studies have demonstrated that food by-products are sources of compounds of high nutritional value that exert beneficial biological properties (known as bioactive compounds) and to improve the sustainability of the food industry (Otero et al., 2022). On the other hand, an under-exploited matrix that has gained attention in recent years are algae and microalgae, due to the discoveries and advances in their chemical and biological characterization. These matrix have considerable potential as a source of bioactive compounds, although commercial exploitation is still limited. Thus, following circular economy approaches, these matrices could be employed as a source of compounds of interest for various applications. In this sense, many emerging extraction technologies have been developed, allowing better extraction of bioactive compounds. Thereby, it would be promising to develop functional food with bioactive compounds from under exploited matrices obtained through new emerging extraction technologies and using 3D food printing (Jankun et al., 2007).

2. 3D food printing

In the literature, 3D printing, also called Additive Manufacturing (AM) or Food layer Manufacturing (FLM) (Wegrzyn et al., 2012), can be used to print food products. It is a three-dimensional technology used for printing objects by adding layer upon layer in a short period of time (Joshi & Sheikh, 2015). This technology allows to design the appearance, shape, taste, color, consistency, and composition of a food. In this process, heat can be used to facilitate the bonding of the layers to each other and obtain a compact shape. Thus, 3D food printers can use solid, liquid, or semi-liquid foods as inputs and formulate food with the desired characteristics (Joshi & Sheikh, 2015). Among the advantages of 3D printing, the customization of food according to the preferences or needs of consumers is one of the most outstanding. With this technology,

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we can make food with different nutritional values, depending on the specific needs of individuals, but with the same appearance as the original food. Hence, personalized meals can be prepared using biometric data and nutritional status, as mentioned by some authors (Lipson & Kurman, 2013). This method of personalizing meals can be a substantial advantage for people who need to avoid some compounds in their meals. For example, food industries could apply 3D printing to obtain foods free of gluten, sugar or lactose, and enrich it with desired compounds (Millen et al., 2012). The perception of food in the mouth is also an important parameter for consumers. Varying the amount of hydrocolloids, it is possible to design foods with different textures, there to change its perception by consumers (Vesco & Lipson, 2009, pp. 807–817). Other advantages include (Vesco & Lipson, 2009, pp. 807–817):

- New components are used in the meal preparation;
- The meals are more accessible and more uncomplicated to prepare;
- There is a possibility to achieve at the same time, the esthetic and customization;
- New textures are developed;
- The shelf life is increased;
- It is easily transportable;
- It brings out new dishes, new design, new creativity in the culinary art;
- Everyone can bring their food designer;
- It is an efficient technique, and it is very economical.

To create the model, 3D printers use Stereolithography (SLT) files, a format of computer-aided design (CAD). 3D printing was initially developed for rapid prototyping, but now it is used for the manufacturing of final objects. 3D food printing is a recent technology (developed in the eighties of the twentieth century) (Izdebska, 2015; F.; Yang et al., 2017). This technology can be applied through different technologies such as fused deposition manufacturing (FDM), selective sintering technology, powder bed binder jetting and inkjet printing (Sun et al., 2015). In FDM, materials are extruded by a heated nozzle layer by layer. According to some authors, this is the preferable technique for the 3D printing of chocolate. Many extruders should be fixed to this printer to enable the printing of several materials simultaneously. In selective sintering technology, particles of powder are melted layer-by-layer. Here, sugar or powder rich in sugar are the expected inputs. Along the x and y axes, a thin powder is applied with a laser or hot air on the bed. To form the final product, it is necessary to repeat applying and sintering the powder, after which it is then purified. There is no post-process in this technology. In powder bed binder jetting, a liquid binder spray is used to combine and apply a uniform layer of powder. As previously, there is a repetition of the process until removing the final product and excess powder. However, to improve the connection between layers, it is required a finishing process (F. Yang et al., 2017). In inkjet printing of foods, the technology is the same as the one used to print books or booklets, but the difference is that here the ink used is edible. The technology used here is print heads with a drop in demand (Sun et al., 2015; F.; Yang et al., 2017).

3D printed food has been described as a useful tool to manage different problems, including: (1) resolve the problem of food scarcity; (2) eradicate malnutrition; (3) reduce the effect of climate mitigations; (4) eliminate unnecessary businesses; (5) resolving the problem of food supply for astronauts and military. So, 3D food printing technology can easily be applied to formulate functional foods (Tran, 2016).

3. Functional foods

Functional foods are defined as foods that have a beneficial effect on health, scientifically substantiated, beyond basic nutrition (Domínguez, 2013). Many terms are used to distinguish functional foods, but in some cases, there is no distinction among: nutraceuticals, bioactive foods, novel foods, designed foods, health foods, medicinal foods, therapeutic foods (Bidlack, 2013; Domínguez, 2013; Guo, 2013; Sankaran & Mouly, 2007). The physiological benefits are attributed to the presence of bioactive compounds or functional ingredients, that are not present in the conventional food (Biesalski et al., 2009). Some examples of these compounds are minerals, vitamins, ω-3 fatty acids, polyphenols, phytosterols, soluble fiber (prebiotics), proteins, amino acids, probiotics, carotenoids, antioxidant compounds, etc., can exert specific actions into the human body (Hasler, 2002). Research in the development of functional food is focused on (Guo, 2013):

- colonic microflora, transit time, nutrient bioavailability, endocrine, and immune activity;
- antioxidant and redox systems;
- the reduction of the risk of pathologic effects associated with cardiovascular disease and insulin resistance;
- infant and fetal diet;
- carcinogenicity or control of toxicity caused by xenobiotics present in food or the environment;
- physical performance, behavior or cognition, and attitude.

According to the criteria defined in food regulations, functional foods should be safe for the consumers. Therefore, the development and validation of new procedures to assess stability, bioavailability, and functional food risks is needed. There is a necessity to carefully monitor the consequences of interaction(s) between the function(s) of the body and functional foods (Biesalski et al., 2009). For the formulation of a functional food that will contribute to the management of type 2 diabetes, the bioactive constituents with dipeptidyl peptidase-4 inhibitors effect, are used as ingredients (Kazeem et al., 2021).The potential adverse interaction with pharmaceutical agents and another dietary component should also be assessed (Hasler, 2002). Communication on the physiological and health benefits of functional foods is essential to prevent consumer confusion and promote public health. Publication in peer-reviewed journals is the best way to share scientific information to improve the product's credibility and consumer awareness.

The production of functional foods can be done by supplementation of a conventional food with bioactive compounds, which could be extracted from different sources. Recently, research has shown that food by-products, algae and microalgae are incredibly useful sources of bioactive compounds. However, to be able to use them in the formulation of any functional foods, first it is necessary to extract them. Food industries are increasingly involved in natural products, product safety, quality, and functionality (Biesalski et al., 2009), and also in the use of green technologies to avoid the use of toxic solvents, protecting environmental safety. In this sense, renewable bio-solvent such as ethanol, supercritical CO_2 hot and subcritical water are widely encouraged to be used for the extraction of bioactive compounds from natural matrices (Crampon et al., 2011; Díaz-Reinoso et al., 2006; Herrero et al., 2006).

4. Emerging extraction technologies of bioactive compounds

The extraction of bioactive compounds from natural matrix can be done through many conventional techniques based on the extracting power of solvents used and the application of heat or mixing. Conventional techniques used to extract bioactive compounds from plants are (1) Hydro-distillation, (2) Maceration, and (3) Soxhlet extraction (Azmir et al., 2013). It is worth mentioning that the solvent's choice depends on the efficiency of all the conventional methods (Cowan, 1999; Joshi & Sheikh, 2015). The choice of the solvent will depend on the polarity of the targeted compound, the affinity between solute and solvent, use of co-solvent, environmental safety, human toxicology, and financial feasibility, among other variables. Table 1 shows different solvents used to extract some bioactive compounds.

Conventional extraction methods have significant limitations, like long extraction times, high cost, high amounts of solvent are required,

Table 1
Example of some extracted bioactive compounds by different solvents (adapted from (Cowan, 1999)).

Water	Ethanol	Methanol	Chloroform	Dichloromethanol	Ether	Acetone
Anthocyanins	Tannins	Anthocyanins	Terpenoids	Terpenoids	Alcaloids	Flavonoids
Tannins	Polyphenols	Terpenoids	Flavonoids		Terpenoids	
Saponins	Flavonol	Flovonol				
Terpenoids	Terpenoids	Alkaloids				
	Alkaloids	Flavones				
		Polyphenols				

evaporation losses, low extraction selectivity, and decomposition of thermo-labile compounds. In this context, emerging innovative extraction techniques have been introduced to come through these limitations. The most well-known are ultrasound-assisted extraction (UAE), pulsed electric field assisted extraction (PEF), enzyme-assisted extraction (EAE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), and supercritical fluid extraction (SFE) (Luque de Castro & García-Ayuso, 1998).

4.1. Ultrasound-assisted extraction (UAE)

Beyond human hearing, ultrasound is a particular type of sound wave. It is usually comprised of between 20 kHz and 100 MHz. These waves create expansion and compression zones when passing into a medium, producing the phenomenon of cavitation with the production, grown and collapse of bubbles (Carreira-Casais et al., 2021, p. 9153). Fig. 1 shows the schematic representation of an ultrasound-assisted extraction equipment (Díaz-Reinoso et al., 2006). Ultrasound energy is efficient for solid plant samples because it eases the liberation of organic and inorganic compounds from the plant matrix (Herrera & Luque De Castro, 2005). Accelerated access of solvent to cell material and mass transfer is the mechanism of this technology. Thus, UAE involves two main phenomena: (a) Diffusion through the cell wall and (b) the breaking of the wall increasing the targeted cell content extract (Mason et al., 1996). The governing factors for efficient and effective extraction are the moisture content, particle size, solvent, temperature, pressure, frequency, and sonication time. UAE has the advantage of reducing extraction time, energy, and the solvent used. This technology uses ultrasound energy to facilitate more efficient mixing, reduce thermal gradients, fast transfer of energy, faster response to process extraction control, selective extraction, quick start-up, reduced equipment size, increased production, and eliminates process steps (Chemat et al., 2009).

Several studies have employed UAE to extract bioactive compounds from natural matrices. For example, UAE was successfully employed to obtain four isoflavone derivatives from soybean namely: daidzin, glycitin genistin, and malonyl genistin (Rostagno et al., 2003). In another study, the extraction of several compounds (rutin, naringin, naringenin, quercetin, ellagic acid, and kaempferol) from strawberries was enhanced by developing a semi-automatic method based on ultrasounds (Herrera & Luque De Castro, 2004). The optimum parameters for chlorogenic acid from fresh leaves, fresh bark, and dried bark of *Eucommia ulmodies* Oliv. by UAE were mehtanol 70%, solvent ratio 20:1 and time 30 min (H. Li et al., 2005). Comparing methods, some studies have reported that UAE showed better extraction efficiency than conventional methods. This is the case of the extraction of rutin and quercetin from *Euonymus alatus* (Thund). Sieb under optimized sonication condition (Yang & Zhang, 2008). For an effective extraction of vindoline, catharanthine, and vinblastine alkaloids from *Catharanthus* spp., UAE extraction with ionic solvent was the most effective strategy (L. Yang et al., 2011). The extraction from grape peel phenol carboxylic acids, and rosmarinic acid has been proved to be more efficient, having a shorter extraction time in UAE compared to conventional methods of extraction (Zu et al., 2012).

4.2. Pulsed-electric field extraction (PEF)

During the last years, pulsed electric field (PEF) was designed to enhance diffusion, drying, pressing, and extraction processes (Angersbach et al., 2000; Lebovka et al., 2002). To increase extraction rate, PEF works on the principle of breaking the cells membrane. During the extraction process, an electric potential pass through the cell membrane. This potential, based on the nature of the dipole, separates molecules according to their charge in the cell membrane. There will be repulsion between charges of the molecules at a potential exceeding the value of 1V, inducing pores expansion in weak areas, and causing an increase of the membrane permeability (Bryant & Joe, 1987). For the treatment of plants intended for PEF, an exponential degenerative pulse circuit is used. The equipment here is composed of two electrodes to place the material between them in a chamber. The PEF process can be conducted in a continuous or batch mode (López et al., 2008). Strength, pulse number, energy input, temperature, and the properties of the materials are the parameters that impact the efficiency of the PEF process (Heinz et al., 2003). Fig. 2 provides an overview of a pulse electric field treatment chamber (Drosou et al., 2017).

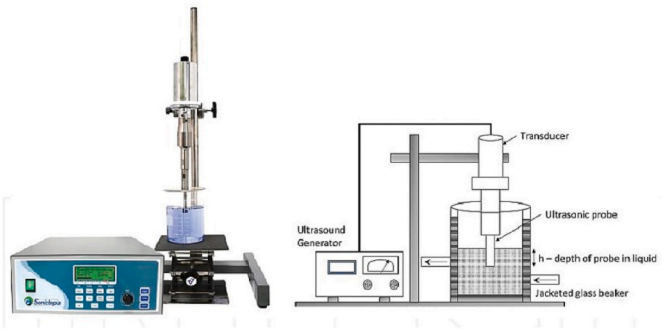

Fig. 1. Schematic representation of an ultrasound-assisted extraction equipment. (Díaz-Reinoso et al., 2006).

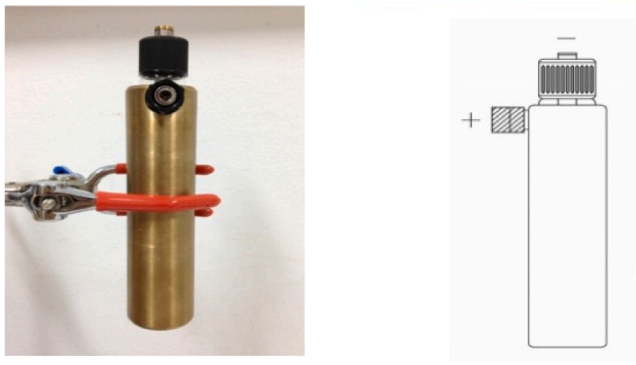

Fig. 2. Schematic representation of a pulse electric field treatment chamber (Drosou et al., 2017).

When the plant's cell membrane is broken, the mass transfer will increase while the needed extraction time decreases during PEF extraction. This technology has the advantage of enhancing the release of intracellular compounds due to the increase in the permeability of the cell membrane (Drosou et al., 2017). A drawback of this technology is that between 500 and 1000V/cm, for 10-4-10-2 s, the cells membrane is damaged with a slight increase in temperature (Fincan & Dejmek, 2002; Lebovka et al., 2002), which could heat-sensitive compounds (Ade-O-mowaye et al., 2001). This techniques is also employed as a pre-treatment before applying a conventional extraction method, to reduce the effort during extraction (López et al., 2009). For example, solid-liquid betanin extraction from beetroots after a PEF pre-treatment (1 kV/cm; 7 kJ/kg energy consumption) has the highest degree of extraction compared to mechanical pressing and freezing (Fincan et al., 2004). Other authors established that when pretreating the plant material with PEF, there is a 32.4% increase in the recovery of phytosterols from maize and an increase of 20–21% in the recovery of isoflavonoids (genistein and daidzein) from soybeans (Guderjan et al., 2005). In another study, it was found that the extraction of anthocyanin mono-glucosides from grape by-product was better with PEF extraction (Corrales et al., 2008). During vinification, applying PEF to grape skin before maceration increases the stability of bioactive compounds such as polyphenols or anthocyanin and reduces the maceration time (López et al., 2008). The Merlot skin permeabilization by a PEF treatment induced the highest extraction of anthocyanins and polyphenols (Delsart et al., 2012).

4.3. Enzyme-assisted extraction (EAE)

Vegetal samples have a complex wall, where several compounds are fixed by hydrogen or hydrophobic bonds in the polysaccharide-lignin network, making their access with solvent extraction impossible. To release bounded compounds in a medium, the use of enzymes for pre-treatment is an approach that can guarantee an increase in extraction yields (Rosenthal et al., 1996). Breaking of cells and hydrolyzation of polysaccharides and lipids during an extraction process can be done by adding enzymes like amylase, pectinase, cellulase or lipase to enhance the recovery (Rosenthal et al., 1996). Enzyme-assisted aqueous extraction (EAAE) and enzyme-assisted cold pressing (EACP) are the two types of EAE approaches (Latif & Anwar, 2009). While dealing with seeds to extract oils, EAAE is usually applied (Hanmoungjai et al., 2001; Rosenthal et al., 2001). When a polysaccharide-protein colloid is not available, with the use of EACP technology, enzymes can hydrolyze the wall of seed (Concha et al., 2004). The main factors in EAE technology are the concentration and composition of an enzyme, the particle size, the ratio of solvent to solid, and the time of hydrolysis. Enzymatic hydrolysis also depends on the water content of the plant (Domínguez et al., 1995). Bioactive compound extraction technology with EACP is ideal for oilseeds (Bhattacharjee et al., 2007). With this technology, the extracted oil has a higher amount of fatty acid and phosphorus than traditional solvent extraction (Puri et al., 2012). A study have found a correlation between the degree of cell wall breakdown by enzyme and the total yield of phenols after a test on phenolic antioxidants with EAE techniques applied on pomace fruits during the production of wine (Meyer et al., 1998). Some authors have shown that the release of phenolics from *Ribes nigrum* pomace increases with different enzymes (Landbo & Meyer, 2001). According to other studies, the best results in the extraction of phenolic contents from five citruses (Yen Ben lemon, Meyer lemon, grapefruit, mandarin, and orange) were obtained with the enzyme celluzyme MX (B. B. Li, Smith, & Hossain, 2006). During their experiments, they also found that there is a positive correlation between the concentration of enzyme and phenolic antioxidants extraction yields (the higher the concentration of enzyme is, the higher is the extraction yields of phenolic antioxidants) (B. B. Li, Smith, & Hossain, 2006). Other authors compared the extraction of bioactive compounds (phenolic acids, non-anthocyanin flavonoids, and anthocyanins) from grape pomace with sulfite-assisted extraction and a mixture of pectinolytic and cellulolytic enzyme in the ratio of 2:1. They established that the second one has a higher yield (Maier et al., 2008). The use of enzymes in hydro-alcoholic extraction of phenolic antioxidants in raspberry solid wastes yields higher yields than a non-enzymatic extraction. It has also been described novoferm enzyme had the highest effect on phenolic release from grape waste, compared to celluclast and pectinex enzymes. Therefore, EAE technology can be another mean for the extraction of bioactive compounds from food byproducts in industries (Domínguez et al., 1995).

4.4. Microwave assisted extraction (MAE)

This extraction technology uses microwave energy to recover a soluble fraction from a material (Jocelyn Paré et al., 1994). Here, the frequency of the electromagnetic fields is between 300 MHz and 300 GHz. These waves have two perpendicular oscillating fields (electric and magnetic fields). Heating with a microwave is based on the polarity of the material heated (Letellier & Budzinski, 1999). The conversion of electromagnetic energy into heat is directed by the dipole rotation and ionic conduction (Cravotto et al., 2008). Foremost, the MAE mechanism operates in three steps: (1) due to the increase of pressure and temperature, solutes are separate from the active sites of the matrix sample; (2) the solvent is diffused across the matrix sample; and (3) solutes are released into the solvent (Pan et al., 2003). Fig. 3 shows schematic representation of a microwave-assisted extraction equipment used at laboratory scale. MAE has several advantages: quicker heating, reduced thermal gradients, reduced equipment size, and increased extraction yield. With this technology, a rapid and better recovery of a bioactive compound is feasible compared to conventional methods (Cravotto et al., 2008). This extraction technique is considered as a green technology because the quantity of organic solvent used during the process is reduced (Pan et al., 2003).

Several studies have employed MAE for the extraction of bioactive compounds. For example, using MAE, extraction of caffeine and polyphenols from green leaf tea is higher at 4 min than any other extraction methods at room temperature for 20 h (Shu et al., 2003). Fifteen minutes of MAE led to higher yields of the ginsenoside obtained from ginseng root than a 10 h extraction with a conventional solvent (Dhobi, 2009). Another study found that the extraction of flavolignin and silybinin from *Silybum marianum* by MAE technology was higher than conventional extraction techniques (maceration and soxhlet) (Asghari et al., 2011). Other study compare MAE and conventional extraction yields of some bioactive compounds (E− and Z-guggolster-one, cinnamaldehyde, and tannin) from many plants. They conclude that MAE was the more accessible and rapid method (Chiremba et al., 2012). MAE has also been applied to extract phenolic acids from sorghum and maize flour and bran fraction of outstanding rigidity (Teng, 2009). MAE extraction was also optimize for the extraction of flavonoids and phenolic compounds from *Pseudocydonia sinensis* in terms of concentration of solvent, time of extraction, and the power of microwave power (Richter et al., 1996).

4.5. Pressurized liquid extraction (PLE)

Pressurized liquid extraction was first described in 1996 (Nieto et al., 2010). PLE has many appellations: enhanced solvent extraction (ESE), accelerated fluid extraction (ASE), or high-pressure solvent extraction (HSPE) (Hayes, 2012). The principle of this technique is to apply high pressure to the solvent beyond its boiling point, thus facilitating the extraction. The remarkable development of PLE technology was the automation, low quantity of solvent, and reduced extraction time. In this technology, the extraction rate is improved by applying a high extraction temperature, leading to reducing the surface tension and viscosity of solvent and increasing the solubility and rate of mass transfer (Kaufmann & Christen, 2002). (Hayes, 2012). In addition, this extraction technology is considered green because of the small quantity of

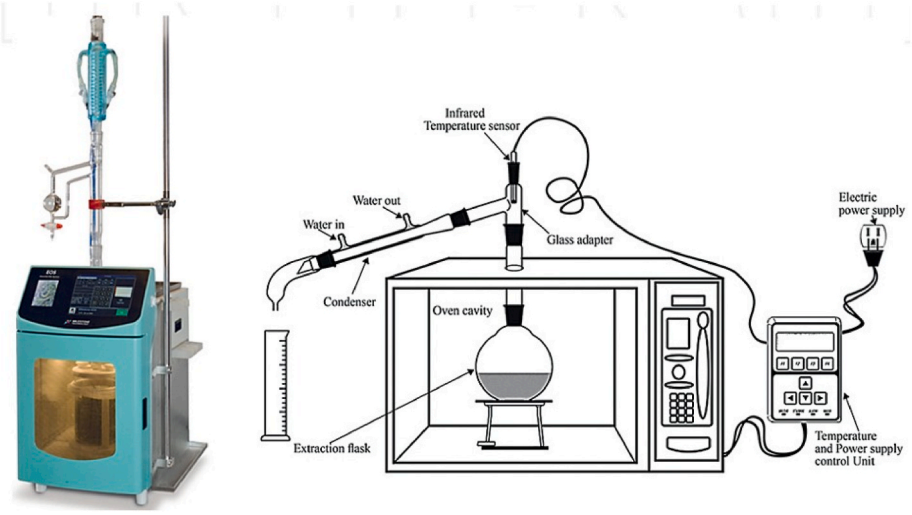

Fig. 3. Schematic representation of a microwave-assisted extraction equipment used at laboratory scale (Castro-López et al., 2016).

solvent required during the process (Nieto et al., 2010). In Fig. 4 the scheme of pressurized liquid extraction equipment is given.

The application of PLE in the extraction of bioactive compounds has been a success in many cases. In optimized conditions, the extraction of isoflavone in frozen and dry soybeans was done without any degradation (Shen & Shao, 2005). Other studies have compared three extraction technologies (PLE, ultrasound-assisted extraction, and Soxhlet extraction) in the extraction of terpenoids and sterols from tobacco (Howard & Pandjaitan, 2008). PLE has been found as an alternative to conventional extraction methods, considering the high yield, reproducibility, low extraction time, and low solvent consumption (Shen & Shao, 2005). The extraction of flavonoids with PLE from spinach with a combination of solvent: water and ethanol (30:70) at 50-150°*C* was better than the only use of water solvent at 50–150 °C (Luthria, 2008). With PLE technology, the extraction of phenolic compounds from parsley (*Petroselinum crispum*) can be influenced by many parameters: solid-to-solvent ratio, particle size, temperature, flush volume, static time, and pressure (Mroczek & Mazurek, 2009). In optimized conditions, lycorine and alan-thamine alkaloids extraction from *Narcissus jonquilla* by the PLE method is more efficient than hot-solvent extraction, MAE and UAE methods (Erdogan et al., 2011).

4.6. Supercritical fluid extraction (SFE)

The SFE was developed by Hannay and Hogarth, but Zosel presented its application in food industry through coffee decaffeination (Zougagh et al., 2004). Many scientists have focused their interest on SFE in the following areas: environment, pharmacy, polymers, and food analysis (Ndiomu & Simpson, 1988). The supercritical state is different from the primary states: solids, liquids, and gas, obtained when a substance is subjected to a temperature and pressure higher than its critical point. The temperature and pressure points above which liquid and gas phases do not exist are critical points (Sihvonen et al., 1999). In that state, the supercritical fluid cannot be liquified with a change in temperature or pressure. This fluid has gas-like properties (viscosity, surface tension, and diffusion) and liquid-like properties (solvation power and density), decreasing the extraction time and increasing the yields during an extraction process. Fig. 5 describes a typical diagram of SFE instrumentation. The most used solvent in SFE is carbon dioxide (CO_2), due to its low critical temperature and pressure and non-toxicity among other advantages (de Hoyos-Martínez et al., 2019; Talmaciu et al., 2016). The limitation of CO_2 is due to its low polarity, making him unsuitable for many pharmaceutical and drugs products, although it is suitable for non-polar substances, lipids, and fat. Nevertheless, chemical modifiers, even at a small amount, can resolve this limitation (Ghafoor et al., 2010; Hawthorne et al., 1994).. To improve the extraction, polar co-solvent can be used. The selection of the co-solvent should be made by the property of the sample and the target compounds (Rodríguez De Luna et al., 2020). Among many, the main factors influencing the SFE process are the size of particle and moisture content of the matrix, temperature,

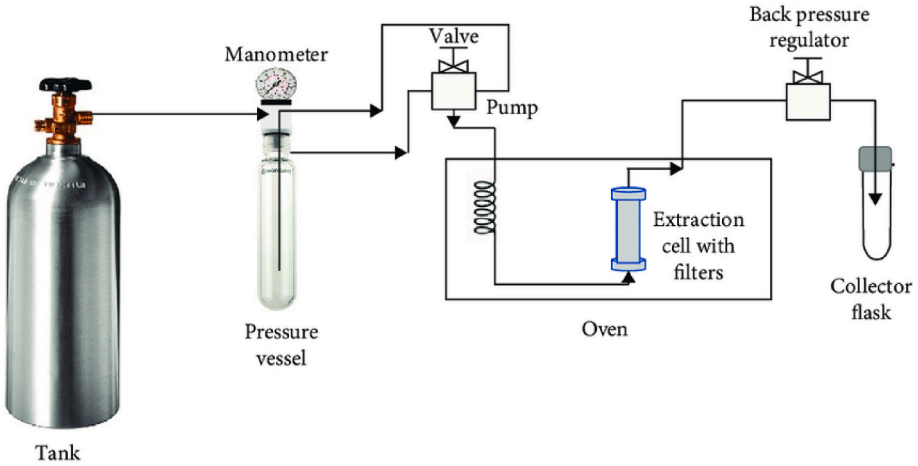

Fig. 4. Scheme of pressurized liquid extraction equipment (Saldaña et al., 1999).

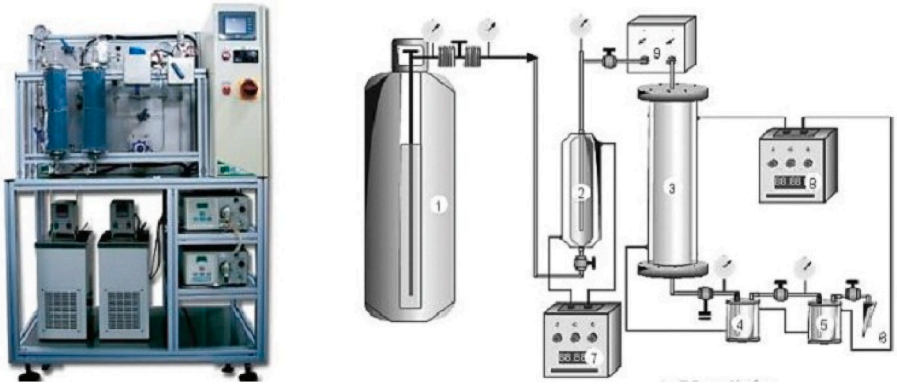

Fig. 5. Schematic representation of a supercritical fluid extraction (SFE) system (Castro-López et al., 2016). 1. CO_2 cylinder; 2. Surge tank; 3. Extractor; 4. and 5. Separators; 6. Collector and gas measuring device; 7. and 8. Thermostatic baths; 9. Isocratic pump.

solvent-to-matrix ratio, pressure, flow rate of CO_2, and extraction time. The control of these parameters is the key to improving the extraction rates (Ghafoor et al., 2010; Saldaña et al., 1999). Extraction of a bioactive compound by SFE has the following advantages (Hawthorne et al., 1994): (1) The diffusion coefficient of supercritical fluid is high, its viscosity and surface tension are low compared to liquid solvent, generating better interring into sample matrix and favorable mass transfer. The time of extraction can be reduced with SFE compared to conventional methods. (2) The complete extraction of the targeted compound is assured by the repeated reflux of supercritical fluid. (3) Supercritical fluid is very selective compared to liquid solvent because the change of temperature and/or pressure can adjust the solvation power. (4) Time could be saved by depressurization of supercritical fluid. (5) SFE is ideal for extracting thermolabile compounds because it can operate at room temperature. (6) Time for the overall experiment could be saved in SFE because, compared to solvent extraction methods, even a small quantity of samples could be recovered. (7) SFE is considered as environmentally accessible technology because it uses a small quantity of solvents. (8) For highly volatile compounds, the coupling of SFE and chromatography has been found to be extremely useful. (9) Waste generation is minimized because supercritical fluid can be recycled. (10) SFE can easily be scaled up to fit a dispositive designed for a small number of samples in a laboratory to tons of samples in an industry. Information provided by SFE operations can be used to optimize the process. (11) SFE process provides information regarding the extraction process and mechanism manipulated to optimize the extraction process.

A study used SFE at 313–343 K temperature and pressure from 14 to 24 MPa for the extraction of caffeine, theobromine, and theophylline from *Ilex paraguaryensis* (herbal mate tea) (Giannuzzo et al., 2003). Modifying supercritical CO_2 with ethanol at 15 wt increases naringin's extraction yields from citrus paradise compared to the only application of supercritical CO_2 at 9.5 MPa and 58.6°C (Ashraf-Khorassani & Taylor, 2004). The extraction from the grape seed of catechin and epicatechin by SFE using as a solvent the methanol modified CO_2 at 40% gives more than 79% of the extract (Carnevali et al., 2021). The extraction from the grape seed of catechin and epicatechin by SFE using as a solvent the methanol modified CO_2 at 40% gives more than 79% of the extract (Carnevali et al., 2021). Optimal conditions for the extraction of indole alkaloids from *Catharanthus roseus* leaves were 25 MPa, 80°C and 6.6% methanol as modifier for 40 min (Baiano, 2014).

Table 2 resume the advantages and drawbacks of the emerging extraction technologies described above. The use of the listed extraction technologies can be applied to food compounds directly, but also in food by-products, bringing more rentability, or they can be applied to algae and micro-algae, to increase their industrial applications. The following part describes the different bioactive ingredients that could be extracted from food by-products and algae, using any of these emerging extraction technologies, before using them in the 3D printing of a desired functional food.

5. Bioactive ingredients from food by-product

Food residues are produced along the food chain. As mentioned before, these by-products are a source of polysaccharides, proteins, fibers, phytochemicals, and flavor compounds, which can be valued as nutritionally and pharmacologically functional ingredients (Gutiérrez, 2004). Nutraceuticals from diverse sources can be used in the formulation of extruded food products. We can mention as examples:

- γ-oryzanol extracted from rice bran, acting as an antioxidant, anticancerogenic, cholesterol-reducing agent, and preventing agent in the treatment of menopausal syndrome (Izydorczyk & Dexter, 2008);
- β -glucans from barley flour, which can increase the metabolism of lipids, lower glycemic index, and reduce plasma cholesterol (Zanwar et al., 2011);
- lignan concentrates recovered in flaxseed, acting as antibacterial, anticancerogenic, antioxidant, anti-inflammatory, and antiviral agents (Kim et al., 2006);
- phenolic compounds from cereal brands, acting as antioxidants, fight against cancer, cardiovascular diseases, free radical damage (Ohtsubo et al., 2005).

γ-Oryzanol is thermolabile, and its quantity decreases with an increase of temperature during extrusion. The oryzanol content has been higher in extruded and puffed pre-germinated brown rice than in non-extruded polished rice (Perretti et al., 2003). The incorporation of β-glucans fractions in noodles, pasta, dairy products, and breakfast cereals has been a success. The enrichment with β-glucans of pearled barley before adding durum wheat gives good cooking properties to pasta (Nawirska & Kwaśniewska, 2005). Flaxseed meal enriched with lignans is suitable for the manufacturing of bakery products. Before extrusion, ingredients should be mixed naturally with phenolic compounds (benzoin, catechin, chlorogenic acid, and ferulic acid) to obtain products more resistant to oxidation while producing rolled oats (Joshi & Sheikh, 2015; Waldron, 2009). In this way, the phenolic content of the final product will be higher than the conventional method, even if the processing conditions reduce the initial amount at a percentage of 24–26%.

Pectin's extracted from fruit pomace and purified play a gelling function in producing foods like sweets, jams, and fillings. Pomace is also the source of food additives (pigments, dietary fibers, lactic acid, natural sweeteners, cellulose, and vinegar) (Waldron, 2009). There is pectin classification according to their degree of methylation. If the degree of methylation is up to 50%, it is high-methoxy pectin, and if the degree of methylation is under 50%, it is considered low-methoxy

Table 2
Advantages and drawbacks of six (6) emerging extraction technologies.

Extraction technology	Advantages	Drawbacks	References
Ultrasound assisted extraction (UAE)	In UAE, the mixing is facilitated, the thermal gradient is reduced, the transfer of energy is faster, the extraction time is reduced, the response to process extraction control is faster, the extraction is selective, the size of equipment is reduced, the production increased, and process steps are eliminated.	In the UAE, a filtration step is required, and, at high frequencies, there is the possibility of destroying some compounds.	(Bimakr et al., 2017; Proceedings of the 3rd International Conference on Materials, 2004)
Pulsed electric field extraction (PEF)	PEF benefits from improving the release of intracellular compounds with increased cell membrane permeability. PEF reduces the effort during extraction.	Between 500 and 1000V/cm; for 10-4-10-2s, the cells membrane is damaged with a slight increase in temperature. PEF deteriorates heat-sensitive compounds.	(Ade-Omowaye et al., 2001; Fincan & Dejmek, 2002; Lebovka et al., 2002; López et al., 2009)
Enzyme-assisted (EAE) extraction	The oil extracted by EAE has a higher quantity of free fatty acids and phosphorus than traditional hexane-extracted oil.	For industrial production, enzymes are relatively expensivePlant cell walls cannot be completely break down with available enzymeEAE could not be always applied in industrial scale since enzymes behave is limited by strict environmental conditions	(Domínguez et al., 1995; Mendes et al., 2006; Onwude et al., 2016)
Microwave assisted extraction (MAE)	Rapid heating for the extraction of bioactive compounds, reduced thermal gradients, reduced equipment size, and increased extract yield, inducing a rapid and better recovery of bioactive compounds. MAE is also recognized as a green technology because it reduces the use of organic solvents.	Low drying rate, especially in the falling rate phase, and reduced product quality due to thermal degradation.	Abbas et al. (2008)
Pressurized (PLE) liquid extraction	Automation is possible with the PLE; a few amounts of solvent and reduced extraction time are required. There is a reduction of the surface tension and viscosity of the solvent and an increase in the solubility and rate of mass transfer. It is considered as a green extraction technique.	Low polarity making it unsuitable for most pharmaceuticals and drug samples	(Ghafoor et al., 2010; Hawthorne et al., 1994)
Supercritical (SFE) fluid extraction	Because the supercritical fluid can be recycled and use a small quantity of solvent, SFE is considered as environmental free technology. SFE can easily be scaled up to fit a dispositive designed for a small amount of sample in a laboratory to tons of samples in an industry. Information provided by SFE operations can be used to optimize the process	SFE complicates system thermodynamics and increases capital costs.	(Godoi et al., 2016; Hawthorne et al., 1994)

pectin. In fruit-based foods, they play the role of gelling agents. For gel of a minimum of 55% of soluble solids and a pH $\leq$ 3.5, the use of high-methoxy pectin's is recommended. In contrast, low-methoxy pectin's are used in a medium having calcium ions (Guerard & LeGal, 1989).

Nowadays, natural ingredients in seafood waste or by-products have been of indubitable interest. The pepsin extracted from fish can play the same function as renin in cheese production (Raa, 1990). For descaling or de-skinning of herring, cod pepsin can successfully be used. In the production of caviar from trout and salmon, pepsin could be added to ease the release of roe from connective tissues (Bordenave et al., 2002). The inhibitory consequence on angiotensin I converting enzyme is the result of the action of the soluble protein fraction from shrimp waste, Alaska pollack, sardines, and cod heads, reducing, therefore, high blood pressure (Sainvitu et al., 2012). Small fish and fish by-products are used to produce a fish sauce (Thongthai & Gildberg, 2020). Considered as a rich source of amino acids, fish sauce can reinforce the food balance of vegetarians. It is also a good stimulator for white blood cells production (Analava et al., 2014).

Fish oil contained in the waste of catfish, cultured eel, ocean-caught tuna, milkfish, sardine, and squid could be extracted by SFE, microencapsulation technology, and enzyme treatment (Analava et al., 2014; Gutiérrez, 2004). Due to the insufficient quantity of ω-3 fatty acids in the modern diet, it is recommended to eat oily fish two or three times a week, improving the intake of polyunsaturated fatty acids, especially eicosapentaenoic and docosahexaenoic acids. Nevertheless, polyunsaturated fats are exposed to oxidation and have undesired fishy smells and off-flavors that can negatively influence their acceptance by consumers. These negative effects can be avoided with microencapsulation of fish oil (Patil et al., 2018).

The blood of animals is an interesting by-product because of their high protein content and heme iron (Ghosh, 2001). In Europe, it is used to produce blood sausages, blood pudding, bread, and biscuits; and in Asia, to make blood cake, curd, and pudding (Ghotra et al., 2002). Although the blood can easily be exposed to microbial contaminations, these products are assumed to be made with pure blood from healthy

animals. Their transportation must be done in a refrigerated stainless-steel material to avoid any recontamination. Otherwise, the use of an elevated temperature through spray drying could eliminate any remaining pathogen. To make margarine and shortening (Weiss, 1983), for frying food (Chrysam, 1985), to produce sausages, or for emulsification (Plaza et al., 2010), lard and/or tallow can be used. The blood of animals is an essential edible by-product because of their high protein content and heme iron (Ghosh, 2001). In Europe, it is used to produce blood sausages, blood pudding, bread, and biscuits; and in Asia, to make blood cake, curd, and pudding (Ghotra et al., 2002).

6. Bioactive ingredients from algae

It exists between one to ten million algae species. Usually, algae are classified in microalgae (unicellular microscopic size) and macroalgae (big multicellular size) (Metting, 1996). Algae are special and unique organisms with the ability to adapt to changes in their environmental conditions (temperature, salinity, nutrients, irradiations) while producing many metabolites with bioactive functions (Plaza et al., 2008). Algae cultivation is easy, its growth rate is high, and the generated bioactive compounds can be controlled by varying the growing medium or genetic approach (Silberstein & Parsons, 2010). These organisms are considered natural reactors and can be used to synthesize some chemical compounds. Therefore, algae in an unlimited field, classified between promising sources in the development of new products because of their great diversity and the constant finding of new bioactive compounds in this group of organisms (Metting, 1996). Many studies show that algae and microalgae are excellent sources of bioactive compounds that could be used as functional ingredients (Silberstein & Parsons, 2010).

Generally, chemical and biological methods are used for testing the bioactivity of algae and microalgae. The following biological activities have been found in bioactive compounds extracted from algae and microalgae (Metting, 1996):

- Antioxidant activity (in phenolics compounds and carotenoids);
- Antihelmintic, antifungal, and antibacterial activity (indoles, peptides, terpenes, phenols, steroidal glycosides, fatty acid, etc.);
- Anticoagulant activity (sulfated polysaccharides);
- Antiviral activity (fatty acids, proteins, terpenoids, sulfated flavones, and polysaccharides);
- Anti-inflammatory activity (shikimate-derivatives, sterols, terpenes, indols and astaxanthin).

Among bioactive compounds found in algae, carotenoids, some lipids and proteins, polysaccharides and dietary fiber, vitamins, phenolic compounds, are the main bioactive compounds. These compounds have the potential to be used as functional ingredients. The list of compounds and combinations could be uncountable due to the incredible biodiversity of algae and the high influence of growing conditions on bioactive formation.

6.1. Carotenoids

Carotenoids, due of their high antioxidant activity, are considered as cancer preventive agents (Kamath et al., 2008), possible life increasers (Kamath et al., 2008), an inhibitor of the development of ulcers (Voutilainen et al., 2006), and preventive compounds of heart attacks and coronary artery disease (Mojaat et al., 2008). In macroalgae, the carotenoids content depends on the type of algae: green algae (chlorophytes) contain zeaxanthin, lutein, violaxanthin, β-carotene, neoxanthin; red seaweeds (rhodophytes) are a source of zeaxanthin, lutein, and α-and β-carotene while brown algae (phaeophytes) present high amounts of fucoxanthin, violaxanthin, and β-carotene (Pereira et al., 2021).

Different methods have been found to extract and isolate β-carotene (Rao et al., 2007). SFE is the most appropriate technique to extract β-carotene from microalgae because of the low polarity of supercritical CO_2 used as solvent (Rao et al., 2007). Under stressful conditions, green algae can produce more than 2–3% of astaxanthin on a dry weight basis (Thana et al., 2008). Many techniques could extract astaxanthin: SFE with supercritical CO_2 (Nobre et al., 2006), supercritical CO_2 with different co-solvents (Jaime et al., 2010), PLE (L. Zhao et al., 2009), MAE (Kang & Sim, 2008), extraction with vegetable oils (Chang & Sang, 2007) or with solvents (Sarada et al., 2006), or the treatment of the cells using different solvents and organic acids at the temperature of 70 °C before the extraction with acetone to facilitate the extraction of astaxanthin (Antonopoulou et al., 2005).

6.2. Lipids

Algae contain a lipid fraction of about 1–3% of their dry weight. In microalgae, mono-galactosyl diacylglycerols (MGDGs), di-galactosyl diacylglycerols (DGDGs), and phosphatidylglycerol (PG) are the principal's polar lipids constituents (Simopoulos, 1996). Most of the lipid's content of algae is composed of polyunsaturated fatty acids (PUFAs) (Metting, 1996). These essential nutrients could not be synthesized by the organism but should only be provided by foods. For cell membrane, ω-3, and ω-6 long-chain PUFAs play a structural and functional role. The ratio ω-3 to ω-6 ratio is particularly important for a balanced diet (Stanley et al., 2007). They are also precursors of eicosanoids playing immunological and hormonal activities. For consuming these two fatty acids, the best ratio ω-6: ω-3 must range from 3:1 to 5:1 (Zuliani et al., 2009). In recent years, the properties of docosahexaenoic acid (DHA) (ω-3 C 22:6) and eicosapentaenoic acid (EPA) (ω-3 C 20:5) have been found very interestingly. In many papers, long-chain ω-3 fatty acids have presented protective effects on the vascular system (Yukino et al., 2005). Regarding macroalgae, green algae have an excellent alpha-linolenic acid (ω-3 C18:3) content, while brown and red algae are good EPA and arachidonic acid (ω-6 C 20:4).

6.3. Proteins

Algae contain proteins near 47% of the dry weight, varying with seasons and species (Morgan et al., 1980). Brown algae have low protein contents (5–15% of the dry weight), while red and green algae have a higher protein content (10–30%). However, *U. pinnatifida* is a brown alga with a protein level between 11 and 24% dry weight (Burtin, 2003), *Porphyra tenera* and *Palmaria palmata*, from the group of red algae, have a protein content of 33-7% (Morgan et al., 1980) and 8–35% dry weight (Burtin, 2003), respectively. These proteins content is close to the one of soybean (Metting, 1996). These algae are high-quality proteins because of their high composition in the following amino acids: arginine, valine, leucine, lysine, threonine, isoleucine, glycine, and alanine, with the predominance of asparagine and glutamine these two last presenting flavor development properties (Metting, 1996).

6.4. Polysaccharides and dietary fibers

Algae are rich sources of polysaccharides. The total content of fibers in algae (33–50%) is higher than that of many plants. The diversity of algae polysaccharide content leads to the presence of minor polysaccharides in his cell wall like fucoidans (in brown algae), xylans (in some green and red algae), ulvans (in green algae), and cellulose (in all genera). Laminarin (β −1,3 glucan) found in brown algae and floridean starch (amylopectin-like glucan) contained in red algae are considered as storage polysaccharides (Slavin & Green, 2007). The central part of these polysaccharides is dietary fibers undigestible by humans. Insoluble fibers primarily improve the laxation effect and the improvement of satiety feeling (Tosh & Yada, 2010). In the large intestine, the central part of the insoluble fibers is fermented, supporting the intestinal microflora growth, comprising probiotics.

On the other hand, soluble fibers reduce cholesterol and regulate the

glucose level in the blood (B. Li et al., 2008). Cellulose, hemicellulose, and lignin belong to insoluble fibers, while oligosaccharides, pectin's, β-glucans, and galactomanna gums are soluble fibers. Sulfated polysaccharides are present in algae providing specific functional properties. For example, brown algae contain a soluble fiber (fucoidans) which possess substantial percentages of sulfate ester groups and L-fucose. In addition the algal polysaccharide ulvan, can suppress growth of hepatoma cells in the treatment of tumors (C. Zhao et al., 2020). In the recent decade, the following biological activities of fucoidans from many brown algae have been established: anti-inflammatory, antiviral, antitumoral and immunomodulatory, antioxidant and anticomplementary properties, anticoagulant and antithrombotic, blood lipids reducing, activity against hepatopathy, renalpathy and uropathy, therapeutic potential in surgery and gastric protective effects (J. B. Lee et al., 2004). Fucoidans are a suitable source of functional ingredients and drugs.

Many brown algae have been used for isolating fucoidans: *U. pinnatifida* (Kitamura et al., 1991) *Laminaria angustata* (Duarte et al., 2001), *Sargassum stenophyllum* (B. Li, Smith, & Hossain, 2006), *H. fusiforme* (Ponce et al., 2003), *Adenocytis utricularis* (Ramazanov et al., 2003), and *Cystoseira canariensis* (S. H. Lee et al., 2008). Galactan, agar, and carrageenans, all soluble sulfated polysaccharides present in red algae. Fucoidans and sulfated galactans (polymers of α-L and α-D or β-D-galactopyranosyl) are the most studied marine sulfated polysaccharides. These sulfated galactans have the following properties: anticoagulant, antitumoral, antiangiogenic, immunomodulation, anti-inflammatory, antiviral, and antithrombotic properties (Osumi et al., 1998). Many red algae are the source of sulfated galactans: *Grateloupia lanceolata, Grateloupia elliptica, Halymenia dilatate, C. Crispus, Sinkoraena lancifolia, Lomentaria catenata, Schizymenia dubyi,* and *Martensia denticulate* (Escrig & Cambrodón, 199 C.E.).

Agar is composed of sulfated galactans, D-galactose, and 3,6-anhydro-α-L-lactose and could be extracted from *Gracilaria* and *Gelidium* genus. The oversimplification of the structure of agar is represented by agarose. Carrageenan belongs to sulfated galactans and could be extracted from many red algae. These carbohydrates have a linear structure with repeated units of 3-linked β-D-galactopyranose and 5-linked α-D-galactopyranose. One of the hot water-soluble fractions of the cell wall is porphyrans, also considered as the main constituent of *Porphyra* sp. They are liners, presenting an alternation of 3-linked β -D-galactosyl units and 4-linked α-L-galactosyl 6-sulfate or 3,6-anhydro-α-L-galactosyl units. Despite the variation of their structure, they have demonstrated antitumor and immuno-regulatory properties (Escrig & Cambrodón, 199 C.E.).

6.5. Vitamins

Porphyra spp. are algae rich in water-soluble vitamins: vitamin C and B complex and fat-soluble vitamins A and E (Kumar et al., 2008). Algae have a large amount of pro-vitamin A. The content of green and brown algae in vitamin C (500-3, 000 mg/kg of dry matter) is comparable to the one of peppers, blackcurrant, and parsley, while the content of vitamin C in red algae is around 100–800 mg/kg (Slavin & Green, 2007). Vitamin C is essential for the organism as they play a role in activating the intestinal absorption of iron. It strengthens the immune defense system, controls the formation of conjunctive tissue and the protidic matrix of bony tissue, and acts in regenerating vitamin E and trapping free radicals (Slavin & Green, 2007).

6.6. Phenolic compounds

Phenols possessed antioxidants and other biological activities. They are essential in the protection of the algae cells against biotic and abiotic stress (Metting, 1996). Phenolic compounds are mainly associated with antioxidant activity of microalgae, and algae (Mišurcová et al., 2009). Anti-inflammatory activity has been related to some phenolic compounds of algae such as epi-gallocatechin gallate, caffeic acid, hesperidin, catechin, morin, catechol, and rutin, identified in *Porphyra* genus (Mišurcová et al., 2009).

7. Conclusion, trends, and recommendations

Table 3 presents selected 3D printing technologies, principles, type of material, applications, machines, and company selling them. Using this table, the formulation of any desired functional food could be done, taking all the presented parameters into consideration.

3D food printing is a modern technology, developed to design and manufacture food of defined properties and characteristics, which can be employed in the development of functional foods to fulfill the consumers demand's for more healthy food. Functional foods contain bioactive compounds in their formulation that can be extracted by emerging extraction technologies. Among many matrix, algae and food waste by-products are rich sources of bioactive compounds. It is possible to use a 3D food printer to design and develop specific foods, with specific functionalities. This can be a way to bring value added to the benefit of the processing activity of a food enterprise or a door to develop an innovative industry with higher specificity only specialized on 3D food printing of functional foods.

This review presents the possibility of using a 3D food printer to manufacture functional food using bioactive compounds extracted by emerging extraction technologies in foods waste by-product and algae. 3D food printing in the manufacturing of a functional food has many advantages: reduction of time, control of the size, shape, color and whole appearance, control of the quantity of nutrient intake and the beneficial effect on health targeted. Nevertheless, it would be necessary to make an economic analysis to see the rentability and to evaluate all the potential risk of this technology to ensure a better implementation and valorization of this technology.

Author statement

Pauline Donn : Writing - review & editing. Miguel A. Prieto : review

Table 3
Selected 3D printing technologies, principles, type of material, applications, machines, and Company selling them.

	Category		
	Extrusion -based printing	*Binder jetting*	*Inkjet printing*
Principle	Extrusion and deposition	Powder binding and binder drop-on demand deposition	Drop-on-demand deposition and Continuous jet printing
Material	Solid-based, Paste material	Liquid-based, Powder-based	Liquid-based, low viscosity material
Applications (example of functional foods)	Chocolate enriched in flavonoids, Candies enriched in B-glycans and phenolics compounds	Chocolate enriched in flavonoids, Pizza enriched with W3-fatty acids (Powder form), Fake food	Chocolate enriched in flavonoids, Liquid dough enriched in B-glycan, meat paste enriched in essential amino acids, cheese with high quality proteins, jams low in sugar, gels enriched in phenolic compounds.
Machine	Choc Creator, AIBOULLY Chocolate, Createbot 3D Food	Chefjet, Fujifilm Dimatix	Foodjet, Filament sixhead 3D
Company	Chocedge, AIBOULLY, Createbot	3D systems, Fujifilm Dimatix	De Grood Innovations, TNO

& editing, Supervision. Juan C. Mejuto: review & editing. Hui Cao: editing & Supervision. Jesus Simal-Gandara : review & Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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