CODEN [USA]: IAJPBB ISSN: 2349-7750

INDO AMERICAN JOURNAL OF
PHARMACEUTICAL SCIENCES

http://doi.org/10.5281/zenodo.3893048

Available online at: http://www.iajps.com *Review Article*

PICKERING EMULSIONS STABILIZED BY POLYPHENOL: A MINI-REVIEW

Eloiza Marcelle Costa Souza[1], Magda Rhayanny Assunção Ferreira[1*], Luiz Alberto Lira Soares[1,2]

[1]Laboratório de Farmacognosia, Avenida Professor Artur de Sá, SN, Cidade Universitária, Recife, 50740-521, Departamento de Ciências Farmacêuticas, Universidade Federal de Pernambuco, Brasil

[2]Programa de Pós-Graduação em Ciências Farmacêuticas, Universidade Federal de Pernambuco, Recife, Pernambuco, Brasil

Article Received: April 2020 **Accepted:** May 2020 **Published:** June 2020

Abstract:

Emulsions are formulations of widespread use in several areas and are configured as a dispersion of liquids that do not mix in the absence of amphoteric molecules. However, conventional emulsions are increasingly obsolete due to problems such as the use of non-biocompatible and biodegradable synthetic surfactants. In this sense, there is currently a quest to develop formulations based on Pickering emulsions that are characterized by being stabilized by particles/polymers, which give them some advantages, with the improvement of stability being the main one. In this article, a general discussion was carried out on the aspects that involve these systems and then the focus is reverted to Pickering emulsions stabilized by particles from secondary plant metabolism, specifically polyphenols. These molecules have a structure composed of rings that gives them an apolar character and hydroxyl groups that provide polarity to the molecule, thus being amphiphilic. Considering these characteristics, it was demonstrated that polyphenols are configured as molecules that have a stabilizing potential in Pickering systems, especially when it comes to using in the pharmaceutical and food industries, since these particles effectively stabilize formulations, contributing to inhibition physical-chemical degradation, such as coalescence, Ostwald maturation, and lipid oxidation, leading to greater stability and a possible increase in shelf life.

Keywords: *Pickering emulsions; particles; stability; polyphenols.*

Corresponding author:

Magda Rhayanny Assunção Ferreira,
Laboratório de Farmacognosia
Avenida Professor Artur de Sá, SN, Cidade Universitária,
Recife, 50740-521, Brasil
Departamento de Ciências Farmacêuticas,
Universidade Federal de Pernambuco
E-mail: magda.ferreira00@gmail.com

QR code

Please cite this article in press Magda Rhayanny Assunção Ferreira et al., ***Pickering Emulsions Stabilized By Polyphenol: A Mini-Review.,*** *Indo Am. J. P. Sci, 2020; 07(06).*

1. INTRODUCTION:

Emulsions are characterized as a heterogeneous dispersion system of two or more immiscible liquids, in which one of the liquids is dispersed as small spherical droplets in a continuous phase. This characteristic of emulsions makes such systems play important roles in different fields, including the pharmaceutical, petrochemical, cosmetics, and food industries [1]. To obtain a stable emulsion that is viable for the incorporation of substances, stabilizers must be added to the formulation, such as amphiphilic molecules, known as surfactants [2-4]. However, it is already known that some of these substances can be harmful to the human organism [5] and the environment [6]. Thus, an alternative may be the use of solid particles or polymers to stabilize the systems, which are now called Pickering emulsions.

Some studies have already reported that these emulsified systems have advantages over conventional ones, such as, for example, the reduction of the possibility of instability phenomena such as coalescence. Another advantage would be that the particle-stabilized interface can be modified after forming the emulsion to provide additional functionality. The improvement of characteristics, such as conductivity, responsiveness, porosity, among others, can also be highlighted as a beneficial factor. Furthermore, solid particles derived from plants (phytoparticles) can be used in these formulations, which is favorable, since it leads to greater safety for *in vivo* use [7-10].

Due to these factors, Pickering emulsions are already well documented in the literature, presenting mainly synthetic stabilizers, such as carbon nanotubes [11], silica nanoparticles [12], cellulose derivatives [13], among others. However, these particles can also present a certain degree of toxicity to the organism [14]. In this sense, in recent years, there has been a more intense search for Pickering emulsions stabilized by phytoparticles.

Phytoparticles, as they are derived from natural products, tend to have greater biocompatibility, being considered "ideal" for the development of Pickering emulsions in the food, pharmaceutical, cosmetic, agrochemical, etc. areas. Some studies have already reported the use of polyphenol particles for stabilizing emulsions [15-17]. Polyphenols are secondary metabolites of plants that have aromatic nuclei in their chemical structure containing hydroxylated substituents and/or their functional derivatives, which give them an amphiphilic character, such as surfactants [18]. Furthermore, this class of compounds, according to the literature, is responsible for many of the biological activities exerted by plants, such as antioxidant and anti-inflammatory potential [19], anticancer [20], antimicrobial [21], among others. Thus, it is observed that the use of these particles has advantages, since, in addition to playing a role in the interface of the emulsion droplets, leading to stability with resistance to coalescence, they are biocompatible.

2. General aspects of Pickering emulsions

The first reports on emulsions stabilized by solid particles were evidenced in the studies of Pickering (1907). Until then, these formulations were exclusively stabilized by surfactants, forming "soap emulsions". A difference that can be highlighted between these two types of colloids is the interfacial characteristic. This is because Pickering emulsions generally have droplets with greater surface charge and thickness due to adsorption of particles at the droplet interface, which can be considered an obstacle to fusion, thus preventing the phenomenon of coalescence [22,23].

The particles, to stabilize the Pickering emulsions, must obey some criteria, such as they cannot be prone to solubilization in any of the phases (aqueous or oily), being, therefore, partially moistened by the two phases simultaneously. The contact angle of a particle represents the wettability of that solid at the interface. Therefore, if the particle angle is less than 90° in the aqueous phase, a larger part of these particles will be present in the aqueous phase, thus stabilizing oil/water emulsions (O/W). And if, on the other hand, the angle in the aqueous phase is greater than 90°, the particle will preferably be present in the oil phase, thus stabilizing water/oil (W/O) emulsions (Figure 1). Another factor that influences the stabilization of these emulsions is the size of the particles. The stability of these colloids is generally inversely proportional to the size of the particles, that is, the smaller the particle, the greater the packaging efficiency, leading to stabilization due to the formation of a more homogeneous interfacial layer. This is because the spontaneous desorption-free energy of the interface (ΔG) is proportional to r^2 (1 - cos θ) where r is the particle radius (for spherical particles) and θ is the particle contact angle at the interface. If the contact angle is not close to 0 or 180, the value of ΔG can be 1000s of kT, therefore, once the particles are adsorbed at the interface, there is a greater difficulty in being removed. In other words, there is a huge energy barrier inhibiting coalescence, generating very stable emulsions [16,23-25].

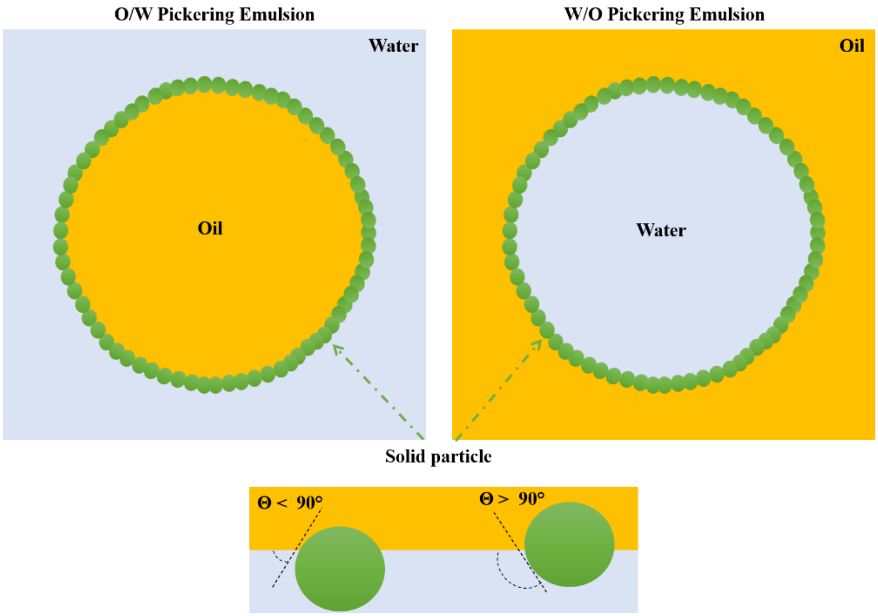

Figure 1. Schematic representation of the stabilization of a Pickering emulsion by particles.

It is also worth noting that studies have already shown that particle-stabilized emulsions have long-term stability against coalescence and Ostwald ripening [26]; besides, when compared with conventional emulsions, the particles present, even with a low amount in the system, greater stabilization capacity [27,28]. Thus, over the past few years, studies have shown success in obtaining Pickering emulsions. Marto et al. (2016) [26] demonstrated the viability of hydrophilic emulsions stabilized by starch, in addition to the high biocompatibility, being a promising vehicle for carrying drugs in the treatment of topical diseases. Shah et al (2016) reported the protective effect of the Pickering emulsion on curcumin transport, enhancing its antioxidant effect [29]. In turn, Gong et al (2017) developed stable O/W emulsions with good size controllability from the use of cellulose nanocrystals as stabilizing particles, thus having the potential to produce new formulations [30].

It is essential to point out that, currently, there is a process of searching for formulations that have renewable and natural elements in their composition [31]. In this sense, there is an increase in the study of Pickering emulsions stabilized by particles derived from plants, such as proteins [32] and carbohydrates [33]. There is also a class of molecules derived from the secondary metabolism of plants and which have aroused interest, the polyphenolic compounds, which will be discussed below.

3. Phenolic compounds

The basic monomer in phenolic compounds is the phenolic ring and, depending on the molecular structure, these compounds can be categorized into several classes, the main ones being phenolic acids, phenolic alcohols, flavonoids, lignans and tannins [34]. Polyphenols are a class of secondary metabolites from plants and are present in most species, such as *Spondias mombin* L. [35], *Eugenia uniflora* L. [36], *Punica granatum* L. [37], being, in each of these species, related to biological activities, such as antimicrobial, antioxidant, anti-inflammatory, antidiabetic, among others. However, in addition to studies on biological properties, in recent years, the technological potential related to these compounds has also been investigated in the pharmaceutical, cosmetic, and food industries.

4. Polyphenols particles as emulsion stabilizers

In 2011, for the first time, Luo and colleagues described the tendency of flavonoid molecules to accumulate in the interface of O/W emulsions, stabilizing them [24]. This is because these compounds have, in their structures, hydroxylated groups that contribute to the hydrophilic nature and rings that confer apolarity to the molecules, contributing to the hydrophobic characteristic, thus being an amphoteric molecule. In 2012, this same research group studied the pH interference in Pickering emulsions stabilized by three different flavonoids - rutin, naringin, and tiliroside - observing a trend towards better stabilization at a higher pH, when the zeta potential was also present in values higher in modulus, which facilitated the dispersion of the droplets. Since then, it has been possible to observe an increase in research related to this topic [38].

4.1 Epigallocatechin-3-gallate

Epigallocatechin-3-gallate (Figure 2) is the major compound in the catechin class [39]. One of the main characteristics of this flavonoid (flavonol) is its antioxidant capacity, being the main compound responsible for this biological response in green tea [40,41]. This molecule has been increasingly studied because of its ability to bind to proteins, for example, improving its functionality in food and pharmaceutical products [42].

Su et al. (2020) produced nanoparticles of lactoglobulin and epigallocatechin-3-gallate complexes to stabilize lutein emulsions, obtaining satisfactory results. This is because the complexed nanoparticles (β-lgENPs) obtained smaller sizes than the lactoglobulin particles (β-lgNPs) due to the formation of a compact structure between the components, in addition to greater thermal resistance, thus being more stable. Another point that should be highlighted is the antioxidant property of the compound that was important for the formulation since lutein is an unsaturated and very passive molecule of degradation in the processing and storage stage due to oxidative processes resulting from chemical reactions and thermal stress [43].

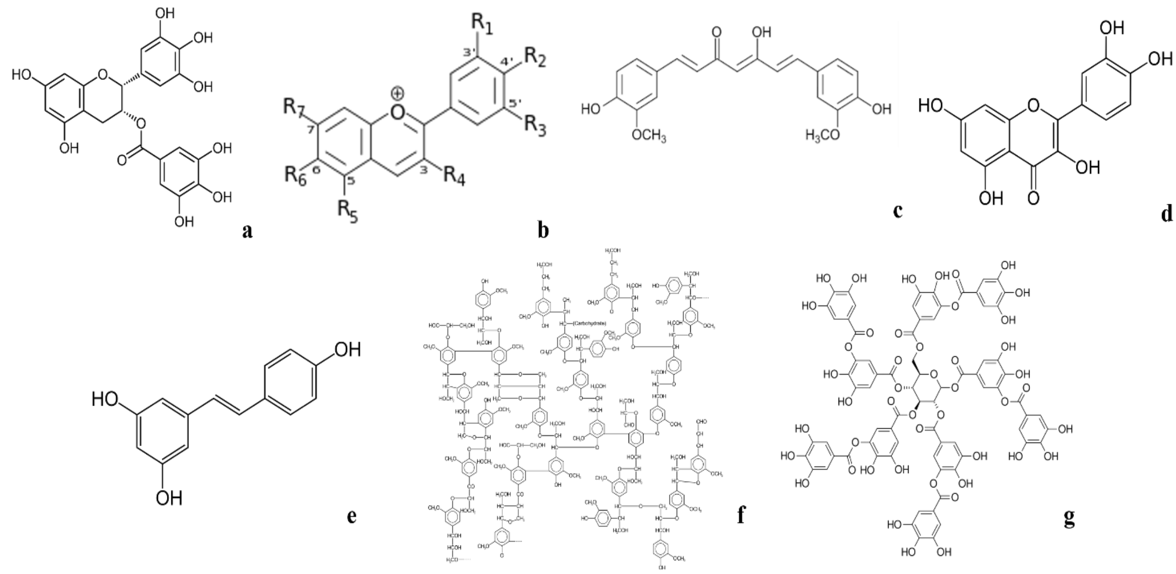

Figure 2. Chemical structures of polyphenols related. a - epigallocatechin-3-gallate; b – flavylium ion (anthocyanins); c – curcumin; d – quercetin; e – resveratrol; f - lignin; g – tannic acid.

4.2 Anthocyanins

It is known that there has been a tendency to complex polyphenolic particles with proteins, aiming to find more efficient stabilizers by adding functional properties to the formulation, such as antioxidant activity [44]. The structure of anthocyanins consists of two aromatic rings and a heterocyclic ring, which gives this molecule antioxidant capacity since it can interact with reactive oxygen species.

Thus, Ju et al. (2020) proposed the development of nanoparticles based on soy protein and anthocyanins, forming the SPI-ACN complex to thus stabilize a nanoemulsion from these solids [45]. In this study, it was observed that the increase in anthocyanins led to a gradual shift from the peak particle size distribution towards smaller sizes, which is ideal for stabilizing Pickering emulsions [16]. Also, antioxidant activity of these nanoparticles was shown against the radicals DPPH and $ABTS^{\bullet+}$, which could also be noticed in other studies with flavonoids [17,46], demonstrating that such activity was a result of hydroxyls present in anthocyanins, which allowed for better long-term stability by decreasing lipid oxidation.

4.3 Curcumin and quercetin

Curcumin is a polyphenol (phenylpropanoid) found in the rhizomes of the Curcuma longa species. Its structure consists of two aromatic rings with two hydroxyl groups and two methoxy groups, being a molecule already known for its antioxidant activity [29,47]. Quercetin, in turn, is considered the main dietary flavonoid [48] and is also considered an antioxidant [49]. The use of these two polyphenols to manufacture a delivery system for bioactive compounds, demonstrating antioxidant capacity, has already been reported [50].

Zembyla and collaborators, since 2018, have investigated the potential of curcumin and quercetin polyphenols to act as stabilizers for emulsified dispersed systems [16]. It was found for the first time that the particles of the two molecules are more hydrophobic, thus stabilizing emulsions of the W/O type. Furthermore, it was observed that, due to the packaging characteristic of the quercetin droplets, the hydroxyl groups are less exposed and, therefore, the pH variation did not affect the contact angle of the quercetin particles, differently from what happened with those of curcumin, leading to a drastic change in the surface charge of this flavonoid. This allowed choosing a more satisfactory pH, since the zeta potential, at pH 3, was closer to zero for both particles, thus favoring hydrophobicity. Besides, in this study, it was also possible to define at which concentrations of curcumin and quercetin there would be the formation of smaller droplets with less free crystals in the continuous phase. As it was the initial study, the particle shapes were also elucidated, with polyhedral curcumin and quercetin being an almost perfect crystalline stick, which is responsible for the greater resistance of the film formed by quercetin particles to curcumin.

In 2019, the same authors proposed, based on previous experiments, the stabilization of emulsions from the formation of a complex between the polyphenol crystals already elucidated and proteins isolated from whey. It was noticed that particles complexed with proteins showed greater efficiency in stabilization, suggesting that the complex is stabilized by electrostatic bonds, in addition to hydrogen bonds, which contributes to this result [51].

Now in 2020, studies have shown that Pickering emulsions co-stabilized by quercetin and curcumin showed greater stability when used with isolated whey protein complex (WPI) or whey protein microgel (WPM), corroborating the previous results. Additionally, it was observed that the WPM particles increase the stability of the formulation by two mechanisms: adsorption on the surface of the droplets and by the formation of mixed crystal flakes composed of polyphenols, WPM particles and small water droplets in the oil phase attached to the surface of the main water droplets [52].

4.4 Resveratrol

Resveratrol is also a phenylpropanoid, consisting of aromatic and hydroxyl rings attached to it [53], thus, like other polyphenols, it has some biological activities, such as antimicrobials and antioxidants, taking into account that such effects are linked to the structure of these molecules. Cheng et al. (2020) developed the resveratrol-zein-pectin complex, that is, in this study, in addition to the phenolic compound - a stilbene - and protein, pectin, a polysaccharide, was also added to the formulation [54]. In this study, it was observed that, in addition to an improvement in the stabilization property of peppermint oil emulsions, the particles of the resveratrol-zein-pectin complex demonstrated synergism in microbial activity, since the value of the Minimum Inhibitory Concentration of microorganisms studied decreased significantly, corroborating studies that demonstrate antimicrobial activity related to this polyphenol [55,56], contributing to an antimicrobial activity over the storage time. Wei and colleagues designed a co-delivery system for coenzyme Q10 and resveratrol by developing a zein and propylene glycol alginate (PGA) nanoparticle for carrying resveratrol [42]. The study aimed to obtain an interfacial stabilization of emulsions for the incorporation of Q10, in addition to studying the resveratrol property of protecting the coenzyme from degradation processes, due to its antioxidant property [57], thus having the potential to be a new vehicle for bioactive ingredients.

4.5 Lignin

Lately, lignin has been the subject of investigation due to its characteristics as a biopolymer and its natural occurrence - second most abundant after cellulose [58]. Various functional groups of this molecule, such as aliphatic hydroxyls, phenolic hydroxyls, carbonyl, and carboxyl, give it this polymeric potential [59]. Considering these characteristics, a range of studies started to be developed to explain the potential of lignin application in different areas, such as nano-engineering [60], in the synthesis of thermoplastics [61], production of carbon fibers [62], among others. In 2019, Bertolo and collaborators obtained nanoparticles based on lignin extracted from the bagasse of the bark and studied its effect on the emulsion interface for curcumin encapsulation. Furthermore, the organosolvent-LNPs was considered the most efficient stabilizer, retaining 73% of curcumin in its encapsulated form after 96 h. Therefore, this study demonstrated the potential of nanostructured lignins for bio-based fields and highlights the influencing factors in the choice of methodologies to produce LNPs [63].

Li et al. (2019) sought to formulate antibacterial phase change microcapsules (microPCM) with n-eicosane core and polyurea (PU) shells via Pickering emulsion modeling, where lignin would function as an emulsion stabilizer and reducing agent to incorporate silver into the microPCM. As a result, Ag/lignin microPCMs exhibited a well-defined spherical morphology of the core-shell, high encapsulation efficiency (69.0%), and good thermal durability. Also, they showed good antibacterial activity, with great potential in industrial applications, such as biomedical, textile, and construction areas [26].

4.6 Tannic acid

Polyphenols have aromatic rings and OH groups that are fully reactive to proteins and amino acids and can interact with proteins over a wide pH range. Tannic acid, rich in hydroxyl groups, can interact strongly with polysaccharides and proteins, in addition to having antioxidant, antibacterial, and antiviral properties [64].

In 2015, Zou and collaborators studied the interaction of zein, a protein derived from corn, with tannic acid, proposing a gel formulation with better application in the food area, since most of the previous studies used synthetic particles [7]. It was observed, in this work, that the ZTP (particles zein/tannic acid) were efficient in stabilizing the oil droplets and lead to a crosslinking phenomenon, forming a continuous network at the oil interface, favoring the formation of Pickering emulsion gels. More recently, in 2018, these same authors studied the influence of ZTP hydrophobicity on the rheology of these gels, varying the amount of tannic acid, reaching the conclusion that, increasing the oil's polarity, the gel would present with a greater or less resistance depending on the hydrophobic or hydrophilic character of the nanoparticles [65]. These results demonstrate that there may be an adjustment of the rheological properties of the formulation, providing interesting resources for various applications in the food industry. This tendency to assess the crosslinking of the zein/tannic acid complex had also been assessed in the studies by Hu and collaborators [66].

In addition, in 2019, Luo and colleagues developed edible oleogel stabilized by polyphenol tea particles obtained from palmitate and in later studies evaluated its drying properties, to develop a more convenient product for the industry, not only for its technological properties such as also antioxidant, coming from polyphenols [67]. The influence of tannic acid on the efficiency of protein emulsification has also been studied for ovalbumin to apply it to food [68]. In 2019, Narukulla and collaborators proposed the study of the influence of this tannin on the stability of re-dispersible emulsions based on polyacrylil hydrazide nanoparticles (PAHz-Ag NP). The authors observed that there was a synergism between tannic acid and PAHz–Ag NP, which, within a formulation, presented as good stabilizers and allowed the obtaining of powders and oils with satisfactory characteristics, being, therefore, an ecological alternative to oil emulsions and powders already available [69].

5 CONCLUSIONS:

Pickering emulsions have been widely described in the literature. In studies related to this formulation, one can see some advantages over conventional emulsions, which further stimulates research on these solid-stabilized colloids, mainly due to the possibility of using plant-derived particles for their stabilization, such as proteins, polysaccharides, among others. In this sense, this review allowed a more specific and in-depth perception of Pickering emulsions stabilized by polyphenolic compounds, molecules derived from the secondary metabolism of plants, and which are well documented due to the range of biological activities they can perform, this being an advantage, a biocompatibility. These studies have shown that, in addition to providing technological characteristics to emulsions, these metabolites, of which flavonoids and tannins are examples, confer antimicrobial and antioxidant characteristics to the final product, which adds to stability. Therefore, it was observed that the formulations resulting from the studies targeted in this article are promising for use in the food and pharmaceutical industry, since they have shown greater physical-chemical stability and, in some cases, have enabled the encapsulation and delivery of bioactive compounds for improved delivery.

ACKNOWLEDGMENTS:
The authors would like to thank the PIBIC-UFPE and CNPq (380696/2020-7; 405297/2018-1 and 307110/2018-4).

REFERENCES:

[1] Kale SN, Deore SL. Emulsion micro emulsion and nano emulsion: a review. Syst Rev Pharm, 2017; 8(1): 39-47.
[2] Kumar A, Mandal A. Critical investigation of zwitterionic surfactant for enhanced oil recovery from both sandstone and carbonate reservoirs: Adsorption, wettability alteration and imbibition studies. Chem Eng Sci, 2019; 209: 115222.
[3] Matsuoka K, Takahashi N, Yada S, Yoshimura T. Solubilization ability of star-shaped trimeric quaternary ammonium bromide surfactant. J Mol Liq, 2019; 291: 111254.
[4] Appah S, Jia W, Ou M, Wang P, Asante EA. Analysis of potential impaction and phytotoxicity of surfactant-plant surface interaction in pesticide application. Crop Prot, 2020; 127: 104961.
[5] Kanno S, Hirano S, Kato H, Fukuta M, Mukai T, Aoki Y. Benzalkonium chloride and cetylpyridinium chloride induce apoptosis in human lung epithelial cells and alter surface activity of pulmonary surfactant monolayers. Chem-Biol Interact, 2020; 317:108962.
[6] Garcia MT, Kaczerewska O, Ribosa I, Brycki B, Materna P, Drgas M. Biodegradability and aquatic toxicity of quaternary ammonium-based gemini surfactants: Effect of the spacer on their ecological properties. Chemosphere, 2016; 154:155-160.
[7] Zou Y; Guo J; Yin SW; Wang JM; Yang XQ. Pickering emulsion gels prepared by hydrogen-bonded zein/tannic acid complex colloidal particles. J Agric Food Chem, 2015; 63(33): 7405-7414.

[8] Jin W, Zhu J, Jiang Y, Shao P, Li B, Huang Q. Gelatin-based nanocomplex-stabilized Pickering emulsions: Regulating droplet size and wettability through assembly with glucomannan. J Agric Food Chem, 2017; 65(7):1401-1409.
[9] Yang Y, Fang Z, Chen X, Zhang W, Xie Y, Chen Y, Liu Z, Yuan W. An overview of Pickering emulsions: solid-particle materials, classification, morphology, and applications. Front Pharmacol, 2017; 8: 287.
[10] Ren X, He S, Liu D, Zhang Y. Multi-stimuli responsive Pickering emulsion stabilized by Se-containing surfactant modified chitosan. J Agric Food Chem, 2020; 68(13): 3986-3994.
[11] Briggs N, Yegya Ramam AK, Barrett L, Brown C, Li B, Leavitt D, Aichele CP, Crossley S. Stable pickering emulsions using multi-walled carbon nanotubes of varying wettability. Colloids Surf, A, 2018; 537: 227-235.
[12] Liu K, Jiang J, Cui Z, Binks BP. pH-Responsive Pickering emulsions stabilized by silica nanoparticles in combination with a conventional zwitterionic surfactant. Langmuir, 2017; 33(9): 2296-2305.
[13] Xie J, Luo Y, Chen Y, Liu Y, Ma Y, Zheng Q, Yue P, Yang M. Redispersible Pickering emulsion powder stabilized by nanocrystalline cellulose combining with cellulosic derivatives. Carbohydr Polym, 2019; 213: 128-137.
[14] Hering I, Eilebrecht E, Parnham MJ, Günday-Türeli N, Türeli A E, Weiler M, Schäfers C, Fenske M, Wacker MG. Evaluation of potential environmental toxicity of polymeric nanomaterials and surfactants. Environ Toxicol Pharmacol, 2020; 76: 103353.
[15] Duffus LJ, Norton JE, Smith P, Norton IT, Spyropoulos F. A comparative study on the capacity of a range of food-grade particles to form stable O/W and W/O Pickering emulsions. J Colloid Interface Sci, 2016; 473: 9-21.
[16] Zembyla M, Murray BS, Sarkar A. Water-in-oil Pickering emulsions stabilized by water-insoluble polyphenol crystals. Langmuir, 2018; 34(34):10001-10011.
[17] Chen Y, Zhang R, Xie B, Sun Z, McClements DJ. Lotus seedpod proanthocyanidin-whey protein complexes: Impact on physical and chemical stability of β-carotene-nanoemulsions. Food Res Int, 2020; 127:108738.
[18] Simões CMO, Schenkel EP, Mello JCP, Petrovick PR. 2017. Farmacognosia: do produto natural ao medicamento. Porto Alegre, Brasil: Artmed Editora Ltda.
[19] Zhang H, Tsao R. Dietary polyphenols, oxidative stress and antioxidant and anti-inflammatory effects. Current Opinion in Food Science, 2016; 8:33-42.
[20] Zhou Y, Zheng J, Li Y, Xu DP, Li S, Chen YM, Li HB. Natural polyphenols for prevention and treatment of cancer. Nutrients, 2016; 8(8): 515.
[21] Singh JP, Kaur A, Singh N, Nim L, Shevkani K, Kaur H, Arora DS. In vitro antioxidant and antimicrobial properties of jambolan (*Syzygium cumini*) fruit polyphenols. LWT--Food Sci Technol, 2016; 65: 1025-1030.
[22] Jafaria SM, Doost AS, Nasrabadi NM, Boostani S, Meeren PV. Phytoparticles for the stabilization of Pickering emulsions in the formulation of novel food colloidal dispersions. Trends Food Sci Technol, 2020; 98: 117-128.
[23] Ortiz DG, Pochat-Bohatier C, Cambedouzou J, Bechelany M, Miele P. Current trends in pickering emulsions: Particle morphology and applications. Engineering, 2020; 6: 468-482.
[24] Luo Z, Murray BS, Yusoff A, Morgan MRA, Povey MJW, Day AJ. Particle-stabilizing effects of flavonoids at the oil− water interface. J Agric Food Chem, 2011; 59 (6): 2636-2645.
[25] Xiao J, Li Y, Huang Q. Recent advances on food-grade particles stabilized Pickering emulsions: Fabrication, characterization and research trends. Trends Food Sci Technol, 2016; 55:48-60.
[26] Li X, Hegyesi N, Zhang Y, Mao Z, Feng X, Wang B, Puckánzsky B, Sui X. Poly (lactic acid)/lignin blends prepared with the Pickering emulsion template method. Eur Polym J, 2019; 110: 378-384.
[27] Marto J, Gouveia L, Jorge IM, Duarte A, Gonçalves LM, Silva SMC, Antunes F, Pais AACC, Oliveira E, Almeida AJ, Ribeiro HM. Starch-based Pickering emulsions for topical drug delivery: a QbD approach. Colloids Surf, B, 2015; 135: 183-192.
[28] Barkhordari MR, Fathi M. Production and characterization of chitin nanocrystals from prawn shell and their application for stabilization of Pickering emulsions. Food Hydrocolloids, 2018; 82: 338-345.
[29] Shah BR, Zhang C, Zi Y, Li B. Bioaccessibility and antioxidant activity of curcumin after encapsulated by nano and Pickering emulsion based on chitosan-tripolyphosphate nanoparticles. Food Res Int, 2016; 89: 399-407.
[30] Gong X, Wang Y, Chen L. Enhanced emulsifying properties of wood-based cellulose nanocrystals as Pickering emulsion stabilizer. Carbohydr Polym, 2017; 169: 295-303.
[31] Wang JS, Wang AB, Zang XP, Tan L, Ge Y, Lin XE, Xu BY, Jin ZQ, Ma WH. Physical and

oxidative stability of functional avocado oil high internal phase emulsions collaborative formulated using citrus nanofibers and tannic acid. Food Hydrocolloids, 2018; 82: 248-257.
[32] Xu Y, Chu Y, Feng X, Gao C, Wu D, Cheng W, Meng L, Zhang Y, Tang X. Effects of zein stabilized clove essential oil Pickering emulsion on the structure and properties of chitosan-based edible films. Int J Biol Macromol, 2020; 156:111-119.
[33] Sufi-Maragheh P, Nikfarjama N, Deng Y, Taheri-Qazvini N. Pickering emulsion stabilized by amphiphilic pH-sensitive starch nanoparticles as therapeutic containers. Colloids Surf, B, 2019; 181: 244-251.
[34] Abbas M, Saeed F, Anjum FM, Afzaal M, Tufail T, Bashir MS, Ishtiaq A, Hussain S, Suleria HAR. Natural polyphenols: An overview. Int J Food Prop, 2017; 20(8):1689-1699.
[35] Sameh S, Al-Sayed E, Labib RM, Singab AN. Genus *Spondias*: A phytochemical and pharmacological review. J Evidence-Based Complementary Altern Med 2018; 2018: 13.
[36] Sobeh M, El-Raey M, Rezq S, Abdelfattah MAO, Petruk G, Osman S, El-Shazly AM, El-Beshbishy HA, Mahmoud MF, Wink M. Chemical profiling of secondary metabolites of *Eugenia uniflora* and their antioxidant, anti-inflammatory, pain killing and anti-diabetic activities: A comprehensive approach. J Ethnopharmacol, 2019; 240: 111939.
[37] Mestry SN, Dhodi JB, Kumbhar SB, Juvekar AR. Attenuation of diabetic nephropathy in streptozotocin-induced diabetic rats by *Punica granatum* Linn. leaves extract. J Tradit Complementary Med, 2017; 7 (3):273-280.
[38] Luo Z, Murray BS, Ross AL, Povey MJW, Morgan MRA, Day AJ. Effects of pH on the ability of flavonoids to act as Pickering emulsion stabilizers. Colloids Surf, B, 2012; 92: 84-90.
[39] Roychoudhury S, Agarwal A, Virk G, Cho CL. Potential role of green tea catechins in the management of oxidative stress-associated infertility. Reprod BioMed Online, 2017; 34(5): 487-498.
[40] Chen W, Lv R, Muhammad AI, Guo M, Ding T, Ye X, Liu D. Fabrication of (−)-epigallocatechin-3-gallate carrier based on glycosylated whey protein isolate obtained by ultrasound Maillard reaction. Ultrason Sonochem, 2019; 58:104678.
[41] Shweta H, Keerthana KP, Rhea R, Daphne NC, Divya G, Srinivas M, Sazada S, Satish KA, Guruprasad K. Epigallocatechin-3-gallate (EGCG) protects the oocytes from methyl parathion-induced cytoplasmic deformities by suppressing oxidative and endoplasmic reticulum stress. Pestic Biochem Physiol [ONLINE] 20 April 2020, 104588.
[42] Wei Z, Huang Q. Impact of covalent or non-covalent bound epigallocatechin-3-gallate (EGCG) on assembly, physicochemical characteristics and digestion of ovotransferrin fibrils. Food Hydrocolloids, 2020; 98: 105314.
[43] Su J, Guo Q, Chen Y, Mao L, Gao Y, Yuan F. Utilization of β-lactoglobulin-(−)-Epigallocatechin-3-gallate (EGCG) composite colloidal nanoparticles as stabilizers for lutein pickering emulsion. Food Hydrocolloids, 2020; 98:105293.
[44] Quan TH, Benjakul S, Sae-leawa S, Balange AK, Maqsood S. Protein–polyphenol conjugates: Antioxidant property, functionalities and their applications. Trends Food Sci Technol, 2019; 91: 507-517.
[45] Ju M, Zhu G, Huang G, Shen X, Zhang Y, Jiang L, Sui X. A novel pickering emulsion produced using soy protein-anthocyanin complex nanoparticles. Food Hydrocolloids, 2020; 99: 105329.
[46] Rengarajana S, Melanathuru V, Govindasamy C, Chinnadurai V, Elsadek MF. Antioxidant activity of flavonoid compounds isolated from the petals of *Hibiscus rosa sinensis*. J King Saud University-Science, 2020; 32:2236-2242.
[47] Rafiee Z, Nejatian M, Daeihamed M, Jafari SM. Application of curcumin-loaded nanocarriers for food, drug and cosmetic purposes. Trends Food Sci Technol, 2019; 88: 445-458.
[48] Yamada N, Matsushima-Nishiwaki R, Kozawa O. Quercetin suppresses the migration of hepatocellular carcinoma cells stimulated by hepatocyte growth factor or transforming growth factor-α: Attenuation of AKT signaling pathway. Arch Biochem Biophys 2020; 682:108296.
[49] Ezzatia M, Yousefi B, Velaei K, Safa A. A review on anti-cancer properties of Quercetin in breast cancer. Life Sci, 2020; 249:117463.
[50] Tavano L, Muzzalupo R, Picci N, Cindio B. Co-encapsulation of antioxidants into niosomal carriers: Gastrointestinal release studies for nutraceutical applications. Colloids Surf, B, 2014; 114: 82-88.
[51] Zembyla M, Murray BS, Radford SJ, Sarkar A. Water-in-oil Pickering emulsions stabilized by an interfacial complex of water-insoluble polyphenol crystals and protein. J Colloid Interface Sci, 2019; 548: 88-99.
[52] Zembyla M, Lazidis A, Murray BS, Sarkar A. Stability of water-in-oil emulsions co-stabilized by polyphenol crystal-protein complexes as a function of shear rate and temperature. J Food Eng, 2020; 281: 109991.
[53] Santos AC, Pereira I, Pereira-Silva M, Ferreira L, Caldas M, Magalhães M, Figueiras A,

Ribeiro AJ, Veiga F. Nanocarriers for resveratrol delivery: Impact on stability and solubility concerns. Trends Food Sci Technol, 2019; 91: 483-497.
[54] Cheng H, Khan MA, Xie Z, Tao S, Li Y, Lianga L. A peppermint oil emulsion stabilized by resveratrol-zein-pectin complex particles: Enhancing the chemical stability and antimicrobial activity in combination with the synergistic effect. Food Hydrocolloids, 2020; 103:105675.
[55] Samprasit W, Chamsai B, Settharaksa B, Opanasopit P. Synergistic antibacterial activity of alpha mangostin and resveratrol loaded polymer-based films against bacteria infected wound. J Drug Delivery Sci Technol, 2020; 57: 101629.
[56] Liu Y, Zhou J, Qu Y, Yang X, Shi G, Wang X,1, Hong Y, Drlica K, Zhao X. Resveratrol antagonizes antimicrobial lethality and stimulates recovery of bacterial mutants. PLoS One, 2016; 11(4): e0153023.
[57] Davies S, Contri RV, Guterresa SS, Pohlmanna AR, Guerreiro ICK. Simultaneous nanoencapsulation of lipoic acid and resveratrol with improved antioxidant properties for the skin. Colloids Surf, B, 2020; 192:111023.
[58] Bertella S, Luterbacher JS. Lignin Functionalization for the Production of Novel Materials. Trends Chem, 2020; 2(5): 440-453.
[59] Wang C, Kelley S S, Venditti RA. Lignin-based thermoplastic materials. ChemSusChem, 2016; 9(8): 770-783.
[60] Gouveia, JR, Costa CL, Tavares LB, Santos DJ. Synthesis of Lignin-Based Polyurethanes: A Mini-Review. Mini-Reviews in Organic Chem, 2019; 16(4): 345 – 352.
[61] Liu C, Li Y, Hou Y. A simple environment-friendly process for preparing high-concentration alkali lignin nanospheres. Eur Polym J, 2019: 112: 15-23.
[62] Li Q, Xie S, Serem WK, Naik MT, Liu L, Yuan JS. Quality carbon fibers from fractionated lignin. Green Chem, 2017; 19(7):1628-1634.
[63] Bertolo MRV, Paiva LBB, Nascimento VM, Gandin CA, Neto MO, Driemeier CE, Rabelo SC. Lignins from sugarcane bagasse: Renewable source of nanoparticles as Pickering emulsions stabilizers for bioactive compounds encapsulation. Industrial Crops and Products, 2019; 140: 111591.
[64] Jia C, Cao D, Ji S, Zhang X, Muhoza B. Tannic acid-assisted cross-linked nanoparticles as a delivery system of eugenol: The characterization, thermal degradation and antioxidant properties. Food Hydrocolloids, 2020; 104: 105717.
[65] Zou Y, Baalen CV, Yang X, Scholten E. Tuning hydrophobicity of zein nanoparticles to control rheological behavior of Pickering emulsions. Food Hydrocolloids, 2018; 80: 130-140.
[66] Hu S, Wang T, Fernandez ML, Luo Y. Development of tannic acid cross-linked hollow zein nanoparticles as potential oral delivery vehicles for curcumin. Food Hydrocolloids, 2016; 61: 821-831.
[67] Luo SZ, Huab XF, Jia YJ, Pan LH, Zheng Z, Zhao YY, Mu DD, Zhong XY, Jian ST . Camellia oil-based oleogels structuring with tea polyphenol-palmitate particles and citrus pectin by emulsion-templated method: Preparation, characterization and potential application. Food Hydrocolloids, 2019; 95: 76-87.
[68] Chen Y, Hu J, Yi X, Ding B, Sun W, Yan F, Wei S, Li Z. Interactions and emulsifying properties of ovalbumin with tannic acid. Lebensmittel-Wissenschaft & Technologie, 2018; 95: 282-288.
[69] Narukulla R, Ojha U, Sharma T. Enhancing the stability and redispersibility of o/w Pickering emulsion through polyacryloyl hydrazide-tannic acid synergy. Colloids Surf., A, 2019; 568: 204-215.