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Unconventional and conventional Pickering emulsions: Perspectives and challenges in skin applications

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ABSTRACT

Pickering emulsions are free from molecular and classical surfactants and are stabilized by solid particles, creating long-term stability against emulsion coalescence. Additionally, these emulsions are both environmentally and skin-friendly, creating new and unexplored sensorial perceptions. Although the literature mostly describes conventional emulsions (oil-in-water), there are unconventional emulsions (multiple, oil-in-oil and water-in-water) with excellent prospects and challenges in skin application as oil-free systems, permeation enhancers and topical drug delivery agents, with various possibilities in pharmaceutical and cosmetic products. However, up to now, these conventional and unconventional Pickering emulsions are not yet available as commercial products. This review brings to the discussion some important aspects such as the use of phases, particles, rheological and sensorial perception, as well as current trends in the development of these emulsions.

1. Introduction

1.1. Emulsions

Emulsions are fluid colloidal dispersions composed of a dispersed and a continuous liquid phase, according to the definition given by IUPAC (PAC, 1972). Conventional emulsions composed of oil and water are frequently found in the cosmetic industry and usually carry functional benefits, which can range from cleaning, protecting skin from UV light, preventing water loss, and delivering drugs into inner skin layers.

Unconventional emulsions are not yet found in commercial products, although they can have different compositions that are associated with many appealing properties. For example, water-in-water (w/w) emulsions are composed of two thermodynamically incompatible water-soluble polymers and have the intrinsic advantage of being oil-free formulations, as reviewed by Dickinson (2019).

There are also non-aqueous liquid–liquid interfaces that can be perceived either as (i) unconventional emulsions composed of an oil and a polar solvent (ii) blends of oil-soluble immiscible polymers (iii) truly oil-in-oil (o/o) emulsions. In the first case, the apolar oil is mixed with a polar non-aqueous solvent (pnas) associated with a high dielectric constant, whilst emulsions in the third case require two immiscible apolar oils with low dielectric permittivity ε, usually lower than 5 (Fernandez-Rodriguez et al., 2017 and Binks; Tyowua, 2016).

Emulsions composed of pnas and oil mixtures or polymers blends are frequently named o/o emulsions, and one reason why these terms are commonly interchanged is that one cannot find a definition for the term “oil” in the IUPAC colour books (Crespy & Landfester, 2011). These emulsions allow the use of agents that react with water and lose their activity, as reviewed by Zia et al. (2020). Several other systems are considered unconventional emulsions as they can present different morphologies such as oil-in-water-in-oil (o/w/o), water-in-oil-in-water (w/o/w), or even fewer common systems such as oil-in-oil-in-water (o/o/w) or water-in-water-in-water (w/w/w). Multiple emulsions are

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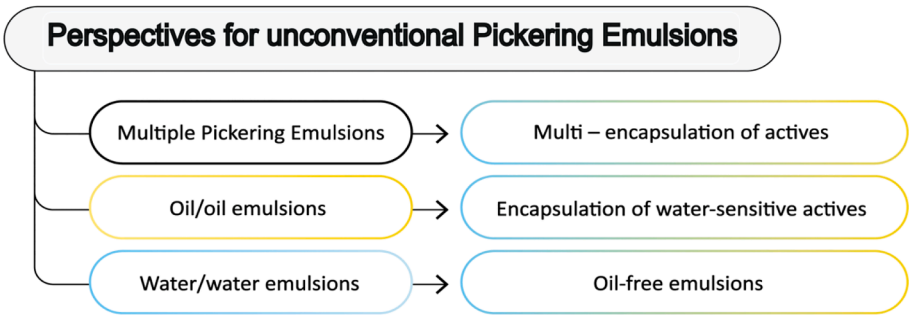

Fig. 1. Perspectives for unconventional emulsions.

Table 1
Measured liquid–liquid interfacial tensions of different emulsion components.

Type of interface	Continuous phase	Dispersed phase	Interfacial tension (γ)/ mN m^{-1}	Reference
w/o	soybean oil	Purified water	28.2 ± 1.6[a]	(D'Apolito et al., 2018)
w/o	pure mineral oil	Purified water	24.5–20.5 ± 0.2[b]	(Posocco et al., 2016)
w/w	PEO	Dextran	0.001[c]	(Balakrishnan et al., 2012)
w/w	xyloglucan	amylopectin	0.001 to 0.01[c]	(Freitas et al., 2016)
o/o	silicone oil	olive oil	2.8 ± 0.2[d]	(Binks & Tyowua, 2016)
	silicone oil	sunflower oil	1.5 ± 0.2[d]	
	silicone oil	rapeseed oil	2.7 ± 0.2[d]	

Measured [a] by a microfluidic setup; [b] by pendant drop technique; [c] by the relaxation of the shape of a droplet; [d] using a spinning drop tensiometer.

closely related to multiple encapsulations and controlled release of active pharmaceutical ingredients (Albert et al., 2019), as observed in Fig. 1.

1.2. Pickering emulsions

Pickering emulsions are systems in which micro or nanoparticles strongly adsorb at the interface of the dispersed phase droplets, and therefore avoid some physical destabilization processes. These Pickering emulsions can be stable for long periods of time, since the particle adsorption at the interface can be irreversible, adding a long-term stability against phase separation mechanisms (Tan and McClements, 2021). The adsorption of solid particles at the interface between the two liquids create stable emulsions without surfactants, known as Pickering effect (Borgia et al., 2008; Schwarz, Weisspapir & Friedman, 1995; Sintov & Shapiro, 2004; Sonneville-Aubrun, Simonnet & L'Alloret, 2004; Wu et al., 2001).

Pickering emulsions are suitable candidates for multi-purpose and diversified functional cosmetics as colloidal delivery systems. Particularly concerning Pickering emulsions, although the phenomenon of particles adsorption at interfaces was described a long time ago, reports of the application of these particle-stabilized materials as topical delivery systems have started to appear near the 2010s for conventional emulsions, i.e, for those composed of oil and water (Eskandar et al., 2010, 2009a, 2009b; Frelichowska et al., 2009b, 2009a; Simovic & Prestidge, 2011).

Unconventional o/o or w/w emulsions began to draw attention looking to understand the physicochemical metastability mechanisms promoted by Pickering particles. A challenge with these unconventional emulsions is associated with their much lower interfacial tension, when compared to conventional ones (Table 1) (Balakrishnan et al., 2012; Binks & Tyowua, 2016; Freitas et al., 2016; Hazt et al., 2020).Table 2..

As the use in topical therapeutics and cosmetic applications of conventional Pickering emulsions was recently summarized by Peito et al. (2022), here we focused initially on unconventional emulsions containing Pickering particles. These emulsions represent a novel frontier in colloid technology and may offer solutions to key challenges faced by the cosmetic and pharmaceutical industries, such as the increase in bioactive loadings, improved compatibility, developing oil-free formulations and creating new sensorial perceptions. Secondly, conventional emulsions were detailed in terms of their composition, stability, and skin permeation, focusing on the effects of particles, oily and water phases on skin permeation, as well as emulsion stability and sensorial properties.

For a Pickering emulsion, there are important parameters associated with the particle adsorption at the interface such as their size, morphology, chemical nature, roughness and density. These parameters were initially established for conventional w/o systems but remain valid for unconventional w/w, pnas/o and o/o emulsions. The particle wettability can be assessed by examining at the contact angle (θ) value (Fig. 2), measured between the solid particle surface and one of the liquids. Based on the particle contact angle, Finkle, Draper & Hildebrand (1923) described an empirical rule which stated that the type of emulsion formed hinges on the particle wettability in water and oil phases, affecting the curvature of the droplet that will be formed (Fernandez-Rodriguez et al., 2017; Balakrishnan et al., 2012).

The physical stability observed in many Pickering emulsions can be explained by the reduction in the interfacial free energy, that occurs when particles are attached to the surface of the dispersed phase droplets (Fig. 2). Even though the interfacial tension for unconventional emulsions is much lower than in conventional ones (Table 1), the process of emulsion formation is still thermodynamically unfavourable. Furthermore, we point out that a metastable state can be maintained associated with the steric and repulsive properties promoted by particle adsorption at the interface, as well as due to the formation of a rigid interfacial layer at higher particle concentration (Gautier et al., 2007; Dickinson, 2012, Zhang et al., 2020; Sarkar & Dickinson, 2020).

The minimum energy needed to desorb a particle from the interface and move it into a bulk phase is represented by ΔG_d, which is related to the squared radius R of the particle and to the interfacial tension between the phases γ (for examples, see Table 1). **Equation (1)**, applied for spherical particles, can be adapted for rod-like particles since they have a higher aspect ratio than spheres (Ngai & Bon, 2015; Binks & Horozov, 2006; Machado et al., 2019).

$$\Delta G_d = \pi R^2 \gamma (1 - |\cos\theta|)^2 \quad (1)$$

Particle-stabilized emulsions are promising systems to operate as pharmaceutical and cosmetic delivery agents, since they present controlled skin permeation properties (Simovic & Prestidge, 2011), and reduction of the irritation and sensitization commonly caused by molecular surfactant-stabilized emulsions (Jiang et al., 2020). Here, the discussion will focus in Pickering emulsions, their perspectives as well as opportunities in skin applications. Before diving into this topic, it is important to understand the skin structure and permeation routes, which are summarized below.

Table 2
Summary of non-conventional Pickering emulsions and their potential application.

Emulsion type	Dispersed phase-in-continuous phase	Stabilizing agent	Experimental findings	Potential application	Reference
o/o	silicone oil-in olive oil or silicone oil-in rapeseed oil or olive oil-in-silicone oil or rapeseed oil-in-silicone oil	20 or 70% SiOH silica particles	Silicone-in-vegetable (S/V) to vegetable-in-silicone (V/S) emulsions occur by increasing the hydrophobicity of the particles.	pharmaceutical and cosmetic preparations	(Tyowua et al., 2017)
o/o/o	vegetable oil-in-silicone oil-in-vegetable oil	the mixture of 20% and 70% SiOH silica particles	Multiple emulsions were completely stable against coalescence at a high concentration of 70% SiOH (2 wt%).		
pnas/o/w	glycerin-in-glycerol monostearate-in-water	fat crystals (glycerol monostearate) and nonionic surfactants	the active rutin encapsulated in the internal oily phase of the double emulsions was stable for 30 days and improved the absolute oral bioavailability by 1.76-fold higher than the active suspension	encapsulation of water-insoluble nutrients (rutin)	(Wang et al., 2017b)
o/pnas	paraffin oil-in-formamide or silicone oil-in-glycerin	kaolinite and nonionic surfactant (Noigen RN10)	The synergism between kaolinite particles with the surfactant improved the stability of paraffin oil-in-formamide emulsion and destabilized the silicone oil-in-glycerin system.	drug delivery	(Tawfeek et al., 2014)
o/pnas/o	paraffin oil-in-formamide-in-paraffin oil		Multiple emulsions were exhibited but were short-lived in terms of stability against coalescence.		
o/pnas	castor oil-in-glycerin	50% SiOH silica particles	the emulsions were stable to coalescence for more than one month and at low concentrations of nanoparticles they sedimented	drug release (aspirin)	(Mohamed et al. 2020)
o/pnas/o or pnas/o/pnas	castor oil-in-glycerin-in-castor oil or glycerin-in-castor oil-in-glycerin	50% SiOH silica particles	with the increase of the glycerin fraction ($\Phi = 0.6$), there was a phase inversion (castor oil-in-glycerin-in-castor oil to glycerin-in-castor oil-in-glycerin).		
o/pnas	olive oil-in-glycerin	50% SiOH silica particles	emulsions stable to coalescence for more than one year	drug release (aspirin)	(Dyab, Mohamed & Taha, 2018)
o/pnas	silicone oil-in-organic liquids	wax crystals	emulsions stable to coalescence for up 6 months	triggered release (antifoam)	(Dimitrova et al., 2014)
o/pnas	vegetable oil-in-honey	$CaCO_3$ particles	emulsions stable to coalescence for up to one year	food industry, cosmetic formulations	(Tyowua et al., 2021)
o/pnas/o	mineral oil-in-acetone-in-mineral oil	SiO_2 nanoparticles/polymers	Hydrophobic surface emulsions maintained their wettability after abrasion and sandpaper scratch tests, exhibiting excellent robustness due to structural nano roughness.	superhydrophobic coatings	(Mani et al., 2022)
o/pnas	paraffin oil-in-TDI (toluene-2,4-diisocyanate)	modified cellulose nanofibers	High encapsulation efficiency of DEET insecticide in stable emulsions (O/O) was obtained by mCNF particles. Furthermore, the barrier properties of mCNF significantly reduced the rate of DEET release.	drug release (DEET - insect repellent)	(Kadam et al., 2019)
o/w/o	paraffin oil-in-water-in paraffin oil	wax crystals	stable to coalescence for up 90 days	agrochemical, pharmaceutical and cosmetic preparations	(Szumała & Luty, 2016)
w/o/w	water-in-dodecane-in-water	50% SiOH silica particles (hydrophobic particles)	The formation of multiple stable emulsions was achieved when the oil fraction ($\Phi o = 0.35$) is destabilized by shearing the emulsion in the presence of hydrophobic silica. W/O/W droplets form with increasing mixing power and increasing particle concentration.	therapeutic or food formulation	(Whitby & Parthipan 2019)
w/w	dextran-in-PEG or PEG-in-dextran	collagen nanofibrils	emulsions presented an enhanced stability, *in vitro* and *in vivo* assessments demonstrated excellent properties for cartilage protection in osteoarthritis treatment	cartilage protection	(Wang et al, 2022b)
o/o	silicone oil-in-vegetal oil or vegetal oil-in-silicone oil	14 or 100% SiOH silica particles	The inversion of the transition phase of emulsions containing equal volumes of the two oils, from silicone in vegetable (S/V) to vegetable in silicone (V/S), occurs by increasing the hydrophobicity of the particles.	triggered release	(Binks et al., 2016)
o/o or o/o/o	vegetal oil-in-silicone oil or		Stable multiple emulsions can be prepared in a two-step procedure using two types of particles of different hydrophobicity.		

(*continued on next page*)

Table 2 (*continued*)

Emulsion type	Dispersed phase-in-continuous phase	Stabilizing agent	Experimental findings	Potential application	Reference
o/o	silicone oil-in-vegetal oil-in-silicone oil vegetal oil-in-silicone oil	silicone, sericite, ZnO, bentonite, $CaCO_3$ or PTFE coated by hydrocarbons or fluorocarbons	Sufficiently hydrophobic particles (clay, zinc oxide, silicone, calcium carbonate) acted as V/S emulsion stabilizers (sunflower oil-in-silicone (20 cS PDMS)).		

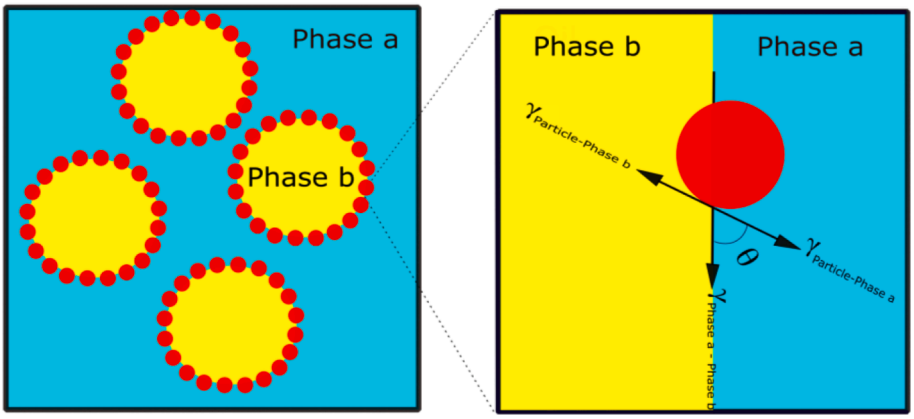

Fig. 2. Illustration of a spherical particle at interface of an unconventional or conventional Pickering emulsions represented by Phase a and Phase b and the contact angle associated to the three surface tensions.

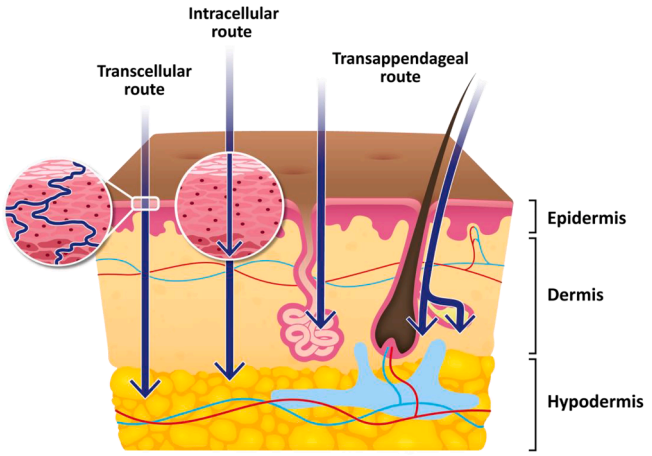

Fig. 3. Schematical representation of skin and skin penetration via intracellular, transcellular and transappendageal routes.

2. Skin structure and permeation routes

The choice of the skin as a drug delivery route can provide local or systemic effects, depending on the therapeutic drug target (Viseras et al., 2019). In surfactant-stabilized emulsions, the surfactant promotes the drug transdermal permeation due to skin irritation properties acting as a permeation enhancement agent. The absorption of the drug occurs into the bloodstream, which makes it difficult to target the therapeutic action in the epidermis and dermis. In Pickering emulsions, drug penetration can be modulated and achieve different routes, such as via hair follicles, sebaceous glands, and pores (transappendageal route), or through diffusion in the stratum corneum (SC) through intracellular or transcellular route (Kováčik et al., 2020), as presented in Fig. 3.

The path taken by the penetrating agent depends directly on its physicochemical characteristics, such as size and solubility. The diffusion of actives to more internal layers beyond the SC can be intercellular or intracellular. By the intercellular mechanism, the drug passes through the interstices between cells, whereas in the intracellular mechanism, hydrophilic molecules diffuse within the corneocytes, whilst lipophilic molecules diffuse intercellular in the lipid content. However, the penetration of the actives is challenging due to the presence of the SC, which limits drug absorption (Kováčik et al., 2020). Overcoming the SC threshold allows the drug to reach deeper layers of the skin, leading to local absorption (in the epidermis) or systemic absorption (such as dermis and diffuse to the bloodstream) (Hadgraft & Lane, 2016).

3. Pickering emulsions and skin applications

3.1. Unconventional emulsions

Unconventional pnas/o, o/o, w/w or multiple Pickering emulsions are interesting systems when the presence of one type of solvent must be avoided or controlled. Additionally, these surfactant-free emulsions are desirable since surfactants are classically irritants to the skin and mucosa (Baravkar, 2014). Unconventional emulsions also have the potential to promote unexplored sensorial aspects, increase drug stability and solubility, and originate oil free emulsions (w/w) as a disruptive innovation in the cosmetic industry.

Among unconventional emulsions, o/o Pickering emulsions are associated with phases composed of a wide variety of vegetable oils such as jojoba, castor, olive, soybean, sunflower, as well as oil solvents like mineral and silicone oil. The most acceptable polar non-aqueous solvent for pnas/o emulsions are poly(propylene glycol), of various molar masses, and glycerin (Baravkar, 2014).

Unconventional pnas/o or o/o Pickering emulsions present some possible advantages compared to classical ones, increasing the stability, solubility, and bioavailability of several drugs (Baravkar, 2014; Dyab, Mohamed & Taha, 2018; Mohamed, Dyab & Taha, 2020). Modifying, hypothetically, the sensorial aspects by controlling the continuous phase

composition (Binks &Tyowua, 2016).

In the literature, the use of vegetable oils and silicone is well described as an ultra-stable and simple way to produce o/o emulsions and multiple emulsion systems with potential uses in skin compatibility and applications (Binks &Tyowua, 2016; Tyowua, Yiase & Binks, 2017).

Measurement of particle wettability could be an easy tool to predict the continuous phase, that could hypothetically affect the sensorial perception. Based on the Finkle rule (Finkle, Draper & Hildebrand, 1923), the phase that wets the particle ($\theta < 90°$) becomes the continuous phase (Robin, Agnely, Tsapis & Huang, 2022).

Simply by modifying the polarity of the particles, the stability of different o/o emulsions can be achieved – such as silicone-in-sunflower oil emulsions with hydrophilic (with 14% SiOH surface groups) particles and sunflower oil-in-silicone emulsions with hydrophobic particles (with 100% SiOH surface groups). The hydrophobic silica particles increased the wettability from sunflower oil to the silicone phase, inverting the continuous phase (Binks &Tyowua, 2016).

Furthermore, multiple emulsions (o/o/o) were obtained with higher viscosity silicone and sunflower oil simply by mixing hydrophilic and hydrophobic particles (Binks &Tyowua, 2016). Total phase separation was obtained in the absence of particles, which highlights the importance of solid particles in the stabilization of the evaluated emulsions (Tyowua, Yiase & Binks, 2017). Other authors used the same strategy of particle surface modification to stabilize o/o emulsions, as Tyowua et al. (2021) and Szumała & Luty (2016).

In terms of cosmetic and pharmaceutical technology, the production of complex multiple emulsions (o/o/o, o/w/o or w/o/w) can be achieved by simply mixing particles with different polarity (Binks &Tyowua, 2016; Tyowua, Yiase & Binks, 2017). They hold great promise as an alternative for both cosmetic and pharmaceutical applications. Multiple unconventional Pickering emulsions for skin applications, for instance, are mainly associated with drug release control and stability (Timgren et al., 2013).

The improved solubility of oil-soluble agents is a highlight point of unconventional o/o Pickering emulsions (Atanase & Riess, 2013; Suitthimeathegorn et al., 2007). Since both phases are composed of oil, insoluble agents can be used in either the dispersed or continuous phase for topical applications. For example, rutin, an antioxidant with very low solubility in water and most oily solvents, is limited in its application. To overcome this setback, an o/o or o/o/w emulsion was developed containing mainly rutin in the inner oil phase, stabilized and co-stabilized by silica particles and surfactants, respectively (Wang et al., 2017a; Wang et al., 2021).

These multiple emulsions could also act reducing hydrolysis and oxidation of pharmaceutical or cosmetic agents, as well as modifying the cumulative release of agents on the skin, without causing skin damage or irritation (Fig. 3) (Dyab, Mohamed & Taha, 2018; Mohamed, Dyab & Taha, 2020).

When necessary, the combination of Pickering particles and surfactants could be a useful strategy to significantly reduce the amount of surfactants in a formulation, thereby improving emulsion stability and minimizing skin and mucosal irritation. From any perspective, total or partial reduction of surfactants could have important implications for skin safety and environmental sustainability (Rebello et al., 2014).

It is necessary to note that, unlike the previously exposed results, the association between particles and surfactants may not always have a synergistic and positive effect on the emulsions. To demonstrate this, one could mention the study by Tawfeek, Dyab & Al-Lohedan (2014), in which the authors observed the behavior of a combination of a non-ionic surfactant (Noigen RN10) and kaolinite particles in the stabilization of non-aqueous emulsions of silicone oil and glycerin. Results showed enhanced stabilization for kaolinite isolated particles, since the addition of surfactant destabilized the o/pnas emulsion.

A key aspect is that particles could, theoretically, alter the sensorial perceptions of emulsions, for example, the starch grains could bring very interesting sensorial properties when in contact with the skin, modifying the after-feel attributes, evaluated as low greasiness, stickiness and slipperiness in Pickering emulsions (Ali et al., 2022a,b). Moreover, these particles can also confer high encapsulation (close to 90%) and stability, suggesting progress in the development of double emulsions for skin applications (Matos et al., 2013).

Antioxidants as vitamin C, anthocyanin and epigallatocatechin can be incorporated into $w_1/o/w_2$ Pickering emulsions, increasing the stability against oxidative degradation (Wang et al., 2022a; Lin et al., 2020; Huang et al., 2021; Zhang et al., 2020). One example found in the literature is an emulsion consisting of an aqueous solution of anthocyanin as the internal phase. The anthocyanin encapsulation efficiency and the encapsulation stability remained high after storage (Lin et al., 2020; Huang et al., 2021).

Unconventional w/w Pickering emulsions are still incipient in literature when compared to o/o or multiple emulsions. However, incorporating this disruptive technology in cosmetics could bring new perspectives to the oil-free emulsions and offer unique sensorial aspects that have not been explored before. Additionally, multiple effects could be associated with this type of emulsion. For instance, Zhang et al. (2019) studied w/w PEG-dextran emulsions stabilized with poly(dopamine) particles cross-linked with poly(acrylic acid), and found that the emulsions formed were stable for more than 16 weeks. PEG and dextran are important moisturizers for improved skin hydration, while large-size hollow polydopamine particles (450 nm) act as an efficient sun protection factor, boosting sunscreens formulations. These particles are biocompatible and can mimic natural melanin, preventing UV-induced DNA damage, and can be used as a safe alternative to sunscreens (Wongngam et al., 2022). This idea of an oil-free moisturizing formulation, with particles as stabilizers and with associated photoprotective properties could be of industrial interest.

Beldengrün et al. (2020) demonstrated the formation of double water-in-water-in-water (w/w/w) emulsions using a similar process to produce w/o/w or o/w/o emulsions. The two aqueous phases, maltodextrin and gelatine, were stabilized with mucin nanoparticles. As this emulsion is formed and stabilized in absence of oil and surfactants, it has promising applications in the biomedical and cosmetic fields. A hydrating formulation was obtained by the authors, as mucin is an effective moisturizer and collagen-stimulator, inducing skin healing and regeneration. Additionally, hydrolysed gelatine could be used in cosmetics as a non-irritating agent, improving skin texture and wrinkles appearance, and maltodextrin is an important moisturizing ingredient.

Other w/w systems seem propitious for skin applications due to their high biocompatibility, such as methylcellulose and dextran (Poortinga, 2008), poly(ethylene oxide) and dextran (Nguyen, Nicolai & Benyahia, 2013; Ben Ayed et al., 2018), starch and locust bean gum (Murray and Phisarnchananan, 2014, 2016), amylopectin and xyloglucan (Freitas et al., 2016; Hazt et al., 2020), pullulan and amylopectin (Machado et al., 2021, 2022), and gelatinized corn starch and κ-carrageenan (You, Murray & Sarkar, 2023).

Although the Pickering effect is observed in many w/w emulsified systems, there are several reports of instability after some period of time, pointing out to the fact that maybe due to its low interfacial tension (Table 1), the particle adsorption at the w/w interface may not be irreversible, unlike o/w emulsions (Dickinson, 2019). There are also some challenges for Pickering-stabilized all-aqueous systems as drug delivery options, including the investigation of mechanical properties, encapsulation of actives, and *in vitro* and *in vivo* tests of the formulations.

It is possible to replace surfactants with Pickering particles to stabilize emulsions. Pickering particles can be used to produce oil-free emulsions in the case of w/w, ultra-stable o/o emulsions, pnas/o emulsions and multiple emulsions, which have been reported as potential carrier systems for bioactive agents with limited water solubility. Multiple Pickering emulsions also favor the multi-encapsulation of actives, bringing new properties and applications, and avoiding some side effects that are associated with a high concentration of surfactants.

3.2. Conventional emulsions

The use of conventional Pickering emulsions presents a significant advantage over traditional emulsions in terms of safety aspects. As surfactants are either absent or used in very low concentrations, the risk of skin sensitization or irritation is usually minimal. However, it is important to note that this assertion holds true only if biocompatible particles are used and appropriated oily phases are selected. Examples of compatible oily phases include caprylic/capric acid triglyceride, vegetable oils, silicones or liquid paraffin. As example of particles, aluminium starch octenylsuccinate (ASt) particles, titanium dioxide (TiO_2) or zinc oxide (ZnO) were investigated toxicologically by Marto et al., (2016a) using an *in vitro* validated skin irritation test method, which uses reconstructed human epidermis EpiSkin® - and an *in vivo* Human Repeat Insult Patch Test (HRIPT). The results of both tests demonstrated that the Pickering particles and the emulsions were considered non-irritant and biocompatible.

Besides the safety aspect, another relevant point is that Pickering emulsions could bring to the formulation new sensorial characteristics such as spreadability, stickiness, hydration, and softness, as demonstrated in studies involving human volunteers (Ali et al., 2022a,b; Marto et al., 2019). All these sensorial aspects are evaluated incipiently at this point and a detailed analysis about the sensorial aspects of unconventional and conventional Pickering emulsions is a good perspective for future investigations.

From the consumer's perspective, the after-feel is a key parameter to determine whether the customer will buy a cosmetic product. Thus, interestingly, when comparing conventional surfactant-based emulsions with Pickering emulsions, the latter have shown distinctive sensorial properties. Ali et al. (2022a,b) pointed out that from the consumers' point of view, surfactant-stabilized emulsions were greasier than particle-based ones right after skin application. In their study, starch granules were used to stabilize o/w emulsions, which were then subjectively evaluated by a human panel and were compared with a rheological investigation, trying to use the measurement of physical properties to predict human sensorial perceptions.

Another feature that Pickering particles can add to conventional emulsions is the control of drug penetration or permeation. Usually, Pickering particles limited the drug permeation through the skin, since no irritating effect is reported for these particles, and that solid particles are unable to cross the skin, which limits drug permeation through the intracellular and transcellular routes (Fig. 3) (Marto et al. 2016a). However, the combination of particles and oily phases could enhance the drug penetration (Taguchi et al., 2019), which is a well-documented property of conventional emulsions stabilized by surfactants.

To illustrate the first scenario of reduced permeation for conventional emulsions stabilized by Pickering particles, Marto et al. (2016a) observed that the permeation of melatonin was reduced for emulsions stabilized with particles, enhancing sunscreen activity by the deposition of the drug onto the skin. Another scenario involves the influence of the oil phase on drug permeation. Taguchi et al. (2019) used CDs as emulsifiers in w/o emulsions with isopropyl myristate as the oil phase. The formulations containing 5% captopril in βCD emulsions were tested on hairless mouse skin to evaluate skin permeation. To confirm the role of isopropyl myristate as a permeation enhancer, liquid paraffin and soybean oil were tested as the oil phase of the emulsion, and the results indicated the use of the CD emulsion with isopropyl myristate as a transdermal drug vehicle.

The evidence suggests that the oily phase in Pickering emulsions plays a more significant role in drug skin permeation than the Pickering particle itself. For instance, Prasanthi et al. (2020) used Pickering emulsions stabilized with bentonite to deliver fluconazole and found that the formulation with sesame oil had low permeation and high skin deposition, whereas the one with oleic acid showed high drug release due to its penetration enhancer properties. By reducing drug permeation, Pickering emulsions can be used topically to deposit the drug on the skin, demonstrating the significant impact of the oily phase composition on the skin permeation and drug deposition onto the skin.

Not only the oil composition is important to define skin penetration. Otto et al. (2022) demonstrated that different polysaccharides (hyaluronic acid, amylopectin or alginic acid) dispersed in the aqueous phase could affect the skin penetration of griseofulvin, an antifungal drug. The modulation of skin deposition/absorption was observed with changing the polysaccharides, and among them, hyaluronic acid-stabilized emulsions showed the best performance regarding drug accumulation in the SC (~13 μg/cm^2). Amylopectin emulsions were found in the innermost layers (~4 μg/cm^2) and alginic acid emulsions presented a transdermal absorption of griseofulvin (~1 μg/cm^2).

The skin penetration/permeation of drugs can also be influenced by Pickering particles formed by polysaccharides. This has been well described in literature for chitosan, a cationic polysaccharide that is an important agent for aiding penetration through the SC. Following the same line of thought, the authors showed that by using a similar particle composed of chitosan/collagen or chitosan/Arabic gum, it was possible to stabilize a classical emulsion through the Pickering effect, in which the oil phase contained either olive oil or paraffin, and the lipophilic drugs resveratrol or cannabidiol. The authors noticed a high deposition of both drugs on the SC, which is consistent with the above-mentioned role of the cationic character of chitosan, which seems to be a generic feature produced by this cationic polysaccharide (Sharkawy et al., 2022, 2021b, 2021a; Wu et al., 2021b).

Skin permeation via hair follicles (transappendageal routes at Fig. 3) is also reported in literature for Pickering conventional emulsions. According to Wu et al., (2021a), in drug delivery through skin, < 3 μm particles were able to be randomly distributed in hair follicles and in the SC, whereas 3–10 μm particles penetrated the hair follicles and bigger particles (greater than10 μm) were prevented from penetrating the SC surface, as described by Hiranphinyophat et al. (2021). So, a very clever way to enhance the skin absorption of drugs in Pickering emulsions is to load both the oil phase and the particles with the compound of interest, as carried out by Laredj-Bourezg et al.(2017), promoting permeation by intracellular, paracellular and hair follicles routes.

Particles that interact significantly with the skin can enhance drug permeation through the skin. For example, Frelichowska et al. (2009 a) produced surfactant-free emulsions stabilized by silica solid particles and tested them on pig skin in Franz diffusion cells. The authors observed that these emulsions could retain lipophilic ingredients in the outer layer of skin, addressing such emulsions for applications in sunscreens. The high storage in the SC, possibly via hair follicles, could enable targeting and promoting a slow release of drug from SC. The same authors also found that hydrophilic drugs such as caffeine could enhance in 3 times the skin absorption. In this case, the strong and specific interaction between the particles and the skin could promote faster drug release into the SC, and the transport associated to caffeine could be considered of relevance in this study (Frelichowska et al., 2009b).

A trend observed in conventional Pickering emulsions is to design particles not only as emulsion stabilizers but also as drug delivery agents, by controlling drug diffusion from the dispersed phase as a barrier, or due to drug encapsulation/incorporation in Pickering particles. As previously mentioned, cyclodextrins are widely used as drug carriers, as their truncated cone shape and inherent inner hydrophobic region with a hydrophilic exterior make them excellent candidates as Pickering particles capable of controlling drug release (Hu et al., 2018; Leclercq & Nardello-Rataj, 2016; Taguchi et al., 2019). Matricial particles could also be incorporated with drugs. For instance, gelatine nanoparticles incorporated with Rutine were tested for photoprotective efficacy, photostability and *in vivo* cutaneous compatibility, resulting in increased antioxidant activity compared to free drugs, without any erythema or effect on skin hydration (Oliveira et al., 2016).

Loading rutin into Pickering emulsions using self-assembled chitosan particles has been shown to improve wound healing by Asfour et al.

Table 3
Summary of Pickering emulsions outputs for skin applications.

Emulsion type	Dispersed phase	Continuous phase	Stabilizing agent	Active ingredient	Output	Reference
o/w	olive oil	water	chitosan with high (96%) and low (78%) degree of acetylation/gum Arabic (CH/GA) particles	cannabidiol (CDB)	Pickering emulsions using NPs with a high degree of deacetylation (DDA) for chitosan were more stable than emulsions with low DDA chitosan, but there was no significant difference between the amount of cannabidiol absorbed from both formulations. Both formulations presented a higher amount of CBD absorbed, when compared to the permeated amount.	(Sharkawy et al., 2022)
o/w	olive oil	water	chitosan/gum Arabic (CH/GA) nanoparticles	*trans*-resveratrol	Pickering emulsions showed an increased *trans*-resveratrol photostability against degradation by UV radiation. Resveratrol was retained in higher levels in the viable epidermis and dermis when using Pickering emulsions.	(Sharkawy et al., 2020)
o/w	medium chain triglyceride (caprylic/capric triglyceride Miglyol 812 N)	water	PLA-b-PEG or PCL-b-PEG block copolymer nanoparticles	retinol (with BHT antioxidant)	Pickering emulsions allowed a large accumulation of hydrophobic drugs in the stratum corneum when compared to the surfactant-based emulsion or an oil solution.	(Laredj-Bourezg et al., 2017)
o/w	propylene glycol and oleic acid	water and acetic acid	self agregated chitosan particles	rutin	Pickering emulsions containing 20% of oil were stable for up to 8 months, and presented an enhanced rutin release efficiency, compared to the plain drug suspension.	(Asfour et al., 2017)
o/w	octyl methoxycinnamate and butanol	water and butanol	colloidal silica particles	octyl methoxycinnamate (OMC) as UV filter; melatonin-loaded (MEL) elastic niosomes as antioxidant	Although advanced characterization studies for emulsions with the surfactant vesicles (niosomes) were not carried out, it was identified that the OMC accumulated on the outer layers of the skin (showing protection against UV-induced skin damage) whilst the niosomes carring MEL were able to penetrate deeper skin layers (as a co-delivery strategy).	(Azizoglu et al., 2017)
o/w	isopropyl myristate, liquid paraffin and soybean oil	water	insoluble β-cyclodextrins complex as solid particles	captopril	Stable emulsions were prepared with increased concentrations of β-cyclodextrins. The highest skin permeability of the model drug captopril was achieved with emulsions containing isopropyl myristate, β-cyclodextrins and water.	(Taguchi et al., 2019)
o/w	octyl and decyl glycerate, glyceryl triacetate, PEG-40 hydrogenated castor oil	glycerin, water	starch modifed with octenyl succinic anhydride (OSA)	resveratrol	The mixture of surfactants modified starch-OSA particles led to more stable Pickering emulsions and enhanced the skin permeation results.	(Wu et al., 2021a)
o/w	olive oil or paraffin oil	water	chitosan/collagen peptides (CH/CP) nanoparticles	cannabidiol (CBD)	*In vitro* skin absorption tests showed a high retention of cannabidiol in the *stratum corneum*. The skin deposition was not influenced by the oil type, but it was enhanced with an increased oil volume fraction.	(Sharkawy et al., 2021b)
o/w	isopropyl myristate	water	poly(2-isopropoxy-2-oxo-1,3,2-dioxaphospholane)-	bifonazole	Pickering emulsions presented an enhanced permeability and skin absorption when	(Hiranphinyophat et al., 2021)

(*continued on next page*)

Table 3 (*continued*)

Emulsion type	Dispersed phase	Continuous phase	Stabilizing agent	Active ingredient	Output	Reference
			modified cellulose nanocrystals (CNC-g-PIPP)		compared to conventional emulsions or a bifonazole control solution.	
w/o	water ethanol	green coffee oil	triethoxycaprylylsilane titanium dioxide, aluminum starch octenylsuccinate, zinc oxide	melatonin	Pickering emulsions were stable and showed to protect melatonin from photodegradation. The results regarding topical delivery and efficacy demonstrated that melatonin provided protection against oxidative stress together with a high sun protection factor.	(Marto et al., 2016a)
o/w	liquid paraffin, caprylic/ capric acid triglyceride, phenoxyethyl caprylate, dimethicone, cetyl dimethicone	water	Quercus Suber Bark (QSB) solid particles	Quercus Suber Bark	Stable Pickering emulsions from organic biocompatible particles were obtained, with protection against oxidative stress as well as a final formulation which did not irritate skin, using an *in vivo* compatibility study.	(Carriço et al., 2019)
w/o	water	liquid paraffin caprylic/ capric acid triglyceride	aluminum starch octenylsuccinate	minocycline hydrochloride	The starch-based Pickering emulsions were efficient in topical delivery of minocycline hydrochloride within a prolonged drug release.	(Marto et al., 2019)
o/w	diethyl adipate	water	Silica (S) or Fuller's earth (FE)	–	Pickering emulsions were used in skin decontamination from a nerve agent. Although the decontamination rate was slightly lower than for dry Fuller's Earth, a liquid formulation should prevent the nerve agent dissemination, and the Pickering emulsions presented a high quantity of warfare agent, when compared to Fuller's Earth in water.	(Salerno et al., 2016)
o/w	water	liquid paraffin or caprylic/ capric acid triglyceride	aluminum starch octenylsuccinate granules	–	The Pickering emulsions were classified as a starch-based vehicle which did not induce any sensitization, being safe for human use. Besides not irritating the skin, they increased both skin hydration and microcirculation.	(Marto et al., 2016b, 2018)
o/w	olive oil	water	hydrophobically modified cellulose nanofibers hybridized with zinc oxide nanoparticles (HCNFZnO)	HCNFZnO	The concentration of Pickering particles from hydrophobically modified ZnO composite cellulose nanofibers was directly related with the UV protection performance as well as with the sun protection factor.	(Lee et al., 2021)
o/w	tea tree oil	water	chitosan nanoparticles	curcumin	The Pickering emulsion presented a high antibacterial efficacy, a significant wound healing property and was also sprayable.	(Bao, Wu, & Ma, 2020)
o/w	miglyol, ethanol and acetone	water	acetylated cashew gum nanoparticles	indomethacin	Then encapsulation efficiency was determined with a steady release profile within 3 h releasing 75 % of indomethacin.	(Cardial et al., 2019)
o/w	medium chain trygliceride from coconut oil	water	carboxymethyl chitosan - sodium alginate nanoparticles	curcumin with poloxamer 407	The study introduced Pickering emulsions hydrogels prepared from carboxymethyl chitosan - sodium alginate nanoparticles and curcumin, which presented antibacterial, hemostasis and healing-promoting properties.	(Wu et al., 2022)
o/w and w/o	caprylic/capric triglycerides	water	titanium dioxide, zinc oxide and silica	–	The authors assessed the sensory perception of Pickering emulsions, relating the type of	(Terescenco et al., 2020)

(*continued on next page*)

Table 3 (*continued*)

Emulsion type	Dispersed phase	Continuous phase	Stabilizing agent	Active ingredient	Output	Reference
					the metal oxide with properties such as film whiteness and screech of the residue. The morphology of the emulsion (W/O or O/W) affected the textural properties of the emulsions.	
o/w	*Melaleuca alternifolia* essential oil	water	silica nanoparticles	tioconazole and *Melaleuca alternifolia* essential oil	The Pickering emulsions containing an azole derivative and antifungal essential oil presented themselves as appropriate candidates for onychomycosis topical treatment.	(Vörös-Horváth et al., 2020)
o/w	medium chain triglyceride, castor oil, isopropyl myristate, diethyl sebacate, limonene, octisalate	water	cyclodextrin with inserted oils	bupivacaine	Different permeation amount of bupivacaine was achieved though skin, only by choosing different oils (a ring-structured one, a linear chain and a triglyceride oil).	(Hu et al., 2018)
o/w	sunflower oil	water	Exopolysaccharides (EPS) produced by *Bacillus halotolerans*	calcipotriol	Stable Pickering nanoemulsions containing calcipotriol reduced the treatment time of psoriasis vulgaris in mice.	(Wang et al., 2020)
o/w	light mineral oil, diethyl sebacate	water, sorbitol	polymeric matrix	halobetasol and tazarotene	Together with emolients and solvents, a polymeric emulsion was formulated which indicate no cutaneous irritation and a uniform disposition, leading to an efficient delivery of actives into the dermal layers.	(Tanghetti et al., 2021)
o/w	linoleic acid	water	spray-dried cellulose nanocrystals	ciprofloxacin hydrochloride	The obtained nanoemulgels presented skin regeneration properties, together with an enhanced inhibition of microbial growth which could be attributed to the use of linoleic acid with the cellulose nanocrystals.	(Kamel et al., 2021)
o/w	medium chain triglyceride	water	poly(lactide-co-glycolide) (PLGA)/poly(styrene-co-4-styrene-sulfonate) (PSS) nanoparticles	tocopheryl acetate	A high rate of encapsulation of tocopheryl acetate (TA) was achieved for stable Pickering emulsions. Encapsulation led to the TA stability against UV radiation improved. The cellular antioxidant activity was increased for the encapsulated TA.	(Wei et al., 2020)

(2017). The authors observed the drug anti-inflammatory activity (lower level of malondialdehyde (MDA) production) in the wound, cells protection from lipid peroxidation and an acceleration of healing rate due to the presence of the emulsion. In the histopathology remarks, the stimulation of hyaluronic acid and collagen type I lead to a fast tissue regeneration with complete re-epithelization of the epidermis (Asfour et al., 2017).

Pickering particles of chitosan are also reported in another manuscript as wound healing enhancers. Bao, Wu, & Ma (2020) produced tea tree oil emulsions containing curcumin as the dispersed phase stabilized by chitosan nanoparticles, leading to a better recovery of mice wounds compared to the drug delivery by dispersing the agent in oil and the chitosan nanoparticles solution. In only five days the wound healing rate was 54.92% compared to 24.56% for classical emulsions, and after ten days, the Pickering emulsion was responsible to 95.06% wound recovery. The use of Chitosan particle-stabilized emulsions instead of surfactant-based emulsions greatly improved the wound healing. Other authors observed similar results using nanoparticles containing chitosan, demonstrating the potential of this particle to stabilize o/w emulsions, promoting a greater wound healing effect than the free drug.

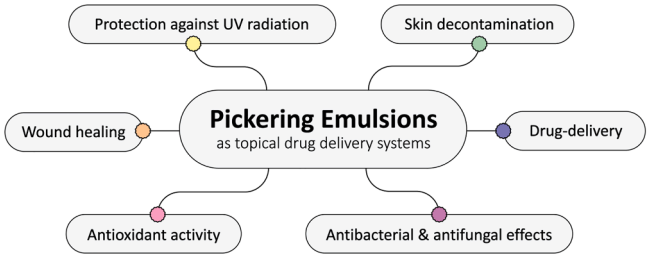

Fig. 4. Main skin applications of Pickering emulsion.

These formulations were also found to reorganize blood vessels, hair follicles and collagen deposition (Wu et al. 2022).

Table 3 describes in detail several emulsions and their associated features, disclosing the main outputs as well as the dispersed/continuous phases used, the stabilizer and the encapsulated compound. Potential applications of Pickering emulsions could be observed with features such as skin decontamination, drug-delivery, antibacterial, antifungal, antioxidant and wound healing effects, together with

protection against UV radiation, (Fig. 4), for example.

4. Perspectives and challenges

Molecular surfactants have been extensively used in traditional emulsions. However, they may be responsible for promoting cutaneous irritation, hemolysis and environment toxicity, which is intrinsically associated with their chemical structure and physical–chemical properties. In unconventional w/w emulsions, the interface length scale is larger than the correlation length of the polymer solution, which requires the use of colloidal particle instead of surfactants to stabilize these emulsions (Lémery et al., 2015; Seweryn, 2018; Freitas et al., 2016).

Pickering particles could offer a new perspective on emulsions, acting not only as a stabilizer but also protecting active substances from degradation, increasing bioavailability through skin permeation, and promoting sustained drug delivery and transdermal applications (mainly for highly interactive particles with skin). Additionally, could promote differences in texture and spreadability, as discussed in this review, improving the sensorial aspects of these emulsions, depending on the kind of particle and oily phase used. This observation highlights the perspective of sensorial and textural analysis of Pickering emulsions. However, detailed rheology and tribology of Pickering emulsions are demanded in a near future, assuming the interplay between them and the consumers sensorial perceptions.

One issue with research on Pickering emulsions is the use of oily phases in both conventional and non-conventional oil-in-oil emulsions or multiple emulsions that are not commonly used in the pharmaceutical and cosmetic industries. While researchers can apply findings from basic studies to some pharmaceutical applications, modifying the oil phase could alter the particle's wettability and completely change its interaction with the skin. As a result, a new system must be examined, thus redoubling the work (Wu et al., 2020).

Another challenge is improving the toxicological safety studies of Pickering particles and, as a result, Pickering emulsions. Some authors have attempted to reduce the likelihood of adverse/toxic effects by employing biomaterials as biocompatible particle sources. However, there is a significant discussion in the literature regarding nanoparticle absorption, as described by McClements & Rao (2011) and Raynes et al. (2014).

It should be noted that each particle must be evaluated independently, as nanoparticles exhibit distinct toxicological behavior compared to microparticles. As a result, the safety of a Pickering emulsion may also depend on the particles used and their intrinsic interaction with the skin. Alternatively, the use of Pickering particles could provide a strategic alternative to molecular surfactants that meets consumers' demand for eco-sustainable products (Marto et al., 2016c; Rebelo et al., 2014).

To our knowledge, there are no commercial products utilizing conventional or non-conventional Pickering emulsions, but there is a growing number of associated patents. Non-conventional Pickering emulsions are a promising system for skin applications, and further investigation of toxicological and sensory aspects will aid in understanding the interaction of Pickering particles at the interface in cosmetic and pharmaceutical formulations.

CRediT authorship contribution statement

Bianca Hazt: Investigation, Writing – original draft. **Gabriela Pereira Parchen:** Investigation, Writing – original draft. **Lilian Fernanda Martins do Amaral:** Writing – original draft. **Patrícia Rondon Gallina:** Writing – original draft. **Sandra Martin:** Writing – original draft. **Odinei Hess Gonçalves:** Resources, Writing – original draft, Funding acquisition. **Rilton Alves de Freitas:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

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.

Data availability

No data was used for the research described in the article.

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