



Utilization of by-products for preparation of Pickering particles

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Abstract

The processing of foods yields many by-products and waste. By-products are rich in bioactive components such as antioxidants, antimicrobial substances, polysaccharides, proteins, and minerals. A novel use of by-products is as materials for the preparation of Pickering particles. Pickering particles are considered appropriate materials for the stabilization of emulsions. Conventionally, emulsions are stabilized by the addition of stabilizers or emulsifiers which decrease the surface tension between phases. Emulsifiers are not always suitable for some applications, especially in foods, pharmaceuticals, and cosmetics, due to some health and environmental problems. Instead of emulsifiers, emulsions can be stabilized by solid particles also known as Pickering particles. Pickering emulsions show higher stability, and biodegradability, and are generally safer than conventional emulsions. Particle morphology influences emulsion stability as well as the potential utilization of emulsions. In this review, we focused on the by-products from different food industries (cereal and dairy) that can be used as materials for preparing Pickering particles and the potential of those Pickering particles in stabilizing emulsions.

Keywords Pickering particles · By-products · Emulsion stability · Co-stabilization · Instability mechanism

Introduction

Many processed foods, personal care products for our skin and face, agrochemical products for crop protection, petrochemicals, and pharmaceutical products [1–3] are based on emulsions. An emulsion is a complex mixture of two or more immiscible liquids which are dispersed in one system [4]. Due to the high surface energy of both liquid phases, emulsions are thermodynamically unstable and can undergo Oswald ripening [5], creaming [6], and coalescence [7, 8]. Conventionally, emulsions are stabilized by adding emulsifiers which decrease the surface tension between phases and can increase the steric hindrance and electrostatic repulsion between droplets [9, 10]. However, some emulsifiers such as polysorbate 80 [11, 12] have been found to cause health issues like inflammation, skin rashes, irritation to eyes, hemolysis, and environmental problems such as contamination of groundwater [13], potentially endangering both the environment and human health [14, 15].

It is important to look for effective, health-promoting, and environmentally friendly stabilizers/emulsifiers to replace fully or partially conventional emulsifiers in a variety of fields such as cosmetics, personal care, and foods as consumers are becoming more aware of the impact of emulsifiers on the environment and health. To overcome the issue of the effects of emulsifiers on the environment and human health, Pickering particles (PPs) could substitute emulsifiers fully. PPs are solid particles that are absorbed at the oil–water interface, making a barrier to prevent coalescence and stabilize emulsions.

By-products from the food industries contain many useful compounds and these compounds have the potential as materials for the preparation of PPs. There is a growing trend towards environmental protection and ecological sustainability which can be achieved through the utilization of by-products. By-products are generated during processing at various stages on the industrial level. The disposal of by-products has become a major issue confronting the food industries globally as the disposal of by-products might contribute to environmental problems including pollution (soil, water, or air) [16].

The disposal of by-products may be prohibitively expensive under some legislative rules (Waste Framework Directive (WFD) – Directive 2008/98/EC, European Union

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community Strategy for Waste Management”). It is not practical to discard by-products, so their utilization has emerged as an alternate strategy to address the issue of safe disposal [17, 18]. By-products include significant amounts of bioactive compounds and functional ingredients including proteins, polysaccharides, fibers, and antioxidants [19]. These compounds can be extracted and processed to be used as PPs for the stabilization of emulsions.

In this review, we highlighted the by-products from different food industries, especially the cereal and dairy industries which can be used as material for the preparation of PPs. The potential of PPs, prepared from by-products, in the stabilization of emulsions is also discussed.

Pickering particles

PPs are solid particles which enable the stabilization of emulsions by the adsorption of particles at the oil–water interface [20]. Ramsden in 1904 [21] and Pickering in 1907 [22] discovered that solid particles are interfacially active and can act as a stabilizer of emulsions.

PPs can vary according to their shape, size, and morphology [23]. The properties of PPs have a significant impact on droplet size, droplet shape, stability, type (O/W, W/O), and characteristics of emulsions. To prepare an emulsion of specific type and properties, it is important to select an appropriate particle [24].

Properties of Pickering particles

The properties of PPs to be used in stabilization of emulsions are as follows: (i) PPs should be partially wetted by both phases yet insoluble in either phase (ii) PPs should maintain intermediate wettability for adsorption at the oil–water interface, and (iii) Size of particles should be smaller than the targeted emulsion droplets size (few order or minimum one order of magnitude) to form a protective layer around droplets [25]. The wettability, particle size, and surface charge are key parameters for consideration while choosing PPs for stabilization [26].

Particle wettability

Particle wettability is characterized by three-phase contact angles (θ). The distribution of particles at the oil–water interface depends on this contact angle. Thermodynamically, θ is interrelated with the balance of surface free energies between particle–oil, particle–water, and oil–water interface [27].

PPs with a contact angle between 30° and 150° are suitable for the stabilization of emulsions. If the contact angle of the particle is below 90° , it will stabilize an o/w emulsion

(i.e., hydrophilic particle). If the contact angle of the particle is above 90° , it will stabilize a w/o emulsion (i.e., hydrophobic particle). The contact angle of the particle should be close to 90° . So, it can be equally absorbed in both dispersed and continuous phases [28]. This phenomenon of contact angle at the oil–water interface is shown in Fig. 1 which has been adjusted according to Klojdová and Stathopoulos [29].

The wettability of particles can be adjusted by physical absorption [30] or chemical modification [31] to increase sufficient adsorption and effective packing of particles at the oil–water interface.

Particle size

The size of PPs is one of the critical factors (others being particle wettability, particles concentration, and surface charge) in the formation of a particle network for developing an emulsion framework. Small particles have been preferred for stabilization as large particles require more time for adsorption at the oil–water interface. PPs should be at least one order of magnitude smaller than the size of emulsion droplets for efficient stabilization [25, 32].

Wang et al. [33] has prepared starch particles by nanoprecipitation and used the particles for stabilization of o/w high internal phase emulsions. The average size of the particles was 120 nm. Hu et al. [34] prepared gliadin particles by anti-solvent precipitation to stabilize o/w high internal-phase emulsion. The average size of the particles prepared was 120 nm.

Surface charge

The distribution of ions on the particle’s surface creates the final surface charge. The electrostatic attraction between the net surface charge and the oppositely charged surrounding surface affects the interfacial region of the adjacent medium. The strong and irreversible anchoring of PPs at the oil–water

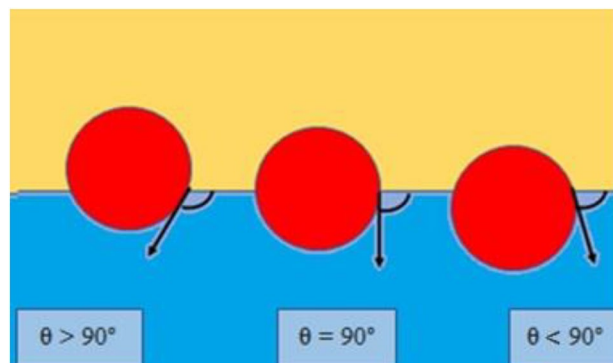


Fig. 1 Adsorption of Pickering particles at the oil–water interface based on wettability [29]

interface has been thought to be the result of the surface charge of PPs caused by both dispersed and continuous phases or any single phase [35].

The addition of salt and adjustment of pH can be used to change the surface charge of PPs [35–37]. The addition of salt can encourage particle adsorption at the oil–water interface by creating a physical barrier in the form of film. A change in salt concentration could alter the thickness of film. A thicker layer can produce more repulsion between droplets which in turn could improve the stability of emulsion [9]. The fluctuation in pH away from the isoelectric point of particles increases surface charge [37]. Changes in pH result in protonation or deprotonation of surface groups which enable the electrostatic interaction [38].

Mechanism of emulsion stabilization by Pickering particles

PPs are characterized by wettability in both aqueous and oil phases, but they are insoluble in any phase. So, they are irreversibly absorbed at the oil–water interface. The adsorption layer, which provides a physical barrier and prevents coalescence, is formed [39].

The mechanism of stability by PPs is shown in Fig. 2 which has been adjusted according to [40].

Co-stabilization with emulsifiers

Emulsions can be co-stabilized by PPs and commonly used emulsifiers. Few studies [41–43] have investigated the combined effect of PPs and emulsifiers on the physical and oxidative stability of emulsions. These studies have suggested that PPs and emulsifiers, when used together, can provide a stable emulsion.

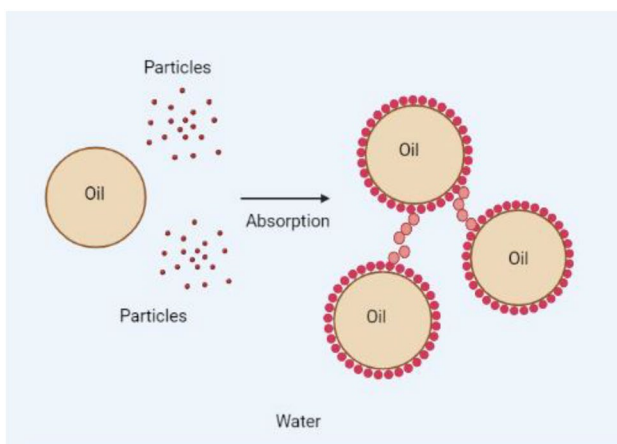


Fig. 2 Mechanism of the stability of Pickering emulsion [40]

The role of co-stabilization is to control the wettability of the particles towards a 90° contact angle for maximum particle adsorption. Binks et al. [44] highlighted the preparation protocol of co-stabilization for o/w emulsion containing a mixture of hydrophilic silica nanoparticles and emulsifiers. When particles were added to an emulsifier-stabilized emulsion, they coalesce and form a tiny population of the big droplet, possibly due to the bridging of adsorbed particles. The addition of an emulsifier to a particle-stabilized emulsion surprisingly boosted coalescence. However, resistance to creaming was increased, probably due to an increase in viscosity. Continuous emulsification by particles and emulsifiers resulted in synergistic stabilization. Emulsions were resistant to creaming and coalescence at lower emulsifier concentrations.

Song et al. [42] have used octenyl succinic anhydride (OSA) modified hydrophobic starch particles and three different emulsifiers (Hexadecyltrimethylammonium (CTAB), sodium dodecyl sulfate (SDS), and polysorbate 20) for preparation of o/w Pickering emulsions. Accelerated oxidation testing at 50 °C was used to evaluate the physical and oxidative stability of emulsions. The droplet size of emulsions co-stabilized by particles and emulsifiers was small compared to emulsions stabilized by OSA-starch particles. It was found that emulsifiers and starch particles when combined can create emulsions with better oxidative stability.

Kim et al. [43] have prepared Pickering nano-emulsions by combining whey protein isolate (WPI) with three different emulsifiers (CTAB, SDS, and polysorbate 20). Their physical stability, turbidimetric, and rheological properties were investigated under food processing conditions. Factors such as pH, heat, freeze–thaw, and salt treatments have been assessed. It was confirmed that steric repulsion for WPI-polysorbate 20 and electrostatic repulsion for WPI-SDS and WPI-CTAB contributed to the emulsion stability. Different studies which have focused on the co-stabilization by PPs, and emulsifiers are presented in Table 1.

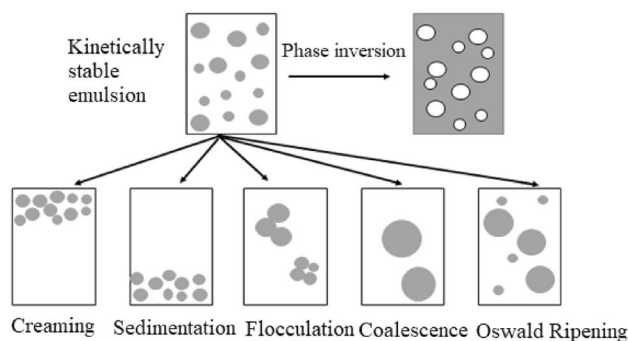
Comparison between PP and emulsifier

PPs have several distinctive benefits compared to the conventional emulsifiers i.e., (i) Irreversible absorption of PPs at oil–water interface prevents droplet aggregation (ii) Pickering emulsions are usually not affected by external factors i.e., pH, temperature, composition of the oil phase (iii) Pickering emulsions require lower or no concentration of emulsifiers compared to conventionally stabilized emulsions (iv) PPs are biocompatible and biodegradable [49] (v) PPs may provide higher stability than conventional emulsifiers [50].

The comparison of Pickering and the conventional emulsion is shown in Fig. 3 which has been adjusted according to Deng et al. [40].

Table 1 Co-stabilization by Pickering particles and Emulsifiers

Pickering particle	Emulsifier	Average droplet size	Emulsion type	References
OSA treated starch	SDS	9.3 ± 0.6 μm	O/W	[42]
	CTAB	29.2 ± 1.6 μm		
	polysorbate 20	19.7 ± 0.1 μm		
Whey protein isolate	SDS	179.7 ± 1.6 nm	O/W	[43]
	CTAB	202.0 ± 0.9 nm		
	polysorbate 20	217.4 ± 2.0 nm		
Whey protein isolate	Phytosterols	0.321–0.409 μm	O/W	[45]
Sodium caseinate	PGPR, phytosterol	5.7 ± 0.3 μm	W/O	[46]
Sodium caseinate	PGPR	422 ± 4 μm	W/O	[47]
High methoxyl pectin	PGPR	6.95 ± 3.9 μm	W/O	[48]

**Fig. 3** Comparison of Pickering emulsion and conventional emulsion [40]**Fig. 4** Schematic diagram of common instability mechanisms in an emulsion system [51]

Instability mechanisms in emulsions

A few phenomena have been considered as the causes of instability in emulsions. These include creaming, sedimentation, flocculation, coalescence, and Oswald ripening.

Creaming

The interfacial membrane that separates the droplets can break, which could result in creaming. Creaming is the rise of dispersed particles to the surface of an emulsion [6]. This phenomenon is shown in Fig. 4 which has been adjusted according to McClements, 2007 [51]. Creaming can be minimized by reducing the droplet size, increasing the continuous phase viscosity, and balancing the density of both phases [52, 53]. The creaming index (CI) can be determined by measuring the height of the serum and the total height of an emulsion [54].

$$CI(\%) = \frac{H_s}{H_t} \times 100$$

where H_s is the height of the serum and H_t is the total height of the emulsion.

Emulsions with a lower creaming index are more stable compared to emulsions with higher creaming index. It has been reported by [55–58] that emulsions stabilized by zein and sodium caseinate particles were stable against creaming.

Sedimentation

Sedimentation happens due to the difference in the density of the phases, resulting in macroscopic segregation. It has been suggested by Ilyasoglu Buyukkestelli and El [59, 60] that sedimentation can be decreased by increasing the viscosity of the continuous phase. Stoke's law describes this phenomenon. It can be seen from the equation that sedimentation is directly affected by the viscosity of the continuous phase and the droplet size.

$$v = \frac{2gr^2(\rho_2 - \rho_1)}{9\eta_1}$$

where v is the gravitational separation rate, g is the acceleration due to gravity, r is the droplet radius, ρ_1 , and ρ_2 are the densities of the continuous phases and dispersed respectively, and η_1 is the viscosity of the continuous phase [61].

Flocculation

Flocculation is an aggregation of emulsion droplets that may result in the formation of 3-D clusters. This phenomenon is reversible, and droplets retain their integrity. This happens when repelling forces (electrostatic) between droplets have been overcome by attractive forces (Van der Waals) [62, 63]. It has been found that emulsions stabilized by sodium caseinate [64, 65], and soy protein [66, 67] were stable against flocculation and sedimentation. The slight or no significant variation in mean droplet size after the storage period was an indication that no flocculation had occurred [64, 67].

Coalescence

Coalescence is the merging of two or more droplets which results in the formation of bigger droplets. Consequently, the emulsion may be separated into two phases. This phenomenon is irreversible [7]. Coalescence can be prevented by the reduction of droplet sizes. Shah et al. [68] has suggested that droplet sizes can be reduced if the concentration of PPs is increased. Some researchers have prepared emulsions stabilized by zein [58, 69, 70], and starch PPs [71–73] which were stable against coalescence.

Oswald ripening

Oswald ripening usually occurs due to the diffusion of small droplets into larger ones. Laplace pressure is the driving force behind this over the time phenomenon in which small droplets from dispersed phase diffuse through continuous phase into large droplets. It is common for emulsions prepared with essential oils and flavors and stabilized by emulsifiers [5, 74]. It has been suggested by [75–78] that emulsions stabilized by zein and starch PPs were stable against Oswald ripening. Liang et al. [78] has prepared o/w Pickering emulsions stabilized by starch nanocrystals. The droplet size and visual assessment of the emulsions showed that Pickering emulsions were stable against Oswald ripening for a storage period of 90 days.

The complete arrest of the Oswald ripening by PPs is related to their exceptionally high adsorption energy. For spherical particles with radius a , the energy for particle adsorption from a fluid interface with interfacial tension σ , is:

$$W = \pi a^2 \sigma (1 - |\cos \alpha|)^2$$

where α is the contact angle of the particle, measured through the aqueous phase. This equation shows that the

adsorption energy is proportional to the particle area, $W \propto a^2$, and that maximal adsorption energy, $W = \pi a^2 \sigma$ is obtained at $\alpha = 90^\circ$ [77].

By-products from different food industries

Food loss is a decrease in the mass of food, at various stages of food supply chain before consumer level, which was initially intended for human consumption. Food which is appropriate for human consumption being discarded or left to spoil at consumer level is food waste [79]. Food loss happens at earlier stages of food supply chain during production, post-harvest, transportation, and processing stage whereas food waste typically happens at retail and consumer. By-product is a secondary product obtained after processing the main product, usually having an economic potential or nutritional value [80–82].

According to the Food waste index report 2021, 931 million tons of food waste was generated worldwide, 61% of which came from households, 26% from food service, and 13% from retail. [83]. According to Food and Agriculture Organization report, 14% of food produced is lost from post-harvest up to the supply chain and 2.2 billion tons of food waste will be generated worldwide by 2025 [84]. Processed fruits and vegetables account for 45–50% of by-products [85], Cereal industries produce 25% of by-products [86], meat processing produces 23% of by-products and the beverage industries produce about 20%–60% of by-products [87]. Cheese production generates 30–35% whey which is either discarded or only used as animal feed [88].

Current situation of by-products utilization and goals

Approximately half of the waste generated by food processing is lignocellulosic; consisting of cellulose, hemicellulose, and lignin [80]. There has been an increased interest in maximizing the use of by-products from the material as a food additive to fortification and other applications [89]. By-products have been used in meat products for delaying protein and lipid oxidation [90–93], in dairy products for improving storage stability, nutritional value, and antioxidant activity [94–99], in bakery products for improving textural and sensory properties [100, 101]. Other potential uses of by-products include the production of fertilizers, fuel i.e., ethanol [102, 103], livestock feed production [104, 105], biomedical application i.e., bone tissue engineering [106], industrial products i.e., lactic acid, gluconic acid [107, 108] or as a carbon source for a variety of purposes [109].

The cause of by-products underutilization is lack of information about value addition and suitable applications. Currently, researchers are focusing on the value addition and

appropriate utilization. The efficient utilization of by-products from the food industries can help reduce industrial costs and environmental pollution, contributing to sustainability in the food industry. This approach will facilitate economic diversity [110]. Waste management strategies should be integrated and coordinated with policies on food, agriculture, food standards, food poverty alleviation, and sustainable production and consumption [80]. The European Commission is now aiming to "halve per capita global food waste at the retail and consumer levels of minimizing food loss along production and supply chains (including post-harvest losses) by 2030," [111]. The necessity of the current situation is to valorize food by-products within the context of the circular economy, reducing the industrial effect on the environment.

PPs trend-why by-products?

By-products from the food industries contain a significant number of bioactive compounds and functional ingredients and these compounds have the potential for the preparation of PPs. By-products contain proteins, polysaccharides, fibers, and antioxidants, [19] which can be extracted, purified, milled, and processed to be used as PPs for the stabilization of emulsion. Some studies have focused on the stabilization of emulsions prepared with these bioactive ingredients [112–115]. Cereal and dairy industries are generating significant amounts of by-products. These by-products are rich in polysaccharides and proteins.

PP prepared from by-products of cereal and dairy industries

Cereal industry

Polysaccharides Polysaccharide particles have been used to prepare emulsions with various functional properties including delivering bioactive compounds, regulating lipid digestion, and preparing low-caloric products [116–118].

Different studies on the PPs prepared from by-products of the cereal industry are presented in Table 2.

Starch Starch is a natural polysaccharide with high molecular weight, found abundantly in cereals. Starch is made up of two glucose polymers, amylose, and amylopectin. Starch is commonly used in the food industry because of its general safety as a food additive, thickening properties, and relatively affordable price. The morphology and composition of native starch granules make it a good stabilizer [39]. Different methods have been used to change the hydrophilic and hydrophobic properties of starch particles to allow the preparation of a specific type of emulsion (o/w or w/o). The commonly used method for the preparation of starch particles is the treating of starch granules with OSA [122–124]. Other methods for the preparation of starch particles include acid hydrolysis [119], high pressure treatment [125], non-solvent precipitation [126], nanoprecipitation [127], and ion gelation [128].

Yusoff and Murray [72] have used OSA-treated starch particles for the preparation of o/w emulsions. The OSA-treated starch particles were freeze milled to reduce their size. Production of diverse-sized starch particles can be indicated by different microscopic techniques such as confocal laser scanning (CLSM), light transmission, and laser doppler light scattering. The prepared emulsions were stable against coalescence with no significant change in droplet size for a storage period of 3 months. Some authors [73, 123, 129, 130] have used OSA to modify starch particles and reported similar results.

Tan et al. [71] have prepared o/w emulsions using starch nanoparticles prepared by nanoprecipitation and treatment with acetic anhydride. CLSM revealed that nanoparticles were mostly absorbed at the interface. When the volume fraction of the oil phase exceeded 0.65, o/w emulsion was reversed to w/o emulsion. An increase in salt concentration increased the average droplet size. This increase in size might be due to a decrease in viscosity of emulsions. It was further found by [71] that droplet size increased with the increase in nanoparticle concentration. The prepared

Table 2 Pickering particles prepared from by-products of the cereal industry

Pickering particles	Modification method	Average Particle size	Particle concentration % (w/v)	Droplet size of emulsions μm	References
Starch	octenyl succinic anhydride	0.5–10 μm	1–3	0.5–15	[72]
Starch	Nano precipitation	–	0.5–2.0	35–60	[71]
Starch	Acid hydrolysis	10–30 μm	0.5–4.0	5–50	[119]
Cellulose	octenyl succinic anhydride	149.2 nm	0.1–1.2	50	[31]
Cellulose	Polymer adsorption	19.576 \pm 0.26 μm	0.5–2	10–40	[120]
Cellulose	Acid hydrolysis	30–80 nm	0.05	10–30 nm	[121]
Zein	Anti solvent precipitation	173.4 \pm 2.16 nm	0.1–2.0	25–54.3	[75]
Zein	–	43.7–60.6 nm	0.1–0.3	42.6–137.9	[57]

emulsions were stable against coalescence for a storage period of 1 month. Similar results have been described by some authors [126, 131–134] who have used starch particles prepared by nanoprecipitation.

Lu et al. [135] have used milled starch particles for the preparation of o/w emulsions. The milling process changed the morphology of starch particles and resulted in irregular shapes, and large size particles. However, particle size decreased rapidly by increasing the milling time and starch concentration. The starch content, oil fraction, pH, and ionic strength influenced the structure and droplet size of the emulsion. The prepared emulsions showed stability against pH, ionic strength, and temperature conditions. Emulsions were stable against coalescence for storage periods of 6 months. Some other studies [136–138] have used milled starch particles for stabilization of emulsions and reported similar results. However, [135, 139, 140] have reported that the storage stability of emulsion decreases at high pH (alkaline).

The starch particle concentration is an important factor that influences the droplet size and creaming index of emulsions. It was found by [71, 119, 126, 130, 132, 139] that the size of droplets reduces initially with increasing particle concentration but remains unchanged after a certain concentration.

Cellulose Cellulose is the structural component of the primary cell wall of green plants and bacteria. Cellulose is made up of linear chains of β (1 \rightarrow 4) linked d-glucose units. Cellulose is a biodegradable polymer that exists in nature as macroscopic fibers or microfibril cellulose [141]. Chen et al. [31] have used OSA treated cellulose particles for preparation of Pickering high internal phase emulsions (HIPE). The microstructure of emulsions was observed by optical microscopy. The droplet size of prepared emulsions decreased with the increase in particle concentration. The prepared emulsions were stable against creaming for a storage period of 7 days. Other studies [142, 143] that focused on OSA treated cellulose particle have reported the similar result.

Dong et al. [144] have prepared o/w Pickering emulsions stabilized by cellulose nanocrystals. The nanocrystals were prepared by acid hydrolysis. The prepared emulsions showed stability against a wide pH range (2–12), ionic strength (0–1000 mM), and temperature (0–100 °C) range. The prepared emulsions were stable against coalescence for a storage period of 40 days [145, 146] have used cellulose particles prepared by acid hydrolysis for stabilization of o/w Pickering emulsion. The authors reported similar results that prepared emulsions were stable for a storage period of several months.

Ahsan et al. [120] has used microcrystalline cellulose (MCC) particles for preparation of o/w Pickering HIPE. Surface modification of cellulose was done through polymer

adsorption with sodium carboxymethyl cellulose. The prepared emulsions were stable against pH, ionic strength, sedimentation, and coalescence for a storage period of 15 days. Some authors [121, 144, 147] have used cellulose particles for stabilization of emulsions and reported similar results. However, Du Le et al. [143] have reported that emulsions stabilized by cellulose particles were sensitive to pH. Owing to emulsions stability toward temperature variation, [121, 144, 148] have reported emulsions stabilized by cellulose particles were stable against temperature variation.

Pectin Pectin is a soluble fiber found in the primary cell wall of plants, mainly in fruits and cereals. Pectin has been used with different PPs such as soy [149], zein [150], pea protein [151], gliadin [152], starch [138] for stabilization of emulsions. Liu et al. [153] have used pectin solely as a PP for the first time in stabilization of Pickering HIPE. Citrus fruit has 3.5% pectin in peel of fruit [154]. Oat bran has 16% total dietary fiber on a dry weight basis, and one third of the total dietary fiber is soluble fiber [155]. Rice bran has 11.5% dietary fiber that is comprised of β -glucan, pectin, and gum [156]. Sugar beet pulp has 70% polysaccharides on dry weight basis, of which 25% is pectin [157]. Pectin can be extracted from these by-products and the potential of pectin as a PPs should be explored.

Proteins Zein Zein is a water-insoluble protein with high concentrations of nonpolar amino acids. It is a byproduct of the cereal industry and has been used in cosmetics, pharmaceuticals, and bio-gels. Feng et al. [158] has prepared o/w Pickering emulsions stabilized by zein nanoparticles. The emulsions were enriched with cinnamon essential oil to partially replace butter in pound cakes and to inhibit mold growth. The prepared emulsions were stable and cinnamon oil prevented yeasts and mold growth on pound cakes for storage for 12 days at room temperature. Santos et al. [70] has prepared o/w Pickering emulsions stabilized by zein-xanthan gum complex. The addition of xanthan gum increased the viscosity of the continuous phase and reduced the creaming during storage. The prepared emulsions were stable against coalescence for a storage period of 3 weeks. Other authors [159, 160] have successfully used zein particles and reported similar results.

Zhou et al. [30] has prepared o/w Pickering HIPE stabilized by zein-pectin particles. Emulsions showed stability against the pH range of 2–5 but a slight separation of the oil and water phase occurred at pH 5. The prepared emulsions were stable against coalescence at room temperature for a storage period of 1 month. Similar results have been reported by [57, 75, 161]. However, Zhang et al. [159] and de Folter et al. [162] have reported that emulsions stabilized by zein nanoparticles were stable against temperature variation and a wide range of pH (2–9). This was due to the addition of xanthan gum which increased the viscosity of the continuous

phase. The high charge density of xanthan gum resulted in strong electrostatic attractions which improved the overall emulsion stability against pH, temperature, and salt concentration [159].

Gluten/gliadin Gluten is a group of proteins found in wheat, and other cereal grains, including rye and barley. Gluten consists of two major groups of proteins, gliadins, and glutenins.

Hu et al. [34] have used gliadin colloidal particles (GCPs) for the first time in stabilization of o/w Pickering emulsions. GCPs were fabricated through anti-solvent precipitation. The prepared emulsions were sensitive at high acidic pH (3.0), but emulsions produced at pH 4.0–9.0 were stable against coalescence for a storage period of 4 weeks. However, Fu et al. [163] have reported that emulsions stabilized by wheat gluten particles showed phase separation at higher pH (≥ 5.0). The addition of gums to emulsions stabilized by gluten has been reported to improve stability against pH; [164, 165] found that the addition of Arabic gum with gluten particles can improve the stability of emulsions at higher pH (≥ 5.0).

Wang et al. [166] has prepared o/w Pickering emulsions stabilized by wheat gluten nanoparticles. Wheat gluten nanoparticles were fabricated by adjusting the pH. It was found that an increase in particle concentration resulted in reducing the emulsions droplet size. The increase in oil phase volume progressively increased the droplet size. This was because increasing the oil phase volume resulted in densely packed droplets. The similar result has been reported by [167, 168]. However, Yuan et al. [169] have reported that the increase in oil phase resulted in a decrease in droplet size. Wang et al. [166] further reported that the prepared emulsions showed long-term storage stability. There was no change in the visual appearance of emulsions after a storage period of 4 weeks at 37 °C. Emulsions showed excellent thermal stability after exposure to 100 °C for 30 min. Emulsions were stable in the pH range of 4–9 but creaming was observed at pH (3.0) Similar results have been reported in previous studies by [34, 164, 170]. Other authors [152, 171–173] have successfully used gluten and gliadin particles for

stabilization of Pickering emulsions for different application, delivery systems of nutraceuticals, and as oil absorbents.

Dairy industry

The dairy industry is an important sector of the global food business. Whey is a common by-product that received industrial interest because it contains significant amounts of bioactive compounds [174]. Whey proteins have been known to exert a positive impact on individual well-being by improving body functions [175, 176]. Milk proteins have been used in the food industry because of their general safety, biocompatibility, biodegradability, nutritional value, and consumer acceptance [9, 177]. Different studies on PPs prepared from by-products of the dairy industry are presented in Table 3.

Whey protein and its fractions Whey protein is a by-product of the cheese industry. Whey is one of the most used food-grade materials in the preparation of ice cream because of its functionality and nutritional value. Whey contains different bioactive fractions such as α -lactalbumin, β -lactoglobulin, bovine serum albumin, and immunoglobulins. The concentration of these fractions is presented in Table 4 which is in line with Asghar et al. [176]. Whey protein gets denatured in food processing due to its heat-sensitive nature. Whey proteins can be modified by various methods to overcome the issue of denaturation [182].

Table 4 Fractions of whey protein from the cheese industry [176]

Whey fractions	Concentrations (g/100 ml)
α -Lactalbumin	1.3–1.8
β -Lactoglobulin	3–5
Bovine serum albumin	0.2–0.5
IgG, IgA, IgM	0.6–1.0
Lacto peroxidase	0.06
Lactoferrin	0.5–2

Table 3 Pickering particles prepared from by-products of the dairy industry

Pickering Particles	Modification method	Particle concentration % (w/w)	Droplet size of emulsions μm	References
Whey protein isolate	High hydrostatic pressure	0.1–3.0	40–55	[178]
Lactoferrin	–	0.2	60–80	[179]
β -lactoglobulin	–	5–25 mg	11–19	[180]
Whey protein isolates	Thermal cross-linking	10	1–5	[181]
Casein	Covalent interaction	3	220–240	[182]
Casein	Crosslinking	0.25–2.5	120–160	[183]
Casein	Covalent cross linking	3	15–35 nm	[184]

Zhang et al. [182] have prepared o/w emulsions stabilized by whey protein isolate nanofibrils. D-limonene (dL) was added to emulsions as an antioxidant and antibacterial additive. It was found that D-limonene improved the antimicrobial and antioxidant properties of emulsions. The prepared emulsions were stable for a storage period of 14 days. Shimoni et al. [179] have prepared o/w emulsions stabilized by lactoferrin nanoparticles. The physical stability to creaming and particle size of prepared emulsions were evaluated. It was found that the prepared emulsions were stable against creaming. Some researchers [178, 180, 181] have found that the pH, ionic strength, particle concentration, and oil fraction are factors that influence the emulsions stabilized by whey proteins.

Gao et al. [180] have prepared o/w Pickering emulsions stabilized by β -lactoglobulin fibrils. It was found that β -Lactoglobulin fibrils can stabilize o/w emulsions in a wide range of pH (2.0–8.0) and particle concentration (5–20 mg/ml). Although, the emulsion prepared at isoelectric pH (5.0) exhibited creaming. The prepared emulsions were stable against coalescence for a storage period of 60 days. Lv et al. [178] have prepared o/w emulsions stabilized by whey protein isolate particles. The droplet's size decreased with the increase in particle concentration and ionic strength. The apparent viscosity increased with the increase in particle concentration, oil fraction, and ionic strength. The prepared emulsions were stable against creaming for a storage period of 14 days. Wu et al. [181] have prepared o/w Pickering emulsions stabilized by whey protein nanoparticles. It was found that stable emulsions can be prepared at a pH above and below the isoelectric point of whey protein and low to moderate ionic strengths (1–10 mM), and with a concentration of 2% (w/v).

Casein Casein is quantitatively and nutritionally the most important protein component of milk, accounting for about 80% of total milk protein. Casein is made up of three different polypeptide chains (α_1 , α_2 , and β). Caseinates are dairy by-products that have been used in many foods [185]. [182–184, 186] have found that particle concentration, pH, and ionic strength influence the emulsions stabilized by casein particles.

Chen and Zhang [183] have prepared o/w Pickering HIPE stabilized by casein particles. The prepared emulsions were stable against coalescence for a storage period of 1 week. The droplets size increased with the increase in ionic strength meanwhile droplets size increased with the decrease in pH. Similar behavior has been described by Sato et al. [187] that the average droplet size increased with the decrease in pH. This is because when pH was dropped towards isoelectric point, the net charge on oil droplets decreased. However, Destribats et al. [188] have reported that the mean droplet size increased with the

increase in pH. This difference of information could be attributed to different modification methods of particles.

Wang et al. [184] have prepared o/w emulsions stabilized by casein gel particles. The casein particles were cross-linked with genipin. The prepared emulsions were stable against flocculation, creaming, and coalescence for a storage period of 1 month. There was no significant variation observed in the droplet size of emulsions during the storage period. Similar results have been reported by Zhang et al. [182]. The droplet size of emulsions stabilized by casein particles decreased with the increase in particle concentration [182–184, 186].

Conclusion

Each year many by-products are generated by the food industry. These by-products have been previously used as fertilizer, animal feed, and in industrial production. By-products contain different bioactive compounds such as polysaccharides, antioxidants, and proteins which make them suitable and valuable materials for the preparation of Pickering particles. In comparison with emulsifiers, Pickering particles are generally safe, biodegradable, and usually not affected by extrinsic factors. Even a partial co-stabilization of emulsions with emulsifiers and the Pickering particles prepared from by-products could be a solution to the rising concern about environmental protection and ecological sustainability. Pickering particles are irreversibly absorbed at the oil–water interface, making a physical barrier that has been reported to provide long-term stability against coalescence and flocculation. Emulsion stability is affected by the concentration of Pickering particles, pH, composition of oil phase, and Ionic strength. Particle size, surface charge, and wettability are key parameters for choosing the ideal particle.

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Declarations

Conflict of interest There is no conflict of interest/competing interest.

Compliance with ethics requirements Not applicable.

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Consent to participate Not applicable.

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