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Stability of Pickering Emulsions with Different Types of Emulsifiers at Different pH Values

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ABSTRACT

Pickering emulsions stabilized by solid particles have potential applications in foods, personal care, and drug delivery. Particle wettability and charge, which depend on pH, are key factors influencing emulsion stability. This scoping review summarizes recent research on the effects of pH on stability of common Pickering emulsifiers. Studies on inorganic particles, polymers, and biopolymers published from 2013-2023 were included. Results indicate pH relative to the emulsifier's isoelectric point impacts stability. Silica nanoparticles showed optimal stability around pH 5 due to increased hydrophobicity and flocculation. Protein-based particles like hordein were more stable at acidic pHs below their isoelectric point. In contrast, nanocellulose Pickering emulsions demonstrated remarkable stability across pH 1-13, attributed to strong van der Waals and hydrogen bonding interactions. Overall, adjusting pH can modify emulsifier surface chemistry to improve Pickering emulsion stability, with exact effects depending on the emulsifier system. Further research directly comparing different particles under standardized conditions is needed. This review summarizes current knowledge on pH effects on emulsion stability for key food-relevant Pickering emulsifiers. The insights could help guide selection of appropriate pH conditions when formulating stable Pickering emulsions.

KEYWORDS

Pickering emulsions; pH values; Stability

1. INTRODUCTION

From the food industry to personal care products, drug delivery and advanced materials, stabilised emulsions offer potential ways to improve product performance and meet the needs of diverse consumers in a sustainable manner. Interfacial layer particles, also known as Pickering emulsifiers, play a decisive role in the stability of Pickering emulsions [1]. Emulsifiers have stabilising and enhancing properties, tuneable properties, and biocompatibility [2]. By summarising the stability performance of several emulsifiers in different pH environments, this review compares the optimum pH of emulsions.

Emulsion usually refers to the unique ability to stabilize an emulsion by adsorbing at the oil-water interface. These particles can be hydrophilic or hydrophobic, depending on the emulsion system and desired properties [2]. When these particles are present at the interface between the oil and water phases, they act as a protective layer, preventing the coalescence of emulsion droplets. The ability to form oil-in-water (O/W) Pickering emulsions or water-in-oil (W/O) Pickering emulsions depends on the wettability of the solid particles at the oil-water interface: if one of the liquids is better at wetting the solid particles than the other, the better wetting liquid becomes the continuous phase, and the other liquid becomes the dispersed phase [3].

Due to its significance for the ionisation of side functional groups carried by the emulsifier, pH is regarded as a critical parameter for determining the complexation of solid particles with emulsions [4]. The isoelectric point of the emulsifier was determined by studying its zeta potential as a function of pH. Typically, the viscosity and shear stress of an emulsifier change with pH. the closer the pH is to the isoelectric point the smaller the charge of the emulsion, the smaller the droplet size, and the more stable it will be.

In the analysis of the factors influencing emulsion stability, it is crucial to differentiate between nanoemulsions and conventional macroemulsions. In contrast to a significant fraction of droplets found in a typical oil-in-water emulsion, which are colloidal or microscopic in nature with sizes of 1 micrometre or greater, the distributed droplets within a nanoemulsion are considerably smaller, with radii reaching up to 100 nanometers.

This distinction carries two implications. In the initial stage, it is seen that the droplets within a nanoemulsion possess a sufficiently small size, enabling them to maintain a relatively uniform distribution due to the influence of Brownian motion, which is characterised by random entropic driving forces. Furthermore, Van der Waals forces between two nanoemulsion droplets are inherently much weaker in comparison to the attractive forces between two droplets on a larger scale. Due to the combination of these characteristics, nanoemulsions exhibit greater stability in comparison to regular emulsions.

The article by Perrier and colleagues examines the pH stability of proteins, polysaccharides, and biopolymers when used as emulsifiers. Their results indicates that Van der Waals forces are not the only reason for droplet size reduction; there are also physicochemical constraints relating to the phase, volume ratio, and emulsifier properties. Protein denaturation or polymer chain size (molecular size). These structural alterations impact the emulsifier's molecular stability, which in turn affects the emulsion's dynamic stability. Furthermore, the extent of structural alterations in hydrocolloids influences the development of systems with diverse physicochemical and organoleptic features .

The effect of generalised pH on emulsion systems has been discovered to be considerable in recent research, and the stability state of the particles in the interfacial layer at different pH values is variable. The following contributing parameters are considered in this review: droplet size, droplet stabilisation time, emulsifier isoelectric point (Zeta potential), emulsifier particle size, and pH. The pattern of emulsions impacted by pH is derived by systematically examining the proved or possible factors of pH on the stability of Pickering emulsions, paving the path for further research. Investigate more modern industrial manufacturing and food processing.

For introductory purposes, the following paragraph introduces several common Pickering emulsions according to the properties of the stable particles:

Inorganic Particles: Pickering emulsions can be stabilised using inorganic substances including metal oxides (such as iron oxide), clays (such as montmorillonite and bentonite), nano-silica particles, titanium dioxide particles, and clays (such as bentonite and montmorillonite). Through adsorption at the oil-water interface and the formation of a shield, these particles offer stability [5].

Polymer particles: Pickering emulsions can be stabilised using polymer particles, such as latex, microgels, and microspheres. These particles can be made of synthetic or natural polymers, such as starch, protein, and derivatives of cellulose [6].

Janus Granules: The grains known as Janus Granules have two distinct surfaces. Without a doubt, the possibility of increased stability of emulsions is inherent in the fascinating characteristics of the particles being examined. The exceptional effectiveness of these materials in this role arises from the intrinsic contrast in their wetting characteristics exhibited on their opposing surfaces, enabling them to efficiently adsorb at the interface that connects oil and water [7].

Delving deeper into this domain, colloidal particles, which include solid nanoparticles and microcolloids, assume significant roles in the process of emulsion stabilisation. The primary function of these entities is to serve as robust physical barriers, successfully preventing the unwanted merging of emulsion droplets. The collection of these colloidal entities encompasses a wide range of materials, including metals, polymers, and ceramics, each playing a unique role in the formation of a strong and protective emulsion layer [8].

Nanocrystals, characterised by their small size and remarkable surface properties, contribute to an additional aspect of emulsion stability. Nanocrystals of metals and semiconductors are especially notable within this category due to their distinct surface properties and complex interaction with oil and water phases, which enable them to effectively enhance emulsions [9].

The attention is redirected onto carbonaceous particles, revealing a specific group of substances that act as stabilisers. These stabilisers originate from the domain of carbon-based materials, including graphene oxide and carbon nanotubes. These carbonaceous materials possess surface features that are naturally suited for successful emulsion stabilisation. They play a crucial role in sustaining emulsions by facilitating unique interfacial interactions [10].

The phenomenon of emulsion stabilisation becomes more complex when mixed particles are introduced, which consist of a combination of several material elements ranging from inorganic to polymer particles. This innovative combination leverages the synergistic effects of diverse elements, resulting in the development of hybrid stabilisers that confer customised emulsion properties and an enhanced perception of overall stability.

In the context of emulsion stability, the interplay of various crucial elements, such as particle size, surface chemistry, concentration dynamics, and the nuanced composition of oil and water phases, significantly influences the distinctive properties of Pickering emulsions. As scholars persist in exploring this complex terrain, they consistently shape and redefine the domain of Pickering emulsions, utilising the unique properties of different particles in accordance with specific contextual requirements.

2. METHOD

PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) is a widely accepted collection of guidelines used in scientific research for performing and reporting systematic reviews and meta-analyses. These recommendations aid in the process of assessing and synthesising existing research literature by ensuring transparency, rigour, and repeatability. This article uses the PRISMA 2020 flow diagram for new systematic review which included searches of database and registers only.

The purpose of writing this article is to summarise the effects of recent pH changes of different substances on the stability of Pickering emulsions in areas related to food, biochemistry and organic chemistry. Therefore, ‘Pickering emulsions’ ‘pH’ ‘stability’ ‘internal’ ‘2013-2023’ are retrieved in a sequential search. The following research areas were excluded from the screening process: ‘Physics’ ‘Agriculture’ ‘Phrmcology Pharmacy’ ’Energy Fuels’ ‘Minerlogy’ ‘Metallurgy Metallurgical Engineering’ ‘Public Environmental Occupatonal Health’ ‘Water Resources’ and etc.. Mainly includued ‘Food Science Technology’ ‘Chemistry’ and ‘Biochemistry’. Finally after manual screening articles: based on emulsifier type, particle size, particle isoelectric point, pH value range, droplet size variations, stability variations.

According to the search results of Figure 1, after the initial screening, 2700 out of the original 3023 articles were excluded for reasons such as: not meeting the target audience of this systematic review, other research areas, published too long ago, etc. The results of this study are summarised in the following table. Some items were eliminated for the reasons stated above, therefore the total number of articles is less than the aggregate total. The remaining 323 articles were evaluated, and an additional 279 were removed for a variety of reasons, including: the kind of literature was conference proceedings and literature reviews, 93 articles did not correctly address the issue, and 8 articles were book chapters with no original research.

Scanning the bibliographies of other periodicals yielded two more papers. Finally, 44 possibly relevant studies were selected after reviewing the entire text of the remaining 57 papers. In terms of study population, 4 other publications were duplicated, and the one with the greatest criteria for examination was chosen. We decided to focus on the 25 most recent papers (published in 2013 or later) after identifying relevant studies by reading the abstracts of the remaining articles and selecting those that were representative of the population (emulsifiers) and clearly stated the relationship between pH and changes in emulsion stability. Table 1 summarises relevant information gathered from these 25 selected research, such as isoelectric point (zeta potential) and pH variation range data.

3. RESEARCH

3.1. Research Questions

To identify the most stable emulsifiers in Pickering emulsions for different pH ranges in the food industry.

3.2. Search Strategy

Databases to be searched: Web of Science

3.2.1. Inclusion Criteria

Studies published in the last 10 years.

Studies conducted on food subjects.

Studies with participants aged 30-80 years.

Study to measure the effect of pH on the stability of emulsifier particles.

Peer-reviewed articles.

Studies available in English.

3.2.2. Exclusion Criteria

Studies on emulsifiers not suitable for the food industry (e.g., Clay Minerals, Solid Lipid Particles).

Studies focusing on temperature, pressure, or ionic concentration.

Reviews, meta-analyses, and opinion articles.

Studies not available in full text.

Studies that do not have a control group.

3.2.3. Search Strategy (for Web of Science):

("Pickering emulsions" OR "emulsifier" OR "pH" OR "stability") AND ("Silica" OR "Polymer" OR " Nanoparticles" OR " Colloidal Particles" OR " Natural ingredients")

3.2.4. Process

Enter the search strategy into database.

Retrieve the list of articles that match the search criteria.

Review the titles and abstracts of the articles to determine their relevance.

Apply the inclusion and exclusion criteria to filter out irrelevant studies.

Review the full texts of the remaining articles to ensure they meet the criteria.

Extract relevant data from the selected articles for analysis.

4. RESULTS

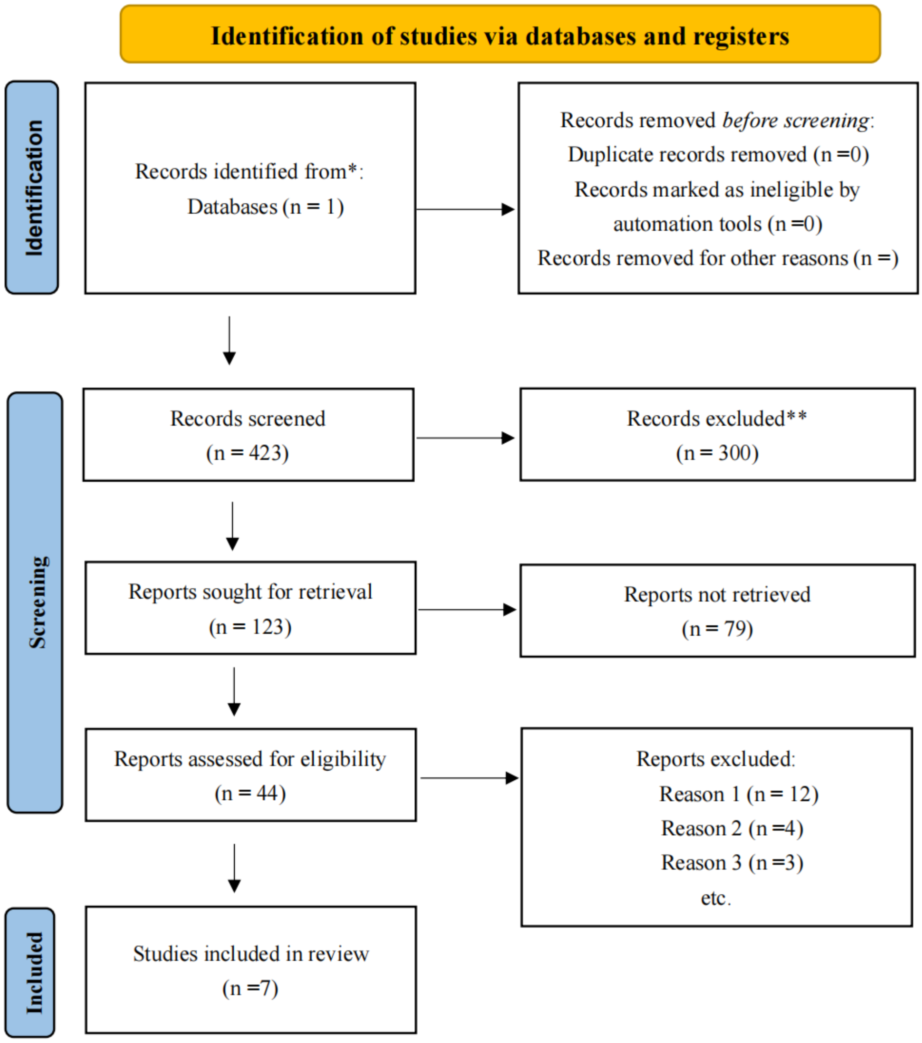

Figure 1. Showing identification and selection of relevant studies for inclusion in review.

4.1. Inorganic Particles

Titanium Dioxide (TiO2) nanoparticles, which typically have dimensions ranging from 30 to 50 nanometers, have received significant attention in several scientific fields within the realm of inorganic chemicals. One notable aspect of their utility is in their capacity as a proficient emulsion stabiliser. The ability of TiO2 nanoparticles to adsorb at the oil-water interface contributes to the notable stability of emulsions. Furthermore, it should be noted that these nanoparticles possess additional characteristics, particularly the ability to provide ultraviolet (UV) protection when integrated into cosmetic compositions. The research undertaken by Demina and Bukreeva [11] is significant as it provides insights into the development of a strong Pickering emulsion by hydrophobizing TiO2 nanoparticles in a solution having a concentration of 2*10^-3 M ODPA. The process of hydrophobization leads to a little reduction in the ζ-potential. Specifically, the ζ-potential was measured to be 35 ± 2 mV before hydrophobization, and 30 ± 4 mV after hydrophobization. The observed persistence of a relatively high ζ-potential after hydrophobization indicates significant suspension stability, which is achieved by the mechanism of electrostatic repulsion.

The systematic examination of the stability of anatase nanoparticles in aqueous solutions throughout a range of pH values (from pH 3 to 12) was a crucial aspect of the research technique, conducted to determine the most favourable conditions for hydrophobization. The findings from these investigations indicate that the addition of TiO2 nanoparticles to both acidic and alkaline water solutions results in a noticeable decrease in pH, with a tendency towards the acidic range, particularly around pH 5.0 ± 0.5. The experimental findings indicate that a pH value of 6.5 can be identified as the isoelectric point for the pure nanoparticles. It is worth mentioning that the hydrophobization process was found to be most effective at a pH of 4.5. This particular pH range is notable because nanoparticles demonstrate a significantly elevated positive ζ-potential. The addition of alkali in the presence of anatase nanoparticles leads to a cessation of pH increase, which can be related to the production of titanium hydroxyl complexes.

Silica Nanoparticles(20nm): According to the research [12] a pH-responsive oil-in-water pickering emulsion was simply prepared using negatively charged nanoparticles of a second silicon oxide and a trace amount of an amphoteric isolated carboxybetaine surfactant as a stabilising agent. The emulsions were aggregation-stabilised at $pH \leq 5$, but completely phase-separated at $pH > 8.5$. They can cycle between stability and destabilisation by alternating the addition of bases and acids. When silicone dioxide particles are exposed to cationic surfactants at low pH levels, the silicone dioxide particles become sufficiently in-situ hydrophobic and flocculated to produce surface activity [13]. The isoelectric point of silicon dioxide nanoparticles is $pI = 6.1$.

4.2. Polymer Particles

The present study proposes a green approach to nanocellulose synthesis and emulsion preparation by utilising enzymatic methods to create nanocellulose (with a size of 41.3nm) for the purpose of stabilising O/W Pickering emulsions. The engineered nanocellulose (ENC) exhibits a diminished zeta potential and a relatively feeble oil/water interface. These characteristics contribute to the facilitation of modest enzymatic reactions and promote the formation of stable Pickering emulsions. In order to examine the emulsification properties of ENC and assess the efficacy of interface adsorption and concentration dependence in ENC-stabilized Pickering emulsions, various techniques including biphasic fluorescent colouring, emulsion polymerization, and rheology were employed. ENC-stabilized Pickering emulsions exhibit remarkable stability across a wide range of pH values due to the strong particle-particle and interface-particle interactions, which are primarily governed by the van der Waals forces and hydrogen bonding [14]. Enzymatic hydrolysis is a process that yields nano-cellulose, a material employed for the purpose of stabilising quench emulsions. The zeta potential and oil/water interface strength of ENC exhibit lower values compared to normal surface-charged nanocellulose. This characteristic proves to be useful in the context of developing stable perylene kleenex emulsions. The oil-water interface can be efficiently modified by ENC to create a compact adsorbent layer. This is primarily attributed to ENC's short axial size and low surface potential, which play a crucial role in regulating the size and morphology of oil droplets inside emulsions. The size and morphology of oil droplets in emulsions can be effectively controlled.

Engineered nanocarriers (ENCs) exhibit robust particle-particle and surface-size properties due to the absence of charged groups on their surface. This absence allows for the maximisation of van der Waals forces and hydrogen bonding interactions. The lack of charged groups present on the surface of encapsulated nanocarriers (ENCs) enhances the formation of van der Waals and hydrogen bonding interactions. These interactions contribute to the establishment of robust connections between particles and between particles and the surrounding surface, hence enhancing the viscoelastic properties of Pickering emulsions.

The low surface potential shown by ENC hinders the formation of a robust electrostatic barrier at the hydrocarbon interface. Consequently, when the concentration of ENC in the continuous phase is elevated, the van der Waals forces and hydrogen bonding come into play, facilitating the additional aggregation of ENC on the oil droplet's surface. This ultimately results in the process of flocculation. The stability of colloidal dispersions is significantly affected by electrolytes, as posited by the DLVO hypothesis [15]. The colloidal surface's charged groups exhibit sensitivity to the electrolytes present in the solution because of the interplay between electrostatic repulsion and the strength of van der Waals forces.

In the context of ENC-stabilized Pickering emulsions, the visual characteristics and structural properties of the oil droplets exhibited minimal alterations across varying pH levels. The emulsification index and the mean diameter of the oil droplets exhibited consistent values of around 85% and 2.7 μm, respectively, throughout the pH range of 1 to 13. The observed outcomes can be ascribed to the predominant influence of intersegmental strength, specifically the van der Waals' force and hydrogen bonding. This intersegmental strength is responsible for the insensitivity of ENC-stabilized Pickering emulsions towards electrolytes.

The self-assembly of alginate-lysozyme nanoparticles (98nm) is facilitated by electrostatic interactions between alginate polysaccharides (Alg), which possess a negative charge, and lysozyme protein (Lyz), which carries a positive charge. This process results in the formation of intricate nanoparticles. The utilisation of Alg-Lyz particles as an emulsifying agent in Pickering emulsions, employing a face-to-face approach through Pickering emulsion technology, exhibits remarkable emulsification efficacy while enhancing the chemical stability of -carotene. The utilisation of Alg-Lyz particles as emulsifiers in a face-to-face Pickering emulsion method has resulted in an enhancement of the chemical stability of β-carotene. The diameter of Alg Lyz particles exhibits a decrease from a pH of 2 to 4, followed by an increase from a pH of 4 to 7. Notably, at a pH of 4, the particles reach their smallest diameter, measuring 96 nm. The observed phenomena can be attributed to the rise in absolute z potential as the pH increases from 2 to 4. This leads to enhanced electrostatic repulsion between Alg-Lyz particles, preventing the formation of larger aggregates. The hydrophilic segments within the Alg chains underwent expansion as a consequence of the dissolution of certain protonated carboxyl groups within the Alg chains, which occurred concurrently with an elevation in pH. This expansion ultimately led to an augmentation in the dimensions of Alg-Lyz nanoparticles. According to Xia et al. [16], there is a notable decrease in particle size as indicated by dynamic light scattering (DLS) when the pH increases from 7 to 11. This decrease can be attributed to the approaching neutralisation of the net positive charge of Lyz, leading to the disappearance of the electrostatic attraction between the polysaccharide and the protein.

4.3. Colloidal Particles

Acid soluble collagen(600-900): Pickering emulsions are those that are stabilised by modest concentrations of surfactants and amphiphilic proteins, which effectively reduce the surface tension of the hydrophobic phase and increase the viscoelasticity of the surface layer. Protein, as an emulsifier, is vulnerable to environmental stresses such as pH, temperature, ionic strength, and so on. Protein-stabilized emulsions are frequently destabilised by flocculation, agglomeration, and phase separation.

According to the research of Zhu and colleagues [17], Pickering emulsion droplet sizes are tiny at pH 2.0, 3.0, 4.0, 5.0, and 6.0, indicating that physicochemical Pickering emulsions are stable at these pH levels. When the pH of a protein-stabilized emulsion is far from the protein pI, the surface of the droplet is charged. The IEP of acid-soluble collagen protein ranges between 7.0 and 8.0. Pickering emulsions made at pH levels lower than 6.0 are positively charged. Gelatin nanoparticles can be uniformly distributed into the nucleus of emulsion droplets in an acidic environment when the pH is lower than the isoelectric point of gelatin (about pH 6.1). In this investigation, as pH was raised from 2 to 6, the drop in net charge resulted in a modest increase in particle size. The oil droplets' electrostatic attraction to one another was lessened at higher pH levels, which encouraged the aggregation and agglomeration of the emulsion droplets and increased droplet size. However, the acid-soluble collagen-stabilized droplet size Pickering emulsion considerably increased, going from 16.8 µm to 74.13 µm, when the pH was raised to 10. Preliminary research indicates that when the ambient pH is higher than 7, acid-soluble collagen proteins are unable to distribute in the aqueous solution and are more likely to precipitate. This could result in a homogenous distribution of collagen protein on the emulsion droplets' surface, which would increase the size of the droplets significantly.

4.4. Natural Constituent Particles

Hordein-based colloidal nanoparticles (400-4000nm): Research is being done on using plant proteins and polysaccharides to replace synthetic surfactants. [18] Alternatives to synthetic surfactants include solid particles manufactured from natural substances. Germanium stabilisation is a stabilising mechanism that solid particles can offer. Pickering emulsions and/or foams are superior to conventional systems in a number of ways, including less stabiliser use, reduced environmental impact, and increased resistance to agglomeration. Additionally, they lack some of the negative impacts of emulsions stabilised by surfactants, such as irritability and unsuitable flavour qualities.

Physical stability eventually deteriorates in a pH-dependent way. In most cases, drainage and decreased physical stability were not noticeable after 1 hour of storage, with the exception of the samples made at pH 6 and 7, where an instability mechanism began immediately after preparation. At pH 3 and 4, as was previously indicated, methionine particles that are soluble in macroalcohol create stable emulsions. The hydrophase separated from these samples after 10 days, but the opacity of the bottom phase was higher than that seen in samples made at pH 6 and 7. This is because the methionite particles are more hydrophilic at an acidic pH than they are at a pH near pI [19].

Food-Grade gelatin(400nm): Animal proteins are also being studied, in addition to plant proteins. The strength of the hydric phase or the particle charge have a significant impact on the adsorption effectiveness of whey protein microgel particles, a novel class of product-grade particles that stabilise Pickering's emulsions. When collagen protein is exposed to acids, alkalis, enzymes, or high temperatures, gelatin is the denaturation result. It is primarily made from the waste materials left behind after processing animal goods, like skin, tendons, and so forth. Theoretically, gelatin is an effective collagenizer. Theoretically, gelatin has good gelling qualities and can be used to create Pickering soft particles [20]. The great hydrophilicity and heat solubility of gelatin make it challenging to produce gelatin nanoparticles, despite the fact that it is inexpensive and widely available, which are needed to stabilise gellan gum emulsions. As a result, there aren't many reports on gelatin nanoparticles and their application to Pickering emulsion stabilisation.

Genipin is an organic compound utilised as a covalent cross-linking agent, derived from the hydrolysis of natural gardenia glycosides by the enzyme β-glucosidase. The compound engages in a chemical reaction with the unbound amino group of proteins, resulting in the creation of a vivid blue pigment that is commonly employed in the production of plant-based dyes. The substance exhibits favourable anti-inflammatory and anti-allergic characteristics. The gold nanoparticles (GNP) exhibited dimensions ranging from 400 to 450 nm and polydispersity index (PDI) values ranging from 0.2 to 0.9 at pH levels between 8 and 11. The Polydispersity Index (PDI) is a measure of the degree of particle dispersion in a solution. A smaller PDI value indicates a more favourable particle dispersion. Hence, it can be inferred that the preparation of GNP at pH levels ranging from 8 to 11 does not result in a homogenous solution. This lack of homogeneity is consistent with the observed poor dispersion, as indicated by the polydispersity index (PDI) value exceeding 0.3. In contrast, the gold nanoparticles (GNPs) exhibited a homogeneous size distribution of around 400 nm and a polydispersity index (PDI) value of approximately 0.285, indicating effective dispersion, when subjected to a pH of 12. Within the pH range of 8-11, the electrostatic repulsion between particles is diminished, while the hydrophobic nature of perillyl alcohol is enhanced. Consequently, this results in the formation of irregular aggregates of gold nanoparticles. Nevertheless, the potent electrostatic repulsion effectively mitigated the influence of hydrophobicity exhibited by perillyl alcohol under alkaline conditions with a pH of 12. As a consequence, this led to the favourable dispersion and uniformity of gold nanoparticles (GNPs) as observed in the study conducted by Feng et al. [21].

Table 1. Summary of trials included in this review

Author/ year	pH/pI	Particles/Size	Stability
Polina Demina/2018	pH3-12/ pI=6.5	TiO2/30-50nm	pH<4.5 stable pH>4.5 gradual decrease in stability
Kaihong Liu/2017	pH3-11/ pI=6.1	Silica nanoparticles/20nm	pH<5 stable pH>5 gradual decrease in stability pH>8.5 Complete Breaking of Emulsion
Ernest M. Hotze/2010	pH1-13/ pI=5	Enzymatic creation of nanocellulose/ 41.3nm	Stable at pH 1-13
Chunmiao Xia/2022	pH2-11/ pI=4	Alginate-lysozyme nanoparticles/ 98nm	pH2-4: stability increase pH4-11: stability decrease rapidly
Qiaomei Zhu/2020	pH3-11/ pI=6.1	Acid soluble collagen/ 600-900 nm	pH<8: Maintaining stability pH>8: stability decrease
Boostani/ 2020	pH3-8/ pI=6.5	Hordein-based colloidal nanoparticles/ 400-4000nm	pH3-4: stable pH4-8: stability decrease
Feng Xin/2019	pH8-12/ pI=12	Food-Grade gelatin/400nm	pH8-11 stability increase pH=12 most stable

5. DISCUSSION

This review summarises the most stable pH of various types of Pickering emulsifiers over a known pH range. In order to prevent droplet aggregation and stabilise the emulsion, one theory for the mechanism of Pickering emulsion stability is that the particles are adsorbed at the oil/water interface and create a particle monolayer or multilayer film. Another argument is that the droplets get caught in the particle arrays when the particles are aggregated in the continuous phase to create a three-dimensional network structure, which lowers the mobility and aggregation rate of the particles. Particle surface wettability, aqueous phase electrolyte, surfactant or solid particle concentration, oil/water phase volume ratio, and initial particle location or shape are the key parameters influencing Pickering emulsion stability. In Pickering emulsion interfacial catalysis (PIC), pH is a simple and efficient triggering mechanism. Environmentally friendly triggers include CO2/N2, temperature, magnetic, and light [22]. pH is now one of the simplest and fastest triggering mechanisms and has so gained special attention. A particle's surface can be changed to adapt to variations in proton concentration, affecting how the material interacts with its surroundings. Such particles are grafted with ionisable groups (carboxyl, amino, or tertiary amine), and emulsions can transition between ‘emulsification’and ‘demulsification’ by adjusting the pH of the aqueous phase, resulting in group dissociation or de-dissociation. The synergistic interaction of commercially available inorganic particles and surfactant molecules is normally fostered by adjusting the pH of the system, which may then be used to generate pH-switching Pickering emulsions. The response mechanism is primarily derived from in situ hydrophobicity, which occurs when inactive hydrophilic particles are charged in aqueous medium and can adsorb the part of the amphiphilic molecules with the opposite charge to theirs; the hydrophilic head group is rooted into the particle surface, and the hydrophobic tail chain is oriented towards the hydrophilic monomolecular layer of water, thereby strengthening the particles' hydrophobicity and surface activity.

Through extensive screening, 7 representative articles were selected. According to Table 1 the emulsifiers studied in these articles include: TiO2, Silica nanoparticles, Enzymatic creation of nanocellulose, Alginate-lysozyme nanoparticles, Acid soluble collagen, Acid soluble collagen, Hordein-based colloidal nanoparticles, Food-Grade gelatin, which can differ greatly because Silica nanoparticles, Enzymatic creation of nanocellulose, and Hordein-based colloidal nanoparticles come from 3 separate categories of emulsifiers and because of the connection between pH and stability. The consequences of these 3 emulsifiers will be discussed in terms of trends, usage scenarios, and applications in this systematic review.

Silica nanoparticles: According to the research, the betaine molecules are positively charged and electrostatically attracted to the negatively charged SiO2 surface when the pH of the emulsion system is below 5. This causes in-situ hydrophobicity to increase the interfacial activity of the particles and stabilise the emulsion. The system's pH is raised above 8.5, which causes the surfactant molecules to change into amphoteric ions and desorb from the surface of the particles (de-hydrophobisation), which causes the emulsion to aggregate and break. The cyclic variations of emulsification and demulsification could be produced by altering the pH value of the aqueous phase. After 4 cycles, some of the electrostatic attraction between carboxybetaine molecules and SiO2 was shielded due to the accumulation of neutral salts inside the system, which weakened the interfacial activity of the emulsifier particles, and the stability of the emulsions deteriorated.

According to another article by the author [18], as a stabiliser, an amorphous hydrophobic SiO2 powder produced by treating hydrophilic SiO2 with dimethyldichlorosilane with a surface area of 300 m2·g-1 was utilised, and the particles were selectively dispersed in toluene before being added to the aqueous phase to generate a water/toluene emulsion. After increasing the pH of the aqueous phase, the uncharged SiOH groups dissolved into negatively charged SiO-, resulting in increased particle hydrophilicity, and therefore the particles were preferentially dispersed in the aqueous phase and formed a toluene/water emulsion.

Dyab created a toluene/water emulsion utilising hydrophobic SiO2 particles as a stabiliser, and then evaluated the effect of pH on the emulsion system's stability. The initial pH of the emulsion was 6.4, and quick pH modification of the emulsion system with HCl and NaOH aqueous solutions resulted in varying degrees of droplet aggregation. The emulsion's stability was optimum when the pH of the system was between 3 and 5; when the pH of the system was 3.5, the emulsion's stability worsened, and SiO2 flocculated and discharged a turbid water layer [23]. Dyab thought that adjusting the pH value in this system may not only influence particle wettability and hence trigger emulsion destabilisation, but also control the degree of flocculation of the particles.

All three articles point out: At pH=5, silica nanoparticles were the most stable emulsions, and it was discovered that the emulsifier alters the stability of Pickering emulsions by influencing particle wetting and flocculation.

Hordein-based colloidal nanoparticles: Changes in pH can have an effect on the efficiency of protein-based particles in germanium stabilisation by altering their surface charge. Egg white is positively charged when the pH is below its point of isoelectricity (pI), and negatively charged when the pH is above its point of isoelectricity (pI) [24]. Particle aggregation caused by charge shielding lowers the emulsifying characteristics of methionine particles. The basic parameters influencing the droplet size distribution in Pickering emulsions, and thus the texture, appearance of shelf-life emulsion formulations, and flavour release, are methionine particle concentration (i.e., concentration of methionine in the aggregated state) and volume fraction of the dispersed phase (Φ). The primary goal of this study was to evaluate the effects of pH and isolation strength on the properties of macroalcohol-soluble protein nanoparticles synthesised by the anti-solvent approach, as well as their final ability to stabilise Pickering emulsions [25].

According to Boostani’s research, Hordein-based colloidal nanoparticles is stable at pH 3-4, with a gradual decrease in stability at pH 5-8. Adsorption to the water-water and oil-water interfaces is caused by the amphiphilic character of this particles [26]. The contact of oil and water. The development of insoluble macroaggregates that encourage foam break-up is responsible for the minimal swelling at pH values near to pI. As ionic concentration increases, the swelling and strength stability of the corresponding Pickering emulsion diminish. As the hydrophilic coating surrounding the bubbles degrades (due to decreased electrostatic repulsion), the resulting rise in ionic concentration reduces the quantity of overflow, resulting in fast agglomeration. By placing more particles at the interface and hence lowering droplet bridging due to particle sharing, increasing particle concentration at the same Φ increases emulsion stability. If a predetermined amount of air is introduced to the emulsion using the right churning technique, raising the fat content of vegetable emulsions to a particular level can enhance the churning power.

According the research [28], for germanium-soluble egg white nanoparticles, similar aggregation behaviour has been seen at pH levels around pI=6.5. The level of aggregation reduces at pH 8. Because the pH of macroalcohol soluble proteins [28] is considerably higher at pH 8, the electrostatic power of repulsion (or absolute value of zeta potential) at pH 8 is significantly larger than that at pH 6 and 7.

Enzymatic creation of nanocellulose: according to the research of Hotze et al. [15], under a range of temperature, pH, and sodium chloride concentration (ionic concentration) conditions, ENC-stabilized Pickering emulsions demonstrate good stability.

The electrostatic interactions of particulate emulsifiers and their adsorption to the oil/water interface are heavily influenced by their surface charge. Although adsorption at the oil/water interface is normally strong for charged micro/nano particles when conditions are sufficiently partially wetted, adsorption is hampered by electrostatic repulsion between these particles. This act of repulsion balances out the inherent energy of particle adsorption at the interface, bringing the entire equilibrium to thermal equivalency and drastically influencing Pickering emulsion stability. However, by altering the ambient pH and ionic strength to lessen electrostatic repulsion between the particle emulsifiers, great stability and oil phase strength can be attained. However, full emulsification of the oil phase and high stability of the Pickering emulsion can be accomplished by altering the pH and ionic strength of the surrounding environment as well as the electrostatic repulsion between the particulate emulsifiers. as well as complete emulsification of the oil phase.

Surprisingly, Pickering emulsions with ENC as stabiliser are very insensitive to changes in pH. As the concentration of ENC rises, greater van der Waals strength and hydrogen bonding interactions produce a continuous grid in the 4-70°C temperature range, which enables the uniform capture of the oil droplets. It is important to note that the grid structure of ENC-stabilized Pickering emulsions is mostly ascribed to strong particle-particle and interface-particle interactions with a preference for proximity strength, as opposed to the tangled grid directly generated by CNF (cellulose nanofibres).

In order to create a stable grid, ENC offers better control over the size, shape, and surface characteristics of oil droplets than CNF. Streptomyces chrysosporium cellulase's cleavage of the -1,4-glycosidic bond makes nanocellulose an excellent option for use in product-grade emulsions because it makes cellulose breakdown to the nanocellulose level easier while maximising the amphiphilic qualities of nanocellulose. It is an ideal candidate for use as a product-grade emulsifier because Streptomyces chloroticus cellulase's cleavage of the β-1,4-glycosidic bond makes it easier to break down cellulose to the nanocellulose level while maximising the amphiphilic nature of nanocellulose. It also significantly reduces the sensitivity of ENC to electrolytes when used as an emulsifier.

The cellulose suspensions are generally reduced by electrostatic repulsion of the charged groups on nanocellulose's surface. Although van der Waals and hydrogen bonding are the predominant particle-particle interactions due to ENC's low surface potential, this results in stable germanium emulsions with outstanding viscoelasticity.

Although van der Waals and hydrogen bonding are the main particle-particle interactions due to ENC's low surface potential, pickering emulsions stabilised with ENC have good viscoelasticity. Additionally, Pickering emulsions have significantly higher viscosities than ENC suspensions, indicating that in addition to strong particle-particle interactions, ENC-stabilized Pickering emulsions also contain strong interface-particle interactions that are influenced by the interface assembly behaviours that control ENC [29].

Discussion of the three different types of emulsifiers revealed that there are a number of ways in which pH affects the stability of Pickering emulsions, most of which are achieved by adjusting the pH to pI, or by reducing the emulsion's sensitivity to pH to bring the emulsion to its most stable state.There is insufficient research covered in this review. Temperature, emulsifier content, ionic concentration, and other particle properties must be taken into account. The effect of ionic concentration, for example, on the stability of protein-based emulsifiers is substantial, and additional comparison trials are required to achieve results that are more reliable.

6. CONCLUSION

This systematic review analyzed recent studies on the effects of pH on the stability of various Pickering emulsifiers, including inorganic particles like silica, polymer particles like nanocellulose, and natural constituent particles like proteins. The results indicate pH impacts emulsion stability through several mechanisms.

For inorganic particles like silica nanoparticles, stability was optimal around pH 5, close to the isoelectric point. At this pH, silica nanoparticles become more hydrophobic which increases their interfacial activity and ability to stabilize emulsions. Below pH 5, the strong repulsion between negatively charged particles hinders their adsorption to the oil-water interface. Above pH 5, increased hydrophilicity causes detachment from interfaces, leading to instability.

Protein-based particles like hordein showed higher stability in acidic conditions below their isoelectric point. At low pH, the positive charge enhances electrostatic repulsion between particles, preventing aggregation. Near the isoelectric point flocculation occurs, reducing stability. However, other factors like ionic strength also impact protein particle stability and need further study.

In contrast, Pickering emulsions stabilized by nanocellulose demonstrated remarkable stability across a wide pH range from 1-13. This pH insensitivity is attributed to the strong van der Waals and hydrogen bonding interactions between nanocellulose particles, forming a continuous 3D network that traps oil droplets. Electrostatic repulsion effects seem less important for nanocellulose compared to other charged particles.

Overall, adjusting pH relative to an emulsifier's isoelectric point and reducing sensitivity to pH changes through mechanisms like hydrogen bonding can improve emulsion stability. However, the effects are complex and depend on other factors like particle concentration, oil phase volume, and ionic strength that require more systematic research. Directly comparing different emulsifier types under standardized conditions is needed.

This systematic review summarizes current knowledge on how pH impacts stability of Pickering emulsions stabilized by key food-relevant emulsifiers. The insights could help guide rational design of stable Pickering emulsions by selecting appropriate pH conditions and emulsifiers. Further work should focus on elucidating stability mechanisms, expanding the range of well-characterized particles, and developing standardized methods to systematically evaluate factors influencing emulsion stability.

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