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# The Formation, Stabilization and Separation of Oil–Water Emulsions: A Review

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**Abstract:** Oil–water emulsions are widely generated in industries, which may facilitate some processes (e.g., transportation of heavy oil, storage of milk, synthesis of chemicals or materials, etc.) or lead to serious upgrading or environmental issues (e.g., pipeline plugging, corrosions to equipment, water pollution, soil pollution, etc.). Herein, the sources, classification, formation, stabilization, and separation of oil–water emulsions are systematically summarized. The roles of different interfacially active materials–especially the fine particles–in stabilizing the emulsions have been discussed. The advanced development of micro force measurement technologies for oil–water emulsion investigation has also been presented. To provide insights for future industrial application, the separation of oil–water emulsions by different methods are summarized, as well as the introduction of some industrial equipment and advanced combined processes. The gaps between some demulsification processes and industrial applications are also touched upon. Finally, the development perspectives of oil–water treatment technology are discussed for the purpose of achieving high-efficiency, energy-saving, and multi-functional treatment. We hope this review could bring forward the challenges and opportunities for future research in the fields of petroleum production, coal production, iron making, and environmental protection, etc.

**Keywords:** oil–water emulsions; emulsification and demulsification; solid-stabilized emulsions; asphaltenes; demulsifiers; oily waste water

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## 1. Introduction

Oil–water emulsions are widely available in food processing [1], pharmacy or clinical production [2], material production [3], the cosmetic field [4], petroleum industry [5], etc. For example, oil–water emulsions could be produced in various processes during oil production, from oil exploitation to petroleum refineries. During the post-production stage, the viscosity of heavy oil (API < 20°) increases sharply, especially in greater depths. Active water flooding, alkali water flooding, polymer flooding, ASP (Alkali-Surfactant-Polymer) flooding, and other technologies are used to ensure regular production and improve crude oil recovery. A large number of chemical additives are used in these flooding technologies, which makes the oil–water emulsions become more stable, and increases the difficulty of oil–water separation. These oil–water emulsions could cause some major corrosion or clogging problems on the pipeline and equipment in downstream plants, which leads to many safety issues [6].

Waste oil–water emulsions are also one of the components of kitchen waste. In China, food waste accounts for 30~50% of household waste [7]. These waste emulsions contain abundant heavy metal ions and pathogenic bacteria [8], which can result in a variety of hazards if not handled properly [9]. However, they will have great recycling value after appropriate disposal due to their high oil content [10]. Additionally, a large number of wastewaters are generated in the coal chemical industry [11]. Phenol, ammonia, nitrogen-containing heterocyclic substrates (NHC), cyanide, polycyclic aromatic hydrocarbons (PAHs), and long-chain hydrocarbons are commonly present in wastewater [12]. In the case of gasification wastewater, for example, the gasification of coal under pressure uses a relatively low gasification temperature and high concentrations of pollutants in wastewater. It has a complex composition, and the chemical oxygen demand (COD) is commonly between 3000 mg/L and 5000 mg/L (up to 6000 mg/L) [13]. Due to the misdistribution of oil reservoirs and consumer sites, half of the world's annual output of oil is transported by tanker to users, which threatens 71% of the oceans with oil pollution [14]. Statistically, at least 5~10 million tons of oil are discharged into water worldwide every year. The annual discharge of oil field wastewater in China exceeds 50 million tons, while the annual discharge of oil processing wastewater in the European Union countries and the Middle East reaches 2 billion tons [15,16]. In China, the maximum permissible discharge concentration of oily wastewater is 10 mg/L. In particular, a series of unexpected events, such as the collision of oil wheels and the leakage of offshore oil fields, has caused incalculable losses to human society. Annual offshore oil spills represent approximately 0.5% of total global oil production. Oil pollution from maritime transport reaches two million tons, of which about 1/3 is caused by oil tanker wrecks. There are more than 500 offshore oil spillage accidents every year, leading to the oil content of seawater in coastal areas being six times higher than that of the national water quality standard [17]. Therefore, how to demulsify oil–water emulsions is an undertaking that is still very relevant to producing oil and protecting the environment.

Chemical surfactants are commonly referred to as amphiphilic molecules comprising hydrophilic and hydrophobic groups. These amphiphilic molecules tend to adsorb at the water/oil interface, with the hydrophilic groups submerged in water and the hydrophobic groups toward the oil, which effectively reduces the interfacial tension [18]. In many cases, the combination of theory and experiment enables a much better investigation of the factors influencing the stability of emulsions. Abbasi A et al. [19] applied the theoretical interaction energy (XDLVO) to calculate the differential interaction energy between droplets of acid solutions in a crude oil emulsion. They found that the most important interaction energy for acids formed in crude oil emulsion is acid–base and the influence of Lifshitz van der Waals, which experimentally proved that 28 wt% HCl solutions formed an extremely stable emulsion with crude oil. Jia et al. [20] applied to a water/surfactant/oil system using MD simulations for determining the behavior of the anionic surfactant sodium dodecyl sulfate (SDS) in both light and heavy oils. Due to the low Gibbs free energy, SDS molecules tend to enter heavy oils, but interestingly, the molecules move significantly stronger in light oils than in heavy oils. Moreover, SDS-water-asphaltic ternary structures can be fabricated in the heavy oil system through hydrogen bonds.

Several review articles on demulsification have been published to clarify the issues and advances in oil–water emulsions [21–24]. Jamaly S. et al. [21] focus on a variety of treatment methods to minimize or avoid the adverse effects of oily wastewater. Recently, Ma et al. [22] reviewed the stabilization mechanisms of heavy oil–water emulsions, especially the significant influence of interfacially active substances (e.g., bitumen, resins, naphthenic acids, etc.) on oil–water interfacial properties. Yongeup et al. [23] reviewed the recent factors contributing to emulsion formation and stabilization in oil fields, as well as the types of emulsions, and also studied multiple demulsification techniques. Idowu Adeyemi et al. [24] analyzed how the use of ultrasound (US) has evolved as a stand-alone, or in combination with other technologies for enhanced oil recovery (EOR) and dewatering in petroleum emulsions. The potential feasibility of techniques such as US-assisted green demulsification and field studies are evaluated.

In this review, the sources of oil–water emulsions from different areas and their harmfulness to the environment and economy will be discussed. The classification, the stabilization mechanisms of oil–water emulsions, and the processes of emulsification and demulsification will be considered. Particularly, the measurement method and the molecular interactions of oil–water emulsions from the micro- to macro-scale are systematically checked. Finally, the methods and techniques for oil–water emulsions separation will be summarized. The advantages and disadvantages as well as the area of application of each technique will also be discussed to shed light on the future development of the demulsification processes for industrial production.

## 2. Generation of Oil–Water Emulsions in Industry

### *2.1. Classification of Emulsions*

Emulsions can be divided into several categories based on various factors [25]. Three common types of emulsions are available [26]: water-in-oil (W/O) emulsion, oil-in-water (O/W) emulsion, and multiple emulsion. The multiple emulsion is also called complex emulsion. It refers to soft materials composed of dispersed droplets, which are made up of smaller droplets inside. The common double emulsions are oil-in-water-in-oil (O/W/O) emulsions and water-in-oil-in-water (W/O/W) emulsions. The definitive composition of these emulsions is shown in Figure 1 [27].

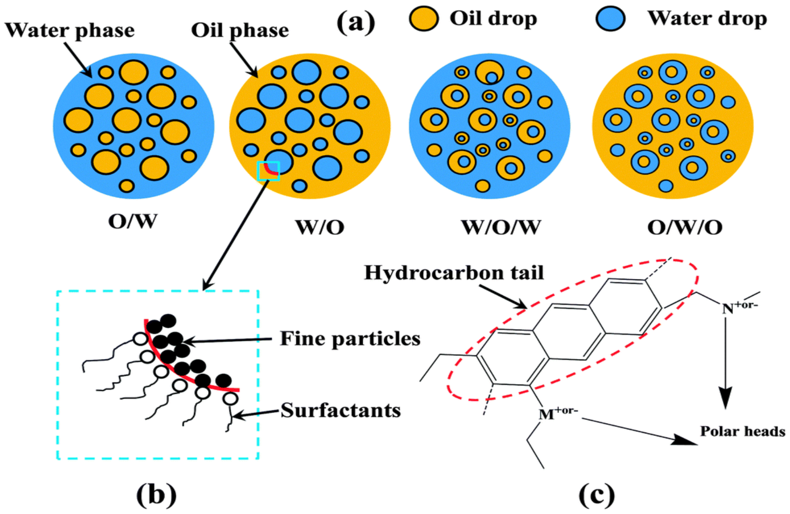


**Figure 1.** Schematic of common types of emulsions and their compositions. (**a**) Emulsions generated in crude oil production and transportation (**b**) Formation of rigid films at the oil–water interface and (**c**) surface activity of asphaltene molecules. Reproduced with permission from He et al., 2015 (ref. [27]). Copyright The Royal Society of Chemistry 2015.

Many researchers have classified emulsions according to their different properties, which is described in Table 1. Winsor [28,29] illustrated the categories of micro-emulsions according to the phase equilibria, which is shown in Table 2. Basically, the macro-emulsion differs from the micro-emulsion in several aspects [30]. Firstly, in the macro-emulsion, the dispersed oil or water droplets contact with each other through an interfacial film (the interface is a different phase), while in the micro-emulsion, the small dispersed droplets cannot come into contact with each other. Secondly, the macro-emulsion is opaque and the micro-emulsion is optically transparent. The differences between macro-emulsion and micro-emulsion are shown in Table 3.

**Table 1.** Various categories of emulsions from different researchers.

| Author | Basis | Categories | Description |
|---|---|---|---|
| Bansbach [26] | The size of droplets in the dispersed phase | Tight emulsion<br>Loose emulsion | Tight emulsions refer to emulsions that contain very small-sized droplets in the dispersed phase and that do not completely separate within a few hours due to their special structure. Loose emulsions, on the other hand, contain relatively large droplets in the dispersed phase, which allows separation within a few minutes. |
| Fingas et al. [31] | The stability, appearance, and rheological measurements | Stable water-in-oil emulsion<br>Meso-stable water-in-oil emulsion<br>Entrained water<br>Unstable water-in-oil emulsion | Emulsions are considered to be in stable and meso-stable states [32]. Asphaltenes and resins trigger off a tough and stable visco-elastic interfacial film. Meso-stable emulsions are those emulsions between stable and unstable states that are not fully stabilized due to insufficient asphaltene contents, resulting in the possibility of degradation. |
| Friberg et al. [33,34] | The size of droplets in the dispersed phase | Macro-emulsion<br>Micro-emulsion | In general, the majority of emulsions are macro-emulsions. The size of the dispersed droplets in macro-emulsions is generally larger than 0.1 μm. Thermodynamically, they are unstable as the oil and water phases tend to coalesce and finally separate over time due to the decrease in interfacial energy.<br>The droplet size in micro-emulsions is generally less than 10 nm. It is formed due to the severe low interfacial energy of two immiscible liquids. The micro-emulsion is considered a thermodynamically stable mixture. |

**Table 2.** Four types of micro-emulsions depend on thermodynamic equilibrium.

| Order | Phase Equilibria | Description |
|---|---|---|
| I | Oil-in-water (O/W) | This type of emulsion contains a water-soluble surfactant, and the surfactant exists in water when forming monomers (Winsor I). |
| II | Water-in-oil (W/O) | This type of emulsion contains an oil-soluble surfactant, and the surfactant-rich oil phase exists at the same time as the water. (Winsor II). |
| III | Three-phase system | It is also called middle-phase micro-emulsion. A middle phase of rich surfactant coexists with superfluous water and oil (Winsor III). |
| IV | Micellar solution | Adding sufficient amounts of surfactant and alcohol can form an isotropic solution of suspended single-phase micelles. |

**Table 3.** Properties comparison between macro-emulsion and micro-emulsion.

| Properties | Macro-Emulsion | Micro-Emulsion |
|---|---|---|
| Transparency | Cloudy | Optically transparent |
| Droplet's size | >0.1 nm | 0.01~0.1 μm |
| Drop shape | Generally, spherical | Spherical |
| Thermodynamic stability | Unstable, stratification after centrifugation | Stable |

P. A. Winsor has categorized the micro-emulsions. The three types of Winsor emulsions are shown and listed in Figure 2 and Table 4 [35].

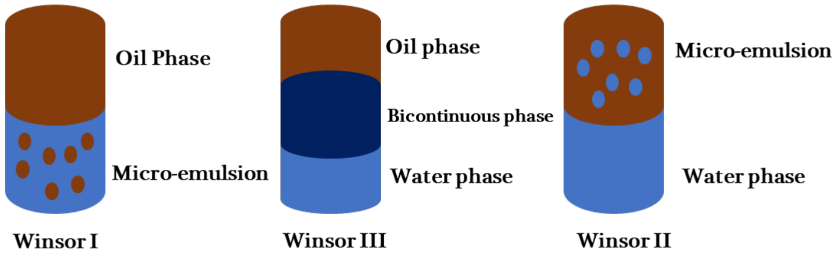


**Figure 2.** Schematic of Winsor I, II, and III micro-emulsion.

**Table 4.** Winsor I, II and III micro-emulsions.

| Type | Diagram | Description |
|---|---|---|
| Winsor I | (a) | The single-phase region is occupied by an O/W micro-emulsion phase, and the two-phase region is occupied by an O/W micro-emulsion in equilibrium with the excess oil phase. |
| Winsor II | (c) | The single-phase region in diagram (c) is occupied by a W/O micro-emulsion, and the two-phase region is occupied by a W/O micro-emulsion in equilibrium with the excess water phase. |
| Winsor III | (b) | In the three-phase region, the micro-emulsion is in equilibrium with the excess water phase and the excess oil phase at the same time, and the three-phase composition does not change with the overall composition (system point). |

## *2.2. Generation and Impacts of Oil–Water Emulsions*

### 2.2.1. Generation of Oil–Water Emulsions in Industry

Oil–water emulsions are generated from many different industrial processes, including petroleum production (exploitation processing, refining, storage, and transportation of oil, oil sludge, etc.) [5], iron and steel smelting (steel rolling water and cooling lubricants, etc.) [3], coal production, food industry, materials manufacturing [1], etc. Table 5 shows the summary of common types of oil–water emulsions in various industries.

**Table 5.** Common types of emulsions in various industries.

| Industrial Fields | Common Types of Emulsions | Description |
|---|---|---|
| Petroleum | W/O, O/W | Further exploitation of the oil field causes the produced fluid to gradually change from W/O to O/W emulsions. |
| Coal chemical | O/W, W/O, sludge | The wastewater is generated from the coal liquification and gasification process, in which the components are resistant to degradation. |
| Metalworking | O/W, W/O | Used hydraulic oil, used lubricating oil, metal cutting fluid, and coolant, etc. |
| Food | O/W, W/O, multilayer emulsions, Pickering emulsion | Various food products, both natural and man-made, exist in part or whole as emulsions, or in the emulsified form at certain times during the manufacturing process, including milk, cream, fruit drinks, infant formula, soups, cake batter, salad dressings, mayonnaise, creamy condiments, desserts, salad cream, ice cream, coffee whitening agents, spreads, butter, and margarine [36,37]. Protein-stabilized Pickering emulsions in the food industry have three main applications including formulation of spread-like products, encapsulation of bioactive components, and protection of lipids [38]. |

**Table 5.** *Cont.*

| Industrial Fields | Common Types of Emulsions | Description |
|---|---|---|
| Cosmetics | O/W, W/O, multilayer emulsions, Pickering emulsion | Cosmetic emulsions are formulated with hydrophilic materials, hydrophobic materials, surfactants, and often additional materials are also added to the formulation to enhance its performance value, improve the sensory, provide fragrance, etc. [39]. With solid particles, Pickering emulsions are widely used in color cosmetics products [40]. |

O/W and W/O emulsions are widespread in the petroleum industry, and O/W emulsions are generally accompanied by oil recovery. Before downstream refining, water is often added to crude oil for desalination, resulting in the formation of W/O emulsions. These emulsions are then demulsified into two phases [41]. There is about 30~50 wt% oil, 10~12 wt% solids, and 30~50 wt% water in these emulsions [42]. The solid particles can improve the stability of the emulsion by adsorbing onto the interfacial film, making the separation of the emulsions much more difficult [43].

In the coal chemical industry, oily wastewater is generated from three sources: coal-gasification wastewater, coking wastewater, and semi-coke production wastewater [44]. Coal-gasification wastewater generally contains tar oil, acid gases ($CO_2$, $H_2S$), acidic substances (phenol, fatty acid, cyanide), alkaline substances (nitrogen, pyridine, amine), heavy metal salts, and other pollutants [45]. Coking wastewater is produced during coking gas purification and the refining of chemical products. It mainly contains phenols, benzene, and other persistent organic matters. The wastewater formed during retort treatment and coal gas purification is semi-coke wastewater. The chemical oxygen demand (COD) in semi-coke wastewater is about 10 times higher than that in coking wastewater.

There are four main sources of wastewater in the metalworking industry, as shown in Table 6. The oil content of steel rolling wastewater is usually between 10 and 2000 mg/L. The raffinate (wastewater) of the solvent extraction process is less than 10 mg/L under normal conditions, and more than 5 g/L under abnormal conditions. The oily wastewater from machine repairing is usually in the form of oil–water emulsions, which consist of 80~90% of water and 10~20% of oil [46].

**Table 6.** Sources of metal processing wastewater.

| Order | Sources |
|---|---|
| 1 | Lubricating oil is generated by lubrication, cooling, transmission, and other systems in the machining process, emulsified oil for cooling and transmission, etc. |
| 2 | Oily wastewater is produced when cleaning machine parts. |
| 3 | Oily wastewater is produced by oil leakage when conducting tractors and other tests, mainly containing diesel oil and gasoline. |
| 4 | Oily wastewater is discharged by rinsing the floor, tanks, and other equipment in the workshop, which is the main source of oily wastewater from mechanical processing. |

In the process of oil and gas refining industries, the fluid produced from oil wells is usually a mixture of hydrocarbon components with various fractions, water, and other organic and inorganic compounds. During this unconventional resource process, natural gas (NG) dissolving in crude oil exists in the form of pure liquid under high pressure (critical pressure: 4.58 MPa). In this process, oil–water emulsions will be formed. The sources and the estimated relative volumes of crude oil and natural gas in the Permian Basin reservoir are shown in Figure 3 [47].

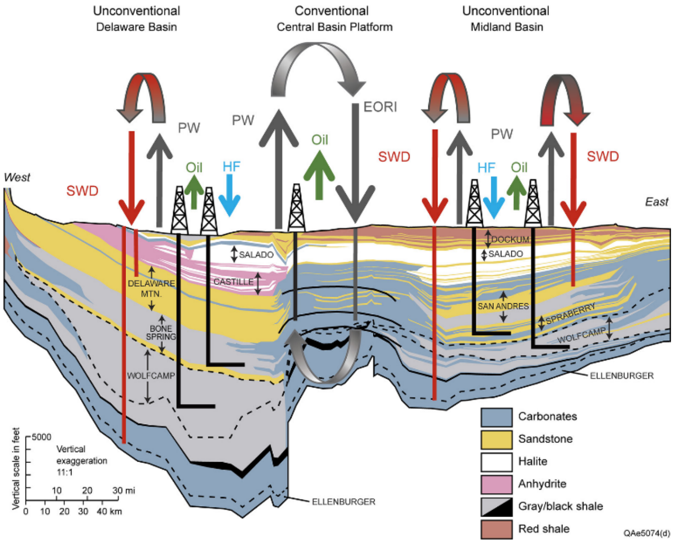


**Figure 3.** East-west cross-section of geological layers for Permian Basin reservoir [47]. Reproduced from Scanlon et al., 2017 (ref. [47]). Copyright 2017 American Chemical Society. (Blue arrows indicate water injection for hydraulic fracturing (HF). These arrows were used to represent the production data and estimate the relative volumes of the produced water.).

To release heavy oil ores, some EOR technologies have been proposed. Applying EOR technologies improves oil yield by 20~40% [48]. However, the process is always accompanied by various problems, such as the formation of strongly stable emulsions and excessive formation of silicate deposits when using high concentrations of alkali [49]. The largest waste streams generated during the extraction of oil and gas occur as the drilling fluids are delivered to the wellhead, where the crude oil is accompanied by produced water or oily wastewater containing a variety of organic and inorganic contaminants. The discharge of this oily water (emulsions) can contaminate both water bodies and soil [50,51]. By adding several chemicals in EOR, such as surfactant-polymer (SP), or ASP, more stable emulsions which are difficult to separate could be formed [52,53].

According to the composition and presence of oil pollutants, the wastewater can be divided into the following five categories, as shown in Table 7.

Water-containing waste oil from the transportation industry and industrial waste oil account for about 55% and 45% of the used lubricating oil, respectively [54]. The oil properties deteriorate with the degradation process, resulting in a large number of acidic compounds, polymers, sludge, etc., prompting factories to discharge the used oil [55]. Industrial waste oil mainly comes from large industrial and mining enterprises, including mines, smelters, non-ferrous metal processing plants, automobile industries, machine processing industries, etc. The waste oil is of hazardous chemicals and must be treated strictly before discharge. The oil change cost mainly consists of the new oil purchase fee, waste oil environmental treatment fee, capacity loss during idle time, and fuel tank cleaning fee, with the waste oil environmental treatment fee responsible for the majority of costs.

### 2.2.2. The Impact of Oil–Water Emulsions

The proper treatment of waste oil–water emulsions has always been an essential issue because of their significant damage and harm to the environment [56]. Statistically, the total amount of oily wastewater in the world reached 10 to 15 billion $m^3$ in 2013, and this figure seems to be increasing significantly in recent years [57]. Chen et al. [58] provided a summary of research on wastewater treatment and emerging pollutants from 1998 to 2021. They found that the number of published papers showed a gradual upward trend year by year, and then reached a peak in 2021 with an annual growth rate of 9.55%. The number of published works can reflect the importance and future development trend of the subject, to some extent.

**Table 7.** Five types of oily wastewater.

| Order | Type | Emulsion Droplet Size | Description |
|---|---|---|---|
| 1 | Floating oil | >100 µm | Also called "oil slick". The oil slick is the present form of most oily wastewater, which, once at rest, quickly floats and can float on the water surface as a continuous oil film. |
| 2 | Dispersed oil | 10~100 µm | The dispersed oil is unstable, which aggregates and forms larger oil droplets that float on the surface. |
| 3 | Emulsified oil | 0.1~10 µm | The surface of emulsified oil is usually covered with a negatively charged bilayer that is relatively stable and hardly floats on the water surface. |
| 4 | Dissolved oil | <0.1 µm | The dissolved oil is dispersed in water as molecules. The uniform system formed by oil and water is very stable and difficult to remove with conventional methods. |
| 5 | Oil–solids mixture | / | The oil adheres to the surface of the small solid particles in water to form an oil–solids mixture. |

Oil–water emulsions from industrial waste have significant impacts on both human health and the environment. Industrial waste emulsions may contain a high concentration of heavy metal elements. Figure 4 shows the generation of heavy metals in the environment [59]. On one hand, heavy metals are harmful to human health. For example, thallium is a cause of alopecia in humans [60]. High exposures to antimony and chromium (i.e., Cr and VI) promote carcinogenicity [61,62]. Lead poisoning could result in intellectual abnormalities in children [63]. Heavy metals are extremely toxic to human organs (kidneys, heart, nerves, skin, etc.); for instance, the Minamata disease is caused by mercury poisoning, and the Itay-Itay disease is caused by excessive exposure to cadmium. Although some naturally occurring vital heavy metals regulate numerous biological activities [64], people still need to properly treat waste oil–water emulsions before they are released, and live in areas that are as far away from heavy metal releases as possible.

On the other hand, heavy metals usually cannot be biodegraded and cause environmental pollution. When untreated wastewater is discharged, most of the heavy metals are absorbed by various organic and inorganic colloids and particles, followed by accumulation and settling at the bottom of the water. Most toxic heavy metals (e.g., lead, thallium, cadmium, arsenic, and antimony) have numerous adverse effects on the environment. For example, mercury is converted to methylmercury in water, resulting in highly toxic sediments [65]. Cadmium pollution in water is useless for plant growth and metabolic processes and occurs through absorption, industrial waste, and surface runoff into sedimentary soils and sediments [66]. A large amount of zinc derived from the mineral processing activities will affect both ecosystems and living organisms [67].

It is estimated that there are roughly 250 million barrels of oilfield-generated water being generated daily as petro-refinery oil–water emulsions, with over 40% of this being dumped into the environment [68]. They contain several toxic substances (identified as potential carcinogens, toxicants, and endocrine disruptors [69]), including benzene, toluene, ethylbenzene, xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs, e.g., phenanthrene, naphthalene, anthracene, etc.), and bentonite, which can harm humans and the environment if discharged without being properly treated [70,71]. Contaminants can have harmful health effects on most organs of mammals. They can lead to skin cancer and affect mental health [72,73]. Bentonite is a major contaminant that can induce genotoxic and cytotoxic harm to lung fibroblasts, and is capable of causing coughs, and eye and skin irritation [74]. BTEX can cause leukemia and tumors. Among all petroleum hydrocarbon pollutants, benzene is the strongest in terms of toxicity. The serious damage it causes includes–but is not limited to–cancer, edema, hemorrhage, and bone marrow damage [75], and xylene can result in hypomnesia, insomnia, and tiredness [76,77]. For example, PAHs reduce oxygen solubility and soil porosity [78]. The presence of long-chain hydrocarbons affects the aqueous environment and results in algal blooms [72]. Water pollution (e.g., red tides or harmful algal blooms (HABs)) is currently occurring around the world, especially after extensive use of chemical dispersants and oil spills; for example, the Bohai Sea Spill (2011) in the Yellow Sea. Phytoplankton species that are harmful to the environment can produce toxins, and their proliferation has negative effects on the environment [79]. An oil spill can cause the death of fish and other aquatic animals, and promote the anaerobic decomposition of organic matter deposited on the bottom, resulting in odor, deterioration of the water, and pollution of the environment [80]. In addition, the coalescence of oil on the water's surface leads to poor penetration of sunlight [81], combustion, or other disasters [82].

**Figure 4.** Graphical representation of heavy metals in the environment [59]. Reproduced from Saikat Mitra et al., 2022 (ref. [59]). Copyright 1969, Elsevier.

## 3. The Stability of Oil–Water Emulsions

### *3.1. The Roles of Emulsifiers*

Emulsifiers are the main reason for the long-term stability of oil–water emulsions. They can form a stable film at the oil–water interface, reducing interfacial tension (IFT) and preventing droplet coalescence. Generally, emulsifiers can be classified into three categories: small molecular emulsifiers, macro molecular emulsifiers, and solids, shown in Figure 5 and Table 8.

### 3.1.1. Small Molecular Emulsifiers

The emulsifiers most commonly found in practice are small molecular surfactants containing hydrophilic and hydrophobic groups. Most hydrophobic groups are alkyl chains. Surfactants can be classified into different types according to the different charges of the hydrophilic groups, including anionic [83–86], cationic [87,88], zwitterionic [89,90] and nonionic surfactant [91]. Usually, a surfactant has a low molecular weight (<1000). It tends to form a monomolecular film at the oil–water interface, which has an oriented arrangement [92,93], as shown in Figure 5a. The adsorption of a single molecular emulsifier could be expressed by Gibbs or Langmuir adsorption theorems [94,95].

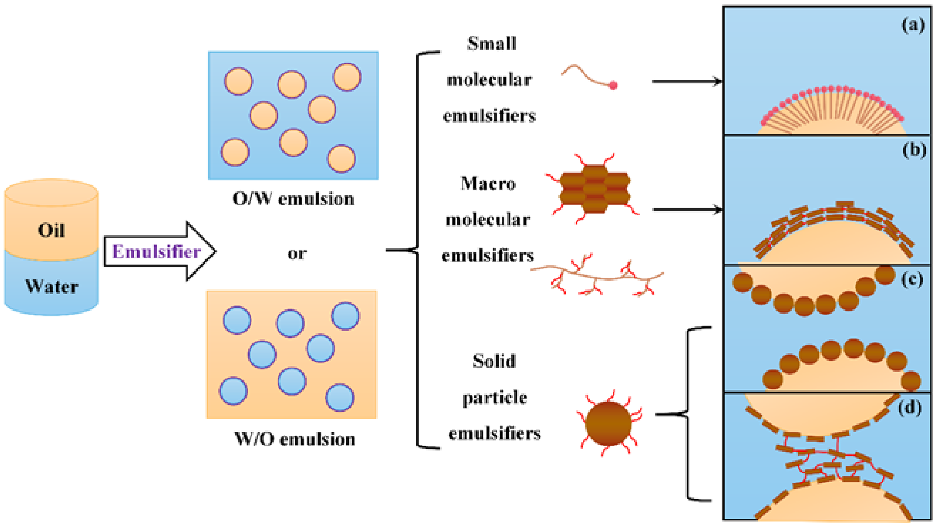


**Figure 5.** The morphologies of the interfacial film are stabilized by different emulsifiers, (**a**) small molecular emulsifiers, (**b**) macro molecular emulsifiers, (**c**) solid particles, (**d**) three-dimensional net structure.

### 3.1.2. Macro Molecular Emulsifiers

The mono-molecule film is the simplest pattern of the aggregation of emulsifiers at the oil–water interface. However, in practice, the interfacial film usually has a more complex morphology. Taking the petroleum industry as an example, the emulsifiers are mainly natural heavy components. Asphaltene is the most typical and most representative component [96,97]. In 2015, Yang et al. [98] reported that a specific sub-component was crucial for the stabilization of the W/O emulsion, which was termed interfacially active asphaltene (IAA). Ma et al. [99] obtained similar results. This phenomenon is directly related to the formation of the strongly stable multi-layered interfacial film, as illustrated in Figure 5b.

The supramolecular film is the association of macro-molecular, and the morphology presents cross-linked multilayers or other supramolecular structures [100]. Asphaltene consists essentially of polycyclic aromatic hydrocarbons, to which multiple side chains containing electronegative heteroatoms (i.e., oxygen, nitrogen, sulfur) are attached [101,102]. Compared to the remaining asphaltene, IAA has a larger molecular weight and more polar groups (i.e., sulfoxide) [98,103]. Polar groups can form a strong positive or negative electrostatic potential. As a result, they facilitate the formation of intermolecular crosslinks through hydrogen bonds. In addition, due to the hydrophilic property of the polar groups, they significantly increase the interfacial activity of the multi-molecular film. The interactions between the multiple layers are Van der Waals forces and $\pi$-$\pi$ stacking [104]. Thus, multi-molecular film possesses high stability and good mechanical properties. Kim et al. [105] proposed that multi-layered film exhibited strong viscoelasticity by the method of mechanical characterizations. Two parameters, including elastic modulus and bulk modulus, are applied to evaluate this film [106]. Multi-layered film effectively prevents floating droplets from coalescing.

Besides IAA, other high molecular weight (>1000) macro-molecular emulsifiers such as resins, biological macromolecules [107–110], polymeric surfactants [111–114], etc., can also form a multilayer film. The polymeric surfactants are classified into the random, block, and graft polymers, as shown in Table 8.

**Table 8.** The typical examples of each kind of emulsifier.

| Large Category | Materials | Example | Systems |
|---|---|---|---|
| Small molecular emulsifier | Simple surfactant | Anionic surfactant: sulfate [83], sulfonate [84], and phosphate [85], carboxylate derivatives [86], etc.<br>Cationic surfactant: mainly ammonium [87,88].<br>Zwitterionic surfactant: anionic ammonium [89], sulfobetaine-type surfactant [90].<br>Nonionic surfactant: mainly oxygen-containing surfactant [91]. | Widely existing in various emulsifying systems, including petroleum, organic synthesis, materials, biological medicine, electrochemistry, food industry, etc. |
| Macro-molecular emulsifiers | Heavy petroleum components | Interfacially active asphaltene [98,103]. | Heavy oil, oil sludge. |
| | Biological macromolecules | Lipid [107], protein [108], polysaccharide [109,110]. | Biological medicine, food industry. |
| | Polymeric surfactants | Random polymer [111,112].<br>Block polymer [113].<br>Branched polymer [114]. | Organic synthesis, materials, biological medicine. |
| Solid particles as an emulsifier | Inorganic solid particles | Silicon dioxide ($SiO_2$), titanium dioxide ($TiO_2$), ferric oxide ($Fe_2O_3$), montmorillonite (MMT), laponite, layered bimetallic hydroxide, etc. | Pharmaceutical industry, oil and gas industry, aerospace industry, etc. |
| | Organic solid particles | Poly (N-isopropylacrylamide) micro-gel particles, polyethylene microspheres, block copolymer micelles, etc. | |
| | Surface modified solid particles | Amine-modified lithium saponite particles [115], etc. | |
| | Janus particles | Polymeric Janus particles (PDVB-PNIPAM) [116], P2VN-PAA/PEO polymeric Janus particles [117], etc. | |

### 3.1.3. Solid Particle Emulsifiers

Pickering emulsion is defined as the emulsion stabilized by solid particles adsorbed at the oil–water interface. The different wettability is derived from the different orientation properties on the crystal planes. The particulate emulsifiers include inorganic solid particles, organic solid particles, surface modified solid particles, and Janus particles. The surface-modified solid particles are produced by physical adsorption, chemical graft polymerization, and other methods [118]. The surface of Janus particles has anisotropy. Pickering emulsions possess a strong designable ability that has been applied in materials [119] and biosynthesis [120]. Besides, due to the mineral paragenesis, the coupled structure of the oil–water–solid system can be regarded as a natural Pickering emulsion. It is widely found in oil sludge [121], causing big problems in separation and purification.

Figure 5c,d show two main factors leading to the high stability of the Pickering emulsion, namely, the solid particle film at the oil–water interface [122] and the formation of a three-dimensional net structure [123]. The theory of solid particle interface film is also known as the mechanical barrier theory. According to this theory, solid particles as emulsifiers are closely arranged on the surface of emulsion droplets, forming a compact film at the oil–water interface. Additionally, Lagaly et al. [123] found that there was a three-dimensional net structure in Pickering emulsions stabilized by bentonite and montmorillonite soil. These barriers enhanced the repulsion effect between droplets and thus improved the stability of the Pickering emulsions.

### 3.2. Interactions between Different Molecules at the Interface: From Macro- to Micro-Scale

Figure 6 shows the different stages in the investigation of emulsion stability. As we all know, the stability of emulsions is determined by interactions between phases.

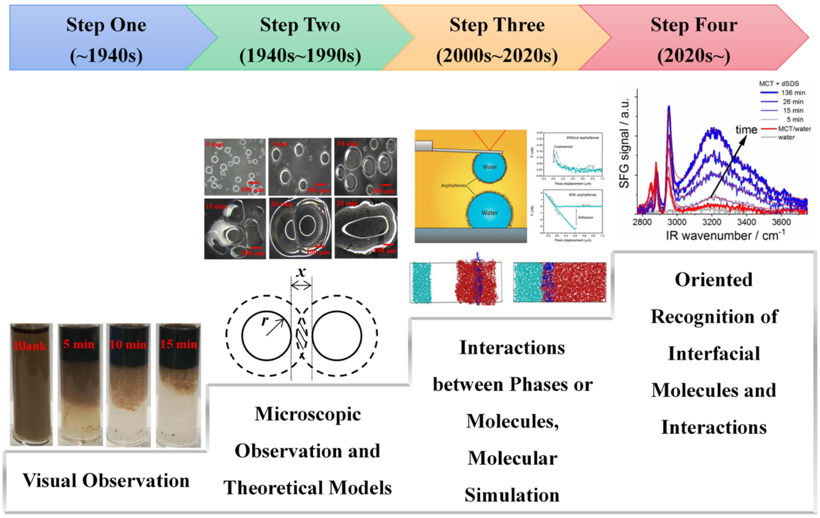


**Figure 6.** The stages in the investigation of the stability of emulsions. Reproduced with permission from (ref. [99,124–126]). Copyrights of 2019 Elsevier B.V., 2021 Elsevier Ltd., 2017 American Chemical Society and 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH, respectively.

#### 3.2.1. Thermodynamics of Colloidal Dispersion Stability: DLVO Theory

The DLVO theory (named after Derjaguin, Landau, Verwey, and Overbek) is one of the most classical interpretations for the quantitative analysis of the thermodynamics of emulsions. In this theory, Van der Waals attraction and electrostatic repulsion are considered to be critical to the stability of suspended colloidal particles, shown in Equation (1) [127], where $V_T$ is the total potential energy between colloidal particles, $V_A$ refers to the potential energy produced by Van der Waals force, and $V_R$ denotes the potential energy produced by electrostatic repulsion. The two types of interactions are collectively referred to as DLVO forces. $V_A$ and $V_R$ are affected by many factors, such as the particle shape, solvent environment, etc.

$$V_T = V_A + V_R \tag{1}$$

This traditional DLVO theory shows good interpretability for simple O/W emulsions since the electrostatic double-layer mainly contributes to the stability of water droplets. However, when applied to other emulsions, the prediction accuracy would be limited. The DLVO theory has been further developed by researchers. For example, Salou [128] adopted the extended DLVO theory, which includes hydrophilic and hydrophobic interactions, and accurately predicted the stability of emulsions formed by bitumen. Vleeschauwer et al. [129] combined DLVO theory with the equation of Ottewill and Walker for the steric repulsion contribution, which has been well used to predict the stability of a mixed phospholipid-non-ionic surfactant stabilized O/W emulsion. Bizmark et al. [130] applied the extended DLVO theory to the calculation of Pickering emulsion that is stabilized by ethyl cellulose nanoparticles. So far, the DLVO theory has been developed in many fields.

#### 3.2.2. Measurements of Interactions between Phases: AFM

The limitation of the DLVO theory is the nature of interactions. The theory was developed as studies dipped to the micro-scale. Petkov et al. [131] confirmed the important effect of non-DLVO forces (i.e., structural, hydration, thermal fluctuations forces) on emulsions by observing the influence of salt concentration on the phenomenon of multiple phases. Atomic force microscopy (AFM) is a very high-resolution technology for the micro-interaction measurement between molecules. The resolution can reach the nanometer level. Although operations aiming at multiphase liquids are difficult, AFM still plays a crucial role in the study of emulsions, which is reflected in the following aspects:

1. Firstly, AFM can quantify the interactions between phases. In 2004, Gunning et al. [132] attached oil droplets to the end of an AFM cantilever, and they monitored the interactions between droplets as a function of inter-droplet separation. In the same year, Dagastine et al. [133] measured the interaction forces between alkane droplets in an aqueous solution. In 2017, Shi et al. [125] applied this method to W/O systems and explored the role of adsorbed asphaltene in interfacial adhesion. These studies provide quantitative insights into the stability of emulsions.
2. Furthermore, AFM improves the theoretical system of colloid science. Liu et al. [134] combined AFM with extended DLVO theory to reveal the stability mechanisms of bitumen droplets. The measured parameters are in excellent agreement with the calculated ones. Wang et al. [135] reviewed the effect of AFM in the theories of deformable droplet interactions, including DLVO forces, non-DLVO forces, and the dynamic film evolution process.
3. Additionally, AFM promotes the rational design of functional emulsions. This is mainly reflected in nano-emulsion in the food industry [136,137], and is better absorbed by the digestive system. Food emulsions can be better understood, predicted, and controlled through the bulk phase interactions, and are better absorbed by the digestive system [36].

### 3.2.3. Visualizing Molecular Interactions: Molecular Dynamics Simulation

Molecular simulation is the technology that examines science at the molecular level in detail, which most instruments cannot realize. The methods include molecular dynamics (MD) [138], quantum mechanics [139], and Monte Carlo [140] simulation, of which MD is the best-studied. The basic idea is to write the inter-molecular interaction potentials into the force field files, and use them to analyze the molecular systems.

The simulation results follow qualitative or quantitative principles. The qualitative analysis focuses on the visualization of the molecular process in the form of simulation snapshots and interfacial molecular orientation [141]. Evaluation parameters are the keys to quantitative analysis and can be divided into two types. Some of the types of the parameters are predictions from macroscopic data (i.e., interfacial tension, interfacial film thickness [142–144]. Other types provide clear recognition of the specific features at the molecular level, and an important function of them is the measurement of molecular interactions. Herein, this section concludes several important micro-parameters in this respect.

1. Radial distribution function (RDF, or $g\,(r)$). RDF describes how density varies as a function of distance from a reference atom, which may reflect the interactions between reference atoms with statistical atoms. This is calculated by Equation (2) [142]. $n_\mathrm{a}(r)$ is the number of particles within a spherical container at distance $r$ from a reference point $b$. $\Delta r$ and $\rho_a$ denote the container thickness and density of atoms in the space, respectively. $g\,(r)$~$r$ functional diagrams are applied for analysis [142,144,145]. Usually, sharp peaks exist in the interval of 0.1~1 nm, which are generated by the interactions between emulsifiers and the bulk phase. The strength is reflected by the peak value of $g\,(r)$, which directly dominates the stability of the emulsion.

$$g_{ab}(r) = \frac{n_\mathrm{a}(r)}{4\pi r^2 \Delta r \rho_a} \tag{2}$$

2. Non-covalent interactions. Non-covalent interactions are general designations of intermolecular interactions other than covalent bonds, including electrostatic interactions (i.e., hydrogen bonds), van der Waals interactions, steric interactions, etc. [36]. The evolving force fields have fitted appropriate molecular potentials that most correctly express them. In addition, several studies discussed the details of non-covalent interac-

tions. Chen et al. studied the wetting mechanism of amphiphilic collagen fibers by MD simulation. It was found that electrostatic interactions and van der Waals interactions are the driving forces of regional wetting in the hydrophilic and hydrophobic regions, respectively [146]. Lv et al. [145] calculated that the hydrogen bonding networks between the carboxyl group and the water molecules stabilized the petroleum emulsion. Ma et al. [124] illustrated the important role of the reconstruction of non-covalent interactions in demulsification by dissipative particle dynamics simulation.

The ideal results are directly related to the accuracy of the models being built, the force field, and the environment. Thus, the difficulty is to target the span-scale analysis of the virtual simulation and the real experiment.

### *3.3. Recent Progress on Molecular Oriented Recognition*

Nowadays, with the development of precise instruments, research on interfacial molecules is not limited to virtual simulation. Traditional optical characterizations (i.e., infrared, Raman spectroscopy) are not limited by interface selectivity. The signals generated by molecules in bulk phases are much stronger than those at the interface, causing great disturbance for characterization. Recently, nonlinear optics facilitate the research at the interface. The interfacial molecules present directional arrangement, and therefore they could be recognized due to special nonlinear optical properties [147]. The most typical spectroscopic technology is Sum-Frequency Generation (SFG) [148] and its derivatives, such as two-dimensional SFG [149], phase-sensitive SFG [126], heterodyne-detected SFG [150], etc. It is difficult to extend the system from a single liquid phase to a liquid–liquid multiphase. Therefore, isotope labeling has often been adopted as an auxiliary method to enhance characteristic peaks to obtain critical parameters. In 2014, Roy et al. studied the one-dimensional [151] and two-dimensional SFG of lipid/water interface and proposed the constraints of hydrogen bonds on interfacial water conformations. In 2021, Pullanchery et al. [152] studied that surfactant increased the ordering degree of the interfacial oil molecules, thus stabilizing the emulsions. They found that strong charge-transfer interactions arose from interfacial C-H···O hydrogen bonds, enhancing the stability of oil droplets in water. Both two types of research adopted the method of phase-sensitive SFG and isotope labeling.

## 4. Separation of Oil–Water Emulsions

### *4.1. Common Processes and Mechanisms of Demulsification*

Emulsions are thermodynamically unstable systems that change slowly. Various phenomena are involved in changing emulsion properties, including sedimentation, creaming, flocculation, Ostwald ripening, coalescence, aggregation, and phase separation. These phenomena can occur together or individually [153]. Flocculation means that droplets in an emulsion collect through attractive interactions to form flocs of droplets [154]. Coalescence occurs when the film ruptures between two droplets, and refers to the combination of droplets [155]. The process of gradual growth from coalesced droplets into large droplets is defined as Ostwald ripening. Table 9 shows the different phenomena during the demulsification process. Figure 7 clearly shows the thermodynamic demulsification phenomenon in nano-emulsions [156].

**Table 9.** Demulsification processes observed in W/O and O/W emulsions.

| Demulsification Process | Definition | Details |
|---|---|---|
| Sedimentation | The difference between water and oil density causes the fall of water droplets due to gravity, and the gravity is greater than buoyancy. | It depends on the difference between oil and water density. |
| Creaming | The separation of emulsions into denser parts (cream) and other parts without actually breaking. | |
| Flocculation | It refers to the agglomeration of suspended droplets in an emulsion, or the formation of floccules, which can accelerate the coagulation of droplets and achieve the purpose of separation. | (a) It is the essential premise of emulsion towards further aging and coalescence.<br>(b) It depends on the surfactant structure and the difference between oil and water density.<br>(c) It occurs frequently in the separation of O/W emulsions. |
| Coalescence | Two or more separate groups pull each other to reach the slightest contact, and the process acts on miscible particles. | The influencing factors of the interfacial film include viscosity, elasticity, and the dynamics of drainage. |
| Aggregation | It corresponds to accumulating the suspended droplets. | It is the most common process, resulting in the instability of colloidal systems. |
| Ostwald ripening | At the later stage of the precipitation phase precipitated by supersaturated solid solution, the size of precipitated phase particles is different. Due to the dissolution of smaller particles, larger particles continue to grow, thus increasing the average size of particles. | It is generally experienced in water/oil emulsions, and other liquid or solid solutions. |
| Phase separation | Oil and water completely separate into two distinct phases. | It relies on time and types of emulsifier. |

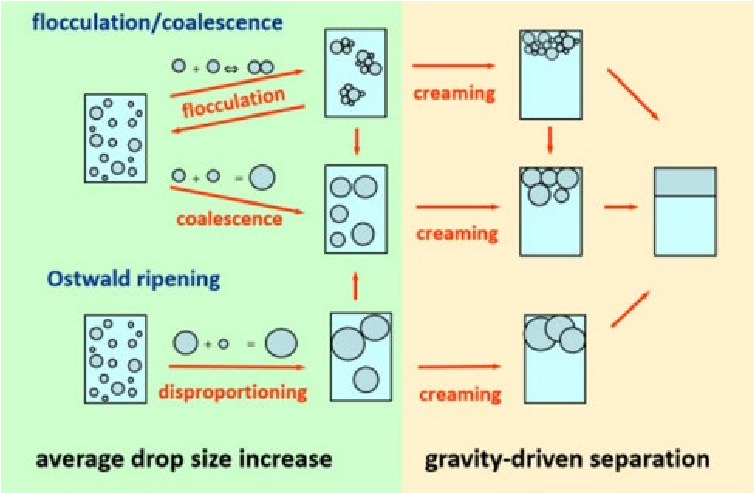


**Figure 7.** Thermodynamic demulsification phenomenon in nano-emulsions [156]. Reproduced with permission of Ravera. F et al., 2021 (ref. [156]). Copyright 2020 Elsevier B.V.

Efficient separation of W/O emulsions can be achieved through four steps [157]: (1) droplets aggregation, (2) interfacial membrane drainage, (3) interfacial membrane rupture, and (4) droplets coalescence and sedimentation [158], as shown in Figure 8.

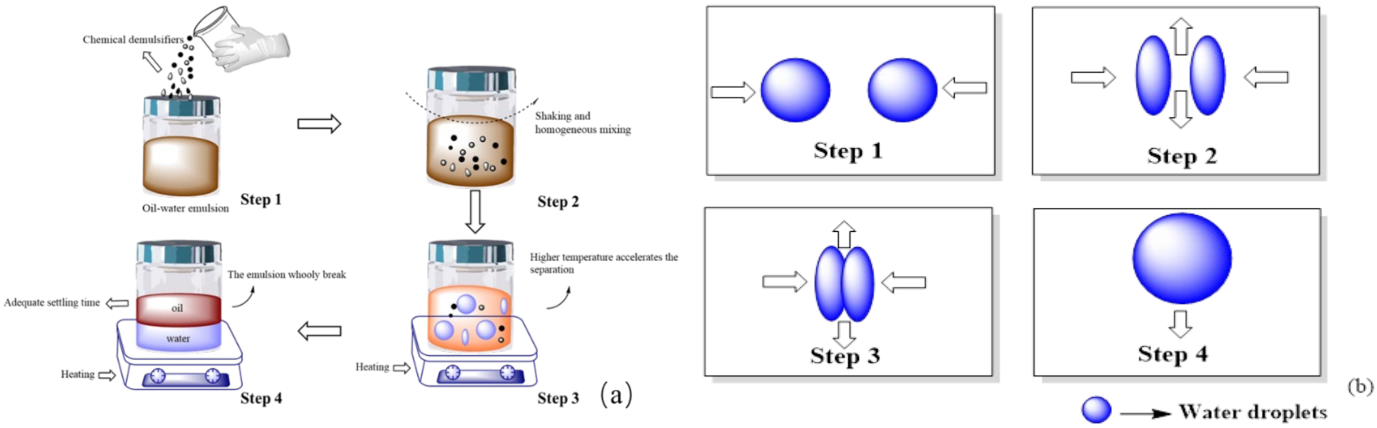


**Figure 8.** The processes of water–oil emulsion separation, (**a**) the four efficient steps to separate oil–water emulsion, and (**b**) the common demulsification process [157,158].

There are many parameters influencing the process of chemical demulsification, changing which can either increase or decrease the emulsion stability. For example, temperature [159–161], salinity [162–165], water and oil content [166–168], etc. Numerous chemical demulsification mechanisms have been reported up to now. However, there is still no universal conclusion that is attributed to the complexity of the destabilization processes involved (diverse knowledge of colloid chemistry, surfactants science, and interface phenomena). The four popular theories of demulsification mechanisms are summarized in Table 10.

**Table 10.** The four common theories of chemical demulsification.

| Order | Theory | Description |
|---|---|---|
| 1 | Replacement or displacement [169,170] | The surfactivity of the demulsifier is higher than that of the natural surfactants in crude oil, thus demulsifier can replace or displace the surfactants at the oil–water interface to disrupt the stability of the interfacial film. |
| 2 | Reverse acting [171] | The demulsifier can change the type of emulsion. Depending on the properties of the demulsifiers, the O/W emulsion and W/O emulsion convert to each other. The oil droplets and water droplets are separated by gravity. |
| 3 | Electrostatic adsorption [172] | The demulsifier having an opposite charge to the interfacial film of the emulsion neutralizes the repulsive force between the interfacial films to demulsify the emulsion. This mechanism is generally applied to ionic demulsifiers. |
| 4 | Dispersion-Solubilization [173] | Some types of demulsifiers have a solubilizing effect. The demulsifier in the emulsion forms micelles and dissolves the surfactants. |
| 5 | Coalescence-Flocculation [174] | The molecular chain of demulsifiers can be adsorbed on the interfacial film of the droplets and form a loose pellet centered on the demulsifier, which increases the contact area between the droplets and the probability of collision. |

Generally, the action mode of demulsifiers is reducing the strength of the interfacial film, aimed at crude oil emulsion. Therefore, it is necessary to reveal the interfacial behaviors of materials at the interface [175]. Figure 9 shows the role of the film drainage process in demulsification. Under gravity force, agitation, and thermal convection, two droplets approach each other, and the thickness of the oil phase film shrinks. Firstly, the concentration of natural surfactant molecules reduces within the film, because they accumulate outside the film due to shear stress. The IFT gradient is developed with low IFT outside the film and high IFT inside the film. Thus, the void left by surfactant in the film provides sites for demulsifiers to be adsorbed. Their adsorption eliminates the produced IFT gradient and improves film drainage. Eventually, the film becomes very thin and the droplets merge due to the proximity of the dispersed droplets [176].

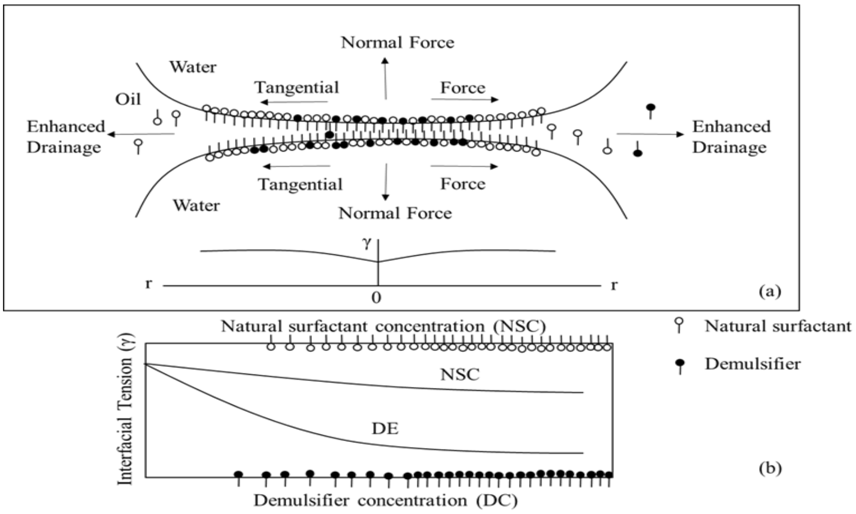


**Figure 9.** (**a**) The film drainage in the presence of demulsifier; (**b**) Influence of concentration of natural surfactant and demulsifier on crude oil and water interfacial tension. Reproduced with permission from A. Bhardwaj et al., 1994 (ref. [176]). Copyright 1994 American Chemical Society.

For O/W emulsions, the demulsification mechanism by ionic demulsifiers has not been explained in detail. One hypothesis is that cationic demulsifiers can demulsify O/W emulsions stabilized by anionic surfactants by neutralizing them with charged heads to form ion pairs [163,177,178]. It has also been reported that cationic surfactants adsorb into the cavity between anionic surfactants and then form ion pairs at the interface itself [179]. The electrostatic repulsive force between the dispersed oil droplets is weakened, allowing the droplets to fuse together, and eventually phase separation occurs.

### *4.2. Technologies for Oil–Water Emulsions Separation*

Oil–water emulsion separation technologies can be classified into four categories: physical method, chemical method, physicochemical method, and biochemical method. The physical method is based on the differences in physical properties such as phase density, conductivity, and sound velocity. The main methods are gravity sinking, centrifugal cyclone, high-voltage electrostatic, high-frequency impulse, microwave irradiation, ultrasonic wave, membrane, in situ extraction, gas flotation [180–187], etc. In chemical demulsification processes, an appropriate dosage of chemical agents (e.g., demulsifiers, polymerization agents) should be added into the oil–water emulsions to break the stable interfacial film and change the emulsification state into a free state, thereby achieving the phase separation of the oil–water emulsion. Physicochemical demulsification processes are a combination of the physical and chemical separation processes. In addition, in biochemical demulsification, biological demulsifiers produced by cell bodies of micro-organisms are used to break emulsions. Each separation method has its own specialty and applicable conditions. Therefore, factors such as oil properties, water content, the intensity of the emulsion, and the dispersibility and stability of the emulsion should be considered comprehensively when selecting the separation methods. Table 11 illustrates the common technologies for separating oil–water emulsions in industry and their advantages and disadvantages.

**Table 11.** Summary of oil–water emulsions separation technologies.

| Treatment | Advantages | Disadvantages |
|---|---|---|
| Centrifugation | High efficiency, lesser operational time. | High cost of maintenance and energy for rotating. |
| Hydrocyclone | High efficiency, compact modules, output for smaller oil particles. | High cost of maintenance and energy, fouling. |
| Bio-demulsification | Better adaptability, strong versatility, non-toxic, eco-friendly, degradable. | High cost. |
| Heating | These techniques are widely used, easy operating and efficient while being used in combination with other methods. | Low efficiency, longer time aimed at O/W emulsion with higher water content, often used in conjunction with other methods. |
| Electric dehydration | | The possibility of short circuiting, will consume lots of energy and increase investment costs. |
| Gravity | | Unsatisfactory demulsification effect, huge equipment demand. |
| Microwave | Fast-speeding, no hysteresis effect. | Low dehydration rate, long settling time. |
| Ultrasonic | No pollution, no emission, low energy consumption, strong universality. | Difficulties in industrial scale-up, high cost of equipment. |
| Magnetic | More suitable for sewage treatment. | Currently in the preliminary stage of research. |
| Membrane | High efficiency, low energy consumption, wide application range. | Low membrane flux, small processing capacity, membrane fouling. |
| In situ extraction | Floating oil can be continuously collected from the water surface. | High cost. |
| Gas flotation | Higher efficiency, fixed parts, robust and durable, easy operation. | Large quantity of skim volume, lateness in separation time, high amount of air generated. |

The chemical demulsification, as introduced in Sections 3 and 4.1, is mainly achieved by adding chemical demulsifiers with strong interfacial activity to the emulsion to achieve the separation. It exerts the merits of excellent demulsification performance, high efficiency, simplicity of equipment, cost-effectiveness, and a wide range of applications. In the physical demulsification method, both sedimentation and centrifugation use the difference in density and immiscibility of oil and water to break the emulsion. In a gravity separator, NaCl can be added to water to increase the density difference between the oil and water phases to improve the floating speed of oil droplets [180]. However, the separation equipment is large and expensive, and the separation efficiency is relatively low. Therefore, it is generally used in conjunction with other separation techniques.

In electric dehydration, it is considered that water in the emulsion is a polar electrolyte, which becomes polarized under the electric field. Under the electric field, the rupture of interfacial film is derived from the collision of polarized droplets. The neighboring droplets are attracted to each other, forming large droplets and promoting oil–water separation [170,179,181].

The ultrasonic method mainly relies on ultrasonic waves, which are elastic mechanical waves with the function of mechanical vibration and thermodynamic interaction. In the process of vibrating the crude oil and water droplets together, the water droplets collide and bond with each other, resulting in an increase in the particle size. Meanwhile, the vibration decreases the strength of the oil–water interfacial film, which is conducive to emulsion breaking. In addition, the thermodynamic interaction of ultrasonic waves can also reduce the viscosity of crude oil. The ultrasonic method can lower the demulsification temperature and reduce energy consumption. However, there is still a lack of large-scale industrialized equipment [182].

The heating method is intended to accelerate the collision and coalescence between droplets. Generally speaking, the heating method is applicable to W/O emulsions with lower water content. Nevertheless, this method has the disadvantages of high production expense, unstable performance, and the process is hardly confined.

The microwave is a type of electromagnetic wave with a frequency of about 300 MHz to 300 GHz, which can generate alternating electric field with frequencies up to hundreds of millions of times per second, and polar molecules under the action of electromagnetic field produce a dipole to polarization resulting in the transformation of internal energy into heat energy, rapidly increasing the system temperature. The microwave method is essentially an indirect heating method, but has the advantages of high speed, uniformity, no temperature gradient, and no hysteresis effect in comparison with the traditional heating method [183].

Gas flotation is used to introduce microbubbles into the water (sometimes it is also necessary to add a flotation agent or coagulant), with which the oil droplets (0.25 to 25 μm) are attached to the bubbles to form aggregates. These aggregates rise to the surface by buoyancy. Finally, oil–water separation is accomplished by scraping off the surface foam. The separation efficiency of the air flotation is determined by the probability of collision between the bubbles and the oil slick. Hence, increasing the specific surface area of bubbles can enhance separation efficiency. Membranes can effectively remove small chemical-free oil droplets (<40 μm) with low energy requirements, low maintenance costs, and low requirements for reliability and space [15,184–186]. However, the major drawback of membrane separation technology is the undesirable deposition of contaminants on the surface of the membrane, which decreases the processing rate and increases energy consumption.

The biological method uses microorganisms to consume surfactants that could break the oil–water interface film. It has the advantages of low concentration, rapid dehydration, high efficiency of dehydration, degradability, and is harmless to the environment. However, the research on the biological method at present is immature and expensive to use. Further research may focus on high efficiency, adaptable, and affordable biological demulsifiers [187].

### *4.3. Oil–Water Emulsions Separation Process*

#### 4.3.1. Combined Demulsification Process

To improve the separation efficiency of the single demulsification method, different methods could be combined in practical applications. Figure 10 illustrates a schematic diagram of the crude oil emulsion separator combining thermal and electrical demulsification methods [188]. The device contains the heating chamber, the degassing chamber, and the electrical chamber. Fire tubes are equipped in the heating chamber and are immersed in emulsion [189]. Heating is favorable for decreasing the viscosity of crude oil emulsion and reducing the resistance of water movement. Demulsification is achieved at around 80–85 °C. Then, the fluids flow into the degassing chamber where the gas escapes. Next, the heated emulsion enters the electrical chamber, where small water droplets could be coalesced under the high-voltage electrical field.

Peng at al. [190] proposed a heat-strengthening double-field (i.e., centrifugation and electrical field) demulsification process to realize efficient demulsification of a waste oil emulsion. As shown in Figure 11, the dewatering-type hydrocyclone which contains high-voltage electrode is applied as a unit body. The W/O emulsion is firstly pumped into the heating tank, where a heating control system is used to rapidly increase the oil temperature. The emulsion quickly flows through the screw pump and enters into the double-field coupling demulsification unit, where the heat-strengthening separation of W/O emulsion is achieved. The separated oil with a small amount of water enters into the overflow tank, while separated water enters into the underflow tank. As the heating temperature raising from 65 to 70 °C, the demulsification efficiency improved by about 6.7%.

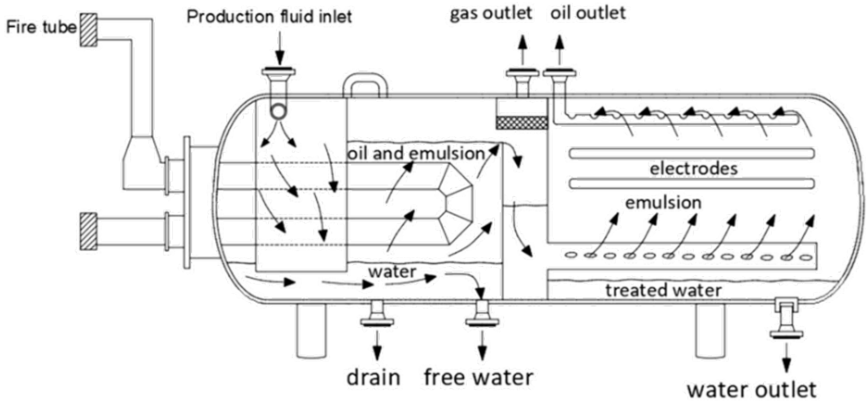


**Figure 10.** Schematic of the flow diagram for electrostatic heater. Reproduced with permission from Choudhary et al., 2017. Creative Commons Attribution 3.0 licence 2017, IOP Publishing Ltd. [188,189].

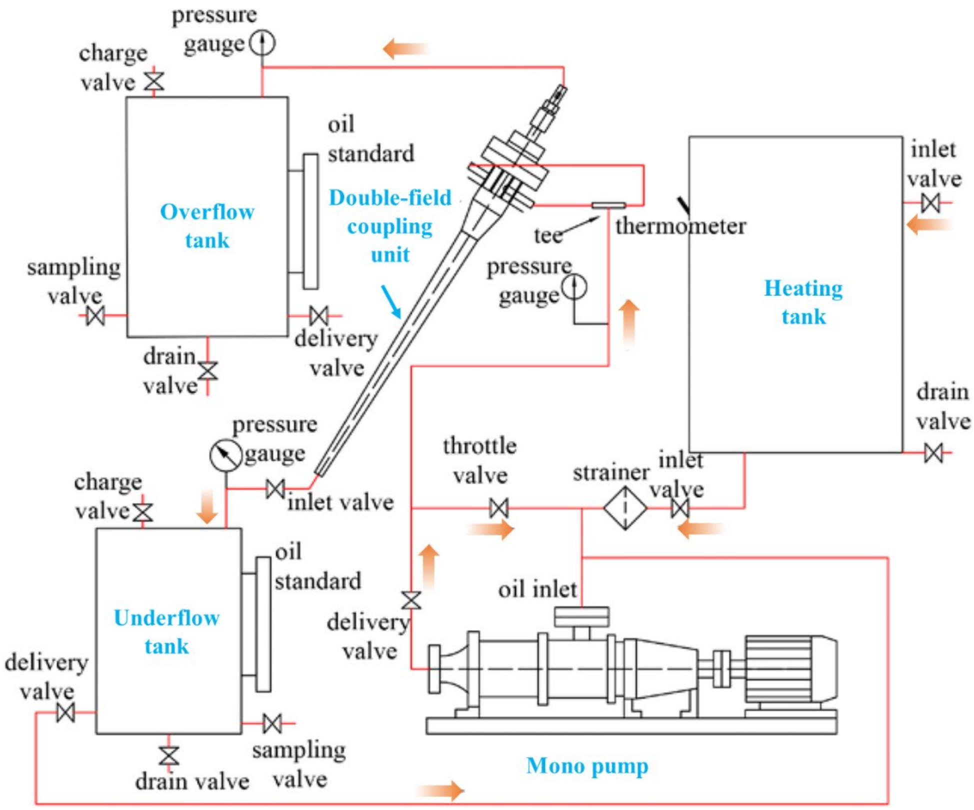


**Figure 11.** Heat-strengthening double-field demulsification process [190]. Reproduced with permission of Peng Y et al., (ref. [190]). Creative Commons Attribution 4.0 International License.

Membrane demulsification is usually combined with other technologies to teat oil–water emulsions [191]. Zhang et al. [192] reported the combination of demulsification as well as reverse osmosis (RO) to treat filature wastewater, which is a type of highly stable O/W emulsion produced by Shen Ma Industrial Co. Ltd. of China. The treatment device is displayed in Figure 12. The filature O/W emulsion was firstly pumped from the underground store tank into the demulsification container. Then, a specific amount of demulsifier was added into the container from the top inlet. Steam was subsequently introduced to the demulsification container from the bottom inlet. The steam was used for heating the emulsion and blending with the demulsifier. When the upper separated oil lifted to the midline of the upper peephole, the steam valve was shut and the inside cooling coil pipe or cooling spray was opened. When the inside temperature was decreased to ambient, the aqueous phase entered into a bag filter and a transfer container, owing to hydraulic pressure. The bag filter was employed to remove suspended solid. The top oil was dis-charged to the follow up section for further treatment or reuse, thus realizing the separation process. The RO system contained a transfer container, a cleaning container, a pre-filter, and a RO equipment. To achieve the designed treatment capacity of 0.1 m$^3$/h, two spirally wound membrane elements were applied. The high-pressure pump equipped with a frequency converter was used to provide steady driving pressure. Condensate water was flowed through to keep the feed temperature below 40 °C, thus preventing the membrane from being damaged. The concentrate was returned to the underground store tank when the recovery rate of water reached 80%. The pilot-scale experiments results show that the removal rate of COD for the waste filature O/W emulsion could reach 99.96% within 30–50 min at 80–90 °C with the dosage of 0.1% (*w/v*), and with a driving pressure of 3.6 MPa at 35–40 °C and a flow rate of 1.5–1.6 m$^3$/h for RO treatment. After treated by this combined process, the water quality of the permeate could meet the first grade discharge standard set in the Chinese National Standards for Integrated Wastewater (GB 8978-1996).

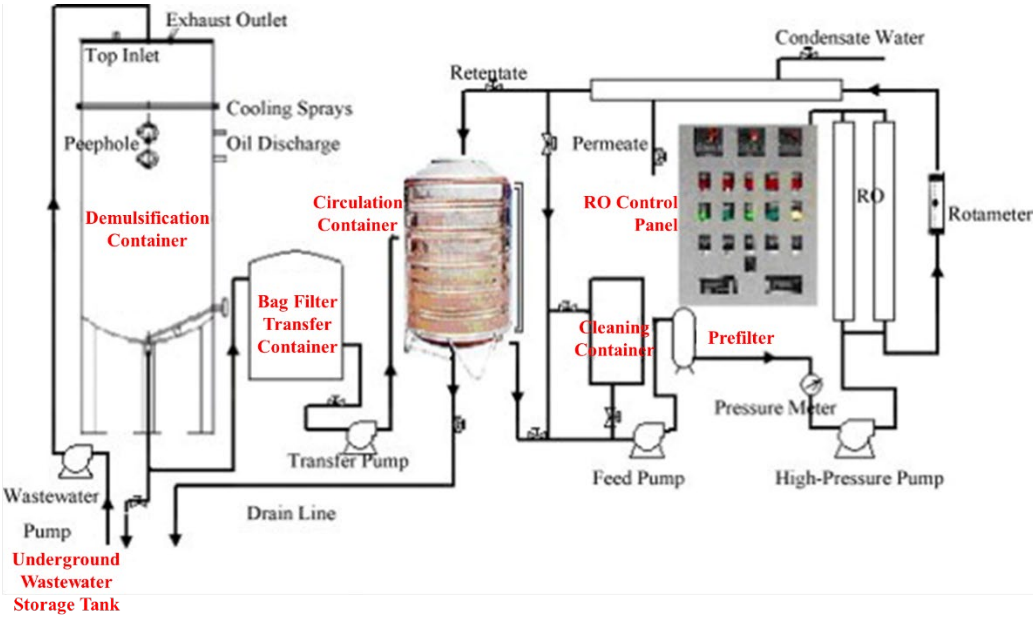


**Figure 12.** Schematic of the pilot-scale demulsification–RO experimental device [192]. Reproduced with permission from H. Zhang et al., 2008 (ref. [192]). Copyright 2008 Elsevier B.V.

Pintarič et al. [193] developed a novel MILP (mixed integer linear programming) model to select optimal demulsification methods with maximum profit. Based on this model, an integrated separation process is reported. As shown in Figure 13, the process consists of chemical pretreatment, mechanical process, evaporation unit, membrane treatment section (re-verse osmosis system), and eventual adsorption treatment by activated carbon. The combination of these methods in sequence presents a flexible design, which could treat various O/W emulsions with COD values as high as 145,000 mg/L. The effluent COD could be reduced to below 120 mg/L. The treated effluent water could be directly discharged into sewage.

Recently, Abidli et al. [194] reported the concept, design, assembly, and testing of a novel pilot-scale skimmer prototype module for oil–water separators. As illustrated in Figure 14, the system is made up of a hydrophilic-hydrophobic porous sorbents-based separation bed and a vacuum-assisted oil collection system. The collection system allows continuous and effective removal of oily contaminants (chemical or oil spills, industrial oily wastewater, etc.) from the water surface. To optimize the separation–recovery process according to the operational needs, the system is designed to provide a suitable oil residence time and flow rate inside the separation column. The prototype is manufactured at the facilities. Operational tests showed remarkable oil–water separation performance during and after the assembly.

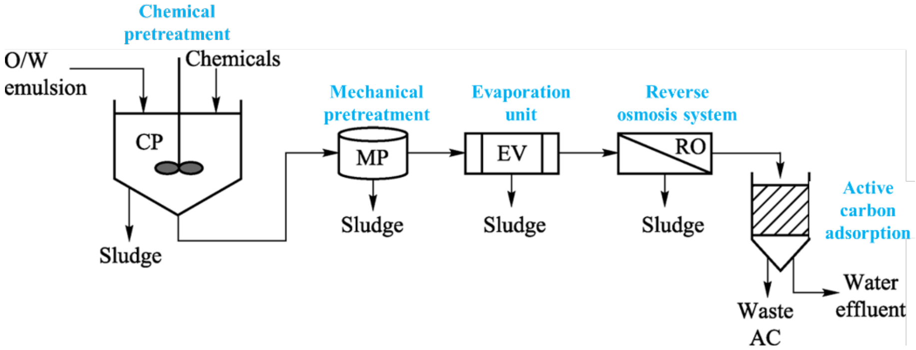


**Figure 13.** Schematic of the integrated process for O/W emulsions treatment [193]. Reproduced with permission from Z.N. Pintarič, et al., 2016 (ref. [193]). Copyright 2016, Higher Education Press and Springer-Verlag Berlin Heidelberg.

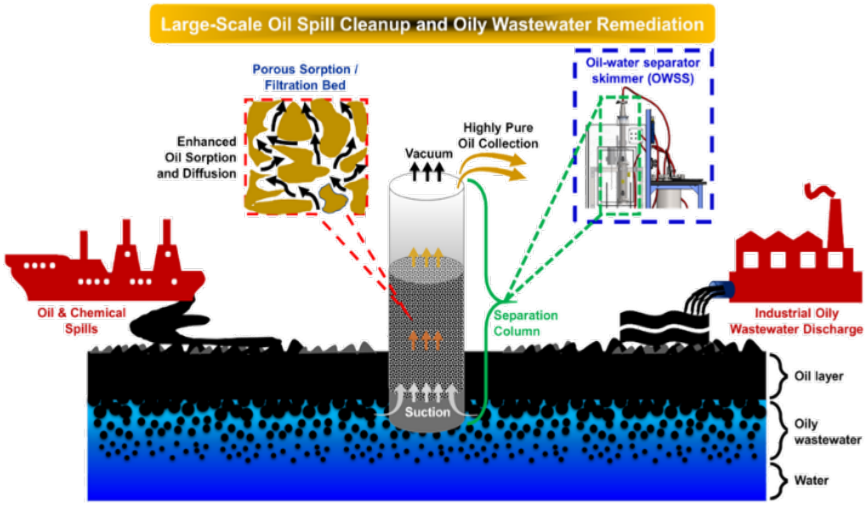
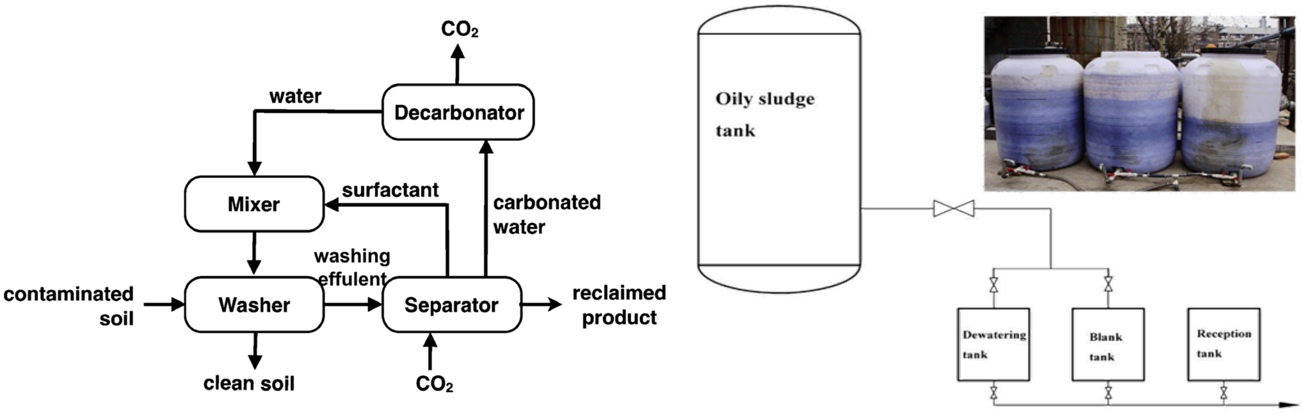


**Figure 14.** Schematic illustration for typical large-scale implementation of the developed oil–water separator skimmer using porous sorbent materials [194]. Reproduced with permission from Abidli et al., 2020 (ref. [194]). Copyright 2020 Elsevier B.V.

### 4.3.2. Demulsification Process in Different Industrial Field

In this section, the oil–water emulsion separation processes that are involved in different industrial fields will be reviewed. Ex situ soil washing is a frequently applied technology in the remediation of contaminated soils. During soil washing, the surfactants are used to liberate the oil from the soil. However, stable O/W emulsions form when surfactants are added. Ceschia et al. [195] proposed a protocol for separating oil–water emulsions after soil washing using $CO_2$ switchable anionic surfactants. As shown in Figure 15a, after the soil washing, the soil had been separated, while the washing effluent was brought into a separator. $CO_2$ was subsequently introduced, allowing the surfactant to be "turned off" and leading to the separation of the emulsified oil and surfactant from the wash solution. The oil could then be reclaimed and recycled, while the carbonated water would be decarbonated, recombined with the surfactant, and re-introduced into the washer. The removal rate of the oil contaminants from the sands reached 97% at the optimum condition, while the residual oil in the washing fluid was about 5%. Remaining surfactants in the aqueous phase and on the sand surface were approximately 0.48% and 0.45%, respectively, indicating negligible accumulation of surfactants during cycling.



(**a**) (**b**)

**Figure 15.** (**a**) A proposed scheme of soil washing using $CO_2$ switchable anionic surfactants. Reproduced with permission from Ceschia et al., 2014 (ref. [195]). Copyright of The Royal Society of Chemistry 2014. (**b**) The experimental setup of pilot scale dewatering of oil sludge. Reproduced with permission of Long et al., 2013 (ref. [196]). Copyright 2013 Elsevier Ltd.

In addition to soil remediation, demulsification is also involved in the treatment of oil sludge. For example, Long et al. [196] applied the biosurfactant rhamnolipid for dewatering of oily sludge at pilot scale. The experiment was performed at the wastewater treatment section in the Shengli refinery of Sinopec Qilu Petrochemical Corporation. As displayed in Figure 15b, 1000 L of the oily sludge with temperature of 30~40 °C was subjected to the dewatering tank for rhamnolipid treatment. A control tank without rhamnolipid was used as a parallel. The oily sludge was settled at ambient temperature (5~10 °C) after mixing for 3 min. The aqueous phase then entered into the reception tank after settling for 2 h. After the pilot treatment, the oil sludge with decreased volume of 60–80% could be pumped into coking tower. Water with soluble COD of about 800 mg/L and residual oil of 10 mg/L could be discharged into the follow-up biotreatment system, thus realizing completely harmless treatment.

Dudek et al. [197] described a typical process for offshore petroleum production at the Norwegian Continental Shelf. The process could be conducted on a FPSO (Floating Production, Storage, and Offloading) unit or on a platform. A ship was designed for production and transportation of natural gas and crude oil. Oil wells are usually connected to a production manifold in an off-shore facility. The fluids flow from the topside of oil wells for further processing (Figure 16). Firstly, the fluids flow into the gravity separator, where the three-phase (water, oil, and gas) separation occur. Owing to the turbulent flow, the existence of resins and asphaltenes and obvious pressure drops in chokes or manifolds, emulsions and foams may be generated, which can impact the separation. Most free gas is separated in the gravity separator. The water and oil are separated after the sedimentation and creaming of dispersed phases. During the three-phase separation, fine solids will follow the fluid streams, whereas larger solid particles settle down in the separator. Afterwards, crude oil is further treated in a second- or even third-stage separator, where the water content in oil is reduced to below 0.5% and meets the export quality. Eventually, the produced water flows into the hydro cyclone and gas flotation in series to achieve the re-injection or discharge quality.

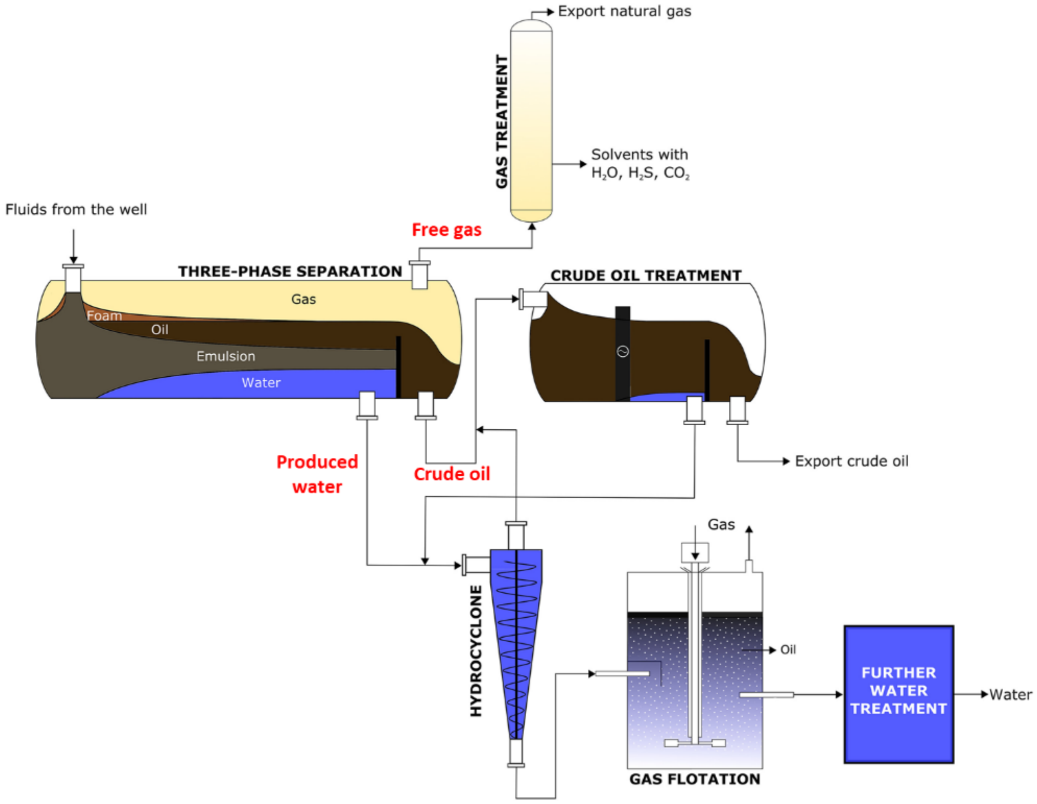


**Figure 16.** Schematic of an offshore crude oil, natural gas and water processing [197]. Reproduced with permission of Dudek et al., 2020 (ref. [197]). Copyright 2020 Elsevier B.V.

During the treatment of hydrocarbon fuels (e.g., naphtha, fuel gas, or jet fuel), amine and caustic solutions and water are usually used to remove or scrub contaminants such as $H_2S$, $CO_2$, sulfur alcohols, or naphthenic acids, forming tight emulsions that are difficult to separate. Salgado et al. [198] has reported an emulsion treatment process by applying membrane coalescence to overcome the tight emulsion problems in a jet fuel treatment unit. As shown in Figure 17, jet fuel from the crude unit entered the caustic and water washing unit, during which stable emulsions were generated. The pre-filter and the membrane coalescer vessel were integrated in a typical process mounted in a single skid. In this case, a horizontal coalescer was selected according to the amount of aqueous phase in the emulsion (48 vol%), as well as an estimated interfacial tension (0.5–1.0 d/cm). The emulsion was fed to the pre-filter and thereafter to the membrane module. The recovered jet fuel flowed upwards and the aqueous phase settled down, caused by their difference in density. The water content in the recovered jet fuel from the coalescence skid varied between 200 and 250 ppmwt, which corresponds to water saturation of the hydrocarbon and indicates acceptable water and caustic entrainment in the recovered jet fuel.

Enzyme-assisted aqueous extraction is considered to be a green oil production technology [199]. In the extraction process, proteins, oils, phospholipids, and other macromolecular sub-stances such as starch and cellulose, are released at the same time. These substances combine with each other to encapsulate the oil, thus forming a stable emulsification system [200]. Cheng et al. [201] investigated the economic feasibility of the enzyme-assisted aqueous extraction process for soybean oil production. As illustrated in Figure 18, there are four steps involved in soybean oil extraction, including: (i) mechanical processing (dehulling and extrusion of soybean flaking), (ii) enzyme-assisted aqueous extraction, (iii) separation of coproducts and cream by three-way centrifugation, and (iv) separation of the cream fraction to release the free oil. Proteases (Protex 6L) was used to degrade olesion and facilitate the phase separation.

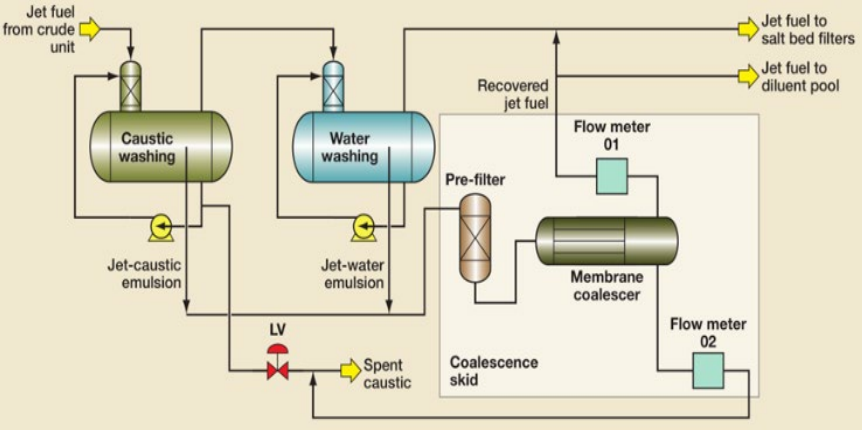


**Figure 17.** Process scheme for recovering jet fuel from emulsions [198]. Reproduced from Hernando Salgado, et al., 2014 (ref. [198]).

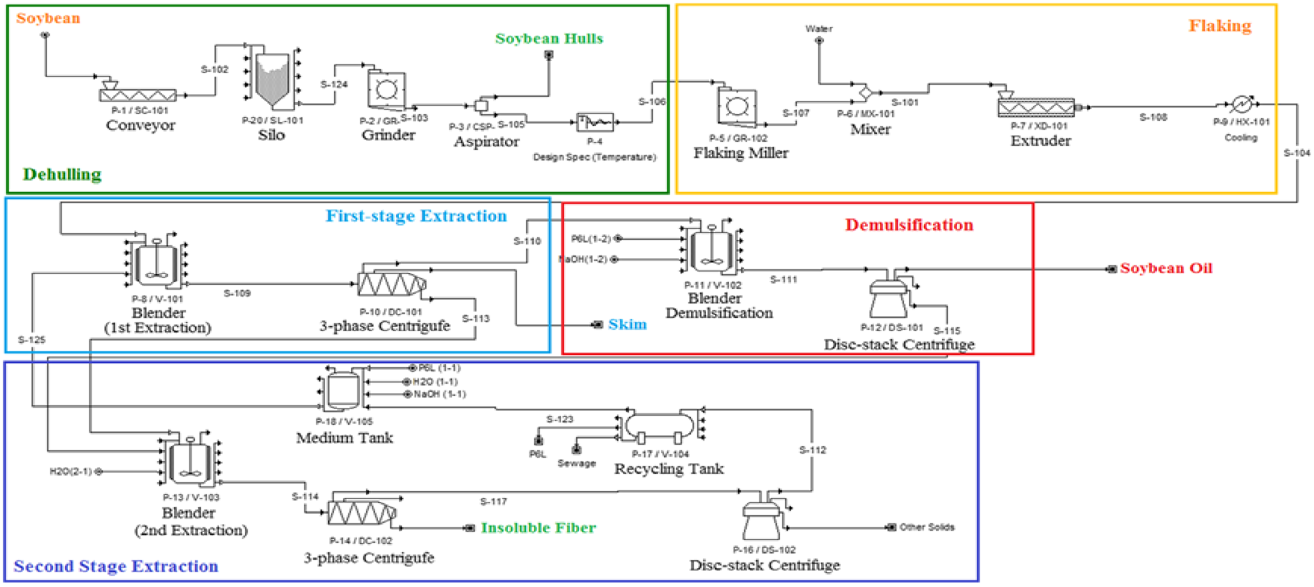


**Figure 18.** Flow diagram of techno-economic analysis model of enzyme-assisted aqueous extraction process for soybean oil extraction [201]. Reproduced with permission of Cheng et al., 2019 (ref. [201]). Copyright 2019, Springer Science Business Media, LLC, part of Springer Nature.

In brief, various demulsification technologies are involved in different industrial processes, both as standalone methods or in combination with other methods. Gravity settling is frequently applied in industry, owing to the convenient operation compared with other methods such as centrifugation, pressure filtration, and vacuum filtration. Gravity separation is also quite suitable for the treatment of large amounts of emulsions. However, the demulsification efficiency of gravity separation is not high enough, thus it is usually combined with other technologies Moreover, some mechanical separation methods, such as centrifugation, hydrocyclone, and filtration, are usually employed in industry for the pre-treatment of complex emulsions. Additionally, chemical demulsification is also one of the most commonly used method in industry, due to its convenient operation and high efficiency. To overcome the disadvantages of high operation temperature and high energy consumption during chemical demulsification, other methods such as adsorption and membrane separation have been applied for treatment of oil–water emulsions and showed potential application prospect.

## 5. Discussions

Studies on the stability of oil–water emulsions have been widely reported, and oil–water separation techniques have been maturely applied in industry. However, there are still many critical issues that need further investigation. The challenges and future developments of oil–water emulsion separation technology are discussed in detail below.

Chemical demulsification is widely used in W/O emulsion separation. The greatest challenge for the demulsification of heavy oil–water emulsions currently arises from the pressing need for novel and efficient demulsifiers. Commercial or conventional demulsifiers are generally characterized by some drawbacks (e.g., low efficiency, high temperature, and use of high concentrations). To achieve industrial applications, the development of complex chemical demulsifiers with easy recycling and high breaking efficiency is urgently needed. The demulsification mechanism at the molecular level is still unclear. Biodemulsifiers seem to be considered promising alternatives to chemical demulsifiers, as they have many excellent properties (good biodegradability, high selectivity, resistance to acids and bases, etc.). However, the manufacturing process of biodemulsifiers would be very expensive (mainly for the purification process as well as for the raw material and fermentation process) [202], and the screening of microorganisms suitable for the fermentative manufacturing would be difficult. The manufacturing cost of the same amount of biodemulsifiers is about 10 to 12 times higher than that of synthetic chemical demulsifiers [203]. In the future, biodemulsifiers will be developed towards lower cost and higher yield.

Physical demulsification methods encompass a variety of techniques, as discussed in the previous section. Each technique has unique strengths and weaknesses. Many researchers have devoted themselves to combining two or more techniques to overcome the shortcomings and enhance the oil–water separation efficiency. In thick oil extraction, downstream separation, and deep-sea operations, the size of the separators and the enormous energy consumption are also some of the existing challenges. Techniques such as gravity or centrifugation, electrostatic precipitation, cyclones, gas flotation, thermal treatment, and adsorption are widely used in many industries. However, these techniques have obvious drawbacks, such as high cost and operational complexity. In particular, the separation efficiency is relatively low (for emulsions where the dispersed phase is very fine droplets) [204–206]. Membrane separation is effective for separating oil-in-water emulsions with fine droplets. Membranes are generally fabricated from polymers and inorganic materials, but are prone to the fouling phenomenon. Ceramic and metal inorganic membranes are capable of performing better separations, but these membranes can be costly to manufacture and difficult to scale up commercially. New materials are being developed to solve these problems, and combining membranes with other technologies will achieve higher oil–water separation efficiency, lower energy consumption, more environmental protection, and a broadening of the range of industrial applications.

## 6. Conclusions

The sources, effects, stabilization mechanisms, and various separation technologies and processes of oil–water emulsions have been comprehensively reviewed herein. The increasing output of oil–water emulsions poses a major challenge to industrial practice and environmental protection. The contribution of fine solid particles and surfactant-active agents to the formation of oil–water emulsions and the difficulties of separation are analyzed. In order to eliminate the influence of solid particles on emulsion stability, the import of unnecessary solid particles, such as sludge and certain metal salts, can be avoided in the process of crude oil recovery. Some natural surfactants in crude oil, especially IAA, play the most important role in stabilizing emulsion produced in oilfield. This provides ideas for the formation of stable emulsions and selection of appropriate chemical demulsifiers. The techniques used to measure oil and water phases interactions of emulsions from micro- to macro-scale are reviewed. AFM can be used to measure the non-DLVO forces, which helps to reveal the molecular interaction mechanisms for emulsions, etc. It is believed that the cognition of the stability of emulsions would rationally promote the design of agent, technological process, and equipment; whether emulsification, demulsification, or other related fields.

The present oil–water separation methods applied in different fields are roundly summarized. The mechanism, advantages, and disadvantages of each method are discussed. The traditional separation methods (heating method, chemical method, electric dehydration method, ultrasonic method, etc.) have been successfully applied in industrial fields. Up to now, microwave, hydrocyclone, and magnetic methods have been studied, which perform better when combined with other methods. Novel oil–water separation methods, such as membrane, in-situ extraction, etc., have broad application prospects. These novel methods have already shown great application potential in the fields of soil restoration, oil sludge treatment, marine oil spills, and other industrial emulsion separation. Electric dehydrators are currently the most commonly used equipment for crude oil dehydration and desalting. However, their high-power requirement means high energy consumption. Metal electrodes also contribute to the deposition of more pollutants.

Oily wastewater consists of oil droplets in the range of 1 to 600 mg/L, with oil droplets less than 40 μm accounting for a significant proportion of it. Nevertheless, the practical situation in industry is that technologies such as flotation, coagulation, hydrocyclones, and API gravity separators are limited in separating oil droplets less than 40 μm. In some novel oil–water separation technologies (such as membranes), high separation efficiency can be achieved and the purpose of separating ultra-fine oil droplets can be accomplished, yet the recyclability of membranes and highly fouling-resistant materials still need to be improved, and easy recovery needs to be further developed in the future. In addition, offshore oil and gas development is increasingly progressing into the deep sea, and the need to develop small, efficient, and integrated pipe-based separators suitable for different conditions appears to be a new way to replace the previous giant tank-based systems, and to solve problems like space constraints on marine platforms. In the future, oil–water emulsion separation equipment will be developed in the direction of short separation time, simple processing process, low energy consumption, green, low-cost, simple operation, and compact structure, and will achieve the goal of high efficiency, energy saving, and multi-functionalization.

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