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Mechanism-Oriented Review of Crude Oil Emulsion Separation: Interfacial Chemistry and Droplet Dynamics.

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Abstract

The presence of highly stable water in oil (w/o) , oil in water (o/w) and oil in water in oil (o/w/o)emulsions have been a major problem to oil production and treatment of oily wastewater, especially, in the presence of sub-micron droplets that are stabilized by asphaltenes, resins and fine solids. Droplets that are less than 10 micrometers cannot be easily separated by any conventional gravity-based method, which means that their efficiency is low and they cost a lot to operate. The present review offers a mechanistic comparison and contrast of the traditional and emerging methodologies of emulsion separation, such as chemical, electrostatic, membrane-based, ultra-sonic and nanomaterial-based methods. The study lays emphasis on recent advances between 2022 and 2025 including ionic liquid-based emulsion separators, biomaterials, and hybrid separation systems. The analysis demonstrates that the effective interface is unstable, which facilitates droplet amalgamation whereby the sub-micron droplets are able to increase to larger droplets (more than 50 micrometers), thereby increasing the efficiency of separation to a considerable extent. In the published literature, oil-water sepa-ration efficiencies of more than 90% are possible under ideal circumstances. In most cases, the performance of separation is mostly influenced by surface characteristics and not by operating intensity. This review gives an overview of the existing weaknesses and emphasizes the potential of semiconductor and hybrid systems in designing efficient and sustainable crude oil emulsion separation technologies.

Keywords: *Demulsification, Water-in-oil (W/O) emulsions, Nanofluids, Coalescence kinetics, Interfacial chemistry*

1. Introduction

Emulsions are also commonly used in numerous industrial applications such as in petroleum refining, petrochemicals, pharmaceuticals and food processing. One of the most challenging problems is crude oil emulsions because of their high stability and complicated physicochemical characteristics. A heterogeneous system whereby a single immiscible liquid is dispersed as fine droplets in a second continuous liquid phase is generally referred to as an emulsion. Water-in-oil (W/O), oil-in-water (O/W) and multiple emulsions are the most common types in petroleum systems, though W/O emulsions are the most common during crude oil production [1]. The emulsions occur naturally in the extraction processes as a consequence of turbulence, pressure variations and the natural occurrence of surface-active agents like asphaltenes, resins, and waxes, which adsorb at the oil-water interface and inhibit coalescence of the droplets[2][3]. Crude oil demulsification is critical because it directly affects the operational efficiency, economic cost, and environmental protection. Water that is emulsified in crude oil increases viscosity and hence, consumes more energy in transportation and pumping and corrods the pipeline as a result of dissolved salts. Stable emulsions increase the apparent viscosity of crude oil, leading to higher flow resistance and consequently a greater drop in pressure along production lines and pipelines, as well as accelerating equipment deterioration[4]. Besides, it has a harmful impact on refinery processes, poisoning catalysts and decreasing the quality of products. Oily wastewater and untreated emulsions may contaminate surface and ground water resources, which are dangerous ecologically and health threatening[5]. Thus, effective separation of crude oil and water is a mandatory process prior to refolding, transportation or reinjection of crude oil. A large quantity of these liquid wastes and stable solids are formed from crude oil, reducing product quality, increasing wear and tear on processing equipment, and leading to higher operating and maintenance costs[3] [2].The distribution of a non-miscible liquid (resolved phase) within another non-miscible liquid (continuous phase) is referred to as an emulsion[3]. The interfacial chemistry and droplet dynamics are two interrelated factors that determine the stability of emulsions and their separation behavior in a mechanistic viewpoint. The interfacial chemistry is important in the sense that it forms viscoelastic films of asphaltenes and other surfactants in the oil-water interface that is resistant to the drainage of the film and prevents the coalescence of the droplets. The interfacial characteristics like interfacial tension and interfacial elasticity do have a direct effect on the energy barrier needed to be overcome in droplet aggregation[6]. Conversely, droplet dynamics govern the separation process at the microscale with the distribution of the droplet size, collision frequency and coalescence kinetics defining the efficiency of phase separation. Specifically, droplets with very small diameter (less than 10 µm) are highly resistant to being separated because the interfaces forces dominate the gravitational forces, and thus droplet growth is a requirement of effective demulsification[4].

A number of past researches have aimed at enhancing the effectiveness of demulsification by the establishment of novel materials and processes. As an example, Ali et al. (2022) were able to synthesize polymeric demulsifiers which had a high level of water separation efficiency, showing that polymer based surfactants were effective to destabilize crude oil emulsions[7]. On the same note, amide-based demulsifiers have demonstrated good effectiveness in the reduction of interfacial tension and improved separation performance[8]. More recently, Abed et al. (2024) created a bio-demulsifier based on corn oil, which has high separation efficiency and at the same time provides an environmentally friendly alternative to the traditional chemicals[1]. Moreover, other superior methods like magnetic nanoparticles have also received significant interest because of their elevated surface area, recyclability and the capacity to react to external magnetic fields which render them very effective in emulsion treatment[9]. All these studies point at the increasing tendency of more efficient and sustainable technologies of demulsification. The objective of this research is to explore the crude oil emulsions with specific reference to the contributions of interfacial chemistry and droplet dynamics in regulating the emulsion stability and separation behavior. The research also aims at determining the performance of the demulsification techniques and effective strategies to enhance the efficiency of separation taking into consideration the operational feasibility and environmental sustainability.

2. Emulsion Removal Methods

Figure 1 provides an overall classification of emulsion removal techniques, showing the key categories of treatment techniques that were taken into account in this review. These techniques vary in their working mechanisms with interfacial modification and droplet coalescence being the simplest and processes such as mass transfer and phase transformation being the most complex.

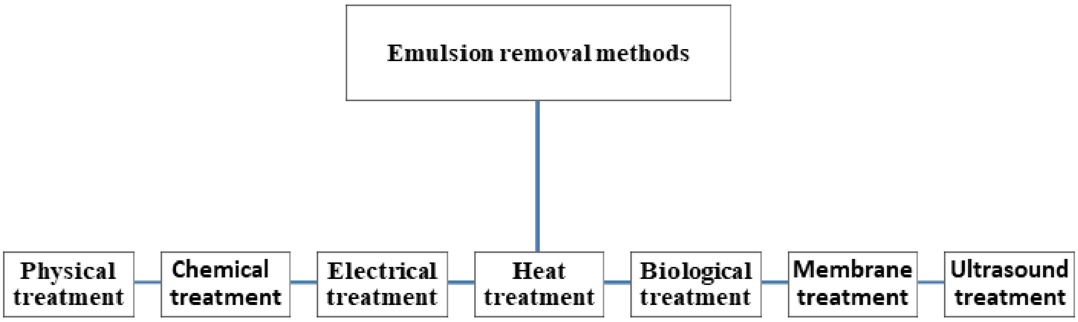

Fig. 1. A schematic arrangement of emulsion removal techniques, such as physical, chemical, electrical, thermal, biological, membrane-based, and ultrasonic.

2.1 Physical Demulsification Techniques

The emulsion is processed using a variety of methods and according to the: -

2.1.1 Gravity separation

The gravity separation is based on the density dissimilarity between the dispersed and continuous phases wherein droplets or solid particles settle at a rate defined by the Stokes law [10]. The balance between gravitational forces and viscous resistance controls this process, and is highly sensitive to interfacial properties and droplet size.

$$V = \frac{2}{9}\frac{(\rho_p - \rho_f) g R^2}{\mu} \tag{1}$$

V = terminal velocity
R = particle radius
g = acceleration due to gravity
ρ_p = particle density
ρ_f= fluid density
μ=fluid dynamic viscosity

According to this law, the settling velocity of the droplets is proportional to the square of the droplet radius and the density difference between the two phases but inversely proportional to the increased viscosity of the continuous phase[11]. At the droplet scale, the larger the droplet the faster it will fall, but smaller droplets (those smaller than the micron scale) will be suspended due to the overwhelming forces between the droplets and the interfaces. Nonetheless, Stokes law has a number of simplifying assumptions such as the assumption of spherical, non-interacting droplets, laminar flow and a Newtonian continuous phase. In practice, these conditions are hardly ever met in real-life emulsions, because the process of sedimentation is disturbed by the effects of droplet collisions, film drainage, and hydrodynamic resistance. Also, droplet coalescence is inhibited by the presence of viscoelastic interfacial films formed by asphaltenes and other surface-active components, which limits droplet growth and thus the efficiency of phase separation[12] , because droplet growth is required to enable effective settling by gravity through interfacial resistance.

2.1.2 Dissolved air flotation

Dissolved air flotation (DAF) is a water treatment method used to remove particles, droplets, or microorganisms typical-ly ranging in size from 10 to 100 µm[13] . It involves a physical separation process whereby under pressure, air is dissolved in water or industrial wastewater and then discharged at atmospheric pressure into the recovery tank. The release of this pressure results in the production of fine bubbles approximately in the m dimension that is attached to suspended solids, oil droplets that are emulsified, oil and grease particles, or agglomerated materials. Mechanistically, the efficiency of DAF is determined by the bubble-droplet interactions at the interface whereby attachment is attained as a result of a combination of hydrophobic interactions, surface forces, and collision frequency. The sticking of the bubbles to the oil droplets decreases the density of the aggregates as a whole making them more buoyant and allowing them to rise upwards to the surface. Interfacial properties like surface tension, wettability, and presence of surfactants or natural emulsifiers play a significant role in the formation and stability of bubble-drop aggregates. They influence the likelihood of attachment and the strength of the bubble-droplet interface, which influences the effectiveness of flotation. The bubble-particle aggregates or bubble-droplet clusters are buoyed and accumulated at the surface, creating a floating foam layer which is taken off by skimming[14]. Figure 2 shows how the dissolved air flotation works with fine air bubbles binding to dispersed oil droplets and suspended particles creating buoyant aggregates that rise to the surface.

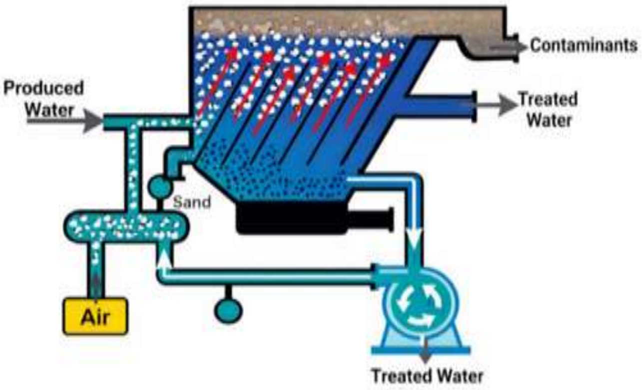

Fig.2:shows how the dissolved air flotation works with fine air bubbles binding to dispersed oil droplets and suspended particles creating buoyant aggregates that rise to the surface [15]

2.1.3 Centrifugation

Centrifugation to separate oils-water mixtures is founded on the difference in density between the dispersed drop-lets of oil and the continuous phase which can be either aqueous or oily[16]. When the mixture is placed at a high rate of rotational speed in a centrifuge, the heavier component, usually water, and suspended solids, radially moves outwards due to centrifugal force. Contrary to this, the light oil phase or the oil droplets move to the axis of rotation (inwards) because of the difference between the density of the phases. Centrifugal acceleration is also useful in this process, which replaces or greatly increases the rate of separation of fine droplets and emulsified oil due to the centrifugal acceleration. In droplet scale, the acceleration is larger and therefore, improves the velocity of droplet migration and decreases the time taken to separate phases[17]. But, just like gravity separation, centrifugation efficiency is highly dependent on the interfacial properties and droplet interactions. The existence of hard interfacial films comprising asphaltenes and additional surface-active constituents may prevent the formation of droplet coalescence, and thus restrict the development of small droplets even with severe centrifugal forces. Moreover, droplet-droplet interactions, collision frequency and coalescence kinetics are important factors that dictate separation efficiency. Thus, despite the fact that centrifugation is a highly effective method of promoting phase separation, successful demulsification is still reliant on overcoming interfacial resistance and facilitating droplet coalescence. Indicatively, recent research on centrifugal separation in the treatment of produced water to be reinjected into production streams of crude oil has demonstrated that centrifugation can be more effective than traditional gravity sedimentation in the removal of suspended solids, and dispersed oil in crude oil production streams[18] . Figure 3 shows the primary categories of centrifugation equipment applied in oil-water separation processes, revealing the variety of designs depending on the mode of operation and designs. The centrifuge design variation has a direct impact on droplet separation behavior because variations in residence time, flow patterns, and centrifugal field strength affect droplet migration, collision frequency, and coalescence efficiency. In the example, high-speed disc-stack centrifuges are used to improve separation of fine droplets whereas decanter centrifuges are best used in situations where loaded with higher solid.

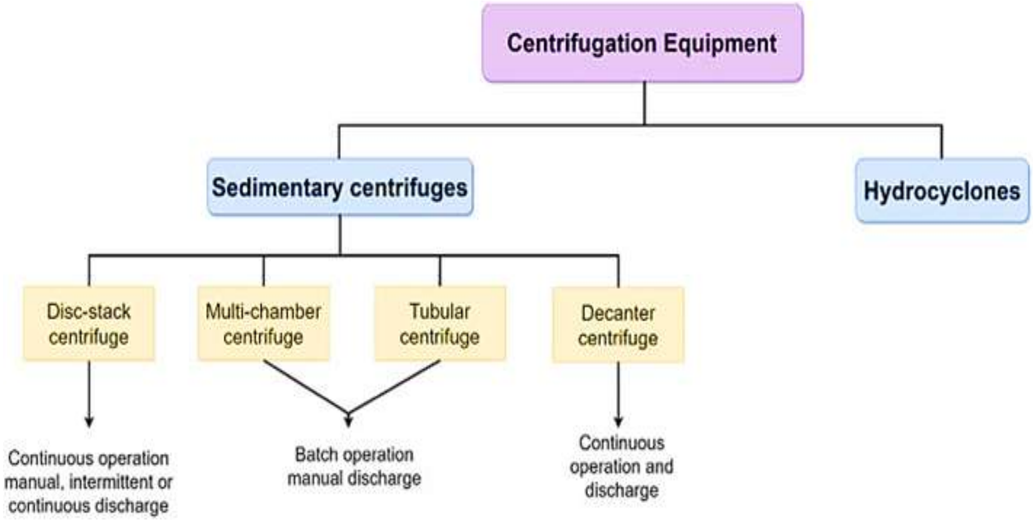

Fig. 3. Categorization of centrifugation equipment employed in the process of oil-water separation, such as sedimentation-based centrifuges (disc-stack, multi-chamber, tubular and decanter centrifuges) and hydro cyclones [19]

2.1.4 Evaporation

Evaporation, especially in solar-driven and vacuum-assisted systems, is founded on the transformation of the aqueous phase into vapor and the preservation of the oil and solid phases. The underlying principle of this mechanism of separation is heat and mass transfer mechanisms, and interfacial transport at the liquid-vapor interface. Recent studies indicate that in the case of oily streams with emulsified oil and high salinity, surface evaporation can be effective at removing the water and leaving the oil phase behind [20]. Mechanistically, in high salinity streams with emulsified oil, surface evaporation is an effective way of removing water and leaving the oil phase behind, as localized heating can be used to enhance the phase change [20]. But, interfacial properties and droplet distribution have a strong impact on the efficiency of evaporation-based separation. The droplets of oil on the interface may create a layer that prevents the transportation of vapor and decreases the evaporation rates. Moreover, the presence of droplets and interfacial deposition may restrict heat exchange and destabilize the continuous delivery of water to the evaporation surface. Moreover, the more modern systems like siphon-based textile evaporators combine the separation and the evaporation by increasing the water flow in the form of capillary movement, hence, ensuring a constant supply of water to the evaporation surface[21]. Likewise, Janus structured evaporators are intended to regulate wettability and interfacial behaviour but oil adhesion on hydrophobic surfaces can prevent water transport and decrease vapour flux [22].

2.1.5 Filtration

The principles of physical interception and size exclusion form the basis of the filtration process of the oily water treatment. The processes of granular media, sand filters, activated carbon and membrane systems eliminate emulsified oil and suspended solids by holding the droplets in pores or holding them on the surface[23]. Mechanistically, interfaces between the droplets of oil and the medium through which the filtration process acts can also determine filtration efficiency; it also depends on the size of the pores. These interactions are wettability, surface energy, and adhesion forces, which dictate the rejection, adsorbing or passage of droplets when passing through the pores. Ceramic membranes used to treat oily wastewater show that the primary processes are droplet-membrane interaction, wetting, and droplet deformation at the pore entrance but interfacial fouling is still a significant constraint in the filtration processes. A fouling layer of oil droplets on the membrane surface can change the surface wettability, close pores and decrease the permeate flux with time. So, interfacial properties and droplet behavior control is vital to enhancing the effectiveness of the filtration process and ensuring high efficiency over the long term [23].

2.1.6 Adsorption

Adsorption can be defined as the separation of residual oil and emulsified droplets out of oily water streams by letting the oil molecules or droplets adsorb onto the surface of a solid absorbent substance, like activated carbon and modified fibers. To illustrate, there are a number of variables in oil-in-water emulsion systems. It has been established that contact time, pH, and surface area of the absorbent material are important factors that influence the process of oil removal by adsorption[24]. Recent reports ascertain that absorption is an economical approach to treat and polish oily wastewater and sewage sludge, particularly where alternative procedures fail[25].

2.1.7 Air or steam stripping

Air or steam stripping is a separation technology that involves removal of volatile and semi volatile substances in oily wastewater streams by forcing air or steam through the liquid phase to enhance the transfer of volatile organic compounds to the gaseous phase. The operation of this process is essentially controlled by the mass transfer across the gas liquid interface with the efficiency being dependent on the interfacial area, volatility of the compounds, and, the dynamics between the gases and liquid. In a mechanistic perspective, the stripping efficiency depends on how well volatile species are diffused out of the bulk liquid to the interface which is then followed by their removal into the gas phase. This process can be influenced by the presence of oil droplets and emulsified phases that can change the interfacial area and mass transfer resistance. Oil layers or interfacial films can inhibit the volatility of the compounds in certain situations thus lowering the efficiency of stripping. Indicatively, in one study, air stripping has been found to significantly lower toxic volatile wastewater streams of oily industrial effluents[26] . Equally, the gas stripping when used on lubricant production wastewater exhibited a better reduction in Chemical Oxygen Demand (COD)[27]. As components of integrated treatment systems, steam stripping towers have recently been used on oily marine wastewater [11].

2.1.8 Oil coalescing

Coalescence process is a physical separation process that helps to facilitate the consolidation of small oil droplets to larger droplets, which is then easily eliminated using gravity or filtration as a method of oily wastewater removal. The interactions of the droplets and interfaces at the droplet scale are fundamental-ly based and drive droplet collisions, film drainage and droplet coalescence. The principle of this process is to decrease the stability of the dispersed droplets by coming into contact with coalescing media or fibers, which increases the frequency of collision and adhesion of droplets[29]. Mechanistically, the process of coalescence takes place when the thin liquid film separating the approaching droplets drains out and breaks, releasing the droplets to join together to form larger objects. Interfacial forces like surface tension, Elasticity of films and presence of surface-active components are very important in defining the coalescence resistance. Film drainage and coalescence can be inhibited with rigid interfacial films, whereas wettability and surface energy alterations can facilitate droplet adhesion and coalescence .It has demonstrated that fibrous and nanostructured materials are very effective in enhancing the efficiency of oily water separation, due to the high droplet-surface interaction and coalescence that takes place at low-energy conditions[30]. Besides that, the hierarchical structures and controlled wettability of materials help to enhance the performance of coalescence because it allows droplet capture, deformation and growth at the interface[31] .

2.1.9 Liquid/liquid extraction

In the treatment of oily wastewater, the liquid-liquid extraction technique is implemented based on the different solubility of the compounds in two immiscible liquid phases, such as an aqueous phase and an organic solvent. This is a technique that eliminates dissolved or emulsified hydrocarbons, whereby they are moved to a selective solvent phase[32]. Mechanistically, liquid-liquid extraction efficiency is controlled by the mass transfer across the liquid-liquid interface, where solute molecules move out of the bulk aqueous phase into the interface and then proceed to partition into the solvent phase. This entails interfacial area, diffusion rates and thermodynamic affinity of the solute with the extracting solvent. At the scale of the droplets in emulsified systems, the droplet-scale behavior is an important aspect, where the existence of dispersed oil droplets may elevate the effective interfacial area and determine the mass transfer rates. Nevertheless, steady interfacial films can become an obstacle to solute transfer since they create an extra resistance at the interface. Thus, interfacial properties, as well as distribution of droplets, directly influence extraction efficiency. Research has revealed that an appropriate choice of solvent and the optimization of phase ratio can help a great deal to improve the process of oil and grease removal in the produced water[33]. The approach works especially well with wastewater streams that have large organic loads and whose physical separation processes are not as effective as this one[48].

2.2 Chemical treatment

One of the most popular ways of demulsifying crude oil emulsions is chemical demulsification, which involves the incorporation of surface-active chemicals, referred to as demulsifiers[36]. Mechanistically, demulsifiers interfere with the stability of natural emulsifiers, asphaltenes and resins, by adsorbing onto the oil-water interface and crowding out or destabilizing the rigid interfacial films, which are also found in natural emulsifiers [37]. This mechanism lowers interfacial tension and changes viscoelastic characteristics of the interfacial layer, which leads to the film drainage and droplet coalesce [38]. When the interfacial barrier is destabilized, the droplets will be able to come closer to each other, which will increase the collision rate and coalescence. This causes small droplets to combine into bigger droplets which can be further separated more easily by gravity or any other physical process. Effectiveness of chemical demulsification is sensitive to a number of variables such as the type of demulsifier to use, the dosage, mixing efficiency, and residence time to enable droplet growth and settling[39]. Moreover, exogenous forces like temperature, electric fields, and mechanical mixing may also be used to further increase demulsification by ac-accelerating interfacial film disruption and droplet coalescence. For example,[40] investigated the performance of different demulsifiers on heavy and medium crude oil emulsions. The findings indicated that the best formulation obtained a water separation of about 80% in the initial minutes. It was also noted that demulsifiers worked better with medium crude oil than in heavy crude oil, which can be explained by the fact that the content of asphaltene and the resulting strength of the interfacial film are different in the latter.

2.3 Biological treatment

Biological treatment is significant in situations where the level of salt in the emulsion is very high or where the levels are abruptly altered [41]. As noted earlier, chemical demulsifiers are very common in the crude oil industry and mi-crobial/biological demulsifiers are being suggested as an alternative. The study of biological demulsification dates back to the 1980s. A biological demulsifier is a type of biologically active compound that has properties that help destabilize the emulsion and is used using biological methods [42]. Bio-demulsifiers are environmentally friendly and are non-polluting. They can work in harsh environments and can be employed to formulate crude oil emulsions with a complex formula. Microbial demulsification's basic idea is that microbial growth and demulsification may occur at the same time as long as the emulsion has enough hydrocarbons to sustain the growth of microbial cells[43].Meanwhile, this type can be regenerated and reused without its efficiency. This comes in handy in the tough environments. The most effective is the bio-emulsifier which is resistant to heat, salinity and acidity. Industrial and agricultural waste can be used to obtain this type of emulsifier [59].

2.4 Electrical treatment

Electrostatic separation plays an important role in promoting the coalescence of droplets dispersed in oil or oil droplets dispersed in water. This operation is performed on the principle of the employment of an external electric field instead of oxidation reduction reactions, in which electrodes are employed in order to create an electric potential across the emulsion[47]. Application of electric field causes an imbalance in the electrical potential of the dispersed droplets resulting in the polarization of the droplets and the formation of dipole. This technique has a number of benefits such as that it is easy to use and it does not require the use of chemical additives[48]. High voltage is fed to electrodes (typically of carbon steel alloys) by electrical transformers in practical systems, providing a powerful electric field between the separation unit. Droplets polarize, and droplets interact in an attractive dipole-dipole interaction as the emulsion passes through this field, increasing collision frequency and facilitating droplet coalescence. As a result, the droplets grow in size and can be more easily separated by gravity [49]. A large electric field is usually necessary since the continuous phase can be weakly conductive or non-conductive. In this case the droplets become induced with opposite charges, causing electrostatic attraction and coalescence. The balance between the interfacial resistance and electrostatic forces determines the efficiency of this process.

$$P_{\mathrm{IN}} = \frac{2\gamma\cos\theta}{r} \tag{2}$$

Equation (2) represents the capillary pressure (P_{IN}) acting within the droplet, where (γ) is the interfacial tension, θ is the contact angle, and r is the droplet radius. This correlation demonstrates that a smaller droplet has greater internal pressure and thus it is more resistant to deformation and coalescence. Hence, effective electrostatic separation of droplets involves the induced dipole forces to surmount this barrier of capillary pressure to allow droplet merging [50].

Figure 4 shows a phase diagram of hexadecane droplets in water under alternating electric field. The horizontal is the dimensionless frequency (τ), the vertical is the modulated capillary number (C_e). This diagram defines three main regimes, namely, weak electrical docking, strong electrical docking and secondary droplet ejection and transition regimes between them. There are symbols that relate to experimental data of different δ/alpha ratios. The microscopic pictures that come with it illustrate the droplet structure before and after being treated with the electric field, indicating that the coalescence of droplets using the electric-field is effective[51].

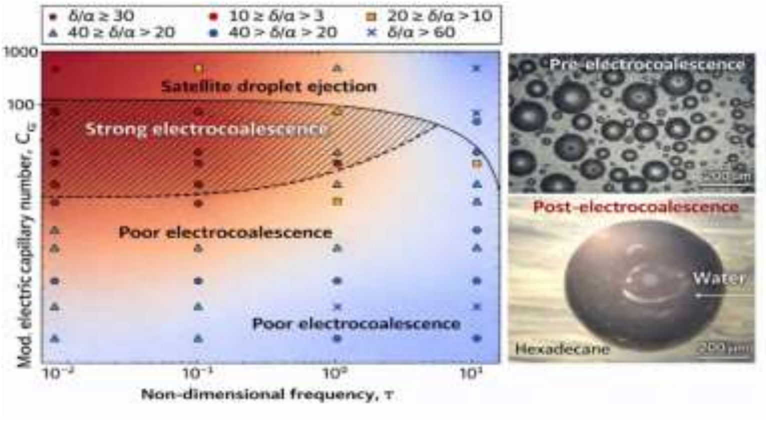

Fig.4: A phase diagram showing electrical bonding patterns of hexadecane droplets in water at different dimensionless frequency and number of electrical capillaries, and with microscopic pictures of pre- and post-electrical bonding [51].

2.5 Heat treatment

A widely used heat treatment technique in oil fields is to subject the emulsions to heat in order to accelerate the process of separating the oil and water phases[52]. Prior to being introduced to the separation vessel, crude oil is normally heated through furnaces or heat exchangers. Mechanistically, rising temperature decreases the viscosity of the continuous phase, leading to higher droplet mobility and a higher collision frequency. Throughout, thermal energy also undermines the interfacial film by diminishing the viscoelastic strength of the film and lowering interfacial tension, which in turn makes the film drain and droplets coalesce. Consequently, droplets are able to combine easier to form bigger droplets, enhancing the effectiveness of gravity separation. Moreover, high temperature increases the rate of diffusion and decreases the mass transfer resistance, further enhancing the phase separation. Practically, heat treatment is commonly added to the chemical demulsification to enhance interfacial disruption and overall efficiency of separation[53].

2.6 Membrane treatment

The recently growing interest in membrane-based demulsification as a viable method of separating crude oil emulsions is explained by the benefits that this technique enjoys over alternative methods[54]. This approach is based on the selective movement of one of the phases under low pressure through a porous membrane with the rest of the phases held back. Mechanistically, the droplet-membrane interactions and interfacial phenomena that dictate membrane separation include wettability, surface energy and capillary forces. Depending on the balance between the capillary pressure and external driving forces, the droplets can either penetrate or be rejected by the membrane. Specifically, droplets have to cross interfacial resistance to enter membrane pores, whereas larger or non-wetting droplets are trapped[55]. This selectivity is critically dependent on the properties of the membrane surfaces including hydrophobicity or hydrophilicity that dictate the adhesion, deformation and transport be-behavior of droplets. But the limitation of this process is the fouling of membranes. The oil droplets on the surface of the membrane may form a foul ant layer which blocks the pores, changes wettability and decreases the permeate flux and membrane life. This means that a lot of maintenance and operating expenses are needed. To mitigate these issues, there has been the development of advanced membrane materials with surface energy and wettability control including super hydrophobic or superoleophobic surfaces in efforts to increase efficiency in the separation process and minimize the impact of fouling.

2.7 Ultrasonic treatment

Ultrasonic demulsification techniques have been of great interest as they are effective and are simple to operate. The coalescence of the dispersed water droplets in crude oil is facilitated by ultrasound through mainly acoustic cavitation, and forms localized high-pressure and high-temperature micro-environment. These forces interfere with the inter-facial film around droplets, which enhances droplet agglomeration and phase separation. Various experiments have examined how the performance of demulsification depends on the various operational parameters of temperature, irradiation time and input power. An example is that optimal input power, temperature, and irradiation time of 57.7 W, 100 C, and 6.2 minutes were reported to give a 99.8 and 84 percent drying and desalting efficiencies, respectively. In a different study, demulsification efficiencies of 65% and 50% were obtained with low-frequency, high-intensity ultrasound without the use of chemical demulsifiers[56]. Although these are promising results, most studies explain ultrasonic separation per-performance without a complete coverage of the mechanism behind the process[2]. In practice, the separation efficiency is not dictated only by the operational intensity (e.g. residence time or applied energy) but by the combination of the properties of the interfacial film and droplet processes[57]. The properties of interfacial membranes and patterns of droplet movement are the main factors that determine the capability of droplets to coalesce prior to total phase segregation [58]. Ultrasonic treatment in this case improves the separation, by weakening or breaking the interfacial membrane by cavitation effects. This destabilization decreases the droplet coalescence resistance and can be increased further by adjusting interfacial properties, including lowering interfacial tension (IFT). As an example, the inclusion of the alkalis can reduce IFT and encourage interfacial film destabilization thus allowing droplets to merge. Thus, ultrasonic treatment and chemical modifications (e.g., addition of alkali) are synergistic to decrease interfacial resistance and improve coalescence efficiency [59].

Table 1 provides a comparative overview of the most important oil-water separation and de-emulsification techniques, including gravity separation, centrifugation, dissolved air flotation, electrostatic separation, ultrasonic treatment, and membrane filtration.

Table 1: Advantages and Disadvantages of physical demulsification techniques

Technique	Advantages	Disadvantages	References
Gravity separation	– Simple design. – Low cost. – No chemical additives	– Inefficient for small droplets (<10 µm). – Slow process. – Sensitive to viscosity and stability.	[10]
Centrifugation	– Rapid separation. – Effective for fine droplets. – Compact system	– High energy consumption. – High capital cost. – Maintenance required.	[18]
Flotation (DAF)	– Effective for light oil removal. – Suitable for wastewater. – Fast process	– Requires chemicals. – Sensitive to conditions. – Sludge generation.	[13]
Electrostatic separation	– High efficiency. – Low chemical usage. – Widely applied industrially.	– High voltage requirement. – Less effective in conductive systems. – Safety concerns.	[47]
Ultrasonic treatment	– Enhances fine droplet coalescence. – Reduces chemical usage. – Flexible operation.	– Energy intensive. – Scale-up challenges. – Possible re-dispersion	[44]
Membrane filtration	– High efficiency for small droplets. – Continuous operation. – High selectivity.	– Fouling. – High cost. – Flux decline.	[23]

Processing Mechanisms: Determining the Key Controlling Variables.

There are a number of key mechanistic variables that dictate the efficiency of emulsion separation processes, which are mainly interfacial properties, droplet interactions, and transport phenomena. All these factors dictate how emulsions can be destabilized and separated under various treatment conditions. Interracially, the stability of emulsion depends heavily on the occurrence of surface-active elements like waxes, asphaltenes, and other natural emulsifiers. Adding or moving these constituents out of the oil-water interface decreases interfacial stability and enables droplet coalescence[60]. Moreover, variations in the surface charge and interfacial forces may facilitate thinning and rupture of the film, thus increasing the droplet merging and separation efficiency[61]. Kinetics of interfacial displacement is another important aspect. Research has indicated that beyond the optimum dose of the demulsifier, a higher dosage of the demulsifier may not always enhance the performance of the separation. Rather, adsorption and displacement of interfacial films are governed by the rate of the overall efficiency meaning that surface kinetics is more dominant than the concentration itself [62]. During the electrostatic separation process, droplet behavior is governed by the polarization when an electric field is applied. The dipole interactions between droplets induced cause attraction and coalescence, both of which are highly dependent on the size of the droplets and the strength of the electric field [79]. Nevertheless, the ineffective charge transfer and unstable droplet interactions can limit the separation efficiency in some working conditions [63]. Nevertheless, operating conditions can reduce the separation efficiency through limitations like ineffective transfer of charge and unstable droplet- droplet interactions [2]. In the case of membrane-assisted processes, pore-scale interaction and interfacial properties are the key determinants of the performance of separation. The wet tenability, surface energy, and pore confinement are some of the factors that determine the deformation of the droplets, their transport, and retention in the membrane structure. Whereas the rate of permeation is a result of operating pressure, the ability to separate is largely a result of interfacial interaction as opposed to pressure[64].

3. Composite Emulsion Separation Operations: The Way Forward from Methodologies

While restructuring the separation process, the hybrid processes seek to nail down as many control mechanisms as possible [65]. The electrostatic and ultrasonic chemical hybrid membrane systems collaborate with their interfacial instability and an accelerated fusion kinetics to allow efficient processing of highly stable emulsions that are found under conditions of high salinity and high temperature [66]. Such systems provide increased industrial application suitability with their chemical and energy-conserving property, which also increases system longevity relative to single-method systems[67].

4. Recent Achievements (22-25): Imagination to Mechanism-based Design.

The research studies performed in 2022-2025 show that there is a paradigm shift between experimental optimization approaches to the use of mechanism-based design approaches to demulsifiers and their working systems[68]. Both ionic liquid de-emulsifiers and bio-derived surfactants are more effective at interfacial surfaces since the two compounds are effective in dismantling interfacial membranes with minimum quantities of their respective active constituents. The assembly of Nano fluid assemblies and multifunctional membranes offers perfect control over interactions of droplets with interfacial sur-faces between Nano and micro level, which facilitates the system to reach separation rates of over 90 percent in extreme operating environments [69]. The adoption of industrial production practices is largely problematic due to the fact that the system must manage various issues of scalability and material stability problems, pollution control issues, as well as technical and economic feasibility must be tested[70].

5. Emulsion Separation Kinetics: A Pseudo First-Order Separation Model

A pseudo-first-order kinetic model has often been used to describe the separation kinetics of emulsions in gravity sedimentation, chemical separation, and electrofusion, especially in the dilute to moderately concentrated emulsions. The time-dependence of the dispersed droplet concentration rate can be given as:

$$\frac{\mathrm{d}C_d}{\mathrm{dt}} = -\mathrm{k}\mathrm{C}_d \tag{3}$$

where: C_d is the dispersed droplet concentration and $\boldsymbol{k}$ is the apparent demulsification rate constant.

Integration yields:

$$C_d(t) = C_o e^{-kt} \tag{4}$$

Where C_d is the droplet concentration at time and C_o is the initial droplet concentration
Mechanistically, this model presupposes that the droplet removal rate is proportional to the constant droplet concentration, meaning that coalescence and separation processes have first-order kinetics. The observed rate constant k, is the sum of multiple effects, such as temperature, concentration of the demulsifier, the strength of the electric field, and the hydrodynamic conditions[62]. The model, however, makes simplifying assumptions, such as a uniform distribution of the droplet sizes, the lack of complexity of droplet to droplet interaction, or constant operating conditions. In actual emulsions, pseudo-first-order behaviour may not be respected because of interfacial viscoelasticity, droplet poly disparity and stabilizing agents like asphaltenes.

6. Interfacial tension behaviour: An empirical model based on adsorption

The decrease in surface tension resulting from the adsorption of a demulsifies is usually described using empirical logarithmic or Langmuir relationships[71]. In a simplified logarithmic equation, we have the following equation[72]:

$$\gamma = \gamma_o - \alpha \ln(1 + \beta C_s) \tag{5}$$

Where γ is the interfacial tension, γ_0 is the initial interfacial tension C_s is the demulsifies concentration, and α and β are empirical constants related to adsorption efficiency. Mechanistically, this model is indicative of adsorption of demulsifier molecules at the interface between the oil and water which lowers the interfacial tension by replacing natural surface-active elements and destabilizing the interfacial film. The greater the concentration of the demulsifier, the greater the number of molecules that are deposited at the interface and the interfacial tension decreases progressively until a point of saturation is reached. Nonetheless, this empirical model presupposes a uniform adsorption behavior, and does not explicitly consider complex interfacial effects like competitive adsorption, multilayer formation, or interfacial viscoelasticity variations. This means that it tends to be applied to those systems where the concentrations of moderate levels of demulsifiers and comparatively straightforward interfacial compositions are found.

7. Emulation stability and incorporation: ratio of stability (Fuchs Theory)

The resistance of droplets to coalescence is commonly evaluated using the stability ratio, originally derived from collision theory and interpreted within the framework of DLVO (Derjaguin–Landau–Verwey–Overbeek) theory [73][2]:

$$W = \frac{k_{obs}}{k_{fast}} \tag{6}$$

where k_{fast} is the diffusion-limited collision rate and k_{obs} is the experimentally observed coalescence rate Low stability ratios indicate a weak interfacial barrier and increased emulsion separation efficiency[2]. The stability of dispersed systems according to the DLVO theory is described as the balance between positive and negative forces between droplets which includes attractive van der Waals forces and repulsive electrostatic forces of the double-layer. The interaction of these forces is what defines the energy barrier that has to be surmounted to cause the droplet coalescence. High energy barrier is an indication of a stable emulsion; whereas low barrier enables the aggregation and separation of droplets and phases. Therefore, low values of the stability ratio (W = 1) correspond to weak interfacial resistance and quick coalescence, whereas high values (distinctly greater than 1) are evidence of strong repulsive forces and high emulsions stability.

8. Dipole interaction model: Electrostatic instability

During the electrostatic emulsion separation process, the droplets are polarized due to the influence of an applied electric field and thus they experience forces of attraction between their dipole poles. The droplet-droplet interaction strength is approximately given by the following. [74]:

$$F_e \propto \varepsilon r^3 E^2 \tag{7}$$

Where: ε is the dielectric permittivity of the continuous phase, $r^3$is the droplet radius, and E^2 is the electric field strength. Mechanistically, this relationship demonstrates that the bigger the droplets and the greater the electric fields, the greater the forces of interaction, thus, the more effective the droplet attraction and coalescence. The cubic dependence on droplet radius shows the significance of droplet expansion in the electrostatic separation procedures whereas the quadratic dependence on electric field strength reveals the role of field strength in hastening coalescence. Nevertheless, this model is based on perfect dipole interactions and ignores other phenomena like deformation of droplets, resistance at interfaces between phases, and non-homogeneous distribution of the electric field. Other effects like the presence of surfactants, interfacial viscoelasticity, and charge relaxation may also have an effect in real emulsions and cause the trend to be deviated. Table 2 shows a comparison between removal methods in terms of Dominant Mechanism, Effect on Droplet Size Distribution, Key Performance Metric, Scalability, Cost, and Typical Separation Performance. The efficiency of emulsion separation is determined primarily by the extent to which each technique affects droplet size distribution and interfacial dynamics, rather than by operating intensity alone.

Demulsification Method	Dominant Mechanism	Effect on Droplet Size Distribution	Key Performance Metric	Typical Separation Performance	Main Limitations	Scalability	Cost	Reference
Gravity separation	Density difference controlled settling governed by Stokes-type hydrodynamics	No active modification;performance depends entirely on initial droplet diameter	Settling velocity ($v \propto d^2$)	Very slow separation; ineffective for droplets <10 μm	Extremely slow kinetics; unsuitable for stable emulsions	Industrial	Low	[11]
Chemical demulsification	Interfacial film weakening, interfacial tension reduction, enhanced coalescence	Promotes droplet growth from micron to tens-of-microns scale	Increase in effective droplet diameter and coalescence rate	High separation efficiency under optimized dosage and temperature	Strong system specificity; sensitive to dosage and mixing	Industrial	Moderate	[3]
Electrostatic demulsification	Droplet polarization, dipole–dipole attraction, electro coalescence	Rapid enlargement even for initially fine droplets	Coalescence rate $(\omega c \propto E^2 r^2)$	Very high separation rates compared to gravity settling	Energy demand; dependence on electrical conductivity	Industrial	Moderate–High	[44]
Centrifugation	Enhanced apparent gravity via centrifugal acceleration	Efficient removal of fine droplets without prior coalescence	Effective acceleration $(g_{eff} \gg g)$	High separation rates even for small droplets	High capital cost and operational energy consumption	Industrial	High	[18]
Dissolved air flotation (DAF)	Bubble–droplet attachment and buoyancy-driven flotation	Apparent droplet size increase via bubble–droplet aggregation	Optimal performance for droplets 10–100 μm	Moderate-to-high efficiency for suitable droplet sizes	Limited efficiency for nano-emulsions	Industrial	Moderate	[14]
Membrane-assisted coalescence	Surface-induced collision, wetting control, and pore-scale coalescence	Converts sub-micron droplets into separable larger droplets	Capillary-controlled attachment and coalescence	High downstream separation efficiency	Membrane fouling; flux decline	Pilot–Industrial	High	[29]
Ultrasonic demulsification	Acoustic cavitation and interfacial film rupture	Rapid droplet agglomeration under optimized acoustic conditions	Cavitation-induced collision frequency	High separation rates at optimal power and frequency	Energy consumption; scale-up challenges	Lab–Pilot	Moderate–High	[75]
Nano-material-assisted coalescence	Surface-mediated collision enhancement and wettability control	Strong promotion of droplet growth under mild conditions	Increased collision efficiency at low energy input	Accelerated separation at relatively low energy demand	Material cost; long-term stability issues	Lab–Pilot	High	[76]

Table 2: Types of demulsification methods and the key step.

9. Surfactant classifications

Organization of these agents, based on chemical structure. Their mechanism of action in turn is determined by their properties when they come in contact with oil and water. It can be divided into ionic and non-ionic, but with other branches on its special chemical nature, according to the basic division. Figure 5 shows the classification and the molecular structure of surfactants, and how they are amphiphilic and thus can be adsorbed at the oil-water interface. Such an amphiphilic structure enables surfactants to decrease interfaces tension, and alter interfaces films properties through alignment of their hydrophilic head groups toward the aqueous environment and hydrophobic tail groups toward the oil environment. Surfactants may stabilize or destabilize emulsions, depending on their type and charge, forming rigid interfacial films or destabilizing natural emulsifiers and reducing interfacial resistance.

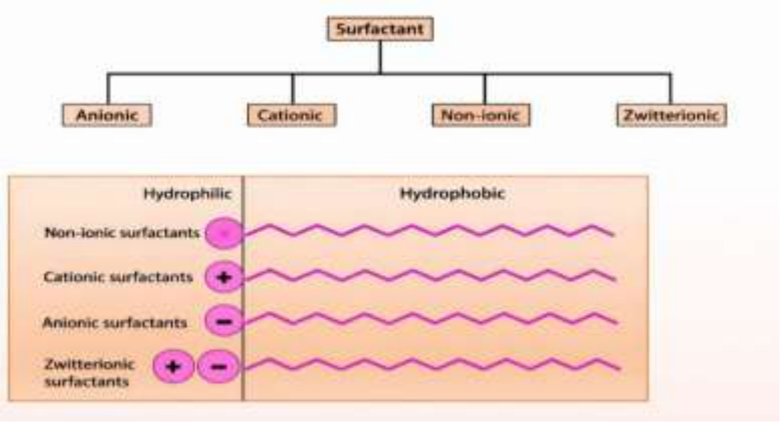

Fig.5. Classification of surfactants based on charge type (anionic, cationic, non-ionic, and zwitterionic) [77].

9.1 Anionic surfactants

Demulsifiers are hydrophilic non-ionic surfactants that are usually made up of hydrophobic and hydrophilic groups. Polyether demulsifiers have a few weaknesses; they are very costly, they need huge quantities of doses and demulsification is not effective. All these shortcomings lead to poor emulsification outcomes as compared to the optimum condition. In contrast, anionic surfactants, examples of which are commonly used sulfates and sulfonates, are characterized. Anionic surfactants interfere and break the stability of the emulsions by decreasing the surface tension of the emulsions and increasing their separation. These materials can be characterized by low cost, low doses, high demulsification efficiency and high adaptability [78].

9.2 Cationic surfactants

Cationic emulsions have the advantage of cationic groups. One typical one is hexadecyltrimethylammonium bromide. The cationic surfactants react with the anions in the emulsion, altering the surface properties of the emulsion, and causing phase separation [79].

9.3 Zwitterionic surfactants

These compounds may alter their behavior depending on the pH of the media since they have positive and negative charges. This two-sidedness allows treating types of emulsions with diversity.

9.4 Non-ionic surfactants

Non-ionic demulsifiers are the most popular emulsifiers used in the petrochemical or crude oil industry and they have zero net electrical charge. The effectiveness of these demulsifiers is based on the fact that they are insoluble at the oil-water interface where they form van der Waals and hydrogen bonds to change their characteristics. Hydrogen and salinity tend to be more sensitive to ionic emulsifiers. Non-ionic surfactants do not have any ionic groups on their molecules. An example is methyl cellulose. Non-ionic surfactants are able to increase dispersement of asphaltenes, lower emulsion viscosity, and phase separation by altering the particle particle size and dispersion [24,25].

10. The Demulsification Mechanism

This is a three-phase process that comprises complicated interactions at the interface between the water and oil phases. This pro-process encompasses relocation of the demulsifier to the oil-water interface and destabilization of the interface. Figure 6 shows the basic mechanism of demulsification, such as flocculation, coalescence and the phase separation by the creaming or sediment. Introduction of demulsifiers changes interfacial characteristics, and leads to droplet aggregation (flocculation) and film drainage and droplet merging (coalescence). The dominance of the gravitational forces increases with the size of the droplets and results in phase separation either by creaming (upward movement of the lighter drop-lets) or by sedimentation (downward settling of the heavier droplets). This sequence emphasises the importance of interfacial change and droplet-size development in defining separation efficiency.

10.1 Agglomeration

The demulsifier overcomes the repulsive forces of the dispersed droplets and the droplets come in contact with each other to create aggregates of clumped particles.

10.2 Coalescence

The demulsifier destabilizes and then destabilizes the interface between the dispersed droplet and the continuous phase, which allows it to combine with the other droplets to create a larger droplet.

10.3 Sedimentation

The higher density of the bigger droplets will cause the bigger droplets to either sink (water-in-oil sedimentation) or to rise to the surface (larger oil-in-water agglomeration), resulting in phase separation. The chemical emulsion removal diagram is an illustration of interfacial displacement and drainage kinetics with the focus being on the reduction in interfacial elastic viscosity (E) and interfacial tension(γ) as variables controlling droplet fusion [80]. A rough equation that characterizes the dependence of the rate at which droplets adhere to the surface on the elasticity of the interfacial membrane, and the alteration in surface tension[81].

$$\frac{d\gamma}{dt} \propto kE \tag{8}$$

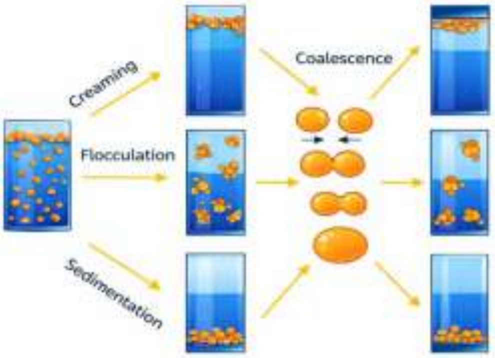

Fig .6. Schematic diagram of demulsification, which shows the successive stages of flocculation, coalescence, creaming and sedimentation[82].

11. Types of demulsifiers and synthesis methods

Demulsifiers are different chemical substances that are aimed at breaking down emulsions, i.e., breaking the line dividing them.

11.1 Polyether-based emulsifiers

Are widely used due to their water-fat tunability and excellent surface activity. Ethylene oxide and propylene oxide make up most of the polymers.

Synthesis Method

Chain polymerization of ethylene oxide (EO) and boron oxide (PO) is carried out on an agent molecule (one of the phenols, alcohols, or amines) using a catalyst (potassium hydroxide, or KOH). The molecular weight, block structure (triblock, di-blocks, and so on) and the EO to PO ratio are carefully adjusted to achieve the best performance[83]. One such type was produced by FYJP emulsion by placing or vaccinating carboxyls on nonioni polyethyne which was produced by ethylene oxide and oxide of arrogance [84].

11.2 Ionic demulsifiers

With characteristics like great thermal stability and controlled solubility, these molten salts at or close to room tempera-ture hold promise for the future.

Synthesis Method: -

Ionic demulsifiers are usually synthesized through organic reactions. For example, PEDA-Br is synthesized with GEDA-Br through a simple two-step process. The first involves specific organic reactions to form the ionic liquid structure. Other ionic liquids, such as GC@DA, are obtained through reactions of glucose derivatives with specific amines and acids to form the desired ionic structure[85].

11.3 Cyclodextrin-based demulsifiers

offer selective interactions at the interface because of their molecular structure, and so are an environmental friendly choice. Nevertheless, their use is hindered by the high cost and manufacturing difficulties.

Synthesis Method: -

This form of degreaser is made by chemically modifying cyclodextrins. As an example, betacyclodextrin was used as the raw material to produce CD-LA. This was accomplished by acylation of the hydroxyl groups followed by dodecylamine grafting. This adjustment increases its contact with the oil-water interface [86].

11.4 Magnetic materials

Of significance since they can be readily recovered and reused through a magnetic field, thus minimizing the utilization of chemicals. However, studies on their long-term stability and concerns on nontoxicity are still in progress ongoing. [86].

11.5 Biomaterials

This type of material is a biodegradable and sustainable option, according to environmental regulations. Nonetheless, its cost of pro-duction is high and research is lacking to make it widely used. [87].

11.6 Traditional surfactants

Cost less, are more efficient, and can be effective in a wide variety of emulsions, but can need greater amounts of them to be as efficient as the advanced types. [88].

11.7 Nano-Demulsifiers

Recent research has indicated that nano-demulsifiers can successfully perform fast and effective separation of crude oil emulsions due to an improved surface activity and surface modification. As an illustration, kaolinite nanoparticles in the form of a new nano-demulsifier (PPA@KAO) prepared by adding polyether-polyquaternium successfully provided high emulsification separation efficiency (around 96.75) of surfactant-stabilized crude oil emulsions in moderate conditions (30 C, 20 minutes). The amphipathic nature of the nanoparticles increased the surface adsorption and droplet agglomeration[89]. In the same vein, Janus magnetic graphene oxide nanoparticles (MJGO) containing $Fe3O4$ was able to separate oil-in-water emulsions with over 96% efficiency, and can be recycled and reduced to lower the electrostatic repulsion which has important mechanical roles[90]. Other articles were on the Fe3N@F magnetic demulsifier, a fluorinated polyether-coated iron nitride nanomaterial, which showed high demulsification performance (removing about 89.4% of water) and high reusability (more than six cycles) under the best conditions [91].

11.8 Hybrid and composite nanomaterials

Composite magnetic nanomaterials are increasingly being of interest because of their dual action (magnetic separation + interfacial destabilization). As an example, magnetic polyether/TiO 2 -carbon heterostructures with induction and neutral magnetic properties can be recycled and recrystallized with emulation separation rates of more than 85 percent in neutral and acidic conditions with high environmental stability[92]. Moreover, research performed on magnetic nano-crystals of cellulose note an environmentally friendly magnetic emulsion separation process has the ability to remove 100 percent of water at high temperatures and significantly decrease surface tension, which is indicative of bio-nanomaterials[93].

12. Functionally modified membranes and hybrid membrane systems

Recent research on functionally modified membrane in the separation of oil-water in emulsions reports on the development of strategies to enhance performance through the functional modification of their surface and minimization of contamination. These hybrid membrane systems aid membrane separation with a specially designed surface chemistry to allow efficient emulsion and phase separation, suggesting a novel category of materials that couples conventional membrane filtration with interfacial destabilization mechanisms[94]. Simultaneously, composite membranes, reinforced with graphene oxide doped with titanium dioxide and silica nanoparticles (PVDF/GO–TiO_2/SiO_2) performed better in oil-in water emulsion separation, which proves the effectiveness of the nanomaterial introduction into the membrane matrices in terms of enhancing the performance of the membrane through its synergistic effect on permeability [95].

13. Comparison of demulsifier types

In Table 3. This section presents a comparison of the demulsifiers types, how they are produced and their key characteristics (merits and demerits).

	Method of synthesis	Key Features	Advantages	Disadvantages	Scalability	Cost	References
polyether	EO/PO chain polymerization on catalyst	HLB adjustable polymer structure,	-High efficiency -Versatile use -Adjustable features	- Heat sensitive - Possibly environmentally hazardous	Moderate	- Heat sensitive - Possibly environmentally hazardous	[62]
Ionic liquid	multistep organic reactions	Adjustable to solubility Molten salts at room temperature High thermal stability	Adjustable structure Tolerance to acidic and salty environments High efficiency with low doses	- High cost - Potentially toxic - Complex to synthesize	High	- High cost - Potential toxicity - Complex synthesis	[85]
Cyclodextrin	Chemical modification of cyclodextrin	hollow structure	Good performance Environmentally friendly Specific interaction with molecules	- Unstable performance - Cost and scalability	Moderate–High	- Unstable performance - Cost and scalability limitations	[86]
magnetic materials	Coating magnetic nanoparticles with chelating agents	Ease of separation Magnetic properties	Use small doses Easy separation Reusable Enhance separation process	- Difficulty in synthesis - Variable stability - Possible toxicity of nanoparticles	High	- Difficult synthesis - Stability issues - Possible nanoparticle toxicity	[96]
Bio-demulsifier	Chemical modification of natural compounds such as plant oils and cellulose	Derived from renewable resources Biodegradable	Good performance Environmentally friendly Sustainable sources	-Performance is variable. - Research is limited. - Cost and scalability.	Moderate	- Variable performance - Limited research - Cost and scalability challenges	[87]
surface active	Various chemical reactions	Reduces surface tension Surfactant	Flexible and efficient Economical	- Requires higher doses - Less specificity than - specialized uncoupling inhibitors	Low	- Requires higher doses - Lower specificity	[88]

Table. 3. A comprehensive overview of the various types of demulsifiers, their advantages, limitations and synthesis methods.

This comparison table highlights the various methods of synthesis or design of demulsifiers as well as the key features, advantages and disadvantages of each method.

14. Effect of variable

14.1 Effect of pH on the Electro Kinetic Properties of Crude Oil Emulsions

The zeta potential of oil droplets is affected by the chemical composition of the oil, aqueous phase pH and salinity, and the existence of surfactants[97]. The zeta potential is the electrical potential at the slipping plane of the droplet interface and has often been employed as a measure of electrostatic stability of emulsions. Increased absolute values of zeta potential denote greater electrostatic repulsion between droplets, resulting in greater emulsion stability, and decreased values prefer aggregation and coalescence of droplets. The figures below compare the change in zeta potential with pH of the various crude oil samples (A, B, and C). In all the samples, the findings indicate that there is a monotonic decrease in zeta potential with an increase in pH, with an increase in salinity leading to a decrease in the zeta potential. As shown in Figures 7–9, the zeta potential decreases with increasing pH, which means the magnitude of the surface charge decreases. This phenomenon implies that the electrostatic repulsive force between droplets is weakened, thus, allowing droplet aggregation and coalescence. Also, rising salinity decreases the magnitude of zeta potential further as a consequence of compressing the electrical double layer and thus a drop in the energy barrier between droplets. This effect increases the probability of droplet collision and coalescence, thus improving the separation efficiency.

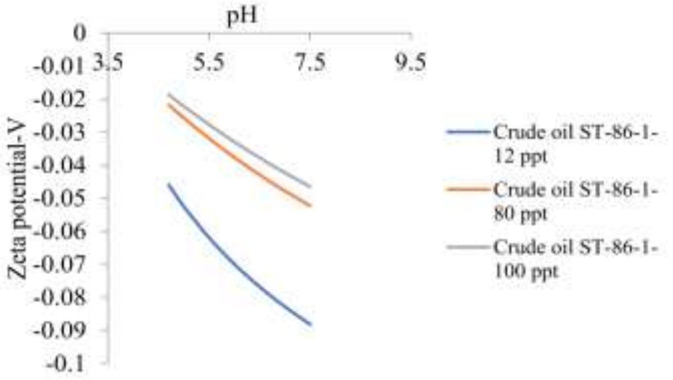

Fig.7: Influence of pH and salinity on zeta potential of crude oil sample(ST-86-1. 9.5) [98].

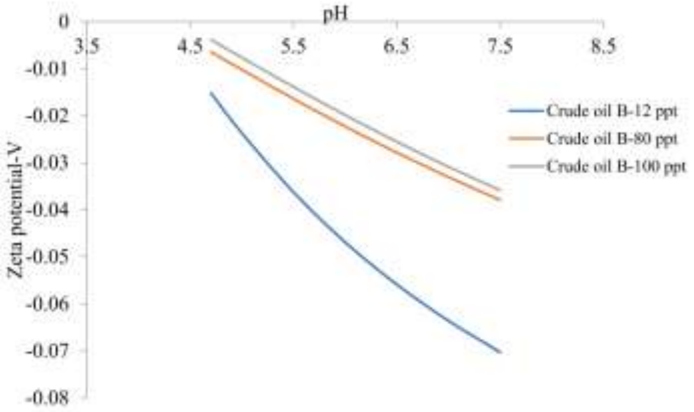

Fig.8: pH dependence of zeta potential of crude oil sample (B) with salinity (S). [98].

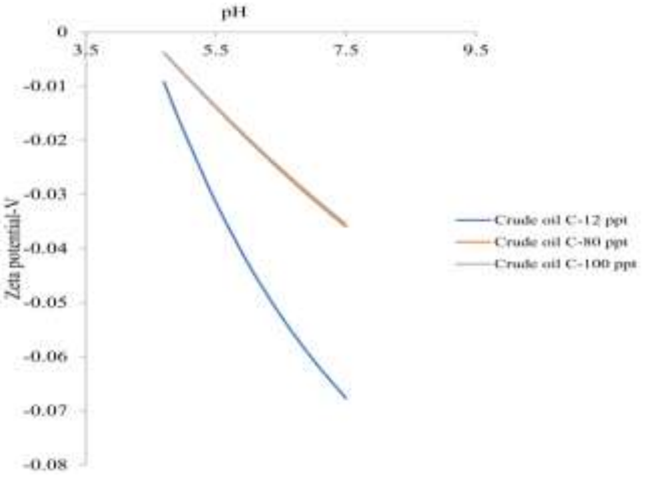

Fig.9: Zeta potential behavior of crude oil sample (C) at different salinity conditions (pH). [98]

where all of the oil samples have a lower zeta potential when the salinity is increased. Therefore, the trends depicted by these figures are similar to the ones reported in association to low-salinity water oil recovery activities.

14.2 Dose of Demulsifier Effect on Efficiency of Water Separation

Demulsifier dosage is a very crucial factor in controlling the efficiency of the separation of water in emulsions especially the water in oil (W/O) systems. The effect of commercial demulsifier Chimec 2439 on the time-dependent water separation efficiency of crude oil emulsions was systematically studied in this study. The Basrah crude oil was used to perform experiments with a constant water content of 20% and demulsifier concentration of 200, 300 and 400 ppm. As shown in Figure 10 water separation efficiencies of 67, 77 and 83 were obtained at these concentrations respectively. A same trend was observed in the separation of Kirkuk crude oil, which is illustrated in Figure 11 where the highest separation efficiency was 88% at the highest dosage of demulsifier (400 ppm). The improved performance of the separation at high concentrations can be explained by the efficient adsorption of the demulsifier molecules in the oil-water interface, which replaces interfacially active asphaltenes. This mechanism destabilizes and dilutes the hard interfacial film around the dispersed water droplets, and eventually causes the film to break resulting in droplet coalescence, thus enabling an effective phase separation[99].

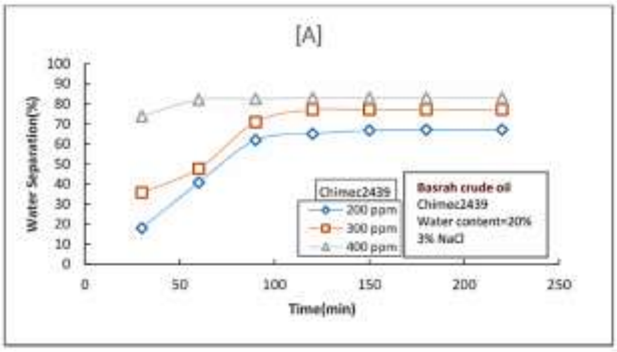

Fig.10: Influence of dose of demulsifier (Chimec2439) on separation efficiency of 20 percent water content in (A): Basrah crude oil.

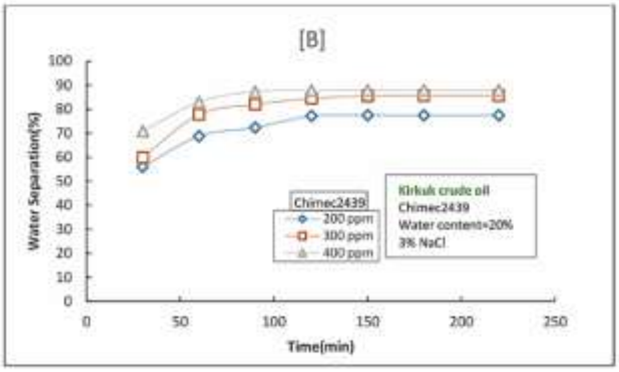

Fig .11: Influence of dose of demulsifier (Chimec2439) on separation efficiency of 20 percent water content of (B)Kirkuk crude oil.

14.3 Effect of temperature on water removal efficiency

The temperature is an influential and important factor in the process of crude oil-water separation, because it directly impacts the dissolution and distribution of demulsifying agents in the oil and water layers, and the coalescence of dispersed water particles [121]. Higher temperatures result in a strong decrease in viscosity of the continuous phase, as well as, a high increase in the mass diffusivity of demulsifying agents in the system. In addition, high temperatures lower the interfacial viscosity of the dispersed (internal) phase, as well as, the interfacial tension of the water-in-oil emulsion, which facilitates the droplet coalescence and enhances phase separation efficiency. Figure 12 shows the dependence of water removal efficiency on temperature. As can be seen in the figure, the efficiency of water separation has a significant impact on raising the temperature. Temperature significantly affects the performance of the demulsifying agents in terms of dehydration. Higher temperature of 50 C to 80 C increased the efficiency of dehydration of the sample treated with the CTAB agent to 90% as compared to 60%.

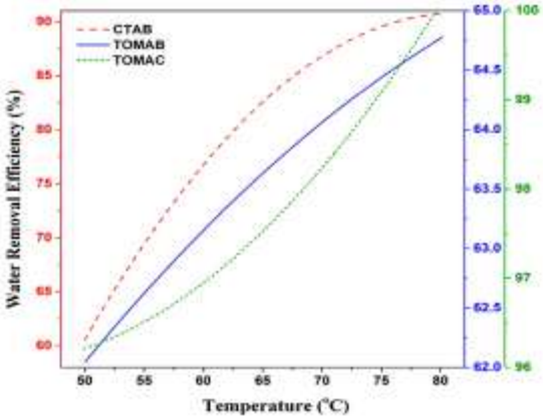

Fig.12. Impact of temperature on the effectiveness of water removal of three agents (CTAB, TOMAB, TOMC)

15. Conclusion

Oily Wastewater and Crude oil emulsions remain a big challenge in the production of petroleum as they have complicated interfacial characteristics and are very stable. This review shows that the interfacial phenomena, the droplet-scale interactions, and the capacity of treatment methods to facilitate droplet coalescence are the basic mechanisms controlling the separation efficiency. Comparative study of the methods of demulsifying shows that methods involving interfacial modification and controlled growth of droplets typically perform better than methods alone involving force-based methods especially in highly stabilized emulsions. Traditional chemical and electrostatic demulsification methods are still in wide use at an industrial level, with new approaches-including ionic liquid-based, bio-derived, cyclodextrin-based, and magnetic demulsifiers-providing a higher level of performance in harsh environments but still restricted by cost, synthesis complexity, and scalability. Notably, there is no universal method of demulsification, and successful treatment involves combining a variety of approaches that are dependent on the properties of the emulsion, working conditions, and financial limitations. In general, film behavior between surfaces and droplet interactions are found to be the major factors that control separation performance and droplet coalescence is a more important factor in separation performance than external forces alone. Mechanism-directed design of demulsifiers, enhanced droplet-scale characterization methods, development of scalable and cost-effective materials, and integration of hybrid treatment systems should then be the focus of future research. Moreover, to close the gap between the laboratory scale innovation and the sustainable implementation in industries, comprehensive techno-economic evaluation and life-cycle assessment are necessary. Better insights into interfacial science, along with material development in an environmentally responsible fashion, will be central to the development of next-generation demulsification technologies, as well as the enhancement of oily wastewater treatment performance.

16. Acknowledgement

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17. References

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