Petroleum Emulsions-Properties, Applications, and Challenges in The Oil and Gas Industry: A Review

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ABSTRACT

Petroleum emulsions play a vital role in water injection enhanced oil recovery (EOR) technologies, as they can significantly increase crude oil production rates. These emulsions, typically formed during the interaction of injected water with reservoir fluids, present several technical challenges, including stability control, ease of transportation, and efficient separation and processing. Understanding the mechanisms that govern emulsion stability is therefore essential for optimizing EOR operations. Over the past decades, substantial research has been devoted to elucidating these mechanisms and developing strategies to control them. Recent trends highlight a shift from traditional synthetic polymer emulsifiers toward more sustainable and environmentally benign alternatives. Natural materials, biopolymers, and solid particles have been explored as promising candidates to replace petroleum-derived stabilizers, thereby reducing environmental impact and improving biodegradability. Surfactants—particularly those with tailored molecular structures—have also gained prominence due to their ability to enhance emulsion stability more effectively than conventional chemical agents. This review provides a comprehensive theoretical framework for understanding emulsion formation, examining factors such as interfacial tension, droplet size distribution, and the role of surfactant adsorption. It discusses common challenges associated with raw water emulsions in EOR processes, including issues of coalescence, phase inversion, and demulsification. Furthermore, it surveys recent advancements in stabilization technologies, with particular emphasis on innovative approaches such as shrinkable surfactants and advanced smart nanomaterials that respond to environmental stimuli. By integrating these emerging solutions, the review underscores the potential for achieving more sustainable, efficient, and adaptable emulsion management strategies in modern EOR operations.

1. Introduction

Petroleum emulsions are formed when water and oil phases disperse, resulting in either oil-in-water (O/W) or water-in-oil (W/O) emulsions. About emulsions concerning production processes, water-in-oil emulsions are by far the most prevalent, where water droplets are suspended within the oil phase [1]. These emulsions are usually generated when water is produced together with crude oil, frequently at the wellhead or during transport. The recovery of crude oil is accompanied by these kinds of emulsions, which are severely detrimental to the succeeding processes. They have to be dealt with in transportation and refining as well as during oil extraction, most significantly in enhanced oil recovery (EOR) processes [2].

Crude oil emulsions significantly alter fluid properties, increasing viscosity and reducing flow rates, which complicates processing, flow rate, and separability of crude oil, making it more challenging to handle and process. Increased viscosity gives higher flow resistance in the pipelines and often requires additional treatment processes for water to be separated from the oil [3]. Emulsions are usually stable, i.e., once formed, they tend to remain for long periods, thus complicating separation efforts, and though this poses a significant challenge, emulsions could also be beneficial, especially in EOR techniques, where their formation could lead to an increase in oil recovery rates by improved mobilization of trapped oil [4].

Traditionally, the oil sector counted on different surfactants and chemical promoters for emulsion breaking and water-oil separation. However, the recent trend has directed the focus more toward the alternative surfactants and solid stabilizers that are environmentally benign and based on nature [5]. This increasing preference is primarily due to changes in affirmative action requiring greener methods in petroleum activities, coupled with more stringent regulations regarding environmental impacts during crude oil production and transport [6].

In the following, we intend to review petroleum emulsions in general and water in crude oil emulsions in particular. Essential tools to study the fundamental mechanism of emulsification, as well as to classify emulsions formed in crude oil, will be discussed. In addition, this work will also review the recent progress of stabilizing these emulsions, mainly focusing on natural surfactants, solid particles, and nanostructures. Last but not least, the potential of emulsion for application in EOR and its impacts on oil recovery efficiency will be discussed [7].

Fig. 1. depicts a geologic cross-section delineating the various strata occurring in an oil and gas reservoir. The structure is partitioned into several key features from base to summit. The Source Rock, or the location of hydrocarbon genesis, exists at the bottom. Above this, we can see the Water layer followed by the Oil layer. Sitting on top of the oil is the Gas layer, and at the uppermost part is the Impermeable Rock cap, which serves to contain the hydrocarbons, preventing them from escaping. This other structure is contained within Porous Rock, which facilitates the accumulation of these resources. The diagram illustrates clearly the arrangement of geology which is usually associated with a hydrocarbon reservoir [8].

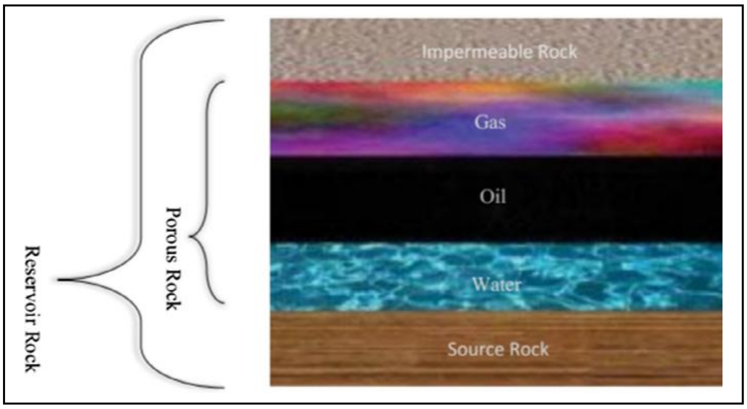

Fig. 1. Reservoir layers

2. Fundamentals of Petroleum Emulsions

Petroleum emulsions are colloidal mixtures of two immiscible liquids, typically water and oil. In an emulsion, one phase (water or oil) is dispersed as droplets within the other phase. The nature of the emulsion-whether water-in-oil or oil-in-water-depends largely on the relative amounts of water and oil present and the nature of the emulsifying agents [8].

2.1. Types of Petroleum Emulsions

Water-in-Oil (W/O) Emulsion: In a water-in-oil emulsion, water droplets are dispersed in the continuous oil phase. This is the most common type of emulsion encountered in crude oil production. These emulsions are created when water is co-produced with crude oil, and water droplets are stabilized in the oil phase [9].

Oil-in-Water (O/W) Emulsion: In an oil-in-water emulsion, oil droplets are dispersed in the continuous water phase. This type of emulsion is less common in crude oil production but may be encountered in some industrial applications where water is used as a dispersing medium [10].

2.2. Mechanisms of Emulsion Formation

An example of an emulsion is produced when two immiscible liquids, such as oil and water, are mixed under certain conditions. However, the amount of energy provided to the mixture must be sufficient to break the inner stability barrier caused by the repulsion between the two phases for the emulsion to be stable. It is on this point that emulsifiers, technically surfactants, become useful [11].

Surfactants: Molecules that contain both water-attracting (hydrophilic) and water-rejecting (hydrophobic) parts are called surfactants. These molecules reduce the interfacial tension between water and oil (both of which are immiscible), enabling water droplets to stay suspended in the oil phase [12].

Solid Particles: Solid particles, other than surfactant, even fine clays, minerals, or nanoparticles, may also act to maintain emulsion stability. Such solid particulates can adsorb at the oil-water interface and act to inhibit coalescence of the droplets and disperse the emulsion [13], as shown in Fig. 2., which illustrates the stabilization mechanisms for nanofluids [14].

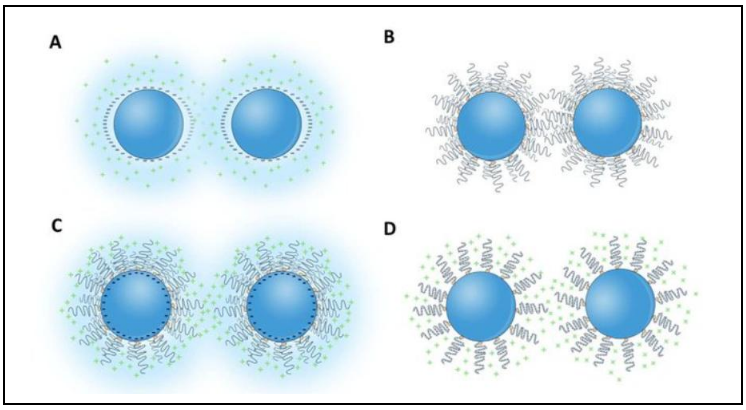

Fig. 2. Schematic of stabilization mechanisms for nanofluids: (A) electrostatic stabilization, (B) steric stabilization, (C, D) electrosteric stabilization.

2.3. Stability of Oil-In-Water Emulsions

The stability of petroleum emulsions has been reported to be influenced by several factors, such as temperature, salinity, and the chemical nature of the surfactants or stabilizers used. Emulsions are not stable systems unless they are stabilized adequately with emulsifiers, and if allowed to stand, they will separate into two or more phases. Environmental parameters like temperature (see Table 1) critically impact stability lifetimes [15], [16].

Table 1. Factors Affecting Emulsion Stability

Factor	Effect on Emulsion Stability
Temperature	High temperatures tend to destabilize emulsions by reducing viscosity and causing phase separation [17].
Salinity	Increased salinity can enhance the stability of certain emulsions, depending on the surfactant [18].
Surfactant Type	The choice of surfactant significantly affects the emulsion's stability and the ease of separation [18].

3. Water-in-Crude Oil Emulsions

Water-in-crude oil emulsions are typically formed during crude oil production when water is co-produced with the oil. These emulsions are formed when water droplets are dispersed within the crude oil phase, making them highly viscous and difficult to process. The stability of these emulsions depends on several factors, including the concentration of water, the type of crude oil, and the presence of emulsifiers [19], [20]. Characteristics of Water-in-Crude Oil Emulsions:

(a) Viscosity of Water-in-oil emulsions raises: the viscosity of the crude oil. This relatively high viscosity results in a considerable frictional loss for oil pipeline transportation [21], [22]. (b) Separation problems: Water-in-oil emulsions are not always easy to separate, and dedicated methods, including chemical demulsification or centrifugation, are needed. (c) Refining impact: This water can also hinder refinement by complicating the separation of water from the crude [23], [24].

4. Challenges in Handling Water-in-Crude Oil Emulsions

Water-in-crude oil emulsions present specific challenges to the petroleum industry and can affect various stages of the petroleum production, transportation, and processing. The emulsions result when water droplets are dispersed into the oil phase of the crude and form a complex and stable mixture that is very viscous. Conversely, the water in the oil increases viscosity, making it challenging to pump the oil with energy-consuming pipes and long-distance transport. These considerations increase not only the amount of energy used for pumping, but also the likelihood of clogging problems and wear in the pipelines, resulting in higher maintenance costs and pump downtime [25].

Water-in-crude oil blend emulsions present complicated problems not just with transportation, but also add complexities to the refining of oil. It is usually challenging to extract the water droplets from the oil owing to their small size and uniform distribution within the crude oil itself. These stable emulsions are particularly difficult to separate in cases where the emulsion is highly viscous or contains stabilizing surfactant droplets that provide additional rigidity, using techniques such as mechanical centrifugation or gravitational settling [26].

Removing water from crude oil is usually expensive and labor-intensive. In many instances, other treatments must be provided to break the emulsion, like adding chemicals, applying heat, or using other specific separation devices. All these operations not only increase operational expenditure but also pose a greater threat to the environment. For instance, the mismanagement of water-in-oil emulsion systems may lead to the discharge of harmful pollutants such as heavy metals and hydrocarbons [27].

The potential for corrosion is another concern. Water present in crude oil is a precursor to various corrosion-producing materials - hydrogen sulfide and dissolved salts - which are extremely deleterious to pipes, storage tanks, and other types of equipment. Sooner or later, this type of corrosion is going to damage the infrastructure, resulting in increased maintenance and repair costs, service cessation, and safety concerns.

Furthermore, water-in-oil emulsions also present challenges in the context of environmental regulations. The discharge of untreated or inadequately treated emulsions into the environment can lead to severe ecological consequences, including contamination of water bodies, soil, and marine ecosystems. This has increased the regulatory scrutiny on petroleum companies, requiring them to adopt better treatment and disposal methods for these emulsions. Table 2 illustrates the challenges in dealing with water-in-crude oil emulsions [8].

Table 2. Challenges in Handling Water-in-Crude Oil Emulsions

Challenge	Description
Increased Viscosity	Higher viscosity due to the presence of water makes pumping and transporting crude oil more challenging [12].
Separation	Difficult separation of water from the oil phase requires additional processing steps [18].
Pipeline Blockages	Increased viscosity and the presence of emulsions can lead to blockages and wear in pipelines [19].

5. Solutions to the Challenges

Several practical solutions have been applied to heterogeneously suspended water-in-crude oil emulsions. One of their more popular methods includes the application of demulsifiers. These agents are thermodynamic constants of a given emulsion system, which drastically lower the stability of water droplets in oil, allowing them to fracture and be removed from the oil phase. They act by changing the interfacial tension of the water phase and oil phase, which breaks the emulsion. The choice of demulsifier is critical and is often made based on the composition of the crude oil and emulsion features like water droplet count, temperature, and constituents of the crude oil [28].

Demulsifiers are often effective in many cases; however, they tend to fall short on highly stable emulsions. In those situations, applying heat has proved to be a better approach. If the crude oil is heated to a specific temperature, the viscosity will decrease, which will make it easier for water droplets to come together. If the droplets combine, they will grow bigger and easier to split. It is important to note that the oil should not be in danger of overheating, which means losing value as traditional oil or other unappealing by-products [29].

Emulsions with water in oil also require some form of mechanical separation that is equally as important as the other types of separation. Water is removed from the oil using centrifugal separators, which utilize high-speed rotation to exploit the difference in density between the two phases. Electric fields are applied in other types of electrostatic separators to encourage the coalescence of water droplets, thereby facilitating the separation process. About other treatments, they are generally used with chemicals so that their efficacy increases and the environmental impact decreases [30].

In the more advanced operations, filtration systems and pipeline heaters are increasingly integrated as part of the architecture. These systems maintain the flow of crude oil and prevent any blockages by it; for example, pipeline heaters would reduce the viscosity of crude oil so that it can flow more easily through the pipe, thus reducing the chance of obstruction happening within the pipeline. On the other hand, filtration systems could add value to crude oil by removing suspended solids and water droplets, thereby reducing corrosion possibilities [31].

Another way of reducing the environmental impact posed by water-in-oil emulsions is by improving disposal techniques. In some cases, reclaimed water from the crude oil separation is reused after treatment in other oil production and refining processes, where it can achieve closed-loop functionality. Such systems prevent their water from going out into the environment, hence reducing contamination risks. Furthermore, there is progress being made in the use of nanotechnology for oil-water separation, which promises more ease and less harm to the environment [32].

Innovative approaches like microfluidic devices are helping scientists find new ways to separate water from crude oil. These devices consist of miniature channels that can control the flow of liquids, enabling them to use the distinct properties of emulsions on a smaller scale. These technologies are in the initial development phases, which makes them ideal for research because they can make the separation emulsion process easier and lessen the environmental issues caused by water-in-oil emulsion [33], [34].

As oil and gas production advances, especially during secondary or tertiary recovery processes, the amount of water produced increases significantly. Next, we see the Oil layer, where crude oil is stored in porous rocks. This layer is what oil production primarily targets. Above the oil is the Gas layer, which consists of natural gas that accumulates above the oil due to its lower density. The topmost layer is the Impermeable Rock, which acts as a seal, preventing oil and gas from migrating to the surface. It plays a crucial role in trapping the hydrocarbons within the reservoir. Between the Impermeable Rock and the Source Rock lies the Porous Rock**,** which holds the oil, gas, and water in its pores. This structure helps maintain the reservoir's ability to store these valuable resources.

6. Crude Oil Emulsions Formed During Enhanced Oil Recovery (EOR) Processes

Enhanced Oil Recovery (EOR) refers to a set of methods used to extract more oil from a reservoir after the primary and secondary recovery methods have been exhausted. Emulsions play a significant role in EOR processes, especially when water is injected into the reservoir to help displace the oil. These emulsions, often water-in-oil emulsions, can either enhance or hinder the efficiency of oil recovery, depending on their stability [34].

EOR techniques can be classified into several categories: (a) Thermal EOR: This involves injecting steam into the reservoir to reduce the viscosity of crude oil, making it easier to extract [31]. (b) Chemical EOR: This involves the injection of chemicals such as surfactants, polymers, and alkaline solutions to increase the efficiency of oil displacement. (c) Gas Injection EOR: CO_2 or nitrogen gas is injected to help force the oil to the surface [32].

6.1. Formation of Emulsions in EOR

In EOR, emulsions form when water is injected into the reservoir to help mobilize oil. These emulsions can significantly improve oil recovery rates by breaking the capillary forces that trap oil in the reservoir. However, their formation also complicates separation and transportation.

Chemical Surfactants in EOR: Surfactants are commonly used in chemical EOR processes to stabilize emulsions and improve oil displacement. However, the same surfactants that enhance oil recovery can also make the emulsions more stable, creating challenges in separation and handling [21], [34].

Nanomaterials for EOR: Recent advancements in nanomaterial technology have shown promise in improving emulsion stability during EOR. Nanoparticles can help stabilize the emulsion, improve recovery rates, and reduce the challenges associated with separating water and oil. Table 3 shows the effect of enhanced oil recovery methods on emulsion formation, stability, and shape. Figure 3 shows how two different types of emulsions [34], [35], [36].

Table 3. EOR Method, Emulsion Characteristics, Recovery Boost, Separation Challenge

EOR Method	Effect on Emulsions
Thermal EOR	Heat can cause instability in emulsions, leading to phase separation issues [37].
Chemical EOR	Surfactants can stabilize emulsions, making oil recovery more efficient, but complicating separation [38].
Gas Injection	Gas injection can lead to the formation of gas-in-oil emulsions, which are more difficult to handle [37].

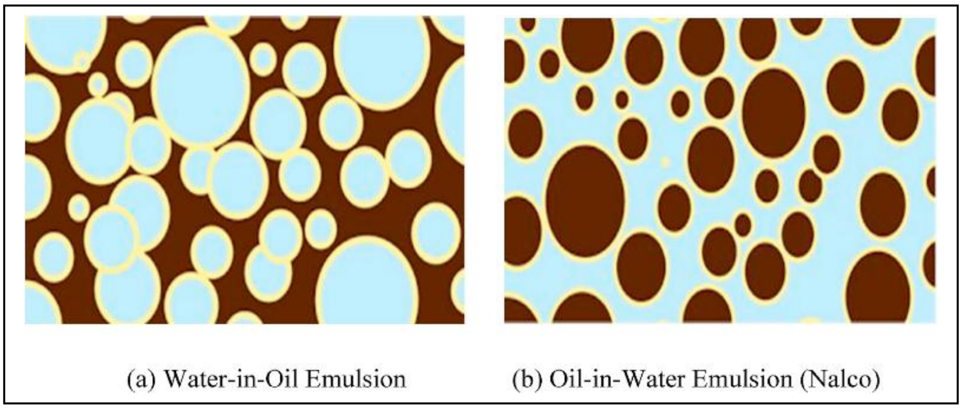

Fig. 3. (a) Water dispersed in oil emulsion (b) Oil dispersed in water emulsion [38]

Water-in-Oil Emulsion: It comprises small droplets of water (depicted by blue circles) dispersed in a continuous phase, which is oil (brown background). Here, the dispersed phase is water, and the continuous phase is oil. Usually encountered in crude oil extraction when water gets mixed with oil, creating problems for extraction as well as transportation [38].

Oil-in-Water Emulsion: Here, the emulsion consists of dispersed oil droplets (brown circles) within a continuous phase of water, represented by the light blue background. This is also the type of emulsion that usually comes across during several industrial processes, particularly in petroleum production, when the oil is dropped suspended in water. The two types of emulsions differ in terms of continuous and dispersed phases and separation treatment methods corresponding to each [9].

6.2. Stabilization of Water-in-Crude Oil Emulsions

Stabilizing emulsion forms of water-in-crude oil is critical for enhancing the efficiency of crude oil transport, storage, and processing operations. The development of new natural surfactants and solid stabilizers has led to new, more environmentally acceptable approaches for emulsion herding [39], [40], [41].

6.3. Ways for Stabilizing Emulsions

Surfactants: The addition of surfactants improves emulsion stability by lowering the interfacial tension of water and oil to a level where well plugging or complete blockage does not happen. Natural surfactants of plant and microbial origin are increasingly getting used to mitigate environmental harm [42], [43], [44], [45].

Solid Particles: Emulsions can be stabilized by solid particles like clay and nanoparticles, which are known to hinder the coalescence of water droplets. Table 4 shows the effect of stabilizers on emulsion stability [46], [47], [48], [49].

Table 4. Effect of Stabilizers on Emulsion Stability

Stabilizer Type	Effect on Emulsion Stability
Surfactants	Surfactants lower interfacial tension, preventing water droplet coalescence [49], [50].
Solid Particles	Solid particles prevent the merging of water droplets and enhance stability [51].

7. New Developments in the Creation of Demulsifying Substances for Oil Petroleum Emulsions

In the past few years, for instance, in the water in crude oil emulsion, the focus on designing materials that demulsify efficiently and more effectively has been intensively pursued by researchers. This system is arguably one of the most complex and stable types of emulsion, requiring attention in the oil and gas industry, specifically in the context of crude oil emulsion. The composition of crude oil emulsion is quite complex owing to the presence of natural surfactants such as asphaltenes and solid particles, which form the outer sheath of the emulsion [52]. Quite a few works were directed to devising and developing new advanced demulsifiers for it, such as amphiphilic polymers, fluorinated demulsifiers, magnetic nanoparticles, surfactants, and herbal surfactants. These materials may manipulate barrier draughts such as lowering interfacial tension, coalescing droplets, and phase separation, which are better than standard chemical treatment. This was done in part to eliminate the damaging effects caused by the use of chemical treatments. The goal, therefore, is to demonstrate some selected works from 2020 to 2024, focusing on synthesis, characterization, and application of such demulsifiers, showing some trends and breakthroughs in this enhancing domain [53].

Management of petroleum emulsions, predominantly water-in-oil (W/O) and oil-in-water (O/W) suspensions, continues to attract attention in the petroleum sector. These emulsions manifest during the processes of oil extraction and transportation, posing several operational as well as environmental challenges, such as petroleum having high viscosity, corrosion, and trouble separating water and oil. Thus, effective demulsifiers are needed to mitigate these problems and enhance the efficiency of the processes performed. Recent works concentrated on the development of novel demulsifiers from diverse materials such as amphiphilic materials, nanoparticles, and modified polymers, all of which are capable of breaking stable emulsions [54].

Previous researchers synthesized two amphiphilic compounds, Tetraethylene glycol - Hexadecylsuccinic anhydride (TGHA) and poly(ethylene glycol) - Hexadecylsuccinic anhydride (PGHA), and tested their performance in water-in-crude oil emulsions. Their results showed that TGHA had greater demulsification performance than PGHA, and this was attributed to the greater hydrophobicity of TGHA. This work discloses that TGHA performed better in high water content situations compared to commercial demulsifier and so-called CD, which was a benchmark demulsifier. Thus, the experiments with TGHA demulsifier proved that the binder's hydrophobicity is very important in demulsification efficiency [51]. And Fig. 4. Schematic illustration of demulsification processes [52].

Previous researchers also pushed this field forward by making a multibranched non-anionic polyether demulsifier; FYJP was created by adding carboxylate onto a non-ionic demulsifier. The study showed that FYJP could reach 94.7% dehydration at the best level, providing a significant improvement over traditional demulsifiers in chemical flooding emulsions [53].

In another relevant study, the use of an amphiphilic Nano-demulsifier, ZIF-8@CNTs, which was synthesized by the combination of metal-organic frameworks (MOFs) and carbon nanotubes

(CNTs). The results indicated that ZIF-8@CNTs achieved a very high demulsification rate of 99.4% O/W emulsions. Such findings further demonstrate the high potential nanomaterials based on MOFs and CNTs have in separation efficiency enhancement due to their superior thermal stability as well as interfacial activities [54].

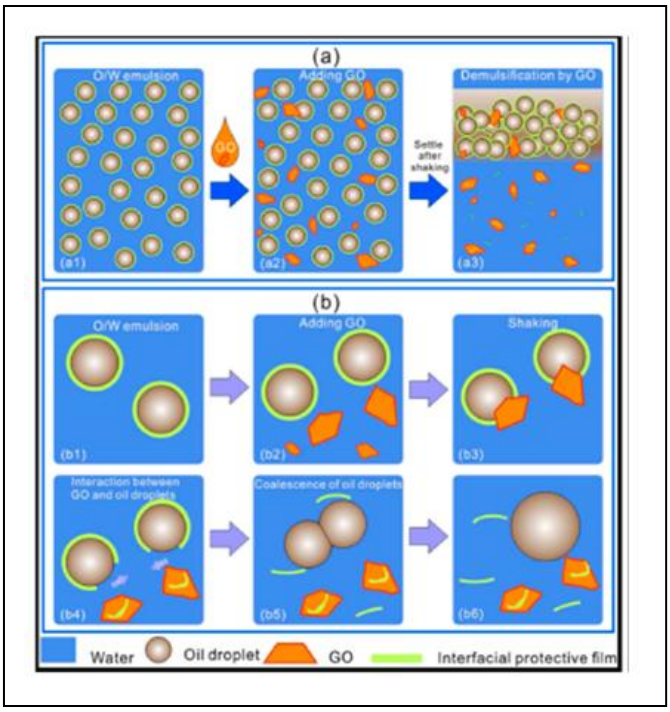

Fig. 4. Schematic illustration of demulsification processes (a) and possible mechanism for coagulation of oil droplets driven by GO nanosheets (b).

In another study, the modification of commercial demulsifier with Fe3O4 magnetic nanoparticles (MNPs) for the broader application of nanomaterials. Their research demonstrated that Fe3O4 MNPs effectively promoted the demulsification of W/O emulsion, which contained high asphaltenes. Under the optimal conditions, the demulsification efficiency of the MNPs was 97.83%, and their reusability was up to three times without loss of efficiency. In addition to the efficacy of nanoparticles in breaking emulsions, this work also emphasizes the reusability and cost-effectiveness from an industrial perspective [55].

In 2023, new non-ionic surfactants based on alkylamine and poly(ethylene glycol) dimethacrylate for the demulsification of W/O emulsions in Arabian heavy oil. These surfactants may be used to break down extremely stable emulsions, as they demonstrated 100% efficiency of demulsification across various water-to-oil ratios in the study. The success of these surfactants would contribute to increased research efforts toward developing non-ionic surfactants capable of successfully dehydrating heavy crude oil [56].

The combined results from these studies show significant advancements in demulsification technologies. From the creation of new amphipathic compounds and non-ionic surfactants to the use of nanomaterials, ionic liquids, and graphene-based systems, the paper marks a wide range of methods for handling petroleum emulsions well. These advances provide possible answers that are not just more effective but also greener, tackling the key issues faced by the oil industry in dealing with emulsions [57].

8. Conclusion

Water-in-crude oil emulsions are highly relevant to petroleum operations, affecting every stage from extraction to transportation and refining. These emulsions, consisting of dispersed water in crude oil, increase viscosity, hinder flow, and complicate separation processes. Higher viscosity not only raises pumping energy requirements but also increases transportation costs. Stable emulsions make water removal more challenging, elevating operational expenses and reducing efficiency.

While emulsions can aid in trapped oil recovery during Enhanced Oil Recovery (EOR), they also introduce complexities in handling and separation. Environmentally, emulsions can promote the formation of corrosive agents such as hydrogen sulfide and dissolved salts, accelerating the degradation of pipelines, storage tanks, and other equipment. This corrosion reduces infrastructure lifespan, poses safety risks, increases maintenance costs, and impacts productivity. Improper management or disposal can release hydrocarbons and hazardous chemicals into ecosystems, causing significant environmental harm.

Recent advances in emulsion management address many of these issues. The adoption of surfactant and solid stabilizer demulsifiers—often derived from plants or microbes—has reduced reliance on harmful traditional chemicals. Solid stabilizers such as nanoparticles and clay effectively prevent droplet coalescence, enhancing stability control. Mechanical separation techniques like centrifugation and electrostatic methods, especially when paired with chemical demulsifiers, have improved separation efficiency, reduced processing time, and lowered costs.

Nanotechnology is transforming the field, with nanomaterial-based demulsifiers such as metal-organic frameworks (MOFs) and carbon nanotubes (CNTs) demonstrating exceptional performance, even under challenging conditions. Their reusability further minimizes environmental impact. Renewable energy integration, such as solar-assisted nanocomposites, adds to the sustainability of these solutions.

Looking forward, further development of cost-effective, eco-friendly methods—such as biodegradable surfactants, advanced nanomaterials, and hybrid separation systems—will be essential. Greater focus on managing emulsions in EOR is also important, as they present both operational challenges and opportunities for sustainable oil recovery.

In conclusion, although water-in-crude oil emulsions remain a significant obstacle, advances in chemical, mechanical, and nanotechnological approaches offer promising, sustainable solutions. By embracing efficient, environmentally responsible technologies, the petroleum industry can enhance production capabilities, meet regulatory requirements, and ensure the long-term sustainability of global energy resources.

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