An overview of recent technique and the affecting parameters in the demulsification of crude oil emulsions

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An overview of recent technique and the affecting parameters in the demulsification of crude oil emulsions

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Abstract. The crude oil mix with water through processing and under significant shear at the wellhead and with the assistance of surface-active substance which is present naturally in the crude oil leading to the formation of water-oil emulsions. These emulsions are undesirable and cause problem like pipeline corrosion, pump malfunctions, poisoning of downstream refinery catalysts, and other problems. Emulsions are needed to demulsify and separate the water. There are various parameters related in crude oil demulsification that can both reduce or rise the stability of the emulsion by altering each. Therefore, this study presents an overview of research efforts on the state-of-the-art demulsification techniques through the last years and the parameters affecting the demulsification process. Firstly, an overview of the crude oil emulsion, kinds, formation, and stability. After that, a short discussion of the different demulsification techniques process. Finally, the study of the parameters affecting the demulsification process, including salinity, temperature, pH, water content, and emulsifier/demulsifier dose. The review of literature culminated in the proposition for future research.

1. Introduction

Crude oil is a composite fluid that contains asphalt elements and resins spread in a combination of aliphatic and aromatic solvents [1]. Water-oil emulsions were produced through oil production and passage in pipelines Due to pressure and shear forces [2-3]. Such emulsions are droplets of water or brine dispersed in a crude oil system and also referred to as water-in - oil emulsions (w/o). There are also emulsions in a continuum of water or brine (o/w) consisting of crude oil droplets, but these are relatively uncommon. [4].

An emulsion may be described as a structure containing two immiscible liquid phases which, are dispersed as globules [5]. The dispersed phase is sometimes referred to as the internal phase, and the persistent phase as the external phase [6]. Derived crude oil from a source includes some impurities such as water and sand [7]. Beside, some hydrocarbons such as asphaltenes, resins, carboxylic acids, waxes and solids from crude oil, which work as natural emulsifiers [8]. Some of these components can accumulate at the water-oil interface and form a stable film around the droplets that prevents coalescence of the water droplets and causes stable water in the oil emulsion [9], where they are usually unwanted and can result in high pumping costs, deterioration of the pipes, reduced capacity and special handling equipment. Therefore, for economic and operational purposes, the water must be isolated from the crude

oil before transporting or refining it [1]. Demulsifiers (or emulsion breakers) are widely used in petroleum-producing industry for demulsification. (Demulsification is defined as an emulsion-breaking process with the purpose to separate water from oil [10]. Currently, available approaches for demulsification of petroleum emulsions can be commonly categorized as biological, electrical, thermal and, mechanical [11]. Chemical demulsification is caused by chemical additives to destabilize the interfacial protective films and thereby speed up the process of separating the emulsion. Chemical additives are commonly used as an economic and efficient method for the dewatering of crude oil emulsions [12]. There are many parameters effected on petroleum demulsification that changing of each one Can decrease or increase the stability of emulsions include temperature, PH value, Salinity, oil content, water content, Emulsifier/demulsifier concentration, mixing speed and time [13].

The present review would investigate the related literature and former studies on the petroleum emulsions, kinds, formation, and stability then, discussion of different demulsifications techniques of removal water from emulsion. Finally, the parameters affecting on the demulsification process including Salinity, Temperature, PH, water content, Emulsifier/demulsifier concentration, Agitation speed, and settling time of emulsion were investigated. Figure 1 briefly illustrates the problem and how to treat the emulsion.

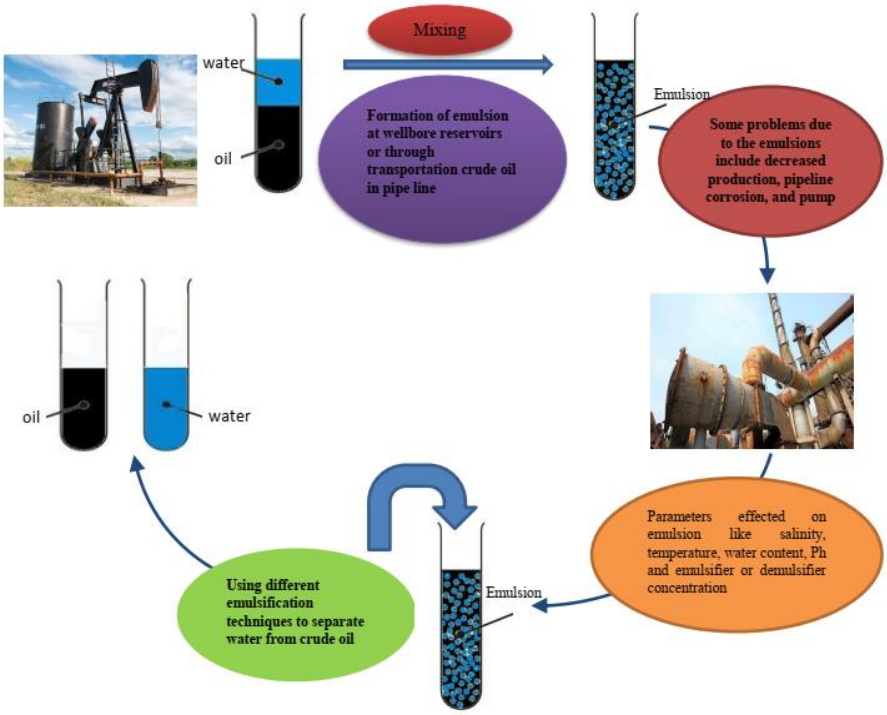

Figure 1. The sketch of the emulsion problem and treatment process.

2. Crude oil emulsions

2.1. Meaning of emulsions

Because of their common presence in everyday life, the emulsion has long been of considerable practical importance. They can be used in significant sectors such as food, cosmetics, pulp and paper manufacturing, pharmacy and farming. Emulsions from petroleum may not be as common, but they have similar historical, widespread and significant industrial occurrences. This can be used in almost any aspect of the oil production and recovery period and can be used at several stages during crude oil exploration, refining, transporting and processing [14]. The emulsion can be described as a dispersed fluid inside another liquid that is assisted by the presence of factors in the interface that prevent it from

separation. In general, these factors are referred to as surfactants or compounds that have polar or non-polar chemical groups in their chemical composition. The dispersed step is usually present in the form of spherical drops in the emulsion [15].

2.2. Types of emulsions

Crude oil is formed as a combination of water and oil. This mixture is known as crude oil emulsion. The formation of emulsions is the product of the co-output water of the oil field. Throughout processing, the pressure that varies during chokes and valves gives enough mechanical forces to disperse water as drops inside the oil [16]. The dispersed step is usually present in the form of spherical drops in the emulsion [17]

It is common that there are two main types of oil emulsions are the water in the oil emulsion (w/o) where the dispersed phase is the water and the continuous phase is the oil and the oil in the water emulsion (o/w) where the phases form the opposite [18-19]. As well as emulsions with multiple phases, such as emulsion of water in oil in water (w/o/w), or emulsion of oil in water in oil (o/w/o) as shown in figure 2. Where these emulsions have multiple uses in the treatment of wastewater, cosmetics, some medicines and the food industry [13].

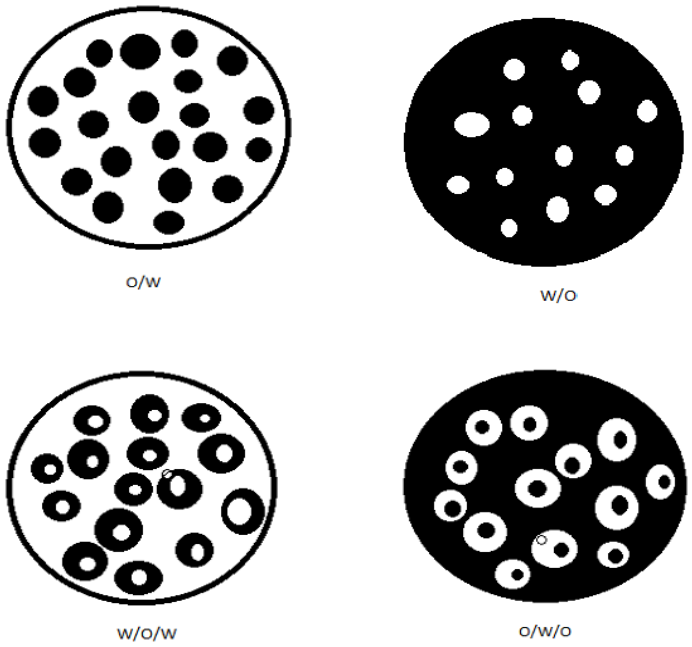

Figure 2. Types of emulsion.

2.3. Emulsion forming and stability in crude oil

One of the most apparent problems in the oil sector is the abundance of water that accompanies the extraction of crude oil. Alternatively, water pumped into the plant during desalination and steam treatment of crude oil [20]. The emulsion forming phase is named "emulsification." Emulsification is a dynamic process that requires a lot of energy to distribute fluid-reducing particles (dispersed phase) in the form of droplets in another liquid which is the continuous phase [21]. Overall, three factors that lead to the formation of the emulsion during the production process are turbulent flows, increased pressure through valves, and the vibratory movement of oil during transport in a pipeline or tanks. There are many methods of emulsification, such as regular mixing of the rotor and pumping of fluid through porous membranes as well as emulsification using ultrasound. During the emulsification process, the shape of the drops changes, and deformation occurs [22-23].

Three conditions must be available to the formation of a stable emulsion. Two liquids immiscible must be in contact, then present an active surface agent (emulsifier) and significant agitation resulting in the mixing of the two fluids and the emulsifier [24]. Emulsifiers contain clay particles, additives applied or components of crude oil such as tar, resins, waxes and naphthenic acid. These emulsifiers help to form a solid layer surrounding the separate drops and prevent fusion [25].

The function of emulsifier is to help to form the emulsion and keep it stable. Other factors that contribute to stabilizing the emulsion are the small size of the dispersed phase drops and the high viscosity of the continuous phase, as well as the decrease in interstitial tension. It is also useful to narrow the distribution of drops of small sizes, as the dispersion will lead to the formation of large droplets compared to the microdroplets, a phenomenon called Ostwald Ripening [26]. Asphalt believed to be an essential factor that contributes to the stabilization of the emulsions [27-28]. It has been shown that asphalt aggregates adsorb on the facade and over time interact to form a solid layer on the surface that gives the emulsion highly stable, as stable films act as a mechanical barrier to coalescence [29]. Table 1 display range of parameters used to prepare emulsion of some studies.

Table 1. Summary of the different parameters used in the preparation emulsion.

Type of emulsion	Water content (v/v)	Mixing time (min)	Mixing speed (rpm)	Type of emulsifier	Emulsifiers concentration	References
W/O	70/30	5-15	1800	Low sulfur wax residue (LSWR) and Triton X-100.		[4]
W/O	Oil content 40–80 wt.%	5-40	1000-15000	Triton X-100	0.5–4 wt.%	[30]
O/W		60		Triton X-100	0.1 %	[31]
O/W	50/50	0.5-1	1000	Ethoxylated nonylphenol family (RENEX) with an ethoxylated amine (Ultramina, 5 EO groups)		[32]
O/W	60/30	10	6000	sodium carbonate (Na_2CO_3)	500–15000 (ppm)	[33]
O/W	69, 72 and 66 vol.%	5-15	1000-2000	Triton X-100	0.3-2.5wt.%	[34]
W/O		15	2000	SPAN 83		[35]
O/W	50/50	5-15	2000	Span 80, Span 83 and Triton X-100)	0.3, 0.5,1 and 1.5wt%	[36]
W/O		30	800	ARMACT	0.6 volume % emulsifier	[37]
W/O	4/1	5	10000	n-heptane (analytical grade) and Toluene		[38]
W/O	70/30	5	1300	Span 80	3%	[39]
O/W		10	16700	Graphene oxide	1000 ppm	[40]
W/O	30/70		1500	Inonic liguid	50-4000 ppm	[41]

3. Demulsification methods

Demulsification is the procedure of separating the emulsion into its initial phases, especially oil and water. The demulsification process in the petroleum industries is an essential method in which emulsions occur usually either naturally or intentionally—separation water from emulsion required in the petrochemical industries and refineries before oil refining. Emulsion resistance depends on fusion and its response to demulsification processes based on the physical and chemical properties of the oil, the

conditions of emulsification and the time of emulsification. This leads to the result that the efforts made and the strategies used to improve the separation of emulsions may differ from one field to another or according to the type of crude oil [42]. Past researchers have addressed various methods of separate the emulsion. There are two main demulsification techniques, which are chemical and physical. The chemical approach is to apply a suitable demulsifier in the demulsification, and traditional physical treatment procedures include heating, electrical or mechanical such as centrifugation [43]. Heating together with the application of the demulsifier, called a thermal chemistry process, and chemical techniques are the most commonly used methods in the industry [44]. Filtration, modification of pH and separation of membranes are techniques used to demulsify the emulsion [45]. Breaking emulsions using chemicals is the most used for all types of oil emulsions, as it promotes flocculation and modifies the properties of the intermittent films, causing coalescence [4].
Atta et al. studied the synthesis of new nonionic surfactants via cardanol containing the amine group. The findings showed strong efficacy as a demulsifier [46]. Hippmann et al. were investigated the influence of alginate as a breaking agent. W/O emulsion consisting of 50/50 of oil/ water brine. It is observed that the emulsion was broken within minutes after alginite added to the emulsion [8].

Auflem and Jiang explained that the mechanical approach depends on the difference in density between phases to break the interlayer to achieve emulsion separation, as there are several mechanical methods used for this purpose such as cyclones, gravity settling tanks, centrifugal separators and so on [47-48] Crude emulsions sometimes contain fairly large droplets and as the flow velocity decreases and due to gravity, it will separate the water from the crude oil. This initial separation is essentially the same as creaming, followed by the coalescence of big droplets. It is usually accomplished in large volume desalters or separators with a typical standing time of 1 hour. The centrifuge has not been used as commonly as other approaches to treating emulsions because of high capital costs and limited efficiency [49].

The thermal approach is the use of heat in both refinery and oil fields to improve emulsion breakage [50]. For laboratory settings, the traditional hot plate used to give the optimum temperature. High Temperatures can also decrease the interface's rigidity, making it easier for droplets to coalesce when colliding. Also, high temperature leads to increased collision rates between droplets and consequently affects the stability of the emulsion. However, the disadvantage of using heat as a demulsifier is the loss of light drops of crude oil, which will negatively affect the density and quality of the oil [51-52]. In many cases, heat is used along with chemical additives to speed up the demulsification process as the temperature helps to reduce the viscosity of the mixture [53].

Electrical demulsification is focused on the use of an electrical field to distort droplets and yield an attractive force among droplets, resulting in coalescence. The electric field causes the drops to be merged into one another, where the Coalescence occurs faster with the distortion and the prolongation of the droplets [54]. This approach is used as an alternate to thermal and chemical therapy. However, it is not well known how this system can be adjusted or adapted to specific emulsion properties to ensure an effective and economically feasible process every time [55]. Li et al. had studied the effect of electric field parameters on ultra-heavy oil dehydration by the airtight oil dehydration system DTS-4C. The separation output and moisture content were respectively 97.81 and 0.37 wt %, which are suitable for refineries [56]. for more detail about the various techniques of demulsification you can read our previous studies [5, 13].

4. Effective parameters

Many variables affect the demulsification process, perhaps changing any one of them may increase or decrease the emulsification stability, which will be discussed in the following sections:

4.1. Salinity

Emulsions are affected by the presence of salts therein, as the increase in the percentage of salts reduces the interaction between water and the surfactant, which is known as the salting effect [57]. Bera et al. studied the impact of salt on interfacial tension between oil and water using several emulsions with

sodium chloride. The results showed that the use of surfactant in the presence of NaCl reduces IFT by a higher rate than when used alone [58]. Increased salt content also results in reduced microwave energy used to heat the device during regulated experiments, resulting in poor performance [14]. Perles et al. studied the influence of Cation and Salinity on (W/O) emulsions on electro coalescence. After the use of the DC electric field. The results showed a negative effect, as the dissolved salt leads to the stability of the emulsion [59].

In another work, Martínez-Palou et al. investigated the effect of salts on the demulsification process of oil emulsions in water using an oil bath and microwave oven for samples of salty water and artificial seawater. The results showed that emulsions are not separated water without using heat [57]. Binner et al. had studied the enhanced separation of water-in-oil emulsions by microwave and investigated the effect of salt content on the separation time. The results show the addition 15 and 35 g/L of NaCl resulted in a decrease in separation time over the entire range of heating periods tested [60]. The Dehghan et al. studied the Effect of Salinity on the separation efficacy of the emulsion, where a constant dosage of the demulsifier was used with different concentrations of sodium chloride salts. Where the emulsion separation was observed quickly at the lower level of the salt but with an increase in the concentration of salts in the emulsion led to a higher separation rate [61]. Saxena et al. had studied the salt effect of the surfactant at Critical Micelle Concentration (CMC), and the result suggested an optimal value of 2% NaCl in CMC surfactant [62]. Akbari, and Biria, had studied the influence of Salinity on the effectivity of bio-demulsifiers. The results showed that sodium chloride had a positive effect on the demulsification efficiency as the percentage of water separation in the samples containing NaCl was higher than the samples that did not include it [63]. Hazrati, et al. had studied the effect of Salinity on interfacial tension with an emulsion called [C14 mim] [NTf2] where 4% of NaCl was used in this experiment. Through the results, it was found that the increase in Salinity leads to the stability of the emulsion [64]. For another study, Xu et al. had tested the impact of NaCl concentration on demulsification efficiency to determine EP@APTESFe_3O_4. demulsification stability. Wastewaters were prepared with various levels of NaCl. The outcomes showed that the adding of Na Cl had little impact on efficiency, indicating that EP@APTESFe_3O_4 had a suitable salt resistance [65]. Table 2 shows summaries of some studies through the literature of salinity effect.

Table 2. The summary some of the recent studies of salinity effect on the demulsification of emulsions.

Type of emulsion	Type of salt	Concentration of salt	Method of demulsifier	Effect of salinity	Reference
W/O			DC electric field	increases the stability of the emulsions	[59]
O/W	deionized water salts& synthetic seawater salts	20,375 & 40,750 ppm	microwave heating	not show any water separation	[57]
O/W	NaCl	15 and 35 g/L	microwave treatment	a reduction in separation time	[60]
O/W	NaCl	150,000 ppm	chemical	faster separation	[61]
O/W	NaCl	1000-9000 mg/L	biodemulsifier	highly effective de-emulsifier	[66]
O/W	NaCl	10 wt%	biodemulsifier	positive effect on the demulsifying activity	[63]
O/W	NaCl	4 wt%	ionic liquids demulsifier	lower efficiencies in demulsification	[64]
oil wastewater	NaCl	0.01-1.0 mol/L	chemical	a little effect on demulsification performance	[65]

4.2. Temperature

In this section, the studies conducted to show the impact of heat on emulsifiers and on the process of breaking emulsions were reviewed. Generally, temperature changes are envisaged to have many advantages; decrease the viscosity of the oil stream, change the disparity between stream densities, It increases the motion of the particles and thus increases the collision between drops. Also, weakening the interlayer around the drops [67]. However, as the temperature rises as a result of a decrease in the viscosity of petroleum, the diffusion rate of asphalt to the interface is increased. Also, consumes a lot of heat in manufacturing, more energy will be used, which will increase the cost of handling crude oil. For this sense, the temperature should be as low as possible while at the same time, achieving an acceptable demulsification [68]. Long et al. had studied the influence of temperature on rhamnolipid dewatering behaviour. A separation efficiency of 75% was obtained using a temperature of 60 ℃, indicating its insensitivity to temperature variations [69].

In the study by Duan et al., six non-ionic demulsifiers based on polyethyleneimine (PEI) have been prepared and their efficiency tested. The oily wastewater created by polymer flooding (OWPF) has been treated at different temperatures by various products. A study showed Temperature effects on the treatment of goods were clearly different. Temperature has not impacted the effect of cationic polymer. However, the temperature affected the impact of PEI products a great deal. With the increase in the heat to 55 °C, all samples performed well and reduced the oil content to 300 mg/L [70]. Al-Sabagh et al. had investigated the effect of temperature on the performance of demulsifier named TE18P. The results showed an improvement in the demulsification efficiency of an asphaltic emulsion using a temperature between 50 to 70 °C [71].

Antes et al. had investigated the influence of heat with ultrasound on dehydration water- in oil emulsion using 160 watts of energy with a temperature ranging from 25-60 °C. The results showed excellent and similar results at these temperatures, but with the temperature increasing above 45, the demulsification performance was reduced [68]. Li et al. studied the effect of heat on removing water from gas emulsions in heavy oil using a column containing porous particles and then performing gravitational separation at temperatures of 60,70 and 80 °C. The results indicated an increase in the removal of water as the temperature rose under the same conditions used [72]. Kumar and Mandal. had studied the effect of temperature on the viscosity of the synthesis of the actor on the polymeric surface where a decrease in viscosity was observed with a rise in temperature above 30 degrees reaching to 70 ℃ [73]. The decrease in viscosity with temperature rises is attributable to the crimping of polymeric surfactant molecules leading to their oxidation and degradation of polymer structure [74]. Yau et al. had studied Impact evaluation of some Marpol oil waste recovery demulsifiers, the study showed that the (O70 PG) acts as the most powerful demulsifier in the separate water between the three demulsifiers at room temperature, while the DP9-6661 and CONC-60 demulsifiers are successful afterwards [75].

Wang et al. investigated the possibility of separating the water from the emulsion using ultrasound and the influence of temperature on the separation rate. The results showed good ratios for removing water with different degrees according to the variability in the volume of water in each sample [76]. Zhang et al. tested the removal of oil from the emulsion using hyperbranched poly amido amine and investigated the difference in temperature over the rate of removing the oil. The results showed a steady increase in the separation rate with increasing temperature, as the percentage of removing oil increased from 34 to 58%, with a temperature increase from 30 to 60 °C as the temperature accelerated the separation process [77]. Table 3 shows summary of some studies through the literature on temperature effect.

Table 3. List some of the latest studies of temperature effect on the demulsification of emulsions.

Type of Emulsion	Method of Demulsification	Range of Temperature	Effect of Temperature	Reference
O/W	chemical	10 - 60 ˚C	Constant dewatering efficiency.	[69]
oily wastewater	Chemical	up to 55 ˚C	good performance reduces the oil content below to 300 mg/L.	[70]
w/o	chemical	50 - 70 ˚C	Improved demulsification efficiency.	[71]
W/O	ultrasound	25,45,60ºC.	Maximum demulsification efficiencies reached at 45 ºC.	[68]
w/o	without	60,70,80˚C	water-in-oil emulsions decreases with increasing temperature.	[72]
w/o	chemical	70 ˚C	Higher removal performance at a higher temperature.	[75]
	polymeric surfactant solution	30 - 70˚C	The viscosity decrease with increases in temperature.	[73]
o/w	ultrasonic treatment	80-100 ˚C	Demulsification become better with the increase of temperature.	[76]
O/W	chemical	30-60 ˚C	The oil removal ratio increases with increasing temperature.	[77]
O/W	chemical	50-70 ˚C	The initiator decomposition rate increases with temperature.	[78]

4.3. pH

The stability of the emulsion is affected by the pH value, the nature of the oil and the composition of the saline solution. The demulsification of the emulsion may also be affected by organic acids or organic soluble organic bases in oil. The Surfactant hydrophilicity seems to increase with increasing pH value. Based on this assumption, water- in oil emulsions are likely to form in an acidic medium at a low pH value, while oil-in-water emulsions can form in alkali medium, i.e. at a high pH. Accordingly, the asphalt films are more strong in the acidic environment and weaken with increasing pH value until they turn into thin, non-coherent films in the alkaline medium. Whereas the resin films are weak in the acidic medium and increase in strength with higher alkaline value. [14, 79]. Liu et al., had researched the impact of pH on the yield and demulsification capabilities of the bio demulsifier of Water-in-Oil emulsion. The results indicate the maximum yield of bio-demulsifier at pH 8 and the highest demulsification ratio of about 84.5 % at pH 9 [80]. Dyab, was studied by adjusting the pH of the silica dispersions in the destabilization of the o/w emulsions. The aqueous dispersions of silica were found to be unstable at a pH < 4.2. The complete separation of water and oil was achieved when the pH of silica dispersion before demulsification changed to a pH of 7-8. [81]. Xuwei et al. Had explored the effect of pH on the efficiency of dewatering by using biosurfactant rhamnolipid. A moderate pH range of 4–10 at 300 mg/L was picked. As shown in the tests, the decrease in pH has improved the rhamnolipid dewatering process. For example, the dewatering performance was 81.2 % below pH 4, while the neutral pH of 7 was 47 percent [82].

Behbahani et al, had studied the impact of pH on cadmium ion Cd (II) extraction recovery between 2–9 pH levels. The results showed an increase in the recovery of cadmium when changing the acidity of the solution to moderate, i.e. at pH seven and then began to descend with an increase in the pH value and its transformation into an alkaline environment. [83]. Liang wt al, tested the demulsification of magnetic nanoparticles for cyclohexane-diluted oil-in-water nanoemulsions, Had investigated the impact of pH on the demulsification efficiency. From the findings, they found efficiency remained stable at pH between (4-7.5). However, a decrease in the efficiency ratio observed with the pH increasing above 8. The reason may be due to the increased dispersion of oil drops in the emulsion [84]. Noah et al. had studied the function of the external phase pH in restoring palladium (Pd) ions and emulsion stability to optimal conditions. Results show that Pd's extraction and recovery performance was

excellent in the acid phase at pH 3. It reached 93 and 95%, respectively. A decrease in Pd recovery level was observed at pH 7, confirming the suitability of the acidic environment for palladium extraction [85]. Xuwei et al. Investigated surfactin's pH-regulated emulsification behaviour and its possible application in the removal of oil towards increased oil recovery (EOR). The surfactant has been found able to stabilize emulsions well above pH 7.4. Also, the oil emulsification ratio at pH 11.0 was around 98%;. In contrast, this emulsification process was fast and fully lost when pH dropped below 3.0, with an oil removal ratio of more than 98% [86].

Saxena et al. had investigated the effect of pH on interfacial tension (IFT) by adding mono-ethanolamine (MEA); IFT was observed to decline at alkali condition [62]. Another study by Wu et al. had been investigated the effects of pH on the dishwasher wastewater treatment efficiency. The successful operating range of Polymer C-572 is to be determined. The results showed that C-572 provided successful care over a pH range of 6.5–9.0, with optimum efficiency between 8.0 and 9.0. About 85 per cent of oil and turbidity were extracted via these pH values. Total oil and turbidity removals were reached at 87 per cent and 90 per cent at 8.5 pH [87]. Table 4 demonstrates the summaries of some studies through the literature of pH effect.

Table 4. The summary of some studies of pH effect on the demulsification of emulsions.

Type Of Emulsion	Method Of Demulsification	Range Of pH	Effect Of PH	Reference
o/w	bio demulsifier	8-9	Improve demulsification ratio	[80]
O/W	chemical	7-8	Improve destabilisation emulsion	[81]
Oily sludge dewatering	bio demulsifier	4-10	Dewatering efficiency below pH 4 of 81.2%.	[82]
cadmium in water		2–9	The extraction recovery of Cd (II), increases as the pH increased to 7.0.	[83]
O/W	chemical	4-11	demulsification efficiency unchanged at The pH range was 4.0–7.5 and reduced from 8.0 to 11.0 as pH increased.	[84]
w/o	liquid membrane process	1-7	The pH of around 3 is adequate for Pd extraction, and pH rises of up to 7 have led to decreases in Pd recovery levels.	[85]
o/w	Biosurfactant	3-11	Active as emulsification at pH 11.0; while improving oil separation when pH decreased to below 3.	[86]
enhanced oil recovery	anionic biodegradable surfactant		IFT decrease with an increase in pH value.	(Saxena et al., 2017
dishwasher wastewater	chemical	5-9	The maximum oil and turbidity removals achieved at a pH of 8.5.	[87]

4.4. Water content

One crucial element affecting on demulsification process is the water content in the emulsion. The stable emulsions rely not only on the content of asphalt, resin and paraffin but also on the content of water [88]. Increasing the percentage of water in the emulsion with the presence of the surfactant facilitates the separation process and enhances the emulsification process and contributes to reducing the amount of the surfactant used and the time required for separation [89-90]. However, an increase in the water content may increase the viscosity of the emulsion [91]. Ali et al, used an P(MMA-AA-DVB)/Fe3O4 magnetic composite nanoparticles as demulgators to test the influence of water content on the separation of w/o emulsion. Such findings suggested the improvement in demulsification efficiency with an increase of 30 to 50 % in water content [92]. Al-Sabagh et al. investigated the effect of water content on the emulsion separation process. Samples were prepared with a water content of 10, 30 and 50 %. The results showed that the samples with high water content would be easier to break in less time[71]. In

another study, Khajehesamedini et al. reported the effect of water content on separation efficacy using low-frequency ultrasound. The results indicated that an increase in the water content leads to an increase in the number and size of water droplets, and consequently an increase in collision and coalescence, which affects the stability of the emulsion and the decrease in the efficiency of breaking the emulsion [93]. On the contrary, Wang et al. used ultrasonic wave to investigated the influence of water ratio on dehydration rate. The findings showed that the percentage of dehydration decreases by more than 70% with the rise in the water ratio. Whereas if the water level reaches 70%. The equilibrium point of the emulsion is due to the water ratio of 70 per cent [76]. Table 5 demonstrates the summaries of some studies through the literature of water content effect.

Table 5. The summary of some recent study of water content effect on the demulsification of emulsions.

Type of Emulsion	Method of Demulsification	Water content	Effect of water on separation	Reference
w/o	magnetic composite nanoparticles	30-50%	The efficiency of demulsification increase with an increased water volume.	[92]
w/o	chemical	10,30 and 50%	the breaking of the emulsion becomes easier with increases the water content.	[71]
	ultrasonic wave	0-70%	the dehydration rate decreases with the increase of water ratio.	[76]
w/o	ultrasonic waves	10-25%	Separated water decreases with an increase in the original water content, while the rate of dehydration decreases.	[93]

4.5. Emulsifier/demulsifier dosage

For treatment, an emulsion with a higher ratio of the emulsifier requires more significant concentration of demulsifier. Usually, third-degree emulsions obtained from enhanced oil recovery process require a more incredible amount of surfactant than first or second-class emulsions. As a result, the use of a little demulsifier may not lead to a complete separation process, while an overdose of the surfactant increases the emulsion stability [94]. Al-Sabagh et al. used the polyester demulsifier to study the effect of the concentration on the separation of water from the emulsion. The results showed that a rapid separation process achieved with an increased level of the surfactant, which significantly reduced the time required to break the emulsion. [71]. Ali et al. investigated the influence of P (MMA-AA-DVB)/Fe3O4 nanoparticles quantity on breaking w/o emulsion. The different amount 100, 300 and 500 ppm of magnetic nanoparticles at 60 ◦C used. The results showed excellent separation results reached 98% throughout one hour by using 500 ppm of concentration [92]. The effect of surfactant concentration in the cycle of emulsion liquid membrane (ELM) extraction is investigated by Othman et al. The results confirmed that phenol extraction increased from 46 to 99% with the increase of the dose of the surfactant to 5% [39].

Liu et al. investigated the effect of the dosage of magnetic graphene oxide (M-GO) on the efficiency separating emulsions. As shown in the results, the concentration of residual oil in the separate water decreased to 841,8 ± 30 mg/L with addition of 0,04 wt percent of M-GO and significantly reduced with an increase in the dosage of M-GO to 0,25 wt % to around 10 mg/L [95]. Zank et al. investigated the effect of the surfactant's concentration on the ratio of oil separation in the o/w emulsion by three types of hyperbranched poly amido amine, where four different concentrations were used, ranging from 10-40 mg / L. The percentages of separated oil were different between the samples according to the concentration and the type of demulsifier used. This confirms the effect of the quantity of the surfactant used on the efficiency of breaking the emulsion and the percentage of oil or water separated [77]. Hazrati et al. studied ionic liquid (IL) application in the isolation of water from crude oil, and investigated the effect of IL dosage on separation efficiency. It was shown that the application of IL leads to separate water from the emulsion of crude oil with a reasonable 86–95 percent efficiency [96]. Li et al. had

researched the treatment of water-in-aging crude oil (WACO) emulsions and examined the effect of dosage on demulsification by the use of polyether tannic acid phenol amine (TAPA). The results indicated that the efficiency of demulsification increases over time for all concentrations. Meanwhile, increasing concentration increases dehydration of the water. When the concentration rises from 50 to 150 mg L^{-1}, removal of water increases significantly [97]. Table 6 demonstrates the summary of some studies through the literature of concentration effect.

Table 6. The summary of some recent study of concentration effect on the breaking of emulsions.

Form of Emulsion	Category of Demulsification	Emulsifier/demulsifier concentration	Influence of concentration on separation	References
W/O	polyester surfactants	25-500 ppm	the increase in concentration reduces the time required for separation.	[71]
O/W	magnetic nanoparticles	100, 300 and 500 ppm	500 ppm of concentration shows excellent demulsification results.	[92]
emulsion liquid	membrane process extraction	1- 5 wt%	increase the phenol extraction with increasing the surfactant concentration	[39]
O/W	magnetic graphene oxide	0.04 – 0.25 wt%	The demulsification efficiency increase with increasing the M-GO dosage.	[95]
O/W	hyperbranched poly (amidoamine)	10, 20, 30, and 40 $mg{\cdot}L^{-1}$	the oil separation ratio change with change demulsifier type at the same concentration.	[77]
W/O	ionic liquids	500-3500 ppm	the demulsification efficiency increase in higher concentrations.	[96]
W/O	polyether	50 to 150 $mg{\cdot}L^{-1}$	The increase of demulsifier concentration improves the water dehydration.	[97]
O/W	copolemer	0.5 wt %	The oil removal decreased at initiator concentration	[78]
W/O	castor oil maleate	100-5000 ppm	The water resolution of approximately 90%.	[98]

5. Conclusion and recommendations

By reviewing the literature, all recent research that has been discussed has demonstrated that the formation of water and oil emulsions is a significant problem in terms of environmental standards, the cost of transporting oil, producing and separating it in refineries and treating waste. These problems in the oil field have aroused a research interest by researchers to find scientific, economically, and environmentally feasible methods to prevent the formation and treatment of these problems. Investigations have shown that different parameters such as salinity, water content, temperature, the concentration of surfactant and pH affect the efficiency and success of using these techniques. Also, each variable has a different degree of efficacy over the demulsification process. Moreover, high efficiency can be obtained to separate the emulsions by involving the synergistic effects of one or more of these parameters. Nevertheless, most researchers used chemicals or thermal methods in the demulsification emulsion. They did not address the use of environmentally friendly processes and techniques that are low cost and give high efficiency. Therefore, efforts should be directed to preparing surfactants from natural materials that preserve the environment and are cost-effective and efficient.

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