



Mimicking the Crude Oil and Heavy Fuel Oil (HFO) Demulsification Process in Power Plants for Preparing a New Demulsifiers

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Abstract:

Water-in-oil emulsions are a big challenge in the production and processing of crude oil due to its bad influence on the fundamental and practical aspects of industrial facilities. Researches for decades gave this phenomena a great deal in the planning to construct power plants, refineries, oil companies and other industrial facilities that uses crude oil as a raw material. In order to overcome the disadvantages and hazards of water-in-oil emulsions researchers used chemical, electrical, thermal and mechanical methods individually or in combination. The chemical method has gained the main interest due to its ease of use and economic feasibility. Demulsifiers have been used extensively to solve the problem of water in oil emulsions. The choice of using the right combination of chemicals had been reached after studying many factors such as cost and safety. This research addresses many fundamental and practical aspects regarding demulsifiers and oil demulsification aiming to find the best selection of chemicals that can be used to treat crude oil before using, refining or transporting it. The crude oil in this research had been demulsified and tested by the spectroil test method while the bottle test method had not been used to mimic the demulsification process used in power plant. The work was carried out using two types of oil, crude oil (containing 7 ppm Na and K salts concentration) and heavy fuel oil HFO (containing 12 ppm Na and K salts concentration). The crude oil

samples were taken from Al – Hilla 2 power plant while the HFO samples were taken from South Baghdad 2 power plant. The results showed that the water miscible chemicals and chemicals with sufficient solubility that used as a demulsifiers like the acrylic derivatives gave the best demulsification when using more wash water percentage. While the combination of water miscible chemicals and chemicals with sufficient solubility and oil soluble chemicals gave the best results in treating heavy fuel oil while using less wash water percentage.

Keywords: Demulsifier, Crude oil, Emulsions, power plants.

محاكاة عملية إزالة أستحلاب النفط الخام و زيت الوقود الثقيل المستعملة في محطات إنتاج الطاقة

الكهربائية لتحضير موانع أستحلاب جديدة

الخلاصة:

تعتبر مستحلبات الماء و النفط تحدي كبير في عمليات إنتاج و معالجة النفط الخام نظرا لتأثيرها على الجوانب الأساسية والعملية للمنشآت الصناعية. لعقود عديدة أعطى الباحثون أهمية كبيرة لهذه الظاهرة عند التخطيط لإنشاء محطات إنتاج الطاقة الكهربائية و مصافي النفط وشركات النفط و المرافق الصناعية التي تستعمل النفط الخام كمادة أولية. لغرض التغلب على مساويء و مخاطر مستحلبات النفط و الماء أستعمل الباحثين طرق كيميائية و كهربائية و حرارية و ميكانيكية بصورة منفردة او بالجمع بين الطرق. الطريقة الكيميائية حازت على اهتمام رئيسي بسبب سهولة أستعمالها و جدواها الاقتصادية. أستعملت موانع الأستحلاب على نطاق واسع لحل مشكلة مستحلبات النفط و الماء. و كان خيار أستعمال الخلطة الصحيحة لمانع الأستحلاب يتخذ بعد دراسة عدد من العوامل المهمة مثل الكلفة و السلامة. هذا البحث يهتم بالعديد من الجوانب الأساسية و العملية التي تتعلق بالمستحلبات و موانع الأستحلاب بهدف الوصول الى أفضل مجموعة مختارة من المواد الكيميائية التي من الممكن أستعمالها لمعالجة النفط الخام قبل استعماله أو تصفيته أو نقله. في هذا البحث تمت محاولة إزالة أستحلاب النفط الخام و من ثم تم فحصه بجهاز SPECTROIL و لم يتم أستخدام طريقة فحص القنينة BOTTLE TEST و ذلك لمحاكاة عملية إزالة الأستحلاب المستخدمة في محطات توليد الطاقة الكهربائية تم العمل على نوعين من الوقود. النفط الخام (CRUDE OIL) (الحاوي على 7 أجزاء بالمليون من أملاح الصوديوم Na و البوتاسيوم K) و النفط الخام الثقيل (HEAVY FEUL (HFO) (الحاوي على 12 جزء بالمليون من أملاح الصوديوم Na و البوتاسيوم). عينات النفط الثقيل تم الحصول عليها من محطة كهرباء الحلة الغازية الثانية بينما عينات النفط الخام الثقيل تم الحصول عليها من محطة كهرباء جنوب بغداد الغازية الثانية. النتائج أظهرت أن المواد الكيميائية التي تمتزج أو تذوب بالماء بدرجة كافية مثل المشتقات الأكريلية أعطت أفضل نتائج إزالة الأستحلاب عند أستعمال نسبة كبيرة من ماء الغسل. بينما المواد التي تمتزج بصورة كافية بالماء و ذوبانية كافية بالنفط أعطت أفضل النتائج عند معاملة النفط الخام الثقيل بنسبة قليلة من ماء الغسل.

الكلمات المفتاحية: موانع أستحلاب – نفط خام – مستحلبات – محطات توليد الطاقة الكهربائية.

Introduction:

In order to eliminate the water in oil emulsions problem many methods have been used including electrical, chemical and thermal processes or a combination of them [14]. Thermal method involves the use of a specific temperature that is not high enough to cause a rise up in water solubility and sometimes the use of chemicals or electrostatic heat are commercially sufficient instead using a high temperatures [14]. Electrical method involves reorientation of the polar molecules and weakens the film around water droplets which lead to the disruption of surface tension of each droplet [14]. Sometimes this method applies alone in solving the emulsion problem and sometimes it requires the addition of heat or chemicals. The use of chemical methods is the most important method of treating the crude oil from emulsification problem. This method involves the breaking of the interfacial film around each droplet effectively by using a combination of chemicals and heat. The use of chemical demulsifiers was due to their high efficiency and economic success [33]. Crude oil is a complex mixture of thousands of components; these components differ in type and percentages due to age, depth and place of the oil field. Crude oil consists mainly of carbon and hydrogen and small amounts of oxygen, nitrogen and sulfur with many metallic molecules like copper, vanadium, nickel and iron [31].

Crude oil main components are:

1- Asphaltenes: a brown to black amorphous powder which is the heaviest component in the crude oil [31]. The structure of asphaltenes is not well known yet but generally asphaltenes are non-volatile and polar fraction of crude oil, decomposes above 300 ° C. Asphaltenes are enhancing the formation and stabilization of water in oil emulsions [23]. Many studies on asphaltenes gave an average molecular weight for their molecules about 750 g/mole [15], while other studies gave a lower molecular weight value of about 400 g/mole [16]. Asphaltenes molecules are mainly aromatic base with cyclic and alkyl chains attached to it with the existence of other heteroatoms like nitrogen, oxygen and sulfur and sometimes a trace amounts of metals like nickel and vanadium [9].

2- Resins: the percentage of resins in crude oil is more than the percentage of asphaltenes but it increases with the increase of the percentage of asphaltenes and vice versa. Resins are brown to dark semi solids [13]. Resins are polar and non-volatile consists mainly of carbon, nitrogen, oxygen, naphthenic acid and sulfur [32].

3- Waxes: are a mixture of alkanes with a high molecular weight, alcohols with a long chain (more than C_{16}) and a long chain ester (more than C_{16}) [5]. The wax molecules can be attached with the carboxylic acids via their fatty tails and stabilize the mixture [26]. The reason for the stable combination of asphaltenes, resins, wax and solids is the crystal structure of wax.

4- Solids: are very small particles materials consists mainly of wax crystals, clay particles and sand. These particles play a big role in stabilizing water in oil emulsions [17]. Solids keep the film around the water molecules thick and increase the strength of the resistance against breaking it. This phenomenon of stabilizing the water in oil emulsions by the presence of solids affected by the size of the solids [20].

5- Hydrocarbons: exist in gaseous, liquid and solid states, depending on the number and arrangement of the carbon atoms in their molecules.

6- Oil field brine: the presence of inorganic salts like sodium chloride and calcium chloride in the crude oil has a big effect in the formation and stabilization of water in oil emulsions and size of water in oil droplets [8]. Many researchers have studied the effect of inorganic salts and pH values on the stability of water in oil emulsions and found that salt concentration has an adverse effect on water in oil emulsion stability and its effect decreased as pH increased ^[34]. The formation of emulsions happens if three main conditions exist:

- 1- Two immiscible liquids should mix with each other.
- 2- The existence of a surface active material that works as the emulsifying agent.
- 3- Enough agitation or mixing should be present to result a dispersion of one liquid into the other as droplets [28].

Researchers have come to a conclusion that the main reason for the stability of water in oil emulsions is the existence of a certain polar components like asphaltenes, waxes and resins which work as natural surface active agents [18]. And by studying the factors that lead to the stabilization of emulsions scientists succeeded in finding the ways to demulsify these emulsions [6]. Chemical demulsification are the most important method for treating water in oil emulsions and the main types of demulsifiers according to their functional groups are polymers, polyhydric alcohols, amines and sulphonates [2]. A demulsifier should diminish the stabilization effect of the emulsifying agents exist in the water in oil emulsions [1]. Demulsifiers are surface-active components just like

emulsifiers and in order for the demulsifiers to work properly they should be chosen carefully through a wide range of surface-active chemicals. The good selection of the demulsifier components is vital for their efficiency, using the right quantity of the demulsifier, enough and accurate mixing, sufficient heat and sufficient retention time in separators are important factors for a good demulsification process [19].

According to [10] chemical demulsification process is the combination of three main effects:

1- The dispersion of the demulsifier into the water/oil interface and the displacement of the asphaltenic film [11, 21].

2- Flocculation, which is the process of joining the small water droplets by the demulsifier and it involves the decrease in interfacial tension gradient and the thinning of the asphaltenic film around the water droplets [24].

3- Coalescence of the water droplets is happening by breaking the emulsifier film around the droplets and joining the droplets which became large enough to separate and settle out.

An ideal demulsifier molecule (which is a surface active agent as stated previously) has two functional groups:

- 1- The hydrophilic group or water preferring group such as amines, sulphate, carboxylate, oxides and other polar groups that have electrophilic properties [27]. There are also water soluble polymeric demulsifiers like the tetra polymer of acrylic acid, butyl acrylate, methyl methacrylate and methacrylic acid.
- 2- The hydrophobic group or water avoiding group such as a long chain of alkyl group.

The behavior, strength and potency of the demulsifier molecule depend on the relative strength of the hydrophilic and hydrophobic groups attached to it. The effects of these groups are not independent; they depend on the hydrogen bonds around the hydrophobic and hydrophilic groups.

Table (1) The development of chemical demulsifier [22, 29]

YEAR	DEMULSIFIER
1920–1930	Soap, naphthenic acid salts and alkylary sulphate, sulphated castor oil
1930–1940	Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosucinic acid ester
1940-1950	Fatty acids, fatty alcohols, alkylphenols
1950–1960	Ethylene oxide/propylene oxide copolymer, Alkoxylated cyclic p-alkylphenol formaldehyde resins
1960–1970	Amine alkoxyate
1970–1980	Alkoxylated cyclic p-alkylphenol formaldehyde resins
1980–1990	Polyesteramine and blends

Aim of the Research:

Mimicking the crude oil demulsification process in power plants for preparing an efficient and economic water in oil demulsifier using a formula from a selection of chemicals and study the effect of the new formula on the Na and K salts concentration as a function of the demulsification process efficiency.

Experimental Section:**Materials and Equipments:**

The chemicals used in this research are chosen according to their suitability, potency and economic feasibility and after reviewing many previous researches dealing with the water in oil demulsifiers. In this research we used the following chemicals:

poly ethylene glycol 99% Fluka company, Acrylic acid 99%, methyl methacrylate 99% and butyl acrylate 99% Aldrich company, trioctyl amine 99% Merck company, dioctyl amine 99% , castor oil commercial grade BIC Chemicals China, trioctyl methyl ammonium chloride 98% Jiangyin Lanyu Chemical company, China.

The main equipments used in this research was the Spectr Oil analyzer from Spectro Scientific company USA (Figure 1) beside other necessary lab equipments.

Experimental Methods:

This research was carried out using two types of oil, crude oil (containing 7 ppm of a total Na and K salts concentration) and heavy fuel oil HFO (containing 12 ppm Na and K salts concentration). The crude oil samples were taken from Al – Hilla 2 power plant while the HFO samples were taken from South Baghdad 2 power plant.

The oil samples have been treated in the laboratory by a selected combination of chemicals then the treated oil analyzed by SPECTROIL Analyzer. A mixture of one liter of a newly brought crude oil and the demulsifier components was heated to (95-97) °C under stirring speed 0.24 Kr/min. by a mechanical stirrer. Then a certain amount of washing water quantity that has been already heated to about 95 °C was added to the mixture and the stirring continues for 10 minutes after the water addition at the same temperature (95-97) °C, then the beaker contents poured into a 2 liter separating funnel and another quantity of washing water added then the mixture was shook up for about 10 seconds and then allowed to settle for about 5 minutes. Some of the lower content of the separating funnel was removed (about 50 mL) and a 5 ml test tubes then filled with the remaining content of the separating funnel, the test tubes put into a centrifuge and processed for 1 minute, the upper part of the test tube has been taken by a syringe and gathered in a 10 mL test tube to be analyzed by the SPECTROIL Analyzer (Figure 1).



Fig. (1) SpectrOil analyzer

Results and Discussion:

Most of the researches dealing with the water and oil emulsions and demulsifiers used the bottle test as a main testing method [4, 25], but in this research the spectroil test has been used according to ASTM6728 (Standard Test Method for Determination of Contaminants in Gas Turbine and Diesel Engine Fuel by Rotating Disc Electrode Atomic Emission Spectrometry) to mimic the demulsification process used in the power plant because many elements used in the oil processing in the power plant do not exist in the bottle test like stirring, washing water and centrifuge. Also the quality test used by the power plants is the spectroil so it's convenient to use the same testing method and by the same testing device.

The materials used in this research combined cost less than the average cost of the commercial demulsifier. Commercial demulsifier barrel cost is (1000 – 1500) IQD while the costs of the prepared demulsifiers are less than 500 IQD a barrel, taking into consideration that the costs vary according to the materials used in it because in this research many combinations have been used according to the type of the processed oil and the amount of the wash water used.

The salts of Na and K have considered the main reasons for the corrosion of equipments and pipes in the factories, refineries and power plants in addition to the water and the existence of these salts give a good indication to the existence of water pockets in the oil sample.

(Figure 2) showed the salt concentration decreased after the treatment of crude oil (contains 7 ppm of Na and K salts) by selected demulsifiers as a function of the demulsification process that happened between water and oil using 30% wash water. (Table 2) showed the components of demulsifier samples used in treating crude oil under test. The analysis data for the Na and K salts concentrations showed that the demulsifier combination of 20% acrylic acid, 20% di octyl amine, 20% methyl methacrylate, 20% trioctyl methyl ammonium chloride and 20% castor oil (Figure 2) gave the best result while the demulsifier combination of 40% acrylic acid, 40% butyl acrylate and 20% trioctyl methyl ammonium chloride gave the worst results (Figure 2). Acrylic acid is miscible in water and that property helped in disperse the acid molecules in the water layer and that's why in the treatment process when using 30% wash water acrylic acid gave the best demulsification result. While adding the trioctyl methyl ammonium chloride to the

combination which is an oil soluble material somehow minimized the good results of acrylic acid and butyl acrylate alone. The combination of 40% methyl methacrylate, 40% di octyl amine and 20% castor oil also gave good results (Figure 2) mainly because the methyl methacrylate has sufficient water solubility (0.1 g / 100 mL) that led to a higher dispersion. The main components that gave the best results have either sufficient water solubility or miscibility so their active groups do not ionize to any great degree so these groups provides the hydrophilic groups that affects the demulsification process [27].

(Figure 3) showed the effect of the demulsifier concentration on the Na and K salts concentration (HFO containing 12 ppm of Na and K salts conc.) with using 30% wash water. Table (3) showed the components of demulsifier samples used in treating heavy fuel oil (HFO). The analysis data on (Figure 3) showed that the demulsifier combination of 80% acrylic acid and 20% castor oil gave the best result. The real shock here is that the combination of 40% acrylic acid with 40% butyl acrylate was not successful at all in treating the heavy fuel oil (Figure 3) and the reason might be based upon the different composition of the heavy fuel oil which needs higher concentration of strong materials in the demulsification process. The composition of the crude oil can vary a lot in the physical and chemical properties of the crude oil [31].

The use of castor oil gave a little enhancement to the demulsifier role as it shown in Figure (3) (the demulsifier in this case was acrylic acid). Castor oil used as a coagulant in the treatment of water in oil emulsions. Coagulation happened in the first step of the demulsification process (the flocculation process) when the small pockets of water became closer to each other and join each other to produce a fish eggs like formation [24].

Figures (4, 5) demonstrated the demulsification of heavy fuel oil (HFO) by various demulsifiers (Table 4) using only 10% of wash water. Reducing the quantity of wash water has made a great negative influence on the separation of the water in oil emulsions.

The demulsifiers that gave good results when using 30% wash water in the demulsification process gave poor results in 10% wash water percentage and that might be because most of the used chemicals were either have a sufficient water solubility or miscibility so they gave good results when there was a big percentage of water [7].

Table (2) Components of demulsifier samples used in treating crude oil containing 7 ppm of Na and K salts concentration and using 30% wash water

Sample	Component
A	20% Acrylic Acid + 20% Di Octyl Amine + 20% Methyl Methacrylate + 20% Trioctyl Methyl Ammonium Chloride + 20% Castor Oil
B	40% Di Octyl Amine + 40% Methyl Methacrylate + 20% Castor Oil
C	80% Trioctyl Methyl Ammonium Chloride + 20% Castor Oil
E	40% Acrylic Acid + 40% Butyl Acrylate + 20% Trioctyl Methyl Ammonium Chloride

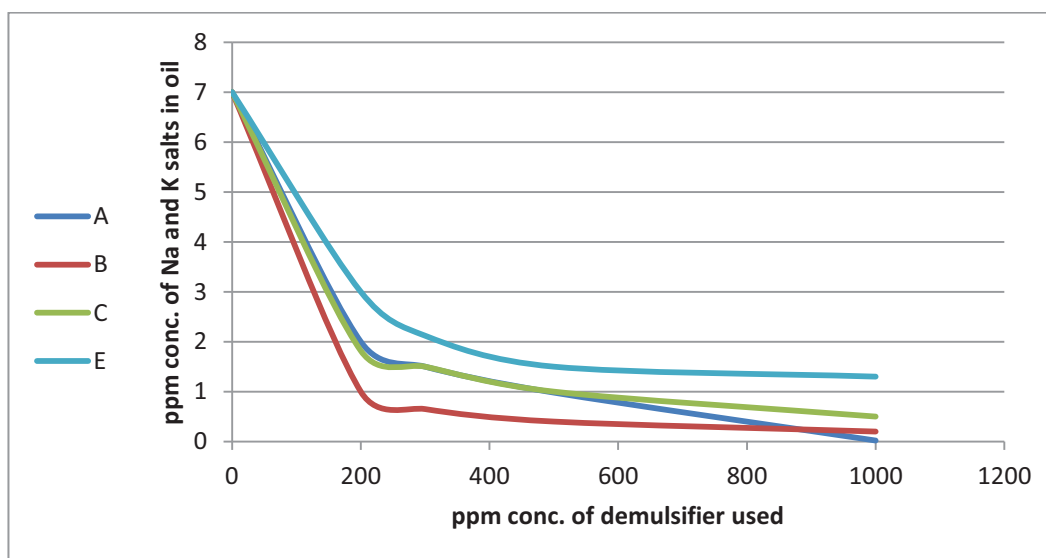


Fig. (2) Effect of demulsifier concentration on the Na and K salts concentration (crude oil containing 7 ppm of Na and K salts concentration) and using 30% wash water

Table (3) Components of demulsifier samples used in treating HFO oil containing 12 ppm of Na and K salts concentration and using 30% wash water

Sample	Component
G	Poly Ethylene Glycol
H	80% Acrylic Acid + 20% Castor Oil
I	40% Acrylic Acid + 40% Butyl Acrylate + 20% Castor Oil
J	80% Methyl Methacrylate + 20% Castor Oil

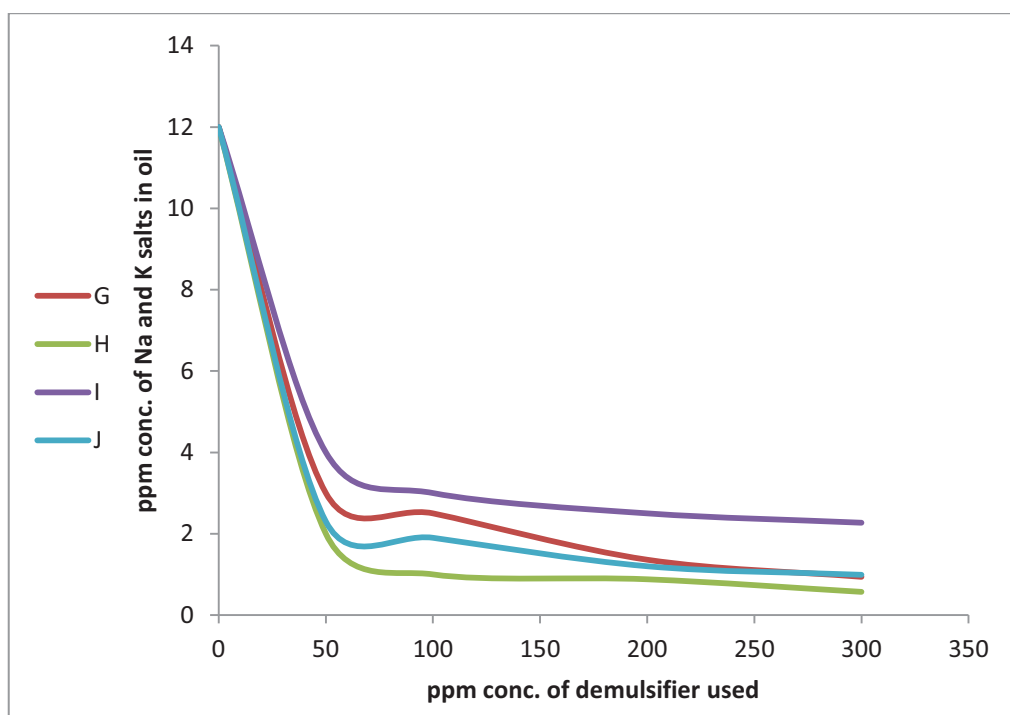


Fig. (3) Effect of demulsifier concentration on the Na and K salts concentration (HFO containing 12 ppm of Na and K salts concentration) and using 30% wash water

Table (4) Components of demulsifier samples used in treating HFO oil containing 12 ppm of Na and K salts concentration and using 10% wash water

Sample	Component
L	35% Acrylic Acid + 35% Trioctyl Methyl Ammonium Chloride + 20% Castor Oil + 10% Toluene
M	Acrylic Acid

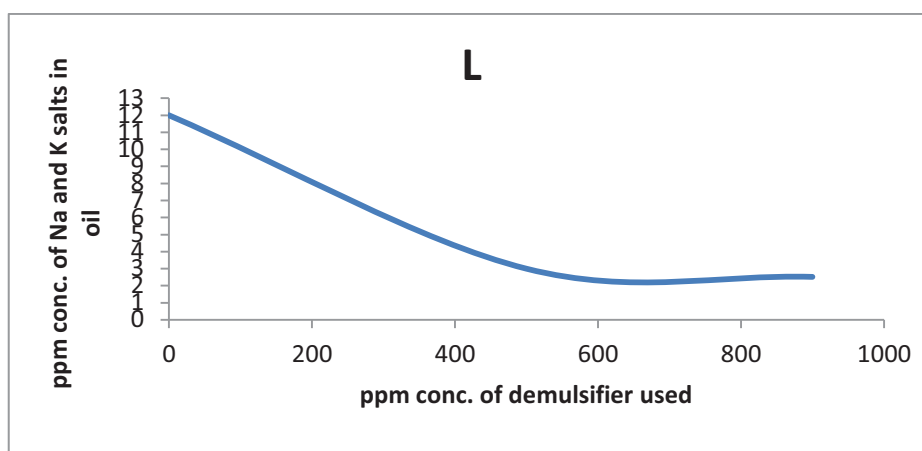


Fig. (4) Effect of demulsifier L concentration on the Na and K salts concentration (HFO containing 12 ppm of Na and K salts concentration) and using 10% wash water

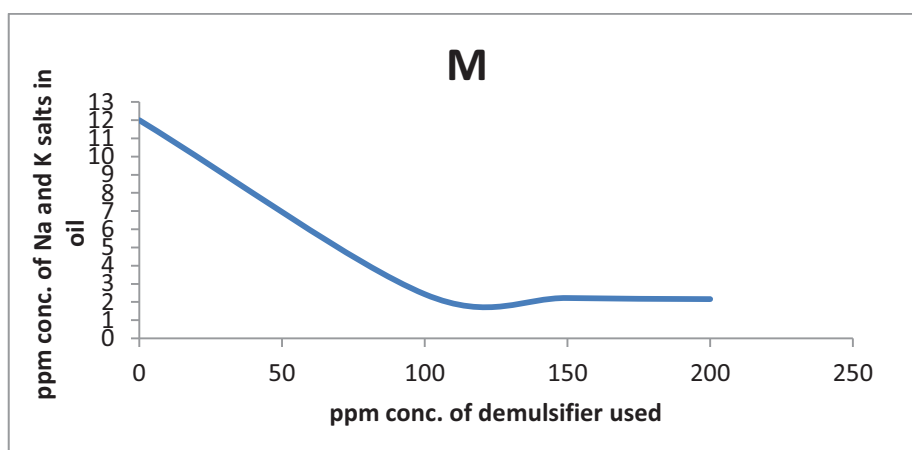


Fig. (5) Effect of demulsifier M concentration on the Na and K salts concentration (HFO containing 12 ppm of Na and K salts concentration) and using 10% wash water

Conclusions:

- 1- More variety of chemicals should be used in treating crude oil. These chemicals should be selected carefully.
- 2- Using more oil soluble surfactants in treating water in oil emulsions. These materials can do more effective role in the demulsification process.
- 3-Regarding the experimental methods, a combination of two methods should be used, the oil treatment and the bottle test to increase the range of demulsifiers and increase the number of experiments for each demulsifier in order to get the best idea of the demulsifier behavior through the use of different concentrations and other experimental conditions.
- 4- In case the combination of the two methods mentioned in point 3 a comparison should be made between the separated water from the bottle test method and the concentration of Na and K salts in the treated crude oil to understand exactly the relation between these two parameters.

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