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Investigation of microwave radiation in conjugate with acidizing as a novel hybrid method of oil well stimulation

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Abstract

In this research, the effect of microwave radiation simultaneous with acidizing on the carbonate rock surface has been investigated. Saturated rock sections were first immersed in the acid solution, and then, exposed to the microwave at 1300 W and 780 W for 1, 2, and 3 min. The surface wettability and hydrocarbon desorption from the rock surface were respectively investigated by the contact angle measurement and Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy. It was observed that the angle under the microwave in the vicinity of the acidic solution improves toward water-wetness and becomes oil-wet. The reduction of the contact angle in the combined mode is tenser due to the simultaneous effect of acid and microwave radiation. According to the ATR-FTIR spectrums, the microwave radiation of the sections during the acid treatment led to desorption of aromatic compounds, long alkanes, polar bonds (O-H and N-H), and the compounds with C=O functional groups. The electrically polar hydrocarbons have more affinity for separation from section during microwave radiation. As a result, microwave radiation could improve wettability alteration through asphaltene desorption during oil well acidizing.

1. Introduction

Acidizing of oil wells is conducted to create new pathways for hydrocarbon production (wormhole) and open blocked passages. The purpose of acidizing oil and gas wells includes reviving the well, opening pores, production improvement, and increasing permeability [1-3]. Wettability stands as a fundamental parameter crucial to oil fluid dynamics, significantly impacting production flow within reservoirs. Its influence extends to key factors like capillary pressure and relative permeability [4].

In the acidification of carbonate formations, acidizing is considered to open a new path for production, but in the acidification of sandstone formations, it leads to the reopening of passages that have been damaged and blocked. The difference between the acidification of these two formations is that in the sandstone formation, the dissolution of the damage that blocked the pores takes place, while in carbonate acidification, in addition to the damage, the reservoir rock is also dissolved by the acid. Precipitation of salts and generating asphaltene sludge are some challenges that most acidizing processes face. Hence, engineering the acidizing process to minimize the risks is always recommended [5].

He et al. [6] applied Formation Microwave Heat Treatment (FMHT) to enhance oil production through fracturing the formation. The findings indicate a notable escalation in fractures induced by microwave energy as the heating time prolongs. These fractures, along with newly formed pore sizes due to microwave treatment, led to a reduction in wave speed (S Pand) within the coal core. Additionally, the frequency spectrum range of the coal core decreased following exposure to microwave energy. Microwave radiation also influenced the frequency distribution range

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within the cores' frequency spectrum. Furthermore, the coal's density, bulk modulus, and shear modulus exhibited a decrease consequent to the microwave energy treatment. Notably, the rate of decrease in bulk and shear moduli surpassed that of coal density [6-10].

Alameedy et al. [11] explored the reaction kinetics of dolomite in carbonate acidification using both fresh and spent acid. Spent acid, characterized as a partially-reacted acid containing calcium and magnesium ions from the acid-rock reaction, was investigated. The findings revealed the dissolution of dolomite mineral within the acid. Moreover, a comparison between spent and fresh acid indicated higher kinematic viscosity and lower pH in the spent acid. The reported results suggested that the dissolution rate and diffusion coefficient of the used acid were greater than those of the fresh acid due to the higher kinematic viscosity and lower pH of the spent acid. These outcomes highlight an unusual ion effect from impurities like iron oxide and aluminum oxide in clay, unrelated to the hydrochloride-dolomite reaction, leading to increased reaction.

One of the important applications of electromagnetic waves is heating oil wells. Among the general advantages of this method of heating the wellbore region are the possible asphaltene cracking, and oil upgrading. The three employed methods are resistance heating, induction heating, and microwave heating [12]. Heating with microwaves has more advantages than other methods, such as less energy loss and not depending on the heat conduction of the environment. In this method, the microwave generating antenna is placed in a well, this well is drilled close to the production well [12]. The fluid in the reservoir that moves towards the production well is heated by microwave energy, in this way, the surrounding area of the well is uniformly heated to a large extent, and this can compensate for the pressure drop around the well area to a large extent. Reducing the viscosity of heavy and extra-heavy oils in this method greatly improves the performance of the reservoir and recovery [13].

In their 2018 study, Taheri-Shakib et al. [14] explored the impact of microwaves on the wettability of carbonate reservoir rock. Through an analysis of alterations in the rock's surface charge and contact angle measurements, their findings suggested that prolonged exposure to microwave irradiation led to an increased water-wet nature of the rock samples.

In their 2021 findings, Karami et al. [15] highlighted that the enhancement of rock wettability through microwave utilization isn't solely attributed to temperature-induced alterations. They observed that microwaves contributed to the breakdown of organic compounds on the rock surface, resulting in the weakening of van der Waals forces and subsequent changes in wettability. Shang et al. [16] investigated the impact of microwaves on crude oil viscosity and determined that variations in viscosity are contingent upon the specific compounds present within the oil. Karami et al. [17] conducted a study on mitigating condensate blockage using both microwave and ultrasonic methods. Their findings indicated that ultrasonic waves and microwaves exhibited a more pronounced impact on eliminating lighter oil compounds compared to heavier ones. Additionally, they inferred that the effectiveness of these methods—microwave and ultrasonic—was contingent upon the dielectric constant and acoustic properties of the respective compounds present within the oil. In their 2023 study, Karami et al. [18] compared the impact of ultrasonic and microwave treatments on asphaltene structure. Their findings indicated that both forms of radiation facilitated the cleavage of covalent bonds within asphaltene molecules. This breakdown resulted in a reduction in asphaltene size and contributed to enhancing its rheological behavior.

In this research, the effect of microwaves on the wettability of carbonate rock has been investigated. After the aging of the rock, they were exposed to microwaves and acid solution for 1-3 minutes with two powers of 780 W and 1300 W. Contact angle analysis has been used to investigate changes in wettability caused by wave radiation. Regarding the fact that asphaltene sludge generated during acidizing leads to wettability alteration of the rock surface, additional treatment is required to prohibit oil-wetness of the near-wellbore region. Because microwave radiation has been proven to be feasible for improving the water-wetness of the rock surface, it was employed to modify the wettability of the rock surface treated by the asphaltene sludge. The wettability of the aged carbonate rock sections was investigated after the acidizing and microwave radiation. The desorption of hydrocarbons from rock surfaces was studied using the Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy.

2. Materials and method

2.1. Materials

2.1.1. Rock sample

A carbonate rock sample was used to investigate the effect of microwaves during acidification on surface wettability. The results of the X-Ray Fluorescence (XRF) of the rock samples are given in Table 1. Based on the XRF analysis, 94.50% of the employed rock sample is comprised of $CaCO_3$. X-Ray Diffraction (XRD) analysis of employed rock sections confirms the rock sections are mainly composed of $CaCO_3$. Based on the XRD spectrum, the mineral contents of the employed rock sections are calcium carbonate, gypsum, microcline, and muscovite. It should be mentioned that the rock sections used in this study had a similar origin to carbonate rock sections employed by Yazdani et al. [19]. The XRD spectrum of the pulverized carbonate rock section is shown in Figure 1.

2.1.2. Oil sample

The oil sample was sourced from a southern oil field in Iran. Table 2 displays the API gravity, viscosity, acid number, and asphaltene content of this oil sample. In addition, the composition of oil sample employed to conduct the tests is shown in Table 3.

2.1.3. Acid solution

The acid solutions were prepared at a concentration of 15% to mimic the rock-acid interaction at the beginning of injection. Three base water of distilled water, seawater, and formation water were used to synthesize the acid solutions.

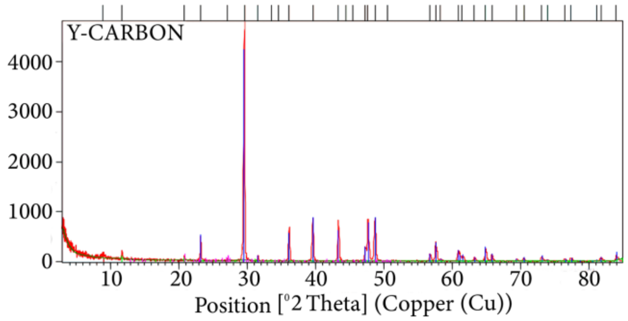

Figure 1. The XRD spectrum of the pulverized carbonate rock section [19].

Table 1. The XRF analysis of the rock sample.

Connie	Apparent percentage	LOI	Actual percentage
Na_2O	0.035	41.09	0.059413
MgO	0.565	41.09	0.95909
Al_2O_3	0.178	41.09	0.302156
SiO_2	0.697	41.09	1.183161
P_2O_5	0.081	41.09	0.137498
SO_3	0.735	41.09	1.247666
Cl	0.009	41.09	0.015278
K_2O	0.037	41.09	0.062808
CaO	55.675	41.09	94.50857
TiO_2	0.067	41.09	0.113733
Fe_2O_3	0.146	41.09	0.247836
Sr	0.684	41.09	1.161093

Table 2. API gravity, viscosity, acid number, and asphaltene content of this oil sample.

Physical properties	Crude oil
API	20.65°
Viscosity (cP)	37
(@ temperature 26°C)	
Acid number	0.6
Asphaltene content (%)	16

The composition of seawater, which is shown in Table 4, was adopted from the Persian Gulf seawater. Besides, the formation water was designed according to the produced water chemistry originated from the same field where crude oil was sampled.

2.2. *Methods*

2.2.1. Microwave treatment

A conventional microwave oven was provided to conduct microwave treatments. The frequency of the device is 2.45 GHz and its radiation power could be adjusted in the range of 260-1300 W. The internal dimensions of the microwave are 10×17×20 cm. Similar to other conventional microwaves bearing a magnetron, the one used in this study could only radiate waves with a single wave frequency. After, immersing the aged rock sections in the provided acid solutions, they were treated by microwave radiation with the radiation powers of 780 and 1300 W for 1-3 min. To investigate the effect of microwave radiation, similar rock sections were also treated with an acidic solution without microwave radiation.

Table 3. The composition of oil sample used for aging the rock sections.

Components	Mole weight	Flashed liquid
Nitrogen	28.01	0
Carbon dioxide	44.01	0
Hydrogen sulfide	34.08	0.0004
Methane	16.04	0
Ethane	30.07	0
Propane	44.1	0.139
I – Butane	58.1	0.127
N – Butane	58.12	1.318
I – Pentane	72.15	1.107
N – Pentane	72.15	3.105
Pseudo C6H14	84	6.109
Pseudo C7H16	96	9.316
Pseudo C8H18	107	9.478
Pseudo C9H20	121	8.252
Pseudo C10H22	134	7.054
Pseudo C11H24	147	6.568
Pseudo C12H26	161	5.547
Pseudo C13H28	175	4.16
Pseudo C14H30	190	3.813
Pseudo C15H32	206	3.12
Pseudo C16H34	222	2.427
Pseudo C17H36	237	2.08
Pseudo C18H38	251	1.733
Pseudo C19H40	263	1.387
Pseudo C20H42	277	1.248
Pseudo C21H44	291	1.04
Pseudo C22H46	305	0.832
Pseudo C23H48	318	0.763
Pseudo C24H50	331	0.693
Pseudo C25H52	345	0.555
Pseudo C26H54	359	0.485
Pseudo C27H56	374	0.416
Pseudo C28H58	388	0.347
Pseudo C29H60	402	0.277
C30+	935	16.666
Total	-	100

Table 4. The composition of brine water compositions (formation water and sea water).

Composition	Concentration (ppm)		
	Distilled water	Sea water	Formation water
NaCl	0	28323	177465
Na_2SO_4	0	4936	0
$CaCl_2$	0	1630	28036
$MgCl_2$. $6H_2O$	0	10510	6561
KCl	0	1032	3440
TDS	0	46431	215502

2.2.2. Temperature changes

The temperature of the rock sections was recorded by a digital laser thermometer (GM-320, Benetech) with an accuracy of ±1°C. Regarding the fact that a digital thermometer measures the material's temperature based on the reflected beam from the surface, it is not possible to measure the temperature continuously. To measure the temperature of treated rock in the middle of the microwave radiation, it was needed to halt the radiation every 30 seconds. Considering the short treatment time (3 min), stopping the treatment for even a short time disturbs the treatment. To avoid this problem, another batch of rock sections was prepared to capture the temperature profile. For instance, to obtain a temperature curve with six data points, six rock sections were treated in six duration times. It should be mentioned that to compare the temperature increase between the oil and rock, the oil samples with a weight equal to the rock section were also treated. The weight of the oil sample and rock section was 40 gr. The rock sections were cut to be in a rectangular cube form with the dimensions of 15 cm×10 cm×5 cm.

2.2.3. Contact angle analysis

One of the most important effective parameters for fluid displacement in the porous medium is wettability. The contact angle test was used to study the wettability alteration of carbonate rock sections before and after the treatments. The rock sections, which were cut from the rock sample described previously, were washed with methanol (two days) and toluene (ten days) to remove petroleum-based and salt-based contamination. The soxhlet device was employed to wash the rock sections. Then, the clean rock sections were saturated with formation water and kept at 90˚C for two days. The formation water-saturated rock sections were injected with crude oil, and then, kept in crude oil at 90 for 35 days. In the end, the wettability of the aged rock sections was restored to the reservoir condition. The rock sections were treated with the acidic solutions for 1hr at 70˚C. Afterward, they were treated by microwave radiation for 1, 2, and 3 min at radiation powers of 780 and 1300 W. At the end of the treatments, the wettability of the rock sections was investigated by using the pendant drop technique. It should be mentioned that the contact angle measurements were conducted 3 times and the median point was reported. Based on the obtained data, the accuracy of the contact angle data was ±0.6°.

2.2.4. ATR-FTIR spectrums

Investigating the wettability alteration by using the pendant drop method gives no information about the chemistry of the desorbed hydrocarbons. The ATR-FTIR of the treated rock sections was investigated by a refractometer (PerkinElmer, USA). The spectrums were obtained from 600-4000 cm^{-1} with a resolution of 1 cm^{-1}. To obtain the computational data from the ATR-FTIR spectrums, the integral area of the hydrocarbon-related peaks was calculated. By implementing the calculated integral areas, the computational characteristic indexes were obtained through equations suggested by Karami et al. [20]. Based on the characteristic indexes, given by ATR-FTIR spectrums, the polar, carbonyl, aliphatic, and aromatic content of the rock sections were addressed.

3. Results and discussions

3.1. Temperature changes

The temperature changes of rock samples under microwave radiation are shown in Figure 2. The temperature of the oil samples increased to 55˚C and 75˚C after microwave radiation for 3 min at radiation powers of 780 W and 1300 W, respectively. Besides, the temperature of the rock sections increased to 94˚C and 120˚C after microwave radiation for 3 min at radiation powers of 780 W and 1300 W, respectively. The reason for temperature increase could be explained by basic laws of physics. Changing the direction of electric dipoles of polar compounds, when it's exposed to the microwaves, leads to thermal energy. The kinetic energy of compounds with high dielectric constants are more absorbent to the microwave, making them good candidate for microwave thermal heating [21,22]. Therefore, higher temperature of the rock sections, respect to the adsorbed hydrocarbon, is explainable based on the higher dielectric constants of the rock sections. An increase in temperature may cause physical and chemical changes to the adsorbed hydrocarbons, leading to cracking and desorption of the polar compounds, such as asphaltenes [23,24].

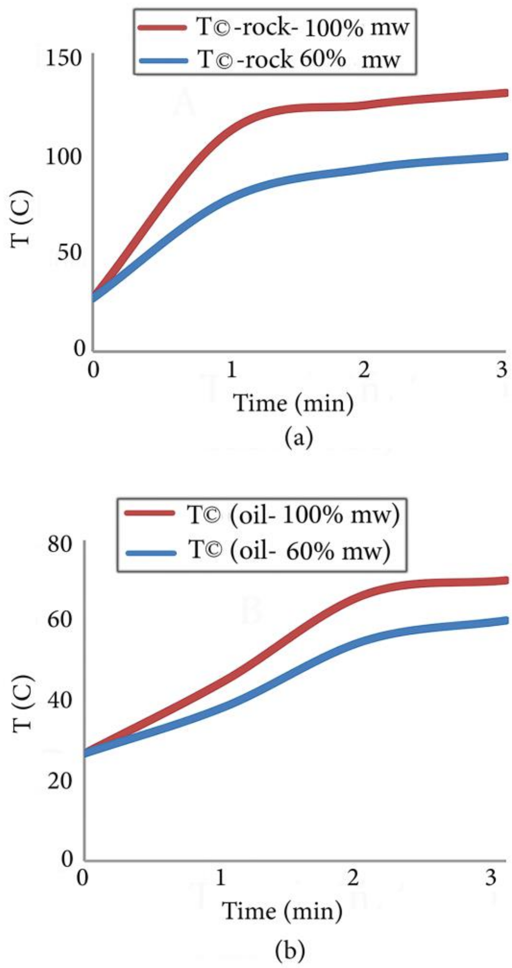

Figure 2. Temperature changes of (a) aged rock sections treated by microwave and (b) oil samples treated by microwave irradiation time.

At first glance, the range of temperature rise is not considerable; regarding other heating methods, higher temperature rise is expected for improving wetting conditions. To explain this issue, the treating condition and heating mechanism of the microwave must be considered. The rock sections were immersed in the solution to mimic the reservoir condition. There is a heat transfer between the rock section and the immersing solution, forcing the rock section to be in thermal equilibrium with the immersing solution. Although the solutions have a much higher dielectric constant with respect to the rock sections, their temperature cannot exceed its boiling point during microwave radiation.

At identical microwave power radiation, exposure time, and wave frequency, the temperature of the materials, including rock sections and oil samples, strongly depends on dielectric constants. The dielectric constant of oil samples, depending on their hydrocarbon content, lies in the range of 1-4.5 [25-28]. In addition, the dielectric constant of the $CaCO_3$ is 9.2 [29]. A higher temperature increase, which was observed for rock sections, confirmed the fact materials with a higher dielectric constant are a better absorbent to microwaves. It should be mentioned that the temperature, which was recorded by the laser thermometer, reports the macroscopic temperature. Crude oil is generally comprised of various hydrocarbons having a wide range of polarity/dielectric constants. The dielectric constant of asphaltene compounds is overall four times of the aliphatic ones, leading to the creation of regions with higher temperatures on a molecular scale. Hence, the temperature of asphaltene molecules is almost four times of the bulk oil sample. As a result, if the oil sample temperature reaches 70°C after 3 minutes of radiation at 850 W, the temperature of asphaltene aggregates reaches 280˚C.

In addition, the lower temperature of the oil sample/rock sections, respect to other thermal methods could also be explained by lower radiation time (3 minutes). After 3 minutes of radiation, the contact angle of some of the rock sections reduced to 62°, while the others were still oil-wet. Increasing the radiation time leads to converging all the contact angles toward the most possible hydrophilic condition, making it impossible to investigate the effect of the microwave radiation and imbibition water composition. Hence, to capture the difference between the various acidizing conditions, the exposure time of 3 min was appropriate.

3.2. Contact angle

According to the reduction of the contact angle in both radiation powers (780 and 1300 W), microwave radiation in conjugate with acid solutions treatment improves hydrophilicity. In the vicinity of an acid solution under a constant temperature of 70°C, the contact angle will decrease due to the loss of light components under the temperature. Due to the polarity of the acidic solution, some of the polar components of the crude oil will react and dissolve with the acidic solution, and as a result, the polar components spread on the surface of the rock will increase slightly, and as a result, the effect of reducing the contact angle due to constant temperature will not intensify. The lowest contact angle related to an acidic solution containing distilled water is 57.1˚ due to less polarity and the highest contact angle related to an acidic solution containing distilled water is 108.2˚ due to polarity. The reduction will be severe, and the greatest reduction of acid solution and water formation will be near the microwave, because high salinity improves the heating power of the microwave.

In the vicinity of acid solution and microwave waves for different periods and different powers, the contact angle will decrease initially due to the loss of light components. By increasing the exposure time, polar compounds will be removed from the section. As a result, the contact angle increases. The lowest contact angle related to the acid solution including seawater and power of 780 W is 55.9˚ and the highest contact angle (114.1˚) is related to the acid solution with a base of sea water and microwave power of 780 W.

The reduction of the contact angle of distilled water, seawater, and formation water will be almost equal in the initial time. The acid solutions with the base of formation water reduces the contact angle to 55° compared to distilled water and seawater base solutions. Also, the high polarity of formation water and seawater causes polar components to dissolve in polar solution (formation water and sea water) and therefore heavy components such as asphaltene and resin are easily separated from crude oil compounds.

According to the contact angles of the sections treated by acid solution, without microwave radiation, the distilled water base acid solution is more feasible for wettability alteration. Besides, a higher hydrophobicity was observed in the sections treated by the formation water base acid solution. Hence, it could be concluded that the presence of the dissolved ion prohibits desorption of hydrocarbon, reducing the ability of acid solution for improving rock surface hydrophilicity.

In Figure 3, the contact angles are shown without the influence of microwaves and only in the vicinity of acid, and it can be seen that the contact angles undergo decreasing changes. Based on the contact angles, shown in Figures 4 and 5, the base water composition and irradiation power and exposure time affect the wettability of the treated rock. The wettability of the rock sections treated by radiation power 1300 W reduces to almost 60˚ after 2 min, and then, increases again at higher exposure times. The reduction of contact angle, indicating rock hydrophilicity improvement, could be desorption of non-polar hydrocarbons from the rock surface. Further microwave radiation could desorb or crack the polar hydrocarbons, such as asphaltenes, leading to increasing the rock hydrophobicity. The composition of base water did not influence the rock wettability at high radiation power (1300 W).

Despite the sections treated by high-power radiation, the base water chemistry influenced the sections treated by microwave power of 780 W. The lowest contact angle was observed in the section treated by the formation water. More salinity of the formation water, representing higher ion concentration, makes microwave radiation more feasible for wettability alteration. The dissolved ions, which are electrically charged, are highly influenced by alternating electric and magnetic fields.

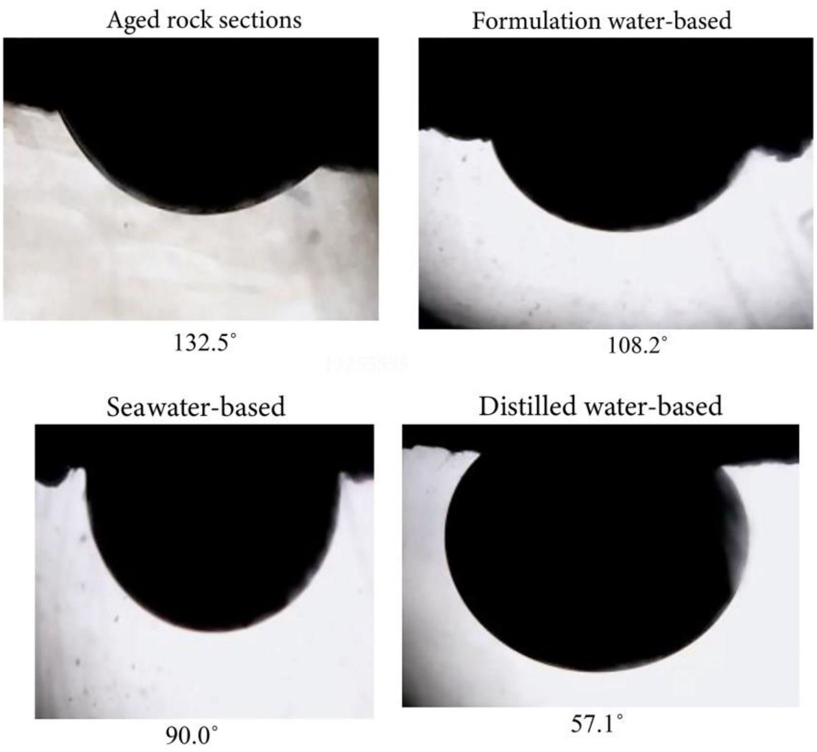

Figure 3. The contact angle between aged rock sections and crude oil being treated with acidic solutions for 1 Hour without microwave radiation .

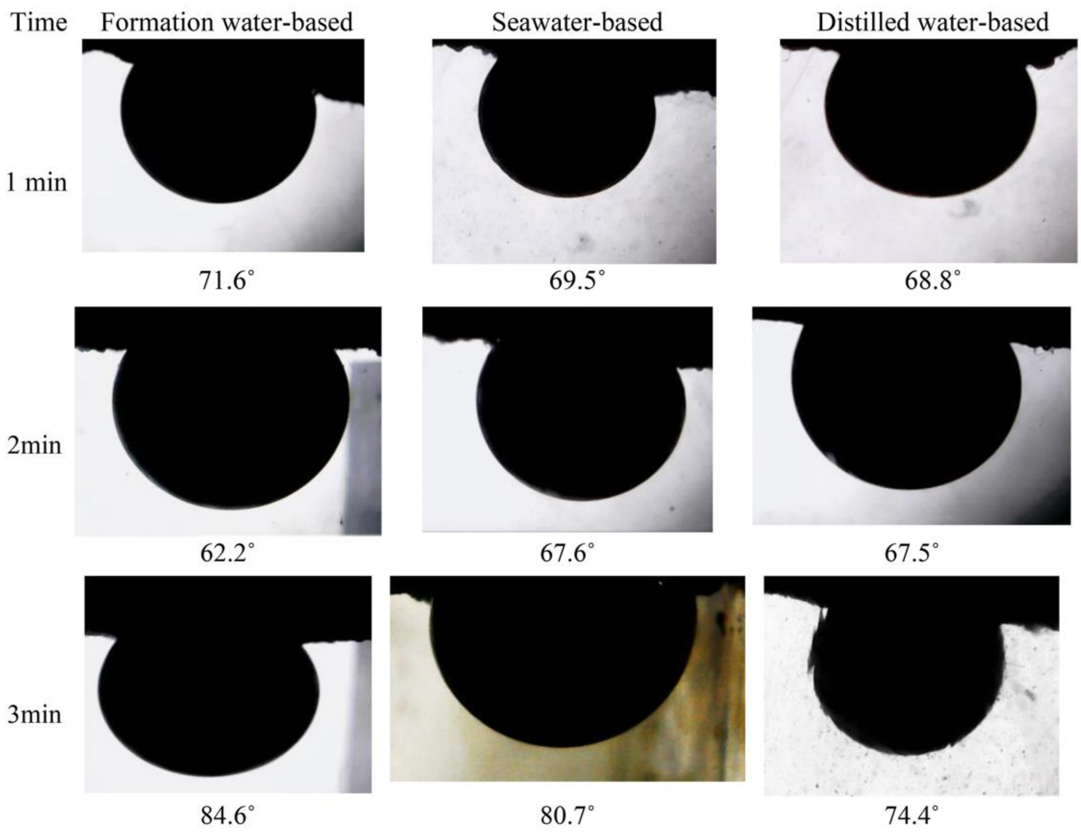

Figure 4. The contact angle between rock sections and crude oil after being exposed to microwave with emission power of 1300 W and acidic solutions for 1, 2, 3 min .

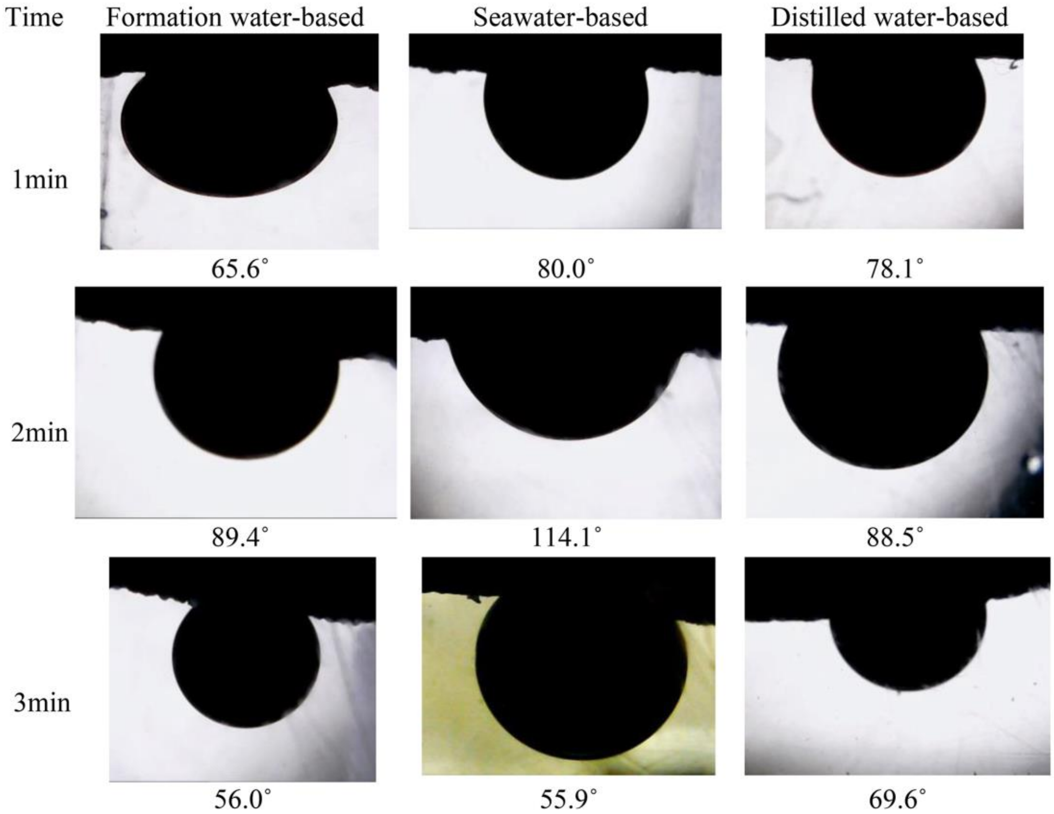

Figure 5. The contact angle between rock sections and crude oil after being exposed to microwave with emission power of 780 W and acidic solutions for 1, 2, and 3 min.

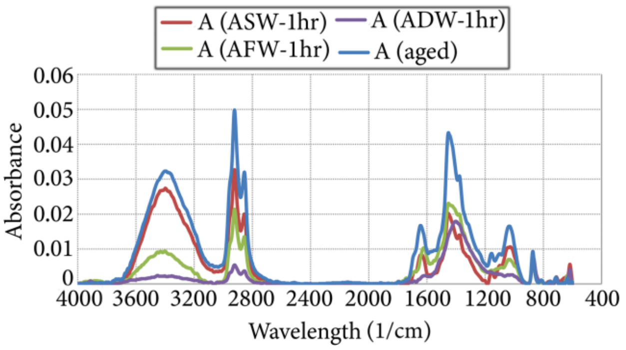

Figure 6. The normalized ATR-FTIR spectrums for acidized rock sections without microwave radiation.

3.3. *ATR-FTIR spectroscopy*

The contact angles, obtained by the sessile drop technique, addressed the wettability status of treated rock sections. But no information was provided regarding desorption of hydrocarbons from the rock surface. The ATR-FTIR spectrums of the Acid-treated rock sections are shown in Figure 6. Besides, Figures 7 and 8 are indicating the ATR-FTIR spectrums of the rock section treated by simultaneous acid solution and microwave radiation with 780 W and 1300 W, respectively.

The peaks in the ATR-FTIR spectrums depict both the adsorbed hydrocarbons and rock minerals. The observed in the ATR-FTIR spectrums could be subdivided into three groups rock-assigned, hydrocarbon-assigned, and common peaks. Regarding the fact that the ATR-FTIR spectrums were employed to address the hydrocarbon chemistry, the peaks that are only assigned to hydrocarbons were taken into calculation. As shown in Table 5, the aliphatic C-H bonds are represented by peaks in the range of 2755-3000 cm^{-1}. Besides, the ranges of 3000-3100 and 1566-1668 cm^{-1} are respectively standing for C-H and C=C bonds in the aromatic rings. Ketone-based functional groups, such as carboxylic acids groups, are vibrating in the range of 1668-1800 cm^{-1}. In addition, the amine and alcoholic functional groups are seen in the range of 3100-3500 cm^{-1}. More information regarding the chemistry of hydrocarbons could be found in Table 5. As mentioned before, to extract numerical data from ATR-FTIR spectrums, the characteristic indexes given by Karami et al 2022 were employed [30]. The Aromatic/Aliphatic, Aliphatic length, C=O/Aliphatic, C=O/Aromatic, Polar/Aliphatic, and Polar/Aromatic indexes were calculated regarding the integral areas of the corresponding peaks. Table 6 shows the characteristic indexes obtained from the ATR-FTIR spectrums [30-33].

Table 5. The assignments of the peaks in the ATR-FTIR spectrums [30-35].

Wavelength	Assignment
3100-3500	N-H, O-H
3000-3100	C–H stretch in aromatic
2946-3000	CH_3 asymmetric stretch
2881-2946	CH_2 asymmetric stretch
2755-2881	CH_2 symmetric Stretch
1668-1800	C=O stretch in ketones, aldehydes, and carboxylic acids
1566-1668	Aromatic C=C stretch

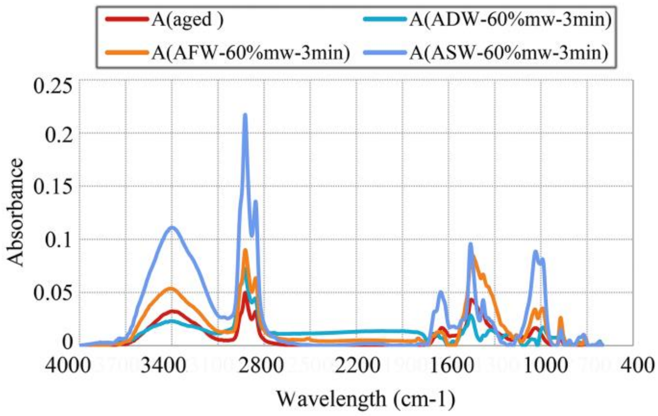

Figure 7. The normalized ATR- FTIR spectrums for crude section and sections treated by acid solutions and the radiation power of 780 W for 3 min.

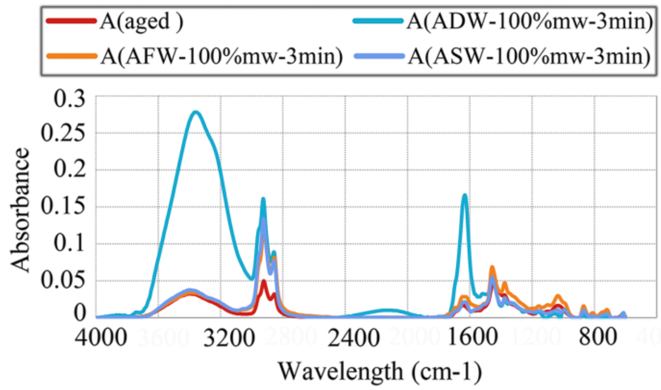

Figure 8. The normalized ATR- FTIR spectrums for crude section and sections treated by acid solution and the radiation power of 1300 W for 3 min.

Table 6. The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-treated rock section (HCl 15%).

Index/treatment solution	Crude	DW-based	SW-based	FW – based
C=O/Aliphatic	0.177	0.223	0.088	0.237
C=O/Aromatic	0.342	0.307	0.259	0.325
Aromatic/ Aliphatic	0.518	0.725	0.339	0.730
Aliphatic length	0.375	0.341	0.382	0.312
Polar/Aliphatic	3.648	2.298	4.640	2.256
Polar/Aromatic	7.036	3.167	13.666	3.089

To investigate the chemistry of the hydrocarbons, which have a greater tendency for desorption from the rock surface, the ATR-FTIR spectrums were analyzed from an analytical point of view. In this regard, the integral area of each hydrocarbon-assigned peak was employed to be used in the characteristic equations given by Refs. [30-35]. Eqs. (1)-(6) show the ratios used to characterize the chemistry of hydrocarbons adsorbed on the rock surface. In Eqs. (1)-(6), the 'A_i' stands with the integral area below the peak in the range of 'i' as following:

$$C{=}O/Apliphatic = \frac{A_{1668-1800}}{A_{2881-2946}}, \quad (1)$$

$$C{=}O/Aromatic = \frac{A_{1668-1800}}{A_{1566-1668}}, \quad (2)$$

$$Aromatic/Apliphatic = \frac{A_{1566-1668}}{A_{2881-2946}}, \quad (3)$$

$$Aliphatic\ length = \frac{A_{2946-3000}}{A_{2881-2946}}, \quad (4)$$

$$Polar/Apliphatic = \frac{A_{3100-3500}}{A_{2881-2946}}, \quad (5)$$

$$Polar/Apliphatic = \frac{A_{3100-3500}}{A_{2881-2946}}, \quad (6)$$

As shown in Table 6, except for the seawater-based acid solution, the Aromatic/Aliphatic index of the acid-treated section is increased. The decrease of the Aromatic/Aliphatic index in the seawater-based acid solution represents more affinity of the aromatic compound to be desorbed from the rock surface due to the presence of determining ions. Aliphatic length, which is lower in the longer aliphatic hydrocarbons, is drastically decreased in the formation of water-based acid solution. Hence, it could be concluded that the high salinity brine water reduces desorption of the long-chain alkanes. Based on the aliphatic length index, the seawater-based solution desorbed the long-chain alkanes with more efficiency. As shown in Table 6, both indexes of the Polar/Aliphatic and Polar/Aromatic only increased in the seawater-based acid solution, representing less potential of the polar functional group (O-H and N-H) for desorption respect to the aromatic and aliphatic hydrocarbons. The lower Aromatic/ Aliphatic index of the section, which was treated with a seawater-based acid solution, indicates that the aromatic hydrocarbon was tenser. Hence, the drastic increase of the Polar/Aromatic index in seawater-based acid solution could be understood by the severe desorption of aromatic hydrocarbons. Both indexes of C=O/Aliphatic and C=O/Aromatic are the least in the seawater-based acid solution, indicating more severe desorption of carbonyl-based functional groups. Based on the characteristic indexes, given by ATR–FTIR spectrums, the chemistry of the hydrocarbons on the rock surface is influenced by the composition of base water.

The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-treated rock section, which were radiated by microwave, are shown in Table 7. The Aromatic/Aliphatic index of the microwave-treated sections is generally lower than the crude aged section, representing that the microwave radiation leads to more efficient desorption of the aromatic compounds, such as asphaltenes. It should be mentioned that the sections, which were not treated by microwave radiation (Table 6). The Aliphatic length indexes of microwave-treated rock sections are higher than the crude rock section. Hence, microwave radiation

Table 7. The characteristic indexes calculated from the ATR-FTIR spectrums of the crude and acid-treated rock section, which were radiated by microwave.

Index	Crude	Radiation power= 780 W			Radiation power= 1300 W		
		DW	SW	FW	DW	SW	FW
C=O/Aliphatic	0.177	0.334	0.148	0.165	0.316	0.083	0.140
C=O/Aromatic	0.342	2.905	0.474	1.27	0.231	0.360	0.362
Aromatic/ Aliphatic	0.518	0.115	0.312	0.131	1.366	0.232	0.387
Aliphatic length	0.375	0.574	0.394	0.387	0.584	0.415	0.374
Polar/Aliphatic	3.648	1.943	3.043	3.272	10.980	1.678	1.649
Polar/Aromatic	7.036	16.892	9.726	24.888	8.036	7.203	4.258

leads to desorption of longer alkanes from the rock surface. Based on the aliphatic length index, desorption of longer alkanes is more severe in the sections treated with distilled water. The Polar/Aliphatic index is commonly lower in the microwave-treated rock sections, indicating the feasibility of microwave radiation for desorption of polar functional groups (O-H and N-H). Despite the Polar/Aliphatic index, the Polar/Aromatic index does not show a consistent trend in the microwave-radiated sections. This irregular trend for Polar/Aromatic could be explained by tense desorption of both aromatic compounds (according to the Aromatic/Aliphatic index) and polar functional groups (observed from the Polar/Aliphatic index). Except for the sections, which were treated by distilled water-based acid solution, the C=O/Aliphatic index of the microwave-treated sections was lower than the crude one. Hence, it could be deduced that desorption of C=O-based functional groups is less efficient without the presence of other ions. Besides, the C=O/Aliphatic index is generally lower in the sections radiated by the power of 1300 W, representing an increase of the C=O bond desorption at higher radiation powers. The C=O/Aromatic index of the microwave-treated sections does not follow a regular trend, which might be due to the tense desorption of aromatic compounds.

By comparing the characteristic indexes, given by the ATR-FTIR spectrums, the microwave radiation of the rock sections during the acid treatment leads to more efficient desorption of aromatic compounds, longer alkanes, polar bonds (O-H and N-H), and C=O based functional group. Hence, simultaneous microwave radiation could be employed to remove the precipitated asphaltene sludge generated by acid treatment. More affinity of the aromatic, polar, and long-chain alkanes for desorption during simultaneous microwave radiation and acid treatment could be explained by the fundamental laws of electromagnetic. The microwave energy absorption of the material is directly proportional to the electric polarity of the material. The material with higher dielectric constants is more absorbent respect to electromagnetic waves, such as microwaves. The hydrocarbons in the crude oil and ones adsorbed on the rock surface lies in a wide range of electric properties. According to the literature review, the dielectric constant of the asphaltenes could also be 3-4 times of the other hydrocarbons, such as alkanes [36-40]. Hence, the energy absorbed by asphaltene molecules could lie in the range of 3-4 times of the other hydrocarbons. The asphaltenes are widely accepted as polycyclic aromatic compounds, attached by aliphatic chains and polar functional groups [41-44]. Hence, the reduction of the mentioned indexes indicates the asphaltene molecule desorption during simultaneous microwave radiation and acid treatment.

4. Conclusion

In this research, the effect of acid solution treatment in conjugate with microwave radiation on the rock-fluid interaction was investigated. Using the contact angle measurement and Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR-FTIR) spectroscopy, the following statements were concluded.

- According to the contact angles, the composition of base water and radiation power and exposure time affects the rock wettability. When there is no microwave radiation applied to the rock section, the addition of dissolving ions prohibits the wettability alteration. In contrast, the saline water (formation water) showed lower oil-wetness when the microwave radiation was combined. Besides, while increasing the radiation power leads to a lower contact angle, increasing the exposure time could either increase or decrease it;
- By comparing the characteristic indexes, given by the ATR-FTIR spectrums, the microwave radiation of the rock sections during the acid treatment leads to more efficient desorption of aromatic compounds, longer alkanes, polar bonds (O-H and N-H), and C=O Based functional group. Hence, simultaneous microwave radiation could be employed to remove the precipitated asphaltene sludge generated by acid treatment.

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Conflicts of interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors contribution statement

Hadi Tanhaei: Formal analysis; Visualization; Writing original draft; Conceptualization; Investigation; Methodology; Validation.

Amir Hossein Saeedi Dehaghani: Supervision; Funding acquisition; Resources.

Saeed Karami: review and editing.

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Amir Hossein Saeedi Dehaghani, received his PhD from Tarbiat Modares University in 2013 and has been working as a faculty member in the Petroleum Department, Faculty of Chemical Engineering since 2013. Some of his research interests are increasing extraction by injecting CO_2, N_2, Natural Gas, laboratory investigation and modeling of wax and asphaltene deposits (solid hydrocarbons), investigation of sediment inhibitors (organic and inorganic) in oil reservoir, smart water injection with nanofluids and surfactants including production enhancement, determining the kinetics of asphaltene precipitation, acidification and investigating the formation of acid sludge, lightening of extra heavy oil by physical and chemical methods, phase behavior of reservoir fluids, membrane construction, and membrane separation for gas sweetening.

Saeed Karami, the Head of the Research and development of Petro Atlas Zagros Company, who graduated from Tarbiat Modares University in 2018 in the field of Petroleum Engineering - Reservoirs, one of his areas of expertise is petroleum chemistry and molecular characterization. He is also the author of several international articles in the fields of smart water and microwaves. He has also been a consultant for MSc students' theses and has cooperated with the subsidiaries of the ministry of oil in the MSc course.