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Article

Sediment Removal from Crude Oil Emulsion using Microwave Radiation

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Radiação micro-ondas em sistema fechado foi utilizada para a remoção de sedimentos de emulsão de petróleo para a posterior caracterização em laboratório. O programa de aquecimento do forno de micro-ondas foi otimizado através da avaliação do tempo de aquecimento (5 a 30 s) e da potência de micro-ondas (300 a 1400 W). O teor de sedimentos foi determinado usando um procedimento de filtração com membrana conforme recomendado pela norma ASTM D 4807-05, antes e após a remoção de sedimentos. Os teores de água e cloreto foram determinados no óleo obtido após a remoção de sedimentos. Até oito amostras de 20 g puderam ser processadas simultaneamente. A eficiência de remoção de sedimentos foi superior a 95%. Foi possível a obtenção de petróleo virtualmente isento de água, sal e sedimentos, permitindo a determinação de parâmetros como gravidade API, densidade, viscosidade e número de acidez total sem interferências causadas por sedimentos ou mesmo sal e água.

Microwave radiation in closed vessels was applied for removal of sediments from crude oil allowing the subsequent crude oil characterization in laboratory. Heating time and microwave power were evaluated in the range of 5 to 30 s and 300 to 1400 W, respectively. Sediment content was determined using the method recommended by ASTM D 4807-05 based on a filtration step in a membrane before and after sediment removal. Water and chloride contents were determined in the oil phase obtained after sediment removal. Up to eight samples of 20 g of crude oil could be simultaneously processed. Sediment removal efficiency was better than 95%. It was possible to obtain crude oil in a suitable condition for determination of routine parameters as API gravity, density, viscosity and total acid number without interferences caused by sediments or even water and salt.

Keywords: microwave radiation, sediment removal, crude oil, emulsion, demulsification

Introduction

Separation of water from crude oil is a challenging task in oilfields due to the high stability of water-in-oil (W/O) emulsions.[1] It is already known that emulsion stability is directly related to oil composition and naturally occurring compounds present in crude oil.[2] Asphaltenes and resins have been shown to promote and stabilize crude oil emulsion. Additionally, some works have demonstrated that inorganic solids can increase the emulsion stability. The influence of these emulsion stabilizers in crude oil was proved using model and natural emulsions and it was concluded that solids play one of the major effects in the stabilization of W/O emulsions.[3,4]

The mechanism of solids in the stabilization of W/O emulsions is contradictory. According to Sullivan *et al.*,[2]

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the presence of inorganic solids could increase the emulsion stability if the particle size is small enough to become interfacially active to cause the adsorption of resins and asphaltenes. The decrease of particle size would enhance the emulsion stability due to increase of interactions between asphaltenes and particles. On the other hand, it was concluded that solids have no effect in the adsorption of asphaltenes on water droplet surface, in spite of their contribution for emulsion stability.[1]

Many efforts have been performed to develop new strategies for achieving an efficient breaking of W/O emulsions in crude oil and, consequently, to remove water, salt and solids. However, despite the importance of demulsification process, the laboratory characterization of crude oil can be more challenging than the step of the emulsion separation.[5] The characterization of crude oil is extremely important for decisions during exploration, production and refining steps. In this way, samples with low content of water and salt are normally required for the determination of crude oil characteristics, such as density, viscosity, among others.[6,7] In this sense, it is necessary to remove water, salts and also solids from crude oil emulsions before laboratory characterization in order to avoid interferences during the analysis.

Water removal in laboratory scale is currently performed using conventional heating and chemical additives since the efficiency of removal can be evaluated by measuring the water content in the oil phase or the salt content in the aqueous phase.[8] Other techniques have been investigated for water removal such as settling by gravity and simple distillation.[9,10] In spite of relatively good efficiency of these methods, they are time consuming, especially for heavy crude oils, and the addition of demulsifiers is frequently required.[11] Additionally, salt and solids are not efficiently removed from the crude oil and can cause interferences especially on density (API gravity) determination.[7]

The determination of sediments in crude oil is usually performed using a method recommended by the American Society for Testing and Materials (ASTM D 4807-05), that is based on a dilution step of samples with toluene, filtration through a 0.45 µm membrane and quantification of solids by weighing.[12] The solids present in crude oil are commonly described as clay particles.[13] However, recent studies have been done in view of solid particles characterization isolated from crude oil samples using the proposed ASTM method and some authors found that these particles were composed mostly of sodium chloride, called salt spheres.[5,14] The characterization of solid particles also revealed other finely divided materials that were composed of calcium and sulfur atoms, indicating the presence of calcium sulfate.[5,14]

In addition to the determination of sediment and water contents, another important parameter to be determined in the crude oil is the salt content. In this sense, a method that consists of extraction using a mixture of solvent and subsequent chloride determination by titration with $AgNO_3$ is usually employed for the determination of salt (expressed as NaCl) in crude oil.[15] However, although some improvements have been proposed, this method is sample destructive and relatively time consuming.[16] The use of microwave radiation in demulsification processes has been reported in several works.[16,17] Microwave electromagnetic field causes fast heating due to molecular rotation and movement of ions as a consequence of induced or permanent molecule dipoles. Thus, the application of microwave radiation to emulsions results in destabilization of interfacial film because of the temperature increase and consequently water droplet coalescence.[16]

Recently, a method using microwave radiation for salt extraction from heavy crude oils has been proposed.[8] The method involves the addition of water to crude oil in a quartz vessel and subsequent microwave irradiation. Using this method, water and oil phases were completely separated and the salt content was determined in the water phase. On the other hand, the separation of water from heavy crude oil using microwave radiation was subsequently investigated and it was possible to obtain crude oil free of water and salt.[18] The main advantage of the proposed microwave-assisted method is that it does not require chemical demulsifiers or other reagents and enables the determination of the salt content in water phase. Moreover, the demulsified crude oil is obtained in a suitable condition for laboratory characterization. In spite of its good performance for salt extraction and water separation, the feasibility of this method was not evaluated up to now for sediment removal.

In the present work, microwave radiation was applied for removal of sediments from real crude oil emulsions with relatively high sediment content (1 to 6%). The efficiency of the proposed method was evaluated based on the determination of sediments in heavy crude oil emulsion without treatment and in the oil phase obtained after microwave heating procedure. Additionally, water and Cl were also determined in the oil phase after sediment removal. Microwave heating program, sample mass and number of extraction steps were evaluated. Samples obtained after microwave irradiation procedure were characterized by performing the determination of sediments, water, S, N and Cl (reported as NaCl). In addition, total acid number (TAN), kinematic and dynamic viscosity and API gravity were evaluated in demulsified heavy crude oil only after the proposed microwave-assisted sediment removal method.

Experimental

Instrumentation

A microwave sample preparation system (Multiwave 3000, Anton Paar, Graz, Austria) equipped with eight high-pressure quartz vessels (80 mL) was used for the proposed microwave-assisted sediment removal method. Temperature and pressure were controlled in real time during all experiments. In order to keep a safe operation, the maximum operational temperature and pressure selected were 260 °C and 70 bar, respectively. This equipment was also used for crude oil digestion by microwave-induced combustion (MIC) for further Cl determination (before and after sediment removal).[19,20]

An ion chromatographic system (Metrohm, Herisau, Switzerland) equipped with a pump (IC liquid handling unit), a conductivity detector (model 819), auto sampler (model 813), anion self-regeneration suppressor (model 833) and a sampling loop of 100 µL were used for Cl determination in crude oil before and after microwave-assisted sediment removals and after microwave-induced combustion (MIC) digestion according to the procedure described in previous work.[20] An anion exchange column (Metrosep A Supp 5, with 150 × 4 mm i.d.) and a guard column (Metrosep A Supp 4/5 Guard) were used. The suppressor column was periodically regenerated with water and 50 mmol L^{-1} H_2SO_4. A solution of 3.2 mmol L^{-1} Na_2CO_3 and 1 mmol L^{-1} $NaHCO_3$ was used as mobile phase at a flow rate of 0.7 mL min^{-1} as well as a dialysis cell composed of a cellulose triacetate membrane. Results were reported as NaCl content.

The determination of TAN in crude oil before and after sediment removal was performed following the method recommended by ASTM[21] using an automatic titrator (Titrando 836, Metrohm, Switzerland) equipped with a combined glass electrode for non-aqueous media. The same equipment was used for water content determination according to ASTM D 4377 standard test method, using a platinum electrode.[22]

For the N and S determinations, a specific analyzer (model 9000 series, Antek Instruments, USA) was used and the procedures were carried out according to ASTM D 4629[23] and ASTM D 5453[24] methods, respectively. Samples obtained after sediment removal using microwave radiation were homogenized, dissolved in toluene and injected into the high temperature combustion tube using a syringe.

The determination of density and viscosity was performed according to ASTM D 7042[25] method, using a Stabinger viscometer (model SVM 3000, Anton Paar, Austria). Samples obtained after sediment removal were homogenized and introduced into the measuring cells with controlled temperature.

Chemicals, solutions and samples

All reagents were of analytical grade. Purified water from a Milli-Q® system (Milipore, Billerica, USA) was used for sediment removal using microwave radiation and also to prepare all reagents, standard solutions and mobile phase. Stock standard solution of Cl (1000 mg L^{-1}) was prepared by dissolving NaCl (Merck, Darmstadt, Germany) in water and analytical standards were prepared by sequential dilution of this solution in water. Sodium carbonate (Merck) and $NaHCO_3$ (Merck) were used to prepare the mobile phase, and H_2SO_4 (Merck) was used to prepare the solution used for suppressor column regeneration. Glass materials were cleaned using toluene and water and further soaked in 20% (v v^{-1}) HNO_3 (Merck) and rinsed with water before use.

Water content was determined in the crude oil before and after sediment removal using Karl Fischer (two-component) reagent Composite 5 (Riedel-de Häen, Seelze, Germany). A mixture of toluene (Vetec Química Fina Ltda., Rio de Janeiro, Brazil) and methanol (Carlo Erba Reagents, Milan, Italy) (3 + 1) was used for sample dissolution. Toluene (Vetec) was also used for sediment determination in crude oil.

Standard solutions for S and N determination were prepared after dissolution of dibenzothiophen (DBT) ($C_{12}H_8S$, ≥ 98%, Merck) and pyridine (Merck) in toluene, respectively. Naturally emulsified heavy crude oil samples, identified as A, B and C, were used. Heavy crude oil A was selected for development and optimization of the proposed method that was subsequently applied for other samples.

Microwave-assisted sediment removal method

Heavy crude oil emulsions were heated at 60 °C for 30 min and homogenized using a mechanical stirrer for 15 min. Subsequently, 20 g of sample were weighted directly into the quartz vessels and 20 mL of water were added. Five glass spheres (ø = 5 mm) were also added to avoid sample projection during the microwave heating. The proposed microwave heating procedure was performed using operational parameters described in Table 1.

After the end of the heating program, the oil phase was transferred to a polypropylene vessel using a syringe. Then, water containing the sediments was removed from quartz vessels and also transferred to vessels. Before characterization, crude oil was centrifuged (7000 rpm)

Table 1. Microwave heating program used for sediment removal from crude oil emulsion

Parameter	
Sample mass / g	20
Water volume / mL	20
Power / W	1400
Ramp / min	5
Heating time / min	5
Cooling / min	20
Maximum temperature / °C	260
Maximum pressure / bar	70

in order to improve the separation of free water droplets, according to the procedure described in a previous work.[18]

Heavy crude oil was characterized by the determination of sediments, salt (as NaCl), water content, viscosity, density, N and S. After each microwave run, vessels were cleaned using, firstly, toluene for removing oil residues, then with concentrated nitric acid by heating in microwave oven for 10 min and rinsed with water.

Determination of sediments in crude oil before and after microwave irradiation

Sediment content in heavy crude oil was determined according to ASTM D 4807 method.[12] Briefly, the procedure consists of filtering a known amount of crude oil with toluene at 90 °C through a 0.45 µm pore size nylon membrane. The weight of membrane is recorded (after drying at 105 °C) before and after crude oil filtration. The mass of solids (in percentage) is calculated by the difference of weight of membrane and related to the amount of filtered crude oil. This procedure was applied before and after sediment removal to evaluate the efficiency of the proposed method for sediment removal from crude oil.

The water phase obtained after microwave-assisted sediment removal method was also filtered through a 0.45 µm pore size nylon membrane for the solid content determination. The membrane was washed with hot toluene to remove oil residues from solid particles, and the quantification was performed by weighing, as it was performed for crude oil. Additionally, water phase was also analyzed for determination of total solid content. In this case, the determination was performed following a procedure commonly used for total solid determination in water.[26] Water phase was transferred to a previously dried and weighed platinum crucible, left in an oven until dry at 80 °C and after at 105 °C for 1 h. After cooling, the weight of crucible plus solids was recorded, and total solid content was calculated considering the mass of crude oil from respective water phase that was submitted to microwave heating procedure.

Results and Discussion

Characterization of the crude oil emulsions

Before optimizing the microwave-assisted sediment removal method, crude oil emulsions were characterized through the determination of sediments and water contents using ASTM D 4807 and D 4377 methods, respectively. Additionally, the determination of Cl (reported as NaCl salt) using MIC was also performed.

Results obtained for sediments, water and salt for samples A, B and C before the proposed microwave-assisted method in closed vessels are shown in Table 2.

Table 2. Sample characterization before proposed microwave-assisted method in closed vessels (n = 3)

Parameter	A	B	C
Water content / %	22.0 ± 0.6	30.8 ± 0.5	3.20 ± 0.05
Sediment content / %	5.15 ± 0.20	3.49 ± 0.15	1.13 ± 0.05
Salt / (µg g^{-1})	41700 ± 3300	19274 ± 670	12128 ± 1156

Sediments and salt content in crude oil emulsion samples were considered relatively high, justifying the interest in developing a unique method that could be suitable for both sediment and salt extractions using the same procedure. It is important to mention that TAN could not be determined in all the emulsions (before the proposed procedure) due to interferences during titration using the ASTM D 664 method. The titration end points were not well defined and no repeatability between results could be obtained during successive titrations. These interferences can be attributed to inorganic salts or sediments present in crude oil emulsions.[27] Additionally, parameters such as density and viscosity could not be determined due to the presence of sediments and water that interfere in the analysis. The S and N determinations were not carried out before sediment removal because the sample is injected into a specific analyzer using a syringe and the presence of solid particles could block the syringe needle.[23,24]

Optimization of the microwave heating program for sediment removal

Microwave radiation in closed vessels has been already applied for salt extraction from heavy crude oil, with addition of water. During the microwave heating, water refluxes inside the quartz vessels and allows washing of the crude oil, transferring salt to the water phase.[8] In case of sediments, it would be expected that water could carry the solid particles from the crude oil to the water. Therefore, preliminary studies were performed for sample A using similar conditions employed in previous work for salt extraction (800 W power; 30 min of irradiation).[8] At the end of the heating program, brown solid particles were observed in the water phase (on the bottom of quartz vessels), showing that microwave radiation could be feasible for sediment removal from heavy crude oil. After this initial test, microwave heating program was optimized, using 5 g of heavy crude oil and 20 mL of water. A three level full factorial design of two variables was used, as shown in Table 3. Experiments were performed in triplicate in random order for combination of levels.

Table 3. Full factorial experimental design used for optimizing the microwave heating program for sediment removal from crude oil emulsions

Run	X_1	X_2
1	–	–
2	0	–
3	+	–
4	–	0
5	0	0
6	+	0
7	–	+
8	0	+
9	+	+

X_1: heating time (5, 15 and 30 min); X_2: microwave power (300, 800 and 1400 W).

Results from the factorial design were processed by analysis of variance (ANOVA) with confidence level of 95%. Sediments were determined in aliquots of crude oil obtained after microwave heating according to ASTM D 4807-05 method.[12]

Sediment removal was more efficient (Table 4) when microwave power was set at 1400 W. In this case, using only 5 min of heating at maximum temperature, the sediment content in sample A was reduced from 5.15 ± 0.20 to 2.9 ± 0.24% (43.7% of removal efficiency). Therefore, this heating program was chosen for subsequent tests.

Evaluation of the sample mass and the use of additional extraction steps

The maximum sample mass that could be submitted to microwave-assisted method was another parameter evaluated using sample A. Crude oil obtained after the proposed sediment removal method, virtually free of sediments, should be suitable for further determination of sediments, water, salt, TAN, among other important parameters. In this sense, experiments were performed using the previously optimized microwave heating program and emulsion amount ranging from 5 to 30 g, with addition of 20 mL of water. The results obtained for efficiency of sediment removal are shown in Figure 1.

Table 4. Results for sediment determination in crude oil by ASTM D 4807 method using full factorial design to evaluate microwave heating program. Sediment content in crude oil without treatment: 5.15 ± 0.20% (n = 3)

Heating time / min	Microwave power / W	Sediment content / %	Removal efficiency / %
5	300	4.77 ± 0.91	7.4 ± 1.4
15	300	4.46 ± 0.86	13.4 ± 2.6
30	300	4.05 ± 0.59	21.4 ± 3.1
5	800	4.18 ± 0.63	18.8 ± 2.8
15	800	3.85 ± 0.53	25.2 ± 3.5
30	800	3.18 ± 0.25	38.3 ± 3.0
5	1400	2.90 ± 0.24	43.7 ± 3.6
15	1400	2.81 ± 0.20	45.4 ± 3.2
30	1400	2.86 ± 0.27	44.5 ± 4.2

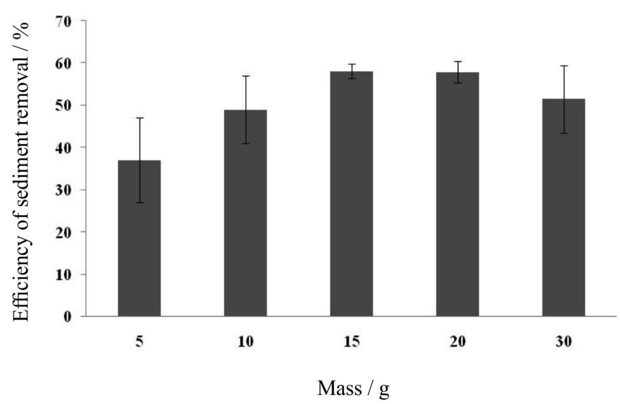

Figure 1. Influence of sample mass on microwave-assisted method sediment removal (n = 3).

An efficiency of sediment removal close to 60% (Figure 1) was obtained with 15 and 20 g of crude oil submitted to microwave-assisted method. The lower efficiencies obtained when 5 and 10 g of emulsion were used could be attributed to difficulties observed during sample removal from quartz vessel. Especially when 5 g of emulsion were used, a relatively high sample mass stuck to the quartz walls and could not be recovered. On the other hand, when 30 g of crude oil were submitted to microwave radiation, probably, this amount (30 g of emulsion + 20 mL of water) was not efficiently heated, and therefore, the efficiency of the sediment removal was even worse. Higher sample amount was not evaluated due to safety reasons (since the maximum internal volume of quartz vessel was 60 mL to assure safety conditions) and an emulsion amount of 20 g was chosen for subsequent experiments. It is important to mention that this amount can be considered enough for crude oil characterization procedures.

The efficiencies of the sediment removal from heavy crude oil emulsion (57.4 ± 2.6%) were not considered suitable for subsequent characterization analysis using one extraction step and 20 g of emulsion. Therefore, the use of additional extraction steps was evaluated, as performed in previous work, to improve salt extraction efficiency.[8] After the end of microwave heating program, the heavy crude oil was transferred to another quartz vessel, a new addition of 20 mL of water was performed and the microwave heating was applied again. The same procedure was repeated up to five sequential steps. The obtained results, calculated in terms of efficiency of sediment removal with the increase of number of extractions applied, are shown in Figure 2.

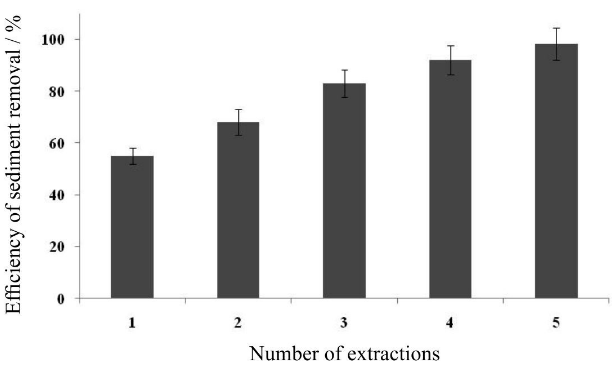

Figure 2. Efficiency of sediment removal from crude oil using microwave radiation in closed vessels employing different steps of extractions (n = 3).

It can be observed in Figure 2 that after 5 extraction steps, the efficiency of the sediment removal was higher than 98%, with a relatively low relative standard deviation (RSD < 7%). The proposed microwave-assisted method can be considered very attractive for sediment removal from crude oil for subsequent crude oil characterization. The sample throughput was considered suitable because even if 5 extractions steps are necessary the microwave heating program takes only 30 min (5 min ramp, 5 min heating and 20 min cooling time) and up to eight samples can be processed at the same time. The conventional methods used for water separation from crude oil are more time consuming and are not suitable for sediment removal.[28]

The optimized conditions employed for sediment removal from sample A (microwave heating program of 5 min ramp and 5 min heating, 5 extraction steps, 20 g of emulsion and 20 mL of water) were applied for emulsions B and C. The sediment content after microwave heating, using 5 extraction steps, in samples B and C were 0.10 ± 0.02 and 0.06 ± 0.01%, respectively. These results correspond to sediment removal efficiencies of 97 and 95%, respectively. As it was observed for crude oil emulsion A, good sediment removal efficiencies were obtained for emulsions B and C, suggesting that the microwave-assisted method is suitable for sediment removal from crude oils with different characteristics.

Total solid content determination in aqueous phase

The water phase obtained after 5 extraction steps using the proposed microwave heating procedure was collected, and the sediment content was determined using the procedure commonly employed for total solids determination in water.[26] Additionally, the water phase was also filtered through a 0.45 µm porous membrane and the sediment quantification was performed following the ASTM D 4807-05 method.[12] According to the results obtained for total solids in water, results were proportional to the reduction of solids in crude oil after each extraction step. In contrast, the sum of solid content determined in water phase after 5 extraction steps using the membrane filtration procedure was 0.52 ± 0.02%. This result is much lower than the expected value because the initial sediment content in crude oil emulsion was of 5.15 ± 0.20%. Then, it could be expected that part of sediments could have been dissolved during the microwave-assisted sediment removal method.

It has been reported in the literature that solid particles isolated from crude oil samples using the proposed ASTM D 4807-05 method[12] were composed mostly of sodium chloride.[5,14] The concentration of salt in crude oil emulsion used in this work was 4.17 ± 0.33% (m m^{-1}). In order to evaluate the possibility that solid particles present in crude oil could be sodium chloride or other chloride salts, the solids isolated by membrane filtration using the ASTM D 4807-05 method[12] were weighed, transferred to polypropylene vessels and filled up with water. After homogenization, samples were centrifuged for 2 min at 3000 rpm (in case of some solids that could remain in suspension) and chloride determination in aqueous solution was performed by ion chromatography (IC). The obtained results showed that salt content (NaCl) in dissolved solids was 64.3 ± 4.0% (m m^{-1}). According to these evidences, it could be expected that part of solids determined in the crude oil using the ASTM D 4807-05 method are composed of chloride salts.

Table 5. Characterization of the crude oil samples after sediment removal using the proposed microwave-assisted method in closed vessels (n = 3)

Parameter	A	B	C
API gravity	18.0	19.6	21.0
Kinematic viscosity / ($mm^2 s^{-1}$), 80 °C	74.825 ± 0.269	87.401 ± 0.380	46.211 ± 0.401
Dynamic viscosity / (mPa s), 80 °C	67.559 ± 0.412	78.072 ± 0.338	36.475 ± 0.390
Water content / %	0.20 ± 0.01	0.45 ± 0.02	0.12 ± 0.01
Sediment content / %	< 0.10	< 0.10	< 0.10
Salt / (µg g^{-1})	< 6.0	9.54 ± 0.67	21.9 ± 1.6
TAN / (mg KOH g^{-1})	0.46 ± 0.02	0.84 ± 0.06	0.45 ± 0.01
Nitrogen / (µg g^{-1})	2160 ± 97	1712 ± 53	3496 ± 89
Sulfur / (µg g^{-1})	3839 ± 201	3236 ± 65	4979 ± 134

Characterization of the crude oil after sediment removal method

Crude oils obtained after the proposed sediment removal method were characterized for comparison of characteristics previously reported, before sediment removal (sediments, water and salt content). Additionally, other parameters, such as TAN, density, API gravity, kinematic and dynamic viscosity were determined after sediment removal and separation of water. The results obtained for samples A, B and C are shown in Table 5.

It is possible to observe that the water content in crude oil samples was lower than 0.50%, giving an efficiency of separation of water better than 96%. This result indicates the good performance of microwave radiation for water separation from crude oil emulsions in agreement with previous work.[18] In the same way, the sediments and salt content were lower than 0.10% and 22 µg g^{-1}, respectively. Several parameters could be determined in the crude oil samples after sediment removal method without interferences, such as the determination of API gravity, kinematic and dynamic viscosity, S and N. In case of TAN, the characteristic titration curves and well defined titration end points were obtained during titration of the crude oil after sediment removal.

The proposed method could be considered advantageous in comparison with other methods used for sediment removal and subsequent crude oil characterization.[27,28] For example, the simple distillation procedure allows removing only water, but not chloride salts.[28] Using microwave radiation in closed vessels, it was possible to remove sediments and salt, as well as to separate water from heavy crude oil emulsion, in a single method, in a relatively short time and for eight samples simultaneously.

Conclusions

The efficiency of the proposed method using microwave radiation in closed vessels for sediment removal was better than 95%. Moreover, the salt and water contents were drastically reduced allowing the determination of several important parameters for crude oil characterization without interferences. Up to eight samples were simultaneously processed in a little time, resulting in a good sample throughput, although 5 extraction steps were necessary for almost complete sediment removal. The sediment removal process could be performed using only water, avoiding the use of toxic reagents or demulsifiers, an important aspect related to the green chemistry recommendations. Additionally, the use of microwave-assisted method is relatively easy to be performed and could be suggested for routine sediment removal from heavy crude oil for subsequent characterization.

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