Microfluidic testing of flocculants for produced water treatment: Comparison with other methodologies

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ABSTRACT

Flocculants are often added during produced water treatment to improve the crude oil droplet growth and separation from the water phase. Prior to use in the field, their performance is tested in laboratory conditions, typically with jar tests that require quite large volumes of sample. In this paper we present a microfluidic method as an alternative to study the efficiency of flocculants on enhancing coalescence between oil droplets. Two crude oil emulsions and four flocculants at different concentrations were tested. The new method is also compared to the more traditional techniques. An anionic flocculant showed the biggest improvement in separation for almost all systems. What is more, marked differences were observed between methods with static (bottle and turbidity tests) and dynamic test conditions (light scattering and microfluidics), where stabilization and dispersion effects were observed for the latter. The microfluidic methodology, with added benefits such as visualization, lower sample volumes and shorter measurement times, yielded similar trends as compared to other techniques. Overall, it was shown that microfluidics is a viable alternative to the standard tests.

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1. Introduction

Many industrial processes utilize flocculation, i.e. formation of loose aggregates, to enhance separation. It is typically induced by adding multivalent metal salts or polymers as destabilizing agents and is commonly used in wastewater treatment (Daifa et al., 2019), within mining (Jang et al., 2010), food (Ahmad et al., 2005) and petroleum industries (Sjoblom, 2001). Polymeric flocculants are often added to improve the treatment efficiency of the large volumes of produced water during petroleum production. In offshore production, the produced water is either discharged to the sea or re-injected into production or disposal reservoirs. Prior to this, it must be treated to a sufficient level of purity, regulated by environmental laws and/or geological specifications of the reservoir (Dudek et al., 2020c).

Conventional flocculants used in produced water treatment are water soluble polymers (often cationic, but also anionic, non-ionic, amphoteric and amphiphilic) with molecular weights ranging from several thousand to several million Da (Kelland, 2014). There are two suggested mechanisms that explain their effect on separation. One possibility is that individual polymer chains become attached to two or more droplets and form "bridges" that keep the droplets in flocs that are easier to separate than individual drops. This is also the classical way of describing flocculation of solids. Droplets, on the other hand, can coalesce and it is possible that the polymer bridges formed between droplets keep them in proximity of each other sufficiently long for drop growth by coalescence to occur. Similar reasoning can be used for drop-bubble bridging in flotation units (Santos et al., 2018). It is, however, unclear, which of the two mechanisms is dominant during produced water treatment, as most techniques for studying flocculation do no allow to visually follow the droplets in dynamic conditions.

Selecting the best flocculant formulation is crucial from an operational point of view. Different fluid properties and process conditions often require that flocculants must be tailored to specific fields, wells, separation trains or even type of separator. Extensive laboratory measurements are performed prior to selection, where the performance of flocculants is frequently tested using bottle or jar tests (Kelland, 2014). In the former, the flocculant is added to an oil-in-water emulsion, shaken and left at static conditions. The time until water clarification can be determined by visual inspection,

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turbidity measurements or sampling followed by extraction and quantification of oil. Jar tests add some level of agitation in the sample container and are often used during field tests with fresh produced water samples. A gas flotation step can also be added after the initial flocculation process if the separation takes a lot of time (for example for water after polymer flooding) (S. Fernandes et al., 2005; Santos et al., 2020). Other methods can be applied if more detailed information about the systems is required. Fernandes et al. used light scattering technique for measuring drop size distribution after adding flocculants (S. Fernandes et al., 2005), while Angle et al. studied the evolution of droplet sizes of diluted heavy oil-in-water including a number of parameters, such as the presence of particles, water pH and the oil phase volume fraction (Angle and Hamza, 2009). Some drawbacks for these methods are the need for large sample volumes and long measurement times.

Droplet-based microfluidics is a technique where droplets can be manipulated and observed in microchannels. It offers precise control over experimental conditions, possibility to study phenomena during flow and use very small (microlitres) sample volumes. It has been applied to study coalescence between droplets or bubbles (Wang et al., 2016, 2020), recently also in crude oil systems (Dudek et al., 2020a; Leary et al., 2020). The objective of this paper is to introduce microfluidic methodology as a viable way of determining the efficiency of flocculants during separation of crude oil from produced water. Microfluidics allows to visually follow the coalescence process between drops, which is the underlying phenomena responsible for improved removal of oil droplets. The novel method was compared to conventional techniques such as bottle testing, turbidity measurements and static light scattering measurements. This allowed for evaluation of strengths and weaknesses between the various methods, as well as some mechanistic considerations.

2. Materials and methods

2.1. Materials

Two crude oils produced at the Norwegian Continental Shelf (NCS) were used in this study. They are designated as crude oil E and G, in accordance with previous studies in our group (Dudek et al., 2020a). Both are light crude oils and are considered representative for the type of oil produced at NCS. Table 1 shows the properties of both the oils. Sodium chloride (analytical grade) was dissolved in deionized water (Millipore Simplicity Systems) at concentration of 35 g/L and used as the water phase. Four commercial flocculants, denoted F1 to F4, were provided by Nouryon Surface Chemistry AB and Schlumberger Production Technologies. Information from the vendors, together with more detailed characteristics performed by the present authors is given in section 3.1. pH of the water phases was not controlled and varied between 5.8 and 6.4.

2.2. Methods

2.2.1. Emulsion preparation

In general, 500 ppm oil-in-water emulsions were prepared as follows: first, crude oil was weighed and appropriate amounts of brine were added. The sample volume was ca. 40 ml for the bottle tests and turbidity measurements, while about 500 ml was required for the light scattering experiments. The sample was then mixed with a high-performance disperser (Ultra-Turrax, IKA) for 3 min at 10 000 rpm. These conditions gave repeatable distribution of drop sizes, regardless of the volume of the emulsion. The majority of the drops were below 60 μm in diameter (see the initial size distribution in Fig. 6).

For the zeta potential measurements, 500 ppm oil-in-water emulsions were prepared by mixing crude oil and 1 g/L of sodium chloride dissolved in deionized water at 10 000 rpm for 1 min. A known volume of flocculant solution was added to the emulsion when required. All the samples were degassed in an ultrasonication bath for 30 s prior to measurements.

2.2.2. Sample characterization

2.2.2.1. Dynamic light scattering. The size of the flocculants in solution and oil drops dispersed in water (with and without flocculants) was measured by dynamic light scattering using a Zetasizer Nano (Malvern Instruments). 200 ppm flocculants were dissolved in deionized water containing 1 g/L sodium chloride. Three scans were made for each sample and two parallels were made for each condition.

2.2.2.2. Electrophoretic measurements. The zeta potentials of dissolved flocculants and oil-in-water emulsions with and without flocculants were obtained by electrophoretic mobility measurements using a Zetasizer Nano (Malvern Instruments). Three scans were made for each sample and two parallels were made for each condition.

2.2.2.3. Interfacial tension measurements. Interfacial tension measurements were performed with a pendant drop tensiometer (PAT1, Sinterface). A crude oil drop was immersed into appropriate solutions by a capillary connected to a micro syringe. The interfacial tension was calculated by fitting the Young-Laplace equation to images of the drop profile. Each measurement lasted 2 h. Three parallels were performed for each system.

2.2.3. Stability measurements

2.2.3.1. Bottle tests. After preparation, the emulsion was stirred at 200 rpm with a magnetic stirrer. A concentrated solution of flocculant was added by a micropipette to give the required concentration. The visual change in the clarity of the emulsion was recorded every 5 min for 30 min or until the water phase was deemed clear. Each measurement was repeated at least two times.

2.2.3.2. Turbidity measurements. Immediately after preparation, the emulsion was transferred into a measurement vial. The flocculant was added in the same way as for the bottle tests. The vial was gently shaken to distribute the flocculant and inserted in the measurement slot of a Turbiscan LAB instrument (Formulaction), where the light transmission through the sample over its entire height (40 mm) was measured every 1 min for 15 min. The average

Table 1
Physicochemical properties of crude oils. TAN and TBN are Total Acid/Base numbers, respectively, while SARA is an abbreviation for different fractions of crude oil (saturates, aromatics, resins and asphaltenes).

Crude oil	Density [kg/m³] @20 °C	Viscosity [mPa s] @20 °C	TAN [mg KOH/g oil]	TBN [mg KOH/g oil]	SARA [% wt.]			
					Saturates	Aromatics	Resins	Asphaltenes
E	830.7	8.3	0.5	0.4	74.8	23.2	1.9	0.1
G	847.8	12.4	0.2	0.6	83.4	14.0	2.4	0.2

light transmission between 8 and 12 mm sample height was reported. All measurements were performed at least three times.

2.2.3.3. Static light scattering measurements. Drop size distributions of the emulsions were measured by static light scattering experiments using a Mastersizer 3000 with a Hydro-EV extension (Malvern Instruments). Prior to experiments, brine was passed through the instrument to measure the background data of the continuous phase. Subsequently, the emulsion was poured into a 600 ml beaker and mounted in the instrument. The sample was stirred at 3000 rpm and continuously pumped through the measurement cell. The light scattered by the droplets were detected at different angles and transformed into a volume size distribution. 100 measurements were performed continuously, each lasting 10 s, adding up to ca. 16 min of experimental time. The concentrated solution of a flocculant was injected into the beaker via a micropipette and distributed by the built-in mixer in the device after the first minute, allowing to obtain initial size distribution. After the measurements, the instrument was cleaned by passing through water, xylene/isopropanol mixture (1:1), isopropanol and finally several times more with water. Three measurements were taken for each condition.

2.2.3.4. Microfluidics. Two chip designs with different ways of introducing the flocculants were investigated: the initial test design and the optimised test design (Fig. 1). In both cases the fluids were pumped with syringe pumps (neMESYS mid-pressure module V3, Cetoni GmbH) into the custom-designed glass microfluidic chip, placed in a chip holder (Micronit Microtechnologies B·V.). All channels had a uniform depth of 45 μm. Monodisperse droplets were generated at a T-junction with 100 μm wide channels. After passing a meandering channel, they got into a 500 μm wide and 33 mm long coalescence chamber, where collisions and coalescence events occurred. In the initial test design, the flocculant was already dissolved in the brine when the droplets were generated at the T-junction, and the length of the meandering channel varied from 3 to 75 mm (Fig. 1 − initial test design). This allowed for different surface ageing of the droplets. In the optimised test design (Fig. 1 − optimised test design), the droplets were generated at the T-junction using brine and then passed through the meandering channel with a fixed length of 15 mm. The flocculant solution was then added at the entrance of the coalescence chamber. The concentration of the flocculant was proportionally higher due to the increased interfacial area (ca. 35 times), but also due to a dilution effect.

During all experiments, a high-speed camera (AX100, Photron), connected to an inverted microscope (Ti−U Eclipse, Nikon), was used to record images at 8500 fps at the inlet and outlet of the coalescence chamber. Approximately 10 000 images were taken for each part of the channel. The recordings were processed with ImageJ to extract the position and size of droplets in each image, which were later used to calculate the coalescence frequency for
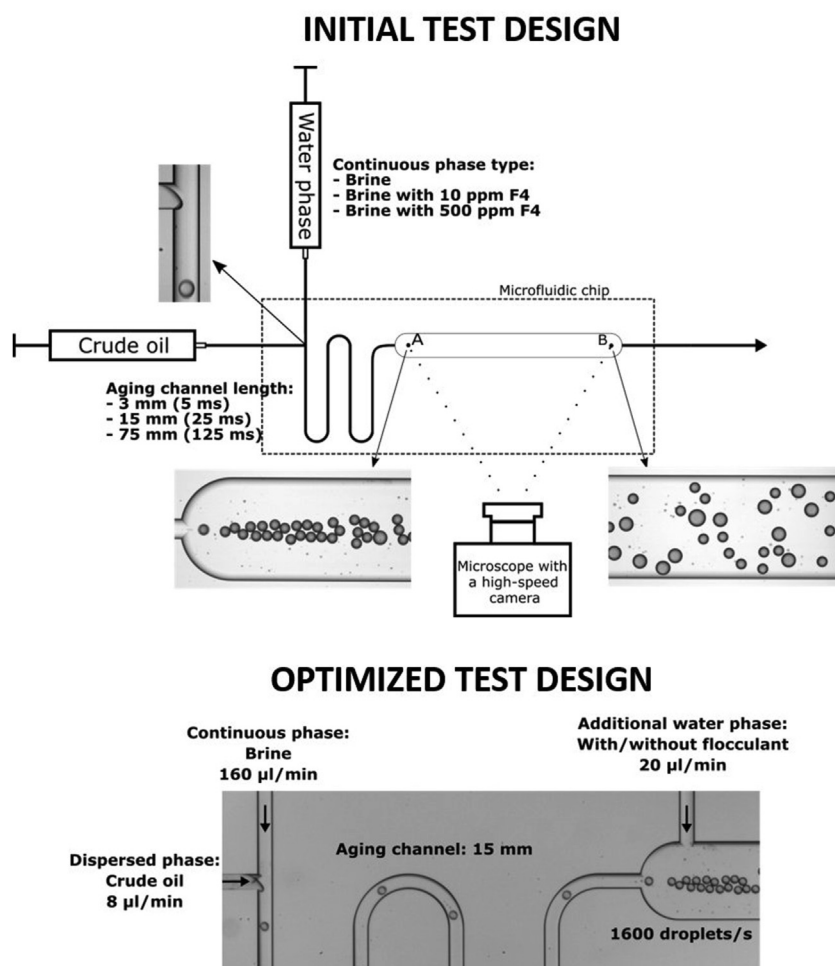

Fig. 1. Different configurations of microfluidic systems used in the present study.

each experiment. More details can be found elsewhere (Dudek et al., 2020a). All reported values were an average of at least three parallels.

3. Results and discussion

The outline of this section is as follows: first, characterization of the flocculant solutions and emulsions with and without flocculants is presented. Next, the principles and results of each technique are presented and discussed. Finally, the flocculants and methods are evaluated with their advantages and drawbacks.

3.1. Sample characterization

3.1.1. Flocculants
Table 2 summarizes the information from the chemical suppliers about the type and molecular weight for the flocculants.

The average size and zeta potential for the flocculants dissolved in aqueous solutions are shown in Fig. 2.

The average size of the flocculants seemed to be related to their molecular weight. The smallest size was measured for F2 with the lowest molecular weight, while F4, with the highest molecular weight, had particles larger than 1 μm. No molecular weight data was available for F3, however the size measurement suggested that it could be in the range of a few MDa. Still, it should be noted that the polymer chain structure (e.g. high deviation from spherical shape) could heavily influence the hydrodynamic radius calculated from the dynamic light scattering experiments. The polydispersity indices (PDI) and size distribution graphs suggested quite high polydispersity within the flocculant molecules or that some of the flocculants could be multicomponent blends (Fig. S1 in SI).

The zeta potentials were in line with the type of flocculant listed in Table 2. The surface charges originate from the presence of dissociated anionic groups or protonated cationic groups in the molecules. The polycationic additives (F1, F3) had the highest positive zeta potentials, the amphiphilic F2 had lower and most likely pH-dependent charge, while the anionic F4 had a significant negative zeta potential.

3.1.2. Emulsions
Fig. 3 shows the zeta potentials for crude oil G emulsions without and after addition of the flocculants (data for crude oil E is shown in Fig. S2 in SI).

Crude oil drops without addition of flocculants had a negative zeta potential of ca. −10 mV. The negative potential is common for

Table 2
Summary of information about flocculants used in the present study.

Flocculant	Type	Molecular weight [Da]
F1	Polycationic	1 000 000
F2	Polyamphiphilic	100 000
F3	Polycationic	N/A
F4	Polyanionic	>10 000 000

dispersed oil in produced water, however the exact value will depend on the oil properties and ionic composition of water (Buckley et al., 1989; Farooq et al., 2013). Addition of three of the flocculants (F1, F2 and F3) reversed the zeta potential of the droplets to positive values and the magnitude of that effect corresponded with the type of the flocculant (cationic or amphiphilic). The presence of the anionic F4 decreased the negative zeta potential of the droplets significantly. While the differences between the addition of any flocculant at 10 and 20 ppm were relatively low, larger absolute charges were always observed for the higher concentration. Similar observations were made for crude oil E (Fig. S2 in SI).

The dynamic interfacial tension graphs for oil E in brine with and without flocculants are plotted in Fig. S3 in SI. Without flocculants, crude oil E reached ca. 21 mN/m after 2 h of measurement. The addition of an additive, regardless of the type, caused a faster drop of the interfacial tension, especially in the initial 10−20 min of the measurement. After that time, the values started to stabilize in a similar manner as without any flocculant, however the value after 2 h was slightly below 20 mN/m for all cases. Overall, the interfacial tension results confirmed that the flocculants are indeed adsorbing at the oil-water interface, however their effect on the interfacial tension is relatively small and apparently did not depend on the type of additive.
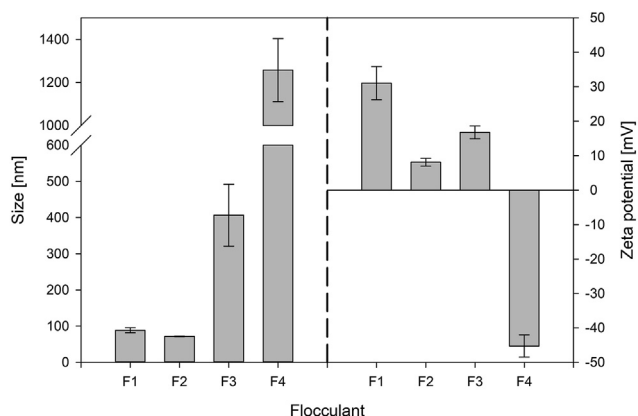
Both the electrophoretic and interfacial tension measurements showed that all the flocculants adsorbed at the oil drop-water interface. There are several mechanisms explaining the adsorption of polyelectrolytes on surfaces, both with the same and opposite charge (Holmberg et al., 2002). The first three flocculants have a positive charge, which should promote the adsorption at a negatively charged crude oil-water interface through Columbic attraction. However, in the abundant presence of electrolytes, as in our case, the adsorption can be decreased. The charge of a surface in water must be balanced by the presence of counterions in the vicinity of the surface. When electrolytes are present, the increase of entropy is not as significant as in an electrolyte-free system. In addition, salt ions can shield the attractive interactions between the polymer and the surface and compete with the polymer for the adsorption sites.

If the surface and polymer have the same charge, as was the case with F4, the attraction is mainly due to van der Waals forces. In contrast to the oppositely charged interfaces, here the addition of salt should increase the adsorption of polymer. When a polymer adsorbs at a similarly charged surfaces, the charge is neutralized by the presence of counterions, which yields local concentration gradient and decrease in the entropy of the system. Higher concentration of electrolytes will diminish this effect. Moreover, it can also shield the electrostatic repulsion between the surface and the polymer. As it will be seen later, the high concentration of the electrolyte could also have contributed to the performance of flocculants during emulsion stability testing.

3.2. Bottle tests

The results from the bottle tests for crude oil E are presented in Fig. 4.

The black line shows the time for clarification for the oil-in-

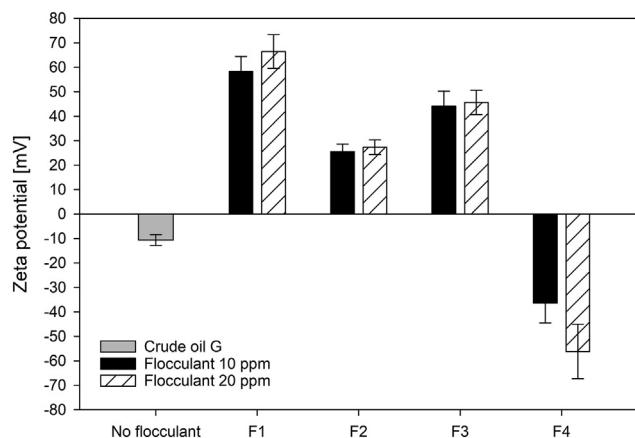**Fig. 2.** Particle size (left) and surface charge (right) of the flocculants in solution.

Fig. 3. Surface charge of crude oil G droplets in brine with and without flocculants.

Fig. 5. Relative change of turbidity for crude oil E emulsions with and without flocculants.
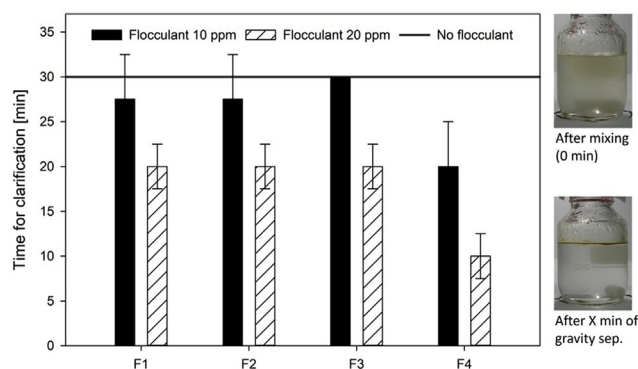

Fig. 4. Bottle test stability of crude oil E emulsions with and without flocculants. The measurements were finished after 30 min and the data showing 30 min without any error bars are samples where separation took longer time.

for all flocculants and concentrations, compared to the initial turbidity of the sample.

The solid line represents the change in transmitted light for the sample without flocculant, with the dotted lines as the corresponding standard deviations. Most of the samples with flocculants experienced changes in transmission within these error bars. The exceptions were F1 at 10 ppm and possibly F4 at 20 ppm. These two flocculants also had the best performance in the bottle tests. Also, for crude oil G (Fig. S5 in SI), F1 and F4 at the highest concentration gave better results. Flocculant 3 at 20 ppm, however, led to stabilization of emulsion, while the rest of the flocculants had a negligible effect on the emulsion stability. Similar to bottle tests, it was difficult to distinguish an improvement in separation, unless major differences in turbidity occurred, for example for F1 at 10 ppm.

3.4. Static light scattering

The evolution of size distributions over time is shown in Fig. 6 for the emulsion without flocculant and when F4 was added to the emulsion.

The initial size distributions (i.e. first few measurements after starting the experiment) are shown as dotted lines. Volume-wise, most droplets were initially between 10 and 50 μm in diameter, however there was also noticeable share of sub-10 μm drops. It should be mentioned that multiple scattering, caused by too high concentration of the dispersed phase, can lead to false signals in the small droplet size ranges. However, care was taken to keep the concentrations low enough to minimize this effect and the main signal (droplets larger than 10 μm) remained largely unaffected.

The arrow in the figures shows the direction towards which the distributions evolve. Without flocculants, the size distribution did not change significantly during the 15 min of measurement. The largest drop diameter increased from ca. 60−80 μm. By contrast, the presence of F4 caused a noticeable shift of the size distribution to the right and positively affected the growth of drops, either by flocculation or coalescence. The largest drop size increased from approximately 40 μm to more than 100 μm.

Another way to describe a size distribution is with the mean value. In the case of volume distributions, volume mean diameters, D (4,3) are often calculated. Fig. 7 shows a summary of evolution of D (4,3) in all systems with crude oil G. The corresponding figure showing data for crude oil E is presented in SI (Fig. S6).

Selected measurement points were shown to avoid cluttering the figure. Standard deviations were omitted for the same reason,

water emulsion without any flocculant present (i.e. equal to or more than 30 min). Adding 10 ppm of any of the flocculants reduced the separation time slightly in most cases. The effect of the higher concentrations was, however, more pronounced. F1, F2 and F3 all reduced the clarification time to ca. 20 min, while F4 decreased it down to 10 min. Similar trends were obtained for crude oil G (Fig. S4 in SI).

Without major improvement in the separation efficiency, it was difficult to compare different systems. The errors in the bottle measurements originated from two sources. Firstly, it was problematic to pinpoint the exact moment when the emulsion was clear. When the measurements are based on visual observations, this is highly operator dependent and can also be affected by other factors (e.g. lighting conditions). The ability to more accurately quantify these results could be improved by oil content measurements, however this prolongs the procedure significantly. Secondly, the clarity of the samples was noted every 5 min, which added some more uncertainty to the results.

3.3. Turbidity

It was challenging to reproduce the initial level of transmitted light for all samples, even with consistent methodology in place. However, the relative change in transmission over time was similar for most parallels and allowed to compare different conditions. Fig. 5 presents the relative change in light transmission after 15 min
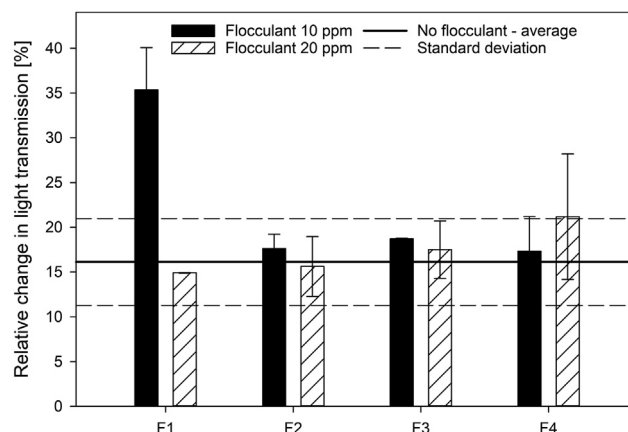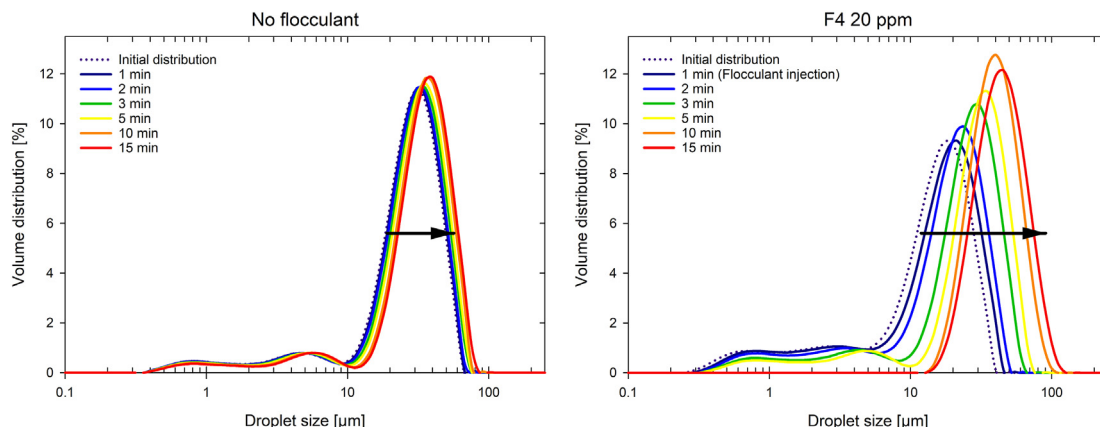
Fig. 6. Evolution of size distributions for crude oil E emulsions without (left) and with F4 at 20 ppm.
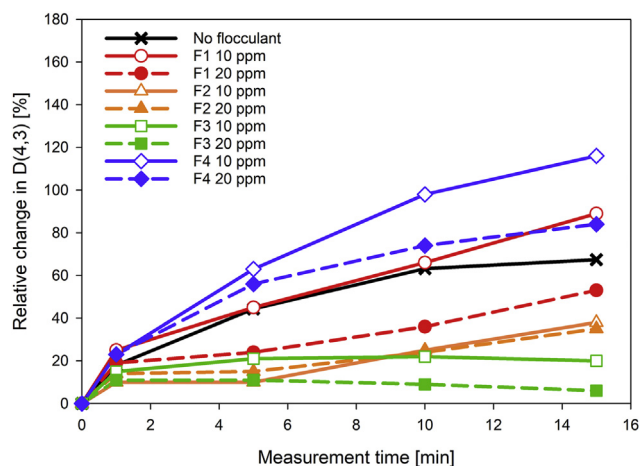

Fig. 7. Relative change in D (4,3) during light scattering measurements for all systems with crude oil G. Lines connecting each data point are added for easier comparison.

which is additionally discussed in section 3.6.2. The flocculants were added after the second measurement point, whereas the next three points show the subsequent evolution of drop sizes. The black line is the drop growth without flocculant. F1 (at lower concentration) and F4 increased the drop growth compared to the sample without flocculants, with the latter being more effective at both concentrations. Furthermore, it took longer time for F1 to have an effect as improvement was only observed for the second half of the measurements. F2 and F3 gave lower D (4,3) values than for the emulsion without flocculant and the effect was largest at the highest concentrations. This suggested that the flocculants led to increased stability and possible breakage of drops due to the mixing and flow through the tubing and cell (flow velocity ca. 0.1 m/s), followed by a slow growth in size. Droplet breakage was probably observed for crude oil G when 20 ppm of F3 was added, as a continuous reduction in drop size was observed over the duration of the experiment.

Another useful way of representing the volume size distributions is with Dx10, Dx50 and Dx90 values. These are defined as threshold values, where 10%, 50% and 90% of drop sizes in the system are smaller or equal to them, respectively. Fig. S7 in SI shows the average Dx values of crude oil E drops for three cases: no flocculant, F3 and F4, both at 20 ppm. Dx10 represents the smallest

droplets in the emulsion − at the beginning of most experiments its value was typically not higher than 5 µm. By the end of the measurement without any flocculant in the system and with F4 at 20 ppm, this value was twice and four times as high, respectively. In the case of F3, only minimal increase was observed. Dx50 can also be defined as a median value for volume distributions. Smaller (relative) increase was observed here, as compared to Dx10, but with similar trends. The same can be said about Dx90, often representing the largest droplets in a system. While for F3 it went up only by 10 µm, it grew by ca. 20 µm without any additives and it doubled to more than 100 µm for the other flocculant.

Dx values can provide additional information on the effect of the flocculant on a particular size range of droplets, for example showing that the chemical is more effective in promoting the coalescence between the smallest, most difficult to remove droplets. This seems to be the case with F4, where the increase of the Dx10 was considerable. Still, the multiple scattering phenomena could have contributed to some changes in the values of Dx10, as explained earlier. Without any flocculant, all drop size classes increased in a similar degree. The addition of Flocculant 3, however, led to size increase only for the largest droplets, while hardly any change in the smaller size classes was observed. Even though larger drops require longer time to coalesce (Dudek et al., 2020b), they are easier to encounter by other drops during flow, which could explain higher coalescence in this size class.

3.5. Microfluidics

3.5.1. Initial test design

Fig. S8 in SI shows how the coalescence frequency was reduced by the length of the meandering channel for crude oil E with different concentrations of F4. F4 was chosen for these experiments, since it generally showed the biggest improvement in separation when using the other experimental approaches. The coalescence frequency clearly decreased the longer the oil drops had to travel before entering the coalescence chamber. This was in line with our previous findings and is due to migration of interfacially active crude oil components (i.e. resins and asphaltenes) to the oil-water interface where they build up an interfacial layer that opposes coalescence (Dudek et al., 2020a). The small difference between the coalescence in the short and medium length channels can probably be explained by relatively large molecular weights for the migrating components, that take longer time to adsorb at the oil-water interface. Similar trends were also obtained for the experiments with the addition of flocculant − in all cases the coalescence was lowest for the
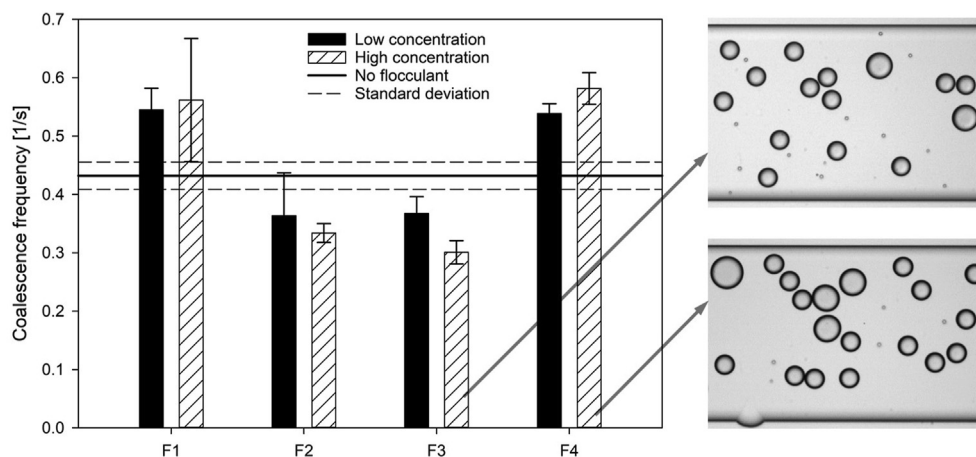
Fig. 8. Summary of coalescence frequencies for all systems for crude oil E. Pictures on the right side show exemplary droplet size distribution at the outlet of the coalescence chamber.

measurements with the longest channel. The measurements without and with 10 ppm of F4 were quite similar, while the coalescence was markedly lower with 500 ppm.

Two important outcomes were noted from these initial tests. Firstly, the presence of flocculant reduced the coalescence between drops. One possible explanation is that adsorption of the flocculant at the fresh oil-water interface stabilized the drops. This is supported by the interfacial tension measurements, where the presence of any of the flocculants caused a small, but noticeable change in the interfacial properties of crude oils. Another explanation could be that the flocculants adsorb less at freshly generated droplets than at aged interfaces, which has different surface properties. The flocculants in solution would then increase the drainage time of the thin liquid film occurring between droplets prior to coalescence, and thereby reduce coalescence. Secondly, the concentration of the flocculant needed to see noticeable effects on the coalescence was considerably higher than for the other tests. This was because the oil-in-water concentration in the coalescence chamber was approximately 100 times higher than in the 500 ppm emulsions. By calculating the total interfacial area for the microfluidic experiments (for droplets of 55 μm) and other techniques (initial Dx50 = 25 μm, taken from the light scattering data), it was seen that this ratio is equal to ca. 35, which was used for further experiments.

3.5.2. Optimised test design

The coalescence frequencies when the flocculants were added at the entrance of the coalescence chamber are presented in Fig. 8. The flocculant concentrations are denoted as low and high concentrations and correspond to 10 and 20 ppm levels from other measurements, as explained before. Similar results for crude oil G are shown in Fig. S9 in SI.

The average coalescence frequency and the corresponding standard deviation for the samples without flocculant are shown as solid and dotted lines, respectively. The injection of additional fluid affects the volume fraction of the dispersed phase and the linear velocity in the channel, both of which impact coalescence in microchannels (Krebs et al., 2012). Therefore, pure brine was also injected at the same flow rate through the additional inlet at the beginning of coalescence chamber to keep total flow rate constant. Both F1 and F4 improved the merging between droplets and the coalescence frequency was generally higher at the concentration equivalent to 20 ppm. By contrast, the lowest coalescence was seen for F2 and F3 at the highest flocculant concentrations.

In this chip design, the flocculant was added in the beginning of the coalescence chamber, perpendicularly to the direction of the main flow. In order to verify the distribution of flocculants and oil drops in the coalescence chamber, the flocculant solution was replaced by a dye-stained water phase. Fig. 9 shows snapshots of this system with varying number of drops in the coalescence chamber. Without any or with only a few droplets present, the laminar flow, typical for microfluidics, inhibited mixing between the injected and continuous phase. Therefore, the distribution of the flocculant was only driven by the diffusion across the water-water boundary. This is seen in the first and second column of snapshots in Fig. 9. The stratified flow of the dye-stained water phase and the continuous phase, normally containing droplets, is visible over the entire length of the coalescence chamber. Similar case occurred when only some droplets were generated. In this situation, there were too few droplets to invoke collisions, so they mostly followed the laminar streamlines of the continuous phase. This resulted in lack of mixing between the two water inlets and two stratified flows were still visible at the outlet of the channel. However, when the flow of droplets was set to the same level as for all microfluidic experiments, the drops started to collide with each other. The collisions forced the droplets to also flow in vertical direction, which disturbed the laminar flow in the channel. The effect could already be seen at the inlet, where the frequent contact between drops caused the interface of the dye-stained water phase to oscillate. Further down the channel the droplets flowing out of the upper part of the channel were disrupting the laminar streams, creating vortices, which resulted in mixing between the two water phases and distribution of the flocculant into the entire cross-section of the channel. Already after 6 mm, the boundary between the two phases was no longer visible and only slight colour gradient across the width of the channel could be observed. To the best of our knowledge, this is the first description of mixing in the continuous phase by the dispersed phase. Previous papers related to mixing in multiphase microfluidics have dealt with mixing inside the dispersed droplets or mixing in the continuous phase during slug flow (Bordbar et al., 2020; Tice et al., 2003).

3.6. Comparison of flocculants and methods/discussion

3.6.1. Performance of flocculants

The comparison of the results obtained with different methods for crude oil E is presented in Fig. 10 (data for crude oil G in Fig. S10 in SI). The values are the relative improvement or, in some cases,
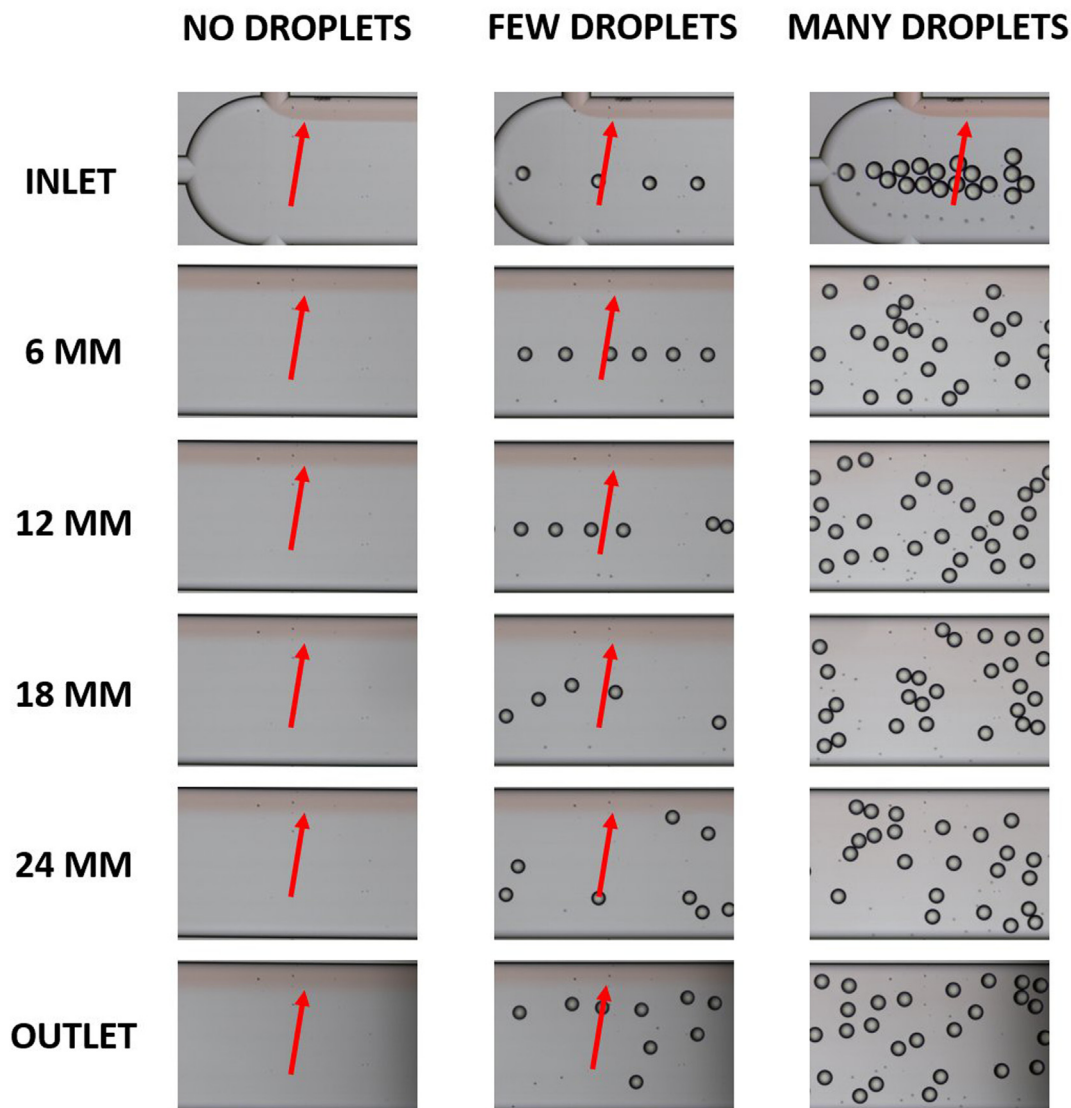
Fig. 9. Snapshots of different parts of the coalescence channel for three concentrations of dispersed phase.

decrease of performance for each flocculant, as compared to the sample without flocculants.

Coalescence of crude oil drops is inhibited by the adsorption of indigenous surface-active components such as resins, asphaltenes, naphthenic acids and various solids at the oil-water interface. This can lead to steric stabilization, elastic interfaces and Marangoni effects, which all can prolong the drainage time of the thin aqueous film formed when droplets approach each other. If this drainage time becomes longer than the contact time between droplets in the dynamic and turbulent produced water systems, coalescence will be scarce and droplet growth slow. The flocculants are added to the water phase in order to create flocs, bridge droplets and facilitate coalescence leading to improved separation. Most tests indicated that the most efficient flocculant for both crude oils was F4. According to our data, it had the largest molecular weight, the largest particle size and, in contrast to other flocculants, a negative zeta potential. Even though the crude oil droplets were also negatively charged, the flocculant still adsorbed at the oil-water interface and decreased the zeta potential even further. Analysis of our results suggests that the impact of the charge neutralization mechanism on the separation efficiency is probably negligible due to high
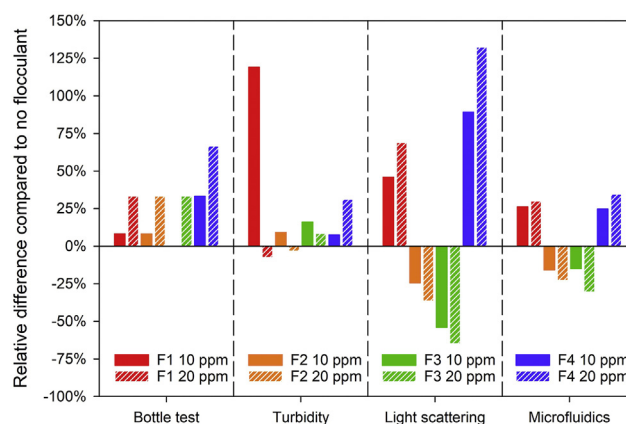

Fig. 10. Summary of the results for all methods for crude oil E. Values presented are improvement or decrease of performance as compared to a system without flocculant.

salinity conditions, which effectively screen the charges at the oil-water interface. It seems that the large molecular weight of F4 was predominantly responsible for its ability to create bigger oil droplets. This conclusion is similar to other studies, where the larger molecular weight of the flocculant has been connected to improved performance during oil removal (S. Fernandes et al., 2005; Santos et al., 2020; Santos et al., 2018). Furthermore, we did not observe any evidence of flocculation during our microfluidic experiments, which suggests that the main principle of flocculants improving separation in our study was promoting coalescence. It is also unlikely that flocculation occurred during light scattering experiments, as the changes in size distribution were relatively smooth. Similar linear flow velocity as in microfluidic measurements and agitation in the vessel probably inhibited formation of unstable flocs, and pointed to coalescence as the main destabilization mechanism.

Some of the flocculants gave worse performance, as compared to the experiments without any additives. In bottle tests and turbidity measurements, almost all flocculants at all concentrations showed a positive response, as compared to tests without additives. Therefore, the comparison of efficiency is mostly based on the magnitude of separation improvement. Methods involving flow, however, displayed stabilizing, or even dispersing effects, which lead to worse separation than without flocculants. Indeed, when F3 was used during the light scattering measurement, one could observe a decline in D (4,3) after a period of initial increase. Even though breakage of droplets was not recorded in our microfluidic recordings, similar trends were seen for F3, which gave the worst overall performance in that technique.

3.6.2. Methodology comparison

Different methods are used to study the efficiency of flocculants in separation processes. Bottle or jar testing is a well-established technique for measuring the efficiency of separation (Gao et al., 2011; Huang et al., 2019; Liu et al., 2013). It is based on the gravity separation of droplets − the better the flocculant, the higher its effect on the coalescence between droplets and the faster the creaming. This methodology is simple to conduct and allows several tests at the same time. The evaluation of the results can be done through visual observation or by sampling and measuring the oil-in-water content with a suitable technique. Visual observation of the sample requires the operator to be present during the entire measurement and is quite subjective. In the case of oil content measurement, more time and resources (chemicals, analytical instruments) are required for extraction and analysis of the oil concentration. There are, however, a few drawbacks. While coalescence or flocculation between droplets is the main mechanism of improving separation, this is not directly observed in this method. Instead, creaming of droplets is followed, which is orders of magnitude slower than the coalescence process between two droplets. Measurements with standard samples are typically quicker, however separation of oil from water after polymer flooding might take several hours (Gao et al., 2011). The tests are also performed in static conditions of column separation, sometimes assisted with some level of agitation.

Turbidity measurements are quite similar to bottle tests. This means that it will take similar time to perform the tests, which can range from several minutes to hours (Zhang, 2017). Other setup configurations are also possible. For example, Fernandes et al. evaluated the efficiency of polymeric flocculants with the use of photometric analyser, allowing to measure light transmission in flow (Fernandes et al., 2004). Compared to bottle testing, an improvement is quantitative, non-subjective data in the form of light transmission measurements over time. This is easier to compare than visual observations of turbidity of the samples and it

offers more detailed information about the progress of separation. The method is also simple, and it is possible to measure several samples at the same time. In our case, the samples were measured continuously for 15 min, however less frequent measurements could allow several samples to be tested by changing them in the instrument, manually or with an autosampler. Nevertheless, the reproducibility is certainly an issue, as it was often difficult to obtain the same initial conditions, even with rigorous sample preparation method. What is more, 500 ppm of oil in the water phase was the lower limit for reliable detection of our instrument. Below that value, the signal was too weak. The strength of the signal is, however, dependent on the type of crude oil. Heavier oils will produce darker emulsions, which could decrease the lower detection limit. Lighter oils will be more transparent and could be problematic during measurements at lower concentrations.

The static light scattering methodology allowed to see the direct effect of the addition of flocculants on the drop size distribution. However, the technique is not without its disadvantages. The error bars in Figs. 7 and S6 were purposely not added to avoid complicating the graphs. The absolute values of D (4,3) for both crude oil emulsions, together with standard deviations, are shown in Tables S1 and S2 in SI. Even though the reproducibility of emulsion preparation method was high, the first measured size distribution often varied quite a lot due to the startup procedure. This impacted the experiment and resulted in large deviations between each parallel. One of the reasons was the unavoidable presence of gas bubbles in the beginning of the experiment, which took up to a few minutes to remove. Another limitation of the method was the oil-in-water concentration. When using too concentrated emulsions, multiple scattering can occur and, as described before, give a false signal from the smaller droplets. When too little dispersed phase is used, the signal-to-noise ratio might be too low. Like in turbidity measurements, the strength of the signal will also depend on the type of oil and its refractive index. Fortunately, 500 ppm was within the acceptable range for reliable measurements. Furthermore, the droplets could also cream to the surface during the measurement due to imperfect mixing in the vessel. Thin oil film formation was observed towards the end of the measurement, however it did not seem to impact the results to a large extent, at least not within our experimental time. On the whole, the results showed similar trends within each parallel and also in comparison with other techniques.

Microfluidics has already become a well-established technology for studying coalescence in emulsified systems (Bremond and Bibette, 2012). Measurement of droplet growth in microfluidic channels is fast and relies on direct observation and recording of coalescing droplets in flow. In contrast, other techniques require following changes in water clarity through subjective visual observation, turbidity or light scattering. Alternatively, time- and solvent-consuming sampling, extraction and analysis of remaining dispersed oil could also be performed. During microfluidic measurements, the droplet size is quite similar to what can be expected in the produced water treatment, and it is also possible to reduce the drop diameter even further. What is more, the droplets were generated *in situ*, which reduced the problems with initial drop size distribution, compared to other techniques. The main difference between our microfluidic method and other techniques used in this study is the concentration of oil. Because of the laminar flow in the channel, the number of generated droplets needs to be quite high to invoke collisions. Otherwise, the droplets would flow in a single row and hardly interact with each other, as observed in Fig. 9. To the best of our knowledge, only one other group attempted to study the performance of an additive to observe the effect on flocculation or improved coalescence with the use of microfluidic chips. Radhakrishnan et al. developed a μFLOC device for testing flocculation of yeast in the presence of polymeric flocculants (P. Radhakrishnan

et al., 2018). They also showed that microfluidics could be a great alternative to more traditional methods, such as light microscopy or light scattering.

Creaming and flocculation and/or coalescence are the main mechanism of oil-in-water emulsion destabilization. However, in the first two methods, flocculation cannot be quantified directly, as both require gravity separation to clarify the water phase and provide a detectable response. Since the oil droplets are in tens of μm size range, this process is rather slow - the rising velocity of a crude oil E droplets of 5 and 25 μm in diameter is ca. 0.2 and 4 mm/min, respectively. Furthermore, the emulsions had quite low concentration of oil, which could limit collisions between drops and decrease coalescence rates, especially considering static conditions of the experiments. By contrast, in light scattering and microfluidics only the fast phenomena are followed. Coalescence in flow conditions takes typically between 10 and 100 ms (Dudek et al., 2020a), and the changes in size distributions are visible very quickly. Additionally, breakage of droplets could also take place during light scattering experiments, due to mixing in the measurement vessel. While bottle and turbidity tests typically took around 30 min to finish, the effect of the flocculant was visible within a few minutes after starting the experiment for the other two methods. However, the lengthy preparation and cleaning procedures also affected the time per sample aspect. Light scattering instrument had to be cleaned thoroughly after each measurement, using several different solvents, bringing the total experimental time close to 60 min for single test condition. Microfluidic method took ca. 15 min to start and 60 min to clean, however several measurements, limited only by the number of chips, could be done during one run. In addition, the droplets were generated on the chip, as compared to other methods, which also saved time and cleaning. When it comes to the volume of the sample, almost 0.5L of emulsion was needed for our light scattering experiments. Significantly less was needed for bottle tests and turbidity (ca. 50 ml) and even less than that for microfluidics (few μl for 1 s recording). The method has the potential to utilize below 1 ml of sample if some optimization steps are implemented, for example simplification of the syringe loading procedure or usage of lower volume syringes.

Bottle (jar) tests and turbidity measurements are often employed in testing of flocculants, even though they have several drawbacks, such as long measurement time and static conditions. This could lead to some problems with screening of chemicals, especially if the flocculant has a long initiation time (e.g. low adsorption kinetics) or causes breakage of drops, impossible to observe in no flow conditions. Light scattering experiments are quite cumbersome to perform, especially considering the lengthy cleaning procedures and large sample volume. However, it provides additional information about behaviour of drops in flow and gives better understanding on the extent of coalescence and breakage in a system. Microfluidics also adds the possibility of testing the efficiency of flocculants in dynamic conditions. It provides very good control over the drop generation process, which compared to the other methods, is much more reliable and repeatable. The volume of samples required for testing is significantly reduced. What is more, with few improvements, one can drastically decrease the measurement time per sample. This can be done through controlling the flocculant concentration injected into the chip, which will further extend the possibility of screening tests.

4. Conclusions

In this paper, we have characterized four flocculants and tested their performance for produced water treatment with a newly developed microfluidic technique. These measurements were compared to three other, more established methodologies, namely bottle tests, turbidity and static light scattering measurements. The results showed that for most systems, the anionic flocculant was most effective, likely due to its large particle size and high molecular weight. Few differences were observed between the methods, which was mostly attributed to the static or dynamic conditions during the measurements or the way the data was collected. Bottle and turbidity tests relied on observing the clarification of the sample, either by eye or measuring the light intensity passing through the sample. However, no direct data on the effect of the flocculants on the droplet size could have been collected from these experiments. In contrast, light scattering measurements enabled to observe the changes in drop size distribution during flow. While the measurements were quite fast and provided additional results on droplet breakage (in some cases), the preparation and cleaning procedures were very lengthy, in addition to high consumption of samples and solvents. Furthermore, all three methods suffered from issues with (repeatable) emulsion preparation and transfer to the measurement vessel. Microfluidic method proved to be a good alternative to standard testing, with additional advantages such as low sample consumption, monodisperse emulsion generation and shorter measurement times. Visual observation of droplets allowed to gain several additional insights into the separation process. Mixing in microfluidics through drop collisions was very effective and helped to distribute the additive in the additive almost immediately after the injection point. What is more, no floc formation was observed during flow in microchannels, which suggested that the main destabilization mechanism responsible for improving separation was coalescence between oil droplets.

Declaration of competing 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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wroa.2020.100073.

References

Ahmad, A.L., Ismail, S., Bhatia, S., 2005. Optimization of Coagulation−Flocculation process for palm oil mill effluent using response surface methodology. Environ. Sci. Technol. 39 (8), 2828−2834.

Angle, C.W., Hamza, H.A., 2009. Effects of sand and process water pH on toluene diluted heavy oil in water emulsions in turbulent flow. AIChE J. 55 (1), 232−242.

Bordbar, A., Kheirandish, S., Taassob, A., Kamali, R., Ebrahimi, A., 2020. High-viscosity liquid mixing in a slug-flow micromixer: a numerical study. Journal of Flow Chemistry 10 (2), 449−459.

Bremond, N., Bibette, J., 2012. Exploring emulsion science with microfluidics. Soft Matter 8 (41), 10549−10559.

Buckley, J.S., Takamura, K., Morrow, N.R., 1989. Influence of electrical surface charges on the wetting properties of crude oils. SPE-16964-PA 4 (3), 332−340.

Daifa, M., Shmoeli, E., Domb, A.J., 2019. Enhanced flocculation activity of polyacrylamide-based flocculant for purification of industrial wastewater. Polym. Adv. Technol. 30 (10), 2636−2646.

Dudek, M., Chicault, J., Øye, G., 2020a. Microfluidic investigation of crude oil droplet coalescence: effect of oil/water composition and droplet aging. Energy Fuels 34 (5), 5110−5120.

Dudek, M., Fernandes, D., Helno Herø, E., Øye, G., 2020b. Microfluidic method for determining drop-drop coalescence and contact times in flow. Colloids Surf. Physicochem. Eng. Aspects 586, 124265.

Dudek, M., Vik, E.A., Aanesen, S.V., Øye, G., 2020c. Colloid chemistry and experimental techniques for understanding fundamental behaviour of produced water in oil and gas production. Adv. Colloid Interface Sci. 276, 102105.

Farooq, U., Simon, S., Tweheyo, M.T., Sjöblom, J., Øye, G., 2013. Electrophoretic measurements of crude oil fractions dispersed in aqueous solutions of different ionic compositions—evaluation of the interfacial charging mechanisms. J. Dispersion Sci. Technol. 34 (10), 1376−1381.

Fernandes, R.S., González, G., Lucas, E.F., 2004. Evaluation of polymeric flocculants for oily water systems using a photometric dispersion analyzer. Colloid Polym. Sci. 283 (2), 219−224.

S. Fernandes, R., González, G., F. Lucas, E., 2005. Assessment of polymeric flocculants in oily water systems. Colloid Polym. Sci. 283 (4), 375−382.

Gao, B., Jia, Y., Zhang, Y., Li, Q., Yue, Q., 2011. Performance of dithiocarbamate-type flocculant in treating simulated polymer flooding produced water. J. Environ. Sci. 23 (1), 37−43.

Holmberg, K., Jönsson, B., Kronberg, B., Lindman, B., 2002. Surfactants and Polymers in Aqueous Solution. Wiley.

Huang, B., Wang, J., Zhang, W., Fu, C., Wang, Y., Liu, X., 2019. Screening and optimization of demulsifiers and flocculants based on ASP flooding-produced water. Processes 7 (4), 239.

Jang, M., Lee, H.J., Shim, Y., 2010. Rapid removal of fine particles from mine water using sequential processes of coagulation and flocculation. Environ. Technol. 31 (4), 423−432.

Kelland, M.A., 2014. Production Chemicals for the Oil and Gas Industry. CRC Press, Boca Raton.

Krebs, T., Schroën, K., Boom, R., 2012. Coalescence dynamics of surfactant-stabilized emulsions studied with microfluidics. Soft Matter 8 (41), 10650−10657.

Leary, T., Yeganeh, M., Maldarelli, C., 2020. Microfluidic study of the electro-coalescence of aqueous droplets in crude oil. ACS Omega 5 (13), 7348−7360.

Liu, D.X., Zhao, X.T., Liang, W., Li, J.W., 2013. The stability and breakage of oil-in-water from polymer flooding produced water. Petrol. Sci. Technol. 31 (20), 2082−2088.

P. Radhakrishnan, A.N., Marques, M.P.C., Davies, M.J., O'Sullivan, B., Bracewell, D.G., Szita, N., 2018. Flocculation on a chip: a novel screening approach to determine floc growth rates and select flocculating agents. Lab Chip 18 (4), 585−594.

Santos, A.S., Oliveira, L.F.S., Marques, A.M.T., Silva, D.C.A., Mansur, C.R.E., 2018. Evaluation of the efficiency of polyethylenimine as flocculants in the removal of oil present in produced water. Colloids Surf. Physicochem. Eng. Aspects 558, 200−210.

Santos, A.S., Marques, A.M.T., Palermo, L.C.M., Mansur, C.R.E., 2020. Influence of molar mass of partially hydrolyzed polyacrylamide on the treatment of produced water from enhanced oil recovery. Colloids Surf. Physicochem. Eng. Aspects 584, 124042.

Sjoblom, J., 2001. Encyclopedic Handbook of Emulsion Technology. CRC Press.

Tice, J.D., Song, H., Lyon, A.D., Ismagilov, R.F., 2003. formation of droplets and mixing in multiphase microfluidics at low values of the Reynolds and the capillary numbers. Langmuir 19 (22), 9127−9133.

Wang, J., Tan, S.H., Nguyen, A.V., Evans, G.M., Nguyen, N.-T., 2016. A microfluidic method for investigating ion-specific bubble coalescence in salt solutions. Langmuir 32 (44), 11520−11524.

Wang, T., Andersen, S.I., Shapiro, A., 2020. Coalescence of oil droplets in micro-channels under brine flow. Colloids Surf. Physicochem. Eng. Aspects, 124864.

Zhang, Z., 2017. The flocculation mechanism and treatment of oily wastewater by flocculation. Water Sci. Technol. 76 (10), 2630−2637.