Journal of Petroleum Science and Technology 13(3): 39, 2023, Pages 16-29
DOI:10.22078/jpst.2024.5171.1889

Journal of Petroleum Science and Technology

Research Paper

https://jpst.ripi.ir/

Stability Analysis of Nanoclay Assisted Water Based EOR Methods

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Abstract

In recent years, nanoparticles have attracted great attention in the oil and gas industry, while one of the most applicable nanoparticles is nanoclay, especially in drilling, which enhances the rheology of the drilling fluids. However, the experimental analysis of nanoclay in EOR processes was rarely investigated. One of the main parameters that play an important role in the success of the EOR process is nanoclay stability. This research focuses on the comprehensive stabilization analysis of montmorillonite nanoclay in the presence of surfactants (SDS, CTAB) and KCl. Sets of experiments such as nanofluid preparation, nanofluid stability via imaging analysis, DLS and Zeta potential, XRD and SEM analysis, and clay swelling tests were performed in this research. All of the experiments were done at ambient pressure and temperature. Four different nanoclay concentrations (0.1, 0.25, 0.5, and 1 weight percentages) and surfactant concentrations of 0.5 are applied. Ultimately, the experiments' results confirm the nanoclay's stability in the presence of the surfactant employed in the study that lasted 24 hours. It is found that the optimum nanoclay concentration during the stability experiments is 0.1.

Keywords: Nanoclay, Stabilizer, Stability, Montmorillonite.

Introduction

In recent years, nanoparticles have greatly affected the oil and gas industry. One of the most interesting properties of nanoparticles used in the upstream sector is their ability to pass through reservoir pores due to their small size [1]. Characteristics of nanoparticles can be altered easily, which will assist in changing favorable IFT, wettability, mobility ratio, and rheological properties of nanofluid as injection fluid that will be useful for EOR[1] methods [2]. Different EOR methods intend to recover more oil with several mechanisms, including wettability and mobility control, gravity drainage, IFT reduction, and changes in rheological characteristics. However, each method has inherent disadvantages that must be mentioned to improve oil recovery. Chemical flooding is one of the EOR methods with significant problems, including low efficiency in IFT and viscosity reduction, an unfavorable mobility ratio, slow diffusion in the pore space, formation damage, and high cost due to the many chemicals required [3]. Nanoparticles are becoming increasingly attractive because they can overcome the abovementioned problems to a large extent.

One of the most applicable nanoparticles is nanoclay. In addition, clay minerals are hydrous aluminosilicates with a sheet-like structure that absorb water on their surface. Although most of the nanoclay applications are in drilling sector of oil industry, it also has the capability to be used as an EOR method assistant. In the following articles, the main concentration of the nanoclay application in EOR is related to modification in rheological behavior [4]. The effects of nanoclay (montmorillonite) on the heavy oil recovery during VAPEX method were investigated by Pourabdollah et al. Quantitative and qualitative analysis of asphaltene and heavy oil resin showed that montmorillonite was able to change the heterogeneity of the matrices. The absorption of asphaltenes in the interlayer spaces of montmorillonite increased and also the oil viscosity decreased [5]. The absorption of polymer on reservoir rock and the role of clay and silica nanoparticles in very small concentrations was investigated by Cheraghian. Nanoparticles play a major role in the absorption of polymer molecules on rock surface. Polymer solutions containing silica nanoparticles have lower absorption based on weight

1. Enhanced Oil Recovery (EOR)

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Received 2024-01-23, Received in revised form 2024-02-14, Accepted 2024-02-14, Available online 2024-04-14

percentage than similar samples containing clay [6]. Also, the effect of nanoclay in production of heavy oil during polymer injection process was investigated by Cheraghian et al. According to their investigations, the injected liquid viscosity is optimized with high concentration of polymer solution and in order to displace heavy oil by the polymer solution, the concentration of nanoparticles in the polymer solution should not exceed the threshold value (0.9% by weight).
The increase in oil recovery by combined injection of polymer (polyacrylamide) and nanoclay was about 5% more than the injection of polymer solution, and the best sample for increasing oil recovery is the polymer containing 0.9% by weight of nanoclay [7].
In another investigation, Cheraghian et al. studied the effect of nanoclay on improving the rheological properties of polyacrylamide solutions used to improve oil recovery. They understand that in a certain range of nanoclay concentration, it positively affects solution viscosity and can compensate for all the negative effects of salinity [8]. Using a glass model, Cheraghian and coworkers investigated the effects of nanoclay addition in surfactant polymer solution for heavy oil recovery. Based on the experimental results, polyacrylamide has good dispersion, and the particle size distribution was uniform when nanoclay was used. Also, with the injection of surfactant and polymer, heavy oil recovery is increased, and when nanoclay is added, the recovery is increased by 6.6% [9].
Cheraghian evaluated the effect of nanoclay and silica foam on the absorption of polymeric surfactant during oil recovery. The results showed that increased nanoclay concentration decreases solution absorption on the sandstone surface. All polymers containing nanoclay have significantly lower absorption than polymeric surfactants. The final oil recovery by nanoclay containing polymer surfactant flooding increases compared to the flood of polymer surfactant by 10.8% [10].
Furthermore, surfactants' effects on the stability of nanoclay Pickering emulsions were investigated by Zheng et al. Surfactants adsorption onto the nanoclay particle surface via electrostatic interactions and hydrophobicity were measured using Zeta potential in water before emulsion formation.
As oil in water emulsions was obtained by nanoclay, stability was improved with surfactant addition [11]. Also, a combination of EOR methods was proposed by Rezaei et al., who integrated surfactant, alkali, and nanofluid flooding. Alkalis and nanoparticles (SiO_2, ZnO, and nano-clay cloisite) were combined with four anionic surfactants. All the additives and NaCl salt (in concentrations lower than 5 wt%) helped to further reduce the IFT and contact angle of the oil droplet on dolomite rock samples compared with the pure surfactants [12].
The study of nanoclay-surfactant-stabilized foam in offshore heavy oil reservoirs to improve the steam flooding oil recovery was conducted by Zheng et al. According to their investigations, the thermal resistance and foam stability experiments showed that foam stability could significantly improve with nanoclay particle addition in an alpha-olefin surfactant system. Also, the system has good performance in terms of plugging effect and thermal resistance [13]. The thermal stability of polymer composites could be improved with nanoclays acting as a barrier to the gad and heat diffusion. The synthesis technique can impact the aspect ratio and interlayer spacing of the nanoclays, which, on the other hand, can improve their thermal stability [14].
Most of the published articles about nanoclay application in the EOR process focus on the rheological flow behavior modification that takes place when nanoclay is used as an EOR method assistant, and the other mechanisms, such as wettability alteration and IFT reduction, are not considered thoroughly. To use nanoclay as a water-based EOR assistant in surfactant flooding, it is necessary to study nanoclay stability in the presence of surfactant in more detail, which is not comprehensively investigated in the old and recent publications. Therefore, the main focus of this research is the stability analysis of the nanoclay in the presence of different surfactants. Several methods are used to enhance nanofluids' stability [15].
These are changing the pH value [16, 17], using surfactants [18], and using ultrasonic vibration [19-21]. Based on the application of nanoclay in this research (surfactant assisted EOR agent), the surfactants are used as stabilizer in order to improve nanoclay stability.
In the following sections, nanoclay preparation methods and the other used materials are described in the material preparation section. In the Experimental Methodology section, the method of nanofluid preparation, nanoclay stability, nanoclay morphology and clay swelling is explained. The results of nanofluids stability, DLS and Zeta analysis, XRD and SEM analysis and the clay swelling analysis are discussed in the Results and Discussion section. Experimental methodology of the stability analysis is described in Fig 1.

Materials and Methods

Materials Preparation

This study used montmorillonite nanoclay (hereinafter nanoclay) to investigate its stability in different fluid solutions. The mechanical and physical properties of the nanoclay are shown in Table 1, and the chemical analysis of the nanoclay is described in Table 2.

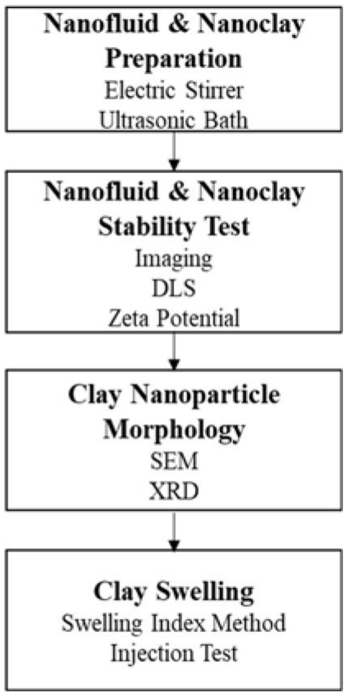


Fig 1. Experimental Methodology of Nanoclay Stability

Table 1 Mechanical and Physical Analysis of Nanoclay.

Mineral Type	Montmorillonite
Density	0.5-0.7 (gr/cm³)
Particle Size	1-2 nm
Specific Surface Area	220-270 (m²/gr)
Electrical Conductivity	-25 MV
Ion Exchange Coefficient	48 (meq/100 gr)
Space Between Particles	60 Aº
Color	light yellow

Table 2 Chemical Analysis of Nanoclay.

Number	Symbol	Percent
1	Na_2O	0.98
2	MgO	3.29
3	Al_2O_3	19.6
4	SiO_2	50.95
5	K_2O	0.86
6	CaO	1.97
7	TiO_2	0.62
8	Fe_2O_3	5.62
9	LOI	15.45

X-ray fluorescence (XRF) spectrometry analysis was done to determine the percentage of elements of the nanoclay. The result of the XRF analysis is exhibited in Fig 2.

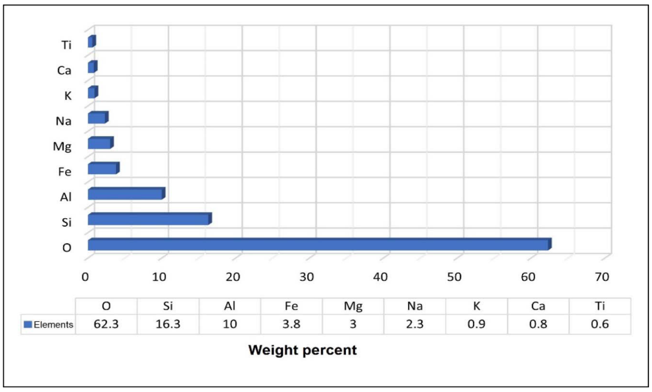


Fig 2 Weight Percentage of Elements in Nanoclay.

On the other hand, to modify nanoclay, a group of surfactants has been used. One of the surfactants that was used is Cetyl Trimethyl Ammonium Bromide (CTAB). The characteristics and molecular structure of tested CTAB are shown in Table 3 and Fig 3a, respectively.

Sodium Dodecyl Sulfate (SDS) is an anionic surfactant used in this research. The characteristics and molecular structure of tested SDS are shown in Table 3 and Fig 3b.

Preparation of Nanofluids

Four different nanoclay concentrations (0.1, 0.25, 0.5, 1 wt%[1]) were selected. Nanofluids were prepared using a two-step method. First, nanoclay was dispersed in distilled water at the above concentrations; then, they were dispersed for one hour in an electric stirrer at a rate of 1200 rpm to homogenize the fluids. Nanofluids were placed in an ultrasonic bath at 30 °C for one hour.

1. Weight Percentage (w/w%)

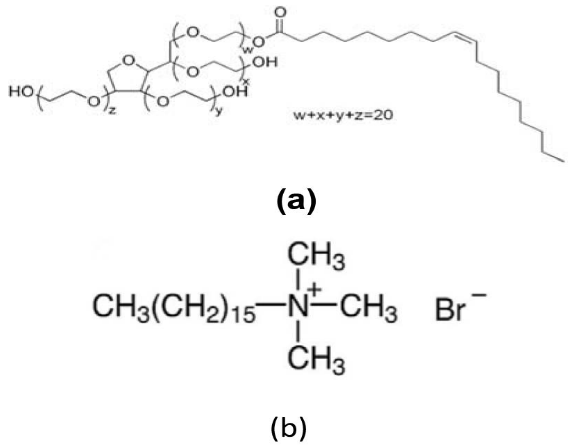


Fig 3 Molecular structure: a) CTAB and b) SDS.

Table 3 Properties of Surfactants: Cationic CTAB and Anionic SDS.

Surfactant	CTAB	SDS
Formula	$C_{19}H_{42}BrN$	$C_{12}H_{25}NaO_4S$
Density (kg/m³)	390	1095
Molar Mass (g/mol)	364.45	288.372
Solubility (g/l)	55	is not mentioned
pH	5-7	5-7

Then, the prepared nanofluids were poured into the Falcon tube in a certain amount. At the moment of nanofluids preparation, the images of all of them were taken inside the falcon tube to comprehensively image the deposition rate of nanoclay in different time intervals of up to 24 hours.

Nanoclays were stabilized by cationic and anionic surfactants. The surfactant concentration was 0.5% (w/v). The nanofluids containing surfactants were prepared using the same method as mentioned.

Nanoclay Stability in Base Fluid

Imaging the deposition of particles with the camera was considered to measure the stability of nanofluids. The imaging time intervals were immediately after sonication, one hour, 6 hours, 12 hours, and 24 hours. The images were compared with each other to analyze the stability of the nanofluid.

Although this approach was performed at a low cost, it cannot provide high accuracy for fluid stability analysis. Therefore, dynamic light scattering (DLS) analysis and zeta potential analysis have been used so that the results can be accurately compared with imaging of particle deposition.

DLS analysis is a physical method to determine the distribution of dispersed particles in solutions and suspensions. After the interaction of laser light with the particle, the scattering and changes in light intensity are evaluated according to the Brownian motions of the particles. Subsequently, the particle size distribution was calculated.

On the other hand, the stability of nanofluids was evaluated via zeta potential by observing the electrophoretic behavior of the fluid. The zeta potential of nanofluids can vary from positive to negative at different pH values. According to the nanofluid stability limit, a zeta potential value of 60 mV has excellent stability, ± 40 to ± 60 mV has good stability, ± 20 to ± 40 mV has medium stability, and for values of ± 10 to ± 30 mV and 0 to ± 5 mV, instability of the nanofluid is considered.

DLS and Zeta tests were measured by a Nanotrac Wave Particle Size Analyzer device capable of measuring particle sizes from 6500 nm to 0.8 nm with a very high weight percentage of up to 40 %. Also, evaluate the zeta potential from negative 200 mV to positive 200 mV. The zeta potential was reported thrice in laboratory conditions at 25 °C and 40% humidity.

Morphology of Clay Nanoparticles

The surface characteristics, structure, and size of nanoclay particles before and after stability were evaluated. The sample of nanoclay was made using a scanning electron microscope (SEM) model. For this purpose, the nanoclay particles were covered with a very thin layer of gold as a conductive material to prevent the deflection of the electron beam. Then, the sample was dried and placed in the center of the sample container under the detector to record the nanoparticle structure. In the next step, one of the most stable nanofluids evaluated by the photography method is passed through filter paper to obtain stabilized nanoclay. Then, the desired material was placed in the oven for 3 hours to dry completely. Finally, in the same way as mentioned, the images of the target sample are taken. In addition, clay nanoparticles were analyzed using X-ray diffraction (XRD). Furthermore, XRD was performed in the 5 to 90 insertions range, and SEM at 20 kW and 30 mA.

Clay Swelling

Clay is widely recognized for its high swelling properties. The swelling index method was used to determine the characteristics of clay swelling. In this research, the ASTM-D5890 test method was used to determine the swelling index. Two grams of nanoclay were dispersed in a 100-milliliter graduated cylinder with an increment of 0.1 gram. At least 10 minutes were allocated between each addition of clay to the water to ensure complete hydration and sedimentation of the clay at the bottom of the cylinder. These steps were followed until the entire 2-gram sample was added to the cylinder. Then, the sample was covered to protect it from disturbances for 16 to 24 hours, and finally, after complete hydration and swelling of the clay, the volume increase in the clay was measured as a swelling index.

On the other hand, an injection test was designed to study the phenomenon of clay swelling and migration simultaneously. For this purpose, absolute fluid permeability was measured on a plug sample whose specifications are listed in Table 4. The method of conducting the test is that first, the plug was saturated entirely with vacuum and then with distilled water. Then, the plug was placed inside the core holder, and a pressure of 1000 psi was applied. In the first test, distilled water was injected into the plug at a flow rate of 0.5 cc/min, and the pressure drop along the plug was recorded during the test.

The absolute permeability of the plug was measured by using the Darcy equation and drawing its pressure drop diagram.

In the second experiment, distilled water containing 0.1% by weight of nanoclay was injected into the plug at a flow rate of 0.5 cc/min and in 5 pore volumes. The pressure drop was recorded again during the injection to check its permeability. Then, distilled water was injected into the plug again in the second cycle. This operation investigated the pressure drop and permeability reduction after the injection of clay nanofluid because the permeability reduction before and after the injection of distilled water indicates the phenomenon of clay swelling and migration.

Table 4 Plug characteristics under clay swelling test.

Feature	Value
Type	Dolston
Length (cm)	5.04
Diameter (cm)	3.765
Dry Weight (gr)	120.595
Wet Weight (gr)	134.75
Porosity (%)	23.66
Bulk Volume (cc)	55.84
Pore Volume (cc)	13.211
Grain Density (gr/cc)	2.85

Results and Discussion

Stability of Nanofluids

The stability of nanoclay to improve the absorption property consists of inorganic modification methods that include the use of acid or hydroxyl metals and organic modification methods that mostly includes the use of surfactants. Modifying clay mineral surface by surfactants changes the clay wetness from hydrophilic to hydrophobic, increasing the distance between clay layers. In this part of the experiment, different concentrations of nanoclay (as mentioned), KCl, anionic stabilizer (SDS), and cationic CTAB (concentration of 0.5% by weight/volume) were used. As shown in Fig 4, all concentrations of nanoclay at the initial time of preparation on distilled water have excellent stability. Still, as time passed, precipitation of nanoclay particles can be seen. Higher concentrations of nanoclay tend to destabilize nanofluids. The images (Fig 4) indicate that nanoclay in concentrations of 0.1 and 0.25% by weight have suitable stability for the next test up to one hour after preparation.

Fig 5 shows the stability of nanoclay with KCl addition. It is clear that nanoclay does not show stability after preparation with this additive, and they begin to precipitate quickly. As a result, KCl does not improve stability; it can be described as a disturbance of stability compared to distilled water. Generally KCl acts as a temporary and efficient clay mineral salt stabilizer, which is widely used in drilling fluids. It is expected that in this research, potassium ion (K^+) did not enter the middle layers of nanoclay, which has smaller distances than conventional drilling clays and was not able to absorb charge and did not reduce the hydration expansion of clay. Figs 6 and 7 show the deposition images of nanoclay with SDS and CTAB, respectively. It is understood that both stabilizers have a significant effect on the stability of nanoclay. The process that takes place between clay and surfactants is the exchange of functional groups of surfactants with cations on the clay surface. It is because the CTAB with a positive head exchanges ions with the negatively charged ions of the nanoclay and increases the interlayer distance of the nanoclay.

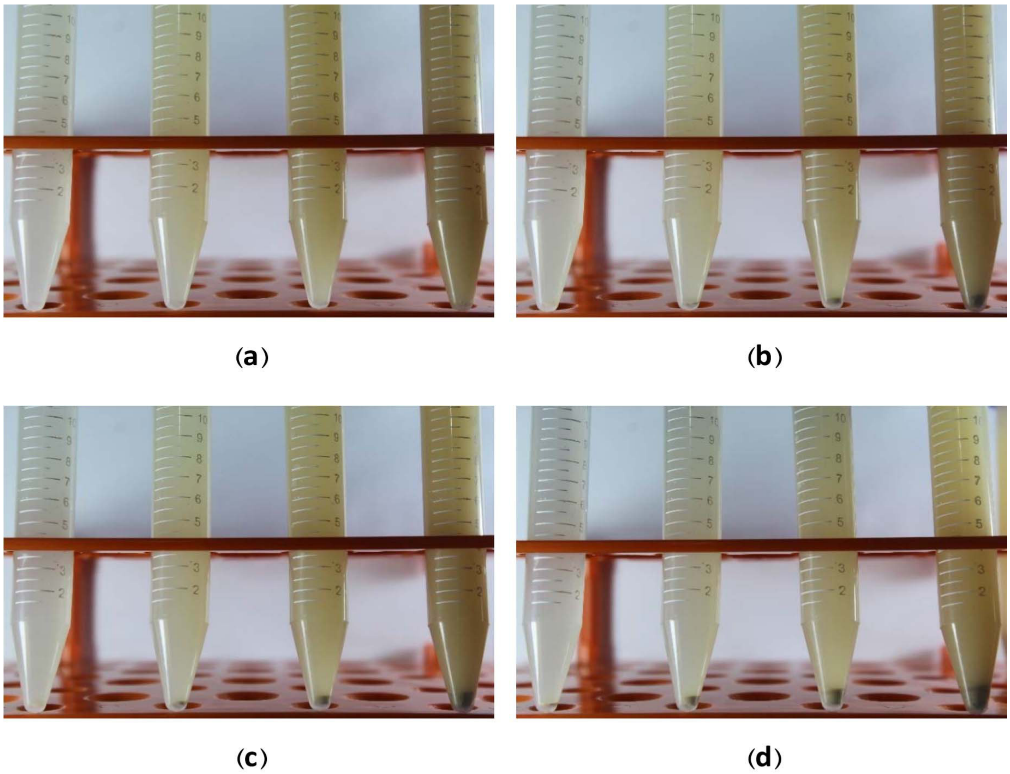


Fig. 4 Images of the deposition of nanoclay in distilled water, from left to right, concentrations of 0.1, 0.25, 0.5, and 1% by weight after: a) immediately after sonication, b) 1 hour, c) 6 hours, and d) 24 hours.

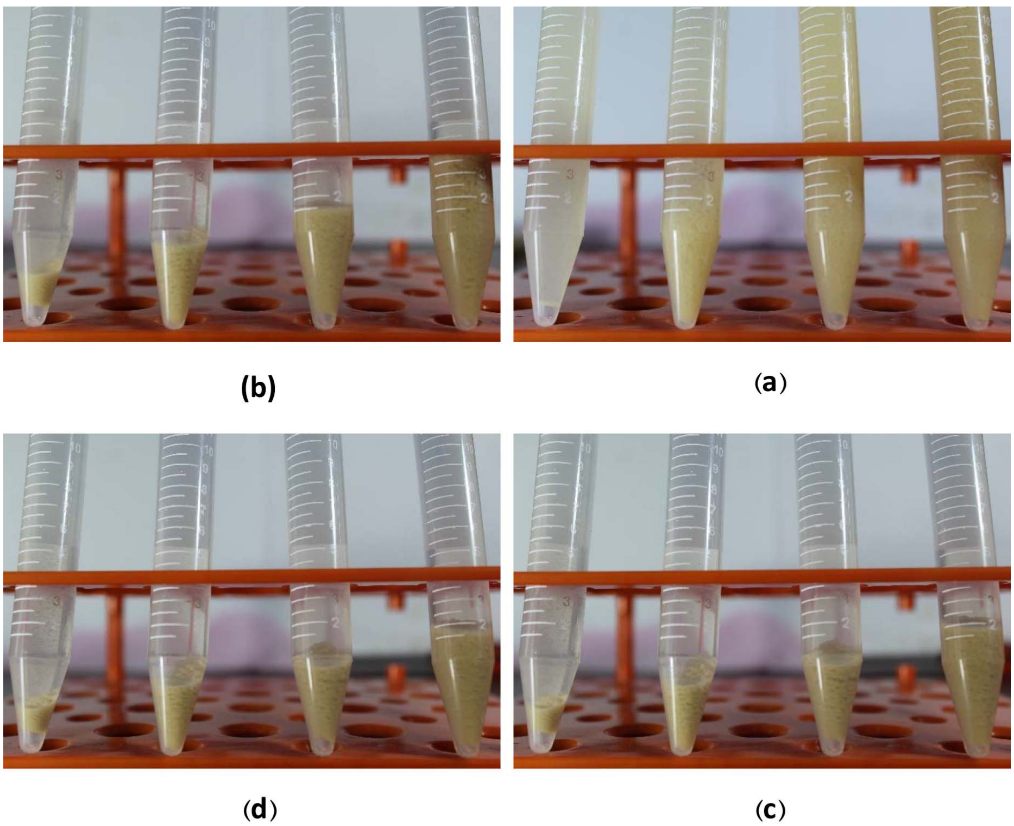


Fig. 5 Photographs of the precipitation of clay nanoparticles with KCl additive, respectively from left to right, concentrations of 0.1, 0.25, 0.5, and 1% by weight after: a) immediately after sonication, b) 1 hour, c) 6 hours, d) 24 hours.

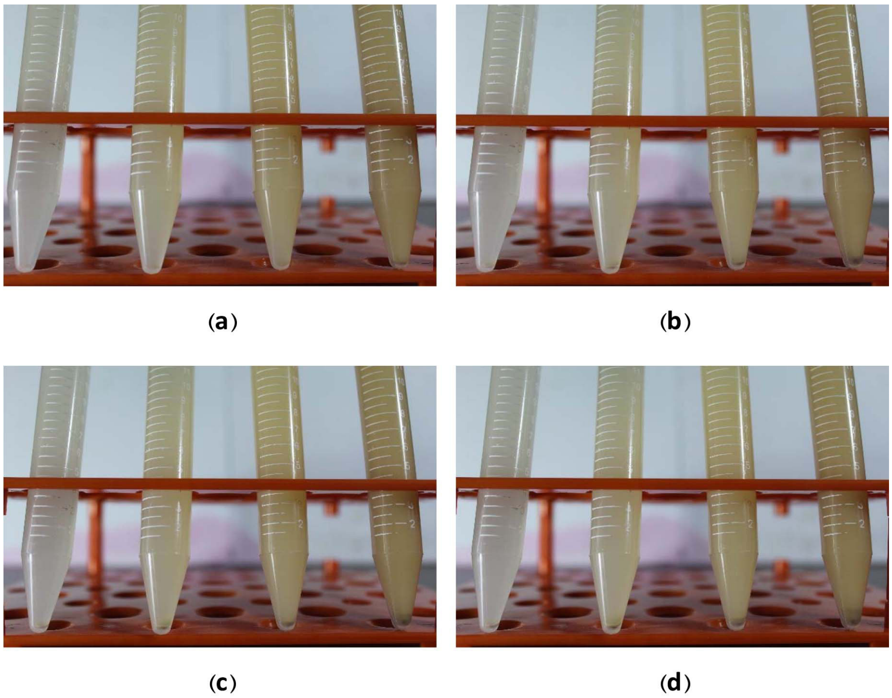


Fig. 6 Photographs of the precipitation of clay nanoparticles with SDS additive, respectively from left to right, concentrations of 0.1, 0.25, 0.5, and 1% by weight after: a) immediately after sonication, b) 1 hour, c) 6 hours, d) 24 hours.

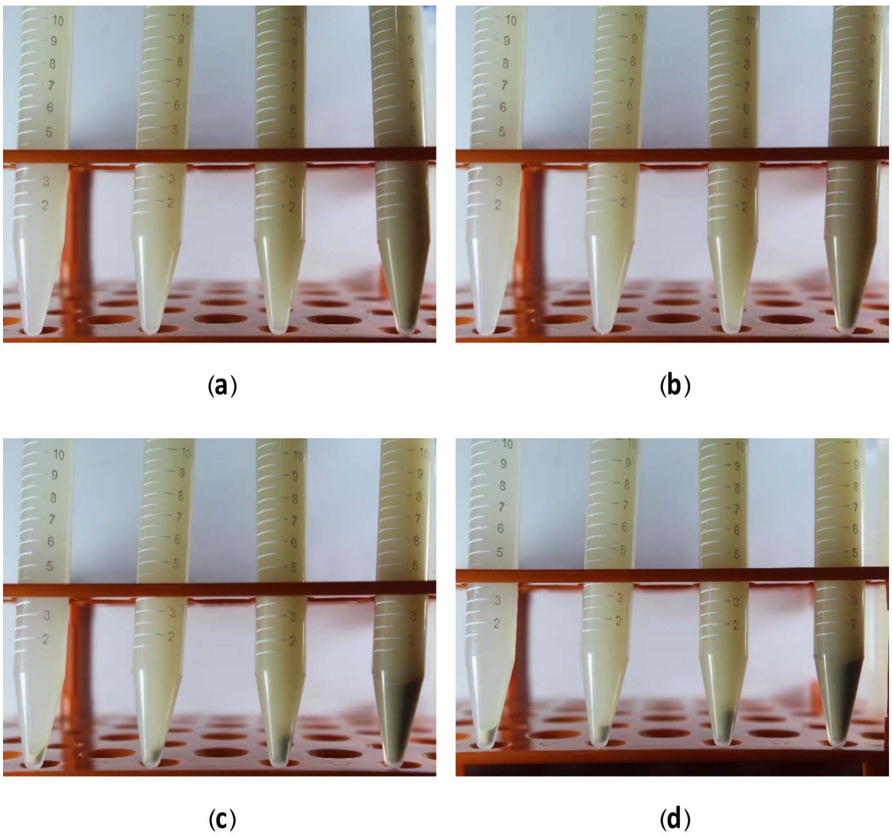


Fig. 7 Photographs of the precipitation of clay nanoparticles with CTAB additive, respectively from left to right, concentrations of 0.1, 0.25, 0.5, and 1% by weight after: a) immediately after sonication, b) 1 hour, c) 6 hours, d) 24 hours.

On the other hand, SDS, which has a negatively charged head, is expected to have no ion exchange effect compared to CTAB. The stability evaluation indicators of nanofluids based on nanoclay deposition from the images taken are summarized in Table 5. After the analysis of the images, concentrations of 0.5 and 1% by weight were excluded from the research process due to the high volume of sediments, and other nanofluids with appropriate stability were selected for DLS and Zeta analyses.

Table 5 Results of Nanofluids Stability.

Base Fluid	Nanoclay Conc. (wt %)	Initial Time	1 Hour	6 Hour	24 Hour
Distilled Water	0.1	Excellent	Good	Intermediate	Intermediate
	0.25	Excellent	Good	Intermediate	Intermediate
	0.5	Excellent	Good	Instability	Instability
	1	Excellent	Good	Instability	Instability
KCl	0.1	Excellent	Good	Instability	Instability
	0.25	Intermediate	Instability	Instability	Instability
	0.5	Intermediate	Instability	Instability	Instability
	1	Intermediate	Instability	Instability	Instability
SDS	0.1	Excellent	Excellent	Excellent	Good
	0.25	Excellent	Excellent	Excellent	Intermediate
	0.5	Excellent	Good	Good	Instability
	1	Excellent	Good	Good	Instability
CTAB	0.1	Excellent	Excellent	Excellent	Good
	0.25	Excellent	Excellent	Excellent	Intermediate
	0.5	Excellent	Good	Good	Instability
	1	Excellent	Good	Good	Instability

DLS and Zeta Potential Results

DLS analysis is a physical method to determine the distribution of particles in solutions and suspensions. The DLS test on the samples was performed in four modes: particle analysis in relation to the occupied surface area, particle analysis in relation to the occupied volume, particle analysis in relation to the number of existing particles, and particle analysis in relation to the intensity of light irradiated to the detector. In general, area and number are used to check the dimensions of nanoparticles, while in higher dimensions, volume and intensity are used.

One of the most important parameters in DLS analysis is the particle distribution index (PDI).

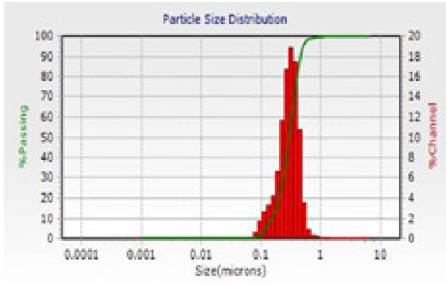
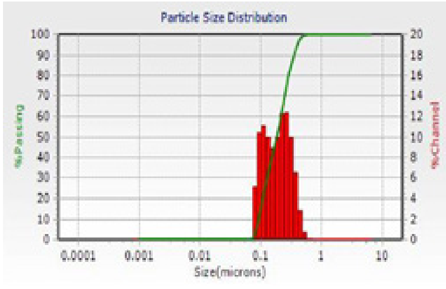
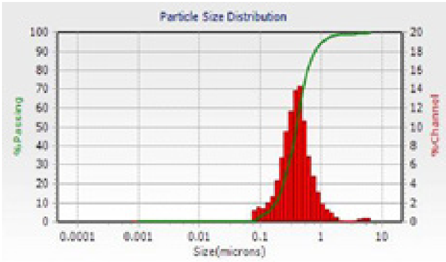
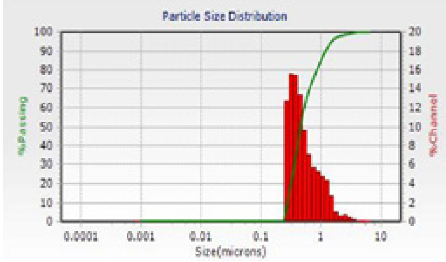
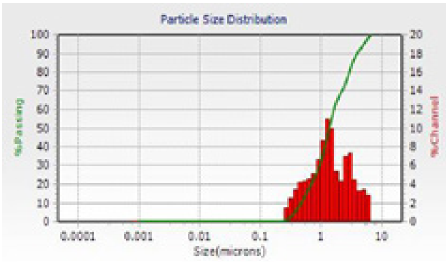
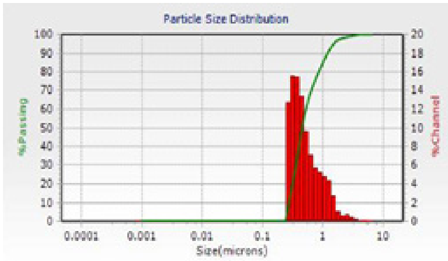
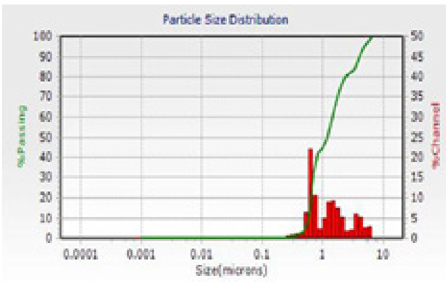
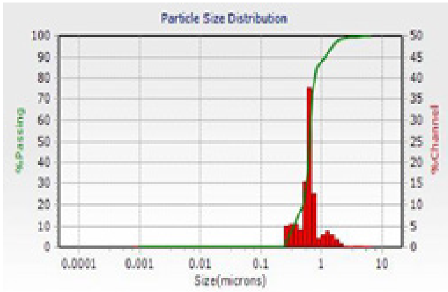
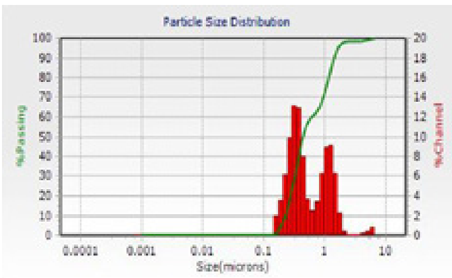
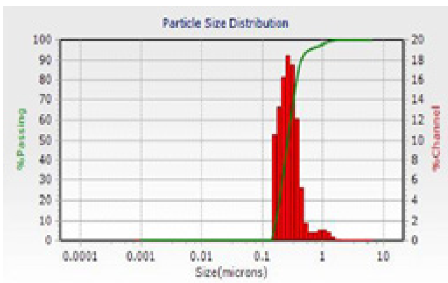
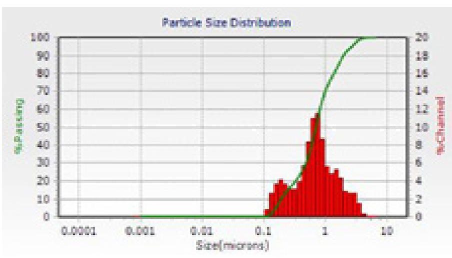
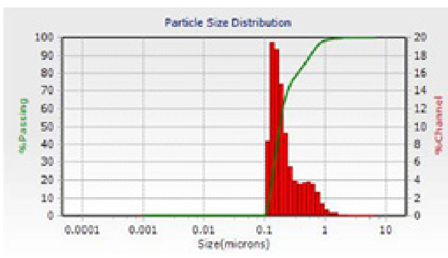
This index examines the standard deviation of the particle diameter distribution relative to the average particle diameter and is used to estimate the uniformity of the particles of a solution so that high PDI values are related to larger particle size distribution in the sample and low values are smaller particle size distribution. It should be noted that PDI in the range of 0.1 to 10 indicates a uniform distribution of particles (prevention of clumping) and excellent stability of the sample. The PDI values of prepared nanofluids are given in Table 6. The lowest PDI related to distilled water with a concentration of 0.1% of nanoclay is 0.841, and the highest value related to nanofluid with 0.25% of nanoclay by CTAB is 19.340. It shows that the distribution of particles in distilled water fluid without any additives is better than in other fluids because ion exchanges in surfactants can lead to disturbances in particle distribution.

Table 6 Nanofluid PDI.

Nanofluid	Nanoclay Conc. (wt.%)	PDI
Distilled Water	0.1	0.841
	0.25	2.584
KCl	0.1	3.040
	0.25	1.314
SDS	0.1	11.820
	0.25	4.170
CTAB	0.1	3.920
	0.25	19.340

Finally, DLS analysis graphs based on area, number, and particle size diameter values according to their volume are drawn for each fluid in Tables 7 and 8, respectively. It is worth noting that the two modes were selected only because of a more comprehensive comparison and a better understanding of the size and distribution of particles. It is clear that the samples containing KCl have the largest particle size in relation to volume percentage, and these results are completely consistent with other analyses carried out by particle deposition imaging and zeta potential. On the other hand, in the distilled water fluid without any surfactant, the concentration of 0.1 nanoclay is in the range of 200 nm, which has much smaller dimensions compared to the concentration of 0.25% by weight, which shows that the particles are not clumped. Therefore, the concentration of 0.1 nanoclay is prioritized for the next tests to determine a more stable fluid.

Table 7 Particle Size Distribution Graphs in Tested Nanofluids.

Nanofluid	Nanoclay Conc. (wt%)	Particle distribution Relative to Area	Particle distribution Relative to Number
Distilled Water	0.1		
	0.25		
KCl	0.1		
	0.25		
SDS	0.1		
	0.25		

countinue table 7

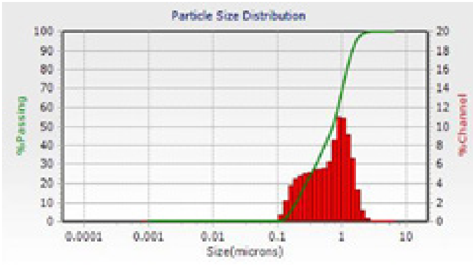
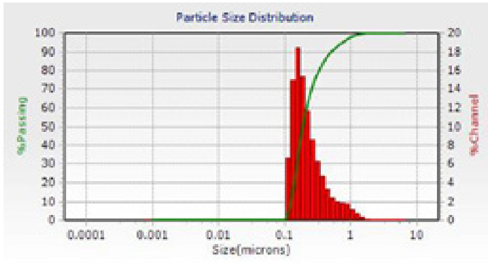
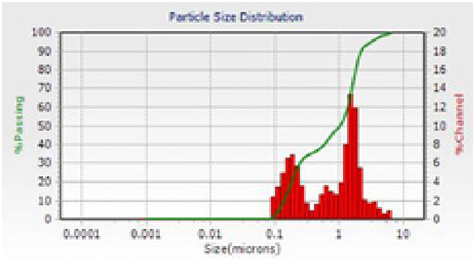
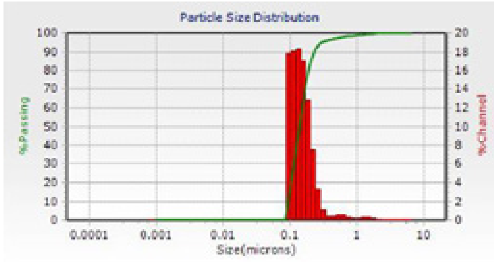
CTAB	0.1		
	0.25		

Table 8 Particle size distribution values in tested nanofluids.

Nanofluid	Nanoclay Concentration (wt.%)	Particle Distribution Relative to Area		Particle Distribution Relative to Number	
		Volume (%)	Diameter (μm)	Volume (%)	Diameter (μm)
Distilled Water	0.1	100	0.2598	56.8	0.2568
				43.2	0.1121
	0.25	99	0.384	54.4	0.2775
		1	4.98	45.6	0.0985
KCl	0.1	29.7	3.21	100	0.442
		70.3	1.035		
	0.25	18.8	4.04	13.1	1.348
		37.2	1.496	68.7	0.626
		44	0.637	18.2	0.331
SDS	0.1	1.5	5.5	100	0.267
		37.4	1.145		
		61.1	0.326		
	0.25	20.7	1.908	100	0.1786
		62.1	0.669		
		17.2	0.1829		
CTAB	0.1	100	0.704	100	0.1917
	0.25	1.1	5.89	100	0.1388
		50.3	1.62		
		12.9	0.638		
		35.7	0.1746		

Regarding the tested surfactants, the concentration of 0.1 nanoclay has a more suitable particle size due to the lack of accumulation of particles, which will lead to an increase in their size and, as a result, less fluid stability. Among the surfactants, CTAB has a particle size of less than 200 nm compared to SDS, which has a particle size of about 300 nm. As a result of the analysis of DLS graphs and particle size, it is clear that CTAB, SDS, distilled water, and KCL have the smallest particle size in fluids containing 0.1% nanoclay.

The most stable samples examined by nanoclay imaging were also tested for zeta potential with three replicates, and the analysis results are shown in Table 9.

Colloidal particles have an electric charge, which creates an electrostatic repulsion force between two adjacent particles. If this electrical charge is high enough, the colloids remain separated and dispersed in suspension, while reducing or removing these charges has the opposite effect. Therefore, colloidal particles easily accumulate and come out of suspension. Based on this and according to Table 9, the suspension of distilled water with nanoclay particles at a concentration of 0.1% weight has a surface charge of -38.6, compared to a higher concentration of nanoclay (0.25 wt.%) has a surface charge of -18.9, which shows the average stability of the sample. On the other hand, the suspension containing KCl (clearly depicted in Fig 4) reported instability and rapid sedimentation in both concentrations.

Table 9 Zeta Potential Test Results.

Base Fluid	Nanoclay Concentration (wt.%)	Zeta Potential (mV)			
		Run 1	Run 2	Run 3	Average
Distilled Water	0.1	-39.1	-38.5	-38.4	-38.6
	0.25	-18.3	-19.3	-19.2	-18.9
KCl	0.1	-5.5	-4.8	-4.9	-5
	0.25	-1.8	-2.2	-2	-2
SDS	0.1	-61.2	-60.6	-60.4	-60.4
	0.25	-58.1	-57.9	-57.7	-57.69
CTAB	0.1	49	49.9	50	49.9
	0.25	67.3	68.1	68.3	67.9

The surface charge in the sample with a concentration of 0.1 and 0.25% weight was recorded -5.0 and -2.0, respectively. According to the result, KCl acts as a stability disruptor.
Meanwhile, the use of surfactant has shown a significant impact on the stability of nanofluids. The results of Zeta potential in the samples using SDS recorded a high surface charge so that it was reported as -60.4 mV in the concentration of 0.1% nanoclay and -57.69 mV in the concentration of 0.25% weight. The results indicate the excellent stability of prepared nanofluids. Zeta results using CTAB cationic surfactant also reported similar results. The use of CTAB in nanoclay with 0.1% and 0.25% weight were measured +49.9% and +67.9% respectively, which shows the excellent stability of the prepared suspensions. With these interpretations, it is clear that the most stable fluids are the ones containing SDS and CTAB.
pH plays a key role in the stability of nanofluids. For this reason, it was measured three times using Hanna Lab's pH meter, and the average of them is described in Table 10. For a better understanding of the relationship between pH and zeta potential with fluid stability, their relationship is shown in Fig 8.
In general, it is known that the values of zeta potential are pushed towards more stability in acidic and basic conditions and by moving away from the neutral environment. The results also confirm that SDS and CTAB have the best stability. In this research, all tested fluids, including distilled water and KCl, reported pH in an alkaline environment but presented low zeta values.

Table 10 pH of Tested Nanofluids.

Nanofluid	Nanoclay Conc. (wt %)	pH
Distilled Water	0.1	9.3
	0.25	9.1
KCl	0.1	9
	0.25	9
SDS	0.1	9.3
	0.25	9.3
CTAB	0.1	8.5
	0.25	8.2

XRD and SEM analysis

The XRD test is one of the basic parameters used to study the distance between layers. Specifically, the reduction of the angle 2θ and the broadening of the peak indicate increased distance between layers. The interlayer distance of the tested particles can be obtained by Bragg's law (Equation 1).

$$2d\sin\theta = n\lambda \quad (1)$$

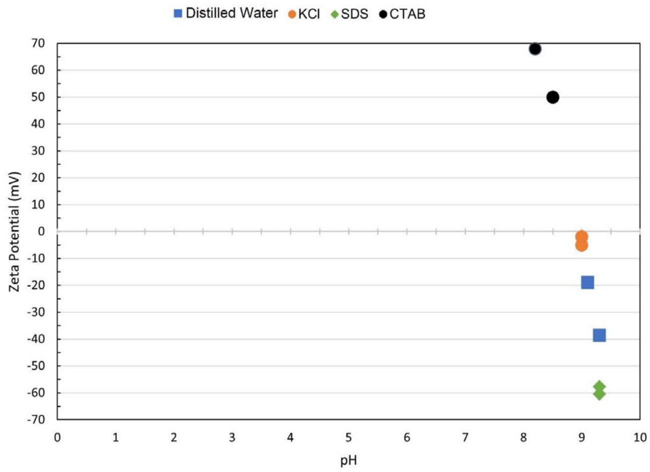


Fig. 8 Comparison of zeta potential and pH results.

where d is the gap between the layers, λ is the wavelength of the emitted X-ray, θ is the angle of the reflected rays, and n is the reflection order. One of the most important properties of layered silicates is the presence of interlayer. This distance can be calculated with data collected from X-ray diffraction.
Fig 9-a shows the XRD graph results, which describe the crystalline characteristics of the nanoclay before stabilization with CTAB (the most stable sample). The X-ray diffraction peaks on the nanoclay before stabilization, for example, at the positions of 20.883°, 27.740°, and 68.188°, have interlayer distances of 4.25, 3.21, and 1.37 Å, respectively. Also, the XRD pattern shown in Fig 9-b is generated after stability with CTAB surfactant. Based on the results, all the peaks related to the nanoclay stabilized with CTAB at the positions of 20.069°, 20.857°, 20.653°, 30.493°, and 67.938° are calculated with interlayer distances of 4.42, 4.25, 3.34, 2.92 and 1.37 Å, respectively, compared to nanoclay before stability. The introduction of CTAB cations between nanoclay layers increases the distance between them. Therefore, by increasing the distance between nanoclay layers, its crystallization will decrease, and as a result, the number of graphite peaks will also decrease, as shown in Fig 9. As a result of these interpretations, when the interlayer distances increase, the nanoclay provides more stability, which is determined in the XRD results.
On the other hand, the analysis of micrograph images was also performed before and after stabilization with CTAB. Investigating the size and morphology of nanoclay particles is very important because they determine the quality of their distribution in the structure and the stability of the suspension in the prepared nanofluid structure.

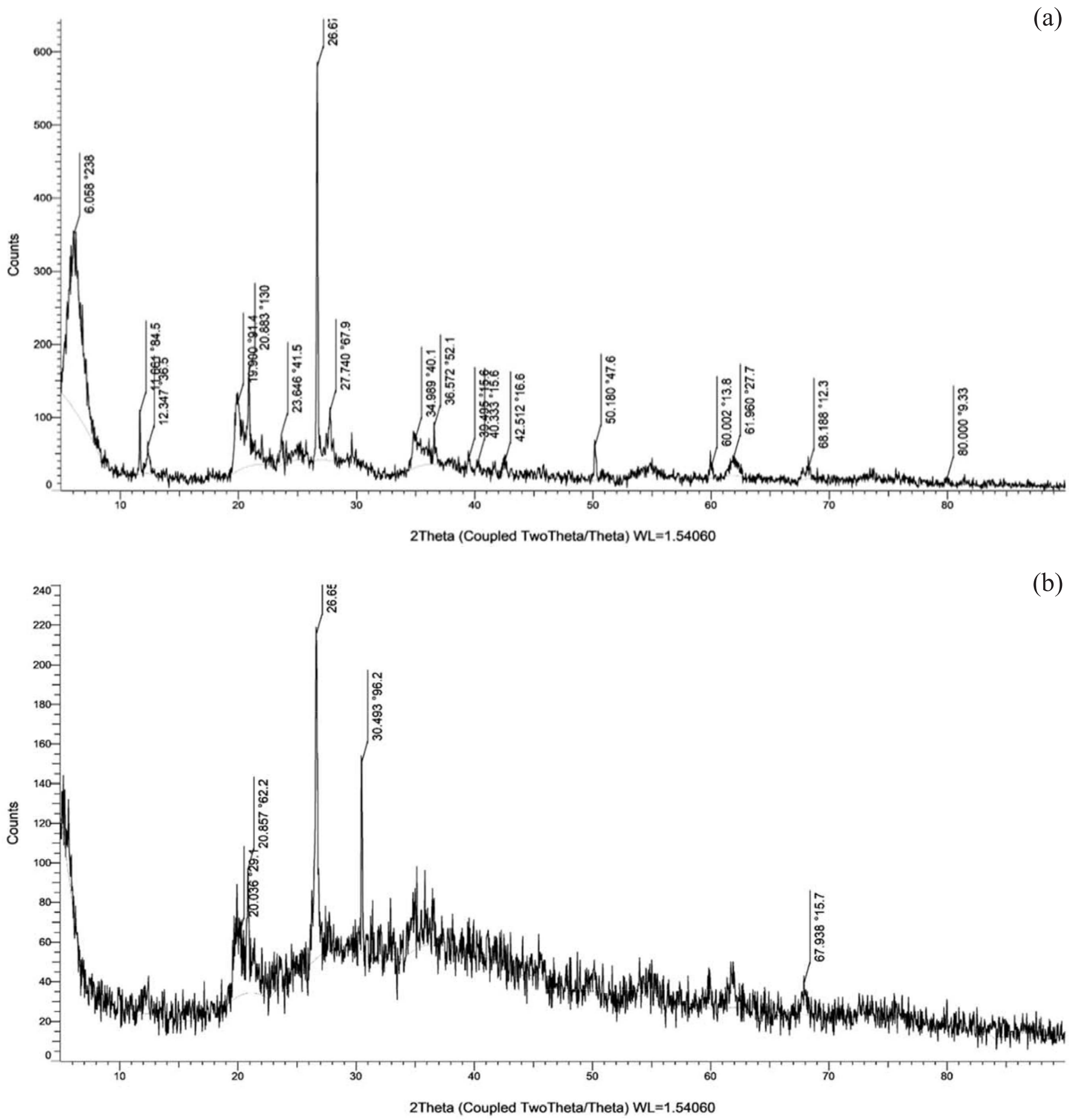


Fig. 9 XRD results: a) nanoclay, b) nanoclay stabilized with CTAB.

It is worth mentioning that using nanoclay particles compared to a micrometer or higher particles leads to better and easier distribution in the composition of base fluids, which is one of the main reasons for using nanoclay particles in porous media. The SEM images were analyzed at two sizes of 2 and 7 micrometers.

In Fig 10, the SEM images of the nanoclay sample before and after stabilization are shown. It is apparent in Fig 10-a that the nanoclay particles have very large plates and are placed very compactly on top of each other. Fig 10-b shows the sheet and plate-like shape of nanoclay and their roughness level. Fig 10-c shows the sample of nanoclay after stabilization with CTAB. The montmorillonite sheet particles have come out of a very compact and lumpy state and have become more accessible and spaced. Also, Fig 10-d shows that the nanoclay particles have changed from a sheet and extreme roughness to a smoother state.

The main reason for these changes is the placement of the organic compound used to produce nanoclay in the space between the layers, leading to proper flaking of nanoclay. Combining surfactants with nanoclay can turn this hydrophilic compound into a material with almost hydrophobic properties. The SEM images of the stabilized nanoclay obtained during the ion exchange process show significant changes in the morphology of the nanoclay.

Clay Swelling Analysis Results

As shown in Fig 11, a clay swelling index of 4.5 (2 gr/100 mL) was measured on distilled water. This index indicates that the swelling of the tested clay is very small, and it can have a promising result for improving oil recovery. Also, the swelling of clay on test additives was evaluated separately, and the results are shown in Table 11. In all cases, the swelling of nanoclay is so low that it can be said nanoclay practically does not swell, and it is far from swelling in all types of test additives, which indicates promising results in porous media injectivity.

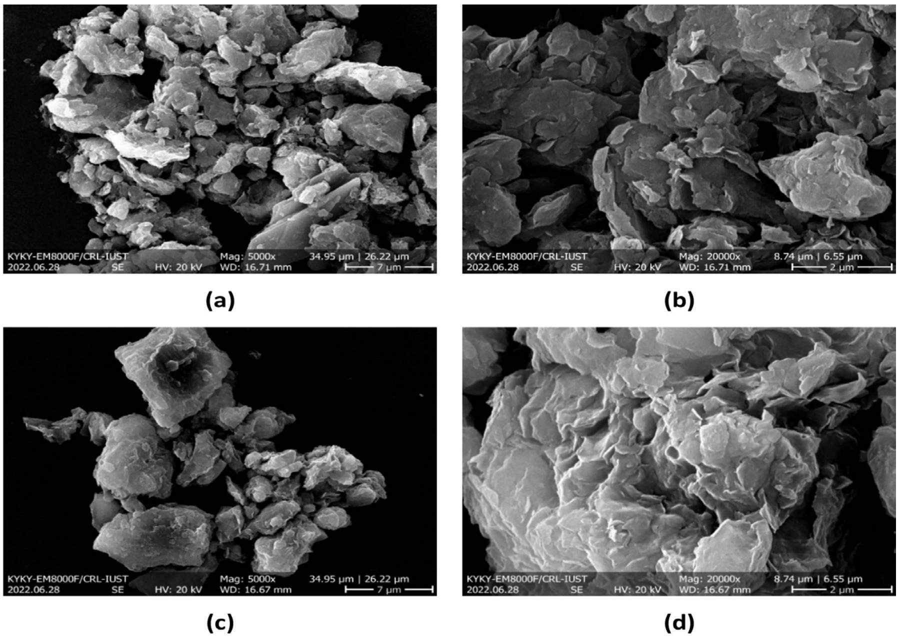


Fig. 10 SEM images of nanoclay: a and b) before stabilization, c and d) after stabilization with CTAB.

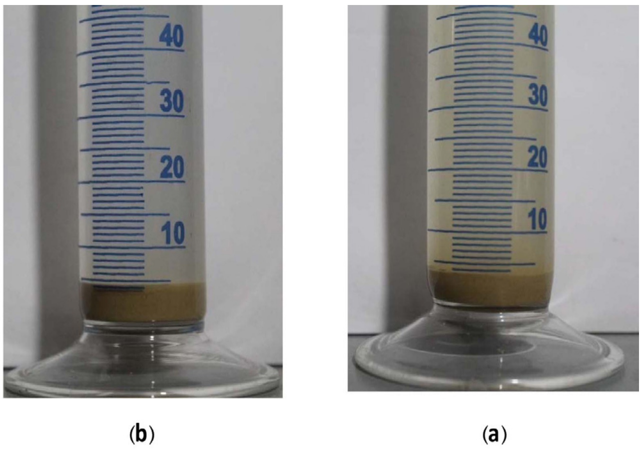


Fig 11 Adding Two Grams of Nanoclay to 100 ml of Distilled Water: a) At Zero Time t0, b) After 24 Hours t1.

Table 11 The Results of Clay Swelling Index.

Fluid	Swelling Index (2 grams/100 ml)
Distilled Water	4.5
KCl solution (0.5% wt)	5
Suspension of CTAB by 0.5 wt%	4.5
Suspension of SDS by 0.5 wt%	4.5

Fig 12 shows the pressure drop across the plug by the injection sequence of distilled water, nanoclay, and recirculation of distilled water. First, the plug was saturated with distilled water by a vacuum pump. Then the plug was placed inside the core holder, and a pressure of 1000 psi was applied on the plug. In the first stage, distilled water was injected with a flow rate of 0.5 cc/min, and the pressure difference along the plug was recorded. As shown in Fig 12, after 5 times of pore volume injection, the pressure difference was 1.1377 bar. Then, the pressure difference increases with the injection of nanoclay, which is fixed at 1.3902 bar. At the same time, if the re-injection of distilled water leads to a higher pressure difference than the injection of the first cycle, it indicates the swelling and confinement of clay nanoparticles in the porous medium.

Distilled water was re-injected with the same flow rate of 0.5 at five times the pore volume. The results indicated that the pressure difference was again equal to the initial pressure difference, and finally, it was reported at a pressure of 1.0320 bar. Therefore, the behavior of nanoclay in this part of the experiment can be explained by two reasons. The first reason is that after 5 pore volumes of nanoclay injection, very little swelling is created, and the distance between the clay plates increases, which leads to an increase in the pressure difference. The second reason is that with the re-injection of distilled water, the slight swelling starts, the nanoclay structure collapses, and the plates migrate through the porous medium, and the pressure difference decreases, as shown in the pressure difference trend in Fig 12.

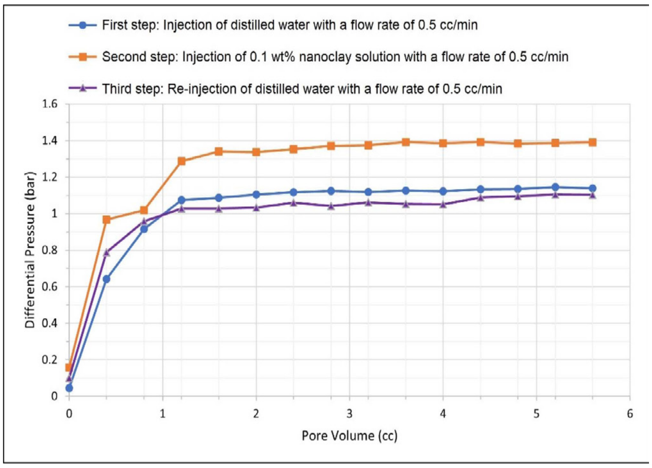


Fig 12 Pressure Difference Along the Plug For the Sequence of Injection of Distilled Water and Nanoclay.

Based on the experiment and considering the Darcy equation, liquid permeability is 3.3 mili Darcy (mD) in the first stage of distilled water injection. In the second stage and after the injection of nanoclay, the liquid permeability decreases to 2.7 mD. Meanwhile, in the third stage and after re-injection of distilled water, the permeability returns to the initial permeability, which it indicates the nanoclay is not trapped in the porous medium.

Conclusions

This research focussed on the stabilization of montmorillonite nanoclay by anionic surfactants SDS and cationic CTAB and in the presence of KCl salt to evaluate its effect compared to the surfactants. Also, nanoclay was tested without any additives and only in distilled water. Because montmorillonite is a type of clay that can swell, standard swelling tests were performed on nanoclay and its injection in the plug. The main results of this research are:

- The stability of four concentrations of nanoclay in distilled water and the presence of KCl, SDS, and CTAB were investigated. Imaging analysis of nanoclay deposition within 24 hours showed that the concentrations of 0.5 and 1.0 % of nanoclay were not stable enough, so they were excluded. The images show excellent nanoclay stability in the presence of surfactants (stabilizers), moderate stability in the presence of distilled water, and a lack of stability in the presence of KCl.
- DLS and Zeta analysis also emphasized the correctness of the results of imaging analysis in such a way that the fluid stability at a concentration of 0.1 and 0.25 % weight in the presence of CTAB was +49.9 and +69.9 mV, SDS was -60.4 and -57.69 mV, distilled water was -38.6 and -18.9 mV, and KCl was -5.0 and -2.0 mV, respectively.
- According to the results, CTAB significantly affected the nanoclay surface's stability and increased the interlayer distance of the nanoclay, so the XRD analysis showed that the unstable nanoclay changed from a crystalline to an amorphous state. With the passage of the stabilizing substance between the nanoclay spaces, its interlayer space has increased so that the number of peaks has reached 4 from 18 in different positions, which shows the effective efficiency of this stabilizer in expanding the space between the layers of nanoclay. The SEM images prepared from the sample also confirm's better dispersion of nanoclay.
- Nanoclay swelling was done using standard clay analysis and injection in a plug. The swelling index of nanoclay on all additives was 0.45 in distilled water, 0.50 in the presence of KCL, 0.45 in the presence of SDS, and 0.45 in the presence of CTAB. Also, the injection of 0.1% (w/w) nanoclay along the plug led to a slight increase in the pressure difference from 1.1377 bar to 1.3902 bar. After the re-injection of distilled water, the pressure difference along the plug was 1.0320, which indicates the inability of nanoclay to swell and lock. The passage of nanoclay through the porous media will reduce the permeability compared to normal clays. In the experiment conducted, the permeability before and after nanoclay injection was reported to be 3.3 and 3.4 mD, respectively, which is considered the same.

References

1. Roy, A., Kabra, D., Pareek, G., Kumari, K., Kashyap, P.P., Naik, S., Chadha, U. and Selvaraj, S.K. (2023). A review of nanomaterials and their applications in oil and petroleum industries, Nano Express, doi.10.1088/2632-959X/acdc40.
2. Sircar, A., Rayavarapu, K., Bist, N., Yadav, K., & Singh, S. (2022). Applications of nanoparticles in enhanced oil recovery, Petroleum Research, 7(1), 77-90, doi.org/10.1016/j.ptlrs.2021.08.004.
3. Ratanpara, A., & Kim, M. (2023). Wettability Alteration Mechanisms in Enhanced Oil Recovery with Surfactants and Nanofluids: A Review with Microfluidic Applications, Energies, 16(24), 8003, doi.10.3390/en16248003.
4. Merino, D., Tomadoni, B., Salcedo, M. F., Mansilla, A. Y., Casalongué, C. A., & Alvarez, V. A. (2020). Nanoclay as carriers of bioactive molecules applied to agriculture. Handbook of nanomaterials and nanocomposites for energy and environmental applications, 1-22, doi.10.1007/978-3-030-11155-7_62.
5. Pourabdollah, K., Moghaddam, A. Z., Kharrat, R., & Mokhtari, B. (2011). Improvement of heavy oil recovery in the VAPEX process using montmorillonite nanoclays, Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles, 66(6), 1005-1016, doi.10.2516/ogst/2011109.
6. Cheraghian, G., Khalili Nezhad, S. S., Kamari, M., Hemmati, M., Masihi, M., & Bazgir, S. (2014). Adsorption polymer on reservoir rock and role of the nanoparticles, clay and SiO2, International Nano Letters, 4, 1-8, doi.org/10.1007/s40089-014-0114-7.
7. Cheraghian, G. K. N. S., & Khalilinezhad, S. (2015). Effect of nanoclay on heavy oil recovery during polymer flooding. Petroleum Science and Technology, 33(9), 999-1007, doi.10.1080/10916466.2015.1014962.
8. Cheraghian, G., Khalili Nezhad, S. S., Kamari, M., Hemmati, M., Masihi, M., & Bazgir, S. (2015). Effect of nanoclay on improved rheology properties of polyacrylamide solutions used in enhanced oil recovery, Journal of Petroleum Exploration and Production Technology, 5, 189-196, doi.org/10.1007/s13202-014-0125-y.
9. Cheraghian, G. (2015). An experimental study of surfactant polymer for enhanced heavy oil recovery using a glass micromodel by adding nanoclay, Petroleum Science and Technology, 33(13-14), 1410-1417, doi.10.1080/10916466.2015.1062780.
10. Cheraghian, G., & Hendraningrat, L. (2016). A review on applications of nanotechnology in the enhanced oil recovery part A: effects of nanoparticles on interfacial tension, International Nano Letters, 6, 129-138, doi.org/10.1007/s40089-015-0173-4.
11. Zheng, W., Tan, X., Jiang, W., Xie, H., & Pei, H. (2021). Investigation of nanoclay-surfactant-stabilized foam for improving oil recovery of steam flooding in offshore heavy oil reservoirs. ACS omega, 6(35), 22709-22716, doi.10.1021/acsomega.1c03008.
12. Rezaei, A., Riazi, M., Escrochi, M., & Elhaei, R. (2020). Integrating surfactant, alkali and nano-fluid flooding for enhanced oil recovery: A mechanistic experimental study of novel chemical combinations, Journal of

Molecular Liquids, 308, 113106., doi.10.1016/j.molliq.2020.113106.
13. Lu, T., Gou, H., Rao, H., & Zhao, G. (2021). Recent progress in nanoclay-based Pickering emulsion and applications, Journal of Environmental Chemical Engineering, 9(5), 105941, doi.org/10.1016/j.jece.2021.105941.
14. Fakhreddini-Najafabadi, S., Torabi, M., & Taheri-Behrooz, F. (2021). An experimental investigation on the low-velocity impact performance of the CFRP filled with nanoclay. Aerospace Science and Technology, 116, 106858, doi.org/10.1016/j.ast.2021.106858.
15. Devendiran, D. K., & Amirtham, V. A. (2016). A review on preparation, characterization, properties and applications of nanofluids. Renewable and Sustainable Energy Reviews, 60, 21-40, doi.10.1016/j.rser.2016.01.055.
16. Russel, W. B., Russel, W. B., Saville, D. A., & Schowalter, W. R. (1991). Colloidal dispersions, Cambridge University Press, doi.org/10.1017/CBO9780511608810.
17. Wen, D., & Ding, Y. (2005). Experimental investigation into the pool boiling heat transfer of aqueous based γ-alumina nanofluids. Journal of Nanoparticle Research, 7, 265-274, doi.10.1007/s11051-005-3478-9.
18. Qiu, F. (2010, October). The potential applications in heavy oil EOR with the nanoparticle and surfactant stabilized solvent-based emulsion, In SPE Canada Unconventional Resources Conference?, SPE-134613, doi.10.2118/134613-MS.
19. Ruan, B., & Jacobi, A. M. (2012). Ultrasonication effects on thermal and rheological properties of carbon nanotube suspensions, Nanoscale Research Letters, 7, 1-14, doi.org/10.1186/1556-276X-7-127.
20. Thangavelu, K., Annamalai, R., & Arulnandhi, D. (2013). Synthesis and characterization of nanosized TiO_2 powder derived from a sol-gel process in acidic conditions, International Journal of Engineering Sciences & Emerging Technologies, 4(2), 90-95, ISSN: 2231 – 6604.
21. Nadler, M., Mahrholz, T., Riedel, U., Schilde, C., & Kwade, A. (2008). Preparation of colloidal carbon nanotube dispersions and their characterisation using a disc centrifuge. Carbon, 46(11), 1384-1392, doi.10.1016/j.carbon.2008.05.024.