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Evaluation of stability and functionality of zinc oxide nanofluids for enhanced oil recovery

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Abstract

Nanofluids for enhanced oil recovery offer a breakthrough solution towards tertiary recovery and consequently higher oil production. Their ability to reduce interfacial tension, alteration of formation's wettability, higher adsorption capacity, and acceleration of disjoining pressure makes them excellent candidates for enhanced oil recovery. The main objective of this paper is to investigate the effect of polymers on zinc oxide (ZnO) nanofluids for enhanced oil recovery (EOR) and the role played by chemical modification using polymer stabilizers on nanoparticle stability in nanofluids. Nanoparticles with an average particle size of 34 nm were synthesized and used to prepare nanofluids of different concentrations and their stability was evaluated using sedimentation and UV–vis spectrophotometry tests. ZnO-synthesized nanofluids were used solely and in addition to Polyvinylpyrrolidone (PVP) and Polyvinyl alcohol (PVA) as stabilizing agents. It was noted that ZnO nanofluids with PVA stabilizer recorded the highest oil recovery of 82%. In contrast, the ZnO nanofluids without stabilizing agents registered the lowest recovery rate during the flooding experiment. The results revealed that a higher injection rate increases the oil recovery and reduces the viscous fingering effect with a better displacement front. Furthermore, nanofluids containing polymeric stabilizing agents achieved better recovery factors compared to ZnO nanofluids without stabilizing agents. This phenomenon was also observed in the interfacial tension test where nanofluids with PVA and PVP stabilizers reduced the IFT by 59% and 61% respectively.

Keywords Zinc oxide, Nanofluids, Enhanced oil recovery, EOR

Introduction

Global energy consumption keeps increasing, which put huge pressure on the oil and gas industry to increase production [36]. However, to overcome this problem, national and international oil companies should focus on innovative ways to increase the current oil production to meet the world's energy demand. Primary and secondary recovery techniques only extend the production life of the reservoir by natural energy or injection of water to displace oil towards producing wells resulting in the recovery of only 15–35% of the original oil initially in place while 60% remained unrecovered (Q. Wang [35]). Since easy-to-produce oil fields have been exhausted, there is an urgent need for better or novel

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enhanced oil recovery (EOR) technologies to replace traditional EOR methods [23]. Enhanced oil recovery is defined as a chemical method of crude oil extraction from the reservoir by injecting materials that are not part of reservoir chemistry which results in the alteration of reservoir fluids properties [14]. The most common chemical-enhanced oil recovery methods include polymers flooding, alkaline, and surfactant flooding and they work by lowering the interfacial tension between the fluids or incremental fluid viscosity which enhances their mobility [12]. One of the remarkable techniques compared to other conventional means is the applications of nanoparticles in enhanced oil recovery and in this case, metal oxides nanoparticles such as ZnO, TiO_2, ZrO_2, $Al2O_3$, and MgO are often employed because of their distinctive chemical and physical properties [20]. Unlike other ordinary particles, metal oxide nanoparticles have unique nanoscale attributes which make them suitable for nanofluids preparation. However, due to their nano size dimension which enables them to move freely in reservoir pores, metal oxide nanoparticles are also coherent and reliable at different reservoir conditions (Hassan, Guan, Chuan, Halilu, et al. [17]). Wettability alteration is one of the main mechanisms in nanofluid-enhanced oil recovery because nanoparticles in base fluids easily rearrange at the formation surface accelerated by an increase in the structural disjoint pressure that enhances oil recovery [33]. This process leads to the alteration of formation rock from oil-wet to water-wet conditions, interfacial tension reduction, and an increase in oil viscosity hence it mobile towards producing wells (Al-Asadi, Arce, et al. [2]). Regardless of nanofluids' capabilities of enhancing oil recovery and increasing recovery rate, their applications are sometimes hindered by stability issues under harsh reservoir conditions, which leads to a decline in system performance after a certain time [8]. The stability issue has been reduced by deploying polymers as stabilizing and capping agents for nanoparticles which improve their suspension, protect them from high temperature and high salinity, and improve molecular interactions with other fluids [24]. Based on recent research, ZnO nanoparticles have been utilized in many nanofluids for enhanced oil recovery simply because of their advantageous attributes related to their low cost, chemical stability, eco-friendly, low-temperature growth, and their ability to adsorb on rock surfaces making them a strong candidate. (Hassan, Guan, Chuan, Hamza, et al. [18]) studied the ZnO nanofluids for enhanced oil recovery and they observed that ZnO nanofluids were able to recover 14% of the original oil initially in place when dispersed in the brine solution. The study conducted by [34] found that ZnO nanofluids reduced the interfacial tension by 6.13% of the crude-oil interface which generally improved sweep efficiency. In addition to their excellent stability, ZnO nanofluids also play an important role in the increment of fluids viscosity in the reservoir and based on an investigation done by [6] it was found that ZnO nanofluids reduced the local viscosity and boosted the recovery factory of oil initially in place by 50%. Furthermore, ZnO nanofluids have a higher adsorption capacity on the rock surface due to the large surface area of its nanoparticles, and [31] found that ZnO nanoparticles have maximum adsorption energy of 253 kcal/mol which accelerates the wettability and capillary reduction hence increasing the recovery factor by 11.82%. Based on several views in many research points, there is a need to explore more advanced materials in enhanced oil recovery in order increase the production output. In this study, the main objective is to increase the recovery rate by deploying ZnO nanofluids as a potential candidate for enhanced oil recovery and to investigate the following: (I) preparation of ZnO nanoparticles using a sol–gel method and to characterize synthesized nanoparticles using various techniques, (II) preparation of nanofluids using the synthesized ZnO nanoparticles and investigating the effect of chemical modification using polymers. To study the stability of nanofluids in the aqueous base. Lastly, (III) fabrication of a microchannel model that represents the porous media of the oil reservoir at which the flooding experiments were executed using synthesized ZnO nanofluids. In enhanced oil recovery processes, microfluidic models are utilized as the subject of research to study the various patterns of fluid flow in subsurface rocks [13]. The use of microfluid for enhanced oil recovery deserves more focus since it is more insightful in the oil and gas sector. The traditional flooding process is associated with certain limitations that can be addressed through the use of microfluidic devices that are accurate, fast, and easy to analyse [11]. Microfluidic models in enhanced oil recovery help in flow visualization to determine the real-time behavior of fluid displacement in porous media. In this study a new design of microfluidic model is introduced to mimic the real rock of petroleum reservoir.

Materials and methods

Chemicals

The chemicals used in this experiment include zinc acetate dihydrate (Zn $(CH_3CO_2)0.2H_2O$) MW 219.51 g/Mol and 99.99% purity provided by Sigma-Aldrich, sodium hydroxide (NaOH) 98% pellets by Merk, methanol CH_3OH anhydrous 99.8% by Sigma-Aldrich, chromium trichloride ($CrCl_3.6H_2O$) by Elami Fine Chemical, India. Polyvinylpyrrolidone (PVP), average MW 3500 K12, Polyvinyl alcohol (PVA) extra pure by Alpha Chemika, India. Deionized water was used to prepare nanofluids and washing of synthesized nanoparticles. Crude oil with API

of 36° was obtained from a local oil refinery company in Alexandria, Egypt. All the reagents used are of analytical grade with high purity with no further purification.

Microchannel matrix design and fabrication

A nature-inspired like structure PDMS microchannel matrix with an obstacle size of (145 × 45 μm) was applied to imitate the porous media of the oil reservoir for the flooding test. Cole-Palmer Syringe pump EW-74900 model was used to inject oil and nanofluids into the microchannel matrix pore system, and Canon EOS-250D digital camera was also used to capture the images of fluids visualization. The PDMS microchannel matrix pattern was manufactured in our lab to mimic the using laser engraving machine VLS3.50 model, Universal Laser System. Table 1, illustrates the microchannel matrix dimensions and properties. To determine the porosity and permeability values, fluid saturation technique was applied where microchannel matrix was fully saturated with the known volume of water. Pressure sensors were connected to the inlet and outlet of the microchannel to measure the pressure drop. With a fixed flowrate and a known pressure drop, Darcy's equation was used to determine the microchannel permeability (Joseph, Siva Kumar Gunda, and Mitra [22]). The determination of permeability and porosity in microchannel using fluid saturation technique relies on assumption that the microchannel mimics the porous media formation.

Synthesis of zinc oxide nanoparticles

Zinc oxide nanoparticles were synthesized using the sol–gel method by carefully adding 10 g of zinc acetate dihydrate to 150 ml of methanol and were subjected to instance stirring using a magnetic stirrer for 60 °C until the solution became clear. 18 ml of sodium hydroxide was added dropwise at the glass wall follows by continuous stirring for three hours. The solution was left to age overnight so that the liquid and precipitates separate. The solution was centrifuged for 30 min at a rate of 500 rpm and deionized water was used to wash the white precipitates and the solution was placed in a sonication bath for 25 min before final separation. The mixture solution was placed in the oven at 80 °C for 24 h and finally calcined at 700 °C for three hours.

Table 1 Microchannel matrix dimensions and properties

Descriptions	Units	Dimensions
Area	(cm^2)	36
Porosity	(%)	40
Permeability	(mD)	750
Diameter	(μm)	300
Depth	(μm)	500

Characterization of zinc oxide nanoparticles

The physical and chemical properties of synthesized zinc oxide nanoparticles were determined using X-Ray Diffraction (XRD) Panalytical Xpert3 powder model, Transmission Electrons Microscope (TEM) JEOL's JEM 2100F Japan, Fourier Transform Infrared Spectroscopy (FTIR) Bruker Vertex 70 V Germany, Zeta Sizer Malvern nano series Germany. UV–vis spectrophotometer Jasco V-630, Japan was used to calculate the spectral absorbance of prepared nanofluids.

Preparation of nanofluids and stability tests

Nanofluids preparation in this experiment considered two-step methods since nanoparticles were prepared separately using the sol–gel method. The prepared zinc oxide nanoparticles, stabilizers, and deionized water was used to prepare nanofluids. 0.2wt% of synthesized ZnO nanoparticles was added to 600 ml of deionized water in three separate bottles equally to form a nanofluids solution and two stabilizers Polyvinylpyrrolidone (PVP) and Polyvinyl alcohol (PVA) were added two bottles subsequently. The bottles were labeled as ZnO, ZnO + PVA, and ZnO + PVA respectively and the bottles were stirred using a magnetic stirrer at room temperature for 30 min and placed in a sonication bath for 45 min for effective dispersion of nanoparticles in the base fluids. To test the stability and agglomeration of nanoparticles in the base fluids, a sedimentation testing method was adopted, and the samples were placed in a stationary environment (Hassan, Guan, Chuan, Halilu, et al. [17]). The color changes of nanofluids were observed every day and photos were taken to differentiate the settling and aggregation behavior of nanoparticles over seven days. The absorbance spectra of ZnO nanofluids were determined at 200–900 nm range with UV–vis spectrophotometer Jasco V-630, Japan. A cuvette of 1 cm was used for baseline adjustment, and each sample's spectrum absorbance was taken and recorded. Zeta potential test was also conducted using Zeta Sizer Malvern nano series Germany to check the stability of ZnO nanofluids. As a function of nanoparticles' surface charge, a zeta potential test is carried out to determine the stability mechanism of nanofluids [16].

Contact angle measurements

Contact angle measurement was used to evaluate the wettability alteration on the surface of PDMS using nanofluids and stabilizers by applying the static sessile drop technique (Al-Asadi, Somoza, et al. [3]). A PDMS acting as sandstone was placed carefully on a secured surface

in stable conditions and an insulin syringe was used to place a droplet of nanofluids on the surface of PDMS. The nanofluid droplets on the PDMS surface were magnified with Canon EOS-250D digital camera which was tethered to a computer and photos were taken once the pictures displayed an equilibrium state. Once clear and focused images are captured, the corresponding contact angle of each droplet was measured using open-source imaging software known as ImageJ which is multidimensional scientific software for imaging processing. Four samples were staged for contact angle measurement (DI water, ZnO, ZnO + PVA, ZnO + PVP nanofluids) and their images of droplets were captured and compared. However, the droplets were subjected to time investigation and their photos were taken every 10 min for 60 min to compare the changes in the contact angle of droplets on the PDMS surface over time.

Interfacial tension measurements

The pendant drop test method was used to measure the effect of the interfacial tension of prepared nanofluids on displaced fluids. A homemade apparatus that consists of a needle, camera, micro-pipette, light source, and computer for image processing was used to experiment. CAST3.0 imaging software was used to measure the interfacial tension values of various nanofluids. The IFT measurements were conducted at ambient pressure and temperature conditions so that the nanofluids' properties are not altered. To measure the IFT of the oil droplet, a sample of oil was placed in a micro-syringe, a drop of specific volume was introduced through a needle, and the contact angle was measured. The same procedure was repeated for various nanofluids and oil, but the system should be cleaned thoroughly before introducing another fluid.

Density measurements

The density of the fluids was measured using analytical density meter DMA 35 Auto Paar instrument Austria-Europe. The density measurements were carried out at a controlled room temperature of 25 °C at atmospheric pressure. The fluid whose density is measured was placed in a beaker and the density meter tube was placed in the beaker to suck the fluids and measurement readings were taken. The process is repeated several times and the instrument was cleaned with distilled water before taking another density measurement of another fluid.

Microchannel matrix flooding experiments

A 2D PDMS mud-crack-like structure microchannel matrix was used as a porous medium, a syringe pump (Cole-Palmer EW-74900 model) was used to inject oil and nanofluids into microchannel matrix pore system, a high-resolution camera (Canon EOS-250D) for capturing images porous flow, and computer for images processing as depicted in Fig. 1. The inlet tube of microchannel

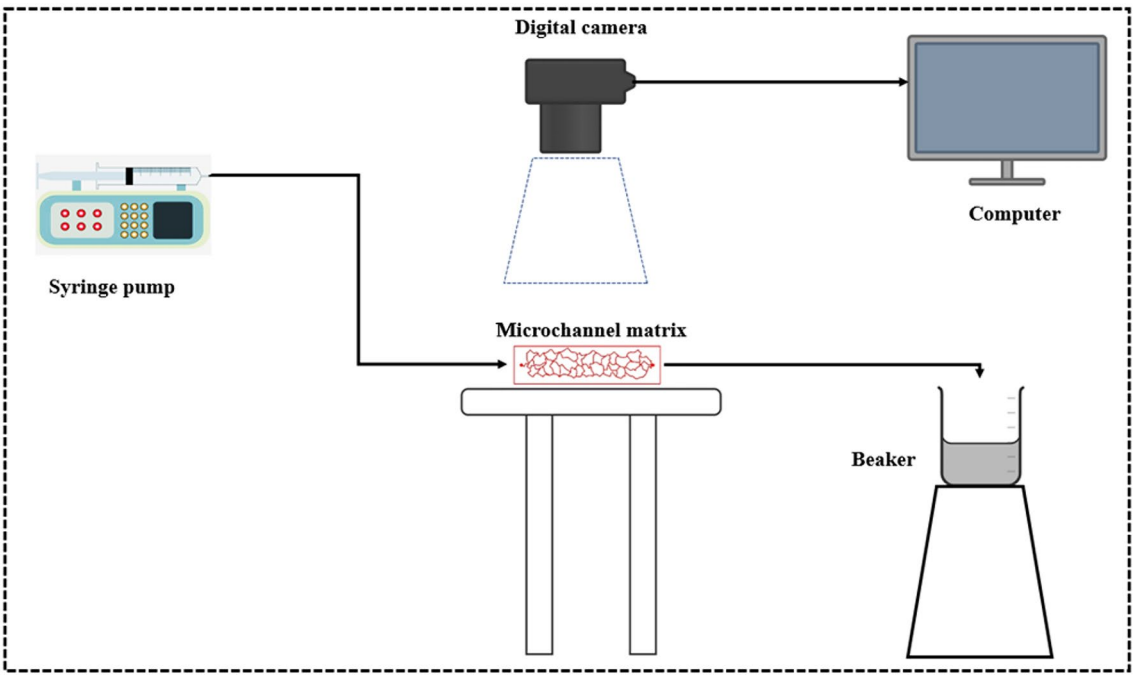

Fig. 1 Schematic diagram of microchannel matrix flooding experimental setup

was connected to a syringe pump while outlet tube was placed into a beaker where fluids were collected as described by [27]. After the experimental setup, sodium hydroxide solution was injected into a microchannel porous medium until it was fully saturated for 40 min to represent the brine formation of the reservoir fluids. Subsequently, distilled water was injected into the microchannel to displace sodium hydroxide and clean any impurities in the porous medium. Thereafter, a solution of chromium trichloride was injected into the matrix to make it an oil-wet condition. After oil-wetting procedures were completed, crude oil was injected into the microchannel matrix at a rate of 30 ml/hr. until it was fully saturated to obtain reservoir conditions (bedrocks and pore throats 100% saturated with crude oil) and was left to age for 2 h. Next, a desirable nanofluid was injected into the matrix and the displaced oil was observed through the transparent matrix until a breakthrough was seen and then, the injection stopped. The experiment was repeated several times with different nanofluids at different flow rate ranging from 30 to 100 ml/hr with flow velocity of $2.5{\cdot}10^3$ to $8.3{\cdot}10^3$ m/s. The amount of crude oil recovered was separated from water and measured volumetrically for every experiment.

Results and discussions

Characterization techniques

X-ray diffraction (XRD) analysis

X-ray diffraction analysis of zinc oxide nanoparticles was determined using (XRD) Panalytical Xpert3 powder model to examine their crystallinity and the patterns were recorded at a range of 20–80 (2 θ) degrees at a scan rate of 12°/min. Based on the main three diffraction peaks at Braggs angles of 2(θ) 36.20, 31.7^0, 56.5^0as shown in Fig. 2, it can be confirmed that the structure of zinc oxide recommended hexagonal Wurtzite structure which is enshrined in JCPDS standard card number 36–1451 [15]. According to the perfect matching of all XRD diffraction peaks in both intensity and positions, it can be concluded that the synthesized zinc oxide nanoparticles carry no impurity with a 99% chance of ZnO without other elements [29]. The average crystalline size (D) was calculated according to Debye–Scherrer's equation.

$$D = \frac{0.9\lambda}{\beta cos\theta} \tag{1}$$

where, D, λ,θ, β is the average particle size, XRD wavelength, Bragg's angle, and full width at haft maximum. The average particle of ZnO nanoparticles was (~34 nm) according to the most intense peak (101).

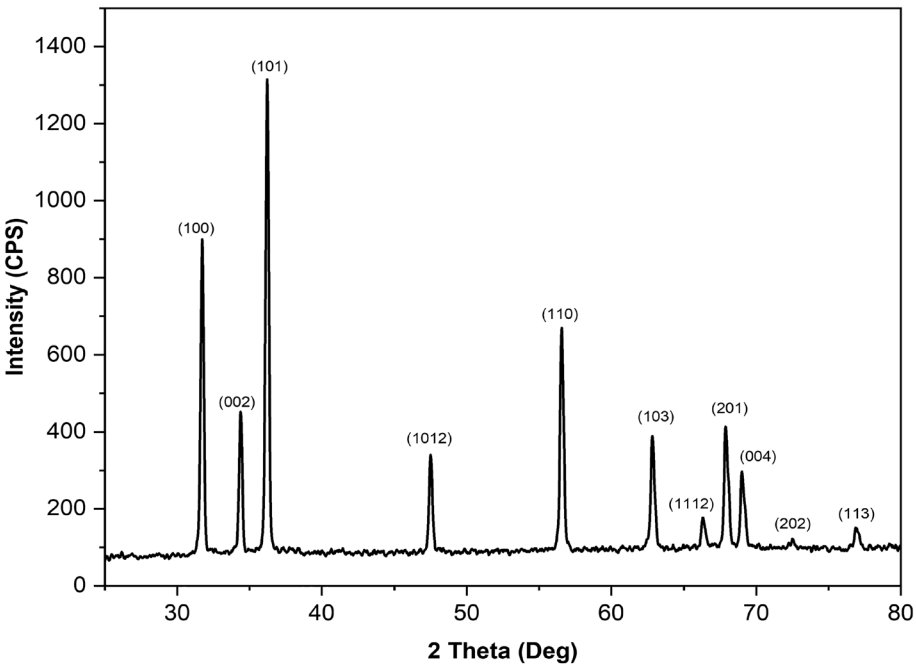

Fig. 2 XRD pattern of Zinc oxide nanoparticles

Transmission electron microscopy (TEM) analysis

The chemicals and physical compositions of ZnO nanoparticles are normally influenced by their shape, size, surface area, and surface energy and generally have a great morphological manifestation on nanoparticle structure [26]. The synthesized ZnO nanoparticles micrography in Fig. 3a are arranged in hexagonal shape without any agglomeration. The investigation of TEM images revealed that ZnO nanoparticles have an average size of 34–93 nm and this study is in good agreement with the literature based on the study conducted by [32].

Fourier-transform infrared spectroscopy (FTIR) analysis

Fourier-transform Infrared Spectroscopy spectra of zinc oxide nanoparticles were analyzed using (FTIR) Bruker Vertex 70 V Germany at a wavenumber range from 400 to 4000 cm^{-1} as depicted in Fig. 3b. Peaks between 3000 and 3600 cm^{-1} are associated with O–H functional groups while peak at 462 cm^{-1} could as a result of oxygen bonds vibration. The lowest peaks are observed between 3200 and 2000 cm^{-1} which could be hydroxyl (OH) groups meanwhile, the carboxylate group (C=O) which can be found around 1619 cm^{-1}, and a peak at 1150 indicates the presence of C-O of alcohol groups. The confirmation of all these peaks indicates the presence of ZnO nanoparticles.

Stability tests analysis

Sedimentation

The stability analysis of nanofluids suspension in the base fluid is one of the prerequisites and key parameters that need to be optimized before the application of nanofluids for enhanced oil recovery. Different nanofluids sets were prepared separately and two stabilizers were added into ZnO nanofluids their stability was examined using a visual test for seven days period as indicated in Fig. 4. ZnO, ZnO + PVP, and ZnO + PVA were all set in stable conditions and their color changes were observed while their photos were recorded each day for comparison purposes. All the nanofluids were well stirred and ultrasonicated to obtain a homogenous solution and after 24 h. there was no change in color which means that the nanofluids displayed good stability. On the third and fifth days of observation, ZnO nanofluid displayed color change whereas nanofluids containing PVA and PVP stabilizers were more stable and never changed any color. On the seventh day of observation, ZnO nanofluids agglomerated and settled faster than ZnO + PVA and ZnO + PVA meanwhile ZnO + PVA has the best stability compared to ZnO and ZnO + PVP nanofluids. However, the addition of stabilizers into nanofluids improved their stability by 10% in PVP and 23% in PVA stabilizers which revealed that stabilizers enhanced the stability of nanofluids based on UV–vis absorbance values in Fig. 5b. A study conducted by (Hassan, Guan, Chuan, Sikiru, et al. [19]) observed similar results in visual test observation.

UV–vis spectral analysis

The UV–Vis absorbance spectra measurement of ZnO nanofluids is important in the characterization of their optical behaviors besides that, their continuing stability in base fluids can also be repeatedly examined by UV–vis absorbance[28]. The dispersion characteristics of ZnO nanofluids were investigated using UV–vis absorbance at a different wavelength from 200 to 900 nm. Figure 5a illustrates the absorbance behavior of ZnO nanofluids and stabilizers at different wavelengths at various concentrations when polyvinyl alcohol (PVA) and

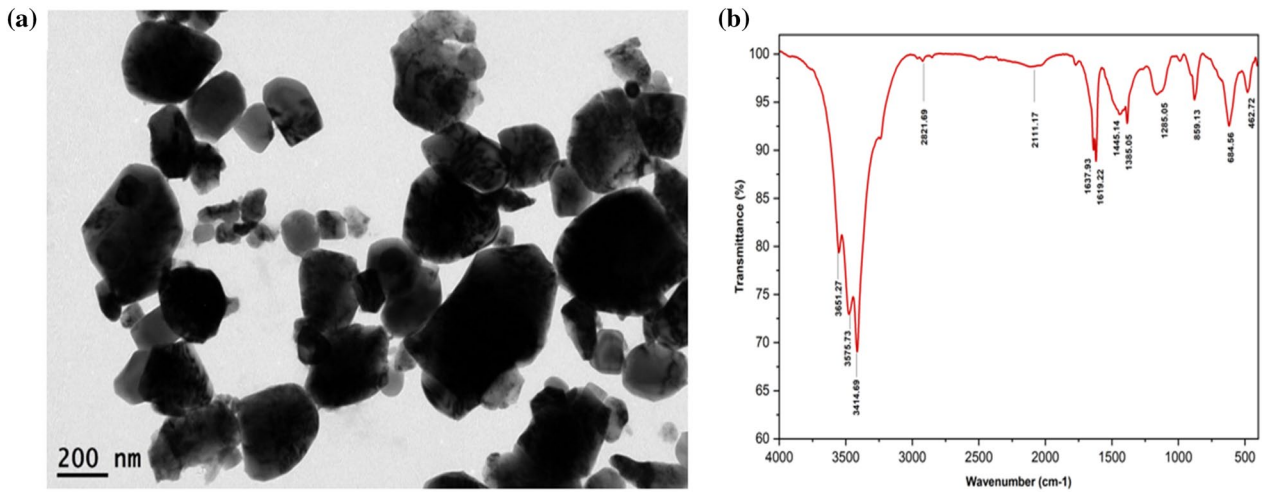

Fig. 3 TEM image of synthesized ZnO nanoparticles (**a**) FTIR spectra of ZnO nanoparticles (**b**)

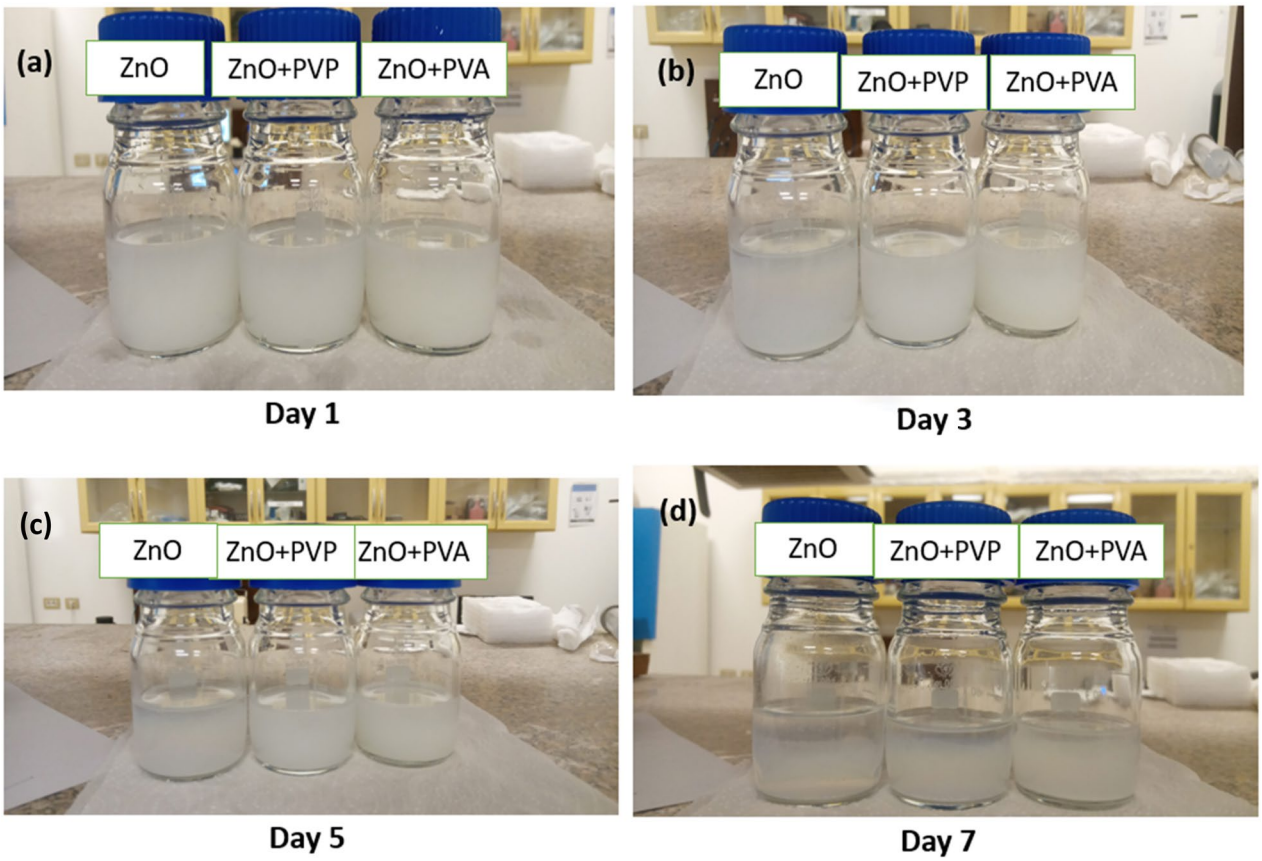

Fig. 4 Images from sedimentation test of nanofluids; freshly prepared (**a**), after three days (**b**), after five days (**c**), and after seven days (**d**)

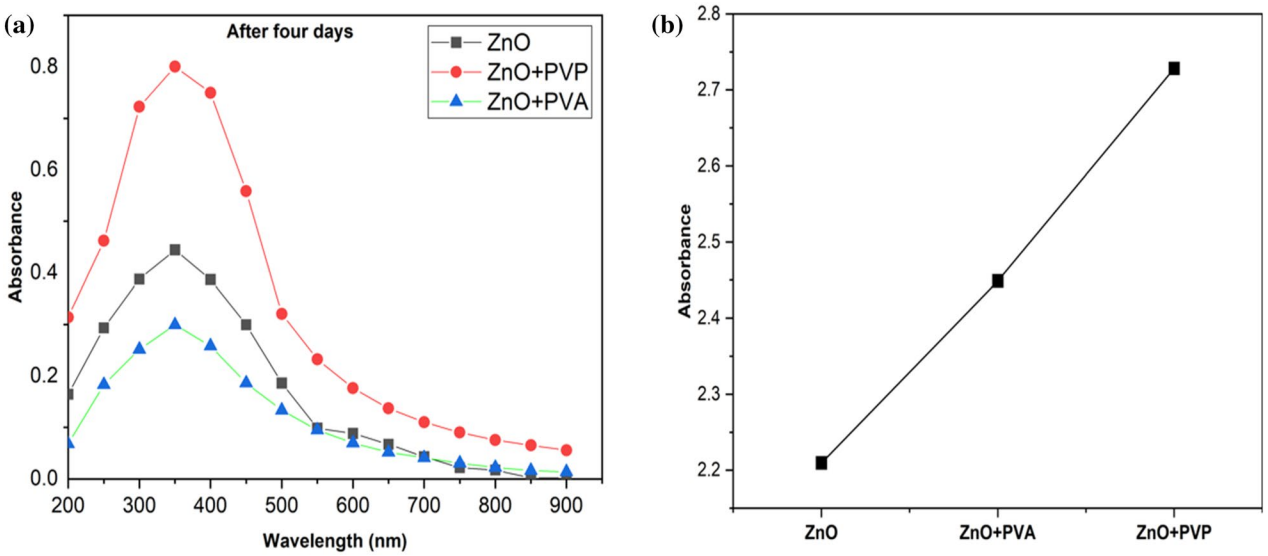

Fig. 5 Absorbance from UV–vis spectrophotometry test of ZnO nanofluids with stabilizing agents at a varying wavelength of 200–900 nm (**a**), Spectra absorbance of ZnO nanofluid with stabilizing agents at a fixed wavelength of 600 nm (**b**)

Polyvinylpyrrolidone (PVP) stabilizers were added. It has been observed that absorbance values increase with the increase in concentrations and decrease with increasing wavelength and this corresponds to Zeta potential values which is above − 43.7 (mV) showing good stability of ZnO nanofluids. However, these experimental results correspond to the study done by [30]. Furthermore, there is a redshift in the ZnO + PVA curve and this may happen due change in refractive index, particle size of PVA and aggregation of ZnO nanoparticles in base fluid or reduction on active sites on the surface of ZnO nanoparticles [38]. In Fig. 5b ZnO + PVP exhibits a higher optical peak because of their high molecular weight which affects nanofluids' optical density compared to ZnO and ZnO + PVA absorbance values.

Zeta potential analysis

Zeta potential is defined as the potential difference between colloids and the base fluids which is used as a dispersed phase [21]. The stability of ZnO nanoparticles in base fluids was also examined using Zeta Sizer Malvern nano series Germany to determine the dispersibility and suspension of ZnO nanoparticles as shown in Fig. 6. To measure the zeta potential of prepared nanofluids, a 0.2 g powder of ZnO nanoparticles was added carefully into 12 (ml) tube of deionized water and sonicated for 30 min to obtain a homogeneous mixture. The ZnO nanofluids sample was loaded in a zeta cell and measured at a room temperature of 25 °C with a dispersant dielectric constant of 78.5 at a viscosity of 0.8872 cp. The obtained zeta potential of − 43.7 (mV) indicates a better dispersibility of the colloidal in the base fluids. Zeta potential test was carried out to validate sedimentation and UV–vis spectrophotometer tests to understand the time taken by ZnO nanoparticles to agglomerate when suspended in base fluids. According to [30] zeta potential value determines the stability of colloidal in the base fluids. However, fluids with a low zeta potential value of ± 5 (mv) have coagulation and flocculation behaviors while nanofluids with ± 40 (mV) have good stability.

Nanofluid wettability alteration

One of the most prominent mechanisms in enhanced oil recovery is the wettability alteration of the reservoir rock formation since the main interest is to alter the formation from oil-wet to water-wet that imbibes the pores media to improve oil recovery [37]. The dynamic spreading behaviors of ZnO nanofluids have different wettability alteration characteristics compared to other convectional EOR fluids because of their ability to change the rock formation from an oil-wet to water-wet (Al-Asadi, Arce, et al. [2]). The contact angle for different fluids was carried out with DI water, ZnO nanofluids, ZnO + PVA, and ZnO + PVP stabilizers on the PDMS surface as depicted in Fig. 7a. Due to the hydrophobic nature of the PDMS, the surface was first immersed in nanofluids for 24 h and then placed in an oven at 70 °C to make it water-wet before the contact angle experiment began. To carry out the contact angle first, droplets were placed on the PDMS surface and images were captured instantly for all the fluids. The corresponding contact angle for DI water, ZnO nanofluids, ZnO + PVA, and ZnO + PVP were 96, 74, 67, and 62° respectively. It was observed that DI water has a higher contact angle compared to nanofluids and this

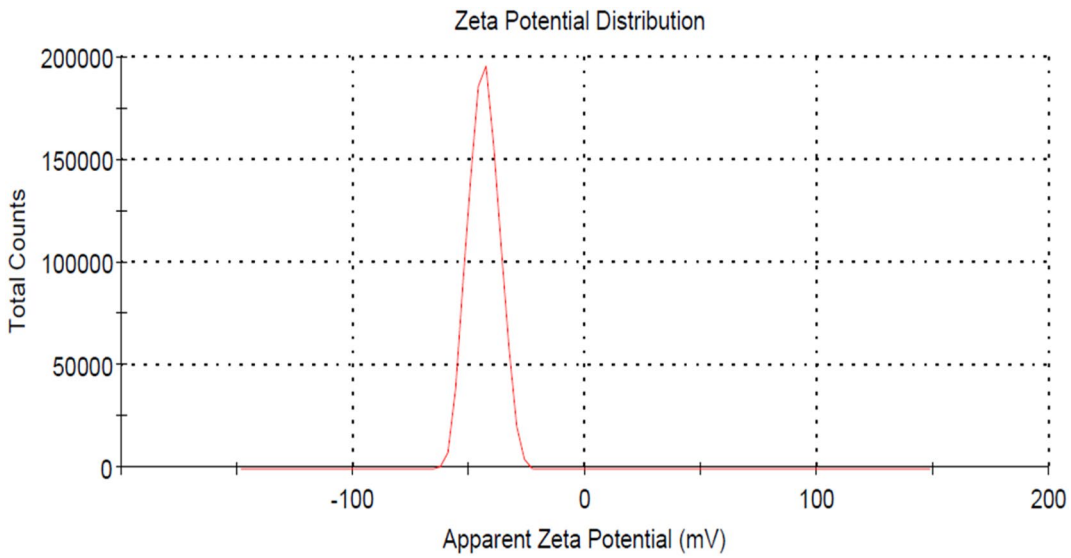

Fig. 6 Zeta potential value of ZnO nanofluids

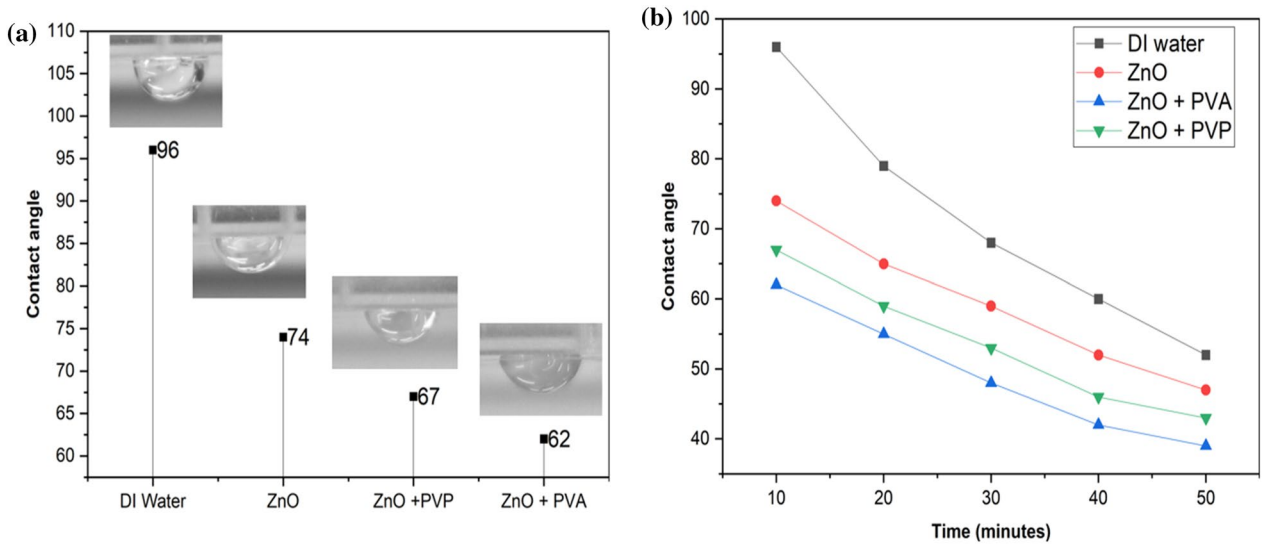

Fig. 7 Dynamic contact angle of ZnO nanofluids on PDMS surface (**a**), variation of contact angle ZnO nanofluids with time on PDMS surface (**b**)

is because PDMS is hydrophobic and hardly changes in pure water. However, the contact angle decreased by 30% when the PVP stabilizer was added to ZnO nanofluids and further decreased by 35% for the PVA stabilizer as well. It was well noted that the addition of PVA and PVP stabilizers into nanofluids decrease the contact angle at PDMS surface than pure nanofluids which changed the PDMS surface to water-wet indicating the capability of nanofluids in altering the reservoir formation wettability. In addition, the contact angle of DI water, ZnO nanofluids, ZnO + PVA, and ZnO + PVP was also carried out at different time intervals as indicated in Fig. 7b and it was observed that the contact angle decreased with increasing time on PDMS surface. PVA nanofluids are easily spread on the surface of PDMS compared to PVP and ZnO nanofluids while DI water has less spreading behavior on PDMS surface over time. In this study, both ZnO nanofluids and stabilizers play crucial roles in the wettability alteration of PDMS surface towards water-wet. However, based on a study conducted by [40] indicated that the wettability alteration on PDMS surface is considered on a macro-scale level whereas, direct proof for wettability alteration of PDMS on a micro-scale is lacking.

Interfacial tension analysis

Interfacial tension (IFT) is a critical factor that needs to be investigated before carrying out nanofluid applications for enhanced oil recovery since it affects different reservoir mechanisms in a porous formation (Ali, Kolo, Khaksar Manshad, et al. [5]). The main aim of the IFT test in this study was to determine the roles played by ZnO nanofluids and PVA and PVP stabilizers on interfacial tension reduction. However, four different concentrations were selected for IFT that was crude oil, ZnO nanofluids with crude, ZnO + PVP with crude oil, and ZnO + PVA with crude oil. From Fig. 8, it was noted that the IFT reduced as nanofluids were introduced. When ZnO nanofluids were introduced the IFT reduced from 63.2 to 26.1 mN/m. Table 2 shows the effect of nanoparticles concentrations in the base fluid where the density of base fluids increases when nanoparticles concentration while reducing the IFT. Further decrease in IFT was also observed when nanofluid containing PVP and PVA stabilizing agents were introduced then the IFT decreased by 59 and 61% respectively. The highest reduction in IFT was achieved by introducing the stabilizing agents into ZnO nanofluids which corresponds to a study conducted by [4, 5]. On the other hand, nanofluids containing PVA and PVP stabilizing agents drastically reduced the IFT because both stabilizing agents and ZnO nanoparticles support each other, and this makes nanoparticles gain better stability in base fluids. Nanoparticles play a critical role in forming a thin layer called nano-film which is distributed equally between injected fluids and oil and this increases the capillary number resulting in interfacial tension reduction of formation fluids (Cheraghian, Rostami, and Afrand [9]). Nano-film is created when nanoparticles coalescence on the formation surface where oil is trapped and this increases the mobility and entropy of nanoparticles in suspension resulting in the reduction of IFT, increase in disjoining pressure, and creation of pressure profile in the reservoir [25].

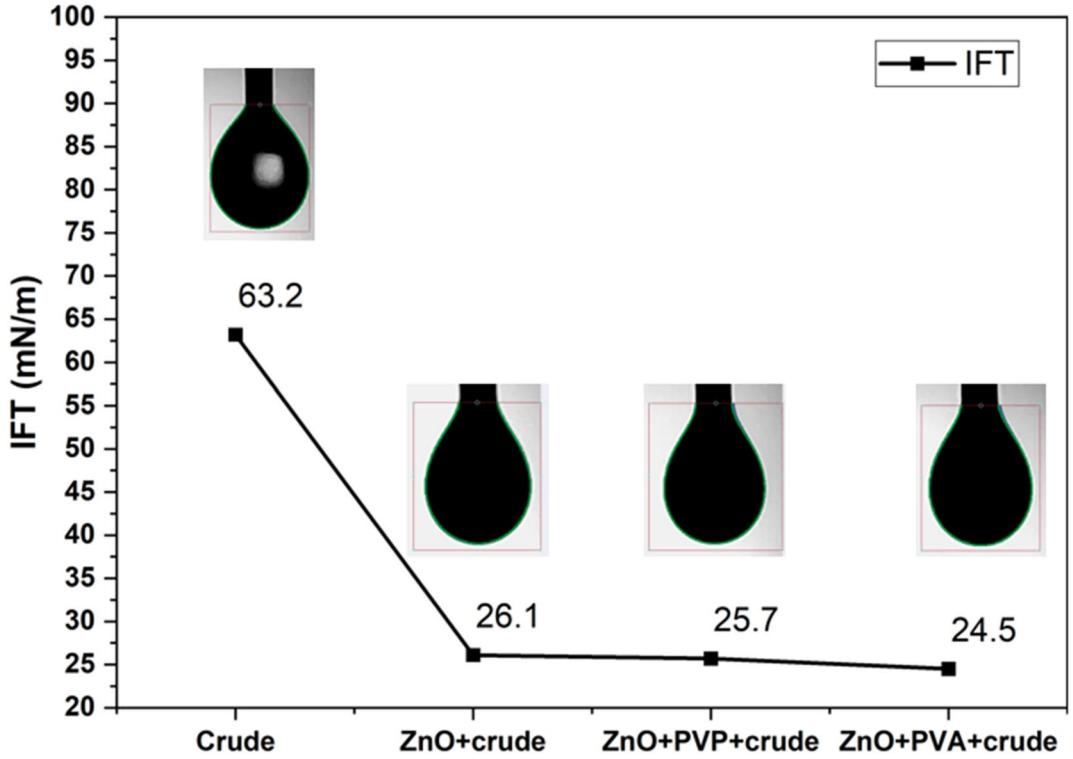

Fig. 8 IFT values of ZnO nanofluids with stabilizing agents obtained from the pendant drop test

Nanofluids flooding in microchannel matrix

To examine the effectiveness of ZnO nanofluids on enhanced oil recovery, different fluids were injected into the microchannel matrix at varying flow rates. Various concentrations of ZnO nanofluids, ZnO + PVA, and ZnO + PVP were injected into the microchannel, and their recovery factors were recorded as shown in Fig. 9a. Microchannel matrix was injected with crude oil until it was fully saturated and ZnO nanofluids were injected to displace the saturated oil until a breakthrough was made. It was observed that ZnO + PVA nanofluids has a higher recovery of 82% followed while ZnO + PVP recorded the second higher recovery factor of 78% and ZnO nanofluids therefore, recorded the lowest recovery factor of 73% respectively. It was worth noting that, at higher injection volume (PV) the recovery factor is almost the same between 70 and 100 (PV). Similarly, a higher recovery rate can also be associated with a higher capillary number which is induced by viscous forces in a higher flow rate. This phenomenon is associated with the adsorption behavior of nanofluids and stabilizers used since nanofluids require a certain amount of time to allow physiochemical interaction between the fluids and reservoir formation [1]. The contact angle spreading behavior over time has confirmed that nanofluids on PDMS surfaces need a certain period to be adsorbed to alter the physiochemical properties of the reservoir fluids. Nanofluids need a longer aging time to alter the physiochemical properties of the reservoir fluids and the PVA and PVP stabilizers may display different chemical properties which need to be investigated. A study conducted by [7] suggested that PDMS wettability alteration depends on the nature of the substrate and stabilizers used in nanofluids. However, any changes that alter the reservoir fluids are mainly determined by the wettability nature of the PDMS surface and the orientation of the stabilizers.

Table 2 ZnO nanofluids and crude oil properties

Concentrations	Density	Interfacial tension
Crude oil	0.7802 g/cm^3	63.2 mN/m
ZnO with crude	0.9981 g/cm^3	26.1 mN/m
ZnO + PVP with crude	0.9985 g/cm^3	25.7 mN/m
ZnO + PVA with crude	1.0010 g/cm^3	24.5 mN/m

Sweep efficiency and visualization

Reservoir sweep efficiency was determined by injecting various fluids into PDMS microchannels as pore saturation was visualized during the flooding process. It was observed when ZnO nanofluids were used, almost 45% of saturated oil remained unrecovered in the pore media. To

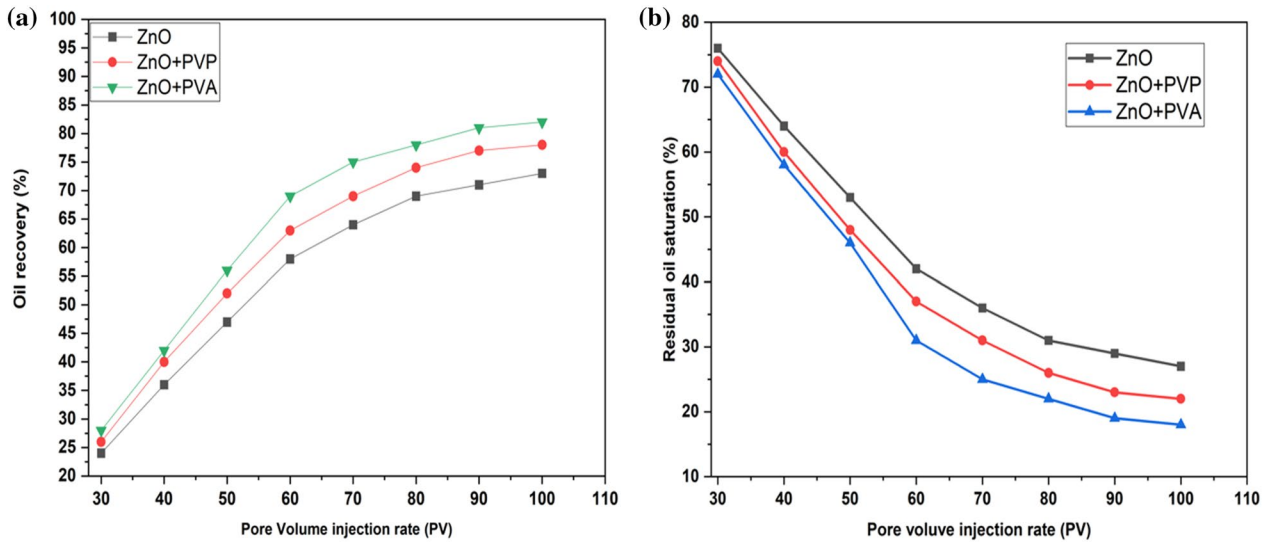

Fig. 9 Oil recovery factors of various nanofluid concentrations as a function of time at different flow rates (**a**), residual oil saturation after porous media after flooding in PDMS microchannel matrix (**b**)

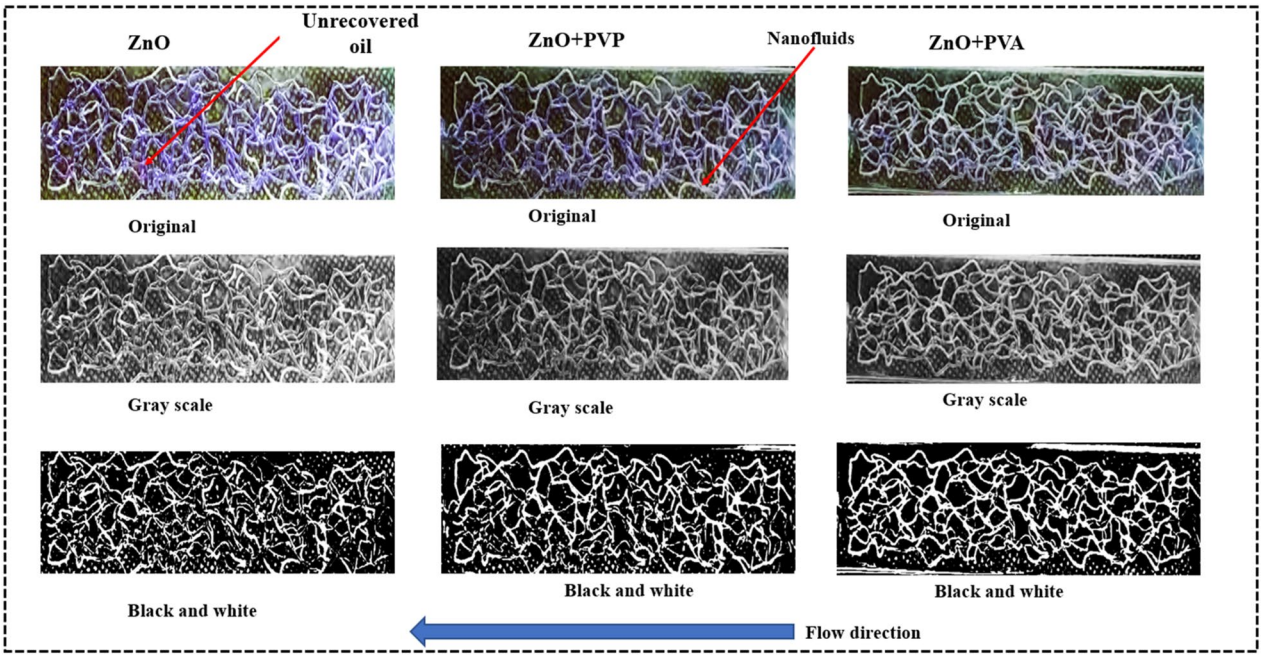

Fig. 10 Images from flow visualization of PDMS microchannel matrix at different nanofluid concentrations

compare the sweep efficiency, nanofluids with PVP and PVA stabilizing agents were injected into the microchannel matrix and Fig. 10 depicts that most oil adhered to the pore throats was able to be recovered. Since PDMS has an oil-wet tendency, it is complicated to mobilize the trapped oil in the pores medium. Therefore, the introduction of nanofluids into the reservoir effectively increased the recovery rate because PDMS wettability was altered to oil-wet conditions. The complexity of the recovery process of trapped oil ganglia is due to the complicated porous media structure and the behavior of trapped oil [39]. Another factor that should be considered is microchannel pore plugging due to the adsorption of nanofluids on the PDMS surface, the physical filtration of larger nanoparticles, and the stability of nanoparticles in harsh conditions [10]. The trapped oil is indicated in dark blue

color areas in Fig. 10 and the nanofluid areas are white spots therefore, the sweep efficiency was estimated from the total volume occupied by the nanofluids to the total volume of microchannel. Based on the visualization of porous media, nanofluids with stabilizing agents displayed a better sweep efficiency than ZnO nanofluids.

Conclusion

Zinc oxide (ZnO) nanoparticles were synthesized using the sol–gel method and were characterized using various characterization techniques such as XRD, TEM, FTIR, and Zeta potential analyzer. The stability of nanoparticles in the base fluid was enhanced by the addition of polymers such as Polyvinylpyrrolidone (PVP) and Polyvinyl alcohol (PVA) as stabilizing agents. Based on sedimentation and UV–vis spectrophotometry tests, nanoparticles remained stable in suspension for seven days indicating better stability in base fluids. The results of the IFT pendant test revealed that PVA and PVP nanofluids significantly reduced the IFT by 59 and 61% compared to ZnO nanofluids without stabilizing agents. It was also noted that the alteration of formation wettability increases mobility and entropy of nanoparticles in suspension resulting in a reduction of IFT, increase in disjoining pressure, and creation of pressure profile in the reservoir. Microchannel matrix flooding experiment results showed that ZnO nanofluids were able to enhance oil by 73% and this slightly increased when PVP and PVA stabilizing agents were added which increased the recovery by 78 and 82%. Future work will focus mainly on the effect of flow rate, differential pressure, and the effect of temperature and salinity on nanofluids in porous formation.

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Declarations

Competing interests

There is no competing of interest, financial or non-financial interests that are directly or indirectly related to the work submitted for publication.

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