

Original Paper

Green-synthesized zinc quantum dots from parsley leaves for enhanced oil recovery: Improving IFT, wettability, and oil recovery performance



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ABSTRACT

Nanotechnology has attracted significant attention in recent decades due to its diverse applications, particularly in chemical enhanced oil recovery (cEOR). By reducing fluid–fluid interfacial tension (IFT) and oil–rock contact angle (CA), nanomaterials offer a promising approach to improving oil recovery. This study explores the application of green-synthesized zinc quantum dots (Zn-QDs)—with an average size of approximately 10 nm and derived from parsley leaves—for EOR applications. The synthesized Zn-QDs were characterized using Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). Nanofluids were prepared by dispersing Zn-QDs in formation water and distilled water at concentrations ranging from 100 to 500 ppm. The stability and quality of the nanofluids were assessed by measuring key properties such as pH, density, and conductivity.

Experimental evaluations, including IFT, CA, emulsion stability, and oil recovery tests, confirmed the effectiveness of these nanofluids. FW1-1-300 nanofluid, prepared by dispersing 300 ppm of nanodots in formation water, reduced the IFT significantly from 28.51 to 8.06 mN/m. Meanwhile, FW1:5-300 and FW1:15-400 were the most effective nanofluids for altering carbonate and sandstone wettability towards a strongly water-wet state, achieving CA values of 29.5° and 36°, respectively. Stability analysis indicated that lower concentrations of Zn-QDs provided better dispersion stability. In contrast, higher concentrations resulted in a significant reduction in droplet size, leading to the formation of a stable emulsion of crude oil and the injection solution. Ultimately, the green-synthesized nanodots enhanced the ultimate oil recovery by 22.28% of the original oil in place (OOIP) for carbonate rocks and 18.03% OOIP for sandstone rocks. These recovery rates represent a substantial improvement over the baseline water flooding recovery factors of 49.24% and 49.18% for carbonate and sandstone formations, respectively.

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1. Introduction

Conventional oil recovery methods typically extract only about one-third of the total oil present in reservoirs (Alhammad et al., 2022). To recover the trapped oil effectively, enhanced oil recovery (EOR) techniques are required (Mandal, 2015). In recent years,

microemulsion flooding with nanoparticles has gained significant attention as an alternative to polymer, alkaline, and surfactant flooding (Ehtesabi et al., 2014). This method is increasingly preferred due to its cost-effectiveness, environmental friendliness, and improved efficiency (Abdulhadi et al., 2025). EOR techniques enhance oil recovery by modifying key factors such as interfacial tension (IFT), rock surface wettability, viscosity, and emulsion formation. However, in low-permeability reservoirs, polymer flooding can pose challenges due to the high molecular weight of polymers (typically 10–25 million Daltons) (Mariyate and Bera, 2021). Similarly, surfactants used in reservoir flooding can degrade through hydrolysis, particularly in high-salinity and high-

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temperature conditions, reducing their effectiveness (Wu et al., 2012).

Nanoparticles (NPs) offer a promising solution due to their small size, which allows them to navigate through the pore spaces in reservoirs with ease (Tabary et al., 2013). Recent studies have demonstrated the potential of nanoparticles such as silicon oxide (SiO_2), titanium oxide (TiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3 , Fe_3O_4), and zinc oxide (ZnO) in reducing IFT. This reduction is primarily attributed to the strong adsorption of nanoparticles at the water–oil interface, enhancing their effectiveness as IFT-reducing agents (Mahmood et al., 2025; Garmroudi et al., 2022). Additionally, nanoparticles enhance oil recovery by modifying wettability. They achieve this by reducing the contact angle between oil and rock surfaces, thereby shifting rock surfaces from oil-wet to water-wet (Bera and Belhaj, 2016; Giraldo et al., 2013). Despite their advantages, previous studies have identified a key limitation of nanoparticle-based EOR: the relatively large particle size (~ 100 nm) often restricts their ability to penetrate tight formations containing nanopores (< 10 nm) and mesopores (~ 25 nm) (Al-Anssari et al., 2016; Mariyate and Bera, 2023). This limitation has significantly hindered their application in unconventional reservoirs (Nwidae et al., 2017). To overcome this challenge, there is an urgent need to develop smaller nanoparticles capable of penetrating these minute pores effectively. Quantum dots (QDs) have demonstrated remarkable potential in various fields, including single-electron transistors (Alharthy et al., 2013), LEDs (Ihn et al., 2010), lasers (Demir et al., 2011), solar cells (Chen et al., 2016), quantum computing (Sargent, 2012), and medical imaging (Veldhorst et al., 2014). However, despite their advantageous properties, studies investigating the application of QDs in EOR remain scarce (Liu et al., 2011).

Enhancing the performance of nanofluid in challenging reservoir condition has been a growing focus of recent research. For instance, even high-salinity brines including multivalent ions (Ca^{2+} , Mg^{2+} , SO_4^{2-}), Modified SiO_2 and Al_2O_3 nanoparticles have demonstrated improved colloidal stability and wettability modification (Kandiel et al., 2025; Zhang et al., 2023). Gholamzadeh et al. (2025) investigated nitrogen-doped carbon quantum dots (CQDs) as effective nanofluid for interfacial tension (IFT) reduction in enhanced oil recovery under varying salinity condition. The results demonstrated that the type of nitrogen dopant and salt ion strongly influence both the stability and interfacial activity of CQDs, with Mg^{2+} and Ca^{2+} ions showing the most significant IFT reduction when CQDs remained stable. The finding highlights that CQDs are promising candidate for EOR application in saline and high-ion reservoirs. Strong synergistic effects have been observed in hybrid nanofluid systems that combine nanoparticle and surfactant. In this system, nanoparticles maintain surfactant films and lower adsorption losses which increase IFT reduction and modify wettability toward water wet condition (Ramadhani et al., 2025). By modifying ionic strength and boosting electrostatic interaction at the rock–fluid interface, low-salinity water mixed with nanoparticles has also been demonstrated to enhanced oil recovery (Ahmadi et al., 2023). These advancements have highlighted the significance of brine composition, zeta potential, and particle surface chemistry in controlling EOR efficiency at high temperatures and salinities.

Despite these developments, most of the research has been on traditional nanoparticles (SiO_2 , Al_2O_3 , Fe_2O_4) that are usually larger than 50–100 nm. Even still, their higher particle size prevents them from penetrating tight or nonporous formation (Zhao M. et al., 2023). Because of their high surface-to-volume ratio, tunable surface chemistry, and ultrasmall size (< 10 nm), quantum dots (QDs) constitute a new class of nanomaterials that may be able to address these difficulties (Sreejith et al., 2024; Yan et al.,

2024). Several studies have explored the potential of nanofluids for oil recovery. Rezvani et al. (2018) investigated an EOR nanofluid formulated with polymer-coated Fe_3O_4 @Chitosan nanocomposites (NCs) in seawater. Their findings indicated that this nanofluid reduced IFT and altered wettability, leading to a 10.8% increase in oil recovery (OOIP). Luo et al. (2016) conducted core flooding experiments using a nanofluid based on amphiphilic graphene nanosheets. These nanosheets spontaneously adhered to the oil–water interface, forming elastic interfacial films and climbing films, which contributed to improved oil recovery. In their study, Izadi and Nasernejad (2022) compared alumina quantum dot-based nanofluid (AQDs, ~ 4 nm) and conventional alumina nanoparticle-based nanofluid (ANPs, ~ 20 nm) to evaluate their stability and oil recovery performance in carbonate reservoirs. The results indicated that both nanofluids effectively altered rock wettability toward a more water-wet state, with AQDs showing superior stability and higher oil recovery efficiency (up to 38% of OOIP). Moreover, AQDs caused minimal permeability impairment (2%–4%) compared to ANPs ($\sim 10\%$), indicating their potential as more efficient and formation-friendly agents for enhanced oil recovery. Mirzavandi et al. (2023) examined the impact of silica-graphene quantum dots (Si-GQDs) on oil recovery using distilled water and seawater as dispersing media. Their results showed that a 1000 ppm Si-GQD solution reduced IFT from 28.3 to 9.5 mN/m and shifted rock wettability from oil-wet to water-wet (contact angle decreased from 134° to 61°), leading to a 14.4% increase in oil recovery. In another study, researchers evaluated the application of silica quantum dots (Si-QDs) for EOR in the Bakken Formation, a tight oil reservoir. They reported that using 0.12 wt% of Si-QDs resulted in an 89.76% reduction in IFT and a shift in wettability toward water-wet conditions. Consequently, the nanofluid improved oil recovery by 25.72%, outperforming conventional surfactant flooding by 7.49% (Zhou et al., 2020). Additionally, Afzalitabar et al. (2020) synthesized a hybrid nanofluid (N-GQDs/ MoS_2) that significantly altered carbonate rock wettability to water-wet, increasing oil recovery by 22% even at very low concentrations (0.01 wt%).

The primary objective of this research is to evaluate the impact of green-synthesized zinc quantum dots (Zn-QDs) on oil recovery enhancement. The authenticity and effectiveness of the synthesized QDs were validated using multiple analytical techniques. A comprehensive series of experimental assessments, including IFT reduction, contact angle measurements, emulsion stability analysis, nanofluid stability testing, and core flooding experiments, was conducted to determine the influence of Zn-QDs on oil recovery in carbonate and sandstone formations.

2. Materials and methods

2.1. Materials

Fresh parsley leaves were purchased from a local market in Soran, Erbil, located in northern Iraq. High-purity zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (analytical grade, 99%) and all other reagent-grade chemicals (99% purity) were sourced from Merck Chemical Company. The synthesis of zinc quantum dots (Zn-QDs) was conducted using thoroughly cleaned and oven-dried glassware to ensure purity and consistency. Crude oil and formation water samples were collected from a Kurdish oilfield. The crude oil composition and specifications are illustrated in Fig. 1(a, b), with a specific gravity of 0.849 g/cm^3 and a viscosity of 2.16 cP at ambient temperature. Methane (C_1) and ethane (C_2) are the main components of the crude oil with the molecular weight of 35.69 and 16.79 mol%, respectively. Meanwhile, in the crude oil

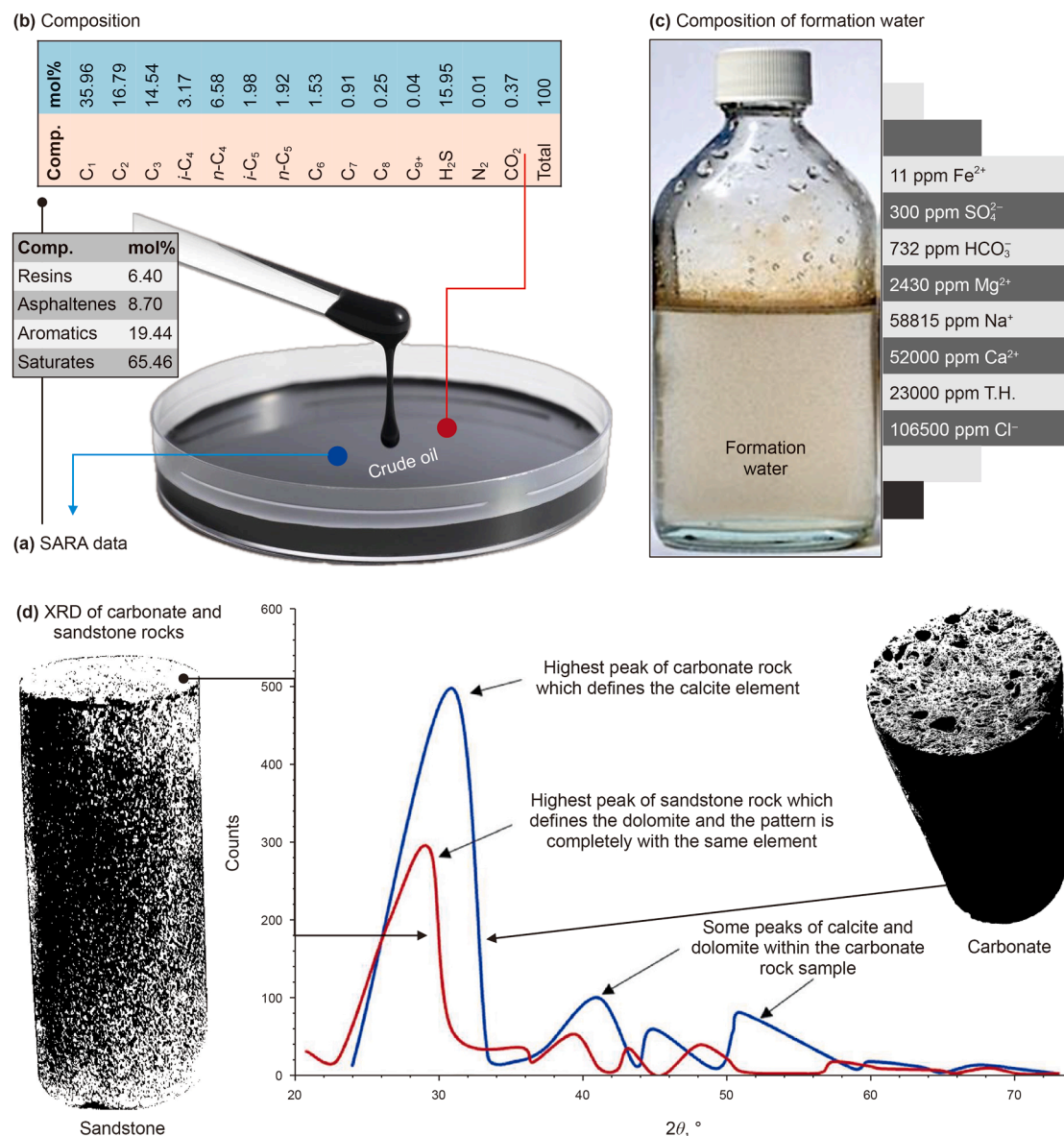


Fig. 1. Composition of the crude oil, formation water, and rock samples: (a) SARA data of crude oil, (b) components of crude oil, (c) composition of formation water, and (d) XRD patterns of carbonate and sandstone rocks.

used, saturates are the predominant fraction in SARA (saturates, aromatics, resins and asphaltenes) analysis (see Fig. 1(a)).

The ion composition of the formation water (FW), predominantly consisting of sodium and chloride ions, is presented in Fig. 1(c). As can be seen, the concentrations of calcium, chloride, and sodium are high, at 52,000, 106,500, and 58,815 ppm, respectively. In addition, sandstone and carbonate rock samples used for contact angle (CA) and core flooding experiments were obtained from outcrops in northern Iraq. Fig. 1(d) displays the X-ray diffraction (XRD) patterns of both rock samples, revealing that the sandstone consists of 40% quartz, 35% calcite, and 25% dolomite, while the carbonate rock is primarily composed of calcite.

2.2. Synthesis of bio-zinc-QDs

Fig. 2 illustrates the procedure used for preparing green zinc nanodots, including the experimental steps, laboratory conditions, molecular structure, and characterization devices. As shown, the

procedure is divided into four main phases: preparation of the plant extract, reduction and stabilization of ions, characterization of the product, and molecular structure analysis.

First, fresh parsley leaves were thoroughly rinsed multiple times with the distilled water to remove any contaminants, followed by grinding. To prepare the extract, 20 g of the ground leaves were mixed with 100 mL of distilled water, heated to 70 °C on a hot plate, and continuously stirred for 2 h. The extract was then cooled to room temperature (25 °C) and filtered through an 11 µm filter paper. The synthesis process began with the preparation of 1 mmol/L zinc precursor solution by dissolving zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in 5 mL of distilled water. This precursor served as the ion source to react with the phytochemicals in the parsley extract. The zinc precursor solution was gradually heated to 40 °C, and 5 mL of the filtered parsley extract was slowly added under continuous stirring. To create a stable medium for the formation of zinc nanodots, the pH of the solution was adjusted to 7 by adding NaOH as an alkali agent (Singh et al., 2018;

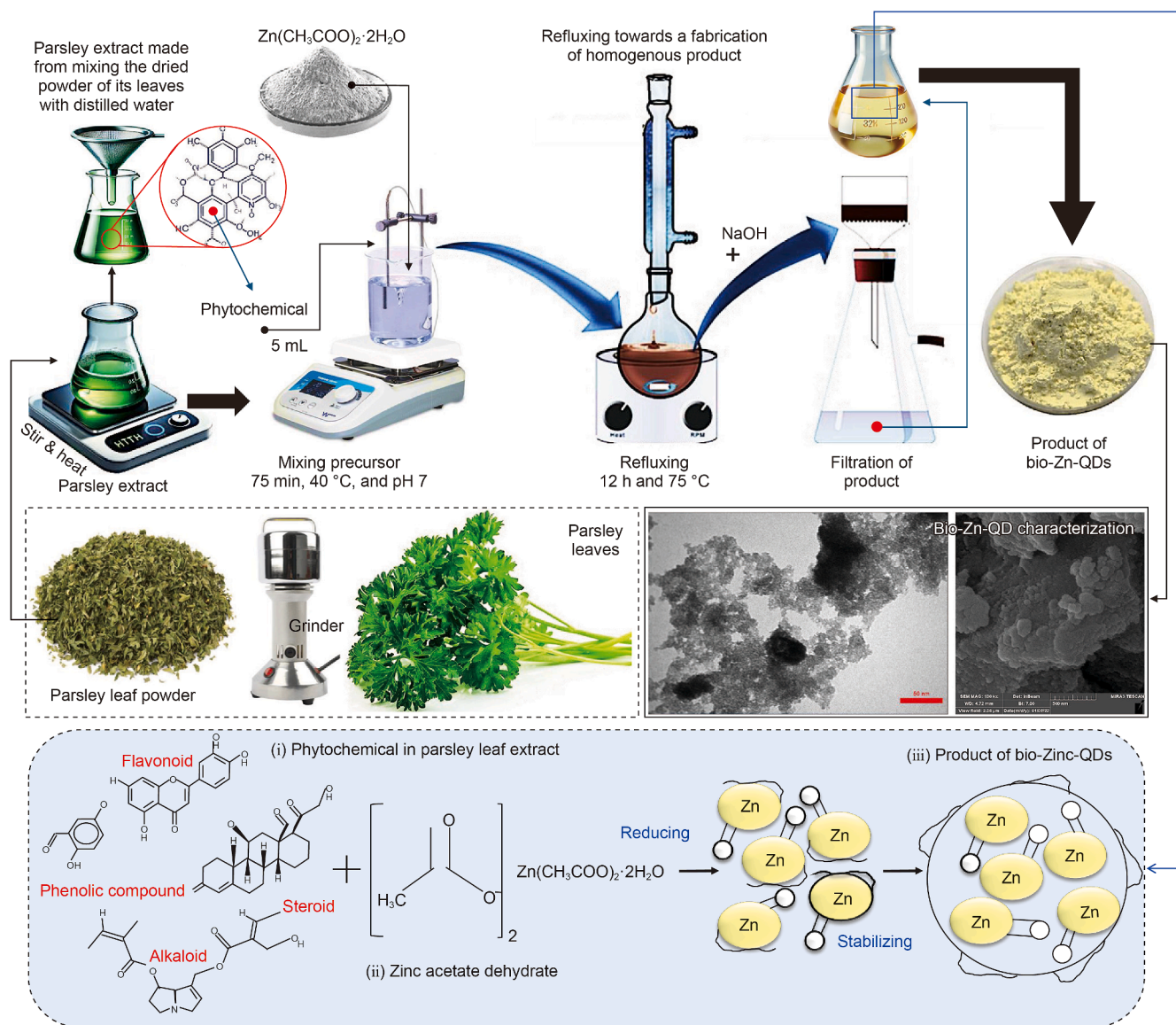


Fig. 2. Schematic illustration of the procedural steps of green synthesis of zinc QDs as nanodots along with the molecular reaction and structure, experimental steps, and laboratory conditions.

Lee et al., 2016). The reaction mixture was stirred for 75 min to promote the formation of the nanodots. Successful synthesis was visually indicated by a color change from dark brown to yellow after continuous stirring. The mixture was then placed in an oven at 50 °C until it completely dried and the liquid phase had evaporated. The final product of bio-Zn-QDs, remained as a fine white-to-yellow powder, ready for characterization.

2.3. Formulation of nano-EOR solutions (nanofluids)

Nanofluids derived from zinc nanodots were prepared by dispersing the synthesized Zn-QDs in the distilled water and formation water at concentrations of 100, 200, 300, 400, and 500 ppm as shown in Fig. 3(c). The experiments began with the preparation of nanofluids in distilled water, using pure distilled water as the baseline. Stable nanofluids were then prepared by introducing Zn-QDs at the specified concentrations, yielding solutions labeled DW100 to DW500 as detailed in Table 1. The formulation strategy begun with low concentrations, based on evidence that smaller nanoparticles exhibit enhanced surface activity and interfacial

effectiveness in enhanced oil (Chakraborty and Panigrahi, 2020; Hama et al., 2023). An initial concentration of 100 ppm was selected, consistent with the literature suggesting that nanoscale particles can achieve significant EOR effects even at low dosages due to their high surface area-to-volume ratio. In this study, the average nanoparticle size ranged from 3 to 8 nm, which is considered relatively small. Previous studies have also demonstrated that the optimal quantum dot concentration is typically below 500 ppm (Magham et al., 2023). In Table 1, light blue cells represent distilled water (DW) and the dark blue cells represent formation water (FW) as aqueous phases. Each square symbol corresponds to 100 ppm concentration of Zn-QDs. All concentrations were tested for density, pH, conductivity, IFT, contact angle (CA), and solution stability, whereas core flooding test and relative permeability measurement were conducted only for the optimal nanofluid concentrations, such as DW 300 ppm, FW1:15, 500 ppm, and FW1:5 400 ppm.

To evaluate the performance of the synthesized nanodots in a saline medium, formation water was used (see Fig. 1(c)). The effect of water salinity was examined by diluting the formation water

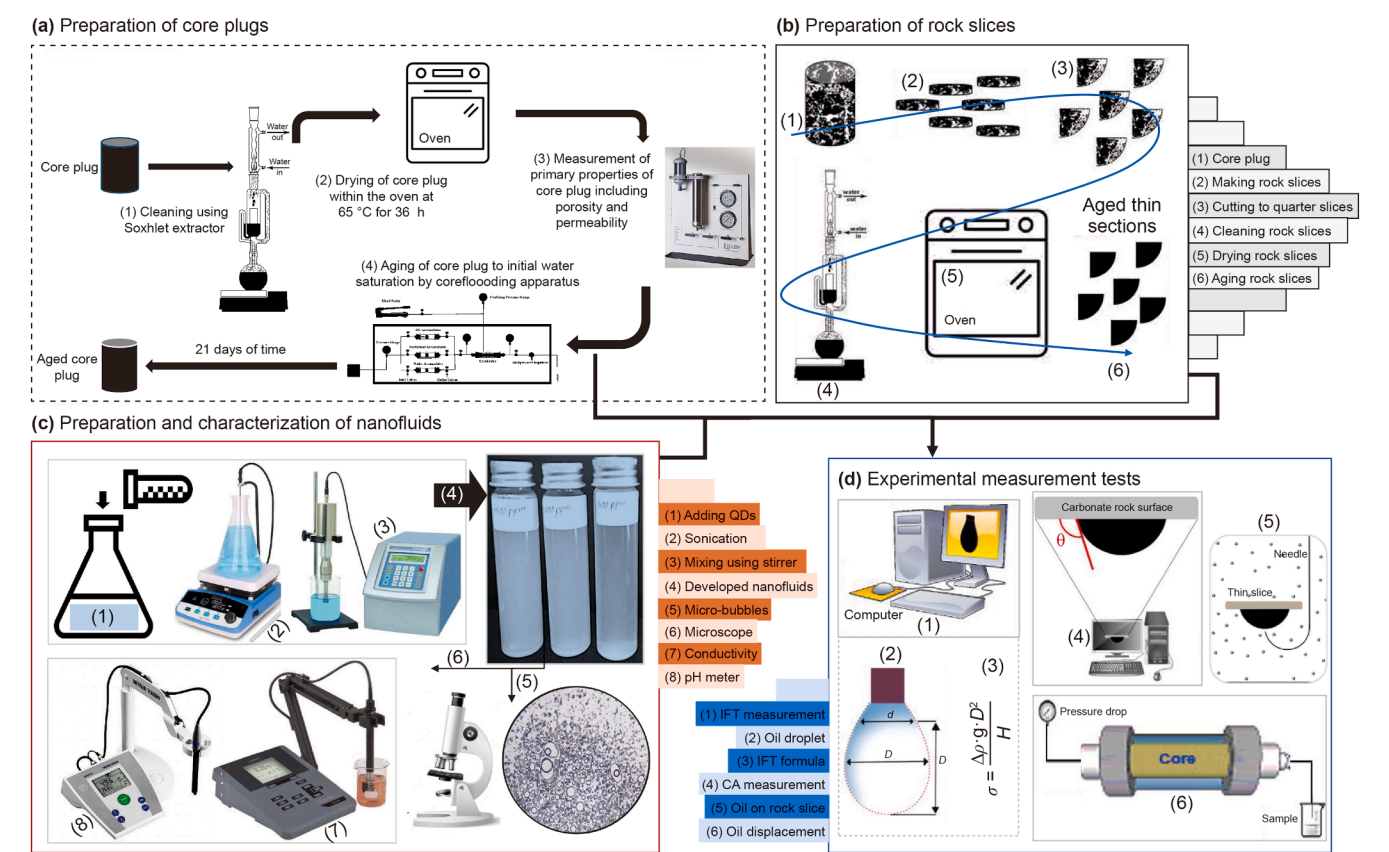


Fig. 3. Schematic demonstration of the experimental workflow: from the nanofluid fomulation to performance testing. (a) Core plug preparation, (b) rock slices (thin sections) preparation, (c) nanofluid preparation and characterization (modified from Modena et al., 2019), and (d) experimental meausremnts of IFT, CA, and oil displacement.

Table 1
Formulated nano-EOR solutions (nanofluids) and laboratory testing. Light blue = distilled water (DW); dark blue = formation water (FW). Each square symbol = 100 ppm.

Water type	Nanodot concentration, ppm					Experimental testing								
	100	200	300	400	500	pH	Conductivity	Density	IFT	CA	Flooding	Emulsion	Stability	Relative permeability
DW	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒							☒☒☒	☒☒☒	
FW	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒									
FW1:20	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒									
FW1:15	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒							☒☒☒☒☒	☒☒☒☒☒	
FW1:10	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒									
FW1:5	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒							☒☒☒☒	☒☒☒☒	
FW1:1	☒	☒☒	☒☒☒	☒☒☒☒	☒☒☒☒☒									

with distilled water. Various dilution ratios ranging from 1:20 (formation water to distilled water) to 1:1, were prepared, resulting in the following salinity levels: 86,500, 34,600, 17,300, 11,533, and 8650 ppm for the FW1:1, FW1:5, FW1:10, FW1:15, and FW1:20 (FW1-20 in Section 2.6) solutions, respectively (see Table 1). In addition to the composition of the formation water (FW) presented in Fig. 1(c), the ionic composition of the diluted formation water is summarized in Table 2. These concentrations are significant as they can influence the adsorption of nanodots and the efficiency of the EOR process. The variation in sulfates,

calcium, and magnesium concentrations among the diluted solutions are expected to affect the adsorption behavior of the nanodots and the resulting wettability alteration of the rock surface. Subsequently, nanofluids were formulated for each diluted formation water variant, with Zn-QDs incorporated at concentrations ranging from 100 to 500 ppm. Several factors, including solution salinity, conductivity, synthesis method, and nanofluid preparation technique, can affect nanofluid stability (Ali, 2023). To ensure high stability of the prepared nanofluids, the solutions were stirred at 600 rpm for 6 h at temperatures below 30 °C using a

Table 2
Ionic composition of diluted formation water for nanofluid preparation.

Ion	Concentration at different dilution rate [FW:DW], ppm				
	FW1:1	FW1:5	FW1:10	FW1:15	FW1:20
Na ⁺	29,425	9810	5362	3670	2815
Ca ²⁺	2630	894	475	316	252
Mg ²⁺	1218	402	223	153	116
Fe ²⁺	5	1.9	1.1	0.7	0.5
Cl [−]	54,132	17,813	9705	6670	5082
SO ₄ ^{2−}	152	49.5	28	19	14.3
HCO ₃ [−]	370	121	67.2	45.5	35
Total hardness (T.H.)	11,495	3832	2090	1437	1941

GUARDIAN TM5000 hotplate stirrer. Afterward, they were sonicated for 2 h with a LABFREEZ UH-92-IIN ultrasonic homogenizer (see Fig. 3(c)). The density, conductivity, and pH of the solutions were measured at ambient temperature and pressure using a PT-D1298-1884 density meter, a BC3020 conductivity meter, and an EUTECH-pH700 pH meter, respectively. Finally, the interfacial tension (IFT), contact angle, emulsion behavior, and stability of each nanofluid solution were evaluated.

2.4. Liquid/liquid/rock interaction evaluation

For oil recovery, the interaction between two aqueous phases is very important; this interaction is described by interfacial tension (IFT). IFT regulates the flow and movement of fluids in porous media. This study applied the commonly used pendant drop method, which involves examining the shape of a suspended oil droplet using high-resolution cameras and computer software. The experimental setup for measuring IFT between crude oil droplets and different liquids, including distilled water, brine, and nanofluids containing synthesized Zn-QDs is shown in Fig. 3(d). In this method, a droplet of crude oil (approximately 4–6 μ L) was formed at the tip of a stainless-steel needle using a motor driven syringe and suspended in the aqueous phase inside quartz cuvette. The tests were conducted at ambient temperature (25 ± 1 °C) and atmospheric pressure. A digital goniometer (model VIT-600) equipped with high resolution camera was used to capture the droplet profile. Each measurement was recorded for 600 s to ensure equilibrium condition, and the IFT value was automatically calculated by fitting the drop shape to the Young–Laplace equation using instrument software. Each test was repeated three times, and the average value was reported to minimize experimental error.

It is important to note that the crude oil contains naturally occurring surface-active components, such as asphaltenes, resins, and organic acids, which can adsorb at the oil–water interface and influence interfacial behavior. These components may contribute to the initial reduction in IFT, even in the absence of nanomaterial. Therefore, all comparative IFT measurements in this study were performed using the same crude oil sample to ensure consistency and to isolate the effect of Zn-QDs in interfacial activity. The IFT values were determined using green Zn-QDs dispersed in distilled water and formation water at various salinity levels. In addition, contact angle measurements were performed to evaluate the effect of Zn-QDs on the wettability of carbonate and sandstone rocks. The sessile drop method, conducted using the VIT-600 apparatus under ambient pressure and temperature conditions, was applied to assess wettability changes (see Fig. 3(d)). An oil–wet state is characterized by a contact angle greater than 90°, while a water–wet state corresponds to an angle of less than 90°, with the latter indicating a neutral wetting system (Jafarbeigi

et al., 2022; Radnia et al., 2018). To examine the influence of Zn-QDs, thin rock slices were cut, cleaned, and aged in oil for 2 weeks at 60 °C to establish an oil-wet condition (see Fig. 3(b)). The wettability alteration was then evaluated by immersing the oil-wet rock samples in nanofluids with varying QD concentrations and different base fluids for three days under static conditions. Contact angles measurement was conducted by placing the rock slices in glass cells containing different nanofluid concentrations. An oil droplet was gently positioned beneath each slice, and the captured images were used to determine the contact angle. This process was repeated at three different points on each thin section to account for surface heterogeneity. These measurements represent the contact angles of a crude oil droplet on the rock surface before and after treatment with nanofluids.

2.5. Emulsification behavior and nanofluid stability

The emulsion behavior of the formulated Zn-QDs nanofluid mixed with oil was examined both visually and microscopically at different concentrations over a specified period, as shown in Fig. 3(c) (Modena et al., 2019). For this analysis, 5 mL of toluene was mixed with the prepared nanofluids in distilled water (DW). The mixture was then shaken for 30 min using a magnetic stirrer. The resulting nano-emulsions were collected in transparent cylinders and visually inspected at various time intervals. To further investigate the microscopic behavior of the emulsion, the samples were sonicated for 30 s using a probe sonication (UH-92-IIN). The vials were placed in an ice bath during sonication to prevent any temperature rise (Ganesh et al., 2019). After 24 h, light micrographs of the emulsions were captured on glass slides using a NOVEL microscope (ECLIPSE NPL-400T), and the emulsion droplet diameters were measured using Digimizer software. Additionally, the dispersion stability of the nanofluids was assessed visually by storing the prepared nanofluids in glass test tubes under undisturbed condition for the required duration. During this period, key characteristics of the nanofluids, such as pH, density, and conductivity, were measured as these characteristics play a significant role in determining the stability of the nanofluids (see Fig. 3(c)).

2.6. Oil displacement

The potential of the fabricated Zn-QDs for enhance oil recovery was evaluated through core flooding experiments. Carbonate and sandstone core samples were selected and prepared to the required dimensions, with both ends trimmed as shown in Fig. 3(a). To remove any residual water, oil, or contaminants, the core plugs underwent a thorough cleaning process using Soxhlet extraction with ethanol and toluene. The extraction was performed at temperatures between 60 and 80 °C for 24 h. Afterward, the core samples were dried in an oven at 65 °C for 36 h. The core plugs were then saturated with water and flooded with crude oil using a core flooding cell for one month (see Fig. 3(a)). Subsequent core displacement tests were carried out using 300 ppm of bio-Zn-QDs dispersed in distilled water (DW) and formation water (FW), labeled as DW300, FW1:5-300 (carbonate rock), and FW1:15-300 (sandstone rock). DW300, FW1:5-300, and FW1:15-300 were prepared by dispersing 300 ppm of bio-Zn-QDs in DW, 1:5 diluted formation water, and 1:15 diluted formation water, respectively. The selection of the nanofluid for tertiary injection was based on the results of interfacial tension (IFT) and contact angle tests. All flooding experiments were conducted at 75 °C and 1350–1380 psi, with an injection rate of 0.3 cm³/min (see Fig. 3(d)). For secondary recovery, approximately two pore volumes (PV) of water were injected at a controlled flow rate. Pressure reading at the injection and production ends was mentioned using two pressure

transducers. After completing secondary recovery, 2 PV of the selected nanofluid were injected into the core plugs, followed by 1 PV of water. The volume of crude oil displaced during the secondary and tertiary recovery processes was subsequently measured.

3. Result and discussion

3.1. Characterization of bio-zinc nanodots (bio-Zn-QDs)

The thermal stability of the synthesized nanodots was evaluated using thermogravimetric analysis (TGA) up to 600 °C as shown in Fig. 4(a). The analysis revealed three distinct thermal regions: the initial region (25–150 °C), the intermediate region (150–300 °C), and the main decomposition region (300–450 °C). In the first region, a 10% weight loss was observed, which can be attributed to the desorption of water and initiator fragments. A gradual and stable weight loss was observed in the second region. However, a significant weight loss of 30%–35% occurred in the main decomposition region corresponds to the decomposition of the bio-Zn-QDs. Additionally, the curve flattens above 500 °C, reaching a residual weight of about 50%, indicating that the remaining materials is mostly Zn-QDs which are thermally stable (see Fig. 4(a)).

Fourier-transform infrared spectroscopy (FTIR) analysis is crucial for identifying the composition and functional groups of the synthesized nanodots. Each characteristic peak in the FTIR spectrum corresponds to a specific vibrational mode of molecular bonds, offering valuable insights into the chemical structure of the zinc nanodots. FTIR analysis is particularly useful for confirming the presence of desired functional groups (Jin et al., 2024). In this study, FTIR analysis was conducted to examine the functional groups present in the synthesized bio-Zn-QDs. Fig. 4(b) presents the FTIR spectrum of the nanodots in the wavelength range of 400–4000 cm^{-1} , revealing multiple peaks associated with various molecular bond systems. According to the standard IR spectral dataset, the broad peak at 3423 cm^{-1} corresponds to the O–H stretching vibration, likely originating from hydroxyl groups in organic compounds such as phenols or alcohols. The peak at 2920 cm^{-1} is attributed to the C–H stretching vibration (Sirdeshpande et al., 2018), which likely arises from organic ligands or capping agents derived from parsley leaf extract. The characteristic peaks at 1622 and 1564 cm^{-1} correspond to C=C stretching vibrations, indicating the presence of conjugated aromatic structures in the organic molecules (Hu et al., 2019). Furthermore, the C–H bending vibrations appear at 1406 and 1344 cm^{-1} , suggesting the presence of aliphatic or aromatic hydrocarbon chains (Jafarirad et al., 2016). Oxygen-containing

functional groups such as alcohols, carboxylic acids, or ethers is indicated by C–O stretching vibrations observed at 1130, 1084, and 1009 cm^{-1} (Bhuyan et al., 2015; Verma et al., 2017). Additionally, the peaks at 924 and 868 cm^{-1} are associated with C–H bending vibrations of alkenes and alkyl groups, respectively, while the peak at 654 cm^{-1} corresponds to =C–H bending of alkynes (Meléndrez et al., 2010). Finally, the successful synthesis of Zn-QDs is confirmed by the peak at 472 cm^{-1} (García et al., 1997).

Fig. 5 presents the morphology and size distribution of the synthesized quantum dots (Zn-QDs) using zeta potential, field emission scanning electron microscopy (FE-SEM), and high-resolution transmission electron microscopy (HR-TEM). The zeta potential analysis shown in Fig. 5(a) was conducted to evaluate the surface charge of the green zinc nanodots, providing essential insights into their colloidal stability. The magnitude of the zeta potential determines the tendency of particles to aggregate or remain dispersed. In general, suspensions with zeta potential values exceeding +30 mV or less than –30 mV are considered stable due to strong repulsive forces that prevent nanoparticle aggregation (Ganguly et al., 2009). For the synthesized zinc nanodots, the zeta potential was measured within the distilled water was –31.9 mV (see Fig. 5(a)). This high negative indicates strong interparticle repulsion, confirming the good colloidal stability of the suspension (Glory et al., 2008). To further investigate the morphology and size of the nanodots, the TEM micrograph shown in Fig. 5(b) provides a precise confirmation of the nanoscale size distribution of QDs, revealing uniformly dispersed zinc dots. Additionally, SEM images captured at different magnifications (Fig. 5(c)) provide a more detailed assessment of the QDs' morphology. The powder samples were analyzed directly without being adsorbed onto a substrate, thereby preserving their natural state. The SEM images show a uniform morphology, with particle sizes consistently in the nanoscale range below 100 nm. This result agrees with TEM observations, which indicate an average size of approximately 10 nm.

3.2. Emulsion and dispersion stability of nano-EOR solutions (nanofluids)

The density, pH, and conductivity of the prepared nanofluids are presented in Fig. 6. The densities of the nanofluids prepared with formation water (FW-based nanofluids) are higher than those with distilled water (DW-based nanofluids). The densities range from 0.9968 to 1.0053 g/cm^3 for DW-based nanofluids and 1.023 to 1.025 g/cm^3 for FW-based nanofluids (Fig. 6(a)). In both cases, the density increases with bio-Zn-QD concentration.

The pH of a colloidal solution plays a crucial role in particle aggregation and suspension stability (Mirzavandi et al., 2023). As shown in Fig. 6(b), pH values range from 7.05 to 6.76 pH for DW-

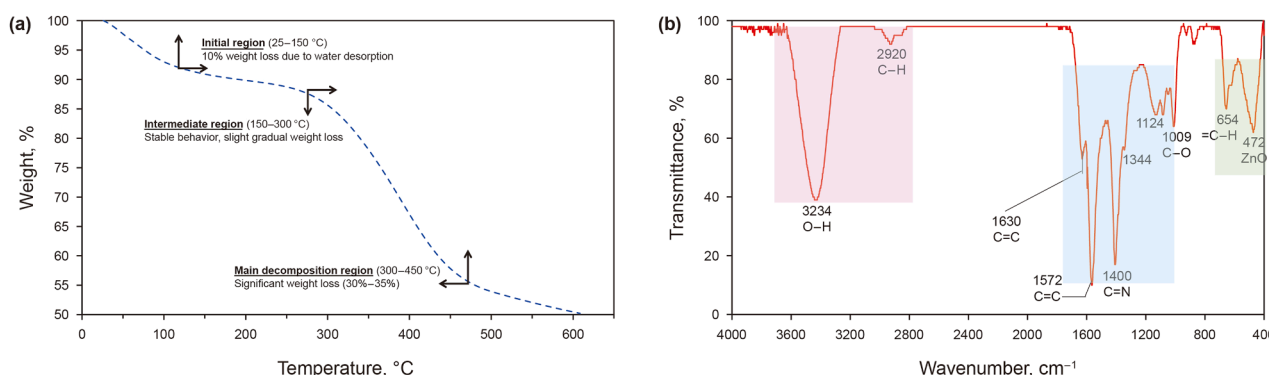


Fig. 4. Characteristics of bio-zinc nanodots: (a) TGA curve and (b) FTIR spectrum.

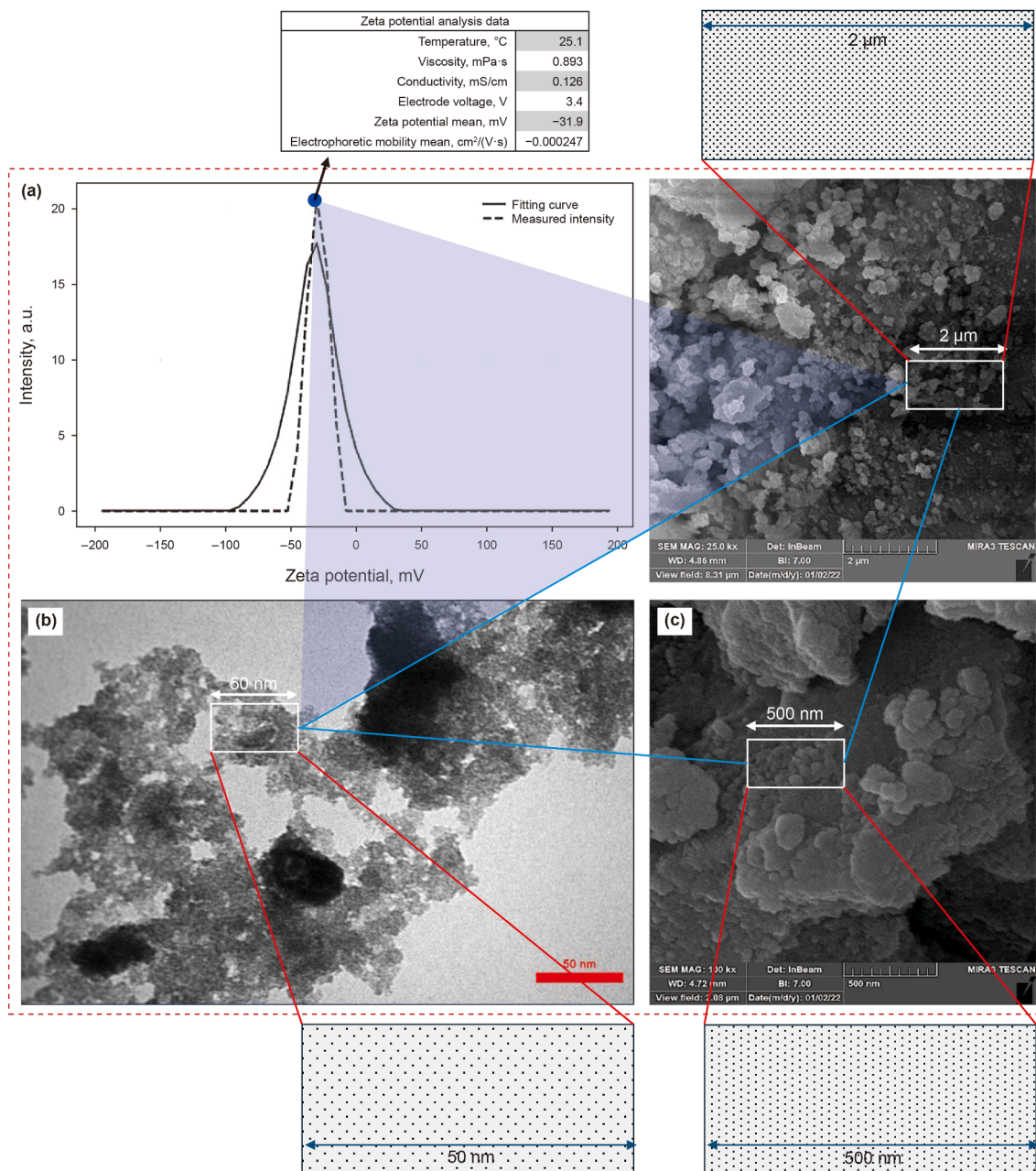


Fig. 5. Characteristics of bio-zinc nanodots: (a) zeta potential, (b) TEM micrograph, and (c) FE-SEM micrographs.

based nanofluids and 5.67 to 6.86 for FW-based nanofluids at different dilution ratios (1:20 to 1:0). The introduction of nanodots altered the solution pH through ion exchange. Specially, the release of Zn^{2+} ions from Zn-QDs slightly increased the pH of FW-based nanofluids, while the pH decreased in the DW-based nanofluid due to the absorption of H^+ ions onto nanoparticle surface.

Furthermore, the ionic strength of each nanofluid was evaluated by measuring its electrical conductivity (see Fig. 5(c)). Conductivity is a key transport property that serves as a useful indicator for assessing the stability of nanoparticles and nanodots in suspension. According to Rao (2010) and Hendraningrat and Torsæter (2015), charge stabilization enhances the stability of the nanofluid. Notably, increasing the bio-Zn-QD concentration in distilled water raises the conductivity, while in formation water,

the concentration has no significant effect. Additionally, reducing the salinity of the aqueous medium—from the FW to diluted-FW and finally to DW—lowers the conductivity. For instance, the conductivity of a nanofluid containing 100 ppm bio-Zn-QDs in FW was 187 $\mu\text{S}/\text{mm}$, increasing slightly to 195 $\mu\text{S}/\text{mm}$ at 500 ppm. In contrast, at the same bio-Zn-QD concentration in FW diluted at a 1:20 ratio, the conductivity varied only between 27.2 and 43.6 $\mu\text{S}/\text{mm}$.

Nanofluids containing bio-Zn-QDs at concentrations of 100, 200, 300, 400, and 500 ppm were used to assess dispersion stability through visual inspection. Following their preparation, the nanofluids were transferred into transparent vessels, and changes in dispersion stability were monitored over time. Initially, all nanofluids appeared milky-white and stable, with an even distribution of nanodots. Fig. 7 demonstrates the images captured

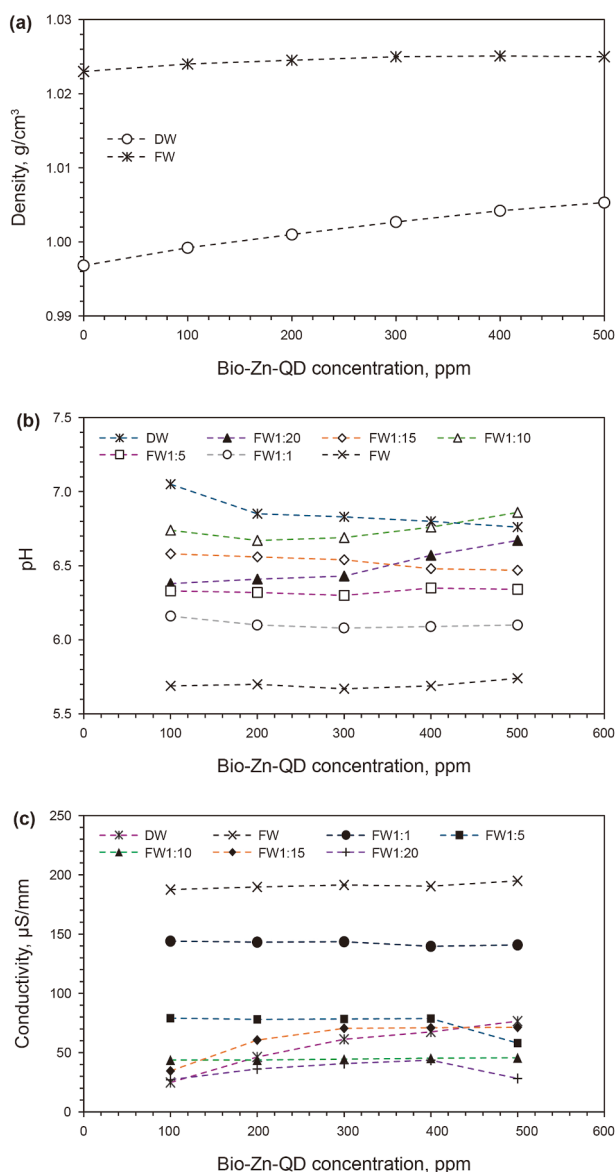


Fig. 6. Physicochemical properties of bio-Zn-QD nanofluids prepared with distilled water (DW) and formation water (FW): (a) density, (b) pH, and (c) conductivity.

immediately after preparation and at regular intervals over one week. Sedimentation of the bio-Zn-QDs became noticeable after 24 h, particularly at higher concentrations of 400 and 500 ppm. The variation in stability is primarily attributed to progressive sedimentation over time. Observations indicate that nanofluids remain stable for the first 24 h, after which the sedimentation became more pronounced, especially at higher concentrations. Additionally, the nanofluid with a concentration of 100 ppm retains a reasonable level of stability for approximately 96 h. After 4 and 5 days, the sedimentation rate increases significantly, and the nanodots accumulate at the bottom of the vessels, leaving a clear and continuous water phase (see Fig. 7). Recent research has demonstrated that ionic strength and multivalent ion concentration have a major impact on nanoparticle aggregation and precipitation in aqueous media. For instance, divalent cations like Ca^{2+} and Mg^{2+} compress the electrical double layer surrounding SiO_2 and Al_2O_3 nanoparticles, increasing aggregation and decreasing suspension stability in high-salinity brine (Rego Barros Rebello et al., 2025). By boosting electrostatic repulsion, surface modification with sulfonate or amine functional groups might

improve nanoparticle stability in such circumstances (Alyousef et al., 2024). In contrast, the bio-Zn-QDs in this investigation showed reasonable short-term stability even in the absence of surfactant modification. This is probably because of their high surface energy and incredibly small particle size (3–8 nm) which encourage stronger electrostatic interaction with nearby water molecules. These results imply that Zn-QDs have intrinsic colloidal stability that make them appropriate for reservoir application, especially in setting that are somewhat salinized. However, additional tailoring would be required to guarantee long-term dispersion in formation fluids that are rich in multivalent ions.

Furthermore, the ability of bio-Zn-QDs to form oil-in-water emulsions at various concentrations was investigated through visual inspection (see Fig. 8). Bio-Zn-QDs were mixed with crude oil at its optimal concentration of 300 ppm, determined based on the IFT and CA outcomes, and the emulsion stability evaluation over the 7-day observation period is presented in Fig. 8. On the first day, the mixture formed homogenous and stable emulsion. However, a slight phase separation of approximately 1 mL was observed at the bottom of the tube. Over time, this separation gradually increased in the samples labeled from day #1 to day #5, as indicated by red lines in Fig. 8, reflecting progressive demulsification driven by droplet coalescence and gravitational settling. By the final day, the separation height reached approximately 4 mL, with the water phase containing dispersed nanodots settling at the bottom of the tube.

In Fig. 9, microscopic images reveal how the concentration of nanodots affects the emulsion characteristics of crude oil/nano-fluid mixtures. As the concentration of bio-Zn-QDs increases from 100 to 500 ppm, the average droplet size of the emulsified oil phase systematically decreases from 8 to 2.3 μm . This trend clearly indicates that higher nanodot concentrations enhance the emulsification process by more effectively stabilizing the oil droplets and preventing their coalescence. At lower concentrations, the stabilization is weaker, resulting in larger, polydisperse droplets. In contrast, higher concentrations provide better surface coverage of the droplets, forming a more robust barrier that inhibits droplet growth and improves emulsion uniformity (Binks et al., 2007; Pilapil et al., 2016; Xu et al., 2015). This demonstrates that zinc nanodots play a crucial role in stabilizing the emulsion, with optimal performance observed at higher concentrations. The primary distinction is that nanomaterials have a stronger tendency to adhere to interfaces, whereas surfactants can dynamically adsorb or desorb from the interface (Binks and Kirkland, 2002; Worthen et al., 2013). According to Binks and Kirkland (2002), the main mechanism for the formation of stable emulsions containing nanomaterials involves the creation of a thin nano-film around the oil droplets. In this case, the surfaces of the toluene droplets are lightly coated with bio-Zn-QDs, leaving gaps without particles between them. These QDs strongly repel each other and form a bond when two droplets come into contact. This bond helps maintain a thin, stable water film in the oil-in-water emulsion. As a result, emulsions stabilized by nanodots are known for their exceptional stability, enabling them to withstand challenging reservoir conditions (Park et al., 2013).

3.3. IFT reduction

The reduction of interfacial tension (IFT) is a crucial mechanism in enhanced oil recovery (EOR), as it directly influences the mobility and entrapment of crude oil within porous rock formations. Lower IFT increases the capillary numbers and facilitates the release of trapped oil. In this study, the IFT between crude oil and both DW and FW was evaluated at various bio-Zn-QDs concentrations (100 to 500 ppm) and different formation water dilution

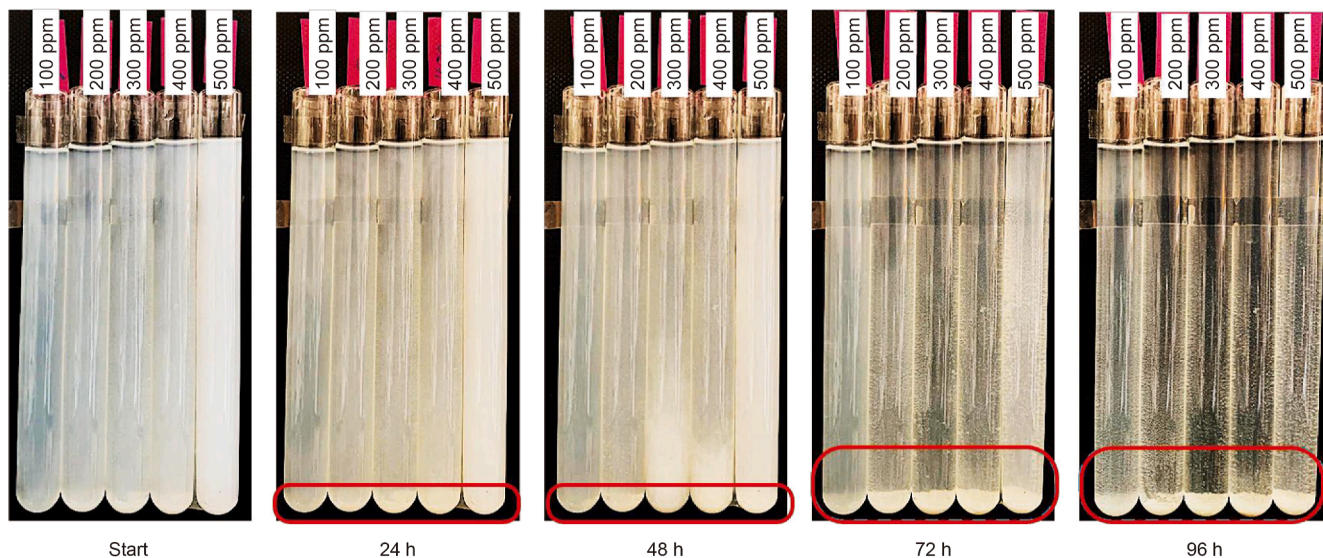


Fig. 7. Dispersion stability of bio-Zn-QDs in distilled water at different concentrations over 96 h.

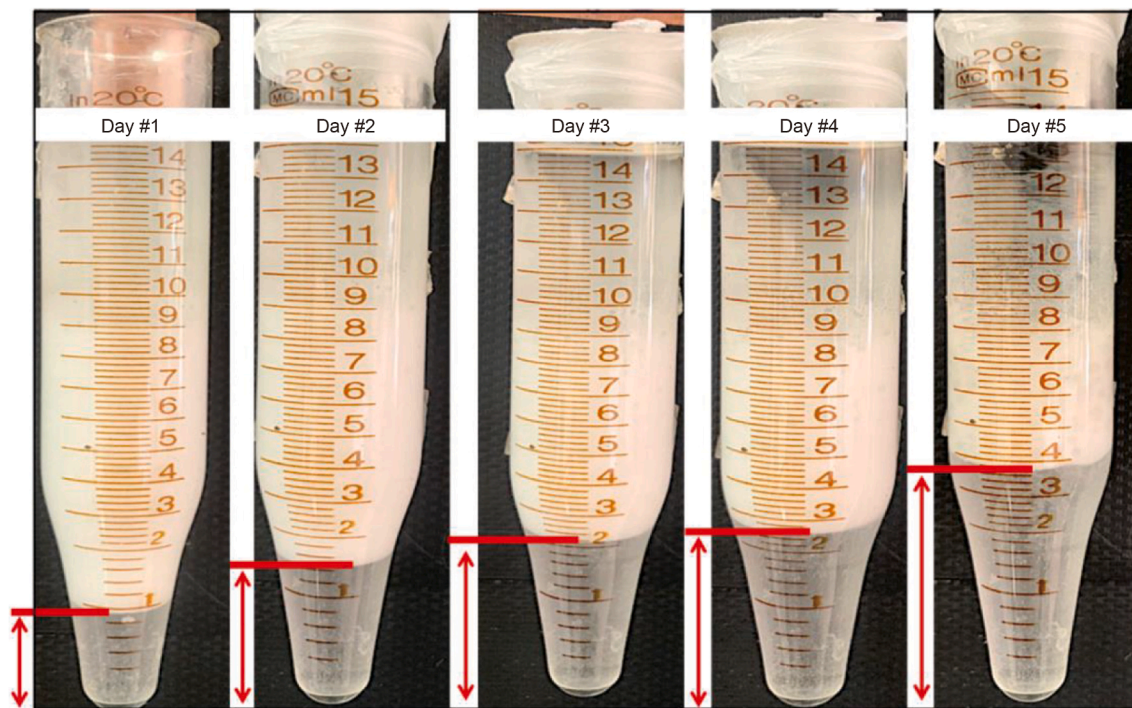


Fig. 8. Emulsion stability of oil/nanofluid system with 300 ppm nanodots for the period of 7 days.

ratios (1:0 to 1:20) as summarized in Table 1. Initially, the IFT between crude oil and DW was 28.51 mN/m, this value decreased progressively with increasing the bio-Zn-QD concentration. At 100 ppm, the IFT was reduced by 35.35% to 18.43 mN/m. With further reductions observed up to 300 ppm, where the minimum IFT of 16 mN/m was recorded. However, at higher concentrations (400 and 500 ppm), a slight increase in IFT was noted (Fig. 10). A similar trend was observed for FW-based nanofluid: the initial IFT value of crude oil/FW was 9.17 mN/m, decreasing to a minimum 8 mN/m at the optimum concentration (see Fig. 10). Thus, for both DW and FW systems, the IFT values decrease with concentration

until reaching the optimum (300 ppm), beyond which the IFT begins to rise.

Fig. 11 presents dynamic IFT values estimated for all FW- and DW-based nanofluids containing bio-Zn-QDs at different concentrations over the period of 600 s until equilibrium state was reached. A consistent decline in IFT was observed throughout the measurement period. FW-based nanofluids consistently exhibit lower IFT value than their DW counterparts across concentrations (100 to 500 ppm). Among the samples, DW-300 showed the lowest IFT throughout the 600-s measurement (see Fig. 11(a)), whereas, FW-300 exhibited the most pronounced IFT reduction of all FW and DW nanofluids (see Fig. 11(b)). The variation in the

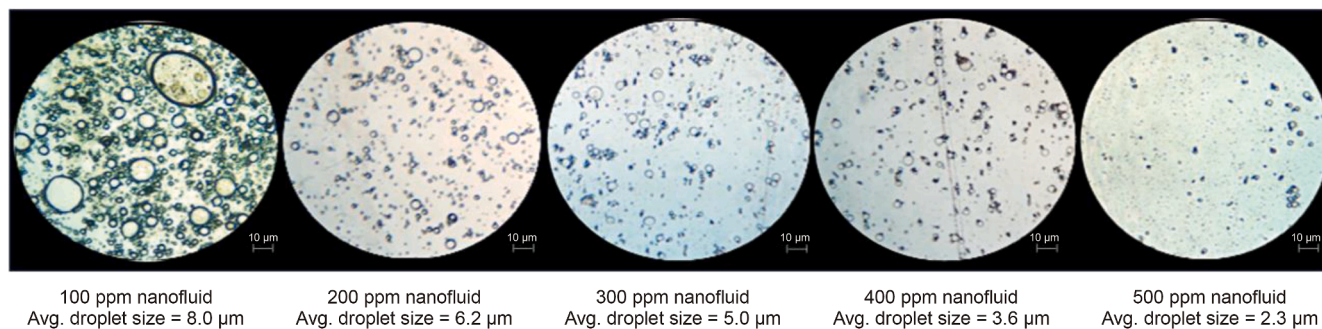


Fig. 9. Microscopic images of oil/nanofluid emulsion at different concentrations of 100–500 ppm.

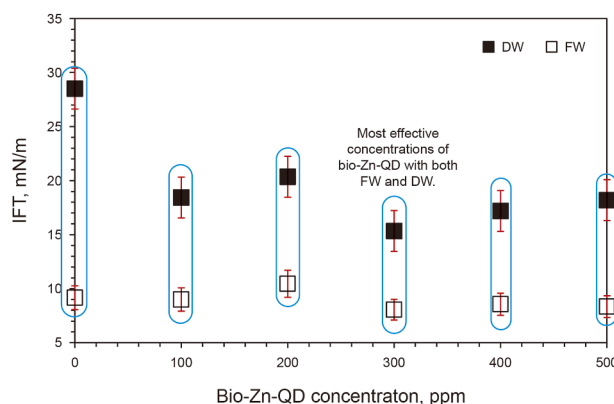


Fig. 10. IFT between crude oil and aqueous phase (DW/FW) with and without synthesized nanodots.

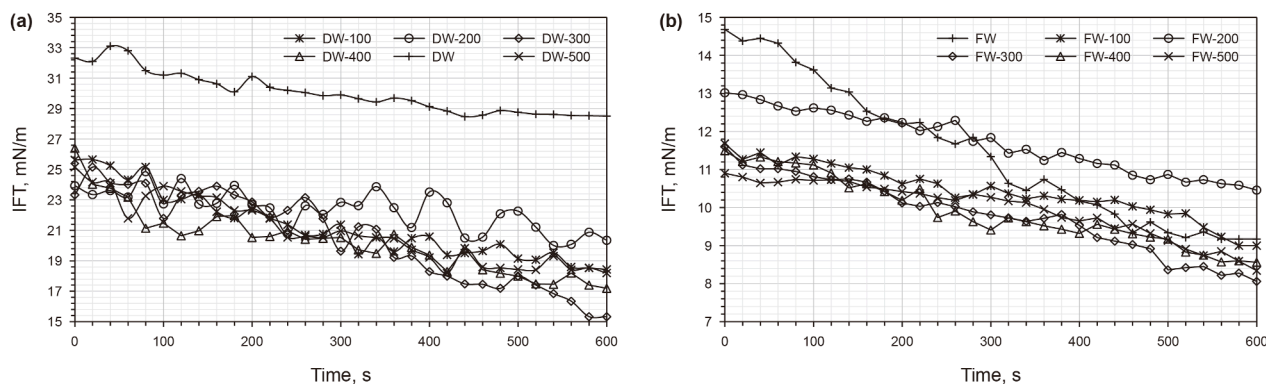


Fig. 11. Dynamic IFT of nanofluids prepared with bio-Zn-QDs in distilled water (DW) (a) and formation water (FW) (b) over a period of 600 s.

reduction trend dependent on the nanodot concentration is consistent with the findings of Eshraghi et al. (2017), Manshad et al. (2020), and Ali et al. (2019). While the exact cause of the IFT increase beyond the optimal point and with higher nanoparticle concentrations is not fully understood, literature suggests a possible explanation. According to Mirzavandi et al. (2023) and Zargartalebi et al. (2014), this behavior can be attributed to capillary forces. When nanoparticles are present at the interface, they either remain suspended or partially submerged in the liquid layer, generating lateral capillary forces. At bio-Zn-QD concentrations above 300 ppm, when the particles are closely packed, these capillary forces become significant, impeding the deformation of the interface and resulting in an increase in IFT. It has been reported that the ionic composition of the aqueous phase plays a

significant role in measuring interfacial behavior (Farhadi et al., 2023; Fattahi et al., 2023). Study by Farhadi et al. (2023) showed that the presence of divalent ions enhances nanoparticle adsorption at the oil–water interface, thereby improving IFT reduction through electrostatic screening and sulfate assisted ion bridging mechanism. In addition, Fattahi et al. (2023) observed that combining SiO₂ nanoparticle with surfactant under high salinity condition results a synergistic reduction in IFT, outperforming either component alone. These findings emphasize that nanoparticles can remain effective under harsh reservoir condition when appropriate ion surface interactions are prompted. In the current study, the stronger IFT reduction observed in formation water compared to distilled water confirms that bio-Zn-QDs interact favorably with saline media, likely due to the

electrostatic interaction between Zn^{2+} surface site and multivalent ions. Such a response differentiates bio-synthesized Zn-QDs from many conventional oxide nanoparticles which often suffer from aggregation and reduced interfacial activity at high ionic strength.

Fig. 12 presents a comparison of various scenarios in which the nanofluid was prepared, with particular emphasis on the IFT test. It is evident from Fig. 12 that using FW instead of DW results in a reduction of the IFT value. Based on this observation, different FW:DW dilution ratios, ranging from 1:1 to 1:20, were tested to determine the optimal salinity of formation water. Notably, the lowest IFT value of 7.31 mN/m was achieved in the FW1:1-300 scenario, where 300 ppm of bio-Zn-QDs were mixed with 1:1 diluted-FW with a salinity of 86,500 ppm. In comparison, the IFT values for the same concentration of bio-Zn-QDs in DW and pure FW were 15.33 and 8.04 mN/m, respectively. Fig. 12(a) illustrates IFTs obtained under the influence of 1 time dilution (FW1:1) at 86,500 ppm salinity with the presence zinc nanodots at different concentrations that are almost similar with what have measured under the impact of FW-based nanofluids. However, as the salinity decreased to 34,600, 17,300, 11,533, and 8650 ppm at dilution ratios of 1:5, 1:10, 1:15, and 1:20, respectively, the IFT values increased. For the 20 times dilution with the salinity of 8650 ppm, FW1:20 nanofluid resulted IFT values close to the DW-based nanofluid for all 100–500 ppm concentrations of the zinc nanodots as shown in Fig. 12(b). In addition to the influence of salinity and bio-Zn-QD concentration, the presence of naturally surface-active component in crude oil can significantly contribute to the observed IFT variation. These species tend to migrate to the oil–water interface, partially reducing IFT and facilitating the adsorption of bio-Zn-QDs. Fattahi et al. (2023) observed that nanomaterials can enhance the stability and performance of these interfacial films under reservoir-relevant condition. The IFT data presented Fig. 12 show the IFT increases as the water salinity decreases. This indicates that the synthesized bio-zinc nanodots are more compatible with saline aqueous media than distilled water.

3.4. Wettability alteration

This section investigates the modification of wettability on oil-wet carbonate and sandstone rock surfaces by measuring the contact angle between crude oil and rock surfaces. The study was carried out using various bio-Zn-QD nanofluid solutions, with distilled water (DW) and formation water (FW) serving as reference system. Initial contact angles (CAs) of crude oil on carbonate and sandstone rock surfaces were first measured without bio-Zn-QDs to evaluate the effect of salinity, as shown in Fig. 13. As observed, the CA of the sandstone rock in DW is slightly lower than that on carbonate rock, which exhibits a CA of 143.5°. However, for

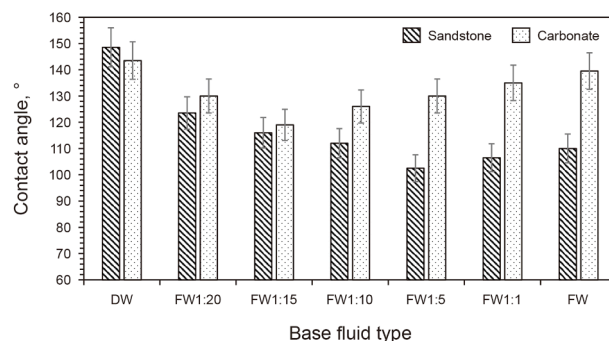


Fig. 13. Contact angles of crude oil droplets on the surfaces of carbonate and sandstone rocks measured at different salinity levels without the presence of bio-Zn-QDs.

FW and diluted FW solution, all measured CAs of crude oil droplets on carbonate pellets are lower than those on sandstone surface. The highest value of CA is 148.5° for carbonate rock in DW, and this value decreased with increasing water salinity. The trend and extent of CA reduction varied across all water types and rock samples depending on salinity level. The minimum CAs recorded were 102.5° for sandstone (with FW1:5) and 119° for carbonate (with FW1:15), as shown in Fig. 13. These results indicate that both carbonate and sandstone rocks exhibit oil-wet behavior without the presence of the synthesized QDs, as all CAs remain above 90°. Among the tested fluid dilution ratios, the FW1:5 and FW1:15 solution produced the lowest contact angle on both rock types. Therefore, these two dilution ratios were selected for further wettability.

The addition of bio-Zn-QDs to the selected reference fluids (DW, FW1:5, and FW1:15) led to a gradual decrease in CA for both rock types, as shown in Fig. 14. Among all tested bio-Zn-QD concentrations, 300 ppm exhibited the lowest CAs for carbonate rock in both DW- and FW-based nanofluids. When DW was used as the dispersing medium, the CA of carbonate decreased from its initial value of 143.5° to 29.5° (Fig. 14(a)). A further reduction was observed when the optimal FW salinity (FW1:5) was used, which resulted in a contact angle of 23.5° (Fig. 14(a)). For sandstone rock, 400 ppm of bio-Zn-QDs yielded the lowest contact angle values for both fluid systems (DW and FW1:15). With 400 ppm to the DW, the CA decreased to 45° (Fig. 14(b)), whereas, using FW1:15 at the same concentration resulted in CA of 60° (Fig. 14(b)). These results indicate that the optimal FW salinity is more effective at reducing the contact angle on carbonate rock, whereas DW is more effective on sandstone rock. This highlights the significant impact of bio-Zn-QDs in altering the wettability of both carbonate and sandstone

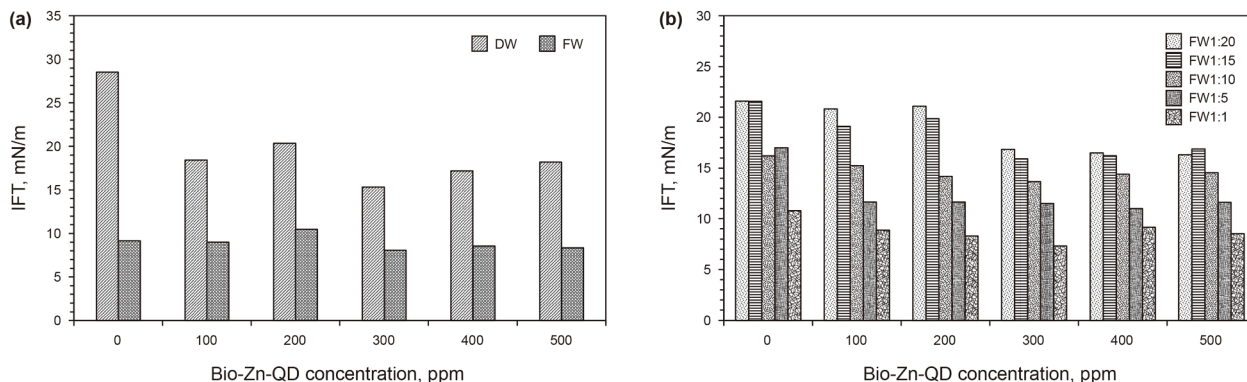


Fig. 12. IFT between crude oil and nanofluids with different concentrations of bio-Zn-QDs in waters of varying salinity: (a) DW and FW, (b) FW1:1 (86,500 ppm), FW1:5 (34,600 ppm), FW1:10 (17,300 ppm), FW1:15 (11,533 ppm), and FW1:20 (8650 ppm).

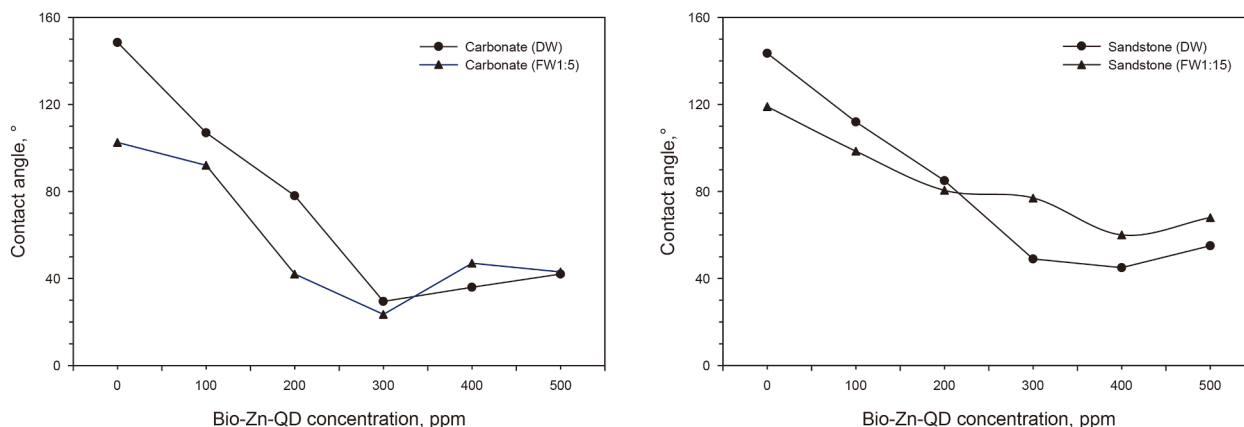


Fig. 14. CAs measured under different concentrations of bio-Zn-QDs: (a) DW- and FW1:5-based nanofluids, carbonate rock pellets, (b) DW- and FW1:15-based nanofluids, sandstone rock pellets.

rocks, shifting them from an oil-wet to a strongly water-wet condition. The reductions in contact angles correspond to substantial enhancement in wettability alteration, with improvements of 84.1% and 74.9% for carbonate and sandstone rocks, respectively. These findings align with recent research trend emphasizing the performance of synthesized nanoparticles under high salinity and multivalent ion environment. Rezvani et al. (2024) and Tong et al. (2023) have reported that divalent ions strongly affect nanoparticle adsorption and wettability alteration efficiency. Modified SiO₂ and Zn based nanofluid have shown improved performance due to electrostatic screening and specific ion interaction in saline systems. Consistence with this finding, the bio-Zn-DQs in this study maintained remarkable wettability altering ability even at salinities exceeding 80,000 ppm, highlighting their compatibility and stability in multivalent ion rich environment.

Aveyard et al. (2003) emphasized that factors such as the nature of the rock surface, fluid temperature, salinity level, and importantly, the concentration and size of the nanomaterials influence the formation of the nanofilm. If no competing mechanisms (i.e., attraction of nanomaterials to the solid surface) interfere with nanofilm development, increasing nanofluid concentration enhance the disjoining pressure, which in turn reduces the contact angle (Nasr et al., 2021; Chengara et al., 2004). The unique properties of the synthesized bio-Zn-QDs—particularly their size, surface charge, and quantum characteristic—play a significant role in wettability alteration. Their interaction with the rock surface is not solely governed by the conventional displacement mechanism observed in typical nanofluid, but also by the distinctive physicochemical behavior of bio-Zn-QDs. A higher concentration of nanodots within the nanofilm increases its effectiveness in modifying wettability. This rise in nanodot concentration elevates the disjoining pressure, ultimately leading to a substantial reduction in the contact angle.

Fig. 15 presents snapshots of oil droplets on the surfaces of prepared carbonate and sandstone rocks, under the influence of DW and FW, with and without the presence of bio-Zn-QDs. When the rock surface is initially oil-wet, the oil droplet tends to spread, forming a flatter shape and resulting in a larger CA. However, as the concentration of QDs increases, the droplet becomes more spherical, leading to a reduction in the outer CA. For instance, the highest CA of 148.5° is recorded for DW without QDs, where the oil strongly adhered to the carbonate surface, indicating a strongly oil-wet state. In contrast, when a 300 ppm nanofluid prepared with FW is used, the CA decreases to 23.5°, signifying a strongly

water-wet state that enhances oil displacement. The mechanism by which nanodots reduce the contact angle between oil and rock surface remains a subject of ongoing debate. Several studies suggest that the wettability alteration occurs due to the adsorption of nanoparticles onto the rock surface, influenced by particle size, surface charge, rock surface chemistry, and the nature of the dispersion medium (McElfresh et al., 2012). One of the most cited mechanisms in the literature is that nanomaterials form a thin layer on the solid surface, and the resulting constraints on the arrangement of nanomaterials within this layer lead to a tendency for the nanomaterials to arrange in distinct ordered structures. This ordered arrangement increases the available space for the nanomaterials to move, which in turn raises the system's entropy (Negin et al., 2016). Consequently, the significant pressure builds up within the confined spaces (Nazari Moghaddam et al., 2015). Accordingly, the thin film formed by the nanomaterials diffuses across the rock surface, effectively displacing bound oil, paraffin and gas, which are responsible for the rock's oil-wet behavior. This separation leads to the establishment of a water-wetting state. The strength of this effect depends largely on the properties of the nanofluid and the dispersed particles in comparison to the fluid and reservoir rock. The formation of the thin film results from changes in the wettability of nanoscale components. At the same time, the pressure buildup in the system creates a wedge-shaped film, often referred to as structural disjoining pressure (Motraghi et al., 2023). This phenomenon arises from the random movement of nanoparticles (Brownian motion) and electrostatic repulsion between the nanoparticles (Ahmadi et al., 2024; Schramm, 1992).

The governing mechanisms of wettability alteration by bio-Zn-QDs in carbonate and sandstone rocks are illustrated in Fig. 16. In sandstone, the rock surface carries negative charges, and the nanofluids likewise contain negatively charged nanodots. As a result, electrostatic repulsion inhibits effective adsorption of the nanoparticle onto the rock surface.

Therefore, at a concentration of 400 ppm, the observed reduction in CA is primarily attributed to Brownian motion of nanoparticles—random movement driven by collisions with surrounding molecules. Disjoining pressure also plays a critical role in modifying the thin liquid films between the oil and the rock surface. The nanodots interact simultaneously with the oil and rock interface and Brownian motion enhances their dispersion and mobility throughout the system. This improved distribution strengthens structural disjoining pressure within the wedge-like films formed on the surface, which helps reduce the CA by

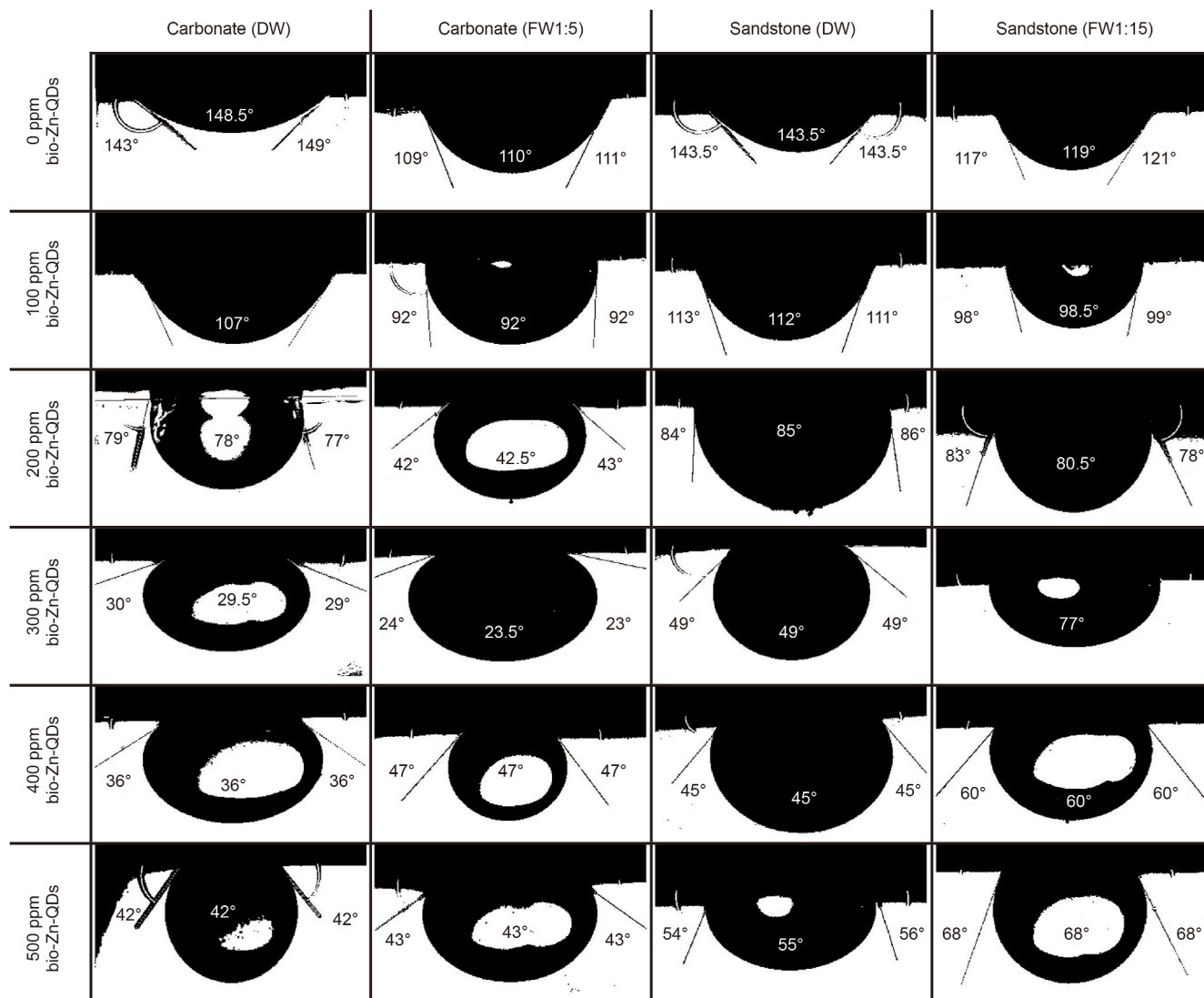


Fig. 15. Snapshots of crude oil droplets on the surfaces of carbonate and sandstone rocks under the influence of FW and DW, with and without bio-Zn-QDs.

enabling the nanodots to overcome electrostatic repulsion. However, when the nanodot concentration exceeds 400 ppm, the disjoining pressure in sandstone becomes less effective. At 500 ppm, excessive particle–particle interactions, reduced mobility, and possible agglomeration diminishes the structural disjoining pressure, leading to an observed increase in CA.

As explained in the preceding sections, when the nanodot concentration reaches 300 ppm, the strong negative surface charge causes the nanofluid to behave similarly to an electrolyte. Since carbonate rocks carry a positively charged surface, this results in an attractive electrostatic interaction between the negatively charged nanodots and the rock surface. The presence of sulfate ions (SO_4^{2-}), which are strongly adsorbed on carbonate minerals, further strengthens this interaction through their association with Ca^{2+} ions (see Fig. 16). This adsorption occurs as the system tends to minimize the Gibbs free energy of the surface. Under these conditions, the electrolyte-like behavior of the nanofluid shifts the dominant mechanism of wettability alteration in carbonate rocks from structural disjoining pressure to direct adsorption of bio-Zn-QDs. For carbonate rocks, the minimum contact angle is achieved at a concentration of FW1:5-300 ppm. However, exceeding this concentration threshold introduces

competing effect. As the concentration increases beyond 300 ppm, disjoining pressure begins to rise, which increases the system's entropy and conflicts with the primary mechanism of minimizing Gibbs free energy for surface adsorption. Moreover, the higher concentration of positive ions in FW—such as Ca^{2+} , Mg^{2+} , Na^+ , and Fe^{2+} —promotes agglomeration of the negatively charged nanodots due to attractive ionic interactions (see Fig. 16). Although adsorption remains the dominant mechanism in carbonate rocks, increasing nanofluid concentration eventually introduces contradictory effects: enhanced entropy, stronger disjoining pressure, and agglomeration. Beyond the optimal concentration of 300 ppm, these competing mechanisms cause the contact angle to rise, thereby reducing the effectiveness of wettability alteration. The observed differences between carbonate and sandstone rocks are consistent with recent findings on ion-specific adsorption and wettability alteration mechanisms. For instance, Ni et al. (2024) noted that while divalent ions enhance nanoparticle adsorption on positively charged sandstone rock, wettability changes are primarily governed by disjoining pressure and Brownian motion. These comparisons reinforce that bio-Zn-QDs alter wettability through dual mechanisms—adsorption-dominated in carbonate and disjoining-pressure-dominated in sandstone—depending on

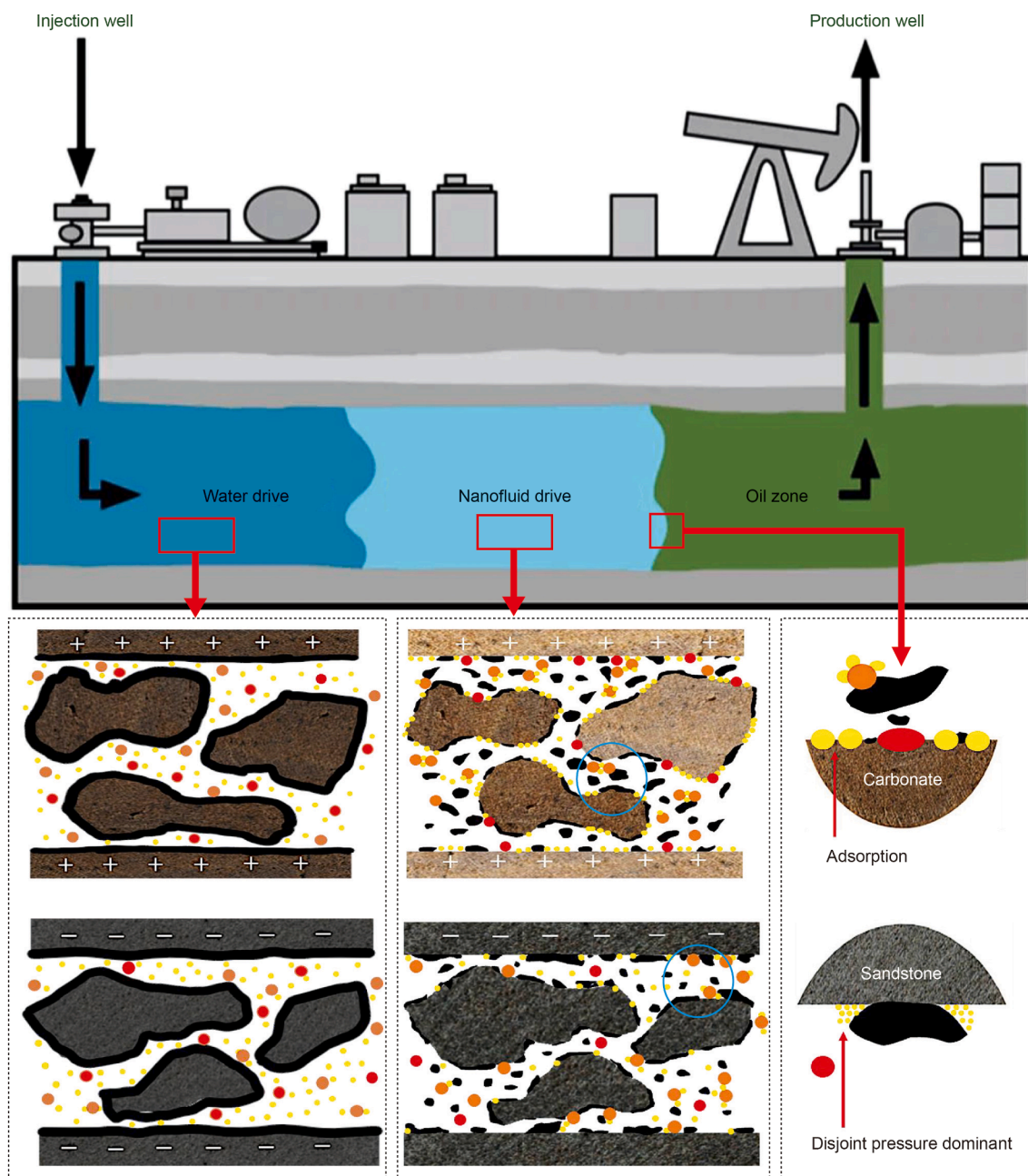


Fig. 16. Schematic illustration of the mechanism of wettability alteration for carbonate and sandstone rocks under the influence of bio-Zn-QDs.

salinity and ion composition. Overall, the green synthesized Zn-QDs represent a sustainable and high-performance alternative to conventional oxide nanoparticles, aligning well with recent advances in environmentally friendly EOR nanotechnology.

3.5. Oil displacement

Oil displacement experiments were performed under four distinct scenarios based on the type of nanofluid and rock substrate (carbonate and sandstone). In the first phase, secondary (waterflooding) recovery performance was evaluated using core samples labeled from C#1 to C#4. During this stage, DW without the presence of the nanodots was injected into cores C#1 (carbonate) and C#3 (sandstone); FW1-5 with the salinity of 34,600 ppm was injected into carbonate core C#2 (carbonate), and FW1-15 with the salinity of 11,500 ppm was used to displace oil in

core C#4 (sandstone). The dilution ratios of the formation water (FW) was selected based on the results of wettability alteration tests.

In the next phase, DW300 nanofluid was injected into cores C#1 and C#3, while FW1:5-300 and FW1:15-400 nanofluids were used to flood cores C#2 and C#4, respectively. All oil displacement experiments were performed under uniform conditions: a temperature of 75 °C, pressures ranging from 1350 to 1380 psi, and an injection rate of 0.3 cm³/min. It is worth noting that although the core plugs showed slight variations in the petrophysical properties, they were all sourced from the same sandstone and carbonate outcrops (Table 3). The porosity ranged from 13.54% to 19.43%, and the permeability varied between 2.54 and 4.23 mD.

Fig. 17 illustrates the oil displacement test conducted on core plugs 1 to 4 for both secondary and tertiary flooding phases. Waterflooding with DW and FW across all sandstone and

Table 3
Characteristics of the carbonate and sandstone core samples used in oil displacement including.

Core ID	Core type	EOR solution	Bulk volume, cm ³	Dry weight, g	Wet weight, g	Porosity, %	Permeability, mD	Oil recovery, % OOIP	
								Waterflooding	EOR
C#1	Carbonate	DW300	77.248	158.81	173.76	19.43	4.21	48.813	20.491
C#2	Carbonate	FW1:5-300	78.533	159.61	172.96	17.07	3.81	49.248	22.277
C#3	Sandstone	DW400	70.644	147.22	147.12	14.07	2.53	49.180	18.030
C#4	Sandstone	FW1:15-400	77.165	160.81	171.22	13.54	2.63	47.694	16.852

carbonate core plugs resulted in an oil recovery ranging from 47.6% to 49.4% of the original oil in place (OOIP). During this secondary recovery phase, prior to breakthrough, high pressure drops were recorded: 185 psi for core C#1, 225 psi for core C#2, 215 psi for core C#3, and 220 psi for core C#4. Following waterflooding, tertiary recovery was conducted using bio-Zn-QDs derived EOR solutions for all core plugs at different concentrations, prepared with the same water types used in the secondary recovery, as shown in Fig. 17.

As is obvious, the lowest incremental recovery, 16.852% OOIP, was observed when FW1:15-400 nanofluid (composed of 400 ppm bio-Zn-QDs in fifteen times diluted FW) injected into the sandstone core plug (C#4), which has a porosity of 13.53% and a permeability of 2.63 mD (Fig. 17(d)). However, the highest tertiary recovery factor of 22.277% OOIP was obtained by displacing the carbonate core plug C#2 with the nanofluid FW1:5-300 containing 300 ppm nanodots in five times diluted FW (Fig. 17(b)).

Meanwhile, injection of DW-based nanofluids with 300 and 400 ppm bio-Zn-QD concentration yielded additional recoveries of 20.49% OOIP from carbonate core C#1 (Fig. 17(a)) and 18.03% OOIP

from sandstone core C#3 (Fig. 17(c)), respectively. In addition, the pressure drop curve during the tertiary phase of the oil recovery by nanofluid injection remained stable and almost linear. This is attributed to the breakthrough that had already occurred in the secondary recovery phase. The rate of the pressure drop varied between 50 and 70 psi for all four injection cases. The oil recovery data indicated that the FW-based nanofluid is more compatible with the carbonate core plug compared with the DW-nanofluid. However, the synthesized nanodots was more effective when deployed in DW for injection into the sandstone rock.

Furthermore, Fig. 18 depicts the relative permeability curves for all flooding scenarios, which correspond to the observed pressure changes and oil displacement. Notably, the pressure difference between the inlet and outlet of the core plug initially increased sharply upon the introduction of the enhanced oil recovery (EOR) agents. This increase continued until the injected fluid encountered the oil and reached breakthrough. After breakthrough, the pressure difference gradually decreased and stabilized, indicating no further oil production. As previously discussed, the nanofluids effectively altered the rock wettability from oil-wet to water-wet.

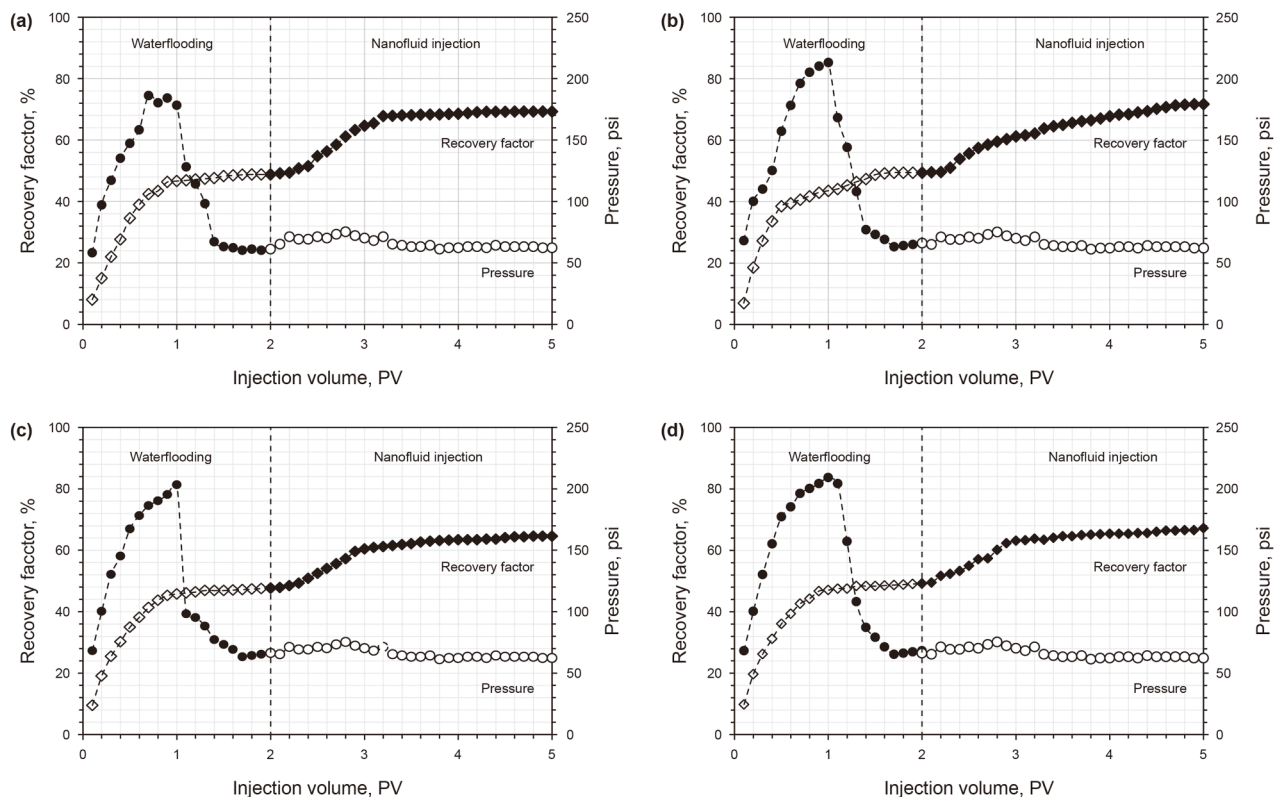


Fig. 17. Oil recovery and pressure profiles from displacement tests: waterflooding (DW and FW) followed by nanofluid injection. (a) DW300 nanofluid injection into carbonate core C#1, (b) FW1:5-300 nanofluid injection into carbonate core C#2, (c) DW300 nanofluid injection into sandstone core C#3, and (d) FW1:15-400 nanofluid injection into sandstone core C#4.

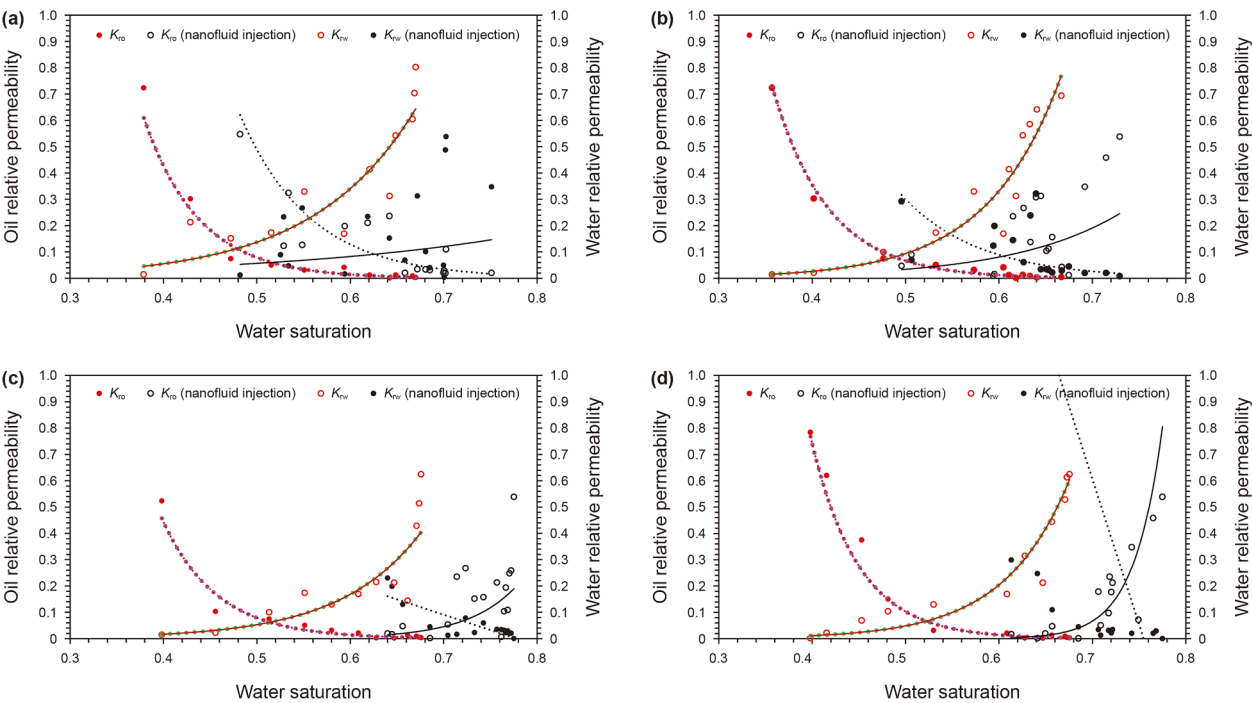


Fig. 18. Wettability alteration indicated by shifts in relative permeability curves upon nanofluid injection: (a) DW-300 nanofluid injected into carbonate core C#1, (b) FW1:5-300 nanofluid injected into carbonate core C#2, (c) DW-300 nanofluid injected into sandstone core C#3, and (d) DW1:15-400 nanofluid injected into sandstone core C#4.

This conclusion is supported by the relative permeability curves derived from the coreflooding results (oil recovery factor, pressure drop, and saturation profile) using the Johnson, Bossler, and Nauman (JBN) method (Johnson et al., 1959). Fig. 18 compares the relative permeability curves of oil and water phases obtained before and after the nanofluid injection. The irreducible water saturation (S_{wir}) decreased significantly from initial values of 0.63, 0.65, 0.61, and 0.61 to 0.52, 0.51, 0.49, and 0.48 for core plugs C#1 (carbonate), C#2 (carbonate), C#3 (sandstone), and C#4 (sandstone), respectively. This shift in S_{wir} confirms the change in wettability from oil-wet to strongly water-wet. Furthermore, nanofluid injection shifted the crossover point of the water and oil relative permeability curves to the right side of the graph. These

notable changes in the relative permeability curves are attributed to the increased disjoining force between the oil phases and the rock surface, resulting from flooding with the synthesized bio-Zn-QDs.

4. Comparative analysis of Zn-QDs with other NPs for EOR application

Table 4 highlights a comparative analysis between current work and previous studies regarding the types of nanomaterials, concentration, experimental conditions, and performance outcomes. While all studies evaluate nanofluids for enhanced oil recovery under elevated temperature and pressure conditions, the

Table 4
Comparison of the performance of Zn-QDs synthesized in this study with nanomaterials reported in the literature in term of IFT reduction, CA decrease, and oil recovery enhancement.

References		Current work	Zhou et al. (2020)	Jafarbeigi et al. (2022)	Zhao G. et al. (2023)	Zhao et al. (2024)
Corresponding address	Type	Czechia	USA	Iran	China	China
	Nanomaterials	Quantum	Quantum	Nanosheets	Nanoparticles	Quantum
	Name	Zinc oxide (Zn-QDs)	Silicon oxide	Graphene oxide (GONs)	Modified carbon black (MCB)	Amphiphilic silicon (A-SiQDs)
Experimental condition	Concentration	0.03 wt%	0.04 wt%	500 ppm	0.25 wt%	0.1 wt%
	Aqueous phase	Distilled water	Distilled water	Water	Water	Water
	Rock type	Carbonate	Bakken core	Carbonate	Sandstone	Carbonate
	Temperature	75 °C	80 °C	120 °C	130 °C	120 °C
	Pressure	1380 psi	–	–	–	–
Performance evaluation	IFT reduction	71.7%	89.76%	52.3%	99.0%	72.9%
	CA decrease	80.13%	19.3%	65.0%	53.0%	68.9%
	Oil recovery	11.48%	9.13%	19.0%	27.27%	17.0%
Morphology						

selection of nanoparticle type and formulation strategy significantly influences efficiency. Zhou et al. (2020) and Zhao et al. (2024) used silicon oxide (SiQDs) and amphiphilic silicon quantum dots (A-SiQDs), reporting additional oil recovery of 9.13% and 17% OOIP, respectively. As can be seen, SiQDs were more effective in reducing IFT but less effective in altering wettability compared with A-SiQDs. In the current work, zinc oxide quantum dots (Zn-QDs) were employed at an extremely low concentration of 0.03 wt% (300 ppm) in distilled water under conditions of 75 °C and 1380 psi. Despite the relatively mild operational conditions and the lowest concentration among the compared studies, the current formulation achieved high performance, with 71.7% in IFT reduction, 80.13% improvement in wettability alteration, and 11.48% increase in oil recovery. This confirms that Zn-QDs demonstrates a strong reactivity and stability even at low concentration due to their high surface-to-volume ratio and quantum-scale interaction effects.

In contrast, Jafarbeigi et al. (2022) utilized graphene oxide nanosheets at a higher concentration (500 ppm) and under a higher temperature condition (120 °C). Despite the more thermally aggressive conditions, their reported enhancement values in IFT reduction, wettability alteration, and recovery improvement were 52.3%, 65.0%, and 19.0%, respectively (Table 4). Meanwhile, Zhao G. et al., 2023 achieved a stronger recovery outcome (27.27%) by incorporating modified carbon black NPs, which improved nanoparticle dispersion and stability at elevated temperatures. Overall, the comparison demonstrates that nanoparticle type and surface chemistry play a more critical role in determining EOR performance than concentration or operating conditions alone. The Zn-QDs in this study deliver superior stability, dispersibility, and functional impact per unit concentration compared to graphene oxide and silicon-based quantum dots.

5. Economic and environmental analyses

The integration of green nanotechnology in enhanced oil recovery (EOR) offers a sustainable approach to maximizing the efficiency of conventional energy resource utilization. This study, for example, employs parsley-based bio-zinc quantum dots (bio-Zn-QDs) to demonstrate that sustainable nanomaterials can be harnessed to increase oil recovery from carbonate and sandstone reservoirs while addressing environmental and economic challenges. From an economic perspective, the locally available parsley-based green synthesis of Zn-QDs substantially reduces processing and material costs (Bera and Belhaj, 2016; Mariyate and Bera, 2023). Compared to other conventional nanomaterials that require a high energy input, toxic reagents, or a high-tech purification procedure, the green synthesis methodology operates at fairly low temperatures with a water solvent. Such features make the technology more applicable for field activities where budget is limited or sustainability is a must. The significant improvements in oil recovery, up to 22.28% OOIP for carbonate reservoirs and 18.03% for sandstone reservoirs, indicate a high return on investment (Abdulhadi et al., 2025).

The biocompatibility of the synthesized nanodots with formation water, even under elevated salinity conditions, reduces the requirement for extensive water pretreatment or modification, thereby lowering operational costs at the field scale. Moreover, the application of bio-Zn-QDs is aligned with global goals for lower environmental footprints for oil production. Green synthesis avoids the application of toxic chemicals, thus preventing the generation of hazardous by-products or residual contaminants in the reservoir environment. The nanodots themselves are synthesized from biodegradable plant material, contributing to safe long-term subsurface interactions and lower chances of environmental

contamination (Zargar et al., 2020). Application of green nanotechnology boosts crude-oil recovery without surfactants or polymers that degrade to environmentally harmful chemicals under reservoir conditions.

This shift from conventional chemical EOR agents to greener agents indicates a promising pathway toward sustainable hydrocarbon production. The stability of nanofluids across a range of salinities and concentrations, combined with encouraging core-flooding results under representative reservoir pressure and temperature conditions, indicates that this technology is nearing readiness for scaled-up field trials (Tabary et al., 2013). The compatibility of bio-Zn-QDs with various formation water chemistries opens the gateway for broad field application without requiring site-specific chemical redesign.

6. Conclusions

This experimental study evaluated the effect of bio-synthesized Zn quantum dots (bio-Zn-QDs) on enhanced oil recovery (EOR) including interfacial tension (IFT) reduction, wettability alteration, and emulsification from carbonate and sandstone rocks under varying water salinity conditions. The successful synthesis of bio-Zn-QDs was confirmed via SEM, TEM, FTIR, and TGA analyses. The resulting nanofluids demonstrated consistent properties in terms of pH, density, and conductivity, indicating high stability of nanofluids. The nanofluid labeled FW1:1-300 significantly reduced the IFT by 74.3% and shifted the wettability of both rock types from predominantly oil-wet to water-wet. Additionally, the nanofluids were successful in the formation of stable emulsions, particularly at higher bio-Zn-QD concentrations. Meanwhile, the FW1:5-300 nanofluid enhanced oil recovery by an additional 22.27% OOIP from a carbonate core plug. The nanofluids prepared at the optimal dilution rate using formation water exhibited a stronger effect in terms of the wettability alteration and enhancing oil recovery compared with the DW-based nanofluids.

CRedit authorship contribution statement

Sarkar Muheedin Hama: Writing – original draft, Formal analysis, Data curation. **Jagar A. Ali:** Writing – review & editing, Supervision, Project administration. **Abbas Khaksar Manshad:** Supervision, Investigation, Conceptualization.

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.

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