



Experimental Study for Improving Oil Recovery Using Organic Alkaline and Nano-Silica for An Egyptian Oil Field

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Abstract The oil and gas industry continually seeks innovative methods to enhance hydrocarbon recovery due to the declining productivity of conventional techniques. Current recovery methods, such as water flooding and chemical flooding, often face limitations like high interfacial tension, unfavorable wettability, and reduced mobility of oil, especially under harsh reservoir conditions of high salinity. To address these challenges, this study explores the implementation of nanotechnology in enhanced oil recovery (EOR), focusing on the distinct and unique properties of nanoparticles. Nanoparticles, particularly SiO₂, were chosen for their ability to significantly decrease interfacial tension, alter wettability, and improve oil mobility. SiO₂ nanoparticles exhibit high surface area-to-volume ratio, stability under reservoir conditions, and effectiveness in high salinity environments, making them superior to other nanoparticles in this context. This study discusses the modeling and optimization of different flooding scenarios using organic alkaline, ethylenediamine, and SiO₂ nanoparticles under harsh reservoir conditions. Organic alkaline was selected to overcome issues related to inorganic alkaline, such as calcium and magnesium ion precipitation and polymer viscosity reduction. The physical properties of the displacing fluids and crude oil were measured, and flooding runs were tested on a linear sand pack unit using various slug concentrations. Wettability alterations were also observed with different concentrations. Design Expert software was utilized to generate and determine the optimum concentrations. The results demonstrated that the highest oil recovery was achieved with 0.7 wt.% ethylenediamine and 0.02475 wt.% Nano silica. These findings suggest that incorporating SiO₂ nanoparticles in EOR can significantly enhance oil recovery efficiency under challenging reservoir conditions, offering a promising advancement over traditional methods.

Keywords: Ethylenediamine; Nanoparticles; Flooding; Oil Recovery

1. Introduction

Enhanced oil recovery (EOR) techniques are essential for improving hydrocarbon extraction, particularly in challenging reservoir conditions. Traditional methods often face limitations such as high interfacial tension, unfavorable wettability, and reduced oil mobility. (Gomaa et al., 2022). Recent studies have explored the potential of polymers and surfactants to address these challenges. The most common EOR techniques are thermal, chemical, and microbial injection. Thermal injection can be steaming injection, in-situ combustion, and sometimes thermal nitrogen injection (Alaa Taha et al., 2021). The microbial technique is applied by providing certain nutrition to the microorganisms present in the reservoir to produce chemicals such as surfactants (Aboelkhair et al., 2022), polymers, or acids. The most applied EOR technique is chemical flooding such as polymer, surfactant, and alkaline. Polymer flooding technology can be considered one of the most economically attractive known techniques for enhanced oil recovery. This is because when it is used, it can extract a large portion of the amount of oil remaining after the primary stage of recovery as it used for the purpose of enhancing the sweep efficiency (Moussa & Attia, 2016). (Mahran et al., 2018) highlighted the significance of key aspects that needed to be considered when employing a polymer flooding project. These aspects include oil viscosity, the temperature of the reservoir in addition to the type of the formation, and the formation brine salinity. (A. Attia & Canal, 2007) shortened many of the empirical studies that established to demonstrate the effect of using viscous polymer solutions. These experimental studies showed that when there is an increase in the viscosity of polymer solutions, there will, in return, be an increase in the mobility ration between the displacing fluid and the fluid being displaced. Polymers are used to increase the water's viscosity and hence lower its mobility and

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Received date 13 June 2024; revised date 28 July 2024; accepted date 02 August 2024

DOI: 10.21608/EJCHEM.2024.297506.9863

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enhance the sweeping efficiency (Mahran et al., 2022), but then polymer can get adsorbed and encounter chemical and mechanical degradation within HTHS conditions (Elsaied Shima et al., 2021), and some new polymers are used for wettability modification (Soliman et al., 2020). A rheological study by (A. M. Attia & Musa, 2015) investigated the performance of Xanthan gum combined with Sodium Magnesium Silicate at varying temperatures (25°C and 60°C) and salinities (0, 3.4, 10, 15, and 20% NaCl). The results demonstrated that salinity, shear rates, and temperature significantly affect the viscosity and stability of the polymers. Notably, Xanthan gum exhibited high thermal and salinity resistance, which was further enhanced by the addition of Sodium Magnesium Silicate nanoparticles, improving viscosity solutions, shear resistance, and thermal stability. (Gomaa, 2018) found that the natural biopolymer Xanthan gum enhances hydrocarbon recovery but undergoes thermal and microbial degradation under harsh conditions. They grafted Xanthan with poly(acrylamide) to improve its stability and performance in chemical flooding, demonstrating its reliability in EOR through tests on a sand-packed model. Surfactants are another key component in EOR, reducing interfacial tension (IFT) and altering wettability. However, their high cost and potential for adsorption pose challenges (Azmi et al., 2022). (Samanta et al., 2009) evaluated surfactant-polymer slugs and observed promising additional recovery rates of 20% for surfactant flooding and 23% for surfactant-polymer flooding, using Sodium dodecyl sulfate and partially hydrolyzed polyacrylamide. Alkaline flooding can be used on large scale, but it is better to merge it with surfactant in order to be more effective and operative (Aurel Carcoana, 1992). Alkaline flooding, which forms in-situ surfactants by reacting with crude oil acids, offers a cost-effective alternative to surfactant flooding. Alkaline's mechanisms include emulsion and entrapment, wettability reversal, and mobility control, enhancing oil recovery by increasing the capillary number and improving vertical and areal sweep efficiency (Arhuoma et al., 2009; Homof et al., 1994; Johnson, 1976; Kumar Sharma et al., 2023; H. Pei, Zhang, Ge, Jin, & Ma, 2013; Sheng, 2015; Zhou et al., 2022). Emulsion and entrainment; where oil can move along with the alkaline flow that can be trapped in the pore throat that is too small for an emulsified oil droplet to fit in, which reduces the mobility of the water and improves the vertical and areal efficiency. Wettability reversal from oil-wet to water-wet; by decreasing the contact angle where oil becomes the continuous phase creating a favorable mobility ratio and increasing the recovery of oil (Hincapie et al., 2021; Mamonov et al., 2018). Wettability reversal from water-wet to weakly oil-wet makes the oil phase a continuous phase and blocks the water channeling also leading to increasing the recovery of oil. Any of these 4 mechanisms can enhance the sweep efficiency of the crude oil to increase its production, and along with these benefits alkaline is a cheap chemical which makes it more desired. There are 2 types of alkaline chemicals organic and inorganic, the most used ones in the oil industry is the inorganic types like sodium carbonate and sodium hydroxide. Some results showed that sodium hydroxide was the most efficient inorganic alkaline chemical (Almalik et al., 1997; Dong, 2011; El-Sayed et al., 1996) but on the other hand, some other results showed that sodium carbonate was the most efficient inorganic alkaline chemical used (H. Pei, Zhang, Ge, Jin, & Ding, 2013; Sun et al., 2008). Sodium metaborate can also be used and increase the recovery of oil (Tang et al., 2013). If the formations contain a high content of calcium and magnesium ions inorganic alkaline causes precipitation of calcium and magnesium salts that damage the formation, so organic alkaline like ethylenediamine, and ethanolamine can be used in such cases (Fu et al., 2016), and if alkaline is being used with polymer, then using organic alkaline would be better as it wouldn't decrease the polymer's viscosity like inorganic alkaline (Chen et al., 2015). One of the problems that can also face alkaline chemicals is adsorption as it can cause losses in its concentration that can reach to up to 50% (Ulas, turksoy & Bagci, 2000). The majority of alkaline floodings are applied during tertiary recovery, but some results showed that applying it during secondary recovery increases the recovery of oil more (El-Hoshoudy et al., 2019; Homof et al., 1994).

Alkaline flooding can be associated with other chemicals such as polymer to provide mobility control (Hincapie et al., 2022; Wang et al., 2022), surfactant to ensure achievement of ultralow (H. H. Pei et al., 2012) and reduce surfactant's adsorption (Campbell, 1982), and co-solvent to improve the solubility of the alkaline to form ultralow IFT and low viscosity emulsion ((Li et al., 2023). Dispersed particle gel strengthened alkali is used as novel combination flooding system, which is polymer with crosslinker and alkaline, it showed very promising results regarding the recovery of oil than alkaline flooding only or polymer-alkaline flooding as its viscosity retention is low and plugs the narrow pores to control high permeable channels (Wang et al., 2022).

In a study presented by (Sayyoub et al., 1993) on the effect of combining alkaline along with the polymer after equilibrium was accomplished at temperatures of 25°C and 70°C, on the behavior of the Petrostep HMW surfactants phase in oil-brine systems, the investigation of this study showed that as the temperature increased from 25°C to 70°C while using the isopropyl alcohol, the miscibility decreased. Conversely, the miscibility increased when the NaOH concentration was raised from 0.5% to 1.0%. Moreover, as the NaCl concentration escalated from 3.84% until reaching 23%, the miscibility decreased.

Recently nanoparticles are introduced to the oil induction and its effect on the recovery of oil was tested (Sircar et al., 2022) and most common type used is nano silica as it increases the viscosity of water, reduces the contact angle, and increases the recovery of oil as it can get into microchannels and displace the crude oil from them (Goharzadeh & Fatt, 2022). Accurate concentrations of nano particles should be applied as high concentrations damage the formation (Elyaderani et al., 2019). Nano particles is mostly used along with other chemicals like alkaline and polymer to enhance their properties more and

recovery more oil (Gong et al., 2022; Salem et al., 2021). (Zargartalebi et al., 2015) introduced research to study the effect of the use of nanoparticles on the properties of the surfactant, after the combination of both silica nanoparticles and an anionic surfactant. Moreover, this research also aimed to analyze the potential of these nanoparticles to boost hydrocarbon recovery. A series of tests were conducted to measure both adsorption and interfacial tension. These implemented tests came up with an observation that when the surfactant mixed with the nanoparticles, its adsorption decreased. Additionally, at high and low concentrations of surfactants, the results of the interfacial tension measurements give out strange behavior. Afterward, the hydrocarbon recovery improved by a noticeable amount as the implemented flooding tests demonstrate that by improving the governing mechanisms, the performance of the surfactant can be enhanced when using the nanoparticles.

Building on these findings, our study explores the combined use of organic alkaline, ethylenediamine, and SiO₂ nanoparticles in EOR under high salinity conditions. By leveraging the unique properties of SiO₂ nanoparticles to decrease interfacial tension and alter wettability, we aim to improve oil recovery efficiency significantly. This research seeks to address the current gaps and limitations in EOR techniques, providing a novel approach to enhance hydrocarbon extraction in challenging environments.

2. Methodology

The methodology is shown in Figure 1. It included experimental design, model setup, and measurements of sand properties.

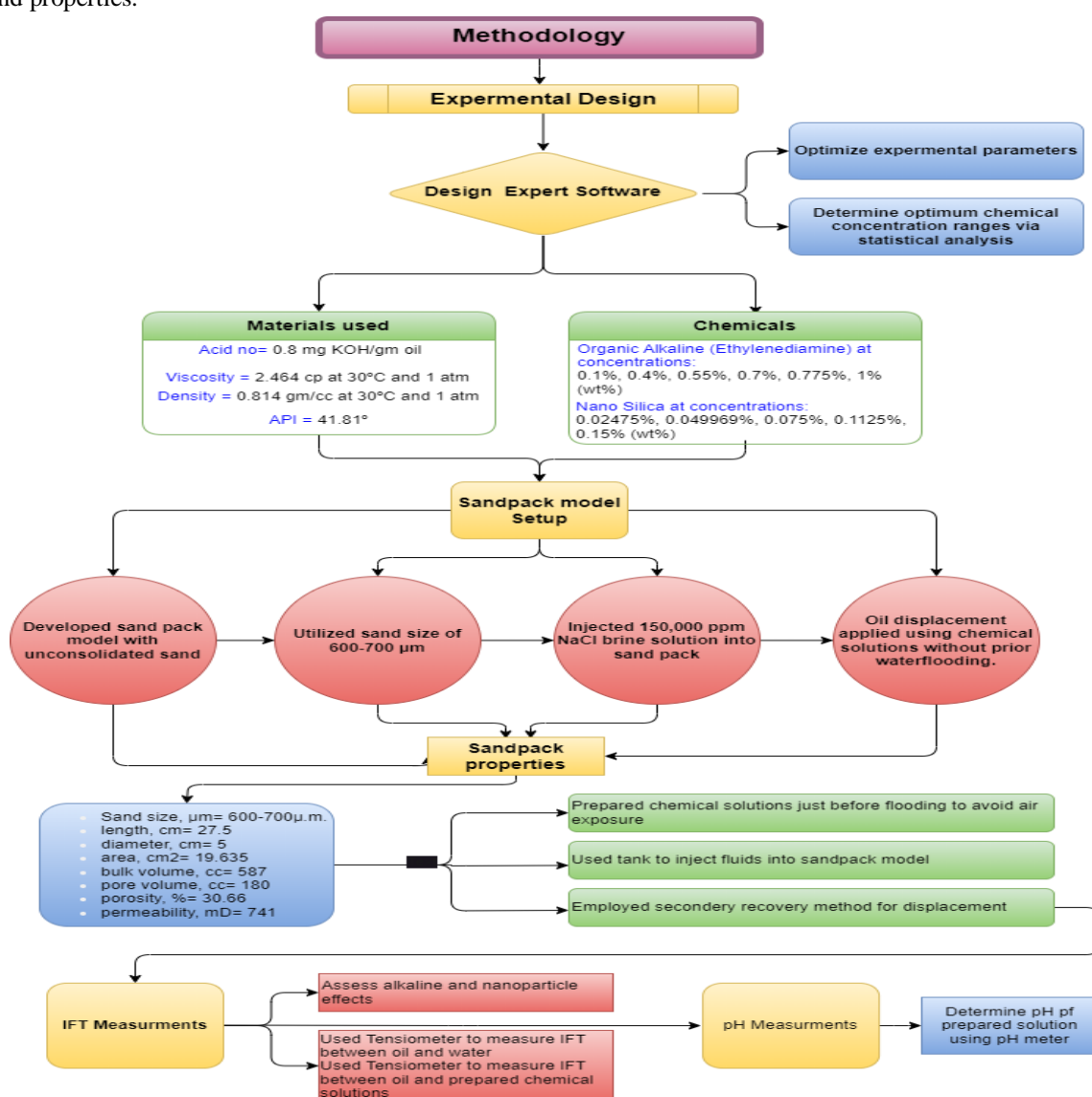


Fig. 1. Methodology Flowchart

2.1. Design Expert Software

Design Expert software was used to generate the optimal experimental design in addition to the gathering and entry of data. Moreover, this software has good potential to make a sufficient model and a reliable statistical analysis along with the entered factors in order to know the optimal chemical concentrations required to perform this study.

2.2. Chemicals

One type of organic alkaline was used which is ethylenediamine with concentrations of 0.1, 0.4, 0.55, 0.7, 0.775, and 1 wt%. This is due to the fact that ethylenediamine solves two major challenges that faces inorganic alkalines as it solves the precipitation of calcium and magnesium ions, which causes formation damage and reduces the permeability in addition to the reduction of polymer viscosity when the inorganic alkalines used with polymer. On the other side, also one type of nanoparticle was used which is Nano silica with concentrations of 0.02475, 0.049969, 0.075, 0.1125, and 0.15wt.%. The usage of these nanoparticles improves the trapped oil mobility along with sand consolidation, while also reducing the interfacial tension and altering the wettability. This is due to the unique properties of these nanoparticles that can be provided an additional control over the situation of the reservoir.

2.3. Oil Samples

Table 1: Oil sample specifications

Density (g/cc)	API Gravity (° API)	Viscosity, (cP) @ 25 ° C	Acidity number (mg KOH per g of crude oil)
0.814	41.81	2.464	0.8

Table 1 shows the specifications of the oil sample used. These specifications include the crude oil sample density of 0.814 grams per cubic centimeter and API gravity of 41.81° in addition to viscosity of 2.464 centipoises and acidity number of 0.8 per milligram of KOH per gram of crude oil.

2.4. Displacement Apparatus

The diagram of the displacement apparatus is shown in figure 2. It consists of a sand pack with all its specifications mentioned in table 2. It includes filters and screens placed at the outlet of the sand pack model to prevent outbreak of the porous medium. One tank is used to inject fluids into the sand pack model. The inlet of the sand pack is connected to a pressure regulator to measure and control the inlet pressure.

Table 2: Sand pack specifications

Properties, unit	Values
sand size, μm	650 μm .
length, cm	27.5
diameter, cm	5
area, cm^2	19.6
bulk volume, cc	587
pore volume, cc	180
porosity, %	30.66
permeability, mD	741

2.5. Displacement Procedures (Chemical Flooding)

The sand pack model is saturated with 150,000 ppm NaCl brine solution and oil is then injected to displace the brine solution to immobile water saturation. The displacement mechanism applied is secondary recovery, injecting the chemical solutions directly without conducting waterflooding first. The preparation of the chemical solutions takes place just before the flooding to avoid air exposure and precipitation effects.

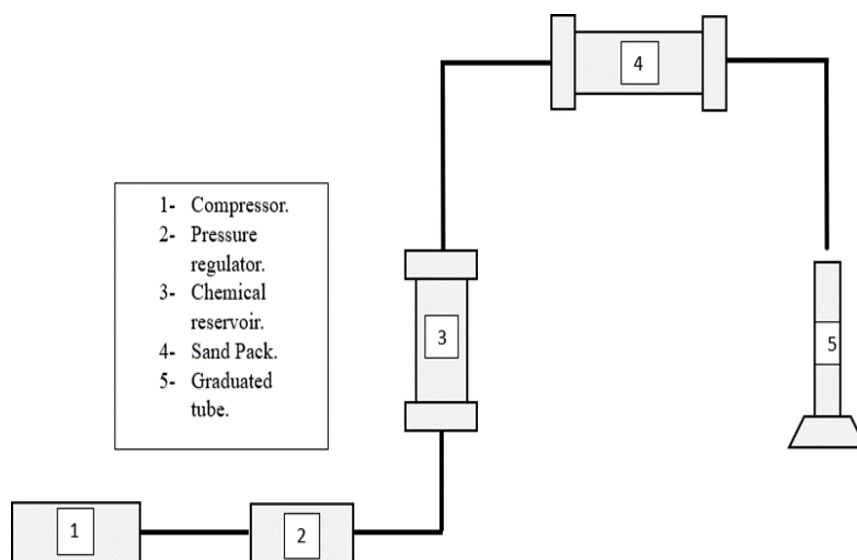


Fig. 2: Displacement set-up

2.6. IFT Measurements

IFT reduction is one of the main effects of alkaline and nanoparticles. So, a Tensiometer was used to measure the IFT between oil and water, and the IFT between oil and the prepared solutions to compare the effectiveness of IFT reduction.

2.7. pH Measurements

The pH of the prepared solution was determined using pH meter.

3. Results and Discussion

3.1. IFT behavior between crude oil and different chemical systems.

The initial interfacial tension (IFT) between the oil and water was measured at 39.18 mN/m. Figure 3 illustrates that the addition of ethylenediamine reduces the IFT. As the concentration of ethylenediamine increases, the IFT continues to decrease. Similarly, the use of nanoparticles decreases the IFT between the oil and water, which enhances oil mobility and increases oil recovery. Figure 4 shows that the addition of nano-silica also reduces the IFT. However, unlike ethylenediamine, the relationship between nano-silica concentration and IFT is non-linear. As the concentration of nano-silica increases, the IFT initially decreases and then increases after reaching an optimum point.

The combined use of ethylenediamine and nano-silica at their optimal concentrations further reduces the IFT to 8.612 mN/m. The reduction in IFT is primarily due to the reaction between the alkaline and the organic acids in the oil, generating in-situ surfactants. These surfactants lower the IFT between water and oil, causing emulsification and altering the rock's wettability. Improved wettability, transitioning from oil-wet to water-wet, significantly enhances oil recovery. Tables 3 and 4 present the specifications and results of the experiments with ethylenediamine and nano-silica, respectively. These tables detail the IFT measurements at various concentrations, demonstrating the effectiveness of both additives in reducing IFT and improving oil recovery.

Table 3: IFT between various OA concentrations and oil

Concentration of the alkaline(mg/g)	1	4	5.5	7	7.75	10
IFT	22.6	19.3	18.3	15.5	10.79	8.9

Table 4: IFT between various Nano Silica concentrations and oil

Concentration of Nano Silica (mg/g)	0.2475	0.49969	0.75	1.125	1.5
IFT	26.09	14.56	10.78	8.612	17.46

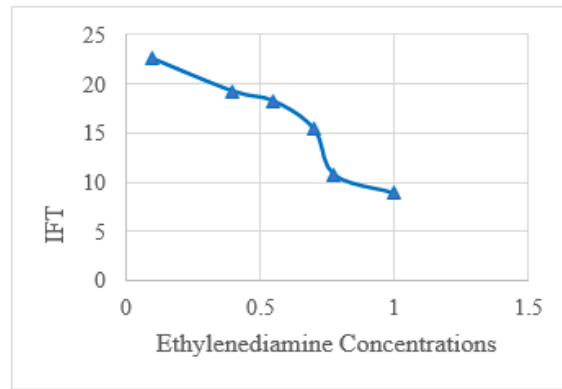


Fig. 3: IFT vs ethylenediamine concentration

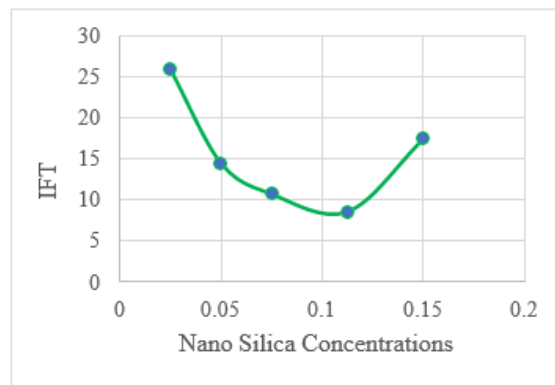


Fig. 4: IFT vs Nanosilica concentration

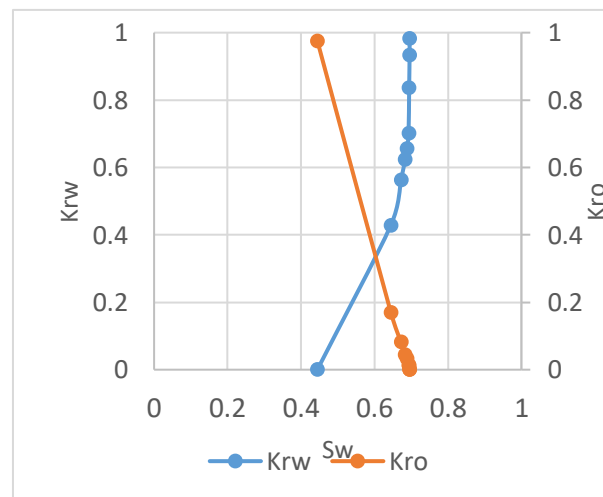


Fig. 5: Relative permeability curve of waterflooding

3.2. Effect of chemicals on rock wettability

Figure 5 illustrates the relative permeability curves (K_{ro} and K_{rw}) as a function of water saturation (S_w) for the water flooding run. The intersection point of the K_{ro} and K_{rw} curves occurs at $S_w = 0.6$, indicating that the sand pack model is originally water-wet.

In general, if the intersection of the K_{ro} and K_{rw} curves occurs at a water saturation (S_w) greater than 50%, the rock is considered water-wet. The farther this intersection point is above 50% S_w , the more water-wet the rock is. This water-wet condition implies a lower residual oil saturation because water can more effectively displace oil from the pore spaces in the rock.

Table 5: Sw at Kro=Krw for OA

Concentration of the alkaline (mg/g)	1	4	5.5	7	7.75	10
Sw atKro = Krw	0.73	0.71	0.72	0.76	0.7	0.75

Table 6: Sw at Kro=Krw for Nano Silica

Concentration of Nano Silica (mg/g)	0.2475	0.49969	0.75	1.125	1.5
Sw atKro = Krw	0.71	0.64	0.65	0.67	0.78

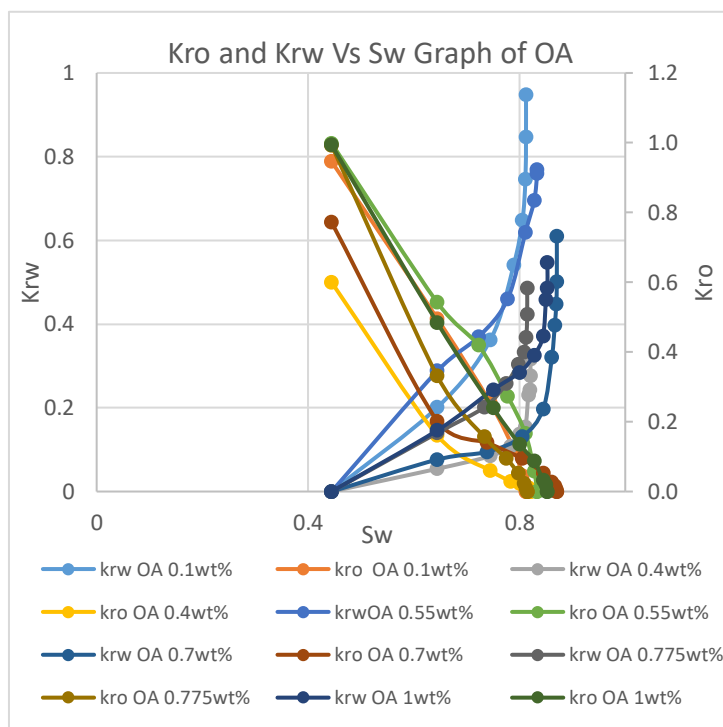


Fig. 6. Relative permeability curve of various OA concentrations

In the ethylenediamine floods the intersection shifts more to the right so the wettability of rock becomes water wet and the best wettability is achieved by 7mg/g ethylenediamine as Sw at the intersection of Kro and Krw is equal to 0.76.

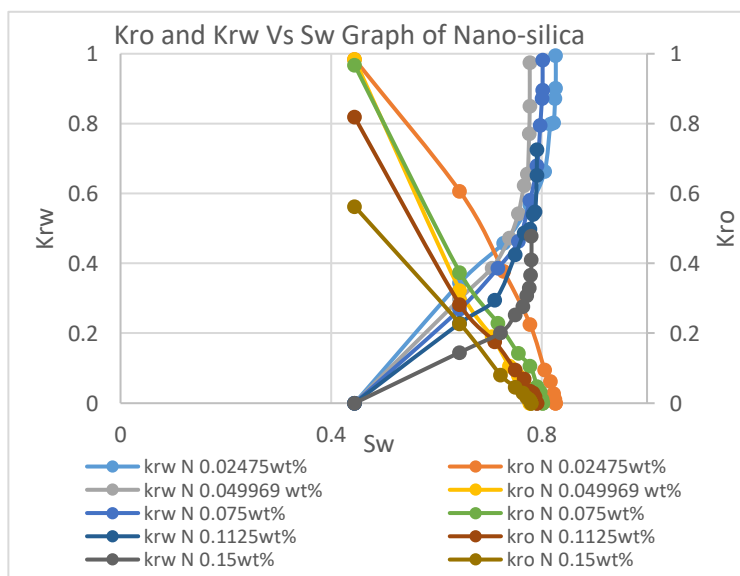


Fig. 7. Relative permeability curve of various nano silica concentrations

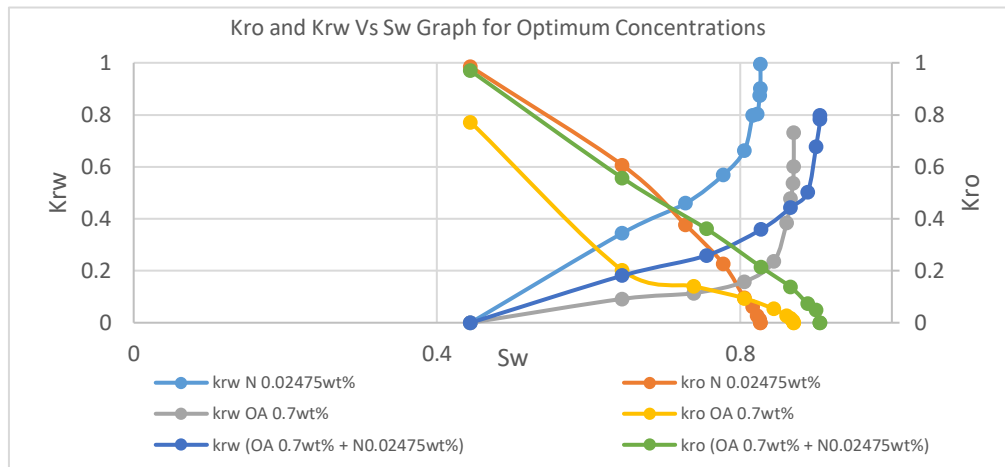


Fig. 8. Relative permeability curve of optimum concentrations

In Figure 7, the nano-silica floods the intersection shifts more to the right, so the wettability of rock becomes more water wet and the best wettability is achieved by 1.5mg/g nano silica so Sw at the intersection of Kro and Krw is equal to 0.78. In Figure 8, the optimum concentrations of organic alkaline and nano-silica gave the best shift of the intersection to the right, so Sw at the intersection is equal to 0.79.

3.3. Effect of Nano Silica concentration on the pH value

In Figure 9, the value of pH increases as the alkaline concentration increases. Figure 10 indicates that as the concentration of the nano-silica increases, the value of pH decreases. This is because of the neutral acidic nature of the nano-silica.

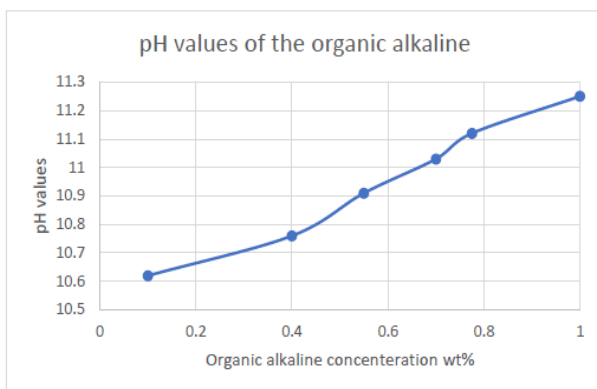


Fig. 9: pH values of various OA concentrations

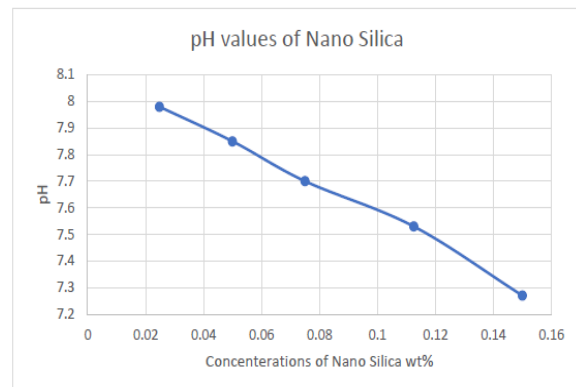


Fig. 10: pH values of various Nano Silica concentrations

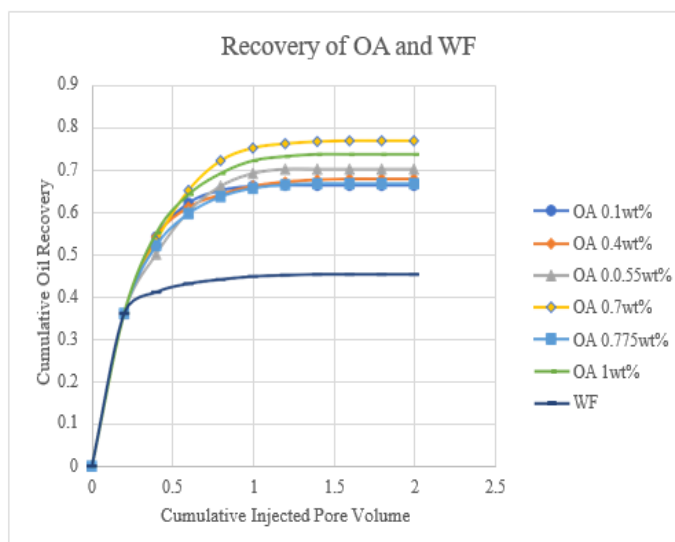
3.4. Effect of different chemicals on recovery of the oil

The lowest oil recovery was achieved by waterflooding and by adding the chemicals the recovery increased, the highest oil recovery was achieved by 7 (mg/g) organic alkaline and 0.2475 (mg/g)-silica. Combining the optimum concentrations of these two chemicals provided the best recovery results.

Table 7: Flooding tests results of Secondary Oil Recovery

Injected fluid	Saturation(%PV)			Recovered Oil (cc)	Oil recovery (% OOIP)
	Soi	Swc	Sor		
Brine	55.56	44.44	30.44	45.2	45.2
			18.78	66.2	66.2
			17.9	67.77	67.77
Organic Alkaline	55.56	44.44	16.67	70	70
			12.94	76.7	76.7
			18.56	66.6	66.6
			14.72	73.5	73.5
			17.33	68.8	68.8
NanoParticles	55.56	44.44	22.28	59.9	59.9
			19.83	64.3	64.3
			20.94	62.3	62.3
			21.94	60.5	60.5
Nano silica with ethylenediamine	55.56	44.44	9.4	83	83

These nanoparticles can cause formation damage when they are used in high concentrations as the concentration of the nanoparticles has no effect on the oil recovery since it precipitates rapidly when their concentrations increase. Furthermore, it has a high resistance to degradation in reservoirs with high temperatures and salinities.

**Fig. 11: Recoveries obtained from organic alkaline compared to waterflooding**

Conclusion

Based on the experimental results of this work, the following conclusions can be reached:

- As the concentration of organic alkaline increases, the IFT decreases.
- The recovery of the oil decreases with increasing the concentration of the nanoparticles, but the recovery of the oil increases then decreases with increasing the concentration of the organic alkaline.
- As the concentration of organic alkaline and nanoparticles increases the wettability tends to be more water wet.
- Combining the optimum concentrations of organic alkaline and nanoparticles, the recovery of the oil and obtained the lowest IFT and altered the wettability to be strong water wet, obtained the highest oil recovery, and provided the best displacement efficiency.
- The oil recovery depends more on the wettability than the IFT.
- As the concentration of the Nano silica increases the IFT decreases then increases.
- The addition of both nano silica and organic alkaline enhanced the displacement efficiency.

4. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work presented in this paper.

5. Acknowledgments

We would like to extend our sincere gratitude to all the researchers, scientists, and industry professionals whose contributions and insights have enriched the contents of this paper. Their dedication to advancing the field of enhanced oil recovery has been instrumental in shaping this comprehensive review. We also acknowledge the support and resources provided by the British University in Egypt that have facilitated the completion of this study.

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