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Original Paper

# Experimental investigation into effects of the natural polymer and nanoclay particles on the EOR performance of chemical flooding in carbonate reservoirs

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A B S T R A C T

This paper aims to investigate the tragacanth gum potential as a natural polymer combined with natural clay mineral (montmorillonite, kaolinite, and illite) nanoparticles (NPs) to form NP–polymer suspension for enhanced oil recovery (EOR) in carbonate reservoirs. Thermal gravimetric analysis (TGA) tests were conducted initially in order to evaluate the properties of tragacanth gum. Subsequently, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) tests were used to detect the structure of clay particles. In various scenarios, the effects of natural NPs and polymer on the wettability alteration, interfacial tension (IFT) reduction, viscosity improvement, and oil recovery were investigated through contact angle system, ring method, AntonPaar viscometer, and core flooding tests, respectively. The entire experiment was conducted at 25, 50, and 75 °C, respectively. According to the experimental results, the clay minerals alone did not have a significant effect on viscosity, but the addition of minerals to the polymer solution leads to the viscosity enhancement remarkably, resulting mobility ratio improvement. Among clay NPs, the combination of natural polymer and kaolinite results in increased viscosity at all temperatures. Considerable wettability alteration was also observed in the case of natural polymer and illite NPs. Illite in combination with natural polymer showed an ability in reducing IFT. Finally, the results of displacement experiments revealed that the combination of natural polymer and kaolinite could be the best option for EOR due to its substantial ability to improve the recovery factor.
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## 1. Introduction

The global demand for hydrocarbon energy continues to rise, highlighting the paramount importance of oil and gas reservoirs in the energy sector. With primary and secondary recovery methods leaving a substantial amount of oil trapped within reservoirs, EOR strategies have garnered significant attention to reduce residual oil saturation (Li et al., 2017; Rezvani et al., 2018). Among EOR methods, water flooding stands out for its cost-effectiveness and widespread applicability, drawing interest in innovative techniques to optimize its efficiency.

Recent advancements have explored various dimensions of water flooding, including low salinity and smart water injection, as well as hybrid approaches (Yousef and Ayirala, 2014; Hassani et al., 2016, 2022, 2023; Ayirala et al., 2018; Al-Kharusi et al., 2018; Abhishek et al., 2018; Veiskarami et al., 2020; Mahboubi Fouladi et al., 2021; Shi et al., 2021; Hassani, 2022; Abdullahi et al., 2022). These methodologies hinge on pivotal factors like wettability alteration, IFT reduction, and viscosity enhancement (Yassin et al., 2015; Hassani et al., 2021; Chen et al., 2021; Horeh et al., 2022; Cheng et al., 2022). To reinforce these mechanisms and amplify oil recovery, the incorporation of chemical additives has emerged as a promising avenue. Surfactants and NPs impact wettability and IFT, while polymers bolster sweep efficiency (Elkady, 2016; AlSofi et al., 2018; Khaleel et al., 2019). Increasing capillary number reduces remaining oil saturation and improves recovery (Jeong, 2005).

Amid these efforts, the introduction of water-soluble polymers into the injection fluid has proven pivotal in controlling water viscosity, thereby curbing finger-like displacements, minimizing

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water cut, and optimizing relative permeability (Firozjaii and Saghafi, 2020). The mobility ratio in the flooding process should be less than one to prevent the fingering and different types of polymers are highly regarded for their ability to dramatically increase viscosity and decrease mobility ratio (Kumar et al., 2008). Synthetic polymers like hydrolyzed polyacrylamide (HPAM) and biopolymers such as xanthan gum have long served the industry, yet temperature and salinity sensitivity restrict their application (Wang et al., 2010; Kamal et al., 2015). Also, chemical methods have a severe reduction in permeability after injection and block the pore throats by adsorption and deposition inside the reservoir rock (da Silva et al., 2007; Olajire, 2014). In enhancing polymer rheology under reservoir conditions — characterized by high pressure, temperature, and salinity — the incorporation of NPs emerges as a solution. NPs have gained traction in EOR research, augmenting injected fluid quality for improved outcomes over conventional methods. NPs contribute to EOR through diverse mechanisms, including IFT reduction, emulsification, and wettability alteration (Suleimanov et al., 2011; Roustaei et al., 2012; Joonaki and Ghanaatian, 2014; Dahkaee et al., 2019; Zhu et al., 2021). NPs have risen as a viable solution, imparting enhanced stability and improved rheological properties under reservoir conditions (Maghzi et al., 2014; Cheraghian et al., 2015; Khalilinezhad et al., 2016; Rezaei et al., 2016; Rahimi et al., 2018; Abdullahi et al., 2019). Notably, NPs navigate small pores without permeability loss (Rodriguez et al., 2009; Yu et al., 2012).

NPs have shown their potential in altering wettability and reducing IFT in oil recovery. Roustaei et al. (2012) reported 90% oil recovery using silica NPs in sandstone cores. $SiO_2$ NPs demonstrated superior wettability effects compared to $Fe_2O_3$ and $Al_2O_3$ (Joonaki and Ghanaatian, 2014). Mahmoudpour et al. (2022) highlighted viscosity enhancement of $SiO_2$ NPs in smart water injection. Esfandyari Bayat et al. (2014) observed wettability alteration and reduced IFT in carbonate formations using $Al_2O_3$, $TiO_2$, and $SiO_2$ NPs, achieving 9.9% oil recovery with $Al_2O_3$ (60 °C). High NP concentrations were found to diminish rock permeability (Maghzi et al., 2012; Hendraningrat et al., 2013), advocating low-concentration NPs in low-salinity fluids. Silica NPs at 0.1 wt% improved oil recovery beyond conventional water flooding, with a critical concentration of 3 wt% (Maghzi et al., 2012). Hendraningrat et al. (2013) noted increased contact angle and IFT reduction with rising nanofluid concentration, with the optimal concentration for oil recovery at 0.05 wt%. Nonetheless, combining polymers and NPs comes with challenges like costly synthesis, substantial injection volumes, and compatibility issues (Cheraghian et al., 2020). Thus, turning to natural polymers and NPs emerges as an eco-friendly alternative.

Cheraghian et al. (2015), Rahimi et al. (2018) and Rezaei et al. (2016) emphasized that incorporating montmorillonite particles with polyacrylamide improves rheology, increasing viscosity while counteracting temperature and salinity impacts on polymer structure, ultimately EOR. Keykhosravi et al. (2021) found that the injection of $TiO_2$/xanthan gum polymer into carbonate reservoirs led to 25% extra oil through IFT reduction and wettability alteration. Effects of tragacanth gum as a natural polymeric surfactant were assessed by Nowrouzi et al. (2020), demonstrating increased water viscosity and 21.4% recovery improvement at high concentrations of polymeric surfactant—alkali solution. However, the influence of tragacanth on wettability remains unexplored despite studies of IFT, viscosity, and recovery factors.

Considering economic factors in EOR, our study examines the synergy of cost-effective natural clay particles and polymers, specifically montmorillonite, kaolinite, and illite NPs. Unlike chemical additives, which often pose sensitivity to temperature and salinity, these natural compounds offer promising solutions for EOR challenges. Investigating their impact on water flooding dynamics, wettability, and rheology, we contribute to a holistic EOR understanding. Core flooding experiments reveal practical efficacy, aiming to identify an optimal formulation for IFT reduction, enhanced viscosity, and modified wettability.

## 2. Materials

### 2.1. Brines and crude oil

Brine (formation brine (30 g/L) and displacement brine (10 g/L)) were made artificially by dissolving a certain amount of NaCl in deionized water (DIW). NaCl salt from Merck Company with 99% purity was used. Our decision to utilize NaCl in our simulated formation water was driven by the need for simplicity and control. By focusing on a straightforward salt, such as NaCl, we could establish a controlled baseline for our research, isolating the effects of particles and polymers. While acknowledging the limitations of this simplified approach, we believe it was a crucial initial step to investigate fundamental interactions before delving into more complex ion compositions found in actual reservoir conditions. In this study, the crude oil used was from one of Iranian oil fields, with a density of 0.8401 g/cm$^3$, a viscosity of 6.0453 cP, and an API gravity of 36.93°.

### 2.2. Natural polymer

Tragacanth gum was used as a natural polymer for EOR application. It is a colorless polymer obtained from Astragalus plant of the species *microcephalus*. The polymer is prepared by Tabib Daru Company (Iran) and its composition is listed in Table 1 ("https://Tabibdaru.Com/," n.d.). The details of polymer structure are present by Nowrouzi et al. (2020).

According to TGA analysis (Fig. 1), the weight loss of 12% occurred at a temperature of about 150 °C. This initial weight loss is due to the evaporation of water and the decomposition of the polymer into smaller molecules. The second weight loss occurred at a temperature of about 200–300 °C, which ultimately shows a weight loss of 45%. With these interpretations, the use of natural polymer is unrestricted at reservoir temperatures.

### 2.3. Clay particles

Three commercial types of mineral clay NPs including montmorillonite, kaolinite, and illite were purchased from SunClay Therapy Co. (France). Scanning electron microscopy (SEM, Tescan, Mira III model) and energy-dispersive X-ray (EDX) spectroscopy (Hitachi, model SU8020) were used to determine the particle size and atomic structure, as shown in Figs. 2 and 3. Montmorillonite NPs have a cornflake morphology with a molecular structure that is mainly composed of K, O, Na, Si, Al, Ca, and Au elements. Kaolinite NPs, on the other hand, had a booklet morphology. And their main

**Table 1**
The composition of the natural polymer used.

| Component | Content, % |
|---|---|
| Arabinose | 35 |
| Galacturonic acid | 21 |
| Xylose | 19 |
| Glucose | 10 |
| Fucose | 9 |
| Rhamnose and galactose | 3 |
| Potassium, calcium, sodium, magnesium, iron, and zinc | < 3 |

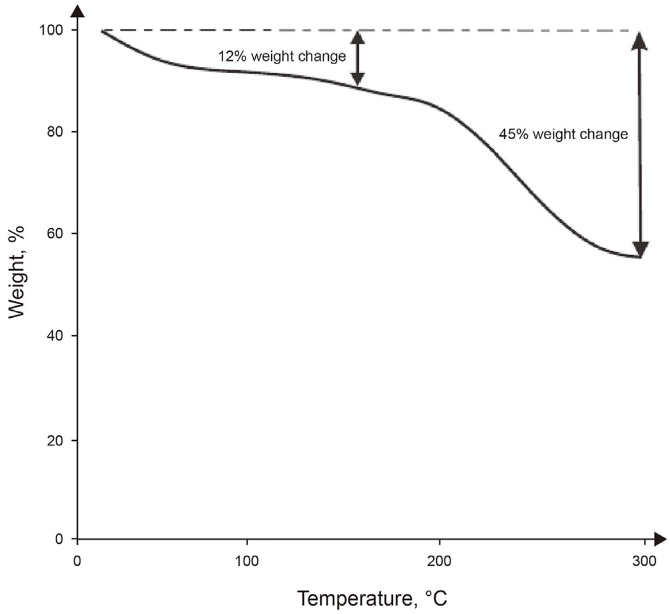


**Fig. 1.** TGA curve of the natural polymer used.

constituent elements are Fe, O, Si, Al, K, Ca, Cr and Au. Analyses of SEM and EDX on illite NPs also show that they have a fiber morphology with a molecular structure consisting of the elements Fe, O, Si, Al, Mg, K, and Au.

### 2.4. Fluid preparation

By dissolving 30 and 10 g of NaCl in 1000 mL of DIW, formation brine and displacement brine were prepared.

Montmorillonite, kaolinite, and illite suspensions were prepared by adding 0.05 g of each clay mineral NPs to 1000 mL of 0.1 wt% NaCl solution. The suspensions were first stirred for 1 h by a mechanical mixer and then ultra-sonicated for another hour using an ultrasonic processor (Hielscher UP400s).

To prepare the solution, natural polymer was first pulverized by the Bosch Mill MKM6000 and its critical micelle concentration (CMC) in 0.1 wt% NaCl solution was obtained by IFT measurement. The powder at CMC was then added to 1000 mL of 0.1 wt% NaCl solution and stirred for 2 h at 250 rpm through a mechanical stirrer. The mixture was then kept under pressure at 5 °C for 24 h.

To prepare NP–polymer suspensions, natural polymer at CMC was added to the pre-prepared NP suspensions and then stirred at 250 rpm through a mechanical mixer and kept at 5 °C for 24 h under pressure. The compositions of different fluids are listed in Table 2.

### 2.5. Porous media

A sample of limestone from the outcrop was used as the porous medium in this study. First, the limestone blocks were broken into smaller pieces and then pulverized by a crusher (BICO powder type). Limestone powder was subsequently sieved through 125- and 200-μm sieves. The sifted powder was then pretreated by a sequential water rinse, ultra-sonication, and drying in an oven at 100 °C to remove impurities. The refined limestone powder was packed in a stainless-steel tube with an inner diameter of 1.7 cm and a length of 30 cm. A 50-μm mesh filter was placed at both ends of the tube to prevent the migration of limestone grains during the displacement process. The porosity and permeability of the

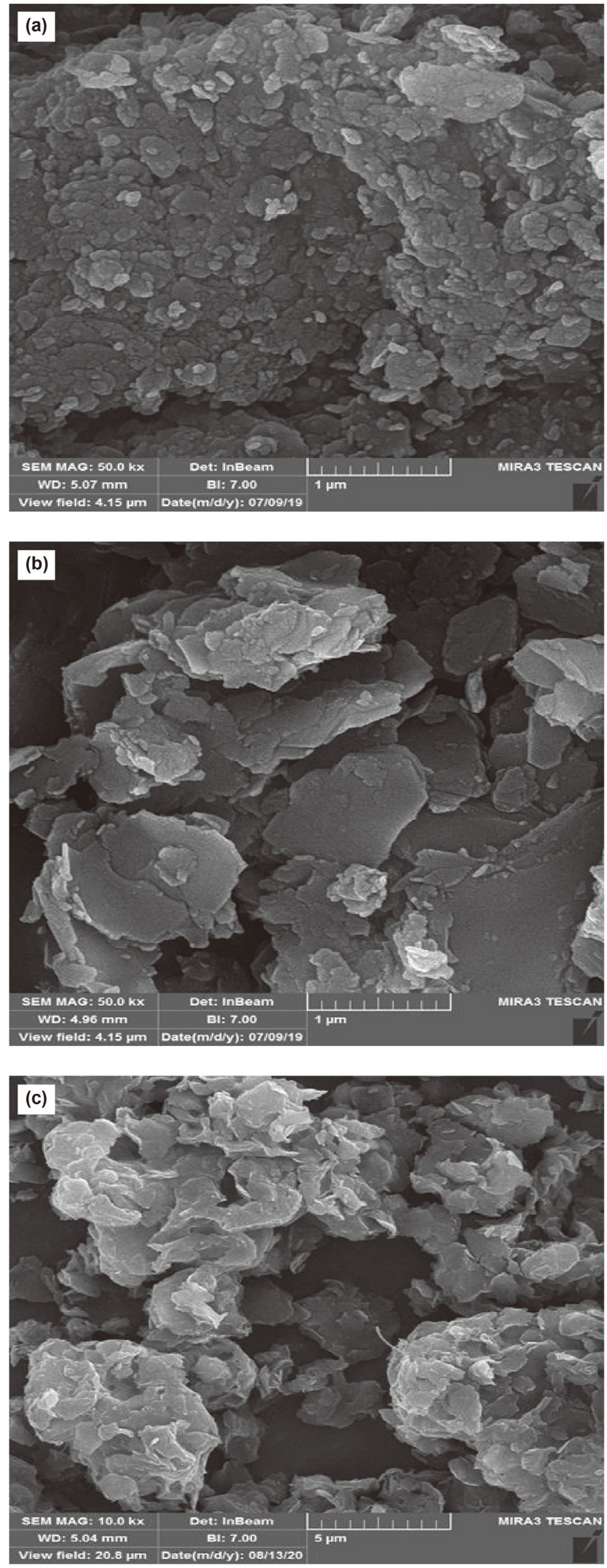


**Fig. 2.** SEM images of illite (**a**), kaolinite (**b**), and montmorillonite (**c**).

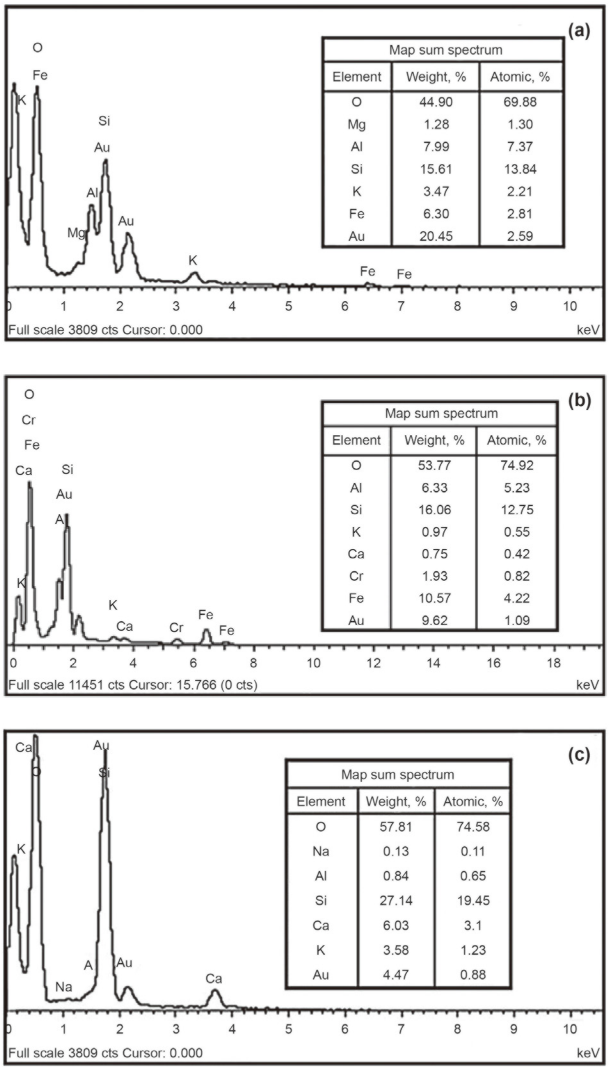


**Fig. 3.** EDX results of illite (**a**), kaolinite (**b**), and montmorillonite (**c**).

limestone pack were measured before each experiment with deionized water. The limestone pack was placed vertically in all experiments. X-ray diffraction (XRD) analysis was also performed on limestone powder to determine limestone components using a diffractometer (Phillips PW1730) (Fig. 4).

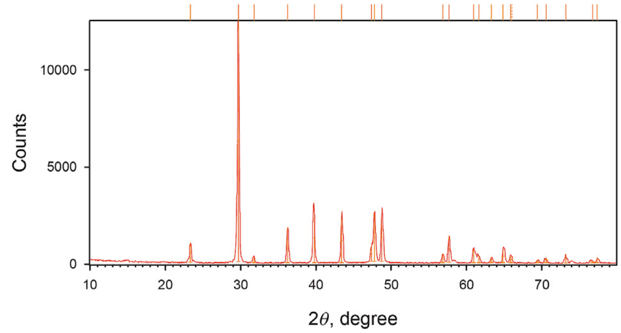


**Fig. 4.** XRD pattern of limestone.

## 3. Experimental apparatus and procedures

Different laboratory systems were used to evaluate the effectiveness of different mechanisms in this process. Viscosity measurements were used to assess mobility ratio, contact angle to check for wettability alteration, IFT experiments, and flood tests to analyze the effect of NPs and polymer on the recovery factor. It should be noted that all measurements were performed at temperatures of 25, 50, and 75 °C. The devices used will be introduced below.

### 3.1. Viscosity test

The viscosity and density of the prepared suspensions were tested using a rotary viscometer (AntonPaar SVM3000). Using this device, fluid viscosity can be measured in the range of 0.2–20,000 mPa s and the temperature can be defined from −56 to 152 °C.

### 3.2. IFT measurement

IFT between suspensions and oil used was measured using DataPhysics DCAT9 instrument (ring method).

### 3.3. Wettability measurement

The wettability of the limestone sample in the presence of the oil and the clay–polymer fluids was evaluated using a series of contact angle measurement tests.

For this purpose, core plugs of the limestone rock with a diameter of 5 cm and a thickness of 2 cm were cut and polished and then immersed in different fluids at different temperatures. The cores were placed vertically in the fluids to prevent deposition of particles on the surface. Hence, the change in wettability can only occur as a result of the adsorption of clay minerals on the surface of

**Table 2**
Fluid compositions.

| Fluid | Concentration, wt% | | |
|---|---|---|---|
| | NaCl | Clay particle | Natural polymer |
| Saturation brine | 3 | – | – |
| Displacement brine | 1 | – | – |
| Illite clay particle | 0.1 | 0.005 | – |
| Kaolinite clay particle | 0.1 | 0.005 | – |
| Montmorillonite clay particle | 0.1 | 0.005 | – |
| Natural polymer | 0.1 | – | 0.1 |
| Natural polymer and illite clay particle | 0.1 | 0.005 | 0.1 |
| Natural polymer and kaolinite clay particle | 0.1 | 0.005 | 0.1 |
| Natural polymer and montmorillonite clay particle | 0.1 | 0.005 | 0.1 |

limestone cores. A drop of the oil sample was then placed on the rock surface via a micro-syringe and the contact angle was measured after 48 h using a micro-lens digital camera. The images were then analyzed using image processing software (ImageJ, National Institute of Mental Health). The schematic diagram of the wettability test is portrayed in Fig. 5.

### 3.4. Flooding test

A core flood system was used to investigate the potential of a natural polymer combined with clay particles to increase recovery factors. The schematic diagram of the displacement device is shown in Fig. 6.

The displacement test method consisted of the complete evacuation of the closed air of the limestone using a vacuum pump, followed by initial saturation of the porous medium with artificial reservoir brine (3 wt% NaCl). The oil was then injected to obtain connate water saturation ($S_{wc}$). The oil flooding process was performed at a rate of 0.2 mL/min via a syringe pump (Chemyx, model Nexus-6000) up to 2 pores volumes (PV) to ensure that the limestone pack was completely saturated with oil. Subsequently, flooding experiments were performed with brine (0.1 wt% NaCl), polymer solution, NP suspension, and NP–polymer suspension at a constant flow rate of 1 mL/min (Darcy velocity $8 \times 10^{-5}$ m/s) up to 4 PV. First, 2 PV of 0.1 wt% brine is injected to ensure that no more oil is produced. Then the prepared suspensions (polymer solution, NP suspension, and NP–polymer suspension) are injected to show the potential and their effects on EOR. Finally, the best solution is introduced, and the involved mechanisms are discussed.

## 4. Results and discussion

### 4.1. Viscosity

In this study, the viscosities of all prepared fluids were measured at different temperatures (25, 50, and 75 °C), as shown in Fig. 7. As it is shown that by adding clay mineral particles to the base fluid (0.1 wt% NaCl), no significant change in viscosity was observed at applied temperatures. For example, the viscosities of montmorillonite, kaolinite, and illite NP suspensions at 25 °C were measured to be 1.195, 1.015 and 0.945 cP, respectively, which was slightly higher than the viscosity of the base fluid (0.94 cP). All NPs with a concentration of less than 5% cannot affect the oil recovery factor in terms of increasing viscosity (Esfandyari Bayat et al., 2014), and the viscosity increases cannot explain the oil recovery enhancement (Ehtesabi et al., 2014).

As predicted, adding a polymer to the injected fluid increases its viscosity (Kamal et al., 2015; da Silva et al., 2007). For example, adding polymer (tragacanth gum) to the base fluid can significantly increase the viscosity of the fluid from 0.94 to 1.941 cP at 25 °C. When clay mineral particles were added to the polymer solution, a further increase in viscosity was also observed. For example, the viscosity of the kaolinite NP–polymer suspension was measured to be 3.613 cP. Also, the same pattern can be seen in the test results of 50 and 75 °C. The viscosity improvement affects both mobility ratio and capillary number. As the viscosity increases the capillary number increases and the mobility ratio decreases, and the two-phase flow shows piston-like behavior. In general, the addition of NPs to the polymer increases its viscosity (Maghzi et al., 2014; Khalilinezhad et al., 2016; Abdullahi et al., 2019). The addition of clay particles to the polymer has a similar effect (Cheraghian et al., 2015; Rezaei et al., 2016; Rahimi et al., 2018). However, in this study, it was observed that among the clay mineral NPs used, kaolinite has a greater potential to increase fluid viscosity at applied temperatures than montmorillonite and illite. Therefore, in terms of viscosity increase, it can be concluded that kaolinite NPs are the best choice for polymer flooding in EOR applications. It is believed that exceptional increase in kaolinite viscosity is caused by a synergistic interaction between its unique surface characteristics, layered structure, and polymer interactions. This interaction includes physical and chemical reactions that are peculiar to the kaolinite–polymer system. Chain entanglement is heightened by the specialized surface chemistry of kaolinite and its structured hydroxyl groups, which intimately interact with polymer chains. A higher-viscosity solution results from this synergy's enhanced network development. To completely comprehend the outstanding viscosity-enhancing qualities of kaolinite, more research and in-depth characterization are required.

### 4.2. IFT

IFT is another important parameter that must be carefully evaluated for EOR applications. Ideally, the amount of IFT should be minimal for successful flood performance in a porous medium. The results of IFT measurements are shown in Fig. 8. Based on the literature, adding chemical NPs can reduce IFT between oil and injectable fluids (Suleimanov et al., 2011; Roustaei et al., 2012; Joonaki and Ghanaatian, 2014; Dahkaee et al., 2019). The same

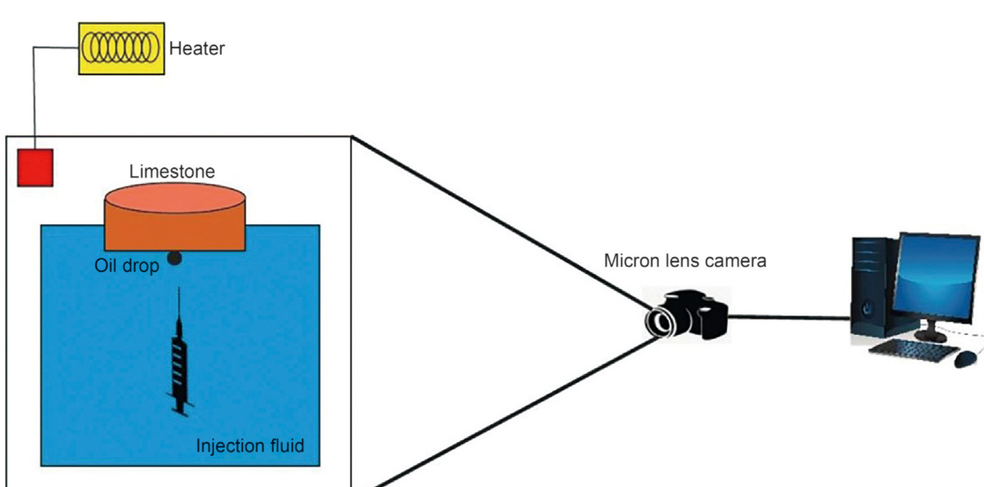


**Fig. 5.** Schematic diagram of contact angle measurement.

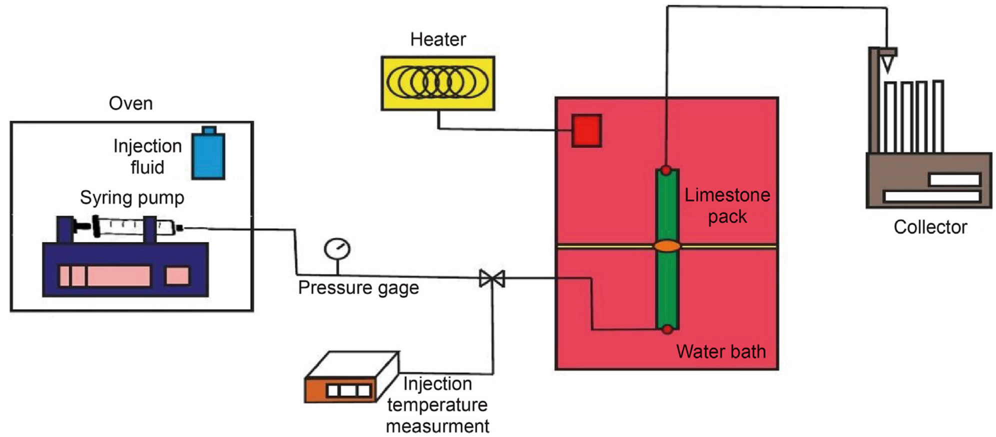


**Fig. 6.** Schematic diagram of the displacement device.

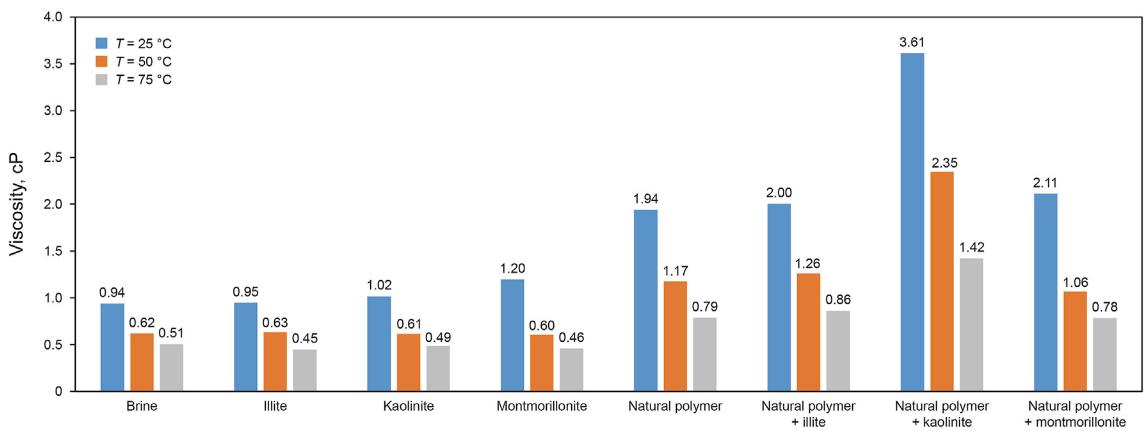


**Fig. 7.** Comparison of injectable fluid viscosities at different temperatures.

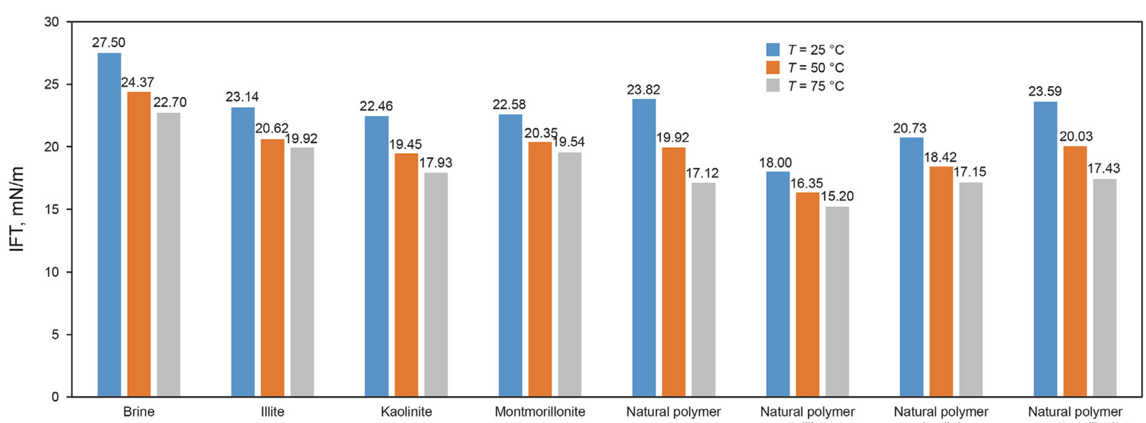


**Fig. 8.** IFT between crude oil and fluids at different temperatures.

effect was also observed in this study. As can be seen, adding the clay mineral NPs and the natural polymer to the base solution significantly reduced the amount of IFT at all three temperatures. For example, at 25 °C, adding montmorillonite, kaolinite, and illite NPs to the base fluid (0.1 wt% NaCl) could reduce the IFT value by 17.89%, 18.32% and 15.85%, respectively, which is similar to a polymer solution with 13.38% of IFT reduction. Similarly, NP–polymer suspension also reduced the value of IFT at all temperatures. The reduction values of IFT for NP–polymer suspension of montmorillonite and kaolinite at 25, 50, and 75 °C were significantly lower than the values of illite NP–polymer suspension. Hence, among applied suspensions, illite in combination with natural polymer is the best choice for reducing IFT at applied temperatures. IFT parameter is directly related to the capillary number. As the IFT reduced, the capillary number increased, and the recovery factor enhancement was observed.

### 4.3. Wettability alteration

The wettability of limestone was determined by measuring the contact angle ($\theta$) between the oil drop and the surface of the limestone in the presence of the prepared fluids. As mentioned earlier, during the wetting experiments, limestone cores were placed vertically in the fluids to prevent the deposition of clay mineral NPs on the rock surface. Thus, the change in wettability can only occur as a result of the adsorption of clay minerals on the surface of limestone cores. Fig. 9 shows the processed optical images of contact angle measurements at 25 °C. As can be seen, the initial contact angle between the oil droplet and the limestone surface in the presence of the base fluid is 54°±2°, which indicates that the rock is water-wet. Details of contact angle values in the presence of NP suspensions and NP–polymer suspensions at different temperatures are available in Table 3. It was observed that as the temperature increases, the contact angle value decreases.

Adding NPs to the base fluid generally changes the wettability to hydrophilicity (Esfandyari Bayat et al., 2014; Maghzi et al., 2012; Hendraningrat et al., 2013; Ju et al., 2006; Karimi et al., 2012). By reducing the contact angle between the oil phase and the rock surface, the wettability of the rock moves to water-wet. This makes the oil droplets less likely to be adsorbed on the rock surface, meaning that the oil can be more easily extracted from the porous medium, which is ideal for applying EOR. The results of contact angle measurements showed that all polymers, clay NPs, and clay NP–polymer fluids were able to change the wettability of limestone cores from water-wet to somewhat extremely water-wet. It was also revealed that the illite NP–polymer suspension caused the highest change in contact angle at applied temperatures, which means that illite NPs have a higher affinity for adsorption on the surface of limestone NPs than montmorillonite and kaolinite NPs.

**Table 3**
Contact angle between oil and different fluids.

| Sample | Contact angle at different temperature, degree | | |
|---|---|---|---|
| | 25 °C | 50 °C | 75 °C |
| Brine | 54 | 48 | 46 |
| Illite | 44 | 40 | 40 |
| Kaolinite | 47 | 43 | 38 |
| Montmorillonite | 46 | 42 | 41 |
| Natural polymer | 42 | 37 | 32 |
| Natural polymer and illite | 32 | 29 | 27 |
| Natural polymer and kaolinite | 40 | 38 | 35 |
| Natural polymer and montmorillonite | 39 | 35 | 33 |

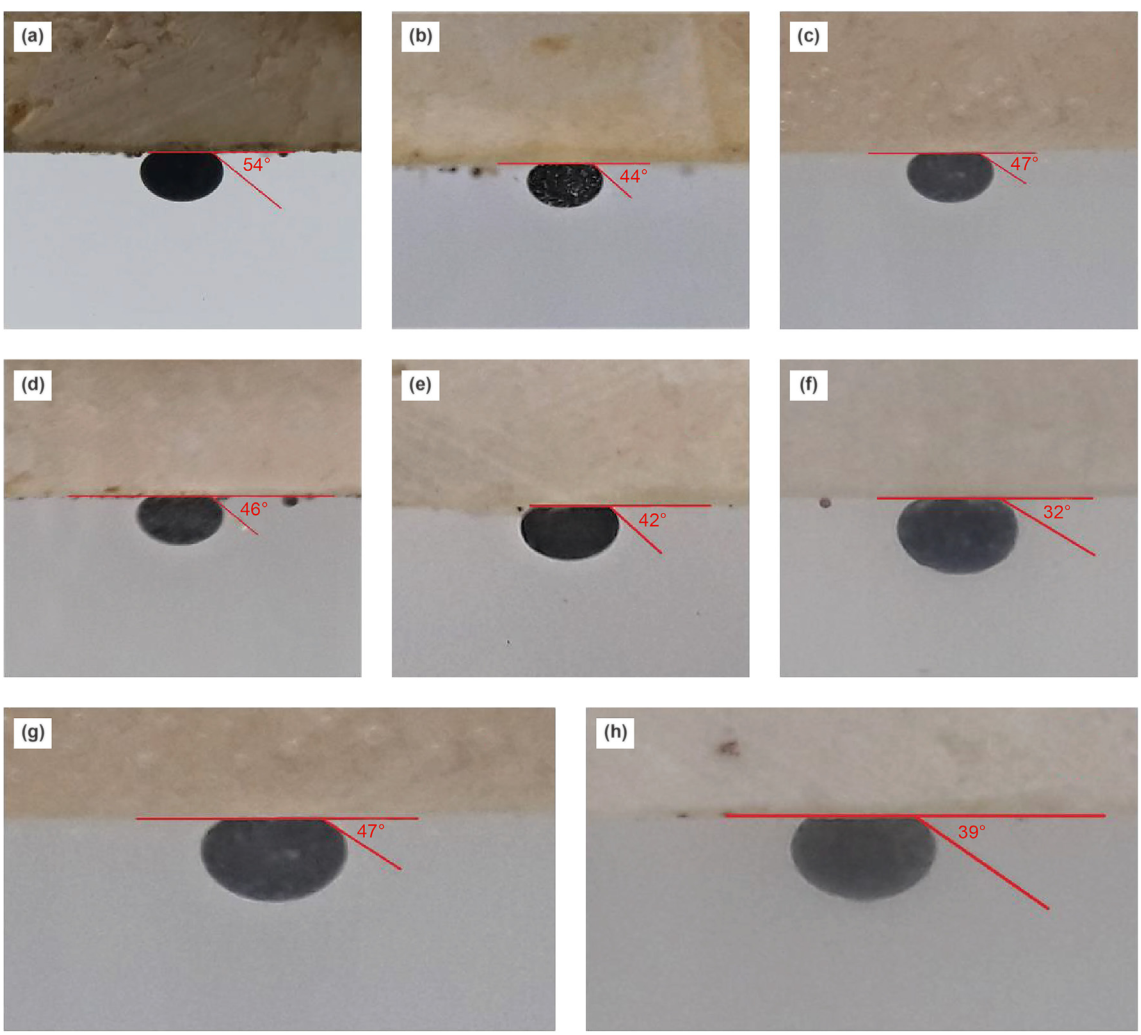


**Fig. 9.** Contact angle measured at 25 °C in presence of brine (**a**), illite (**b**), kaolinite (**c**), montmorillonite (**d**), natural polymer (**e**), natural polymer and illite (**f**), natural polymer and kaolinite (**g**), and natural polymer and montmorillonite (**h**).

Therefore, it can be concluded that illite NP–polymer suspension is a relatively better option for changing wettability within the porous limestone environment and consequently a successful application of EOR.

### 4.4. Core flooding results

As depicted in Table 4, the impact of temperature on tertiary recovery is evident. Kaolinite fluid without polymer has the most tertiary recovery at 25 °C. Notably, the illite fluid exhibits superior recovery factors at elevated temperatures of 50 and 75 °C. This phenomenon can potentially be attributed to the presence of additional metal elements, as indicated by the EDX test, along with improved thermal conductivity. The reduction of tertiary recovery at 50 and 75 °C compared to 25 °C is due to more oil production in the first stage of flooding with 1 wt% brine and thus reducing the remaining oil saturation. The natural polymer in all temperatures has more tertiary recovery than 1 wt% brine and less recovery than clay fluids.

The results reveal a nuanced relationship between natural polymers and clay NPs. In the hybrid scenarios, the combination of natural polymer and kaolinite results in the highest oil recovery (81.1%) at 25 °C, surpassing the recovery achieved with illite (78.8%) and montmorillonite (77.3%). This outcome resonates with the findings in the literature (Cheraghian et al., 2015; Rezaei et al., 2016; Rahimi et al., 2018) emphasizing the potential synergy between natural polymers and clay particles in boosting recovery efficiency. Furthermore, Keykhosravi's investigations with xanthan gum polymer and $TiO_2$ NPs emphasize the nuanced effects of NP–polymer suspensions on EOR. The study indicates that while the nanofluid and the polymer solution contribute to extra oil recovery values of 12% and 19% of OOIP, respectively, an additional 25% of oil recovery is achieved through the incorporation of NP–polymer suspension. This remarkable enhancement can be attributed to the combined effects of water viscosity improvement and wettability modification. Indeed, the incorporation of specific materials, whether in the form of NP–polymer suspensions or the synergistic combination of natural polymers with NPs, has consistently demonstrated its efficacy in significantly enhancing oil recovery. This consistency underscores the relevance of key mechanisms such as water viscosity enhancement and wettability alteration in diverse contexts of EOR.

Interestingly, the introduction of the natural polymer combined with kaolinite consistently outperforms the brine injection in tertiary recovery across all temperature conditions. This observation reinforces the benefits of incorporating natural polymers and kaolinite in enhancing oil recovery, demonstrating their superiority over traditional brine flooding methods. The results of the flooding tests through the injection of different fluids are shown in Figs. 10–12.

## 5. Conclusions

In this study, the effects of three nanoparticles of illite, kaolinite, and montmorillonite with natural polymer and its composition on increasing oil recovery at 25, 50, and 75 °C in a carbonate reservoir have been studied. For this end, the effects of these fluids on the mechanisms involving reduction of IFT, wettability alteration, and increase of viscosity have been investigated.

(1) It has been observed that clay particles alone cannot significantly increase the viscosity of the injection fluid. The addition of natural polymer increases the viscosity and the addition of clay particles also increases the viscosity of the natural polymer. Among all fluids, the combination of natural polymer and kaolinite has the highest viscosity at all temperatures.
(2) Nanofluid has shown its ability to change the wettability of rock and reduce the contact angle. The wettability of the rock changes to a hydrophilic state for all occasions. Among these fluids, the combination of natural polymer and illite had the greatest effect on decreasing the contact angle at all temperatures.
(3) The tested fluids also could reduce IFT and the combination of natural polymer and illite showed the greatest ability to reduce IFT.
(4) The results of flooding tests showed that the combination of natural polymer and kaolinite has the greatest improvement

**Table 4**
Results of core flooding experiments.

| Fluid | $\phi$, % | $k$, D | $T$, °C | $S_{wc}$, % | $S_o$, % | Oil recovery by water flooding, % | Tertiary oil recovery, % | Total oil recovery, % |
|---|---|---|---|---|---|---|---|---|
| Brine | 38.10 | 2.26 | 25 | 28.13 | 71.88 | 61.0 | 2.9 | 63.9 |
| | 41.68 | 2.32 | 50 | 28.57 | 71.43 | 68.1 | 2.4 | 70.5 |
| | 41.68 | 2.41 | 75 | 20.00 | 80.00 | 73.8 | 1.7 | 75.5 |
| Illite | 38.63 | 2.17 | 25 | 34.38 | 65.63 | 61.0 | 10.4 | 71.4 |
| | 43.47 | 2.37 | 50 | 18.92 | 81.08 | 68.9 | 11.6 | 80.5 |
| | 42.25 | 2.51 | 75 | 22.86 | 77.14 | 74.0 | 12.8 | 86.8 |
| Kaolinite | 37.94 | 2.27 | 25 | 25.81 | 74.19 | 61.2 | 13.5 | 74.7 |
| | 44.06 | 2.69 | 50 | 18.92 | 81.08 | 67.9 | 12.9 | 80.9 |
| | 41.68 | 2.34 | 75 | 20.00 | 80.00 | 73.8 | 11.5 | 85.3 |
| Montmorillonite | 42.25 | 2.57 | 25 | 22.86 | 77.14 | 60.6 | 11.1 | 71.6 |
| | 41.52 | 2.39 | 50 | 20.00 | 80.00 | 68.3 | 10.8 | 79.1 |
| | 36.91 | 2.12 | 75 | 29.03 | 70.97 | 73.8 | 9.9 | 83.7 |
| Natural polymer | 38.10 | 2.31 | 25 | 28.13 | 71.88 | 61.2 | 9.2 | 70.5 |
| | 35.99 | 2.18 | 50 | 20.69 | 79.31 | 68.4 | 8.1 | 76.5 |
| | 41.68 | 2.41 | 75 | 22.86 | 77.14 | 73.6 | 7.3 | 80.9 |
| Natural polymer and illite | 39.29 | 2.36 | 25 | 27.27 | 72.73 | 61.0 | 17.8 | 78.8 |
| | 38.63 | 2.29 | 50 | 18.75 | 81.25 | 68.4 | 17.1 | 85.5 |
| | 42.25 | 2.48 | 75 | 22.86 | 77.14 | 74.1 | 15.9 | 90.0 |
| Natural polymer and kaolinite | 38.10 | 2.22 | 25 | 26.56 | 73.44 | 61.3 | 19.8 | 81.1 |
| | 39.29 | 2.38 | 50 | 22.73 | 77.27 | 68.6 | 18.9 | 87.5 |
| | 40.48 | 2.31 | 75 | 16.18 | 83.82 | 74.2 | 17.8 | 92.0 |
| Natural polymer and montmorillonite | 41.68 | 2.44 | 25 | 14.29 | 85.71 | 61.3 | 16.0 | 77.3 |
| | 42.28 | 2.51 | 50 | 19.44 | 86.56 | 68.3 | 15.8 | 84.1 |
| | 44.06 | 2.64 | 75 | 21.62 | 75.38 | 73.6 | 14.7 | 88.3 |

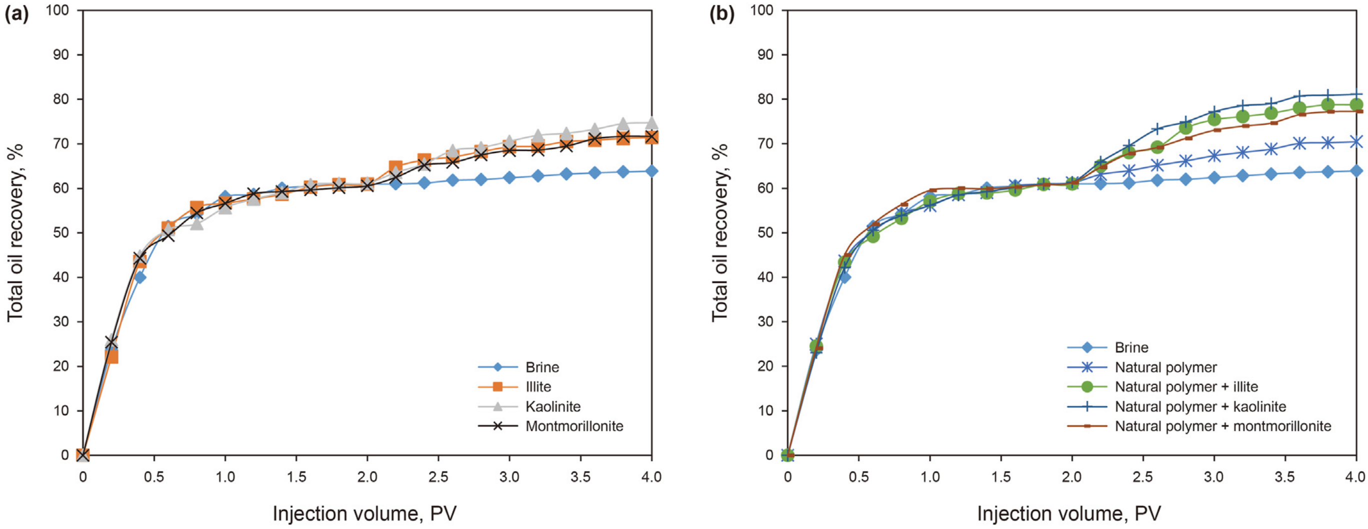


**Fig. 10.** Oil recovery for water flooding and different suspension flooding at 25 °C. (**a**) Clay NP suspensions; (**b**) Clay NP–polymer suspensions.

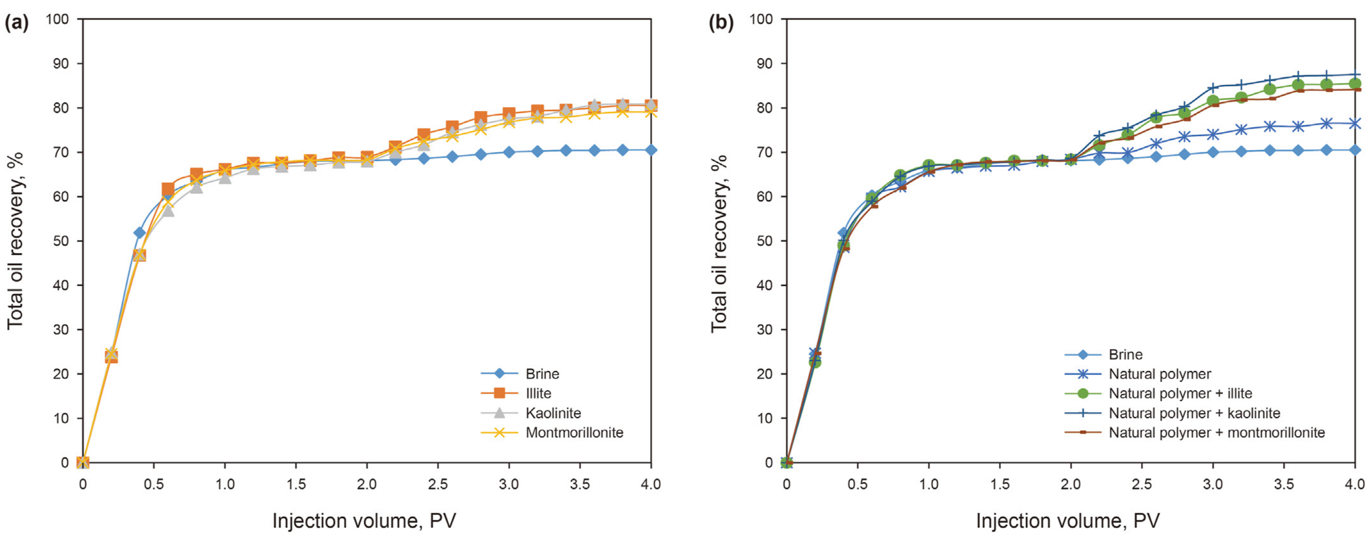


**Fig. 11.** Oil recovery for water flooding and different suspension flooding at 50 °C. (**a**) Clay NP suspensions; (**b**) Clay NP–polymer suspensions.

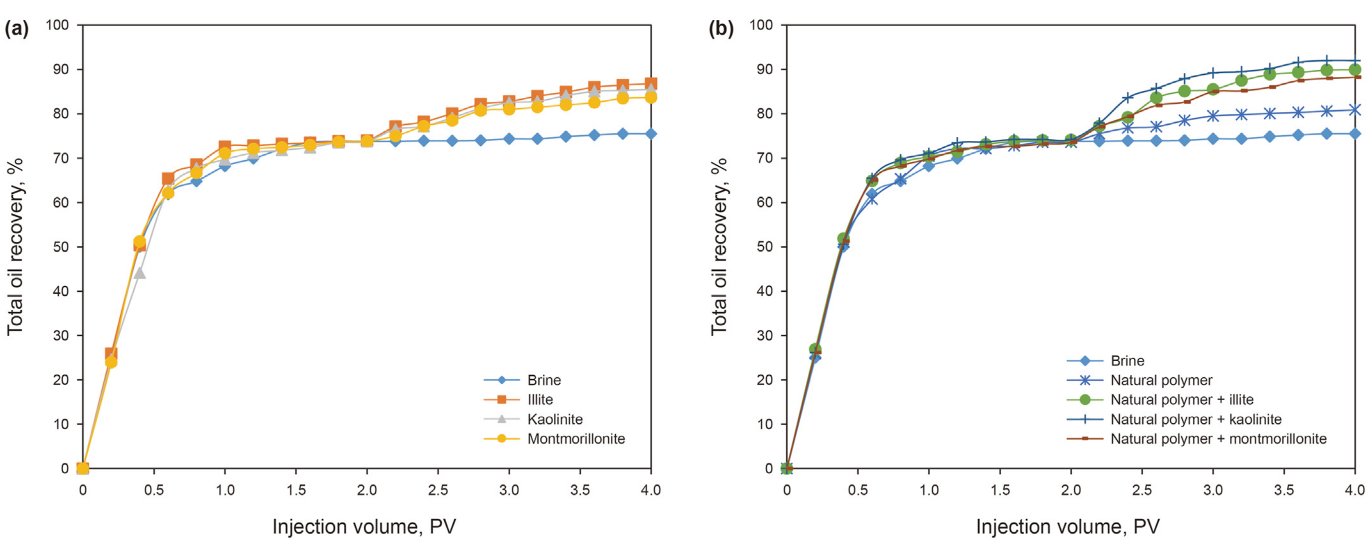


**Fig. 12.** Oil recovery for water flooding and different suspension flooding at 75 °C. (**a**) Clay NP suspensions; (**b**) Clay NP–polymer suspensions.

in oil recovery factor and can be a good option for oil production operations. Then natural polymer and illite suspension is the best option to increase oil recovery at all temperatures.

(5) It is concluded that illite, kaolinite, and montmorillonite nanoparticles and their combination with the natural polymer can reduce capillary forces by changing rock wettability and reducing IFT. They also increase the viscous forces and reduce the mobility ratio by increasing the viscosity of the injection fluid. The results of flooding tests showed that among the three mechanisms studied, increasing the viscosity of the injection fluid has the greatest impact on the EOR process.

## CRediT authorship contribution statement

**Amir Mohammad Zamani:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization. **Ashkan Moslemi:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization. **Kamran Hassani:** Writing – original draft, Writing – review & editing.

## Declaration of competing interest

None.

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