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The Effect of TiO2 Nanoparticles on The Performance of Kappaphycus Alvarezii Biopolymer for Enhanced Oil Recovery

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ABSTRACT - This study investigates the performance of a novel, environmentally friendly nanocomposite, utilizing the natural biopolymer Kappaphycus alvarezii enhanced with TiO₂ nanoparticles, for Enhanced Oil Recovery (EOR) via polymer flooding. The application of this nanocomposite was aimed to simultaneously enhance microscopic displacement and macroscopic sweep efficiency. The research method used was laboratory testing which included solution stability, viscosity, interfacial tension (IFT), and rock wettability tests in various polymer concentrations (2,000–6,000 ppm), TiO₂ (2,000–4,000 ppm), and salinity (6,000–30,000 ppm) at temperatures of 30–80°C. Quantitative laboratory results confirm fluid property improvements: TiO₂ addition increased the solution viscosity by up to 11 cP where an average increase up to 7.11% in high-salinity brines, reduced the Interfacial Tension (IFT) from 7.54 dyne/cm to 6.80 dyne/cm (a 9.8% reduction), and decreased the contact angle from 39.05° to 28.51°, confirming enhanced water-wetness. Core flooding experiments demonstrated that the polymer flooding yielded an incremental oil recovery factor after waterflooding ranging from 6.67% to 27.67%. The maximum total oil recovery achieved was 69.17% at the optimal concentration of Polymer 4,000 ppm and TiO₂ 2,000 ppm. These specific findings highlight the significant potential of the Kappaphycus alvarezii–TiO₂ nanocomposite as an effective EOR agent.

Keywords: kappaphycus alvarezii, TiO2 nanoparticle, salinity, enhanced oil recovery, wettability.

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INTRODUCTION

Polymer flooding is a chemical flooding method that can increase oil recovery by reducing the mobility of the injection fluid and reducing water permeability (Navaie et al., 2022; Lamas et al., 2024). In field applications, polymer flooding has been shown to increase oil recovery by 12-15% and can produce oil more quickly and effectively (Koottungal 2010; Wang et al., 2003).

Problems with polymer use in reservoirs include adsorption and environmental impacts. Adsorption due to the interaction of polymers and rocks causes a decrease in polymer concentration in solution and can lead to narrowing or clogging of rock pores. Polymer adsorption and degradation are affected by salinity and temperature (Sun et al., 2023), which reduce the effectiveness of polymer function (Li et al., 2021).

An advantage of biopolymers is their environmentally friendly nature (Obuebite et al., 2021). Kappaphycus alvarezii is a biopolymer widely cultivated in Indonesia, particularly in Sulawesi (Mualam et al., 2022), Maluku (Labenua & Aris 2021), Jawa (Abdullah 2021), Nusa Tenggara (Radiarta et al., 2014), and Papua (Padawan et al., 2020). In general, seaweed is rich in polysaccharides. Types of polysaccharides found in seaweed include alginate, carrageenan, agar, and small amounts of other polysaccharides. Seaweed polysaccharide content is generally 48% (Martone et al., 2019; Subagio & Kasim, 2019). Kappaphycus alvarezii is the seaweed species with the highest carrageenan content, at 62-68% of its dry weight. Kappa-carrageenan, a hydrocolloid extracted from Kappaphycus alvarezii, has similar characteristics to gelatin, acting as an emulsifier, stabilizer, thickener, and gelling agent (Erniati et al., 2022; Aprianti et al., 2023; Nurani et al., 2024).

The application of nanotechnology can address some of the drawbacks of polymer flooding. Applied nanoparticles are categorized into metal oxide, magnetic, and organic nanoparticles (Soleimani et al., 2018; Ehtesabi et al., 2013). The use of nanoparticles in polymer flooding can reduce residual oil saturation by more than 20% (Nguyen et al., 2012), reduce the IFT from 26% to 76%, and stabilize emulsions (Sharma et al., 2016; Keykhosravi et al., 2021; Rezvani et al., 2018). The addition of nanoparticles can also reduce the average contact angle by 52.5%. So that the wettability of the rock becomes more water wet caused by the adsorption of nanoparticles

on the rock surface (Al-Anssari et al., 2016; Tola et al., 2017). As a result, polymer adsorption is reduced (Cheraghian et al., 2014). The addition of nanoparticles can also increase the viscosity of the solution by 2.1% to 770% (Corredor et al., 2019a).

Polyacrylamide-grafted TiO, nanoparticles (TiO₂-PAM) demonstrated superior properties in terms of performance compared to the grafted SiO₂ and Al₂O₃ (SiO₂-PAM and Al₂O₃-PAM); TiO₂-PAM was the only one capable of significantly increasing the viscosity of the polymer solution (6.9% increase) and enhancing cumulative oil recovery by 5% to 7%, which was attributed to its smaller particle size favoring the formation of a better elastic network. However, in general, all three nanopolymers equally improved the surface properties of the nanoparticles, lowered the Interfacial Tension (IFT), and were able to alter the wettability of the substrate from oil-wet to intermediate-wet conditions (Corredor et al., 2019b). Therefore, TiO2 nanoparticles were used in this study to improve the performance of polymer.

Kappaphycus alvarezii contains carrageenan which has a viscosity of 3.73-6.13 cp and can undergo degradation and adsorption (Mulyani et al., 2012; Tarman et al., 2023). The addition of TiO₂ nanoparticles to the polymer flooding is expected to improve the performance of the Kappaphycus alvarezii polymer. The mechanism of action is that nanoparticles added to the polymer flood will increase the viscosity of the polymer solution, reduce the interfacial tension between the polymer solution and the oil, and reduce adsorption by changing the wettability of the rock due to the interaction of the nanoparticles with the rock. This will increase the ability of the polymer solution to sweep oil from the pores of the rock. The purpose of this study is to apply Kappaphycus alvarezii as a natural and environmentally friendly polymer in an effort to increase oil recovery. In addition, the use of TiO₂ nanoparticles as an additive that can affect the performance of Kappaphycus alvarezii in the polymer flooding.

METHODOLOGY

This research included the collection of materials and equipment for laboratory experiments. The results were used to evaluate the characteristics and performance of Kappaphycus alvarezii polymer and ${\rm TiO}_2$ nanoparticles in an effort to improve oil recovery.

Materials

The materials used in this study include natural polymers from Kappaphycus alvarezii and TiO₂ nanoparticles. Several solutions were prepared with various concentrations of Kappaphycus alvarezii and TiO₂ nanoparticle. Synthetic salt solutions (NaCl solutions) used to dissolve the polymers and nanoparticles were prepared with low to moderate salinity. The oil used was intermediate crude oil with a specific gravity of 28.5°American petroleum institute and a viscosity of 22.5 cp. Berea core was used in this study as a porous medium representing reservoir rock.

Equipments

The research was conducted using equipment at the Enhanced Oil Recovery Laboratory of Trisakti University. Several researches were performed in the Integrated Physics Laboratory and the Ogrindo Laboratory at the Bandung Institute of Technology.

Laboratory experiments

The studies conducted include density test, aqueous stability test, transmittance test, viscosity test, filtration test, wettability (contact angle) test, IFT and thermal stability test, adsorpsion test, and coreflooding test. The first four experiments were conducted on all solution samples with various combinations of Kappaphycus alvarezii concentrations, nanoparticles, and salinity. The remaining experiments were conducted on solution samples with a salinity of 6000 ppm.

Viscosity tests were conducted at room temperature (≈30°C), 40°C, and 80°C. The room temperature reflects laboratory and ambient handling conditions, 40°C approximates near-surface or shallow reservoir temperatures, and 80°C represents medium-depth reservoir conditions where viscosity is critical for fluid mobility and sweep efficiency (Minakov et al., 2022). Wettability, IFT, and thermal stability tests were conducted at 60°C. Testing at 60°C ensured that the polymer or nanofluid performance (in altering wettability, reducing IFT, and maintaining thermal stability) reflected subsurface thermal conditions rather than ambient ones (Yekeen et al., 2020). Other tests were conducted at room temperature.

RESULT AND DISCUSSION

Preparation of polymer solution

The brine solution was prepared first. The salinity of the brine solution used was 6,000 ppm, 18,000 ppm, and 30,000 ppm. The salinity of the brine represents the conditions of several reservoir fluids in Indonesia and Malaysia (Johnson & Worthington, 1991; Yusof et al., 2020; Yusof et al., 2021; Putra et al., 2025; Sheng, 2011). Kappaphycus alvarezii polymer solution was prepared with concentrations of 2,000 ppm, 4,000 ppm, and 6,000 ppm. These concentrations were selected based on previous works indicating that biopolymer viscosities suitable for mobility control in polymer flooding are typically achieved within this range, providing adequate injectivity while minimizing shear degradation (Ofulue, 2023; Sutiadi et al., 2024). Meanwhile, the nanocomposite polymer solution was prepared with TiO₂ nanoparticle concentrations of 2,000 ppm and 4,000 ppm. This concentration was chosen based on previous nanofluid-enhanced polymer flooding studies, which found that TiO2 nanoparticle additif between 2,000-4,000 ppm can reduce IFT, change the rock wettability to water wet, and provide additional oil recovery (Corredor et al., 2019b). The solutions used in the experiment are shown in Table 1.

Preparation of berea core samples

Cylindrical Berea cores were used for wettability (contact angle) and coreflooding experiments. Core parameters measured included diameter, length, porosity (ϕ), and permeability. Porosity and permeability were measured using a porosimeter and a permeameter, respectively. Berea core samples used for four consecutive coreflooding experiments are shown in Table 2.

Density test

Liquid density was measured using a pycnometer and a digital scale. The density measurement results for 27 polymer solution samples are shown in Figure 1. The total density of the solution was affected by the mass of NaCl salt, Kappaphycus alvarezii polymer, TiO₂ nanoparticles, and distilled water. The density of polymer solutions with TiO₂ additive varies from 1.076 to 1.098 gr/cm³. The largest influence on the density of the polymer solution was given by TiO₂ nanoparticles with a density of 4.23 gr/cm³. The average increase in density for the addition of 2,000 ppm TiO₂, NaCl, and Kappaphycus alvarezii was about 0.138%, 0.119%, and 0.046%, respectively.

Aqueous stability and transmittance tests

The aqueous stability test was carried out for 7 days. The aqueous stability measurement is a visual measurement to obtain qualitative measurement results. The addition of Kappaphycus alvarezii generally causes the solution to remain clear. Meanwhile, the addition of TiO₂ causes the solution to become cloudy and whitish. TiO, nanoparticles precipitate over time due to gravity. Observations on the seventh day in the polymer solution with the addition of nanoparticle additives are that the solution becomes clear again with the presence of TiO, deposits. The aqueous stability test was carried out using a Duran laboratory bottle at room temperature. Table 3 shows the results of the aqueous stability test for 27 polymer solutions. In addition to the aqueous test, a transmittance test was also conducted to quantitatively measure the clarity of the solution. The transmittance test was conducted using a UV-Vis spectrophotometer at a wavelength of 600 nm. Table 4 shows that all solutions were quite clear with transmittance values above 55%. The table

Table 1. Polymer solutions with various combinations of salinity, Kappaphycus alvarezii, and TiO₂ nanoparticle concentration

Solution	Salinity, ppm	Kappaphycus alvarezii conc., ppm	TiO ₂ concentration, ppm	
1	6,000	2,000	0	
2	6,000	4,000	0	
3	6,000	6,000	0	
4	6,000	2,000	2,000	
5	6,000	4,000	2,000	
6	6,000	6,000	2,000	
7	6,000	2,000	4,000	
8	6,000	4,000	4,000	
9	6,000	6,000	4,000	
10	18,000	2,000	0	
11	18,000	4,000	0	
12	18,000	6,000	0	
13	18,000	2,000	2,000	
14	18,000	4,000	2,000	
15	18,000	6,000	2,000	
16	18,000	2,000	4,000	
17	18,000	4,000	4,000	
18	18,000	6,000	4,000	
19	30,000	2,000	0	
20	30,000	4,000	0	
21	30,000	6,000	0	
22	30,000	2,000	2,000	
23	30,000	4,000	2,000	
24	30,000	6,000	2,000	
25	30,000	2,000	4,000	
26	30,000	4,000	4,000	
27	30,000	6,000	4,000	

Table 2. Berea core sample size used in coreflooding experiments

No	Diameter, cm	Length, cm	Porosity, fraction	Permeability, mD
1	2.5	2.8	16.654	126
2	2.5	2.8	17.016	129
3	2.5	2.8	12.020	93
4	2.5	2.8	12.020	93

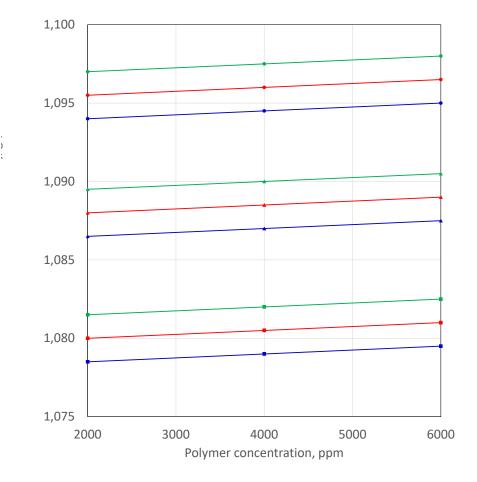




Figure 1. Density measurement results for 27 polymer solutions.

shows that transmittance values tend to decrease with increasing concentrations of polymers, nanoparticles, and salinity. Increasing the concentration of these substances reduces the clarity of the distilled water, which reduces the amount of light that can pass through the material. In other words, the more turbid the solution, the lower the transmittance value. The largest decrease in transmittance was caused by the addition of TiO₂. The average decrease in transmittance for the addition of 2,000 ppm TiO₂, NaCl, and Kappaphycus alvarezii was about 9.75%, 1.24%, and 4.98%, respectively.

Filtration test

According to Tobing and Hestuti (2013), if large amounts of sediment or impurities are retained on the filter paper, the solution is considered unsuitable because filtration will reduce the concentration of the chemical. Therefore, the results of the filtration test will determine the quality of the polymer. Polymers that are able to pass through the filter (filter paper) well and do not clump indicate that the polymer can function effectively in the EOR process. In this experiment, Whatman filter paper no. 41 with a

pore size of 20 µm was used. Based on the filtration measurement data, the filtration ratio (FR) can be calculated for all solutions. The results of the friction ratio calculation are given in Table 5 (Sugihardjo & Eni, 2022; Mohd, et al., 2018; Verma & Mandal, 2021).

Based on the table, the FR value varies from 0.95 to 1.73. The tolerable FR value is 1.2. Table 4 shows that the FR of solutions with Kappaphycus alvarezii concentrations of up to 4000 ppm has an FR value below 1.2. Meanwhile, solutions with Kappaphycus alvarezii concentrations of 6000 ppm show an FR value above 1.2, indicating that the solution has the potential to cause pore plugging.

Viscosity test

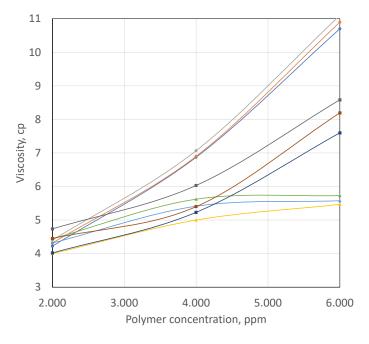
Viscosity (µ) is an important property of polymers used for oil displacement. Viscosity testing is also one of the tests for polymer selection. Polymer viscosity measurements were carried out using a rotational viscometer at temperatures of 30°C, 40°C, and 80°C. The results of the viscosity measurements are shown in Figures 2 to 3.

These Figures show the effect of Kappaphycus

Solution	Aguagus Stability (168 hrs)	Transmit
	*	

Table 3. Aqueous stability and transmittance test results

Solution	Aqueous Stability (168 hrs)	Transmittance%
1	Clear	94.1
2	Clear	89.7
2 3	Clear	64.9
4	Clear, Sediment	90.4
5	Clear, Sediment	82.3
6	Clear, Sediment	81.3
7	Clear, Sediment	86.2
8	Clear, Sediment	85.3
9	Clear, Sediment	84.3
10	Clear	90.7
11	Clear	89.1
12	Clear	84.3
13	Clear, Sediment	89.0
14	Clear, Sediment	78.4
15	Clear, Sediment	74.9
16	Clear, Sediment	82.2
17	Clear, Sediment	80.8
18	Clear, Sediment	62.2
19	Clear	90.7
20	Clear	89.1
21	Clear	84.3
22	Clear, Sediment	88.5
23	Clear, Sediment	86.6
24	Clear, Sediment	80.5
25	Clear, Sediment	81.9
26	Clear, Sediment	64.6
27	Clear, Sediment	55.7



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TiO2 = 0 ppm; Salinity = 6,000 ppm
TiO2 = 2,000 ppm; Salinity = 6,000 ppm
TiO2 = 4,000 ppm; Salinity = 6,000 ppm
TiO2 = 0 ppm; Salinity = 18,000 ppm
TiO2 = 2,000 ppm; Salinity = 18,000 ppm
TiO2 = 4,000 ppm; Salinity = 18,000 ppm
TiO2 = 0 ppm; Salinity = 18,000 ppm
TiO2 = 0 ppm; Salinity = 30,000 ppm
TiO2 = 2,000 ppm; Salinity = 30,000 ppm
TiO2 = 4,000 ppm; Salinity = 30,000 ppm
TiO2 = 4,000 ppm; Salinity = 30,000 ppm
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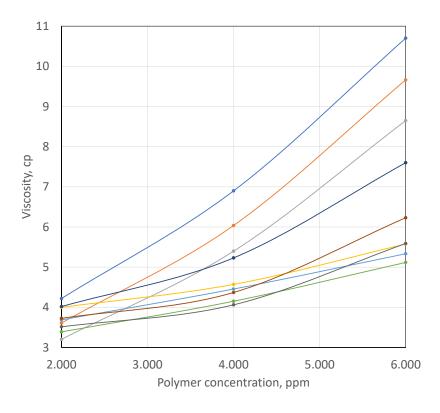
Figure 2. The effect of TiO₂ concentration and salinity on the viscosity of the Kappaphycus alvarezii solution

Table 4. Filtration ratio (FR) of polymer solution

Solution	FR	Solution	FR
1	1.11	15	1.60
2	1.10	16	1.12
3	1.09	17	1.12
4	1.17	18	1.57
5	1.18	19	1.03
6	1.56	20	1.11
7	0.96	21	1.37
8	1.20	22	0.99
9	1.73	23	1.18
10	1.11	24	1.42
11	1.12	25	0.95
12	1.67	26	1.07
13	1.17	27	1.26
14	1.13		

alvarezii concentration on viscosity increase for various salinities and TiO₂. The viscosity increase for the addition of 2,000 ppm Kappaphycus alvarezii concentration varied from 1.04% to 21.12%.

The effect of salinity on viscosity can be analyzed based on Figures 2 to 3. Based on these Figures, the average viscosity of the polymer solution with a salinity of 6,000 ppm is 6.84 cp. The average viscosity of the polymer solution at a salinity of 18,000 ppm is only 4.68 cp. The addition of salt (increasing salinity) causes the viscosity of polymer solutions to decrease. This decrease in viscosity is caused by the added Na⁺ and Cl⁻ ions neutralizing the repulsion of like charges along the polymer molecular chain. The polymer chain becomes more coiled, so the solution loses its viscosity (Sadeghi & Jahani 2012; Zhao, 2016; Fang 2013). Furthermore,



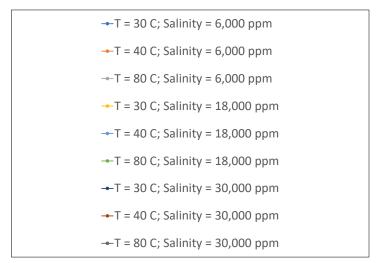


Figure 3. The effect of temperature and salinity on the viscosity of the Kappaphycus alvarezii solution

in polymers that form networks through hydrogen interactions or complexation, salt ions can compete with these bonds. This results in shorter polymer chains and reduced solution viscosity (Afdi 2022; Frigrina et al., 2017; Ulfa 2023).

A further increase in salinity to 30,000 ppm causes a slight increase in the viscosity of the polymer solution. The average viscosity of the polymer solution at a salinity of 30,000 ppm was 5.56 cp. This increase in viscosity can occur due to the increasing thickness of the solution due to the

high salt content.

The effect of TiO₂ addition on the viscosity of polymer solutions is shown in Figure 2. Based on these Figures, the percentage increase in viscosity occurs highest in solutions with salinity. The average percentage increase in viscosity with the addition of TiO₂ for solutions with salinity of 6,000 ppm, 18,000 ppm and 30,000 ppm is 3.70%, 4.97%, and 7.11%, respectively. This phenomenon can be attributed to the interaction between TiO₂ nanoparticles and NaCl ions through ion adsorption and agglomeration. TiO₂

possesses a high surface charge density and strong affinity toward both cations (Na⁺) and anions (Cl⁻), leading to the formation of an electrical double layer that promotes partial flocculation of polymer chains and restricts their mobility (Ehtesabi et al., 2013; Keykhosravi et al., 2021). Such electrostatic interactions enhance intermolecular bridging between TiO₂ and polymer functional groups (-OH and -SO₃-), increasing the overall hydrodynamic volume and viscosity of the nanofluid (Corredor et al., 2019b; Sun et al., 2023). Moreover, under saline conditions, TiO2 nanoparticles can act as crosslinking sites that stabilize polymer conformation by reducing charge screening effects from NaCl, thus improving viscosity retention even at high ionic strengths (Cheraghian et al., 2014; Sharma et al., 2016). The formation of weak agglomerates between TiO₂ and dissolved ions also increases the effective particle size and local network density, resulting in the observed viscosity enhancement (Rezvani et al., 2018; Minakov et al., 2022).

The effect of temperature and salinity on the viscosity of polymer solution is shown in Figure 3. Increasing the temperature of the polymer solution causes an increase in the thermal energy of the molecules. This increase in thermal energy causes the solvent molecules and polymer chains to move faster. This mechanism causes expansion that reduces internal friction, thus reducing viscosity. Increasing the temperature from 30 °C to 80 °C causes an average decrease in viscosity of 17.7%.

Wettability test

Wettability is a critical parameter in enhanced oil recovery (EOR) as it governs the distribution and flow of fluids within porous media. It describes the tendency of a solid surface to be preferentially wetted by one fluid in the presence of another immiscible fluid. The contact angle (θ) is the most common indicator of wettability; it is the angle formed at the interface where the solid, liquid, and vapor phases meet. When the contact angle is less than 90°, the surface is considered water-wet, meaning water preferentially spreads over the solid surface, while a contact angle greater than 90° indicates an oil-wet condition (Anderson, 1986; Morrow, 1990; Al-Anssari et al., 2016). In this study, wettability testing was conducted using a pendant drop tensiometer at 60 °C, as shown in Table 5. The measured contact angle for brine (NaCl 6,000 ppm) was 39.05°, while for the Kappaphycus alvarezii polymer solution (6,000 ppm), it decreased to 27.47°. The addition of TiO₂ nanoparticles slightly increased the angle to 28.51°, indicating that both polymer and nanocomposite solutions made the rock more water-wet compared to brine. The reduction in contact angle signifies enhanced water-wetness due to the adsorption of polar functional groups and TiO₂ particles on the rock surface, which modify surface energy and polarity (Cheraghian et al., 2014; Tola et al., 2017; Keykhosravi et al., 2021). From a reservoir engineering perspective, increasing waterwetness improves oil displacement efficiency. In water-wet systems, water tends to occupy smaller pores, displacing oil from larger pores, leading to improved microscopic sweep efficiency and higher recovery factors (Craig, 1971; Sheng, 2011). Conversely, in oil-wet systems, oil adheres to rock surfaces and becomes more difficult to displace, reducing oil production. Therefore, the observed decrease in contact angle in this work confirms that both Kappaphycus alvarezii and TiO2 contribute to altering rock wettability toward a more water-wet condition, facilitating easier oil flow during polymer flooding.

Table 5. Contact angle test results

Surfactant Solution	Rock Type	Contact Angle	Visual
Brine NaCl 6,000 ppm	Berea sand-stone	39.05°	13.00
Kappaphycus alvarezii 6,000 ppm	Berea sand-stone	27.47°	nar nar
Kappaphycus alvarezii 6,000 ppm+TiO ₂ 1,000 ppm	Berea sand-stone	28.51°	21.47

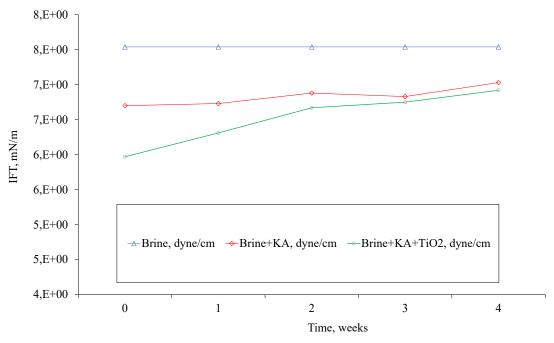


Figure 4. IFT and thermal stability test results

Interfacial tension and thermal stability test

Measurement of interfacial tension (IFT) is essential in this study to understand the microscopic displacement efficiency mechanism that complements the macroscopic effects of polymer flooding. Although polymer flooding primarily enhances macroscopic sweep efficiency by improving mobility control (Li et al., 2021; Lake et al., 2014), the reduction of IFT at the oil-water interface facilitates the mobilization of trapped residual oil droplets within the pore spaces, thereby enhancing total oil recovery (Sheng, 2011). In polymer–nanoparticle systems, nanoparticles such as TiO2 can further influence IFT by modifying interfacial interactions and stabilizing emulsions, thus improving microscopic displacement efficiency (Sharma et al., 2016; Rezvani et al., 2018; Keykhosravi et al., 2021). Therefore, IFT measurement is an important indicator of how Kappaphycus alvarezii biopolymer and TiO2 nanoparticles interact at the oil-water interface to support both microscopic and macroscopic displacement mechanisms (Sun et al., 2023; Corredor et al., 2019a).

In the IFT test for the Kappaphycus alvarezii polymer, the tool used was a spinning drop tensiometer TX 500D in the OGRINDO ITB laboratory. The test results can be seen in Figure 4. The Figure shows the results of the IFT thermal stability test of 6,000 ppm brine for four weeks, which has a relatively stable IFT value of 7.54E+00

dyne/cm. In addition, Figure 4 shows the results of the thermal stability test of the solution with a salinity of 18,000 ppm and Kappaphycus alvarezii 6,000 ppm which had an IFT value that tended to be stable until the third week and experienced an increase in the IFT value in the fourth week. Meanwhile, the results of the thermal stability test of the solution with a salinity concentration of 6,000 ppm, Kappaphycus alvarezii 6,000 ppm, and TiO₂ 10,000 ppm shown in Figure 4 have an IFT value that tends to increase during the four weeks of testing.

Based on Figure 4, it can be seen that the application of Kappaphycus alvarezii is able to reduce the IFT from 7.54E+00 dyne/cm to around 6.80E+00 dyne/cm. The increase in IFT to 7.03E+00 dyne/cm in the fourth week can be caused by the degradation process experienced by Kappaphycus alvarezii. The application of TiO₂ nanoparticles can reduce the IFT of brine more to 5.97E+00 dyne/cm on the first day. The IFT of Kappaphycus alvarezii polymer solution with TiO₂ additive continues to increase approaching the IFT curve of Kappaphycus alvarezii polymer solution. This can occur due to the gradual precipitation of TiO₂ due to gravitational force.

Coreflooding experiments

Coreflooding tests were conducted on four solutions as follows:

Coreflooding A was conducted for a solution

with a salinity of 6,000 ppm and a Kappaphycus alvarezii concentration of 6,000 ppm.

- Coreflooding B was conducted for a solution with a salinity of 6,000 ppm, a Kappaphycus alvarezii concentration of 6,000 ppm, and a TiO₂ concentration of 2,000 ppm.
- Coreflooding C was conducted for a solution with a salinity of 6,000 ppm, a Kappaphycus alvarezii concentration of 4,000 ppm, and a TiO₂ concentration of 2,000 ppm.
- Coreflooding D was conducted for a solution with a salinity of 6,000 ppm, a Kappaphycus alvarezii concentration of 4,000 ppm, and a TiO₂ concentration of 2,000 ppm.

Table 6. Core flooding scenario for water flooding.

Core flooding	Solution	RF Water Flooding
A	3	40.88 %
В	6	41.11 %
C	5	62.50 %
D	4	60.71 %

The application of solutions with a salinity of 6,000 ppm for coreflooding is due to their higher

The four coreflooding scenarios can be expressed in Table 6.

Figure 5 shows the results of coreflooding A and B. Coreflooding A and B were carried out by injecting 3 PV of brine for waterflooding followed by injecting 5 PV of polymer solution for polymerflooding. During coreflooding A, waterflooding produced 0.70 cm³ of oil with a recovery factor (RF) of 40.88%, while polymer flooding produced 0.4 cm³ of oil with a RF of 23.53%. Meanwhile, in coreflooding B, waterflooding produced 0.74 cm³ of oil with a RF of 41.11%, while polymer flooding produced 0.5 cm³ of oil with a RF of 27.67%.

Figure 6 shows the results of coreflooding C and D. Coreflooding C and D were carried out by injecting 4 PV of brine for waterflooding followed by injecting 4 PV of polymer solution for polymerflooding. During coreflooding C, waterflooding produced 0.75 cm³ of oil with an RF of 62.50%, while polymer flooding produced 0.08 cm³ of oil with an RF of 6.67%. Meanwhile, in coreflooding D, waterflooding produced 0.85 cm³ of oil with an RF of 60.71%, while polymer flooding produced 0.11 cm³ of oil with an RF of 7.86%.

Table 7 shows the additional oil recovery factor with polymer addition after water addition (second

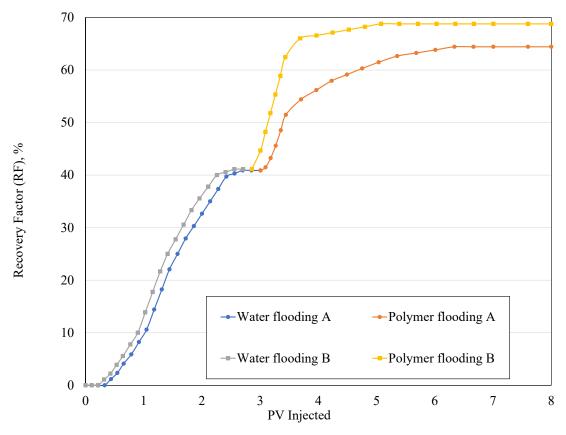


Figure 5. Test of coreflooding A and B

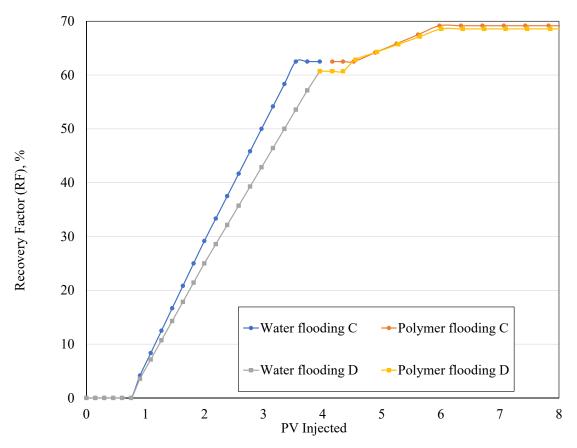


Figure 6. Test of coreflooding C and D

column). The third column shows the total oil recovery factor, which is the sum of the oil recovery factors using water flooding and polymer flooding. The table shows that the use of Kappaphycus alvarezii polymer with a concentration of 6000 ppm and a salinity of 6000 ppm (core filling A) can result in a total oil recovery of 64.41%. The application of TiO₂ additives as in core flooding B can increase the oil recovery factor by 4.37%. Nevertheless, this oil recovery factor is higher than the application of the Kappaphycus alvarezii with lower concentrations as in core floodings C and D.

In addition, Table 7 shows the highest total oil recovery factor, which is 69.17%, obtained by applying coreflooding C. The recovery factor of coreflooding C using a solution with a concentration of Kappaphycus alvarezii of 4,000 ppm, is higher than that of coreflooding B using solution 6 with a concentration of Kappaphycus alvarezii of 6,000 ppm. This is likely due to clogging. As shown in the filtration test (Table 5), the FR of the solution with a concentration of 6000 is more than 1.2 which has the potential to cause plugging in the rock pores.

Based on the results in Table 7, the addition of

TiO₂ nanoparticles to the Kappaphycus alvarezii polymer solution enhanced the total oil recovery factor compared to the base case without nanoparticles. The recovery increased from 64.41% (core flooding A) to 68.78% (core flooding B), while tests C and D achieved up to 69.17%. This improvement indicates that TiO2 effectively enhances polymer flooding performance by slightly increasing viscosity, reducing interfacial tension (IFT), and altering rock wettability toward a more water-wet condition, which promotes better oil displacement. Similar effects of TiO₂ in improving viscosity stability and wettability have been reported in previous studies (Ehtesabi et al., 2013; Cheraghian et al., 2014; Corredor et al., 2019b; Keykhosravi et al., 2021), confirming that the use of nanoparticles can improve both microscopic and macroscopic recovery efficiency.

CONCLUSION

The experimental results demonstrated that the Kappaphycus alvarezii biopolymer possesses favorable rheological and interfacial characteristics for enhanced oil recovery (EOR) applications. The incorporation of TiO₂ nanoparticles effectively

improved the overall performance of the polymer solution by increasing its viscosity up to 11 cP, enhancing its thermal and salinity tolerance, and stabilizing its flow behavior. Wettability and interfacial tension (IFT) analyses confirmed that the addition of Kappaphycus alvarezii and TiO2 nanoparticles altered the rock surface toward a more water-wet condition, reducing the contact angle from 39.05° to 27.47° and lowering the IFT from 7.54 dyne/cm to 6.80 dyne/cm. These physicochemical changes enhanced both the microscopic and macroscopic displacement mechanisms during flooding. Coreflooding tests further validated these findings, showing incremental oil recovery factors ranging from 6.67% to 27.67%, with the highest total recovery factor reaching 69.17% at polymer and nanoparticle concentrations of 4,000 ppm and 2,000 ppm, respectively. However, higher polymer concentrations (6,000 ppm) were found to increase the risk of pore plugging, indicating that an optimal formulation is crucial for field application. Overall, the Kappaphycus alvarezii-TiO, nanocomposite system offers a promising, sustainable, and environmentally friendly alternative to synthetic polymers for chemical EOR operations.

This study identified limitations in the form of TiO₂ aggregation risks and potential plugging at high concentrations, which point to the need for future work to validate long-term stability, injectivity, and conduct field pilot studies under more complex reservoir conditions. Furthermore, research should compare its performance directly with conventional polymers in terms of cost-performance ratio to validate its economic and practical feasibility.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
API	American Petroleum Institute gravity	
IFT	Interfacial Tension	mN/m

PV	Pore volume	cm
φ	Porosity	
μ	Viscosity	cР

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