ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

Artigo de Revisão

WETTABILITY MODIFICATION IN OIL RESERVOIR ROCKS: A COMPREHENSIVE REVIEW ON THE USE OF POLYMERIC NANOFLUIDS FOR ENHANCED OIL RECOVERY

Modificação da molhabilidade de rochas reservatório de petróleo: uma revisão abrangente sobre o emprego de nanofluidos poliméricos para otimização da recuperação de petróleo

Maria Eduarda R. Vaz[1]*, Priscila F. Oliveira[1], Luiz Carlos M. Palermo[1] e Claudia R. E. Mansur[1,2]

[1]Instituto de Macromoléculas Eloísa Mano, IMA/UFRJ.
[2]Programa de Engenharia Metalúrgica e de Materiais – PEMM, COPPE/UFRJ

Submetido em: 20.09.2024; Aceito em: 08.10.2024; Publicado em: 28.10.2024.

***Autor para correspondência:** mariaeduardariente@ima.ufrj.br

Resumo: A crescente demanda por petróleo, impulsionada pelo aumento populacional, tem gerado um interesse crescente na área de pesquisa promovida pelo setor industrial, que busca métodos de recuperação avançada mais eficientes. Nesse cenário, os métodos químicos se destacam devido ao seu custo-benefício e à variedade de opções disponíveis. Entre essas opções, destaca-se a aplicação de agentes que podem restaurar a molhabilidade à água das rochas de reservatório, especialmente em campos maduros, com o objetivo de aumentar o fator de recuperação de óleo a longo prazo. Entre os agentes químicos utilizados, os polímeros são notáveis por sua eficácia na melhoria da eficiência de varrido, embora a aplicação desses compostos como modificadores de molhabilidade ainda seja limitada. O sinergismo entre polímeros e nanopartículas para essa finalidade tem mostrado resultados promissores e constitui o foco desta revisão.

Palavras-chave: Polímeros; nanopartículas; modificadores de molhabilidade; EOR.

Abstract: The growing demand for oil due to the population increase generates an increasing interest in the research area, driven by the industrial sector in the search for increasingly efficient advanced recovery methods. In this context, chemical methods stand out due to their cost-effectiveness and their range of possibilities. Among them, there is the use of agents capable of recovering water wettability from reservoir rocks, especially from mature fields, thus increasing the oil recovery factor in the long term. Among the chemical agents used, polymers stand out, already widely used to increase sweep efficiency, but the exploitation of these compounds as wettability modifying agents is still limited. The synergism between polymers and nanoparticles for this purpose already presents promising results, thus being the focus of this review.

Keywords: Polymers; nanoparticles; wettability modifiers; EOR.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

INTRODUCTION

Oil, being still one of the largest sources of energy resources, has a high global demand, leveraged by population growth. However, the production of oil from more mature wells is not advantageous due to the large volume of water produced, generating losses in production and cost to treat this effluent before its disposal. The produced water can present volumes 10 times greater than the produced hydrocarbons, reaching 98% of the extracted fluid. Produced water composition is a complex mixture of organic and inorganic compounds, featuring heavy metals such as lead (Pb), nickel (Ni), cadmium (Cd) and chromium (Cr) (KHATIB; VERBEEK, 2002; NSIAH *et al*., 2023).Therefore, a more efficient exploitation of already known reserves is necessary. Brazil is considered the largest energy consumer in Latin America, representing more than 40% of the region's consumption. Its energy matrix is dominated by renewable energy sources and oil, the latter still prevailing in the market due to the cost-benefit of its production (IEA, 2020; LASHARI *et al*., 2023).

The growing demand for oil must be met through the discovery of new wells or by increasing the oil recovery factor of already explored or mature wells (MOHSENATABAR FIROZJAII; SAGHAFI, 2020). The *Recovery Factor* is the parameter that indicates the percentage of the volume of oil that was extracted from a reservoir or well in relation to the total volume in it. Primary oil recovery is achieved through the differential pressure naturraly present between the reservoir and the oil well, displacing the oil by mechanical drag strength. Subsequently, to maintain the reservoir pressure, water is injected in a process called secondary recovery (MOHSENATABAR FIROZJAII; SAGHAFI, 2020; ROSAS, 2005).

However, approximately 60% of the oil is still retained in the carbonate reservoirs, due to their heterogeneity and capillary trapping (AGI *et al*., 2020). The recovery of oil from this type of reservoir through water injection (secondary recovery) is not very efficient because the fractured carbonate reservoirs present greater wettability to the oil. Thus, the injected water is not able to properly penetrate the rocky pores, resulting in a low crude oil recovery factor (WU *et al*., 2008).

Carbonate reservoirs account for more than 60% of world oil reserves and 40% of world gas reserves, and their production is only 2% of national production capacity (GHOSH; SHARMA; MOHANTY, 2019; YAO; WEI; KANG, 2021; ANP, 2021).

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

Thus, the rapid decline in crude oil production and the great demand for it have forced the industry to develop new Enhanced Oil Recovery (EOR) technologies that can improve production not only from mature fields, but also from new fields such as those in the pre-salt. Among the EOR techniques, one can mention gas injection, thermal recovery, biological and chemical injection (cEOR), which has gained prominence due to its high efficiency associated with reduced capital investments (KUMAR *et al*., 2022; YEKEEN *et al.*, 2023).

The injection of fluids for EOR may be able to change some properties of the reservoir, among them, the wettability of the reservoir rock stands out. The wettability of most carbonate reservoirs is characterized as oil-wet or mixed wettability and its change to water-wet becomes an important factor to facilitate the drag of oil soaked in the pores (through negative capillary forces) (SAGBANA; SARKODIE; NKRUMAH, 2022).

To this end, the rock surface must be modified through chemical interactions, such as hydrogen bonds, acid-base interaction or polar interactions, changes in surface charge or film formation (MOHAMMED; BABADAGLI, 2015; YAO; WEI; KANG, 2021).

In the context of cEOR techniques, the injection of polymeric fluids to increase viscosity, and consequent reduction of the mobility rate and increase in sweeping efficiency, is already widely used, and its application as a wettability modifier is still a subject under study (TAVAKKOLI *et al.*, 2022).

Synthetic polymers, such as partially hydrolyzed polyacrylamide (HPAM), are applied worldwide, on a large scale, to EOR purposes and has been also being applied as a wettability modifying fluid (OLIVEIRA *et al.*, 2019). HPAM is an anionic polymer, due to acrylate groups presence. Upon contact with the oil-coated rock surface, an elestrostatic repulsion is generated between the HPAM and the asphaltenes present in the oil. Thus, the oily layer is expelled and HPAM adsorbs on the rocky surface with its polar clusters exposed to the medium, thus changing the wettability to water-wettable (AHSANI; TAMSILIAN; REZAEI, 2021).

However, under conditions of high salinity (TDS > 5% w/w), high shear rate ($\gamma > 20.000\ s^{-1}$) and high temperature (greater than 60°C), this polymer has low stability, because the amide functional groups hydrolyze with increasing temperature (CASTRO *et al.*, 2020; SERIGHT *et al.*, 2010). This condition, combined with the high concentration of salts, favors the flocculation of polyacrylic acid, requiring chemical modifications or addition of fillers, such as nanoparticles, for example, to minimize this disadvantage (CANCELA *et al*., 2022).

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

Biopolymers, such as xantham gum, guar gum, cellusose and chitosan, appear as an alternative to the use of HPAM because they have a more rigid structure, composed of double or triple helices containing free side chains, thus being more stable under conditions of high temperatures and salinity (ALI *et al.*, 2020; AZARHAVA *et a*l., 2021; KEYKHOSRAVI; BAGHERI; AGHAYARI, 2021; RELLEGADLA *et al*., 2021; REZVANI *et al*., 2018; SOLIMAN; EL-HOSHOUDY; ATTIA, 2020). Allied to this fact, biopolymers are extracted from natural sources, configuring a sustainable strategy to produce polymers, in addition to being biocompatible and biodegradable. Due to the aforementioned facts, biopolymers can be employed for injection purposes in an environmentally friendly and more efficient manner than synthetic polymers (LOPES *et al*., 2014; LI *et al*., 2017, PU *et al*., 2018; RODRIGUES *et al*., 2021; COSTA *et al*., 2022; CARVALHO *et al*., 2022).

In another aspect, the use of nanoparticles (NPs) in synergism with polymers already shows promising results for this purpose, in addition to also presenting the ability to reduce water-oil interfacial tension and increase the viscoelasticity, adsorption and stability of the polymeric fluid under severe reservoir conditions (KAKATI; BERA; AL-YASERI, 2022b; RELLEGADLA *et al.*, 2021; TAVAKKOLI *et al*., 2022).

Thus, this study will review the literature on the application of nanoparticles and polymers to change wettability, an area of study that has been increasingly explored over the years (Figure 1).

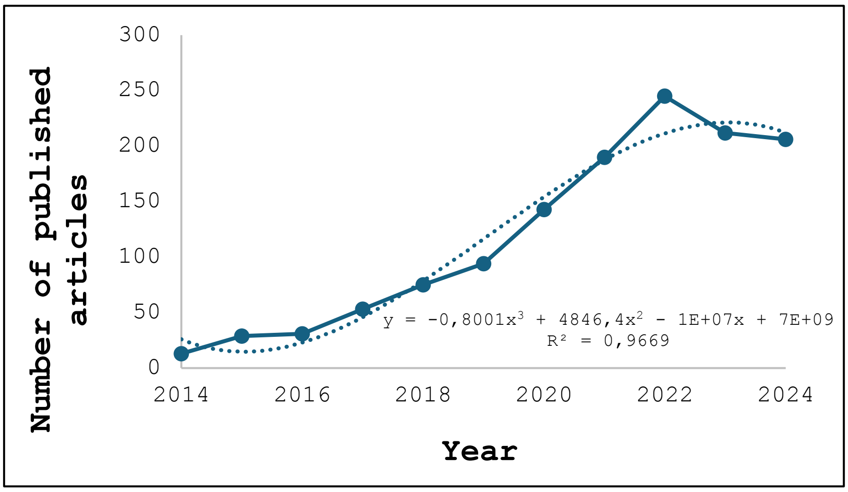

Figure 1. Number of publications on polymeric fluids containing nanoparticles to change wettability for EOR. Data obtained through the *ScienceDirect* platform using the terms “polymers AND nanoparticles AND wettability AND EOR”. Fonte: própria autoria.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

ENHANCED OIL RECOVERY (EOR)

Extraction of crude oil from reservoir rocks occurs through primary, secondary and advanced recovery methods. The primary stage uses the well's own high geological pressure conditions for recovery, while the secondary stage is based on the injection of water, gas or water/gas into the reservoir rock (RELLEGADLA *et al*., 2021). However, primary and secondary recovery processes are only able to extract between 30 and 40% of the local original oil (OOIP), requiring investment in enhanced recovery techniques (EOR) (ALI *et al*., 2020).

EOR techniques are responsible for increasing the displacement and scanning efficiency in a macro and microscopic way, using methodologies that can be broadly divided as thermal methods, gas injection, microbiological and chemical methods of EOR (JUNIOR *et al.*, 2023).

Thermal methods involve the use of heat to reduce the viscosity of the oil, in addition to acting on the thermal expansion of the oil, reducing interfacial tension, thus increasing the mobility of the oil, also acting as a wettability modifier of the reservoir. Thus, this method is able to promote an increase in oil displacement efficiency (BEALESSIO *et al*., 2021; JUNIOR *et al.*, 2023). However, thermal EOR has its limitations related to the large loss of energy to maintain heat flow and formation of preferred heat injection paths.

Aiming to minimize the loss of energy from this process, AFRA *et al.* (2021) used nanomaterials to compose thermal insulators. Ceramic and silicon nanoparticles (SiO_2) were used, obtaining a 44% reduction in energy loss with an increase of only 3% in investment, while procedures already used, such as increasing the rate of heat injection, increase the cost by around 35%, in addition to causing an energy loss of 90% (AFRA *et al.*, 2021).

Recovery using gas injection can be done using oil-miscible or oil-immiscible gases. When using oil immiscible gases, the only effect present is that of maintaining the reservoir pressure, so the injection of miscible gases is more common. In this case, CO_2 or gaseous hydrocarbons that interact with the oil are usually used, promoting changes such as reduction of interfacial tension, reducing the viscosity of the oil, thus facilitating its displacement to the producing well (JUNIOR *et al.*, 2023).

The disadvantage of this technique is related to the difference in viscosity and density between the gas and the crude oil, promoting the formation fingerings that lead to reduced sweep efficiency. In order to solve this problem, alternating water and gas (wag) injection was proposed, first applied in 1957 in Canada.

This methodology combines the advantage of the two injections, controlling the gas-oil mobility rate, making it possible to maintain sweep efficiency and, consequently, increase oil recovery (WANG *et al*., 2020).

Regarding microbiological methods, they employ microorganisms *in situ* and *ex situ*. In the first classification, biological agents are added to reservoirs producing metabolites, gases and bioproducts capable of altering reservoir and oil properties. *Ex situ* application, on the other hand, involves the use of bioproducts previously produced by microorganisms for subsequent injection into the reservoir. Among the bioproducts produced by such agents, biopolymers can be highlighted, which act as viscosifying agents, and biosurfactants, capable of reducing fluid-oil interfacial tension in addition to acting as a wettability modifying agent (JUNIOR *et al.*, 2023; NAJAFI-MARGHMALEKI *et al*., 2018).

In this context, Najafi-Marghmaleki et al. (2018) evaluated the impact of the use of an isolated strain, *Alcaligenes faecalis*, in changing reservoir properties and consequently increasing oil recovery. The microorganism in question was able to produce a biosurfactant *in situ*, responsible for reducing the contact angle of the reservoir rock from 156° to 86°, changing its wettability from oil wettable to mixed wettability. The reduction of interfacial tension between oil and brine from 28.1 to 8.4 $mN.m^{-1}$ was also observed. Finally, the applied microorganism showed an increase of up to 8.4% in the final oil recovery (NAJAFI-MARGHMALEKI *et al.,* 2018).

However, among the EOR techniques, chemical methods (cEOR) are promising techniques, using the injection of chemical compounds to modify reservoir properties or reduce fluid-fluid interfacial tension (JAFARBEIGI *et al.,* 2023; KEYKHOSRAVI; BAGHERI; AGHAYARI, 2021). Commonly, surfactants, alkalis and polymers are used, together or not, and polymeric fluids are the most applied class worldwide due to their effects already known as the increase in viscosity and consequent decrease in mobility rate that prevents the formation of preferred paths (BEALESSIO *et al*., 2021; JUNIOR *et al*., 2023).

The use of nanoparticles (NPs) in cEOR techniques is also an area of interest, since they have the ability to reduce water-oil interfacial tension and increase the viscoelasticity, adsorption and stability of the polymeric fluid under severe reservoir conditions (KAKATI; Bera; AL-YASERI, 2022; RELLEGADLA *et al*., 2021; TAVAKKOLI *et al*., 2022).

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

WETTABILITY

- **Wettability basic concepts**

As a definition, the wettability of a reservoir can be defined as the ability of a fluid to adhere to, or spread over, the rocky surface in the presence of other immiscible fluids (ALNOUSH; SHAAT; ALYAFEI, 2022; SAGBANA; SARKODIE; NKRUMAH, 2022). It can also be described as the affinity of the rock for oil or water that is dependent on the interactions between oil, brine and the rock surface (MOHAMMED; BABADAGLI, 2015). Figure 2 illustrates the ability of a fluid to wet or not wet a solid surface. It is noted that if the fluid does not have affinity for the surface, that is, it does not wet it, it tends to organize itself in such a way as to have the least contact, and therefore the geometric arrangement in the shape of a sphere is favored.

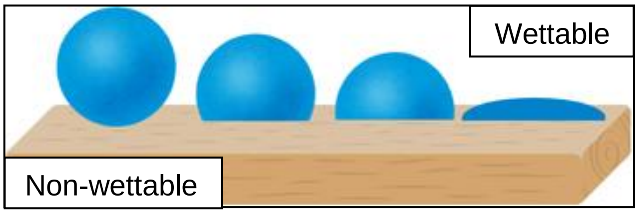

Figure 2. Distribution of a fluid on the surface of a solid in different wettability scenarios. Fonte: própria autoria.

Reservoir rocks tend to prefer being in contact with oil or water and knowing their preference is important in understanding the flow behavior during water injection to displace oil (ALYAFEI, 2021). In the initial state of the reservoir rock, a thin layer of water is formed on its surface. However, when the attractive forces between the brine/rock and oil/brine interfaces are greater than the repulsion force between them, this water layer collapses, allowing contact between the rock and the oil. Thus, the rocky surface goes from water wettable to oil wettable (MOHAMMED; BABADAGLI, 2015; SAGBANA; SARKODIE; NKRUMAH, 2022).

In petroleum reservoirs, the term alteration of wettability generally refers to the process of restoring wettability to the original reservoir, which is assumed to be water-wettable. The target of this restoration treatment is unrecoverable oil by the conventional recovery process (DENG *et al*., 2020). The *water flooding* flow in a reservoir, whose rock is water wettable, will be different from an oil wettable rock. This phenomenon happens due to the low mobility of the water, which will preferably adhere to the surface causing the oil to be expelled easily. Therefore, wettability can be considered as a transport property that affects flow in porous media (YAO; WEI; KANG, 2021).

In the oil reservoir the difference between the attractive and repulsive forces determines the way the fluids are distributed in the porous medium. Thus, the fluid with greater attractive interaction with the rock will maximize the contact between these two phases. On the other hand, the fluid with higher repulsion will minimize contact with the rock. The analysis of the behavior of the fluid against a rocky surface allows classifying the wettability of an oil reservoir between water wettability, intermediate wettability or neutral wettability, oil wettability or neutral wettability (JOHN *et al*., 2003; TIAB *et al*., 2003; ALYAFEI, 2021):

- Water-Wet - when the rock surface prefers to be coated with water, allowing water to spread on the surface. This means that the contact angle will be less than 90° as the water spreads on the surface (Figure 3a).
- Intermediate-wet or neutral-wet - when the surface has an equal tendency to be coated by one of the fluids (oil or water). This means that the contact angle will be around 90° (Figure 3b).
- Oil-wet - when the rock prefers to be in contact with the oil, allowing its spreading. In this case, the contact angle will be greater than 90° (Figure 3c). The cohesive forces between the water molecules are stronger than the adhesive forces between the water molecules and the surface, and therefore the water droplets come together to form a sphere. Every system goes through an energy minimization phenomenon, in which the system tends to go to the lowest energy state and therefore the droplet takes the form of a sphere, as the spheres have the smallest surface area.
- Mixed-Wet - when parts of the rock prefer to be in contact with oil and other parts prefer to be in contact with water. Mixed wettability may also be called fractional wettability, and the contact angle varies depending on the region of the rock.

Although the literature indicates that water-wettable reservoirs produce more oil, some authors observed in their studies higher production in reservoirs with neutral and mixed wettability. As was the case with Salatiel in 1973 who, in a field-scale experiment, showed that reservoirs with mixed wettability can exhibit greater oil recovery during water injection than water-wettable reservoirs.

JADHUNANDAN & MORROW (1991) also tested the effect of reservoir wettability on oil recovery during water injection and concluded that final oil production reached its maximum near the state of neutral wettability and not in a strongly water-wettable state.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

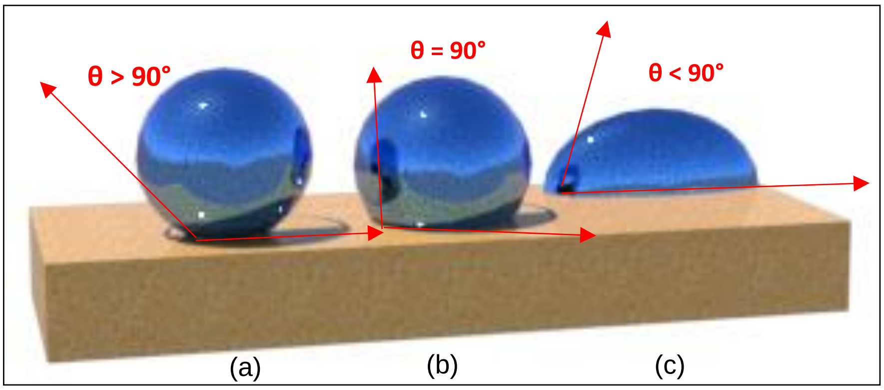

Figure 3. Scheme showing the contact angle measurement on a solid surface for: (a) oil wettability, (b) intermediate wettability or neutral wettability, (c) water wettability. Fonte: própria autoria.

While there is a consensus that changing the wettability of reservoirs to water-wettable or strongly water-wettable is favorable, no conclusive statement can be made about the extent of the change that would lead to optimal recovery of the oil.

WETTABILITY OF CARBONATE RESERVOIRS

- **Electrical charge on the surface of carbonate rocks**

Over the years, oil reservoirs have accumulated hydrocarbons in rocks that were originally filled with water, which remains present in the form of a thin film whose thickness is between 1 and 100 nm and is located between the crude oil and the rock surface (MOHAMMED, BABADAGLI, 2015). When the oil invaded the porous medium, it did not completely displace the water due to the wettability of most of the minerals that form the reservoir rock, such as silica and carbonate (ABDALLAH *et al*., 2007).

The wettability of the reservoir changes when the water layer is destabilized as a result of the oil/water/rock interaction. As a result of this interaction, the reservoir may become wettable to oil (BUCKLEY, 1989).

Understanding the properties of the solid-liquid interface are essential to understand the rupture mechanism of the water film and the adsorption behavior of the oil (YAO *et al.*, 2021). If the rock/water interface and the water/oil interface have identical charges, an electrostatic repulsion force may exist between the two interfaces, as a result, the water film tends to be stable. In contrast, the opposite charge results in an attractive force between two interfaces, which tends to destabilize the water film.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

In carbonate reservoirs, the charge at the water/rock interface is positive, while the water/oil interface has a negative charge when the pH of surrounding brine is greater than 3 (HIRASAKI, 1991; MOHAMMED; BABADAGLI, 2015; SAGBANA; SARKODIE; NKRUMAH, 2022). In addition to the rupture of the water film, McCaffery and collaborators in 1970 showed that stearic acid can bind strongly to calcite. Kaminsky and Radke in 1997, went further in explaining that the asphaltenes and resins components present in the crude oil could alter the wettability with the presence of the water film. According to the authors, these components can diffuse through the thin film of water, and then their polar functional groups adsorb to the rock surface to change the wettability of the rock.

STANDNES *et al*. (2000) presented studies that prove the affinity of carbonate rocks for the acid components of crude oil and point to them as mainly responsible for the oil wettability of rocks of carbonate origin. In this study, the authors showed that the acidic compounds in crude oils bind to the basic surfaces of carbonates.

The presence of an excess of positive species (Ca^{2+}, $CaHCO^{+}_3$ and $CaOH^{+}$) is expected under low pH conditions, while under high pH conditions, in contrast, the excess of negative species (HCO_3^- and CO_3^{2-}) occurs (YAO *et al*., 2021). Knowing the zero point of charge (ZPC) is of great value for the proposal to develop a wettability modifier, as is the case of this project. For Jarrahiam et al., 2012 and Deng et al., 2020, values above the rock sample ZPC indicate negative surface, while below ZPC indicate positive surface.

- **Crude oil/brine/rock interaction**

As previously mentioned, after the collapse stage of the water film, surfactant components present in the crude oil can adsorb onto the surface of the rock to form a hydrophobic layer making it oil-wettable. The hydrophobic layer can be induced by three main categories of crude oil/brine/rock interactions, as indicated in Figure 4, they include polar interactions, surface precipitations, and acid/base interactions (MOHAMMED; BABADAGLI, 2015; YAO; WEI; KANG, 2021).

- <u>Polar interactions</u> - The polar components of crude oil can interact with some polar rock surface locations, in particular asphaltenes and resins showed high surface activity affecting the wettability state, with N, S and O atoms frequently observed in adsorbed components (SALEHI; JOHNSON; LIANG, 2008). According to SUN (2016), polar interaction is a physical adsorption process, which is generally weak and easily reversible.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

- Surface precipitation - Asphaltenes are expected to precipitate on the rock surface, provided that the dissolution capacity of crude oil for asphaltenes is reduced, making the rock surface more oil-wettable. API gravity and oil refractive index are effective for quantifying oil solvency to asphaltenes. It has been indicated that crude oil with higher API gravity is more likely to be a poorer solvent for asphaltenes and vice versa. The refractive index decreases linearly with increasing API gravity of the oil (YAO; WEI; KANG; 2021).
- Acid/base interactions - With the existence of water, polar components at the oil/rock interface could act as acids (capable of donating protons and having charge) or bases (capable of releasing hydroxide ions). As the surface of the carbonate rock is generally positively charged, the adsorption of acidic species tends to be increased (Figure 4). The carboxylate groups can ionize and behave like carbonate anions, while the long fatty acid chains can intertwine with each other to form a compacted hydrophobic layer to strengthen adsorption stability (MOHAMMED; BABADAGLI, 2015).

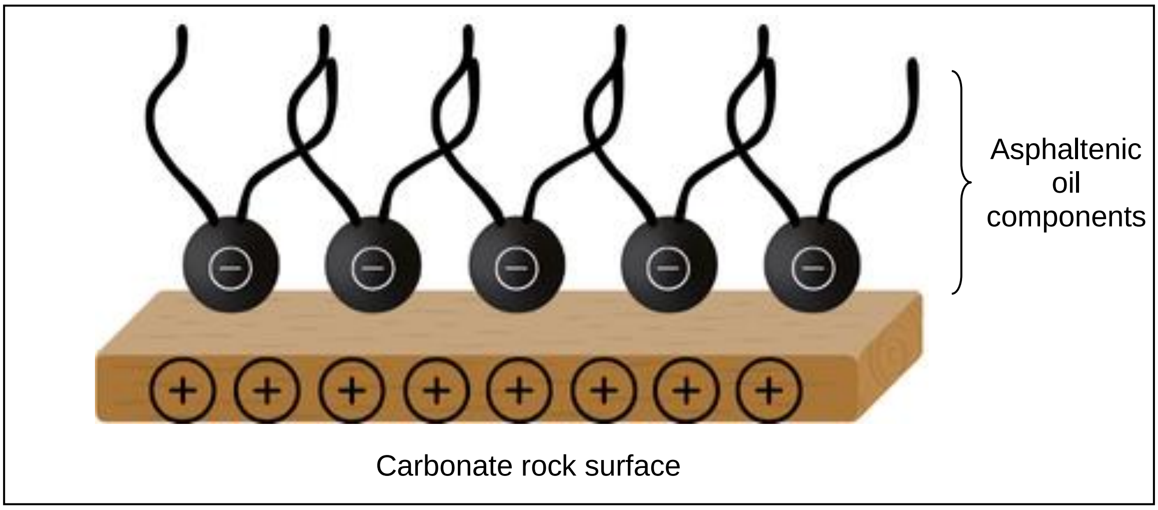

Figure 4. Mechanisms of crude oil/brine/rock interactions. With the presence of water, asphaltenic oil componentsionize and become negatively charged, which can adsorb to the surface of the positively charged rock. Fonte: própria autoria.

MEASUREMENT OF WETTABILITY CHANGE

Among the conventional techniques, the following stand out: (i) contact angle measurements, (ii) Amott-Harvey index, (iii) United States Bureau of Mines (USBM) index and (iv) spontaneous imbibition curve.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

Contact angle measurements are made at the rock surface, however wettability at the rock surface may be different from that within the rock, i.e. at the pore surface. The Amott tests and the USBM provide a value that describes the general wettability of a rock sample (FRANCISCO, 2021).

- **Contact angle**

It is seen in the literature that the contact angle is the most used indicator to quantify wettability. Usually, the contact angle is measured through the aqueous phase when a water/oil interface meets a solid surface. There are many ways to measure the contact angle, among which the most used is the sessile drop method. With this method, the contact angle can be easily measured between the solid/water line and the water/oil line.

- **Amott-Harvey Index**

It is a variation of the Amott method, being widely used to evaluate the wettability of reservoir rock in general. For this, two spontaneous imbibition tests and two forced displacement tests are used. The spontaneous imbibition processes are conducted submerging an oil-aged rock sample in the wettability modifying fluid. Over the time, the wettability alteration occurs and the displaced oil is determined using the graduated apparatus used in this assay. Meanwhile, in forced displacement processes, centrifuges or coreflooding itself are used to induce the flow of imbibing fluid and displace the non-soaked fluid. Thus, the fluid is displaced until it reaches its residual saturation in the rock (AMOTT, 1959; SAGBANA; SARKODIE; NKRUMAH, 2022).

In the case of water and oil wettability assessment, spontaneous water imbibition is first performed until oil production reaches a plateau, followed by forced water imbibition until residual oil saturation is obtained via coreflooding. Such a process is repeated using the oil as the imbibing fluid in place of the water. Thus, the imbibition saturation values (S_{wi}) and total water (S_{wt}) and the imbibition saturation values (S_{oi}) and total oil (S_{ot}) are obtained, which are applied in Equation 1to obtain the Amott-Harvey index (I_{AH}) (SAGBANA; SARKODIE; NKRUMAH, 2022; YAO; WEI; KANG, 2021).

$$I_{AH} = \left(\frac{S_{wi}}{S_{wt}}\right) - \left(\frac{S_{oi}}{S_{ot}}\right) \qquad \text{(Equation 1)}$$

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

- **USBM Index**

The test is conducted in the same way as the Amott-Harvey test. Its wettability index, I_{USBM}, is defined in two parameters: the area under the oil conduction curve, A_o, and the area under the water drive curve, A_w, according to Equation 2.

$$I_{USBM} = log\left(\frac{Ao}{Aw}\right) \qquad \text{(Equation 2)}$$

Table 1 shows the wettability classification according to the methods of evaluation of contact angle, Amott-Harvey index and USBM index, ranging from water-wettable, intermediate, oil-wettable to strongly oil-wettable.

Table 1. Types of wettability based on contact angle

TYPE OF WETTABILITY	Contact angle (°)	AMOTT-HARVEY INDEX	USBM INDEX
Water Wettable	0 - 80	0.3 - 1.5	>0
Intermediate wettability	80 - 100	0.3% - 3%	~0
Oil wettable	100 - 160	1 - 3	<0
Strongly oil-wettable	160-180	-	-

Adapted from DENG *et al.*, 2020.

- **Spontaneous imbibition curve**

Obtaining data for making the spontaneous imbibition curve is done by adding an oil-saturated rock sample to an Amott cell containing water or the fluid that is desired to evaluate the wettability change potential. Over time, if the wettability change actually occurs, oil contained in the rock will be expelled due to its greater affinity for water (Figure 5). The volume data of oil produced, and the time required for this, are plotted in a graph giving rise to the spontaneous imbibition curve (YAO; WEI; KANG, 2021).

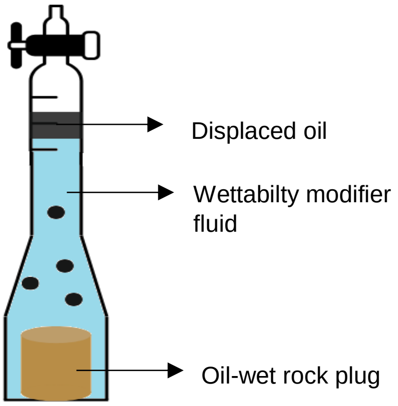

Figure 5. Scheme of an Amott cell containing an oil-saturated rock plug immersed in a modified wettability fluid to obtain the spontaneous imbibition curve. Fonte: própria autoria.

POLYMERS AND NANOPARTICLES AS WETTABILITY MODIFYING FLUIDS

Figure 6 shows a bibliometric analysis on wettability change for EOR in the last ten years. To obtain this graph, the terms: “wettability modifiers” AND “EOR” were used, using the Scopus database and the VOSviewer software. Analyzing the terms representative of the trends of this line of research, it is possible to observe that the injection of polymers and the use of nanoparticles, especially those of silica, appear in evidence indicating that in fact they are resources that present relevance.

Several studies have been conducted in the context of changing the wettability of the reservoir rock for the purpose of an advanced oil recovery process. In general, the interactions between the rock, brine, and oil can be modified through coating or cleaning mechanisms when surface-active substances are used. The first is the formation of a layer of hydrophilic material on the oil-wettable surface. The cleaning mechanism, on the other hand, encompasses the use of substances capable of interacting and, consequently, desorbing the oil from the rocky surface, reestablishing its wettability to water.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

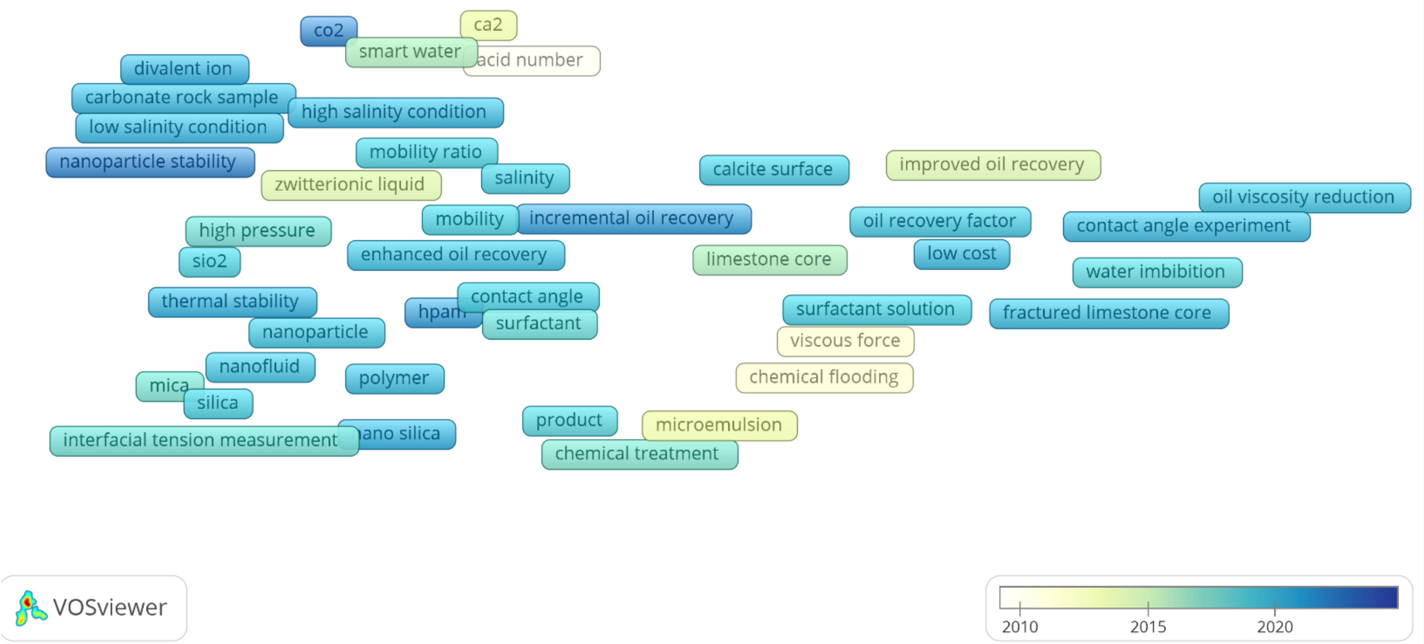

Figure 6. Bibliometric analysis using the VOSviewer software and the terms “wettability modifiers AND EOR” in the Scopus database. Fonte: própria autoria.

Until then, surfactants, alkalis, polymers, nanoparticles, smart waters (brines containing lower concentration of specific cations and anions) and their combination have been analyzed as wettability modifying agents (MOHAMMED; BABADAGLI, 2015; YAO; WEI; KANG, 2021).

NANOFLUIDS

The application of nanotechnology in the petrochemical industry has stood out and attracted the attention of several researchers. Nanoparticles are defined as structures of reduced size, which have between 1 and 100 nm, and can be used in various functions such as drug vehicle, solar cells, image acquisition and in EOR (JOSEPH-IGBOR; ORODU; AFOLABI, 2016; SHAMSIJAZEYI *et al*., 2014).

Due to the size of these particles being smaller than the pore diameter of the rocky surface, they are able to permeate pores that are difficult to access, not swept by injection fluids, allowing them to be covered and functionalized with a small number of nanoparticles. In addition, nanoparticles have some advantageous peculiarities such as superior thermal stability, when compared to some polymers and surfactants, possibility of diameter control and functionalization of their surface, being able to acquire hydrophobic, hydrophilic and even amphiphilic character (ZHANGALIYEV; HASHMET; POURAFSHARY, 2022).

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

The vast surface area of the nanoparticles ensures the increase of properties using reduced concentrations of these. For EOR application, nanofluids enhance oil recovery as they reduce capillary pressure in rocky pores by reducing interfacial tension, oil viscosity, and contact angle, thereby altering the wettability of the reservoir rock. According to McElfresh *et al.* (2012), the nanoparticles are organized in a wedge shape at the three-phase oil-water-solid interface (Figure 7), which increases their ability to displace the oily phase from the rock surface. This layer of nanoparticles, in the confined space of the film, generates a pressure at the end of the drop (disjoining pressure), presenting sufficient magnitude to disrupt the oil-rock interaction, detaching the oil drops from the rock, thus causing the wettability change of the rock surface (KAKATI; BERA; AL-YASERI, 2022; SOLIMAN; EL-HOSHOUDY; ATTIA, 2020).

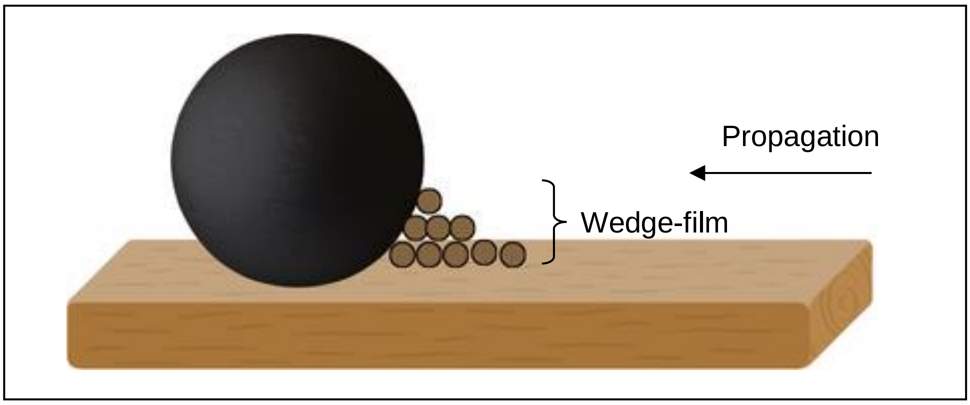

Figure 7. Nanoparticle film displacing crude oil from a solid surface. Fonte: própria autoria.

When hydrophilic nanoparticles adsorb to the rock surface, a thin nanotexture is formed, coating the rock surface. As a result, surface wettability becomes water-wet (GIRALDO *et al.*, 2013; KARIMI *et al.*, 2012).

Studies report that particle size is directly related to the ability to modify the contact angle. Thus, smaller particles, due to their larger contact surface, would act more effectively by reducing the contact angle, thus changing the wettability of the rock (SEFIANE; SKILLING; MACGILLIVRAY, 2008).

Hendraningrat et al. (2013), using lipophobic and hydrophilic nanoparticles (LHP) composed by 99.8% of SiO_2, observed that decreasing particle size increased oil recovery and displacement efficiency. The highest oil recovery was achieved for 7 nm size indicating that nanofluid optimization should consider reducing nanoparticle size to a minimum.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

An important factor that must be taken into consideration is the stability of the nanoparticle in the fluid. This stability is influenced by several factors, including size and shape (sphere, rod, sheet) nanoparticle concentration, salinity of the medium and temperature (AL-ANSSARI *et al*., 2017).

In relation to size, smaller particles tend to present greater stability in solution because, at submicron sizes, the dispersion is maintained due to Brownian motion. As particles have larger diameters, gravitational forces begin to act more effectively, promoting their precipitation. The shape is also an important parameter, since isotropic particles, that is, they have the same size in all directions, are more stable than anisotropic ones. This is due to the more uniform distribution of partial charges in isotropic particles, thus prevailing the repulsive forces that keep the particles separated (KUMAR *et al.,* 2022).

Within the scope of the concentration, there is a limit where the repulsive forces still overlap the attractive ones, preventing the agglomeration and sedimentation of the particles and may cause blockage of the pores of the reservoir rock. This limit varies from one nanoparticle to another, depending on characteristics such as charge and structure (KAKATI; BERA; AL-YASERI, 2022a; KUMAR *et al.*, 2022).

The influence of temperature and salinity on the stability and adsorption of NPs is of great interest in the oil industry, due to high salinity conditions and higher reservoir temperatures. Studies report that higher salinities generate a drop in the zeta potential of nanoparticles, favoring their agglomeration (KUMAR *et al*., 2022). However, the addition of polymers has been shown to be efficient in preventing this agglomeration, and the increase in salinity would favor the adsorption of particles on the rocky surface (KADHUM *et al*., 2017).

The temperature factor is still something under study, as it will depend on other factors such as the influence on the distribution of charges around the particle. At high temperatures, reducing the interfacial tension is extremely important for increasing oil recovery, so if the particle is able to continue exercising this purpose without agglomerating, its performance will continue to be satisfactory (KUMAR *et al.*, 2022).

A major challenge in the production of nanofluids lies precisely in this issue of the stability of their dispersions. Since such nanoparticles tend to agglomerate with increasing concentration, strategies for the preparation of nanofluids have been developed. Among them, we can mention the use of ultrasonic probes and the association with polymers, where the particles would be trapped in the polymer chains, stabilizing them (KEYKHOSRAVI; VANANI; AGHAYARI, 2021; MOHAMMED; BABADAGLI, 2015).

Among the commonly used nanoparticles, those composed of metal oxides such as aluminum oxide, titanium, zirconium and silicon stand out (Table 2).

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

Table 2. Literature review with some of the most used nanoparticles in EOR

Nanoparticle	Diameter (nm)	Type of water	Obtained results	REFERENCE
Hydrophilic SiO_2	4 – 20	Brine	Imbibition tests showed a 10% increase in oil recovery	(MCELFRESH; HOLCOMB; ECTOR, 2012)
ZrO_2	24	Brine	Contact angle reduction Recovery of 60% OOIP through imbibition test	(KARIMI *et al.*, 2012)
Hydrophilic SiO_2	19	Brine	Recovery of 55% of OOIP	(WASAN; NIKOLOV, 2003)
Al_2O_3/SiO_2		Brine + CTAB	80% reduction in contact angle Final recovery of 92% of OOIP	(REZVANI *et al.*, 2020)
Carbon nanotubes/CTAB	<20 nm	Low salinity water	IFT reduction to 0.33 mN/m contact angle Recovery increase by 21%	(MAHDAVINEZHAD *et al.*, 2022)
TiO_2	21	Smart water	IFT reduction around 70% Reduction of around 40% in contact angle Increase in OOIP recovery Zeta potential analysis indicating the impairment of mono- and divalent cations at pH higher than ZPC.	(SHIRAZI; KORD; TAMSILIAN, 2019)
$TiO_2/MgO/\gamma\text{-}Al_2O_3$	10/20/20	Low salinity water	Reduction of IFT for all nanofluids, with the best result obtained for Al_2O_3	(NOWROUZI; MANSHAD; MOHAMMADI, 2019)
CeO_2/Montmorillonite	14	Distilled water	Reduction of IFT by 33% and contact angle by 87%	(BAHRAMINEJAD *et al.*, 2024)

ESFANDYARI BAYAT *et al.* (2014) investigated the influence of different metal oxide nanoparticles (NPs) on EOR processes. The effect of aluminum (Al_2O_3), titanium (TiO_2) and silicon (SiO_2) oxides on an intermediate wettability carbonate rock in a temperature range ranging from 26 to 60 °C was studied. The contact angle measurement results indicated a more efficient wettability change of SiO_2 (26±2°) against the TiO_2 (57±2°) and Al_2O_3 (71±2°) NPs.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

However, due to the greater availability of raw material for its production and greater cost-benefit ratio, studies involving silicon oxide (SiO_2) have been highlighted in this area. Such oxide can be obtained through synthetic routes or through waste extraction, such as for example from rice husk and straw (LU; HSIEH, 2012; YEKEEN *et al*., 2023; ZAKY *et al*., 2008).

Silicon dioxide is a compound abundant in nature in the form of quartz or sand, forming part of the structure of various natural and synthetic materials. Due to the ease of controlling size and shape through the control of reaction conditions, SiO_2 is widely used for nanoparticle production (FAKOYA; SHAH, 2017; SCHNEIDER *et al*., 2023).

Its properties such as ease of surface functionalization using macromolecules and polymers, obtaining particles of various sizes, shapes, porosity in addition to their biocompatibility, made silica nanoparticles (SiNP) to be used for various purposes. SiNPs can be applied as a drug carrier, thermal and electrical insulators, moisture sensors in addition to their use in the agricultural and energy sector (FAKOYA; SHAH, 2017; GUPTA; QUADROS; MOMIN, 2023).

In the petroleum industry, silica nanoparticles can be exploited in various ways such as drag reduction, rheological control of fluids, stability of emulsions and foams for advanced oil recovery and as wettability modifying agents (FAKOYA; SHAH, 2017).

The silica nanoparticles have silanol groups in their outer layer, conferring a negative surface charge in addition to a hydrophilic character. The presence of silanol groups is also responsible for the anchoring of functional groups of other molecules, thus making it possible to modify their surface (GUPTA; QUADROS; MOMIN, 2023).

As already presented in this work, carbonate rocks tend to have partially positive charges on their surface, so the negative charges present on the surface of SiNPs would facilitate their adsorption on the rocky surface.

There are several methods of obtaining silica nanoparticles, commonly divided between top-down and bottom-up. Top-down methods involve physical phenomena of size reduction of a silica feedstock, while bottom-up methods refer to chemical routes capable of synthesizing silica at the atomic or molecular level (NEGI; ANIRBID; SIVAKUMAR, 2021). The most common methods of obtaining SiNPs will be presented below.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

AGI *et al.* (2020) subjected the rice husk to a temperature of 700° C for 4 hours using a muffle, followed by wet milling with a ball mill. Shrestha and collaborators added a previous washing step for 5 hours with hydrochloric acid followed by muffle burning at 600 °C, while Kumari and collaborators (2023) chose to perform the bleaching step after burning at 750 °C (AGI et al., 2020; KUMARI *et al*., 2023; SHRESTHA *et al*., 2023). In all cases, amorphous silica particles were obtained and followed for milling to reach the nanoscale.

In the case of the production of SiNPs through rice straw, a chemical extraction is usually carried out, using bleaching processes to remove organic matter. YEKEEN *et al*. (2023) applied a rice straw digestion process using anthraquinone soda solution followed by neutralization with sulfuric acid to obtain silica gel, converted into nanoparticles through sonication. LU *et al*. (2012) combined the burning of rice straw at high temperatures with silica extraction through a sodium hydroxide digestion process, thus obtaining ultrapure silica particles (LU; HSIEH, 2012; YEKEEN *et al.*, 2023).

POLYMER AND POLYMER/NANOPARTICLE BASED FLUIDS

The injection of polymeric fluids for advanced oil recovery is already known to promote effects of increased viscosity, reduced mobility rate and, consequently, increased sweep efficiency (AZARHAVA *et al*., 2021; KEYKHOSRAVI, BAGHERI, *et al*., 2021). Partially hydrolyzed polyacrylamide (HPAM) is a polymer widely used in advanced oil recovery (EOR), whose main objective is to viscosify the pressure fluid and improve its mobility rate (OLIVEIRA *et al*., 2019; VIEIRA *et al*., 2021).

However, the role of this polymer as wettability modifying agent has remained a topic of debate. Some studies have been advancing in this regard, in order to mainly analyze the influence of these types of synthetic polymer together with nanoparticles, in increasing oil recovery (SHAMSIJAZEYI *et al*., 2014; NEGI *et al*., 2021; SONTAKKE *et al*., 2022; KUMAR *et al*., 2022).

KUMAR *et al*. (2022) studied the viscosification properties, reduction of interfacial tension and change in wettability of HPAM-GO and HPAM-SiO_2 composites. The results indicated that the addition of GO and SiO_2 in HPAM significantly improved rheological properties, reduced IFT, and decreased contact angle. GO performed better than SiO_2 in terms of improving rheological properties and reducing IFT. However, the addition of SiO_2 in the HPAM resulted in a lower contact angle compared to the HPAM-GO nano-polymer solution. Another positive point to be highlighted was that the synergistic effect of GO and SiO_2 with HPAM showed promising results under severe conditions.

In a more recent study, LASHARI *et al.* (2023) investigated the efficiency of a HPAM/GO-SiO_2 composite in altering the wettability of a carbonate rock from coreflooding assays. In this study, a novel HPAM/GO-SiO_2 polymer nanocomposite for advanced oil recovery was investigated experimentally. An investigation of the structural integrity of the composite, morphological interactions and possible binding effects was conducted. The response surface method was used to replicate the contact angle measurements. Experiments obtained with assays in porous media showed that the HPAM/GO-SiO_2 composite was superior in terms of pressure drop, water cut and final oil recovery. Fluids containing HPAM and HPAM/GO-SiO_2 at concentrations of 0.05% wt resulted in 15.5 and 30.8%, respectively, increase in oil recovery.

Biopolymers, due their rigid structure, have greater tolerance and stability at higher temperatures and higher concentrations of cations, in addition to being a more ecological alternative because of their biodegradability and biocompatibility (SOLIMAN; EL-HOSHOUDY; ATTIA, 2020). Among the biopolymers, xanthan gum, guar gum and cellulose and chitosan derivatives are the most used biopolymers in EOR, also being used to polymeric nanofluids production for wettability alteration (REZVANI *et al*., 2018; SOLIMAN *et al*., 2020; ALI *et al.*, 2020; FRANCISCO *et al*., 2020; RELLEGADLA *et al*., 2021a; RELLEGADLA *et al*., 2021b; AZARHAVA *et al*., 2021; MANSHAD *et al*., 2022; GARMROUDI *et al*., 2020; KEYKHOSRAVI *et al*., 2021).

REZVANI *et al.* (2018) synthesized Fe_3O_4@Chitosan nanocomposites and investigated for the first time the effects of this fluid on EOR. To this end, several static and dynamic experiments, including contact angle, zeta potential, absorption spectroscopy, oil viscosity, interfacial tension (IFT), and injection into unconsolidated carbonate sand medium, were conducted. Zeta potential and absorbance measurements indicate a good stability condition for the nanocomposite synthesized in seawater during dynamic experiments.

The results of the contact angle measurements indicate a 42 to 53° reduction for nanocomposites of 0.01, 0.02 and 0.03% in seawater at ambient conditions, which resulted from the accumulation of nanocomposites in the vicinity of the rock surface. In the end, a 10.8% increase in oil recovery with fluid containing 0.03% was obtained, compared to injection with seawater.

SOLIMAN *et al.* (2020) investigated the efficiency of solutions of Xanthan Gum (GX), physical mixture of Xanthan Gum/SiO_2 (GX/SiO_2) and Xanthan Gum grafted with silica nanocomposite (GX-g-SiO_2), in the ability to recover oil and change rock wettability.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

The authors observed that mixing or grafting of silica derivatives considerably improved the rheological properties of the xanthan gum solutions to resist salinity of the medium and higher temperatures. Relative permeability curves and fractional flow curves indicated that the presence of silica precursors modifies the wettability of rocks to more water-wettable and improves displacement efficiency which in turn increases oil recovery.

Cumulative oil recovery increased with increasing xanthan gum fluid concentration and maximum oil recovery is achieved at 2.0 g/L. Oil recovery increases with increasing concentration of XG/SiO_2 physical mixture up to 1.5 g/L, but with further increasing concentration of XG/SiO_2 physical mixture, the amount of oil decreased. The XG-g-silica composite can be considered a reasonable agent to enhance oil recovery where it has a great effect on reducing interfacial tension and changing wettability.

Franciscos et al. (2020) evaluated the ability to modify the wettability of oil-wet carbonate rocks from chitosan derivatives such as trimethylchitosan (TMC) and trimethylchitosan hydrophobized with myristoyl chloride (TMC-C14). Tests were conducted through contact angle measurements, atomic force microscopy, and oil recovery testing in the unconsolidated porous media. The authors observed efficiency of the products in modifying the wettability of the carbonate rocks, making them wettable in water, promoting oil displacement increases of 25% for TMC and 16% for TMC-C14. TMC showed a better performance for wettability change than TMC-C14, confirming the hypothesis that the higher the positive charge density in the polymeric surfactant structure, the more efficient the system is as a wettability modifier and as an EOR agent.

In this context, AZARHAVA *et al*. (2021) produced and investigated poly γ (glutamic acid) (PGA), a biopolymer synthesized by the bacterial strain *Bacillus licheniformis LMG 7559* that has properties similar to polyacrylate, such as high-water absorption. Its application in EOR proved to be efficient, since it promoted a reduction in the contact angle in 22 units, more positive values of surface charge, indicating the desorption of asphaltenes and, consequently, promoting an oil recovery of 31.45% for the concentration of 0.5% (m/v) of PGA. KEYKHOSRAVI *et al.* (2021) also investigated a polymeric nanofluid using xanthan gum, but associated with TiO_2 nanoparticles. The zeta potential results showed more positive values, indicating the desorption of asphaltenes, corroborating the contact angle measurement, reduced from 128° to 21°, confirming the change from wettability to water wettable. Finally, the nanofluid containing only the nanoparticles was able to generate a 12% increase in OOIP recovery, the polymeric solution accounted for 19% and the polymeric nanofluid resulted in an additional 25% recovery.

In order to save the environment and preserve human health by reducing the production of toxic compounds, the study and application of green nanocomposites has expanded. Considering this context, ALI *et al.* (2020) developed a nanocomposite of Fe_3O_4@SiO_2@Xanthan Gum using the extract of the *Alocasia macrorriza plant* as a reducing agent. In order to analyze the efficiency of these systems, interfacial tension and contact angle analyses were conducted. The concentration that resulted in a better IFT reduction was 1500 ppm of nanocomposite, promoting a reduction from 28.3 mN/m to 8 mN/m, while for the contact angle a better result was obtained at a concentration of 1000 ppm, causing a reduction from 134° to 34.5° (Figure 15) (ALI *et al*., 2020).

Still with an environmental bias, AHMADI *et al.* (2023) developed nanocomposites from eucalyptus (ENC) and walnut shells (WNC) associated with xanthan gum and compared them with a nanocomposite consisting of Xanthan Gum@magnetite@SiO_2 (NC). The nanocomposites were analyzed under different salinities through CA and spontaneous imbibition assays. The best results were obtained by the ENC at salinities of two (2SW) and 10 times (10SW) the regular salinity, leading to a reduction of contact angle to 49 and 43.4°, for the respective salinities (Figure 16). Regarding oil recovery, the imbibition tests showed values of 64.13 and 60.12% of increment for 10SW and 2SW, respectively, compared to only 46.16% of the reference nanocomposite (AHMADI *et al*., 2023).

AHMADI *et al*. (2023) were also responsible for conducting other research developing another type of nanocomposite: SiO_2@ZnO@Xanthan Gum from biosynthesis using pomegranate seeds. This fluid was also evaluated at the 2SW and 10SW salinities, with reductions in the contact angle and increased oil recovery being analyzed. An IFT drop to 80 and 78° values and an oil recovery factor increase to 25.1 and 34.1% was observed for 2SW and 10SW salinities, respectively (AHMADI; JAVADI; KIKHAVANDI, 2023).

CONCLUSIONS

Currently, the polymers most used for EOR purposes are synthetic and besides being non-biodegradable, can generate toxic by-products. Associated with this, there is the fact of the lower resistance of such polymers to severe conditions of salinity and reservoir temperature. Thus, biopolymers emerge as an ecological alternative that offers greater chemical and thermal resistance due to the rigidity of their chemical structure.

Studies using polymers as wettability modifiers are still scarce, and their association with nanoparticles is more common. Such structures, despite not presenting a cheap synthesis route, become a cost-effective option due to the small concentration necessary to observe significant results. In light of this consideration, several researchers have concentrated efforts to develop nanoparticle extraction routes from industrial waste.

The combination of biopolymers and nanoparticles is a good strategy for obtaining a wettability modifying agent, since the cost of extracting polymers from natural sources, often higher than the cost of producing synthetic polymers, can be compensated using low-cost nanoparticles, thus also allowing the use of a lower polymer concentration. Thus, further studies in the area become necessary, since the change in wettability promotes significant impacts on oil recovery by, for example, reducing the amount of water produced. With this, the recovery yield is increased in addition to minimizing the costs of treating oily water, a by-product of the process that can reach values of up to 90% of the composition of the fluid produced by the reservoir well.

ACKNOWLEDGMENTS

This research was carried out in association with the R&D project registered as ANP 23186-0, “Desenvolvimento de biopolímeros, biocidas e biossurfactantes e tratamento de água como soluções para recuperação de petróleo com aplicação offshore” (Universidade Federal do Rio de Janeiro (UFRJ) / Shell Brasil / ANP) – “Development of biopolymers, biocides and biosurfactants and water treatment as solutions for oil recovery with offshore application”, sponsored by Shell Brasil under the ANP R&D levy as “Compromisso de Investimentos com Pesquisa e Desenvolvimento”. This work was also supported in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES), Finance Code 001, the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) and the Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ).

REFERENCES

ABDALLAH, W. *et al*. Fundamentals of wettability. **Oilfield Review 19**(2), 44–61, 2007.
AGI, A. *et al*. Synthesis and application of rice husk silica nanoparticles for chemical enhanced oil recovery. **Journal of Materials Research and Technology 9**(6), 13054–13066, 2020.
AHMADI, Y. *et al*. Application of Green Polymeric Nanocomposites for Enhanced Oil Recovery by Spontaneous Imbibition from Carbonate Reservoirs. **Polymers 15**(14). 2023.

AHMADI, Y.; JAVADI, F.; KIKHAVANDI, T. Effect of different salinity on low permeability carbonate reservoir recovery using a new green polymeric nanocomposites. **Energy Sources, Part A: Recovery, Utilization and Environmental Effects 45**(1), 1091–1103, 2023.

AHSANI, T.; TAMSILIAN, Y.; REZAEI, A. Molecular dynamic simulation and experimental study of wettability alteration by hydrolyzed polyacrylamide for enhanced oil recovery: A new finding for polymer flooding process. **Journal of Petroleum Science and Engineering 196**, 2021.

AL-ANSSARI, S. *et al*. Effect of temperature and SiO2 nanoparticle size on wettability alteration of oil-wet calcite. **Fuel 206**, 34–42, 2017.

ALI, J. *et al*. Greenly Synthesized Magnetite @ SiO 2 @ Xanthan Nanocomposites and Its Application in Enhanced Oil Recovery : IFT Reduction and Wettability Alteration. **Arabian Journal for Science and Engineering 45**(9), 7751–7761, 2020.

ALNOUSH, W.; SHAAT, A.; ALYAFEI, N. What is the Optimum Wettability for Oil Recovery Through Waterflooding? **Society of Petroleum Engineers - SPE Conference at Oman Petroleum and Energy Show, OPES 2022**, 9–11, 2022.

AMOTT, E. Observations Relating to the Wettability of Porous Rock. **Transactions of the AIME 216**(01), 156–162, 1959.

AZARHAVA, H. *et al.* Journal of Petroleum Science and Engineering Stability and performance of poly γ - (glutamic acid) in the presence of sulfate ion for enhanced heavy oil recovery. **Journal of Petroleum Science and Engineering 196**, July 2020, 107688, 2021.

BAHRAMINEJAD, H. *et al*. Nanocomposite synergy for enhanced oil recovery: Macro and micro analysis of CeO2/montmorillonite nanofluids in carbonate and sandstone reservoirs. **Fuel 360**, 2024.

BEALESSIO, B. A. *et al.* A review of enhanced oil recovery (EOR) methods applied in Kazakhstan. **Petroleum.** KeAi Communications Co.**,** 1 fev. 2021.

BUCKLEY, 1 5. **Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils**. [s.l: s.n.]. Disponível em: <http://onepetro.org/RE/article-pdf/4/03/332/2631821/spe-16964-pa.pdf/1>.

CANCELA, BR. *et al*. Rheological study of polymeric fluids based on HPAM and fillers for application in EOR. **Fuel 330**, 2022.

CARVALHO, RTR *et al.* Extraction, Characterization and Rheological Behavior of Tamarind Gum Under High Salinity. **Brazilian Journal of Analytical Chemistry 9**(35), 62–75, 2022.

CASTRO, RH. *et al*. Polymers for eor application in high temperature and high viscosity oils: Rock–fluid behavior. **Energies**, **13**(22), 2020.

DENG, X. *et al*. **A Review on Wettability Alteration in Carbonate Rocks: Wettability Modifiers**. **Energy and Fuels,** 2020.

ESFANDYARI BAYAT, A. *et al*. Impact of metal oxide nanoparticles on enhanced oil recovery from limestone media at several temperatures. **Energy and Fuels 28**(10), 6255–6266, 2014.

FAKOYA, MF; SHAH, SN. Emergence of nanotechnology in the oil and gas industry: Emphasis on the application of silica nanoparticles. **Petroleum**. KeAi Communications Co., 1 dez. 2017.

GHOSH, P.; SHARMA, H.; MOHANTY, KK. ASP flooding in tight carbonate rocks. **Fuel 241**, 653–668, 2019.

GUPTA, J.; QUADROS, M.; MOMIN, M. **Mesoporous silica nanoparticles: Synthesis and multifaceted functionalization for controlled drug delivery**. **Journal of Drug Delivery Science and Technology.** 2023.

HIRASAKI, GJ. Wettability: fundamentals and surface forces. **SPE Formation Evaluation 6**(2), 217–226, 1991.

JAFARBEIGI, E. *et al*. Identification of novel applications of chemical compounds to change the wettability of reservoir rock: A critical review. **Journal of Molecular Liquids 371**, 121059, 2023.

JOSEPH-IGBOR, B; ORODU, OD; AFOLABI, RO. **Evaluating the Oil Mobilization Properties of Nanoparticles Treated with Arabic Gum and Xanthan Gum for Trapped Oil in Porous Media**. [s.l: s.n.]. Disponível em: <http://onepetro.org/SPENAIC/proceedings-pdf/16NAIC/All-16NAIC/SPE-184332-MS/1375393/spe-184332-ms.pdf/1>.

JUNIOR, AN *et al*. Assessing EOR strategies for application in Brazilian pre-salt reservoirs. **Geoenergy Science and Engineering 223**, 211508, 2023.

KADHUM, MJ *et al.* Polymer-Stabilized Multi-Walled Carbon Nanotube Dispersions in High-Salinity Brines. **Energy and Fuels 31**(5), 5024–5030, 2017.

KAKATI, A; BERA, A; AL-YASERI, A. A review on advanced nanoparticle-induced polymer flooding for enhanced oil recovery. **Chemical Engineering Science 262**, 117994, 2022a.

KAKATI, A.; BERA, A.; AL-YASERI, A. **A review on advanced nanoparticle-induced polymer flooding for enhanced oil recovery**. **Chemical Engineering Science**, 23 nov. 2022b.

KARIMI, A. *et al.* Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. **Energy and Fuels**, **26**(2), 1028–1036, 2012.

KEYKHOSRAVI, A.; BAGHERI, M.; AGHAYARI, C. Journal of Petroleum Science and Engineering TiO 2 nanoparticle-induced Xanthan Gum Polymer for EOR : Assessing the underlying mechanisms in oil-wet carbonates. **Journal of Petroleum Science and Engineering 204**, 108756, 2021.

KHATIB, Z; VERBEEK, P. **Water to Value-Produced Water Management for Sustainable Field Development of Mature and Green Fields m3/d PD O AFPC SPDC BSP Expro Norske Shell Gabon Thai Shell SSPC SSB NAM Figure 1: History and Forecast W ater Production in Shell E&P operations; colors refer to different operating fields**. [s.l: s.n.]. Disponível em: <http://onepetro.org/SPEHSE/proceedings-pdf/02HSE/All-02HSE/SPE-73853-MS/2925703/spe-73853-ms.pdf/1>.

KUMAR, D. *et al*. A review on application of nanoparticles in cEOR: Performance, mechanisms, and influencing parameters. **Journal of Molecular Liquids 353**, 118821, 2022.

KUMARI, A. *et al*. Green synthesis and physical properties of crystalline silica engineering nanomaterial from rice husk (agriculture waste) at different annealing temperatures for its varied applications. **Journal of the Indian Chemical Society 100**(5), 100982, 2023.

LASHARI, N. *et al*. Coreflood investigation of HPAM/GO-SiO2 composite through wettability alteration. **Journal of Molecular Liquids 371**, 2023.

LU, P; HSIEH, Y. LO. Highly pure amorphous silica nano-disks from rice straw. **Powder Technology 225**, 149–155, 2012.

MAHDAVINEZHAD, M. *et al*. Efficacy of f-MWCNT-CTAB nano-complex in low-salinity seawater EOR operation. **Journal of Petroleum Science and Engineering 208**, 2022.

MCELFRESH, P.; HOLCOMB, D.; ECTOR, D. Application of nanofluid technology to improve recovery in oil and gas wells. **Society of Petroleum Engineers - SPE International Oilfield Nanotechnology Conference 2012**, **2003**, 46–51, 2012.

MOHAMMED, M.; BABADAGLI, T. **Wettability alteration: A comprehensive review of materials/methods and testing the selected ones on heavy-oil containing oil-wet systems**. **Advances in Colloid and Interface Science.** 2015.

MOHSENATABAR FIROZJAII, A.; SAGHAFI, HR. Review on chemical enhanced oil recovery using polymer flooding: Fundamentals, experimental and numerical simulation. **Petroleum 6**(2), 115–122, 2020.

NAJAFI-MARGHMALEKI, A. *et al*. Experimental investigation of efficiency of MEOR process in a carbonate oil reservoir using Alcaligenes faecalis: Impact of interfacial tension reduction and wettability alteration mechanisms. **Fuel 232**, 27–35, 2018.

NEGI, G. S.; ANIRBID, S.; SIVAKUMAR, P. **Applications of silica and titanium dioxide nanoparticles in enhanced oil recovery: Promises and challenges**. **Petroleum Research.** KeAi Publishing Communications Ltd, 1 set. 2021.

NOWROUZI, I.; MANSHAD, AK.; MOHAMMADI, AH. Effects of TiO2, MgO, and γ-Al2O3 nano-particles in carbonated water on water-oil interfacial tension (IFT) reduction in chemical enhanced oil recovery (CEOR) process. **Journal of Molecular Liquids 292**, 2019.

NSIAH, F. *et al*. Impact assessment of high-risk analytes in produced water from oil and gas industry. **Marine Pollution Bulletin**, **191**, 2023.

OLIVEIRA, PF *et al*. Hydrolysis and thermal stability of partially hydrolyzed polyacrylamide in high-salinity environments. **Journal of Applied Polymer Science 136**(29), 2019.

PU, W. *et al*. **A comprehensive review of polysaccharide biopolymers for enhanced oil recovery (EOR) from flask to field**. **Journal of Industrial and Engineering Chemistry.** Korean Society of Industrial Engineering Chemistry, 25 maio 2018.

RELLEGADLA, S. *et al*. Wettability Alteration of the Oil-Wet Carbonate by Viscosity- Augmented Guar Galactomannan for **Enhanced Oil Recovery**. 2021.

REZVANI, H. *et al.* Experimental investigation of interfacial properties in the EOR mechanisms by the novel synthesized Fe3O4@Chitosan nanocomposites. **Colloids and Surfaces A: Physicochemical and Engineering Aspects 544**, 15–27, 2018.

REZVANI, H. *et al*. A novel foam formulation by Al2O3/SiO2 nanoparticles for EOR applications: A mechanistic study. **Journal of Molecular Liquids 304**, 2020.

ROSAS. **Reservatorios de Petroleo 20016**(202), 2–3, 2005.

SAGBANA, PI; SARKODIE, K; NKRUMAH, WA. A critical review of carbonate reservoir wettability modification during low salinity waterflooding. **Petroleum**, 2022.

SCHNEIDER, M. *et al.* Synthesis and characterization of silica-based nanofluids for enhanced oil recovery. **Journal of Materials Research and Technology 24**, 4143–4152, 2023.

SEFIANE, K.; SKILLING, J.; MACGILLIVRAY, J. Contact line motion and dynamic wetting of nanofluid solutions. **Advances in Colloid and Interface Science**, 19 maio 2008.

SERIGHT, R. *et al.* **This paper (SPE 121460) was accepted for presentation at the SPE International Symposium on Oilfield Chemistry SPE Journal**. [s.l: s.n.]. Disponível em: <http://onepetro.org/SJ/article-pdf/15/02/341/3299452/spe-121460-pa.pdf/1>.

ISSN 1984-5693
Vol.16, 2024,
http://dx.doi.org/10.22407/1984-5693.2024.v16.p.e20241609

SHAMSIJAZEYI, H. *et al*. Polymer-coated nanoparticles for enhanced oil recovery. **Journal of Applied Polymer Science 131**(15), 1–13, 2014.
SHIRAZI, M.; KORD, S.; TAMSILIAN, Y. Novel smart water-based titania nanofluid for enhanced oil recovery. **Journal of Molecular Liquids 296**, 2019.
SHRESTHA, D. *et al*. Rice husk-derived mesoporous biogenic silica nanoparticles for gravity chromatography. **Heliyon 9**(4), e15142, 2023.
SOLIMAN, AA; EL-HOSHOUDY, AN; ATTIA, AM. Assessment of xanthan gum and xanthan-g-silica derivatives as chemical flooding agents and rock wettability modifiers. **Oil and Gas Science and Technology 75**(12), 1–13, 2020.
TAVAKKOLI, O. *et al*. Effect of nanoparticles on the performance of polymer/surfactant flooding for enhanced oil recovery: A review. **Fuel 312**, 122867, 2022.
VIEIRA, HVP *et al*. Thermal stability of polymers based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid in different temperature and salinity conditions. **Journal of Applied Polymer Science 138**(44), 2021.
WASAN, DT; NIKOLOV, AD. Spreading of nanofluids on solids. **Nature 423**(6936), 156–159, 2003.
YAO, Y; WEI, M; KANG, W. A review of wettability alteration using surfactants in carbonate reservoirs. **Advances in Colloid and Interface Science 294**, 102477, 2021.
YEKEEN, N. *et al.* Synthesis and pore-scale visualization studies of enhanced oil recovery mechanisms of rice straw silica nanoparticles. **Journal of Petroleum Science and Engineering 221**, 2023.
ZAKY, RR *et al*. Preparation of silica nanoparticles from semi-burned rice straw ash. **Powder Technology 185**(1) 31–35, 2008.
ZHANGALIYEV, MM; HASHMET, MR; POURAFSHARY, P. **Laboratory Investigation of Hybrid Nano-Assisted-Polymer Method for EOR Applications in Carbonate Reservoirs.** 2022.