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BIOPOLYMERS COMPOSITES AS OIL IMPROVING CANDIDATES-ARTICLE REVIEW

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Abstract

To help with understanding the advancement of biopolymers in enhanced oil recovery (EOR), this article gathers and outlines the accessible information out of the blue and altogether talks about the structural properties of EOR execution relationship from flagon to handle scale application. Considerations were given to xanthan, hydroxyethyl cellulose (HEC), Scleroglucan, carboxymethylcellulose (CMC), gum, guar, hydrogel and other recently grew relatives. This audit gives an abstract of the EOR biopolymer, which is quickly developing as eco-accommodating and extreme injection agents contrasted with engineered polymers.

Keywords: Enhanced oil recovery; Carboxymethylcellulose; Surfactants; Hydrogel.

1. Introduction

Conventional reserves of crude oil progressively decline, so the recovery for heavy oil acauire progressive attention on the scale of the oil industry ^[1]. At the present time, chemical displacement through enhanced oil recovery (EOR) patterns in geological reservoirs increased gradually due to continual energy request ^[2]. Moreover, the oil left after exhausting conventional recovery processes estimated by seven billion barrels ^[3]. Chemical EOR relies on reducing interfacial tension and/or improving mobility ratio in order to solubilize oil ^[4]. EOR through biopolymer overflowing including starch, xanthan gum, scleroglucan, hydroxyethyl cellulose (HEC), carboxymethyl cellulose (CMC), guar gum, cellulose and lignin ^[5] as a natural, lowpriced, plentiful and ecologically friendly agents ^[6-7] is an evolving and guaranteed tendency relevant to chemical submerging, so modified biopolymers anticipated to substitute hydrophobically associated polyacrylamides (HPAM) in the near future concerning EOR techniques ^[8]. Biopolymers produced via different raw materials including straw, sugar cane, corn, polyhydroxyalkanoates (PHA), in addition to cellulosic materials [9]. For commercial EOR projects, HPAM is the most extensively implemented water-soluble polymer ^[10], however, hydrolyzed polyacrylamides (HPAMs) are enormously vulnerable to reservoir environment (temperature, salinity, shearing) which in turn result in remarkable loss of the thickening properties ^[5] due to increased hydrolysis rate of amide groups which in turn form acrylic acid-vulnerable to brine hardness causing HPAM flocculation ^[5]. Moreover, owing to imminent environmental protocols and incremental industrial regulating laws biopolymer-based EOR formulations will be more promised in the future ^[4]. Original biopolymers have some restrictions concerning industrial processing, so it is subjected to physical-chemical modifications ^[11], including etherification, esterification, grafting and crosslinking with other rheology-modifying agents ^[12] to be implemented in enhanced oil recovery patterns, drag reduction, and water shutoff ^[13]. The application of starch derivatives in petroleum industry starts in the 1980s [14], comprising pregelatinization and etherification of starches ^[15]. Recently, many cationic and amphoteric starch grafted copolymers, and other biopolymers attain augmented consideration on the hypothetical and manufacturing interest owing to their unique structure and reactivity as a water-responsive shale or a clay-hydration suppressant. Modified biopolymers exhibit higher resistance to salt and thermal disintegration, which renders biopolymer as a prominent thickening agent in the condition of the harsh reservoir condition ^[5]. Their solutions exhibit high viscosity competency and low responsive behavior towards shear degradation coupled with the intrinsic viscoelasticity and favorable rheological and adsorption criteria ^[16]. Splicing of vinyl monomers on biopolymers generated by water-soluble initiators as well as redox pair initiators ^[17-18]. Some literature discusses the grafting of different vinyl monomers on the biopolymer substrate through free radical initiation reactions and usage as a viscosifier in chemical submerging processes ^[19-23]. Others discuss the implementation of etherified biopolymers in EOR by replacing hydroxyl groups by ether group as reported in our previous literature ^[22, 23] since hydroxyl substitution boost salinity and thermal resistance ^[24].

2. Mechanism of biopolymer flooding

Biopolymer flooding can provide additional oil recovery by 3% after water flooding ^[5]. The process aims to increase aqueous phase viscosity, reducing permeability contrast ^[4] so reduce mobility ratio and improves the sweeping efficacy ^[25]. The technique of biopolymer flooding involves the injection of the biopolymer slug over long years trailed with continued water overflowing to direct the biopolymer slug and the oil toward the producing wells. Injected water seeks the path of the highest permeable zones. If the displaced oil viscosity is higher than the injected water, the water will finger through the oil causing rapid breakthrough or bypassed oil. Consequently, the term mobility ratio (M) used for an initial reservoir evaluation through assessment of the water and oil relative permeabilities and viscosities based on Darcy's Law ^[26]. $\lambda W KW/\mu W KW\mu O$

$$M = \frac{\lambda W}{\lambda O} = \frac{KW/\mu W}{KO/\mu O} = \frac{KW\mu O}{KO\mu W}$$

(Eq.3)

Mobility ratio (M) expressed as displacing phase mobility divided by the displaced phase mobility. Biopolymer decreases water mobility through: (1) increasing the water phase viscosity; (2) reducing the water relative permeability to the porous rock via adsorption and/or retention of the biopolymer in the pore throats. By reducing the mobility ratio, the sweeping efficacy and oil recovery are improved ^[27]. If the mobility ratio ($M \leq 1$), the sweeping and displacement efficiencies of the oil by the water phase will be effective and pistons like fashion. On the other hand, when the mobility ratio (M > 1), the mobile displacing water phase will flow more readily than the displaced oil fluid and lead to serious viscous fingerings or channeling through the oil causing "breakthrough" leaving behind regions of unswept oil. As a result, some of the residual oil is bypassed resulting in poor recovery ^[28]. Moreover, biopolymers can recompense the reservoir pressure after its passage ^[27]. This behavior resort to the biopolymer ability to builds up a resistance to flow in the porous media ^[27]. This incremental flow resistance forced the injected water into poor swept zones. Biopolymer retention reduces the wetting phase relative permeability more than the relative permeability of the non-wetting phase in the water-wet reservoirs due to the improved gelling properties of the biopolymers.

3. Flooding experiments

The sandstone flooding experiments carried out as described in our literature ^[2, 22, 25, 29-33] with brine solution, crude oil and aqueous biopolymer solutions to obtain certain reservoir parameters such as porosity, permeability, initial oil and water saturation, in addition to predict the polymer performance and recovered oil amount with respect to slug size and concentration through two steps.

3.1. Brine overflowing

The sandstone was evacuated and then saturated with brine solution after 10 pore volumes flooding at a constant low flow rate. The brine solution flew first through the sand packed model to produce the equilibrium pressure (P_0), where the differential pressures between the

inlet and the outlet were monitored. After saturation was achieved, permeability (K_w) to the brine solution was calculated by monitoring the pressure drop through the model, and the flow rate using Darcy's equation ^[34]. The biopolymer solution displaces the brine solution to yield another equilibrium pressure (P₁). Finally, the brine solution was injected again to flush the non-adsorbed biopolymer from the sandstone at the end of the biopolymer injection process. When the pressure drop stabilized across the model, the experiment was finished, record the pressure (P₂). Based on their pressure difference (ΔP), the resistance factor (R_f) and a residual resistance factor (R_{rf}) estimated from equations 1&2 respectively.

$$Rf = \frac{(\Delta P)p}{(\Delta P)w}$$
(1)
$$Rrf = \frac{(\Delta P)w(Afterpolymer)}{(\Delta P)w(Before polymer)}$$
(2)

3.1. Crude oil flooding

The stock tank oil was injected at a low rate of 60 cc/h by a syringe pump until the water production ceased. Crude oil permeability at initial water saturation (S_{wi}) was also measured. The sandstone was allowed to age for 14 days to attain equilibrium under reservoir conditions, and overburden pressure of 500-1000 psi was applied to the sandstone during the aging time and flooding conductance. The purpose of this aging procedure was to alter sandstone wettability to oil-wet. The sand pack flooding tests represented schematically in Figure 1. After oil injection, the sand pack was brine flooded. Brine injection was everlasting till the ceased oil production. At this stage recovered oil by primary and secondary methods is exhausted. After brine injection, about 3-5 pore volumes (PV) of biopolymer slug was injected and left for about 24 hours, endowed by an extended water flood until oil cut became less than 1%. The recovered oil was determined on a volume basis to calculate the recovery percentage. The effect of biopolymers' concentration on oil recovery was studied by carrying out several floods with different concentrations.

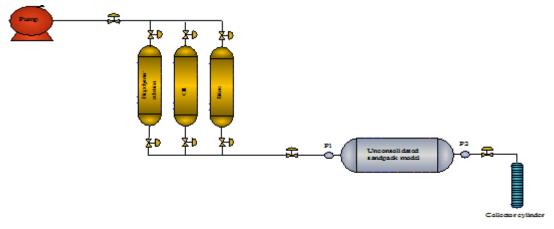


Figure 1. Flow sheet of brine, crude oil, and biopolymer flooding

4. Commonly used biopolymers in EOR

This section gives hints on some of the most common used biopolymers in enhanced oil recovery and polymer flooding.

4.1. Xanthan gum

Xanthan is a bacterial biopolymer used in many foods, pharmaceuticals, cosmetics, paint, textile, agricultural products, and petroleum industries ^[5]. It is produced through a fermentation process with sugar cane broth or glycerol as a carbohydrate raw material, in the presence of <u>Xanthomonas campestris</u> strain, then purified, dried, and milled into a powder. The manufacturing process is detailed elsewhere ^[35]. The viscosity of their solutions falls with higher

shearing rates, so exhibit pseudoelasticity behavior, where the thinning effect disappear by removing the shearing action. A pilot field test of xanthan gum overflowing was held from 1994 in Ng 5.5 zone of the 7th block in ShengLi Gudong Oilfield to revolutionize conventional EOR technique. During this operation, the viscosity of xanthan gum solution, water cut, and oil production rate to biopolymer injection was observed. Xanthan gum displayed excellent thermal steadiness and low viscosity loss at the reservoir temperature. ^[5, 36].

4.2. Scleroglucan

Scleroglucan is a natural biopolymer produced by fermentation of the filamentous fungi <u>Sclerotium rolfsii</u> in the presence of starchy materials like glucose and sucrose ^[37], where the detailed biosynthesis and fermentation process stated elsewhere ^[38-39]. Its chemical architecture comprises a linear β (1-3) D-glucose units with one β (1-6) D-glucose side chain. The rigid chain and triple-helical geometry of Scleroglucan boost its excellent rheological properties, including effective shear resistance and reasonable temperature resistance. Scleroglucan solutions are also robust to pH and high-ionic-strength due to their non-ionic features ^[5].

4.3. Hydroxyethyl cellulose

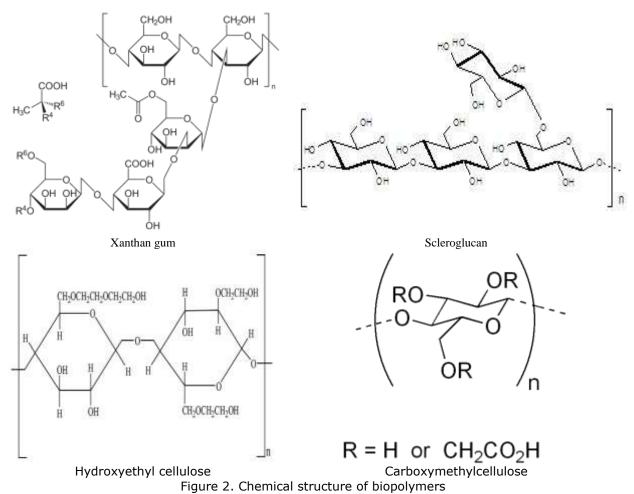
Hydroxyethylcellulose, also known as Natrosol, is a gelling and thickening candidate derived from cellulose. It is widely used in cosmetics, cleaning solutions, and other household products. As well as in EOR, well drilling and completion, and hydraulic fracturing. This biopolymer has high molar mass and a fairly rigid backbone ^[40]. It is produced from the raw cotton linter or refined pulp as follows; Immerse the cotton linter or refined cotton pulp in 30% liquid base. Remove after pressing. Followed by pulverization, followed by reaction with pre-cooled ethylene oxide to produce crude hydroxyethyl cellulose. Then washed with alcohol, and acetic acid washed and neutralized. Then add glyoxal cross-linked aging, followed by fast washing with water, then subjected to centrifugal dehydration, drying, and milling.

4.4. Carboxymethylcellulose

Carboxymethyl cellulose or known as (tylose powder) is a cellulose derivative with carboxymethyl groups (-CH2-COOH) binds to hydroxyl groups of the glucopyranose moieties which form cellulose skeleton. It is usually applied as sodium carboxymethylcellulose, and synthesized by the alkali-catalytic reaction of cellulose with chloroacetic acid. It is synthesized from cellulosic materials such as refined cotton and sugarcane bagasse as stated elsewhere ^[41-42], the synthesis process including two steps, alkalization and etherification of pure cellulose under heterogeneous conditions. In the alkalization step, 1 gram of cellulose powder weighed and added to 20 ml of isopropanol with continuous stirring. Then, 4 mL of NaOH solution (5-25%; w/v) was added to the mixture with further stirring for an hour at room temperature. The carboxymethylation started by monochloroacetic acid (0.6; 0.8; 1.0; 1.2; and 1.4 g) addition with continuous stirring for 3 hours at 55°C. The slurry neutralized with 90 % of acetic acid to pH 7 and then filtered and washed with ethanol 70%, dried at 60 °C in the oven, and kept in a dry desiccator. Figure 2 represents the chemical structure of the aforementioned biopolymers.

5. Surfactants in EOR

There are distinctive sorts of surfactants: ionic, non-ionic, and amphoteric. This assortment of surfactants starts from the specific structure of surfactants, which has a polar segment and a nonpolar segment. The polar part is either ionic or nonionic. The polar segment is known as the head, and the nonpolar part, which is a hydrocarbon chain, is known as the chain of the surfactant. The go to be solubilized in watery solvents, for example, salt water, and the chain in natural solvents, for example, oil. Subsequently, surfactants settle in the interface between oil and salt water. Such a situation of surfactant in the middle of two stages is called solubilization and brings down the interfacial pressure among oil and salt water. Bringing surfactants into immiscible organic aqueous blend prompts the development of smaller scale emulsion. In contrast to emulsion blends, small-scale emulsions are homogeneous blends and are thermodynamically steady. The arrangement of the miniaturized scale emulsion is exceedingly invaluable in water flooding since the miniaturized scale emulsion brings down the interfacial strain among oil and water and prompts higher portability proportion. Various parameters influence achieving a stable small-scale emulsion in a water-oil-surfactant arrangement. The surfactant composes the salinity of the saline solution, oil composes, and working weight and temperature affect the strength of the arrangement. Upgrading the activity parameters can prompt the development of a heterogeneous stable small-scale emulsion, which eventually results in bringing down interfacial pressure in the oil-salt water surfactant blend and at last achieving higher oil recuperation by salt water surfactant flooding ^[43-44].



5.1. Nano surfactants in EOR

As of late, the utilization of nanoparticles in concoction infusions for enhancing proficiency has been essentially researched. For example, an investigation about utilizing an anionic surfactant with the expansion of non-ferrous metal nanoparticles has been performed. Subsequently, the outcomes uncovered that the utilization of nanofluid allowed a 70– 79% decrease of surface strain. What's more, it was asserted that within sight of nanoparticles the adsorption procedure is steadier. In addition, in another exploration, it has been demonstrated that the use of Al_2O_3 nanoparticles with an anionic surfactant could modify the wet ability of framework from oil-wet to water-wet and furthermore make an impact on expanding extreme oil recuperation. What's more, a few specialists explored about consequences of the nearness of nanoparticles on rheological changes and interfacial properties and increment impact of surfactant arrangement on oil recuperation forms. The effects of these exploratory works indicated how scattered nanoparticles in a watery stage could alter the interfacial properties of the fluid/fluid frameworks if their surface is altered by the nearness of surfactant. Apparently, among the numerous highlights that influence the liquid appropriation, oil recuperation in permeable media, wettability is ended up being a pivotal factor [45-54]. Some exploration of the impacts of nanoparticles on wettability adjustment furthermore, extreme oil recuperation has been performed. The outcomes uncovered that the utilization of nanoparticles could change shake wettability and its ensuing impact on oil recuperation. Also, a few specialists introduced broad writing surveys on the impact of wettability on the minuscule relocation of the liquid stream on the pore scale. In any case, no examinations have been done to explore the impact of nanoparticles alongside surfactants on the pore-scale perception of the job of ZrO₂ nanoparticles on wettability adjustment and IFT decrease amid nano surfactant flooding. In addition, examinations on the impacts of nanoparticles/fluid surfactants arrangements on various parts of enhancing EOR proficiency have not essentially been directed yet. Besides, the component of fluid surfactants containing nanoparticles in enhancing plainly visible and tiny proficiency of substantial oil recuperation especially in a cracked 5-spot display has been less researched. Likewise, as it is notable that, in EOR forms, versatility proportion is the portability of the infused uprooting liquid to that of the oil being uprooted. Great portability control is acquired when the consistency of the infused liquid is higher than the thickness of the oil in the supply and can prompt a cylinder like the relocation of the oil from the infusion well to the creative well. Be that as it may, poor versatility control because of the lower thickness of the infused liquid can result in low recuperations because of thick fingering. Accomplishing great versatility control in the mix with other systems, including low interfacial pressure or wettability change is subsequently fundamental for fruitful synthetic EOR. The high consistency of the infused stage can prompt enhanced portability control ^[44, 55]. The straightforward materials like glass have been utilized to develop micromodels and to ponder different parts of miniaturized scale uprooting. By utilizing micromodels, the movement of the liquids can be watched and explored as far as small-scale geometry and physical qualities of the exhibited fluids, gases, and solids The outcomes and discoveries from micromodel studies can be utilized to enhance our comprehension about infinitesimal and naturally visible practices of removal forms, and maybe the demonstrating of the stream system. Perception in 5-spot micromodel can better recreate the conduct in permeable media; in this way, we in this utilized these sorts of micromodels [56].

5.2. Biosurfactants in EOR

The development of supportable advancements has driven the look for common, biodegradable mixes to remediate destinations defiled by hydrocarbons. This has prompted the revelation of surfactants of a characteristic starting point. A large portion of these surfactants are integrated by living creatures, for example, saponins delivered by plants, glycolipids created by microorganisms, and bile salts created by creatures. Mixes with surfactant properties created by microorganisms are designated biosurfactants. Biosurfactants are, for the most part, created by oxygen-consuming microorganisms in fluid media with a carbon source feedstock, for example, starches, hydrocarbons, fats, and oils. It is trusted that biosurfactants are discharged into the way of life medium to aid the development of the microorganism by encouraging the translocation of insoluble substrates crosswise over cell layers. These mixes have amphipathic atoms with hydrophobic and hydrophilic parts that demonstration between liquids of various polarities (oil/water and water/oil), enabling access to hydrophobic substrates and causing a decrease in surface strain, an expansion in the zone of contact of insoluble mixes, (for example, hydrocarbons) and the improvement of the versatility, bioavailability, and biodegradation of such mixes. The lipophilic moiety can be a protein or peptide with a high extent of hydrophobic side chains or a hydrocarbon chain of unsaturated fat with 10 to 18 carbon particles. The hydrophilic moiety can be an ester, hydroxy, phosphate, carboxylate gathering, or sugar. Biosurfactants are, for the most part arranged into low atomic mass particles, which proficiently bring down the surface and interfacial pressures and high sub-atomic

mass polymers, which are more successful as emulsion-balancing out operators. The real classes of low-mass surfactants are glycolipids, lipopeptides, and phospholipids, though high-mass surfactants incorporate polymeric and particulate surfactants. Biosurfactants offer various points of interest over concoction surfactants, for example, biodegradability because of their basic synthetic structure, ecological similarity, low lethality, which permits use in the corrective, pharmaceutical and sustenance industry, high selectivity because of essence of particular utilitarian gatherings, permitting specificity in the detoxification of particular poisons, and action under states of extraordinary temperatures, pH and saltiness. These attributes add to the pertinence of biosurfactants in various enterprises. The way that biosurfactants are described by a tremendous auxiliary assorted variety and show a wide scope of properties may clarify why this gathering of atoms keeps on picking logical intrigue. Because of their different mechanical applications, numerous creators have petitioned for licenses on biosurfactants. To be sure, licenses have been issued for biosurfactant delivering organisms, particularly Pseudomonas spp., Acinetobacter sp, Bacillus sp, and Candida sp, kinds of biosurfactant, the generation procedure and mechanical applications. The financial aspects of biosurfactant creation justify specific consideration. The aggregate creation of surfactants in 2012 was ~ 12 million tons, just 3.5 million tons of which were biosurfactants. Also, incomes from the bio-based segment of the market were US\$ 6.588 million. In any case, the attention on maintainability and new ecological enactment have prompted the look for characteristic surfactants as options in contrast to existing items. Businesses are right now trying to supplant a few or every single synthetic surfactant with feasible biosurfactants, yet the high creation cost is a noteworthy disadvantage ^[57-67]. A key factor overseeing the achievement of biosurfactant generation is the improvement of a sparing procedure that utilizations ease materials and offers a high return. To be sure, the decision of an ease substrate is imperative to the general financial matters, as the substrate represents up to half of the last creation cost. Luckily, biosurfactants can be delivered with conservative, sustainable assets, for example, vegetable oils, refinery waste, and dairy squander. Biosurfactants are the better option of synthetic surfactants; they have high surface movement, natural inviting, bring down danger, biodegradability, biological worthiness and don't lose physical properties of the substance at outrageous temperatures, pH and saltiness levels. The greater part of the biosurfactant delivering microorganisms has been confined from oil polluted soil or water, oil squanders, or slime and oil wells. At the point when the microorganism was developed with an insoluble carbon source in the development media, for example, hydrocarbon, they will create some emulsifying operator to solubilize hydrocarbon in the water that outcomes increment the accessibility of carbon in the media for the microorganism. Utilization of organisms or their items Biosurfactant for Enhanced Oil Recovery is known as microbial improved oil recuperation. They are generally utilized in microbial-improved oil recuperation, horticulture, nourishment, beautifiers, and pharmaceuticals enterprises. Today unrefined petroleum and oil-based goods are the real wellsprings of hydrocarbon poisons for soil and marine situations. Because of the insoluble idea of these contaminations in water, their expulsion from the earth is extremely troublesome. Biodegradation of hydrocarbons by microorganisms is one of the promising approaches to expel them from the dirt and marine conditions. Biosurfactants can emulsify unrefined petroleum and diminish the consistency of raw petroleum that is one of the instruments for microbial EOR. Biosurfactant properties stay stable under extraordinary physical-compound conditions; this makes it achievable for upgraded oil recuperation activities.

As indicated by their compound nature, biosurfactant is delegated glycolipids, lipopeptides, phospholipids, polymeric microbial surfactants, and particulate biosurfactants. Lipopeptides are most well known and proficient biosurfactant; they have high surface and interface action, emulsion shaping limit and adjustment, wetting, hostile to cement and the antimicrobial exercises. Surfactin, a lipopeptide biosurfactant is a standout amongst the most surface-dynamic biosurfactants. It is a flexible bioactive particle being able to repress fibrin clump development, improved oil recuperation, bioremediation for cleaning soil and water. These properties of surfactin mirror its potential business applications. In our past investigation, Candida tropicalis

MTCC230 are adjusted in high hydrocarbon condition for biosurfactant generation and streamlining. Emulsification capacity was additionally examined, and <u>Bacillus</u> <u>subtilis</u> utilized as a standard surfactin. Biosurfactant delivering strain for relative examination. Surface pressure and emulsification power were done at the distinctive temperature, pH and saltiness for deciding the adequacy of biosurfactant under extraordinary ecological conditions. Moreover, a dirt section soaked with motor oil was washed with biosurfactant by group compose soil washing; this delights its potential use in MEOR. Squander versatile oil-defiled soil was washed with biosurfactant delivered from a versatile strain Candida tropicalis ^[68].

6. Hydrogels for Enhanced Oil Recovery applications

Hydrogels are delicate solids or strong like materials that immobilize a lot of water in a three-dimensional (3D) organize held together by covalent bonds, non-covalent or topological cooperation. As of late, scientists have endeavored to create salt-coldhearted microgels utilizing exceptional salt-heartless changed polymers. For instance, the incomplete charged polymeric hydrogel, integrated by means of copolymerization of acrylic corrosive gatherings with sodium acrylate, played out steady swelling conduct subsequent to engrossing the salt arrangements. In addition, the salt tolerant polymers, created from ammonium derivatives, demonstrated a lessened affectability to salt and pH. In addition, nonionic polymers, arranged by polymerizing monomers like vinyl liquor or vinyl pyrrolidone, demonstrated diminishing the salt impact by lessening the contact territory of a polymer chain and water [69-72]. A portion of the uses of hydrogels in (bio)medical fields incorporate sensors, actuators, gadget coatings, wound dressings and glues, fluid engrossing cleanliness items, conveyance vehicles for dynamic mixes or cells, delicate contact focal points, and frameworks and embeds in tissue building and regenerative pharmaceutical. Gelled polymers framed by the response between a polymer arrangement and crosslinker are being utilized progressively in various applications, including the control of overabundance water creation in synthetically upgraded oil recuperation (EOR) through profile alteration or on the other hand hindering the ways with high penetrability to water. During the gelation process, the fluid as a gelant arrangement is changed over into a high thickness three-dimensional organize material with some versatile conduct that is exceptionally impervious to stream and is not eluted promptly. The gel quality and its viscoelasticity is administered by the arrangement creation and furthermore by the level of crosslinking. The most broadly utilized gelant framework is the watery arrangement of in part hydrolyzed polyacrylamide/Cr (III). Polyacrylamide/Cr (III) framework was first proposed to decrease water porousness or level of water coning and thusly expanding oil clear productivity in EOR stages. In this procedure, polymer and crosslinker game plans are mixed and a short time later either implanted into the store shake through the implantation well or age well. The level of accomplishment depends upon (a) the advancement of an unfaltering gel inside the pore spaces of the stones with enough flexibility and quality at the store condition and (b) the level of the decline of water vulnerability in the nearby well-bore zones. Gelation time and diverse characteristics of the molded gel are known to be a component of the reactant's obsession and the polymer form (sub-nuclear weight, level of hydrolysis (DH)), and besides the pH and saltiness of the planned water. In addition, the Injectivity of the gelant game plan depends on the normal consistency at the archive temperature. More basic is the quality of the polymer gel towards expanded age inside seeing the game plan water made of the irregular condition of divalent cations (Ca²⁺, Mg²⁺) capable of complexing the carboxylate clusters attached to the polyacrylamide chains, inciting the gel shrinkage besides, syneresis, in view of addition in the gel crosslink thickness. For a gelled polymer, syneresis is in a similar manner overhauled by growing the crosslinker obsession with the remote possibility that a high modulus orchestrate is needed. Starting late, consider on organic-inorganic nanocomposites has appeared as a crucial research field. Starting at now half and parts of polymer with a little proportion of montmorillonite nanoclay have pulled in unprecedented interest because of their incredible mechanical, warm, and distinctive properties that develop their specific esteem. The unquestionable properties shown by the polymer/nano clay composite materials have been credited to the specific sort of microstructure, in which the nanoclay layers are either scattered

through the polymer cross-section (shedding morphology) or on the other hand, the polymer chains are diffused between the nanoclay layers (intercalation). In the two sorts of morphology, the high relationship between the polymer areas, moreover, earth layers prompt the change of immovability, warm robustness, and quality. Furthermore, part of morphology headway in polymer/nano clay cross breeds, exclusively

Starting late, to crush the inadequacy and limitations of the polymeric gels generally sustaining the gel arrange while keeping the crosslinker thickness at low degree, arrangement of nanocomposite make hydrogels (NC gels) in perspective of nano clay/polyacrylamide has pulled in extra besides, more attention as an aftereffect of their high capacity to acclimatize a ton of water while keeping incredible mechanical quality and warm soundness and what's more high flexibility and extensibility. This class of hydrogels has been observed to be appropriate for being utilized in oil fields for EOR processes, and in different regions, for example, agriculture [73-74]. Lately, there has been expanding research in self-recuperating hydrogels that can detect the adjustment in their condition and likewise adjust their function. Given the distinction of multi-useful properties and conditions, hydrogels have been custom-made to react to pH, light, redox, and so forth. These elite hydrogels are relied upon to have different applications, for example, sedate conveyance frameworks remotely activated biosensors, shape memory materials and improved oil recovery. Injecting a polymer arrangement with a cross-linker, as a synthetic technique for EOR to shape a polymer gel in underground arrangement amid a couple of hours to a few days for water close, has been generally utilized in developing oil supply advancement. In any case, there are a few drawbacks of these self-recuperating hydrogels, for example, low-temperature opposition, poor salt resistance, and simple oxidative corruption. Aware of the poisonous quality, ecological concerns, and the potential contamination of groundwater and private wells by downhole synthetic concoctions, the need to moderate substance use in upgraded oil recuperation tasks are unavoidable. Consequently, our nanocomposite hydrogel was planned with simply normal muds, without the use of traditional compound crosslinkers. Furthermore, the expense of such substance crosslinkers far supersedes normal dirt. Besides, measure avoidance chromatographic issues, as a rule, emerge amid infusion. Because of noteworthy contrasts in the sub-atomic weights of polymer contrasted with crosslinker, crosslinkers tend to travel quicker than polymers amid downhole organization, to such an extent that an uneven proportion of polymer/crosslinker happens at close wellbore, in this manner modifying the first gallant arrangement and subsequently shaping gels with less mechanical exhibitions than anticipated. Consequently, for these few impediments, the utilization of artificially crosslinked hydrogels is confined. It is thus that our ebb and flow explore proposes a nanocomposite hydrogel, including just polymer and dirt, without the fuse of natural crosslinkers. The target and oddity of the present work include building up an effortless physical crosslinking to get ready polyacrylamide (PAM)-based nanocomposite gels with altogether enhanced mechanical properties for the potential application in upgraded oil recuperation. Laponite is an engineered layered silicate that has been utilized in a wide assortment of utilizations including surface coatings, horticulture, individual consideration, and oil field applications. A circle formed a crystalline colloid with an angle proportion of ca. 27 nm (circle measurement ca. 25 nm and thickness of ca. 0.92 nm). It has a compound equation Na+0.7[(Si₈ Mq_{5.5} Li_{0.3}) O_{20} (OH)4] -0.7. The precious stone surface is adversely charged while the edges of the gem have positive charges. It is named an inactive intensify that isn't corrupted by high temperature or high shear scattering forms. Henceforth, as a nanomaterial, it will confer thixotropy, enhance steadiness and syneresis, and go about as multifunctional physical crosslinks [75-76].

7. Conclusion

Recently enhanced oil recovery through different technologies increased by the foregoing days. Biopolymers and their composites are a cost operative and eco-friendly agent, which exhibits numerous benefits over other EOR processes. Flooding process through biopolymers acquires increased potential to replace the traditional EOR chemical methods. This article gives

short notes on the applied biopolymers, biosurfactants and hydrogel produced through microorganisms in the field of the oil industry. Moreover, the mechanism of biopolymer flooding to improve sweeping efficiency was handled in more detail. We recommend carrying out more research investigation on the applicability of these biopolymers on the field scale at harsh reservoir conditions of high ionic strength and thermal degradation.

Nomenclature

М	Mobility ratio
λ_W	Water phase mobility
λΟ	Oil phase mobility
KW	Relative permeability of water phase, MD
КО	Relative permeability of oil phase, MD
μW	Water phase viscosity, cP
μΟ	Oil phase viscosity, cP
$(\Delta P)_P$	The pressure difference during polymer flooding
$(\Delta P)_w$	The pressure difference during water flooding
$(\Delta P)_{w(Before \ polymer)}$	The water pressure difference before polymer flooding
$(\Delta P)_{w(After \ polymer)}$	The water pressure difference after polymer flooding

References

- [1] Wu Z, Huiqing L, Wang X, Zhang Z. Emulsification and improved oil recovery with viscosity reducer during steam injection process for heavy oil. Journal of Industrial And Engineering Chemistry 2018; 61:348-55.
- [2] El-Hoshoudy A, Desouky S, Betiha M, Alsabagh A. Use of 1-vinyl imidazole based surfmers for preparation of polyacrylamide–SiO2 nanocomposite through aza-Michael addition copolymerization reaction for rock wettability alteration. Fuel, 2016;170: 161-75.
- [3] Bai M, Zhang Z, Cui X, Song K. Studies of injection parameters for chemical flooding in carbonate reservoirs. Renewable and Sustainable Energy Reviews, 2017;75: 1464-71.
- [4] Sveistrup M, van Mastrigt F, Norrman J, Picchioni F, Paso K. Viability of biopolymers for enhanced oil recovery. Journal of Dispersion Science and Technology, 2016;37(8): 1160-9.
- [5] Pu W, Shen C, Wei B, Yang Y, Li Y. A comprehensive review of polysaccharide biopolymers for enhanced oil recovery (EOR) from flask to field. Journal of Industrial and Engineering Chemistry, 2018; 61: 1-11.
- [6] Pei X, Zhai K, Tan Y, Xu K, Lu C, Wang P, et al. Synthesis of monodisperse starch-polystyrene core-shell nanoparticles via seeded emulsion polymerization without stabilizer. Polymer, 2017; 108: 78-86.
- [7] Wang S, Xu J, Wang Q, Fan X, Yu Y, Wang P, et al. Preparation and rheological properties of starch-g-poly (butyl acrylate) catalyzed by horseradish peroxidase. Process Biochemistry, 2017; 59: 104-10.
- [8] Guo Q, Wang Y, Fan Y, Liu X, Ren S, Wen Y, et al. Synthesis and characterization of multiactive site grafting starch copolymer initiated by KMnO₄ and HIO₄/H₂SO4 systems. Carbohydrate Polymers, 2015; 117: 247-54.
- [9] Klemm D, Heublein B, Fink HP, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. Angewandte Chemie International Edition 2005; 44(22): 3358-93.
- [10] Gao C. Application of a novel biopolymer to enhance oil recovery. Journal of Petroleum Exploration and Production Technology 2016; 6(4): 749-53.
- [11] Men Y, Du X, Shen J, Wang L, Liu Z. Preparation of corn starch-g-polystyrene copolymer in ionic liquid: 1-Ethyl-3-methylimidazolium acetate. Carbohydrate Polymers, 2015; 121: 348-54.
- [12] Zhao W, Yang R, Hua X, Zhang W, Tang Y, Chen T. Inactivation of polyphenoloxidase of pear by Pulsed Electric Fields. International Journal of Food Engineering, 2010; 6(3): 4.
- [13] Zhang L. The Study of Starch-Based Chemicals for Oilfield in China. Chemicals; 1997.
- [14] Zhang L, Tan Y, Li Z. New water-soluble ampholytic polysaccharides for oilfield drilling treatment: a preliminary study. Carbohydrate polymers, 2001; 44(3): 255-60.
- [15] Fanta GF, Felker FC, Shogren RL. Recent Processing Methods for Preparing Starch-based Bioproducts. In book: Food and Industrial Bioproducts and Bioprocessing, Chapter 2,2012: 37-83, https://doi.org/10.1002/9781119946083.ch2.

- [16] Wei B, Romero-Zerón L, Rodrigue D. Improved viscoelasticity of xanthan gum through selfassociation with surfactant: β-cyclodextrin inclusion complexes for applications in enhanced oil recovery. Polymer Engineering & Science, 2015; 55(3): 523-32.
- [17] El-Hamshary H, Fouda MM, Moydeen M, El-Newehy MH, Al-Deyab SS, Abdel-Megeed A. Synthesis and antibacterial of carboxymethyl starch-grafted poly (vinyl imidazole) against some plant pathogens. International journal of biological macromolecules, 2015; 72: 1466-72.
- [18] Umar A, Sanagi MM, Salisu A, Ibrahim WAW, Karim KJA, Keyon ASA. Preparation and characterization of starch grafted with methacrylamide using ammonium persulphate initiator. Materials Letters, 2016; 185: 173-6.
- [19] Sorour M, El-Sayed M, El Moneem NA, Talaat H, Shaalan H, El Marsafy S. Free radical grafting kinetics of acrylamide onto a blend of starch/chitosan/alginate. Carbohydrate polymers, 2013; 98(1): 460-4.
- [20] Yang Z, Wu H, Yuan B, Huang M, Yang H, Li A, et al. Synthesis of amphoteric starch-based grafting flocculants for flocculation of both positively and negatively charged colloidal contaminants from water. Chemical Engineering Journal, 2014; 244: 209-17.
- [21] Zahran MK, Ahmed EM, El-Rafie MH. Synthesis and characterization of hydrolysed starch-gpoly (methacrylic acid) composite. International Journal of Biological Macromolecules, 2016; 87: 473-80.
- [22] El-Hoshoudy A, Desouky S. Synthesis and evaluation of acryloylated starch-g-poly (Acrylamide/Vinylmethacrylate/1-Vinyl-2-pyrrolidone) crosslinked terpolymer functionalized by dimethylphenylvinylsilane derivative as a novel polymer-flooding agent. International Journal of Biological Macromolecules, 2018; 116: 434-42.
- [23] El-Hoshoudy A, Desouky S, Attia A. Synthesis of starch functionalized sulfonic acid co-imidazolium/silica composite for improving oil recovery through chemical flooding technologies. International Journal of Biological Macromolecules, 2018; 118(Pt B): 1614-1626.
- [24] Hasan AM, Abdel-Raouf ME-S. Cellulose-Based Superabsorbent Hydrogels. Cellulose-Based Superabsorbent Hydrogels, 2018: 1-23.
- [25] El-hoshoudy A, Desouky S, Elkady M, Al-Sabagh A, Betiha M, Mahmoud S. Hydrophobically associated polymers for wettability alteration and enhanced oil recovery–Article review. Egyptian Journal of Petroleum 2017; 26(3): 757-62.
- [26] A.N. El-hoshoudy, Desouky SM. Hydrophobic Polymers for Enhanced Oil Recovery: Preparation, Characterization, Rheological Properties. Lambert Academic Publishing; 2016.
- [27] Zheng C, Gall B, Gao H, Miller A, Bryant R. Effects of polymer adsorption and flow behavior on two-phase flow in porous. SPE/DOE Improved Oil Recovery Symposium. Society of Petroleum Engineers; 1998.
- [28] Seright RS. Clean up of oil zones after a gel treatment. SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers; 2005.
- [29] El-hoshoudy A, Desouky S, Al-Sabagh A, Betiha M, MY E-k, Mahmoud S. Evaluation of solution and rheological properties for hydrophobically associated polyacrylamide copolymer as a promised enhanced oil recovery candidate. Egyptian Journal of Petroleum, 2017; 26(3): 779-85.
- [30] Hoshoudy A, Desouky S, Al-sabagh A, El-kady M, Betiha M, Mahmoud S. Synthesis and characterization of polyacrylamide crosslinked copolymer for enhanced oil recovery and rock wettability alteration. International Journal of Oil, Gas and Coal Engineering, 2015; 3(4): 43-55.
- [31] El-Hoshoudy A, Desouky S, Attia A. Synthesis of starch functionalized sulfonic acid co-imidazolium/silica composite for improving oil recovery through chemical flooding technologies. International Journal of Biological Macromolecules, 2018; 118: 1614-26.
- [32] El-hoshoudy A. Quaternary ammonium based surfmer-co-acrylamide polymers for altering carbonate rock wettability during water flooding. Journal of Molecular Liquids, 2018; 250: 35-43.
- [33] El-Hoshoudy A, Desouky S, Elkady M, Alsabagh A, Betiha M, Mahmoud S. Investigation of optimum polymerization conditions for synthesis of cross-linked polyacrylamide-amphoteric surfmer nanocomposites for polymer flooding in sandstone reservoirs. International Journal of Polymer Science, 2015; 2015.
- [34] Germann PF. Viscosity—The weak link between Darcy's law and Richards' capillary flow. Hydrological Processes, 2018; 32(9): 1166-72.
- [35] Faria S, de Oliveira Petkowicz CL, de Morais SAL, Terrones MGH, de Resende MM, de França FP, et al. Characterization of xanthan gum produced from sugar cane broth. Carbohydrate Polymers, 2011; 86(2): 469-76.

- [36] Guo X, Li W, Tian J, Liu Y. Pilot test of xanthan gum flooding in Shengli oilfield. SPE Asia Pacific Improved Oil Recovery Conference. Society of Petroleum Engineers; 1999.
- [37] Castillo NA, Valdez AL, Fariña JI. Microbial production of scleroglucan and downstream processing. Frontiers in Microbiology, 2015; 6: 1106.
- [38] Survase SA, Saudagar PS, Singhal RS. Production of scleroglucan from Sclerotium rolfsii MTCC 2156. Bioresource Technology, 2006; 97(8) :989-93.
- [39] Farina J, Sineriz F, Molina O, Perotti N. High scleroglucan production by Sclerotium rolfsii: influence of medium composition. Biotechnology Letters, 1998; 20(9): 825-31.
- [40] Abbas S, Sanders AW, Donovan JC. Applicability of hydroxyethylcellulose polymers for chemical EOR. SPE Enhanced Oil Recovery Conference. Society of Petroleum Engineers; 2013.
- [41] Asl S, Mousavi M, Labbafi M. Synthesis and characterization of carboxymethyl cellulose from sugarcane bagasse. Journal of Food Processing and Technology, 2017;8(8).
- [42] Sunardi, Febriani NM, Junaidi AB. Preparation of carboxymethyl cellulose produced from purun tikus (Eleocharis dulcis). AIP Conference Proceedings. 1868. AIP Publishing; 2017: 020008.
- [43] Healy RN, Reed RL, Stenmark D. Multiphase microemulsion systems. Society of Petroleum Engineers Journal, 1976; 16(03): 147-60.
- [44] Ma G, Shen Y, Gao R, Wang X, Wu Z. Research and application of ultralow interfacial tension oil displacement agent. Journal of Dispersion Science and Technology, 2017; 38(10): 1459-64.
- [45] Szulczewski ML, MacMinn CW, Herzog HJ, Juanes R. Lifetime of carbon capture and storage as a climate-change mitigation technology. Proceedings of the National Academy of Sciences, 2012; 109(14): 5185-9.
- [46] Orr jF, Taber J. Use of carbon dioxide in enhanced oil recovery. Science, 1984; 224(4649): 563-9.
- [47] Eddi A, Winkels KG, Snoeijer JH. Short time dynamics of viscous drop spreading. Physics of Fluids 2013; 25(1): 013102.
- [48] Andrew M, Bijeljic B, Blunt MJ. Pore-scale contact angle measurements at reservoir conditions using X-ray microtomography. Advances in Water Resources ,2014; 68: 24-31.
- [49] Song W, Kovscek AR. Functionalization of micromodels with kaolinite for investigation of low salinity oil-recovery processes. Lab on a Chip, 2015; 15(16): 3314-25.
- [50] Trojer M, Szulczewski ML, Juanes R. Stabilizing fluid-fluid displacements in porous media through wettability alteration. Physical Review Applied ,2015; 3(5): 054008.
- [51] Holtzman R, Segre E. Wettability stabilizes fluid invasion into porous media via nonlocal, cooperative pore filling. Physical Review Letters, 2015; 115(16): 164501.
- [52] Zhao B, MacMinn CW, Szulczewski ML, Neufeld JA, Huppert HE, Juanes R. Interface pinning of immiscible gravity-exchange flows in porous media. Physical Review E, 2013; 87(2): 023015.
- [53] Rabbani HS, Zhao B, Juanes R, Shokri N. Pore geometry control of apparent wetting in porous media. Scientific Reports, 2018; 8(1): 15729.
- [54] Osei-Bonsu K, Shokri N, Grassia P. Foam stability in the presence and absence of hydrocarbons: from bubble-to bulk-scale. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015; 481: 514-26.
- [55] Zhao X, Blunt MJ, Yao J. Pore-scale modelling: Effects of wettability on waterflood oil recovery. Journal of Petroleum Science and Engineering, 2010; 71(3-4): 169-78.
- [56] Thammachart M, Meeyoo V, Risksomboon T, Osuwan S. Catalytic activity of CeO₂-ZrO₂ mixed oxide catalysts prepared via sol-gel technique: CO oxidation. Catalysis Today, 2001; 68(1-3): 53-61.
- [57] Silva RdCF, Almeida DG, Rufino RD, Luna JM, Santos VA, Sarubbo LA. Applications of biosurfactants in the petroleum industry and the remediation of oil spills. International Journal of Molecular Sciences, 2014; 15(7): 12523-42.
- [58] Franzetti A, Caredda P, Ruggeri C, La Colla P, Tamburini E, Papacchini M, et al. Potential applications of surface active compounds by Gordonia sp. strain BS29 in soil remediation technologies. Chemosphere, 2009; 75(6): 801-7.
- [59] Marchant R, Banat IM. Microbial biosurfactants: challenges and opportunities for future exploitation. Trends in Biotechnology 2012; 30(11): 558-65.
- [60] e Silva NMPR, Rufino RD, Luna JM, Santos VA, Sarubbo LA. Screening of Pseudomonas species for biosurfactant production using low-cost substrates. Biocatalysis and Agricultural Biotechnology, 2014; 3(2): 132-9.
- [61] Malik Z, Ahmed S. Degradation of petroleum hydrocarbons by oil field isolated bacterial consortium. African Journal of Biotechnology, 2012; 11(3): 650-8.

- [62] Lin M, Liu Y, Chen W, Wang H, Hu X. Use of bacteria-immobilized cotton fibers to absorb and degrade crude oil. International Biodeterioration & Biodegradation, 2014; 88: 8-12.
- [63] Silva EJ, e Silva NMPR, Rufino RD, Luna JM, Silva RO, Sarubbo LA. Characterization of a biosurfactant produced by Pseudomonas cepacia CCT6659 in the presence of industrial wastes and its application in the biodegradation of hydrophobic compounds in soil. Colloids and Surfaces B: Biointerfaces, 2014; 117: 36-41.
- [64] Makkar RS, Cameotra SS, Banat IM. Advances in utilization of renewable substrates for biosurfactant production. AMB express, 2011; 1(1): 5.
- [65] Dzięgielewska E, Adamczak M. Evaluation of waste products in the synthesis of surfactants by yeasts. Chemical Papers, 2013; 67(9): 1113-22.
- [66] Aparna A, Srinikethan G, Hedge S. Effect of addition of biosurfactant produced by Pseudomonas ssp. on biodegradation of crude oil. International Proceedings of Chemical, Biological & Environmental Engineering, 2011: 71-5.
- [67] Campos JM, Montenegro Stamford TL, Sarubbo LA, de Luna JM, Rufino RD, Banat IM. Microbial biosurfactants as additives for food industries. Biotechnology Progress, 2013; 29(5): 1097-108.
- [68] Muthusamy K, Gopalakrishnan S, Ravi TK, Sivachidambaram P. Biosurfactants: properties, commercial production and application. Current Science, 2008: 736-47.
- [69] Zhang L, Zheng L, Pu J, Pu C, Cui S. Influence of hydrolyzed polyacrylamide (HPAM) molecular weight on the cross-linking reaction of the HPAM/Cr3+ system and transportation of the HPAM/Cr3+ system in microfractures. Energy & Fuels, 2016; 30(11): 9351-61.
- [70] Bueno VB, Bentini R, Catalani LH, Petri DFS. Synthesis and swelling behavior of xanthanbased hydrogels. Carbohydrate polymers 2013; 92(2): 1091-9.
- [71] Lopérgolo LC, Lugao AB, Catalani LH. Direct UV photocrosslinking of poly (N-vinyl-2pyrrolidone)(PVP) to produce hydrogels. Polymer, 2003; 44(20): 6217-22.
- [72] Tongwa P, Nygaard R, Bai B. Evaluation of a nanocomposite hydrogel for water shut-off in enhanced oil recovery applications: Design, synthesis, and characterization. Journal of Applied Polymer Science, 2013; 128(1): 787-94.
- [73] Al-Sharji HH, Grattoni CA, Dawe RA, Zimmerman RW. Pore-scale study of the flow of oil and water through polymer gels. SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers; 1999.
- [74] Albonico P, Lockhart TP. Stabilization of polymer gels against divalent ion-induced syneresis. Journal of Petroleum Science and Engineering, 1997; 18(1-2): 61-71.
- [75] Muller F, Salonen A, Glatter O. Phase behavior of Phytantriol/water bicontinuous cubic Pn3m cubosomes stabilized by Laponite disc-like particles. Journal of colloid and interface science, 2010; 342(2): 392-8.
- [76] Mongondry P, Tassin JF, Nicolai T. Revised state diagram of Laponite dispersions. Journal of Colloid and Interface Science, 2005; 283(2): 397-405.

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