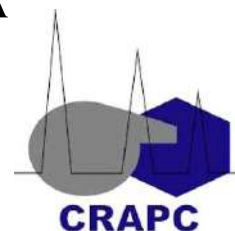


DEMOCRATIC PEOPLE'S REPUBLIC OF ALGERIA
MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH
UNIVERSITY OF KASDI MERBAH OUARGLA



Faculty of applied sciences
Department of Process Engineering



End of Studies Thesis

In order to obtain an ACADEMIC MASTER'S DEGREE

Field: Science and technology
Major: Petrochemical industries
Specialty: Petrochemical Engineering

Presented by

BENMERAD Meriem Rim

Topic

Development and Physicochemical Evaluation of Hybrid Nano-Biosurfactant Systems for Enhanced Oil Recovery

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Acknowledgments

﴿وَنُفِّقَ كُلٌّ فِي عِلْمٍ عَلِيمٍ﴾

First and foremost, I would like to express my deepest gratitude to my supervisor, Pr. BACHA Oussama, for his unwavering guidance throughout this work. His constant encouragement to aim higher and strive for excellence has been a true source of motivation throughout this experience.

I am equally grateful to my co-supervisor, Dr. BOURICHA M'hamed, for his invaluable presence, patience, and support throughout the experiment of this research. My sincere appreciation is extended to Dr. BELKHALFA Hakim, the Director of CRAPC Ouargla; also, Dr. RAHMANI Youcef and all the staff of the research center for providing access to the laboratory facilities and supporting the successful completion of this work.

I would also like to thank KHENFER Siham and ZATOUT Rabab for their insightful advice and continuous support throughout the past months. Their experience and guidance were highly beneficial to the progress of this study.

Special thanks are extended to all my teachers and professors who have supported my academic journey and broadened my perspective over the years.

Finally, I carry deep gratitude for everyone who, in one way or another, became part of this journey and contributed to shaping my resilience and multidisciplinary outlook, each of which played a role in shaping the person and researcher I continue striving to become.

Dedication

To Mom & Dad,

Who never asked me to become anything other than myself, and who never questioned the paths I chose to follow, as long as they were mine.

To my siblings,

The source of love and inspiration and a motivation I did not even know I needed.

To family and friends,

Whose presence accompanied me through the different phases of life and remained a part of this journey.

Development and Physicochemical Evaluation of Hybrid Nano-Biosurfactant Systems for Enhanced Oil Recovery

Abstract

Enhanced Oil Recovery (EOR) involves modifying rock-fluid interactions to mobilize trapped residual oil. This study develops and evaluates a sustainable hybrid bio-nano system combining a microbial biosurfactant with environmentally friendly synthesized Zinc Oxide (ZnO) nanoparticles. The biosurfactant, extracted from *Pseudomonas* sp., achieved a high yield of 82%. Spectroscopic analyses (UV-Vis and FTIR) and GC-MS confirmed its amphiphilic glycolipid structure, with 1,2,3-propanetriol triacetate as the main component. ZnO nanoparticles, synthesized using pomegranate peel extract, showed a spherical shape and ZnO characteristic vibrations. The hybrid system successfully integrated both components, as confirmed by their combined spectral picks. Interfacial tension (IFT) tests indicated that the pure biosurfactant initially performed better than the hybrid, reducing the oil-brine baseline by 12.1% at 25°C and 10.7% at 80°C. However, aging the hybrid system for one week significantly improved its interfacial performance, lowering the IFT to a 5.4% reduction at 25°C. The time-dependent improvement indicates progressive interfacial stabilization and nanoparticle bioavailability. The results confirm the eco-friendly synthesis of a bio-nano hybrid system and highlight the importance of longer formulation aging to optimize sustainable nano-biosurfactants for EOR.

Keywords: Enhanced oil recovery (EOR), bio-nano hybrid system, biosurfactant, Zinc Oxide nanoparticles (ZnO), green synthesis, interfacial tension (IFT).

Développement et évaluation physicochimique de systèmes hybrides nanoparticules–biosurfactant pour la Récupération Assistée du Pétrole

Résumé :

La récupération assistée du pétrole (RAP) consiste à modifier les interactions roche-fluide afin de mobiliser le pétrole résiduel piégé. Cette étude développe et évalue un système bio-nano hybride durable combinant un biosurfactant microbien à des nanoparticules d'oxyde de zinc (ZnO) synthétisées de manière écologique. Le biosurfactant, extrait de *Pseudomonas* sp., a permis d'obtenir un rendement élevé de 82 %. Les analyses spectroscopiques (UV-Vis et FTIR) et GC-MS ont confirmé sa structure glycolipidique amphiphile, dont le principal composant est le triacétate de 1,2,3-propanetriol. Les nanoparticules de ZnO, synthétisées à partir d'extrait d'écorce de grenade, présentent une forme sphérique et les vibrations caractéristiques du ZnO. Le système hybride a permis d'intégrer efficacement les deux composants, comme le confirment leurs spectres combinés. Les tests de tension interfaciale (TIF) ont indiqué que le biosurfactant pur était initialement plus performant que l'hybride, réduisant la tension de base huile-saumure de 12,1 % à 25 °C et de 10,7 % à 80 °C. Cependant, un vieillissement d'une semaine du système hybride a significativement amélioré ses performances interfaciales, réduisant la TIF de 5,4 % à 25 °C. Cette amélioration au fil du temps témoigne d'une stabilisation interfaciale progressive et d'une biodisponibilité accrue des nanoparticules. Ces résultats confirment la synthèse écoresponsable d'un système hybride bio-nano et soulignent l'importance d'un vieillissement prolongé de la formulation pour optimiser les nano-biosurfactants durables destinés à la récupération assistée du pétrole (EOR).

Mots-clés : Récupération assistée du pétrole (RAP), système bio-nano hybride, biosurfactant, nanoparticules d'oxyde de zinc (ZnO), synthèse verte, tension interfaciale (IFT).

تطوير وتقييم الخصائص الفيزيائية والكيميائية لأنظمة هجينة نانوية-حيوية خافضة للتوتر السطحي من أجل

الاستخلاص المعزز للنفط

ملخص: بالعربي.

تتضمن عملية استخلاص النفط المعزز (EOR) تعديل تفاعلات الصخور مع السوائل لتحريك النفط المتبقي المحتجز. تُطوّر هذه الدراسة نظامًا حيويًا نانويًا هجينًا مستدامًا، وتقييمه، حيث يجمع بين مُستحلب حيوي ميكروبي وجزيئات أكسيد الزنك النانوية المُصنّعة بطريقة صديقة للبيئة. وقد حقق المُستحلب الحيوي، المُستخلص من بكتيريا *Pseudomonas sp.*، إنتاجية عالية بلغت 82%. وأُكدت التحليلات الطيفية (FTIR و UV-Vis) و GC-MS بنيته الجليكوليبيدية الأمفية، حيث يُعد ثلاثي أسيتات 1،2،3-بروبانetriول المكون الرئيسي. وأظهرت جزيئات أكسيد الزنك النانوية، المُصنّعة باستخدام مُستخلص قشر الرمان، شكلًا كرويًا واهتزازات مميزة لأكسيد الزنك. وقد نجح النظام الهجين في دمج كلا المكونين، كما يتضح من قمم الطيف المُدمجة. أشارت اختبارات التوتر السطحي البيني (IFT) إلى أن المادة الفعالة السطحية الحيوية النقية أظهرت أداءً أفضل في البداية من المادة الهجينة، حيث خفضت مستوى الزيت في المحلول الملحي بنسبة 12.1% عند 25 درجة مئوية و 10.7% عند 80 درجة مئوية. ومع ذلك، أدى تعريض النظام الهجين للتقادم لمدة أسبوع إلى تحسن ملحوظ في أدائه السطحي البيني، حيث انخفض التوتر السطحي البيني بنسبة 5.4% عند 25 درجة مئوية. ويشير هذا التحسن مع مرور الوقت إلى استقرار تدريجي للسطح البيني وتوافر حيوي للجسيمات النانوية. وتؤكد هذه النتائج على فعالية التخليق الصديق للبيئة لنظام هجين حيوي نانوي، وتُبرز أهمية تعريض التركيبة للتقادم لفترات أطول لتحسين المواد الفعالة السطحية النانوية الحيوية المستدامة في عمليات استخلاص النفط المعزز..

كلمات دلالية: الاستخلاص المعزز للنفط، نظام هجين حيوي نانوي، مادة فعالة سطحياً حيوية، جسيمات نانوية أكسيد الزنك، التخليق الأخضر، التوتر البيني.

Table of Contents

Acknowledgments.....	
Dedication	I
Abstract.....	II
List of Figures	VIII
List of Tables.....	XI
Acronyms	XII
Introduction	XIII
I. Literature Review.....	4
I.1 Introduction	5
I.2 Reservoir Rock Properties.....	5
I.2.1 Porosity.....	5
I.2.2 Permeability	6
I.3 Reservoir Fluid Properties.....	6
I.3.1 Oil viscosity	7
I.3.2 Density gravity (°API).....	8
I.4 Rock–Fluid Interactions	8
I.4.1 Wettability.....	8
Types of Wetting	8
I.4.2 Interfacial tension.....	10
I.4.3 Capillary pressure	10
I.4.4 Saturation.....	12
I.5 Oil recovery Mechanisms	13
I.5.1 Primary oil recovery	13
– Natural Flow:.....	13
– Mechanical lifts:.....	13
I.5.2 Secondary oil Recovery.....	14
a. Water-flooding	14
b. Gas injection	15
I.5.3 Enhanced Oil Recovery (EOR)	15
I.5.3.1 Classification of EOR Methods.....	16
i. Thermal EOR (TEOR).....	16

ii.	Gas based EOR (GEOR).....	16
iii.	Chemical EOR (CEOR).....	17
iv.	Emerging EOR.....	17
v.	Advanced approaches.....	17
1)	Microbial EOR	17
	Pseudomonas aeruginosa for biosurfactant production in MEOR.....	20
2)	Nanoparticle assisted EOR (Nano-EOR)	21
	Limitations	25
3)	Low-salinity waterflooding (LSW)	25
4)	Synergistic effects	26
II.1	Introduction	29
II.	Materials and Methods	29
II.2	Methodology	30
1)	Biosurfactant Production.....	30
2)	Green Synthesis of Zinc Oxide Nanoparticles (ZnO NPs).....	33
3)	Hybrid System formation (Biosurfactant-Capped Nanoparticles).....	37
4)	Oil	38
	Crude Oil Classification.....	39
5)	Brine	39
	Preparation of low Salinity Brine	39
III.	Results and Discussion	42
III.1	Introduction	43
III.2	Biosurfactant Characterization.....	43
a)	UV–Visible Analysis	45
b)	FTIR Characterization	46
c)	GC-MS Characterization.....	47
III.3	Zinc Oxide Nanoparticles (ZnO NPs) Characterization.....	50
a)	Visual analysis.....	50
b)	UV–Visible Characterization	51
c)	FTIR Characterization	51
d)	Scanning Electron Microscopy (SEM) Characterization	52
III.4	Biosurfactant-capped ZnO nanoparticles (Bio–Nano) Characterization.....	53
a)	UV–Visible Characterization	53
b)	FTIR Characterization	54
III.5	Interfacial Performance Evaluation	55

Conclusion.....	42
References	43
Appendices.....	42

List of Figures

Chapter I: Literature Review		
Figure I.1	Comparison of low and high porosity in oil sands.	5
Figure I.2	Comparison of low and high Permeability in oil sands.	6
Figure I.3	Schematic representation of an oil reservoir.	7
Figure I.4	Perfect wetting.	9
Figure I.5	Neutral wetting fluid.	9
Figure I.6	Non wetting fluid.	10
Figure I.7	Capillary pressure within capillary tube.	11
Figure I.8	Oil and Gas Extraction Systems.	13
Figure I.9	Beam pump.	14
Figure I.10	Primary and secondary recovery phases of conventional oil extraction. (a) Primary recover. (b) Secondary recovery.	14
Figure I.11	Enhanced oil recovery methods.	15
Figure I.12	Schematic illustration of EOR classification.	16
Figure I.13	The Role of microorganisms in MEOR.	17
Figure I.14	Adsorption of surfactant on oil water interface.	18
Figure I.15	Biosurfactants And its applications.	19
Figure I.16	Mechanism for enhanced oil recovery by biosurfactants.	20
Figure I.17	Rhamnolipid biosurfactant molecule.	21
Figure I.18	Nanoparticles recovery mechanism.	22
Figure I.19	Tetrahedral structure of ZnO.	23
Figure I.20	ZnO 3D illustration.	23
Figure I.21	Nanofluids mechanisms within porous media.	25

Figure I.22	Mechanism of low salinity water injection in dolomite rock.	26
Chapter II: Materials And Methodes		
Figure II.1	Culture medium Autoclaving.	30
Figure II.2	Culture medium incubation.	31
Figure II.3	Culture medium centrifugation.	31
Figure II.4	Supernatant.	32
Figure II.5	Lyophilizer.	32
Figure II.6	Solvent extraction.	33
Figure II.7	Organic phase.	34
Figure II.8	Pomegranate peels powder.	35
Figure II.9	shaker.	35
Figure II.10	Vacuum filtration.	35
Figure II.11	Centrifuge.	36
Figure II.12	Zinc acetate + Peel extract water bath heated.	36
Figure II.13	Precipitate formation.	36
Figure II.14	The precipitate.	37
Figure II.15	Calcination furnace.	37
Figure II.16	Bio-nano solution agitation.	38
Chapter III: Results And Discussion		
Figure III.1	Visual comparison of phase separation behavior.	43
Figure III.2	Visual evaluation of oil droplet dispersion.	44
Figure III.3	Visual comparison of dispersion behavior.	44
Figure III.4	UV–Visible absorption spectrum of the extracted biosurfactant.	45
Figure III.5	FTIR spectrum of the extracted biosurfactant	46

Figure III.6	GC-MS chromatogram of the biosurfactant.	48
Figure III.7	Enlarged GC–MS chromatogram in the retention time range of 15–25 min	49
Figure III.8	Visual observation of precipitate formation post green synthesis of ZnO NPs.	50
Figure III.9	UV–Visible absorption spectrum of green-synthesized ZnO NPs	51
Figure III.10	FTIR spectrum of green-synthesized ZnO NPs.	52
Figure III.11	SEM image of biosynthesized ZnO NPs	53
Figure III.12	UV–Visible absorption spectrum of the a) biosurfactant b) biosurfactant – ZnO nanoparticle system.	54
Figure III.13	FTIR spectrum of the biosurfactant–ZnO NPs system (BNPs).	55

List of Tables

Chapter I: Literature Review		
Table 0.1	Physiochemical properties of ZnO nanoparticles	24
Chapter II: Materials And Methodes		
Table II. 1	Measured Properties of the Crude Oil	39
Table II.2	Engineered brine salts composition	40
Chapter III: Results And Discussion		
Table III.1	Interfacial Tension Measurements.	56

Acronyms

OIIP Original oil in place

EOR Enhanced oil recovery

API The American Petroleum Institute

MEOR Microbial Enhanced Oil Recovery

ZnO Zinc Oxide

TEOR Thermal Enhanced Oil Recovery

GEOR Gas Enhanced Oil Recovery

IFT Interfacial Tension

CEOR Chemical Enhanced Oil Recovery

Nano-EOR Nanoparticles assisted Enhanced Oil Recovery

CMC Critical Micelle Concentration

BS-MEOR Biosurfactant Mediated Microbial Enhanced Oil Recovery

NPs Nanoparticles

ZnO NPs Zinc Oxide Nanoparticles

IOR Improved Oil Recover

COBR Crude Oil / Brine / Rock

LSW Low Salinity Waterflooding

BS Biosurfactant

BNPs Biosurfactant - ZnO NPs system

OB Oil–Brine

OBBS Oil–Brine–Biosurfactant

OBNPs Oil–Brine–ZnO NPs

OBBNPs Oil–Brine–BNPs

Introduction

In the middle of the rising global energy demand, fossil fuels remain a strong reliance in the energy sector despite its ongoing transition towards renewable alternatives. such as solar, wind, hydroelectric, biomass, and geothermal energy¹ some of those technologies are still in their early development stages, and some face technical or economic, regulatory, and integration challenges².

Hydrocarbons still represent the backbone of the global energy supply, and it is projected that world energy consumption will increase by almost 50% between 2020 and 2050³. However, many major oil fields have already reached maturity and are experiencing production decline, and numerous others are approaching it, while a substantial proportion of the original oil in place (OOIP) remains unrecovered⁴.

There comes the necessity of overcoming the challenges of maximizing the production of existing reservoirs for an increased supply, fulfilling future demands⁵. During the primary and secondary stages of the oil extraction, approximately 20-30% of the OOIP is recovered from the well, leaving around 70% of the OOIP over the reservoir⁶.

Enhanced Oil Recovery (EOR) techniques are applied to those depleted and mature reservoirs⁷. Whereas the secondary oil recovery techniques only sweep the oil through the wellbore by injecting water or gas, with no hydrocarbon's properties altered, enhanced oil recovery methods, on the other hand, get in action by changing the reservoir's properties: rock, fluids, and rock-fluids interaction⁸. Specifically, EOR methods change the natural physical and chemical properties of the reservoir, like the density and viscosity of the crude oil, making the disposition process smoother. EOR is widely implemented to ameliorate the extraction efficiency of the residual trapped oil; depending on the employed technique, oil recovery can rise up to 75% in EOR approaches⁷.

Even with the operational effectiveness conventional EOR techniques have shown, they are significantly contributing to environmental concerns associated to governmental regulations, leading researchers to develop more ecological mechanisms and sustainable alternatives for enhanced oil recovery⁹.

In this context, emerging EOR technologies are progressively being explored. Among those approaches, microbial enhanced oil recovery (MEOR) and nanotechnology-based EOR have attracted significant attention due to their promising individual performances resulting, an innovative, emerged interest toward investigating their combined application and potential synergistic effects¹⁰.

Building upon the promising potential of hybrid enhanced oil recovery approaches, this study investigates the development of a biosurfactant–ZnO nanoparticle hybrid system as a sustainable alternative for petroleum applications. By combining the surface-active properties of biosurfactants with the unique physicochemical characteristics of nanoparticles, the proposed system aims to exploit potential synergistic interactions that may improve oil–fluid interactions and interfacial behavior.

To achieve this objective, the work is structured into three chapters:

Chapter 1 presents the theoretical background covering the fundamental characteristics of reservoir rocks and fluid properties, as well as fluid interactions within porous media and oil recovery mechanisms, and provides an overview of enhanced oil recovery (EOR) technologies with particular focus on emerging EOR approaches, including hybrid and combined mechanisms that integrate multiple recovery strategies.

Chapter 2 describes the materials and experimental procedures.

Chapter 3 discusses the obtained results, including the characterization of the extracted biosurfactant, synthesized ZnO nanoparticles, and the developed hybrid system.



I. Literature Review



Introduction

Oil recovery is a complex process influenced by the properties of the reservoir's rock and the behavior of the fluids within it. In particular, parameters such as viscosity porosity and permeability play a critical role in determining the efficiency of oil production. Despite the use of conventional primary and secondary recovery methods, a significant portion of oil remains trapped in the reservoir due to capillary forces and high viscosity. Therefore, advanced techniques such as enhanced oil recovery (EOR) are required to improve oil mobilization and increase overall recovery efficiency

I.2 Reservoir Rock Properties

I.2.1 Porosity

Porosity refers to the void spaces found in rocks that might occur between particles or within soil or rock cavities or cracks¹¹. in other words, porosity is the storage capacity that can indicate the amount of fluid that the porous rock can store¹².

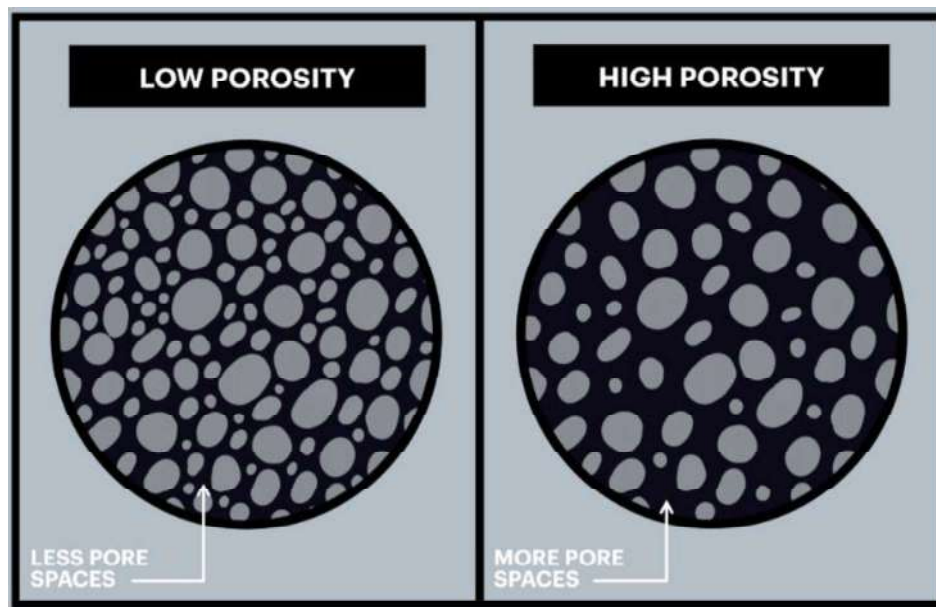


Figure I.1: Comparison of low and high porosity in oil sands¹³.

Porosity is measured as void volume in a porous medium to the total volume of that medium¹⁴:

$$\Phi = \frac{V_p}{V_t} \quad \text{Eq. 1}$$

Φ Porosity.

V_p is the pore volume [cm³].

V_t is the total volume [cm³].

I.2.2 Permeability

The ability of fluids to flow through porous media is known as permeability. It measures the fluid's capacity to move from the porous media through the reservoir rock to the producing well's wellbore; the greater the permeability, the faster the fluid moves¹.

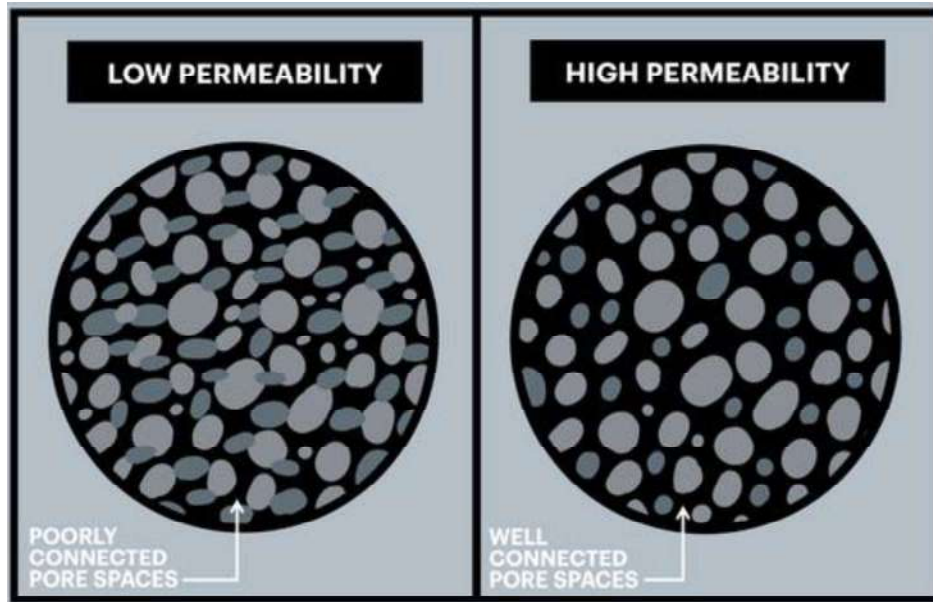


Figure I.2: Comparison of low and high Permeability in oil sands³.

Darcy's law Equation for single phase liquid permeabilities in the hydrocarbon:

$$Q = \frac{KA(P_i - P_o)}{\mu L} \quad \text{Eq. 2}$$

K the permeability (Darcy).

Q the flow rate (cm³).

P_O the outlet fluid pressure (dynes).

P_i the inlet fluid pressure (dynes).

μ the fluid viscosity (cP)

L the tube length (cm).

A the area of the sample (cm²).

I.3 Reservoir Fluid Properties

In a typical oil–gas–water system, the fluids naturally arrange vertically segregated by gravity so that the lightest phase, gas, occupies the uppermost region of the reservoir, followed downward by oil and then by formation water. This stable configuration results in nearly planar gas–oil and oil–water contacts, reflecting the difference in fluid densities and the hydrostatic equilibrium established within the porous medium.¹⁵

There are three types of reservoir fluids: hydrocarbon and non-hydrocarbon gases, liquid hydrocarbons (crude oil), and an aqueous phase with dissolved salts (formation water or brine).

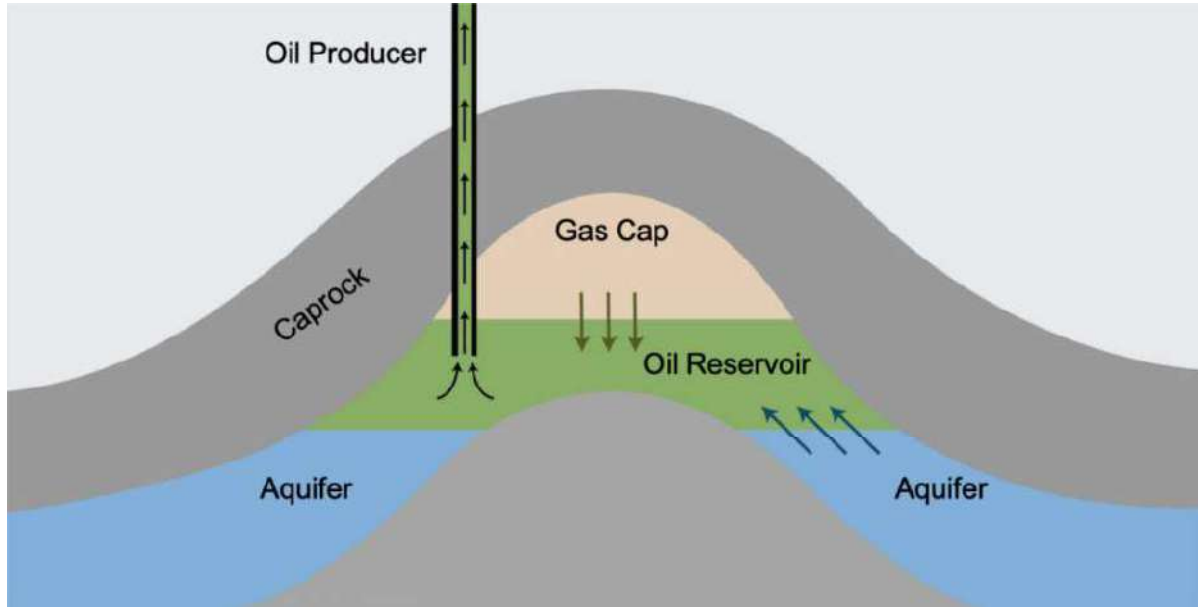


Figure I.3: Schematic representation of an oil reservoir.

I.3.1 Oil viscosity

Oil viscosity is the resistance of a fluid to flow as it indicates the ability to flow easily in the reservoir¹⁶. Acting as internal friction that determines how thick or thin the fluid is, viscosity is also defined by Newton's law as the ratio of shear stress (pressure) to shear rate (flow rate), measured in *(Pa.s)* or *(cP)*:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad \text{Eq. 3}$$

η dynamic viscosity

τ shear stress

$\dot{\gamma}$ shear rate

Water is tended to have better mobility in porous media compared to oil as it's less viscous, and light oil flows quite easily through porous media, conversely to heavy viscous crude, which requires more energy to flow towards the wellbore: the lower viscosity the better the fluidity.

The heavier the hydrocarbon deposits are the harder it is to recover and it necessitates unconventional methods of recovery.¹⁷

I.3.2 Density gravity (°API)

The American Petroleum Institute gravity, or API gravity is a measure of a petroleum liquid density compared to water in order to determine whether the oil is light or heavy³.

API gravity is derived parameter calculated using the following formula:

$$API\ gravity = \frac{141.5}{SG} - 131.5 \quad Eq. 4$$

SG: specific gravity is the ratio of density of the material to the density of a given reference

$$SG = \frac{\rho_{substance}}{\rho_{substance}} \quad Eq. 5$$

Water at 4 °C for liquids and solids, Air at 20 °C for gases, also can be calculated conversely using their API gravity value as:¹⁸

$$SG = \frac{141.5}{API\ gravity + 131.5} \quad Eq. 6$$

I.4 Rock–Fluid Interactions

I.4.1 Wettability

Wettability is the tendency of a fluid to spread over a surface in the presence of another fluid, Consequently, determining a contact angle. Wetting occurs when a fluid's contact angle $\theta < 90^\circ$.

The polar components in the oil or the products adsorbed onto the rock surface are what cause oil to be wettable.¹⁹

In reservoir systems, wettability is a rock property measures the rock's preference for oil or water. Affected by several parameters like fluid composition, rock mineralogy, surface chemical interactions, temperature, and pore characteristics²⁰. And it strongly influences residual oil saturation and fluid distribution within pore throats. Changing the wettability from oil-wet to water-wet conditions helps reduce capillary trapping by increasing the water affinity to the rock which facilitates the displacement of the trapped oil²¹.

Types of Wetting

Wettability determines which fluid is in contact with the rock. This behavior is described by a quantity called the spreading parameter S, which measures the difference between the energy of the wetted substrate and the energy of the dry substrate.

$$S = \gamma SG - (\gamma SL + \gamma) \quad Eq. 7$$

With:

S: Spreading quantity;

γ_{SG} : Solid/air surface tension.

γ_{SL} : Solid/liquide surface tension.

γ : Liquide/air surface tension.

The liquid/substrate system adopts the configuration that minimizes energy. thus, we distinguish two types of wetting depending on the sign of the spreading parameter S ,

The different configurations for spreading a liquid on a substrate as shown below²²:

$S \geq 0$ or Total wetting (complete spreading):

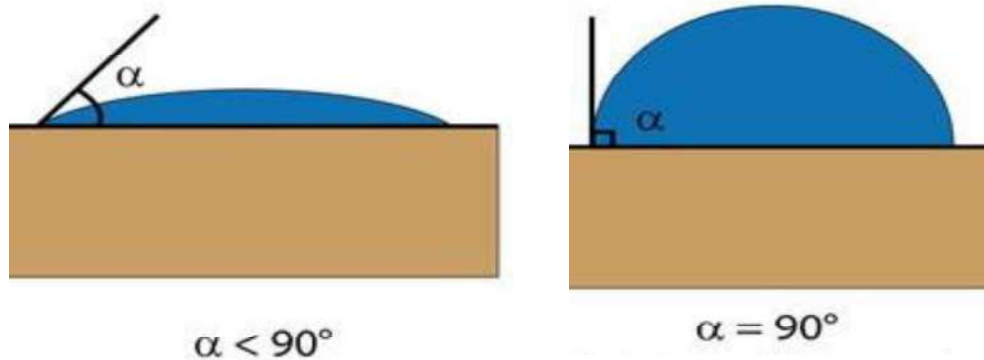
The liquid spreads spontaneously to form a thin a film covering the entire surface. Contact angle $\theta_E = 0$.



Figure I.4: Perfect wetting.

$S < 0$ or Partial wetting:

A liquid that does not fully spread on a solid surface form a spherical-cap-shaped droplet, with an equilibrium contact angle θ_E satisfying $0^\circ < \theta_E < 180^\circ$. Wettability is



classified by the value of θ_E : when $\theta_E < 90^\circ$, the surface is hydrophilic and exhibits good wetting; when $\theta_E > 90^\circ$, the surface is hydrophobic and exhibits poor wetting.

Figure I.5: Neutral wetting fluid.

$S \ll 0$ Super hydrophobicity (non-wetting):

The droplet remains almost perfectly spherical and barely touches the solid surface known as the lotus effect. The angle is defined by the Young-Dupré equation linking the contact angle to interfacial energy:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad \text{Eq. 8}$$

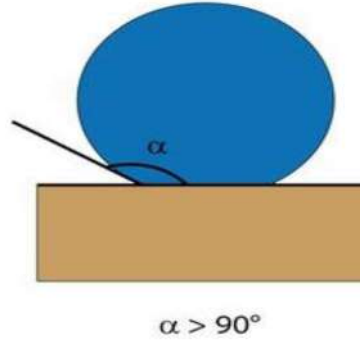


Figure I.6: Non wetting fluid.

I.4.2 Interfacial tension

Interfacial tension is the Gibbs free energy per unit area of interface at fixed temperature and pressure. Interfacial tension occurs because a molecule near an interface has different molecular interactions than an equivalent molecule within the bulk fluid.

Interfacial or surface tension exists when two phases are present. These phases can be gas/oil, oil/water, or gas/water. Interfacial tension is the force that holds the surface of a particular phase together and is normally measured in dynes/cm²³.

I.4.3 Capillary pressure

Capillary pressure P_c is defined as the pressure difference across the discontinuity of the curved interface separating two immiscible fluids, where one is wetting and the other is non-wetting ²⁴.

Consider a capillary tube of radius r with two incompatible liquids, one wetting and one non-wetting, separated by an interface, for example water and oil.

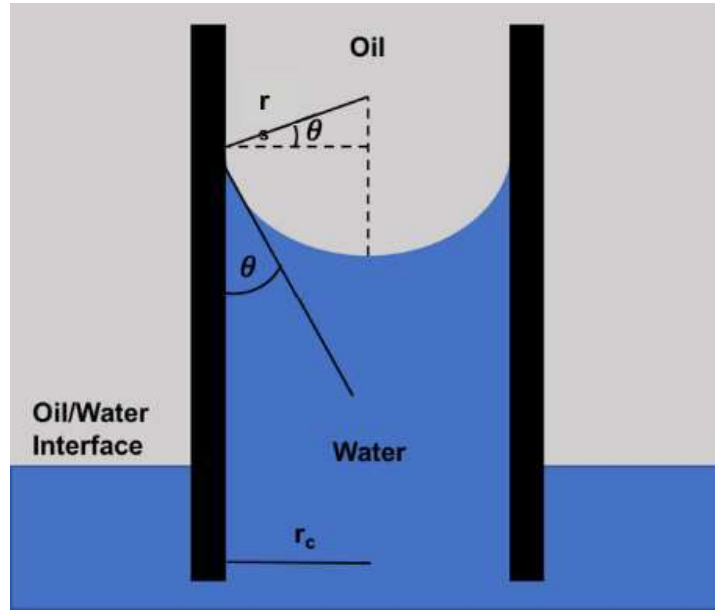


Figure I.7: Capillary pressure within capillary tube¹⁶.

The Young–Laplace equation is the force-up description of capillary pressure and the most commonly used variation of the capillary pressure equation :²⁵

$$P_c = \frac{2\gamma \cos \theta}{r_c} \quad \text{Eq. 9}$$

γ is the interfacial tension.

r is the effective radius of the interface.

θ is the wetting angle of the liquid on the surface of the capillary.

The force down formula for capillary pressure is seen as: ²⁶

$$P_c = \frac{\pi r^2 h (T_w - T_{nw})}{\pi r^2} = h(T_w - T_{nw}) \quad \text{Eq. 10}$$

where:

h the height of the capillary rise.

T_w the density gradient of the wetting phase.

T_{nw} the density gradient of the non-wetting phase.

Regardless of the system, a pressure difference arises at the resulting curved interface between the two fluids¹⁴. in oil-water systems for example water is often the wetting phase, while for gas-oil systems, oil is typically the wetting phase¹⁵.

The wetting phase is identified by its ability to selectively diffuse across the capillary walls prior to the non-wetting phase distinguishes the wetting phase. The wettability of a

fluid depends on its surface tension, the forces that drive a fluid's tendency to take up the minimal amount of space possible, and it is determined by the contact angle of the fluid¹⁶.

I.4.4 Saturation

Saturation is defined as the fraction, or percentage, of the pore space of a rock (volume) occupied by a specific fluid (oil, gas, or water). This property is expressed mathematically by the following equation:

$$\text{fluid saturation} = \frac{\text{fluid's total volume}}{\text{pore volume}} \quad \text{Eq. 11}$$

By Applying the above mathematical concept of saturation to each reservoir fluid yields:

$$S_O = \frac{\text{Oil volume}}{\text{pore volume}} \quad \text{Eq. 12}$$

$$S_G = \frac{\text{Gas volume}}{\text{pore volume}} \quad \text{Eq. 13}$$

$$S_W = \frac{\text{Water volume}}{\text{pore volume}} \quad \text{Eq. 14}$$

Where:

S_O : Oil saturation

S_G : Gas saturation

S_W : Water saturation.

all saturation values are based on pore volume and not on the gross volume of the reservoir.

The saturation of each individual phase varies between zero and 100%. By definition, the sum of the saturations is 100%¹⁴.

$$s_O + s_G + s_\omega = 1 \quad \text{Eq. 15}$$

I.5 Oil recovery Mechanisms

Oil recovery is known as the process of extracting subterranean reserves of hydrocarbons (crude oil).

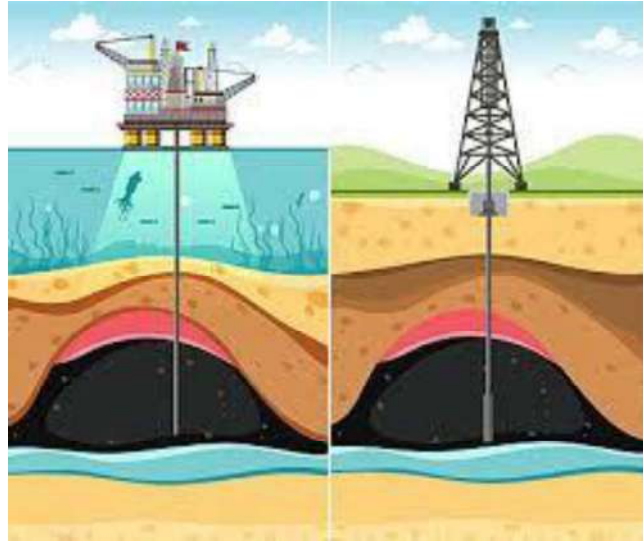


Figure I.8: Oil and Gas Extraction Systems²⁷.

Oil recovery can be categorized into three main stages: primary oil recovery, secondary oil recovery, and tertiary oil recovery.

I.5.1 Primary oil recovery

Primary oil recovery is the first technique used to pull the oil up to the surface through the wellbore and begin the production, depending only and mainly on the natural energy of the reservoirs either by natural flow or artificial lifts.

- Natural Flow: The reservoir has sufficient natural pressure itself that is capable of driving hydrocarbons upward, granting an efficient oil recovery without any artificial support.
- Mechanical lifts: after the depletion of the natural energy and pressure becomes is insufficient, artificial lift mechanisms such as pumps are implanted to assist oil production to bring oil to the surface⁶.



Figure I.9 : Beam pump²⁸.

I.5.2 Secondary oil Recovery

The main natural engine of the reservoir pressure, decreases early in the productive life of the well so secondary oil recovery methods are used to re-pressurize the reservoir in order to prolongate the productivity life of the reservoir by fluids injection to increase recovery rates and oil disposal⁸. in a cost-effective manner²:

a. Water-flooding

is pumping pressurized saline water to maintain the pressure of the well after falling down⁸ the injected water can control the pressure of the reservoirs and the displacement of oil to the producing wells²⁹.

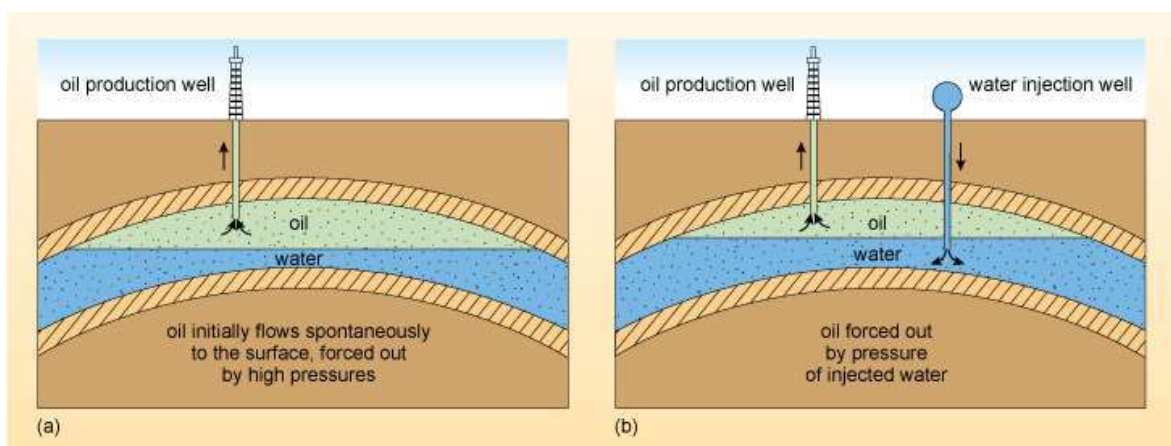


Figure I.10: Primary and secondary recovery phases of conventional oil extraction. (a) Primary recover. (b) Secondary recovery³⁰.

b. Gas injection

Gas injection can be applied before or during the recovery process as the pressure decreases²⁰. gases such as; CH₄, CO₂, associated petroleum gases, nitrogen, glue gases and air are usual injection gases.

I.5.3 Enhanced Oil Recovery (EOR)

Only a 20-30% of the total original oil in place (OOIP) can be extracted with primary and secondary recovery stages, leaving a substantial amount underground unrecovered²⁰ as long as it is economically feasible, enhanced oil recovery (EOR) methods techniques aim to increase the recovery factor by extracting a higher percentage of oil in place beyond what is achievable with traditional recovery operations.³¹

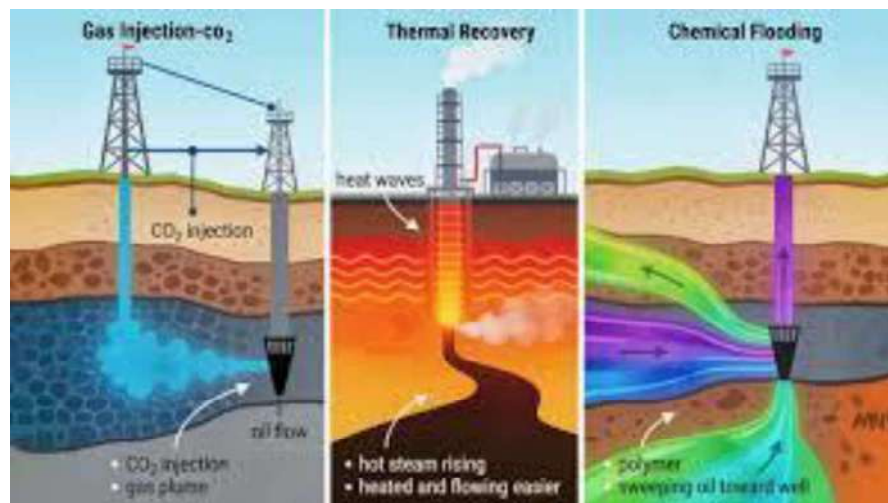


Figure I.11: Enhanced oil recovery methods³².

EOR mechanisms focuses on properties modification of the oil, the injected water and the rock fluid system, enhancing the displacement efficiency and capillary forces reduction improving hydrocarbons mobilization within the porous medium.^{33 34}. By implanting EOR strategies, up to 75% of OOIP can be extracted it differs depending on the technology.³⁵

The primary objectives of EOR processes are recognized to be pressure maintenance, increasing reservoir fluid mobility, and recovering trapped oil^{7 36}.

I.5.3.1 Classification of EOR Methods

EOR can be categorized into four main categories: thermal, gas-based, chemical, and emerging hybrid methods.^{37 38}

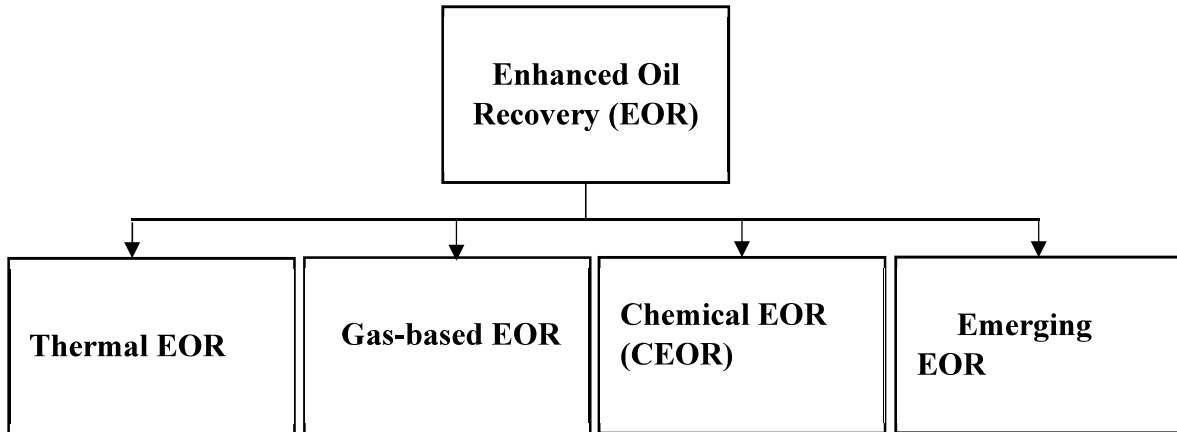


Figure I.12: Schematic illustration of EOR classification.

i. Thermal EOR (TEOR)

Thermal oil recovery is an enhanced oil recovery method that involves using heat in order to change the properties of the reservoir's rock and reduce the high viscosity and density of heavy crude oil, by injecting heat into the formation as steam or generating it electrically or electromagnetically underground.^{8 39}. It mainly targets heavy oil reservoirs with an API number of less than 22⁴⁰. heterogeneous reservoirs with high porosity sandstone⁴¹. And not designed for high depth or low profit zones unrewarding⁴². The applied thermal energy increases the reservoir's temperature that reversely, decreases the viscosity and improves displacement towards the production well⁴³.

ii. Gas based EOR (GEOR)

Gas EOR method is broadly executed in heavy oil fields to boost residual oil displacement and improves recovery overall, via interfacial tension (IFT) minimization, viscosity reduction and oil swelling mechanisms^{44 45}. this process depends on the reservoir's conditions of pressure, temperature and most importantly the gas interaction with crude oil so two types of gas injections are distinguished⁴⁶:

- The miscible gas injection: uses CO₂, N₂, or hydrocarbon gases to dissolve in oil, reducing its viscosity⁴⁷.
- The immiscible gas injection method pushes oil without fully mixing the gas⁴⁸ could become semi miscible with oil under reservoir conditions.

- This classification is based on the interaction with oil and not the nature of the used gas.

iii. Chemical EOR (CEOR)

Chemical EOR is an enhanced residual oil recovery method aimed for a physicochemical characteristic modification like wettability, interfacial tension, and relative permeability of the reservoir's rock and trapped fluids, by water flooding a variety of combined chemicals, conventional like surfactant flooding, polymer flooding and alkaline flooding, or modern techniques and hybrid chemical systems such as smart polymers, nanotechnology and alkaline-surfactant-polymer (ASP) flooding⁴⁹.

In order to preserve the performance of these chemical agents under harsh reservoir conditions of elevated temperature, high pressure and high salinity, also the presence of divalent cations, engineers are implying advanced strategies to develop more stable formulations^{50 51}.

iv. Emerging EOR

In spite of the promising outcomes and its efficiency in increasing the recovery factor, EOR methods still present several limitations, what shifts the attention towards the development of new emerging and compounded technologies as a potential solution to overcome conventional EOR challenges.

One of the most widely recognized are: hybrid chemical–thermal processes, microbial EOR (MEOR), nanoparticle assisted EOR (Nano-EOR), and low-salinity waterflooding (LSW).⁵²

53

v. Advanced approaches

1) Microbial EOR

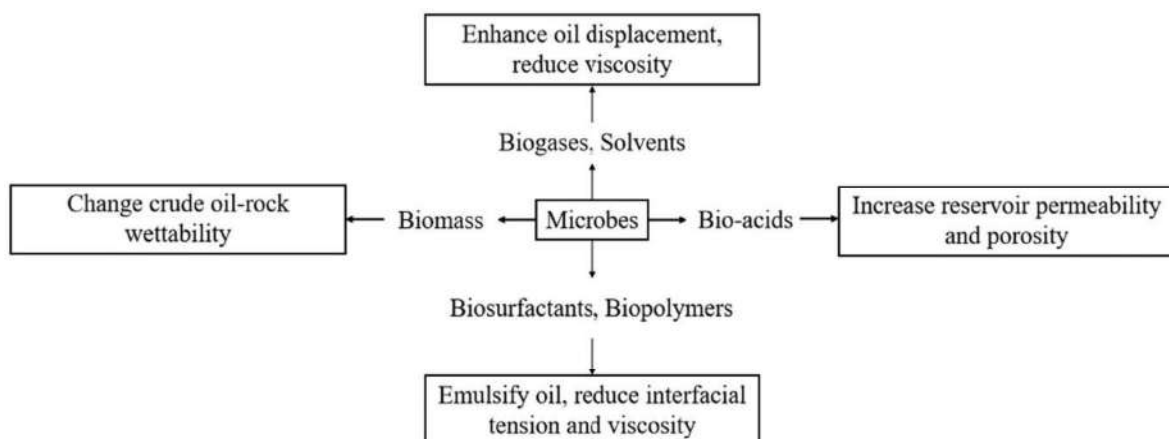


Figure I.13: The role of microorganisms in MEOR⁵⁴.

Microbial enhanced oil recovery (MEOR) is a general term for various techniques that use microorganisms to enhance the oil recovery factor⁵⁵.

MEOR is one of the most vital techniques used to recover residual oil trapped in the capillaries of reservoir rocks by employing microorganisms or their metabolites such as biosurfactants, solvents, or biopolymers. That can improve extraction through⁵⁶:

- Rock wettability alteration.
- Reservoir's dispersed porosity and permeability modification.
- Decreasing water/oil mobility ration.
- Reducing interfacial tension (IFT).
- Increasing emulsification process.

The Goal in MEOR is to mobilize residual oil by altering oil properties or creating displacement forces. However, MEOR is a slow process, and the reservoir conditions (temperature and salinity) must support the microbial growth ⁵⁷.

Due to their amphiphilic molecular structure, Surfactants position themselves at the interface and thereby lower the interfacial tension. Between two fluids with different polarity degrees in oil/water or water/oil mixtures ⁵⁸.

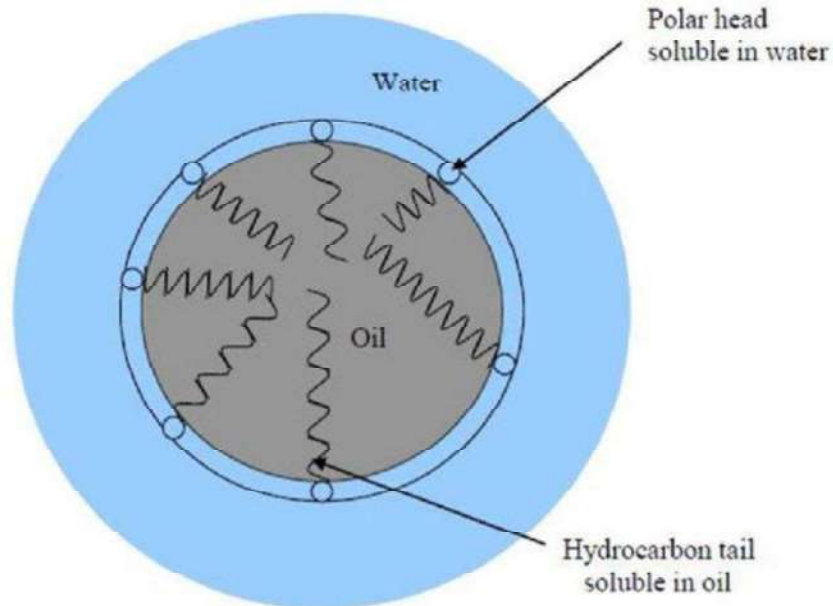


Figure I.14: Adsorption of surfactant on oil water interface³⁰.

This is, formed by non-polar and polar groups, presenting ionic (anionic or cationic) and non-ionic or amphoteric constitutions ⁵⁹. Offering a wide range of utilization as

emulsifying agents, detergents, humidifiers, solubilizers, and phase dispersers ⁶⁰ therefore surfactants are widely employed in different petroleum processes ^{61 62}.

Biosurfactants are biological amphipathic compounds, composed of hydrophilic and hydrophobic moieties similar in principle structure and function as conventional surfactant ⁶³. While it exhibits significant advantages such as lower critical micelle concentration (CMC), renewable, biodegradable, good activity under wide range of harsh environmental conditions, and comparatively lower toxicity⁶⁴.

High-molecular mass biosurfactants are superior bio emulsifiers, but low-molecular mass biosurfactants are better at reducing surface and interfacial tensions⁶⁵

Biosurfactant mediated MEOR (BS-MEOR) could be categorized in two primary methods: in-situ and ex-situ.

In-situ BS-MEOR is applied by injecting biosurfactant producing microorganisms in the reservoir with or without nutrients. followed by shut-in phase where the injected microorganisms are then given a few months for adaptation to the reservoir's environment while monitoring metabolites production and oil recovery process.

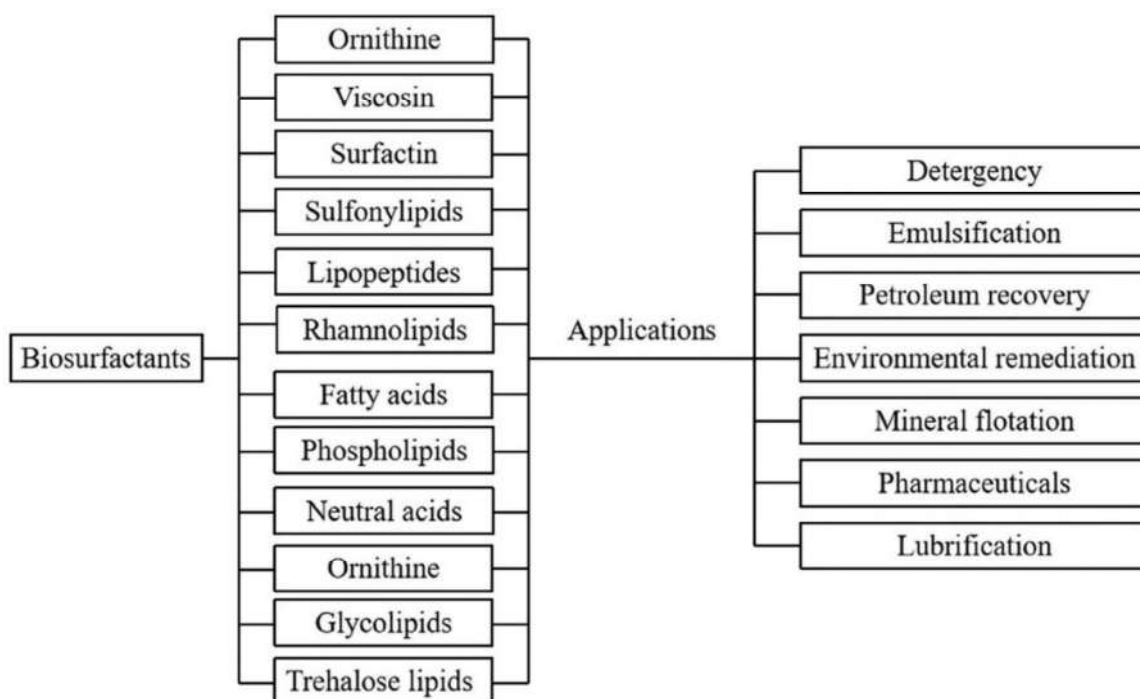


Figure I.15: Biosurfactants And its applications⁵².

ex-situ BS-MEOR the biosurfactant is produced outside the wellbore and then injected directly

Both techniques are designed to enhance oil displacement mechanisms, still present some differences as in-situ is considered economically favorable but limited in production conversely ex situ tends to be more productive but with higher costs due to additional operational requirements such as the purification process of the microbial produced metabolites⁶⁶.

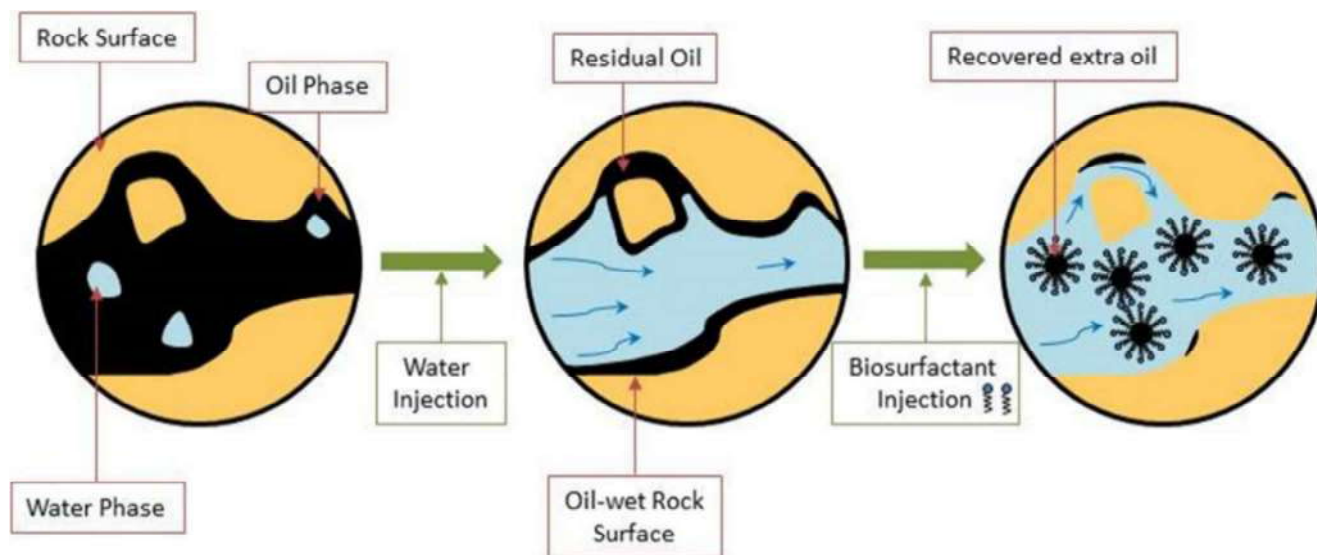


Figure I.16: Mechanism for enhanced oil recovery by biosurfactants⁶⁷.

***Pseudomonas aeruginosa* for biosurfactant production in MEOR**

Among the most intriguing biosurfactants; Rhamnolipids, are glycolipid compounds produced by *Pseudomonas* genus which could reduce water surface tension and emulsify oil^{68 69}. These compounds are biodegradable and have applicability in advanced oil recovery processes in both marine and terrestrial settings⁷⁰.

Pseudomonas aeruginosa was the most frequently employed biosurfactant-producing species during the millennium, less than 20% of the total number of studies did not employ this species, including studies employing only one strain or many species. the extensive time period used in the research justifies *P. aeruginosa* prevalence in experimental biosurfactant studies⁷¹.

This species has a natural ability to reproduce and survive in various conditions like extremophile areas and hydrocarbons contaminated soils^{72 73}.

Compared to other EOR techniques MEOR is considered as an inexpensive method, because microbes and their nutrients that are essential for metabolites production, are considered cheap and the low environmental impact and sustainable nature of this approach have driven

petroleum industry scientists' attention, as its danger and risk free due to the biodegradability of all used components positing MEOR as a promising option for enhanced performance⁷⁴.

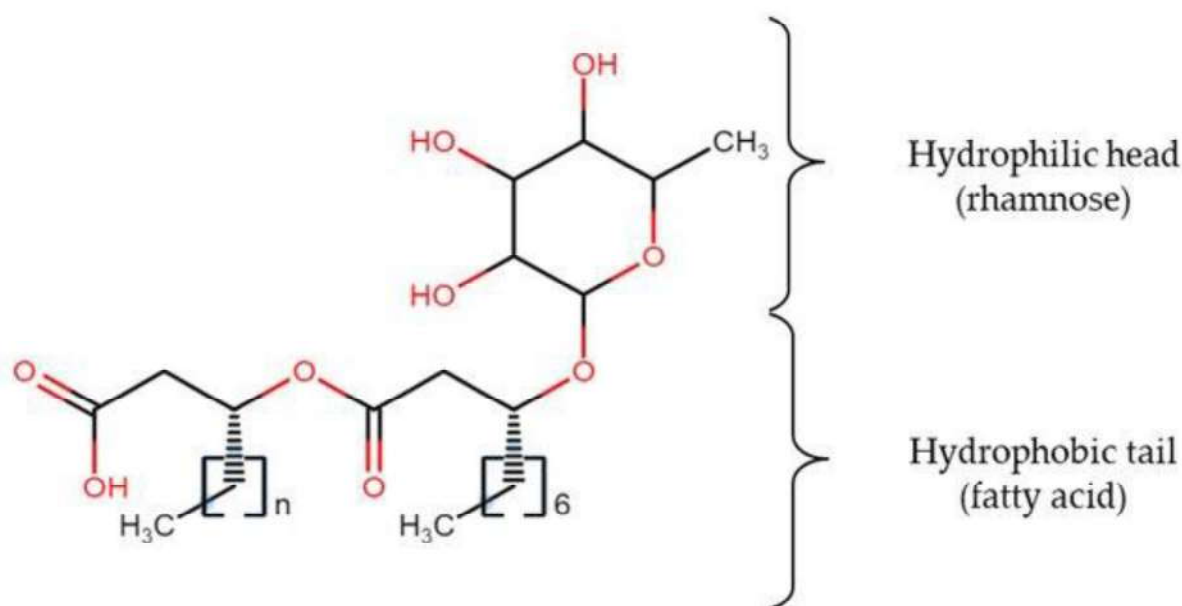


Figure I.17: Rhamnolipid biosurfactant molecule⁷⁵.

2) Nanoparticle assisted EOR (Nano-EOR)

Numerous scientific disciplines and applications have been upgraded and improved by nanotechnology as a cutting-edge technology⁷⁶, oil & gas industry also been influenced by this transition as it elevates the work of engineers and supports research to improve innovative modern materials⁷⁷.

Tertiary recovery methods promise a recovery factor of 0.3 to 0.5. while nanotechnology guarantees a future hydrocarbons recovery growth of 0.5 to 0.6 oil recovery factor.⁷⁸

Nano-EOR integrates synthesized nanoparticles to improve oil recovery through fluid and rock interactions adjustment at the nanoscale⁷⁹, Unlike traditional chemicals that mainly change the overall properties of fluids, nanoparticles improve enhanced oil recovery by altering interfacial mechanisms. These include modifying wettability, redistributing interfacial energy, increasing disjoining pressure, and controlling localized mobility. As it addresses specific weaknesses of thermal, gas, and chemical methods these features make nanoparticle-assisted EOR as a natural extension of current EOR techniques instead of a replacement⁸⁰.

NPs could stabilize emulsions and reduce the mobility ratio of heavy oil and its viscosity, change the wettability of particles toward more water-wet conditions,^{81 82} as it was noted that water wet formation wettability was better than oil-wet formation.

The unique physicochemical properties of nanoparticles (NPs) like their high surface area to volume ratio, different shapes and small particle size ranged 1–100 nm^{83 84} and thermal stability. it can penetrate transport through tight porous rock spaces with 5 to 50-micron size pore diameters and modifies rock-fluid and fluid-fluid interactions facilitating residual oil mobilization⁸⁵ in harsh salinity and high-temperatures and pressure in the subsurface of oil reservoir environments⁸⁶.

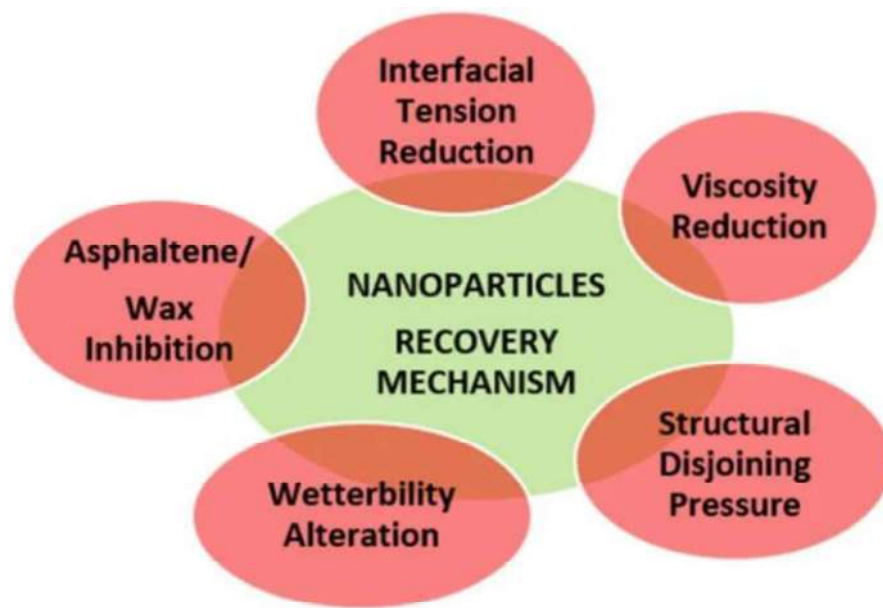


Figure I.18: Nanoparticles recovery mechanism⁸⁷.

Nano-EOR core floods keep tracking changes in contact angle, natural adsorption rates, resulting cumulative oil recovery pace before and after nanoparticle implantation⁸⁸. due to the wedge effect, nanoparticles can create an obvious change resulting from a strong detachment or separation between the oleic phase and the solid phase meaning the rock⁸⁹.

Different types of nanoparticles have been studied and performance evaluated by Ogolo et al, in EOR applications, such as Al₂O₃, MgO, Fe₂O₃, ZrO₂, SnO, SiO₂, and ZnO.⁹⁰ the scientists classify metallic nanoparticles as an environmentally benign technology that must be invested in to overcome efficiency challenges development⁹¹.

Zinc oxide nanoparticles ZnO in nano-EOR:

ZnO nanoparticles falls within the metallic oxide's nanoparticles category, that are capable of creating strong interactions with the oil, water, and rock interface through their

high specific surface area given by the small size of the particles⁹², with a great thermal stability it remains structurally stable at a very high temperature which makes it suitable for EOR subsurface conditions⁹³.

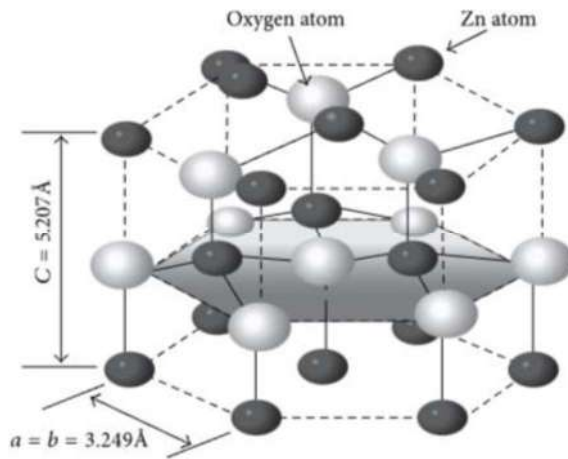


Figure I.19: tetrahedral structure of ZnO⁹⁴.



Figure I.20: ZnO 3D illustration⁹⁵.

ZnO nanoparticles exhibit amphoteric behavior, meaning they can associate with both acidic and basic fluids, which improves its stability in water and changes its wettability, and carry a positive charge under mildly acidic conditions and a negative charge under alkaline conditions. This pH-dependent surface behavior is reflected in high zeta potential that enhances electrostatic repulsion ensuring good colloidal stability under typical reservoir parameters, noting that ZnO NPs have one of the highest zeta potentials across all the metal oxide nanoparticles⁹⁶.

ZnO nanoparticles offer multifunctional characteristics⁹⁷:

- Low priced.
- Strong chemical and thermal stability.
- Chemical corrosion resistant.
- Considerable mechanical strength.
- High hardness and wear resistance.
- Low electrical conductivity.
- A catalyst support or mediator in certain chemical reactions, like titania and iron oxide nanoparticles.

By increasing the sweep efficiency and disjoining pressure, ZnO NPs support EOR applications as it can efficiently lower interfacial tension, alter rock wettability toward water-

wet conditions, and enhance the mobility of trapped oil and able to form stable combinations in brine despite different interaction with chemicals and other reservoir surface conditions like temperature⁹⁸.

Table I-1 Physiochemical properties of ZnO nanoparticles

Properties	
Formula	ZnO
Color	white
Odor	Odorless
Molecular weight	81.40 g/mole
Sizes	between 10 and 80nm ⁷⁷
Density	5.6 g/cm ³ ⁷⁸
Thermal stability limit	about 400°C ⁷⁸
Zeta potentials	From - 20 to -40mV ⁷⁹
Melting point	1975°C

Nanoparticles effectiveness in reducing heavy crude oil viscosity and modulating rock's wettability, was studied by Tajmiri *et al.* demonstrated that the use of 0.2wt% ZnO nanofluid in heavy oil-saturated sample plugs results in an additional recovery of 8.89% of the original oil in place (OOIP) in carbonate formations and 20.68% in sandstone cores⁹⁹.

Despite the significant improvements achieved by metal oxide nanoparticles in enhancing oil recovery, certain limitations persist, notably aggregation and precipitation formed due to challenges like poor stability of the NPs at high-temperature and high-salinity¹⁰⁰ around 10% salinity¹⁰¹. This agglomeration led to reduced permeability by blocking pore spaces²⁰. Accordingly, researchers have emphasized that the choice of surfactant, pH control, and use of ultrasonication are crucial for improving the stability and mobility of nanofluids. Hybrid formulations for example like NP-surfactant can overcome these challenges through cooperative interactions, greatly enhancing EOR performance⁸⁴.

Limitations

In Nano-EOR, maintaining stable nanoparticle dispersion over reservoir-representative distances remains difficult, as aggregation and retention on rock surfaces can severely limit transport efficiency⁹⁸. Additionally, the long-term environmental impact and cost-effectiveness of nanoparticle injection are active areas of debate¹⁰².

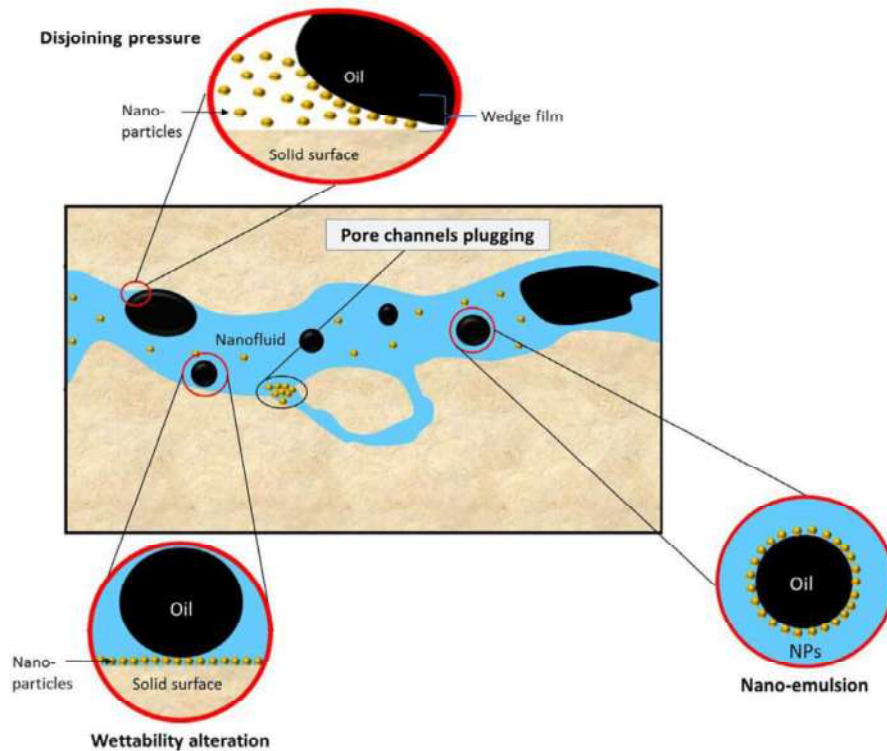


Figure I.21: Nanofluids mechanisms within porous media¹⁰³.

Hendraningrat et al. (2013) studied various concentrations of nanoparticles and their effect during core flooding experiments; their work suggests that nanoparticle concentrations between 0.01 and 0.05 wt% are favorable. Less concentration of nanoparticles has a small impact. At the same time, there are negative impacts of using more nanoparticles dispersed in brine, which may lead to the blocking of pores¹⁰⁴.

3) Low-salinity waterflooding (LSW)

Waterflooding is a secondary and the most widely adopted improved oil recovery (IOR) technique, mainly used for pressure maintenance after primary depletion and displacing oil by harnessing viscous force. This technology has attracted the industry's interest because of its simplicity, high availability and low cost.

Consequently, several studies are investigating the role of injected waters chemistry on the displacement efficiency and its impact on oil recovery. the results indicated that brine injection with a salinity in the range of 1000–2000 ppm can indeed affect crude oil/brine/rock

(COBR) interactions productively, thereby reducing the remaining oil saturation and enhancing oil displacement¹⁰⁵.

Low-salinity LSW or "smart" water injection operates through several mechanisms primarily attributed to wettability alteration via modifications to the electrical double layer influencing both the mineral–oil interface interactions and the stability of reducing fine migration within the porous medium¹⁰⁶.

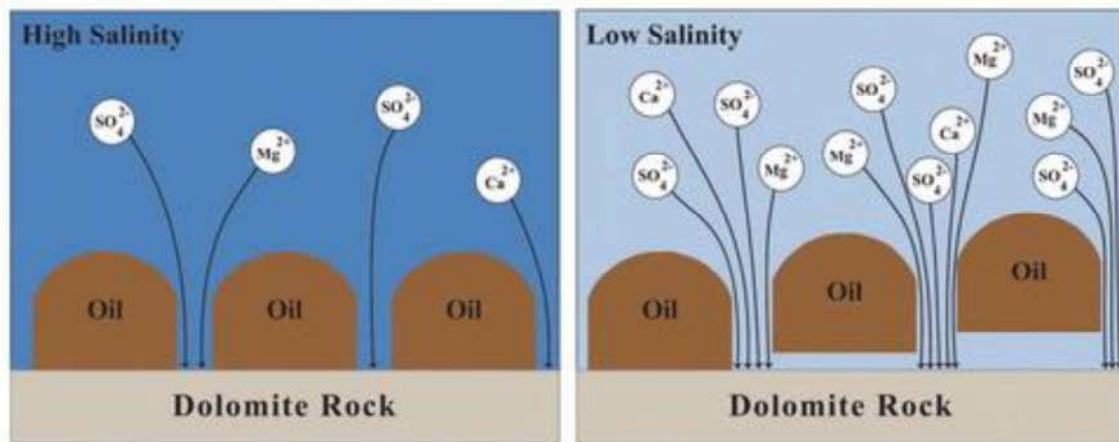


Figure I.22: Mechanism of low salinity water injection in dolomite rock¹⁰⁷.

Studies are investigating the precise effects of low-salinity water. Although its synergy with chemical EOR methods, such as surfactant, had a proved enhanced performance¹⁰⁸, limited by the high cost of these chemicals, this limitation has shifted focus to alternatives; hybrid approaches.¹⁰⁹

4) Synergistic effects

Synergy refers to the interaction where the combined effect of multiple elements exceeds the sum of their individual contributions. This concept, derived from Greek roots meaning "working together," applies across fields like science, biology and engineering¹¹⁰.

Synergy is also well established in emerging hybrid processes to activate the combined efficacy of multiple recovery mechanisms, such as combining nanoparticles with engineered low-salinity brines creating synergistic nano-brine formulations or coupling chemical injections with electromagnetic heating¹¹¹.

In heavy oil reservoirs, the synergy between nanoparticles and LSW is essential for managing asphaltene deposition, a major cause of permeability reduction and pore blockage¹¹². Nanoparticles possess a high surface area-to-volume ratio, allowing them to adsorb asphaltene molecules onto their surfaces, thereby stabilizing them and preventing self-assembly into damaging aggregates¹¹³. When these nanoparticles are combined with

LSW-based hybrid systems (such as ZnO/SiO₂/xanthan in diluted sea water), they not only prevent precipitation but also improve the viscosity and mobility ratio of the injected fluids¹¹⁴. This multi-agent approach has been proven to significantly enhance displacement efficiency, outperforming conventional chemical EOR by 5–25% OOIP under challenging conditions¹¹⁵.

The integration of nanotechnology with conventional chemical EOR addresses the inherent limitations of standalone agents⁴. While surfactants are effective at reducing interfacial tension (IFT), they often suffer from high retention and excessive adsorption onto reservoir rock surfaces, which diminishes their economic and technical viability. Nanoparticles, specifically metal oxides like Zinc Oxide (ZnO) and Silica (SiO₂), act as stabilizing agents that protect surfactant molecules, effectively reducing their adsorption by 50–70% and increasing the formulation's efficiency¹¹⁶. Conversely, surfactants such as sodium dodecyl sulfate (SDS) improve the colloidal stability of nanoparticles by preventing particle growth and sedimentation, ensuring that the nanofluid remains functional under harsh reservoir conditions.¹⁰¹ For example, SiO₂-CTAB hybrids improve wettability change and mobility control, delivering an additional recovery of 12–30% by addressing nanoparticle retention and surfactant partitioning¹¹⁷.

A critical synergistic mechanism is the achievement of significant IFT reduction and favorable wettability shifts. nanoparticles tend to gather at the oil-water interface, creating a rigid interfacial layer that disrupts cohesive forces more effectively than surfactants alone. For example, a formulation of 0.05 wt% ZnO NPs in 0.2 wt% SDS was shown to reduce IFT from 32.5 mN/m to 7.1 mN/m, facilitating an 8% increase in oil recovery compared to conventional surfactant flooding¹¹⁸. Furthermore, the presence of nanoparticles generates a structural disjoining pressure within the wedge-shaped film at the oil–water–rock contact zone. This mechanical overpressure detaches oil droplets from the rock surface, shifting the system toward a strongly water-wet state and allowing trapped oil to flow more freely¹¹⁹.

The use of Low Salinity Water (LSW), or "smart water," serves as a vital multiplier in nano-surfactant systems by optimizing the chemical environment for particle transport¹²⁰. High salinity environments typically suppress repulsive forces between nanoparticles, leading to aggregation, sedimentation, and potential pore-throat blockage⁸¹. By utilizing diluted seawater or LSW, the formulation maintains a higher zeta potential, which ensures colloidal stability and deep reservoir propagation. Research has demonstrated that silica nanoparticles dispersed in smart water can improve the recovery factor by up to 65.07% of

the original oil in place (OOIP). This synergy is driven by the "Low Salinity Effect," which expands the electrical double layer while nanoparticles simultaneously stabilize asphaltenes and reduce IFT¹²¹.

More experiments examples as Singh *et al.* study on a low-cost microemulsion using olefin sulfonate surfactants (ENORDET) stabilized by silica nanoparticles (SiO₂) for enhanced oil recovery, post characterization of its phase behavior, low interfacial tension, and wettability change using tensiometer, dynamic light scattering, and pendant/sessile drop analyses. Core flooding in sandstone cores showed the superior performance of the surfactant-nanoparticle hybrid, achieving about 29% OOIP recovery compared to about 20% for the surfactant-only microemulsion following secondary waterflooding. This study adds proven stabilization and better displacement efficiency of the combined system making it a strong potential candidate for sustainable EOR⁵³.

According to Yarahmadi et al., applying a combined formula of silica nanoparticles, a cationic surfactant, and low salinity water resulted in significant changes to the rock's wettability, reductions in interfacial tension, and increased oil recovery from carbonate reservoirs with this new hybrid nanofluid¹²².



II. Materials and Methods



Introduction

This chapter presents the experimental work conducted from January 20, 2026, to June 4, 2026, at CRAPC Ouargla. The study investigates the efficiency of the synergistic effect between Zinc oxide Nanoparticles and microbial produced biosurfactants in hydrocarbon media. The main objective is to evaluate the ability of this system to reduce crude oil viscosity and modify water–oil interfacial properties, with the aim of improving oil mobility and enhancing recovery performance.

II.2 Methodology

1) Biosurfactant Production

Step 1 : Bacterial culture medium preparation

A Nutrient Broth (BN) was prepared by dissolving 5 g of peptone and 3 g of yeast extract in 1 L of distilled water. After agitation, the solution is aliquoted into 150 mL bottles and then sterilized by autoclaving (Figure II.1) at 120°C for 20 minutes.



Figure II.1: Culture medium Autoclaving.

- The glycerol was sterilized separately in a water bath at 100 °C for 10 minutes.
- The sterilized medium and glycerol were stored in a refrigerator until use.

Step 2: Activation of the bacterial strain

A reference strain of *Pseudomonas aeruginosa* was used, isolated from soil contaminated with hydrocarbons and stored at low temperature.

The *Pseudomonas aeruginosa* strain was inoculated into a glycerol medium (3 mL of the sterilized glycerol in 150 mL of BN) and incubated at 37°C. After 24 hours, bacterial growth was observed, and portions of this culture were then inoculated into the 150 mL nutrient broth medium (BN) bottles containing 3 mL of sterilized glycerol. The incubation (Figure II.2) was carried out at 37°C for 48 to 72 hours.



Figure II.2: Culture medium incubation.

After incubation, the culture was centrifuged (Figure II.3) at 4000 rpm for 10 minutes to eliminate bacterial cells.



Figure II.3: Culture medium centrifugation.

A lyophilizer (freeze-dryer) was used to reduce water and concentrate the supernatant

To concentrate the supernatant shown in (Figure II.4) a lyophilizer, also known as a freeze-dryer, was used. This instrument removes water by freezing the supernatant and then applying a vacuum to sublime the ice directly into vapor, bypassing the liquid phase. As a result, the water content is significantly reduced, leaving behind a more concentrated and stable product without exposing it to damaging high temperatures. An image of the lyophilizer apparatus is shown in (Figure II.5).



Figure II.4: Supernatant



Figure II.5 Lyophilizer

Step 3: Biosurfactant Extraction

Biosurfactant extraction was performed using acid precipitation followed by organic solvent extraction. The supernatant was collected and acidified to pH 2 with 6N HCl. A chloroform and methanol mixture (2:1 v/v) was then added to the acidified sample. The mixture was stirred for several minutes, transferred to a separatory funnel, and left to stand overnight. The following morning, the first phase was decanted. The organic phase, containing the biosurfactant, settled to the bottom, while the aqueous phase remained on top as presented in (Figure II.6).



Figure II.6: Solvent extraction.

The solvents were then dried from the extracted recovered organic phase (Figure II.7) under vacuum in an oven at 40°C until complete evaporation.



Figure II.7: Organic phase.

2) Green Synthesis of Zinc Oxide Nanoparticles (ZnO NPs)

Plant-based biosynthesis of metal oxide nanomaterials is considered an alternative to chemical synthesis as a result of the plants' biodiversity and the different varieties of phytochemical compounds adding the 'greenness,' rapidity, low cost, and simplicity of the process, accelerating research to expand its role in modern applications.¹ Organic wastes

contain a significant concentration of bioactive compounds that can be implanted in the biofabrication of metal and metal oxide nanomaterials such as Ag, CuO, MgO, and ZnO¹²³¹²⁴. these bioactive compounds act as natural reducing and stabilizing (capping) agents¹²⁵¹²⁶ ZnO leading the group of nanoparticles that have been thoroughly investigated because of their safety profile. Those nanoparticles are being biosynthesized using a variety of plant extracts. such as *Mentha pulegium* L.¹²⁷, *Thymbra Spicata* L.¹²⁸, and *Punica granatum* L.¹²⁹.

Specifically, it has been determined in literature that it is rich in concentration of bioactive compounds such as phenolic, flavonoid, anthocyanin, and hydrolysable tannin compounds, and it varies according to the pomegranate cultivar, fruit ripeness, extraction methods, and storage conditions¹³⁰¹³¹.

Step 1: Plant Extract Preparation

Fresh pomegranate peels were thoroughly washed with distilled water and air-dried until completely dehydrated. The dried peels were ground into a fine powder and stored in amber glass jars.



Figure II.8: Pomegranate peels powder.

For extraction, 7.5 g of powder per 100 mL of distilled water was agitated continuously overnight at room temperature using an orbital shaker (Figure II.9).



Figure II.9: shaker.

The next morning, the suspension was subsequently filtered and clarified by centrifugation at 4000 rpm for 10 min to obtain a clear aqueous extract.



Figure II.10: Vacuum filtration.



Figure II.11: Centrifuge.

Step 2: Green Synthesis of Zinc Oxide Nanoparticles (ZnO)

In an Erlenmeyer flask, 500 mL of 10 mM Zinc acetate solution was mixed with 100 mL of the prepared pomegranate peel extract. Then heated in a water bath at 80 °C under continuous agitation for 2 hours (Figure II.12). then incubated at 75 °C for 12 hours.

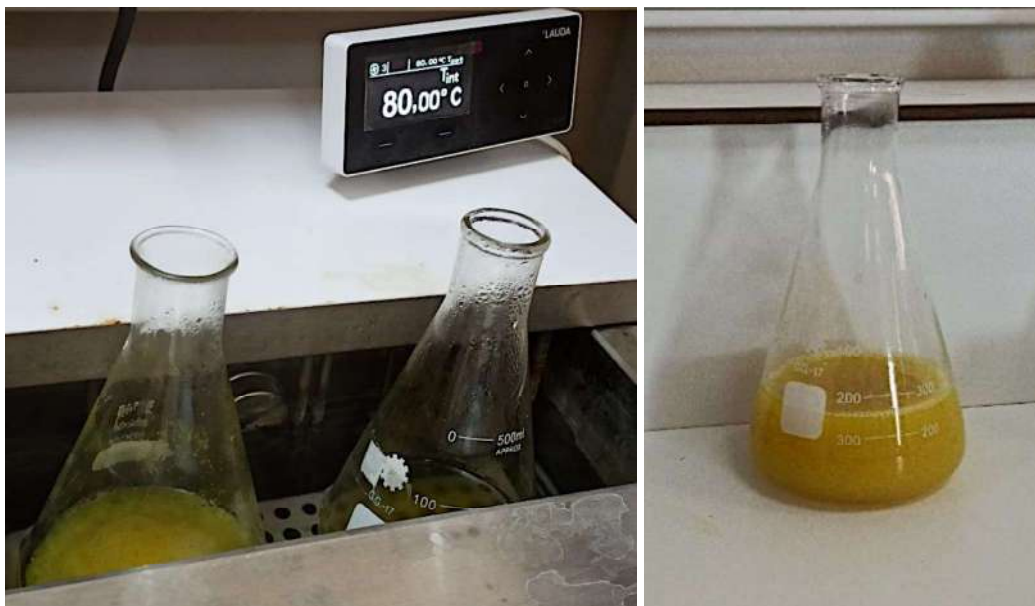


Figure II.12: Zinc acetate + Peel extract water bath heated.

After incubation, a change of color was observed with precipitate formation at the bottom of the flask (Figure II.13), which indicates the presence of ZnO nanoparticles.



Figure II.13: Precipitate formation

Additional characterization techniques (e.g., XRD, SEM, UV-Vis spectroscopy) are necessary for structural and morphological confirmation. Purification was carried out using four sequential centrifugation cycles :

- Firstly, to separate the precipitate from the aqueous phase.
- Then, washing cycles with distilled water of a precipitate to eliminate unreacted species were performed.

- Finally, the washing step uses ethanol to eliminate water.

The precipitate was then placed in an oven at 75°C until completely dry. The resulting material is shown in (Figure II.14).



Figure II.14: The precipitate.

The dried material was then ground into a fine powder and prepared for the calcination step.



Figure II.15: Calcination furnace.

3) Hybrid System formation (Biosurfactant-Capped Nanoparticles)

Biosurfactant-Capped Nanoparticles are an engineered structure where surface-active agents (biosurfactants for this study) are adsorbed on the surface of metal or metal oxide nanoparticles to stabilize them for the purpose of controlling their growth and prevent agglomeration, to maintain particle uniformity in the nanometer range, and to secure their stability in colloidal dispersions.

The bio-nano hybrid system was prepared by dispersing 100 mg of nanoparticles in 10 mL of distilled water under manual agitation. The suspension was subsequently treated in an ultrasonic bath to improve nanoparticle dispersion and minimize aggregation.

Separately, the dried biosurfactant extract was dispersed in 10 mL of distilled water.

5 mL of the nanoparticle suspension was added to the biosurfactant solution under continuous magnetic stirring agitation overnight (Figure II.16) to promote interaction between the biosurfactant compounds and the nanoparticle surface.



Figure II.16: Bio-nano solution agitation.

The prepared hybrid formulation was then used for experimental analyses subsequently.

4) Oil

In this study, Petroleum vacuum distillation residue (VDR), a sample from Adrar refinery Sbaa RA1D, is used as a modeling fluid to replicate the characteristics of heavy oils found in oil reservoirs in the context of enhanced oil recovery (EOR). The heavy fraction is rich in high-molecular-weight compounds such as asphaltenes, as well as in heteroatoms and heavy metals¹³². These constituents give the residue properties similar to those of actual heavy oils, notably high viscosity, strong polarity, and a tendency to aggregate^{133 134}, which promotes the trapping of oil within the reservoir's porous media. The use of vacuum residue allows for a representative simulation of the complex conditions encountered during EOR processes.

Crude Oil Classification

The viscosity measurements were performed using a Kinematic viscometer, SVM 3001. the obtained properties are summarized in the table below:

Table II. 1 Measured Properties of the Crude Oil

Propriety	Value
Specific density ρ	0.90214 g/cm ³
Specific gravity SG	0.9100
Dynamic viscosity μ	644.42 mPa·s
Kinematic viscosity	714.32 mm ² /s
API	24°

This combination suggests complex rheological behavior, whereby the fluid may exhibit flow characteristics more typical of heavy oils despite its medium API classification.

5) Brine

Brine was used as the dispersion solution for the hybrid system to replicate reservoir salinity and realistic ionic conditions. Unlike distilled water, saline formation water influences the physicochemical behavior of the injected fluids.

Salinity affects the stability, solubility, adsorption and interfacial behavior and may lead to precipitation or reduced efficiency at high ionic strengths^{135 136}. Changing water chemistry to increase recovery So the Use of brine ensures optimal formulation performance in the context of the study.

Preparation of low Salinity Brine

The preparation of the engineered low-salinity brine was executed through a systematic dissolution process. Initially, the required salts, with their respective compositions explicitly outlined in Table II.2, were carefully weighed and introduced into a volumetric flask containing deionized water¹³⁷.

Table II.2 Engineered brine salts composition¹³⁸.

Salt	Formula	g/L
Sodium chloride	(NaCl)	11.815
Potassium chloride	(KCl)	0.5675

Calcium chloride dihydrate	(CaCl ₂ .2H ₂ O)	0.9075
Magnesium chloride hexahydrate	(MgCl ₂ . 6H ₂ O)	6.1115
Sodium sulfate	(Na ₂ SO ₄)	3.3575
Sodium bicarbonate	(NaHCO ₃)	0.169

To facilitate the complete dissolution of the chemical components and to ensure a uniform, homogeneous mixture, the solution was continuously agitated for a duration of 30 minutes. Throughout this entire mixing period, the temperature was strictly maintained at ambient room conditions to prevent any premature evaporation and to preserve the physicochemical stability of the final brine solution.



III. Results and Discussion



III.1 Introduction

This chapter focused on the characterization of the biosurfactant and the green synthesized nanoparticles, separately then as a combined system in order to evaluate their performance in oil water interaction using various analytical techniques such as Gas chromatography mass spectrometry (GC-MS), UV-Vis Spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM).

III.2 Biosurfactant Characterization

The extracted biosurfactant was subjected to a series of physicochemical tests to confirm its nature.

Test N°1:

Tubes are represented in Figure III.1 from right to left as follows below:

- 1: Oil + Water
- 2: Oil + aqueous phase
- 3: Oil + organic phase



Figure III.1: Visual comparison of phase separation behavior.

We recorded the following observations for each tube, as detailed below:

- Tube 1: A clear phase separation, which indicates the absence of interfacial interaction between the two phases.
- Tube 2: A clear phase separation in the oil aqueous phase post solvent extraction proving or validating that the surface-active compounds are not present with the aqueous phase.
- Tube 3: A homogeneous one phase appearance and an improved fluidity and mixing behavior were observed, indicating the presence of surface-active compounds within the organic phase extract.

Despite the equal initial volumes in the 3 systems, this tube appeared visually reduced, suggesting strong potential for emulsifying and partial dispersion of oil and improved interfacial activity.

Test N°2:

Oil droplet in the same volume of water and organic extract phase as represented in Figure II.2.

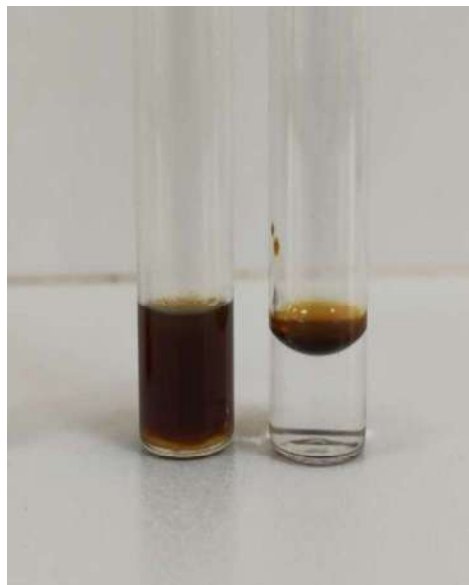


Figure III.2: Visual evaluation of oil droplet dispersion.

It was observed that the oil droplet maintained a distinct and stable interface separation in the water, indicating limited affinity. While the oil droplet showed altered behavior and better dispersion in biosurfactant phase with the same volume of water

Test N°3:

From left to right (Figure III.3) oil droplet for visual test was remained as following:



Figure III.3: Visual comparison of dispersion behavior.

Oil droplet + organic extract phase

Oil droplet + water droplet

Oil droplet

It was observed that the water droplet remained visually distinct. Within the oil phase, reflecting poor interaction between the two fluids and interfacial resistance. A noticeable spreading and distribution suggesting a potential reduction in interfacial tension

As a result, the visual observations revealed a significant difference in phase behavior between untreated and organic extract-treated systems, enhancing interaction with the oil phase, improving dispersion behavior, and reducing visible interfacial resistance. These observations support the successful extraction of surface-active compounds.

a) UV–Visible Analysis

The UV-Visible spectrum (Figure III.6) of the extracted biosurfactant exhibited a major absorption peak at 259 nm, confirming the presence of biosurfactant-related organic compounds.

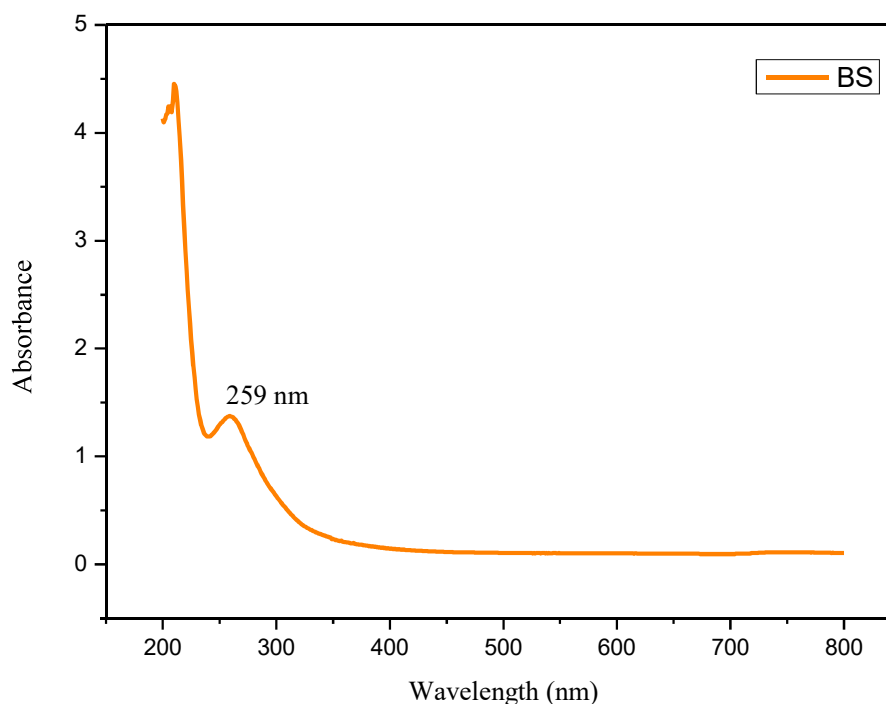


Figure III.4: UV–Visible absorption spectrum of the extracted biosurfactant

Sultana, Shahnaz et al,¹³⁸ reported the UV-Vis absorption spectra of biosurfactant and they found that the wavelengths ranged between 200 and 800 nm, suggesting the presence of rhamnose in the sample.

b) FTIR Characterization

The FTIR spectrum of the extracted biosurfactant exhibited characteristic absorption bands at 3289, 2920, 1683, 1450, 1200-1000, 688, and 506 cm^{-1} , confirming its amphiphilic molecular structure.

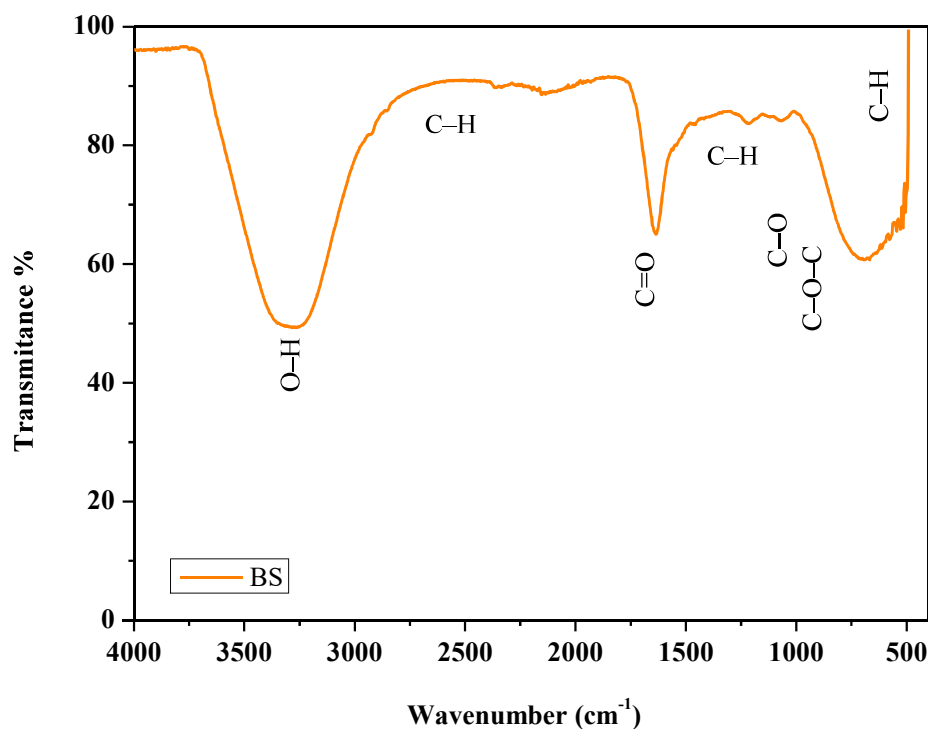


Figure III.5: FTIR spectrum of the extracted biosurfactant.

The broad and intense band observed at 3289 cm^{-1} is attributed to O–H stretching vibrations, indicating the presence of hydroxyl groups involved in hydrogen-bonding interactions, which is characteristic of the carbohydrate moiety in glycolipid biosurfactants^{139 140}.

The absorption bands in the 2920-2850 cm^{-1} region correspond to asymmetric and symmetric C–H stretching vibrations of methylene and methyl groups, confirming the presence of aliphatic hydrocarbon chains indicative of the fatty acid/lipid tail component^{2 141}.

The strong absorption band at 1683 cm^{-1} is assigned to C=O stretching vibrations of ester or carboxylic acid functional groups, typically corresponding to ester linkages between the fatty acid chain and sugar moiety or carboxylic acid groups in the lipid portion³.

The band around 1450 cm^{-1} corresponds to C–H bending vibrations, further confirming the aliphatic chain structure, while the multiple absorption bands in the $1200\text{--}1000\text{ cm}^{-1}$ region are characteristic of C–O stretching vibrations and C–O–C glycosidic linkages, confirming the presence of carbohydrate structures and ester functionalities^{2,3}.

The bands at 688 cm^{-1} and 506 cm^{-1} fall within the fingerprint region and are associated with out-of-plane C–H bending vibrations of long-chain aliphatic compounds and skeletal vibrations, respectively, confirming the presence of long fatty acid chains^{4,142}.

The combination of these functional groups confirms the amphiphilic nature of the extracted biosurfactant, with hydroxyl groups and C–O bonds representing the hydrophilic portion from carbohydrate groups, aliphatic C–H chains representing the hydrophobic portion from fatty acid components, and ester/carbonyl groups serving as the linkage region connecting both portions. Compared to previous studies, all these main chemical groups were in line with the structural characteristics of rhamnolipid, but it needs further characterization.

c) GC-MS Characterization

The GC–MS analysis revealed 109 different compounds in the extracted biosurfactant at retention times ranging from approximately 12 to 39 min, indicating the presence of various bioactive metabolites belonging to different chemical classes, including lipids, fatty acid derivatives, sugars, organic acids, and secondary metabolites. The chromatogram (Figure III.6) showed one dominant peak corresponding to 1,2,3-propanetriol triacetate (triacetin), indicating that this compound represents the major constituent of the biosurfactant extract.

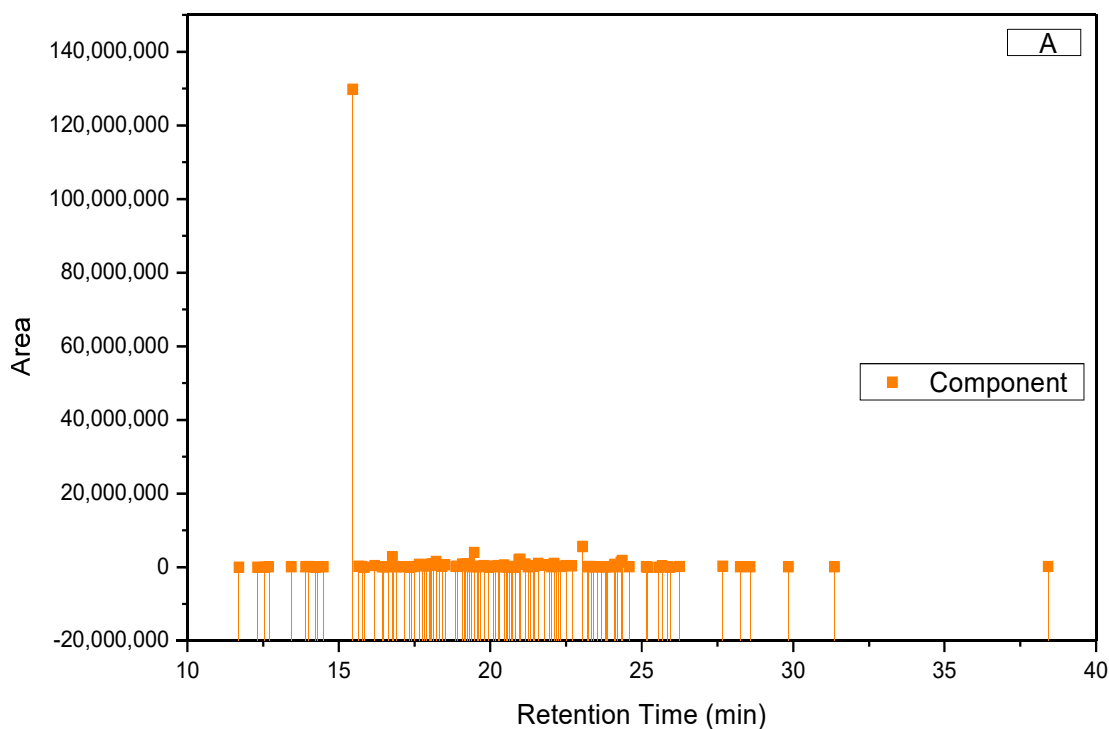


Figure III.6: GC-MS chromatogram of the biosurfactant

Several lipid-associated and esterified compounds were identified, including triacetin, glycerol diacetate, octadecanoic acid, and isopropyl myristate. The occurrence of glycerol-derived esters may be associated with the microbial metabolism of glycerol present in the culture medium, while the presence of long-chain fatty acid compounds and fatty acid esters reflects lipid-associated metabolic activity in *Pseudomonas* sp, in particular, the detection of octadecanoic acid supports the lipidic nature of the produced metabolites¹⁴³.

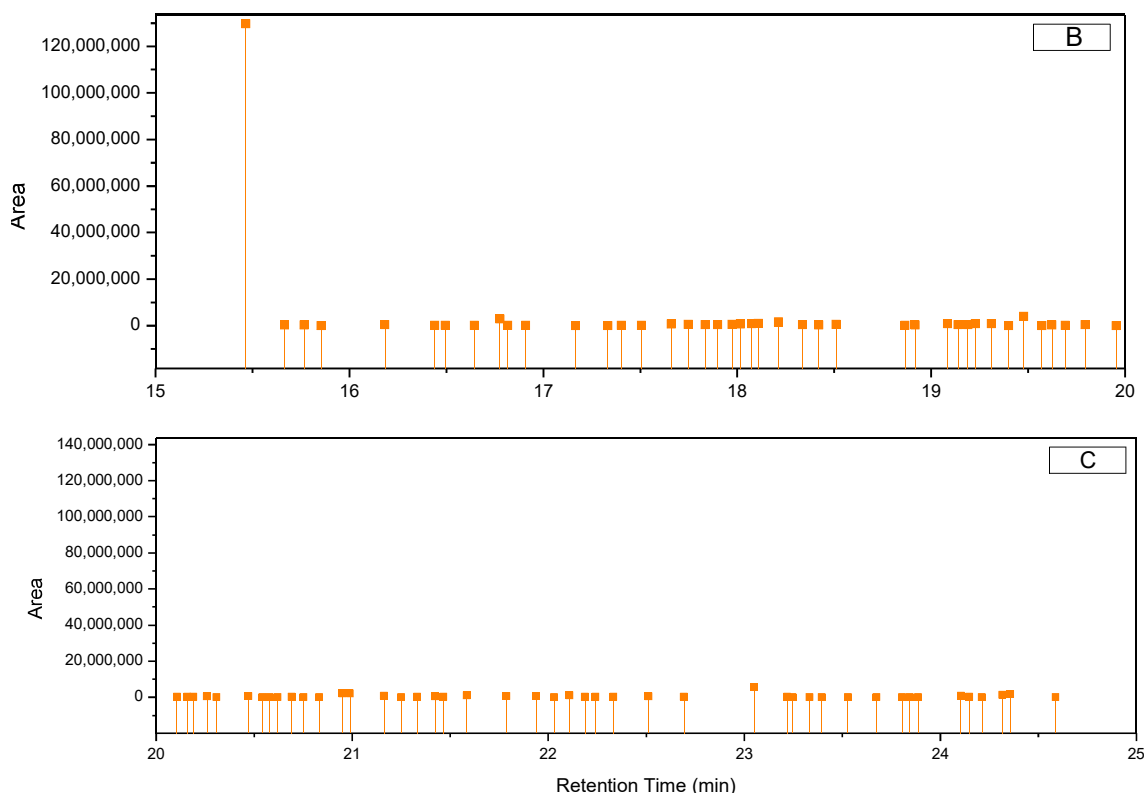


Figure III.7: Enlarged GC–MS chromatogram in the retention time range of 15–25 min.

Glycerol can serve as a precursor for rhamnose biosynthesis, whereas fatty acids contribute to the formation of the lipid moiety, followed by the coupling of these intermediates during mono- and di-rhamnolipid biosynthesis¹⁴⁴. In the present study, the detection of glycerol-derived esters and fatty acid-associated compounds is consistent with metabolic pathways involved in glycolipid biosurfactant production.

Previous studies reported that triglycerides are enzymatically hydrolyzed into glycerol and free fatty acids, which act as important intermediates in biosurfactant biosynthesis pathways¹. The detected fatty acid and esterified compounds are consistent with metabolites commonly associated with glycolipid biosurfactants and support the possibility of rhamnolipid-type biosurfactant production¹⁴⁵. Furthermore, the identified esterified and fatty acid-derived compounds may contribute to the emulsification and surface-active properties exhibited by the produced biosurfactant.

Although the chromatographic profile did not directly identify characteristic rhamnolipid molecules, the obtained results suggest the possible production of a glycolipid-type biosurfactant by *Pseudomonas* sp.

III.3 Zinc Oxide Nanoparticles (ZnO NPs) Characterization

a) Visual analysis

During the green synthesis process of ZnO NPs, a strong color change was observed following the 12 h incubation at 75°C post the addition of pomegranate peel extract to the zinc acetate solution under continuous heating and agitation.

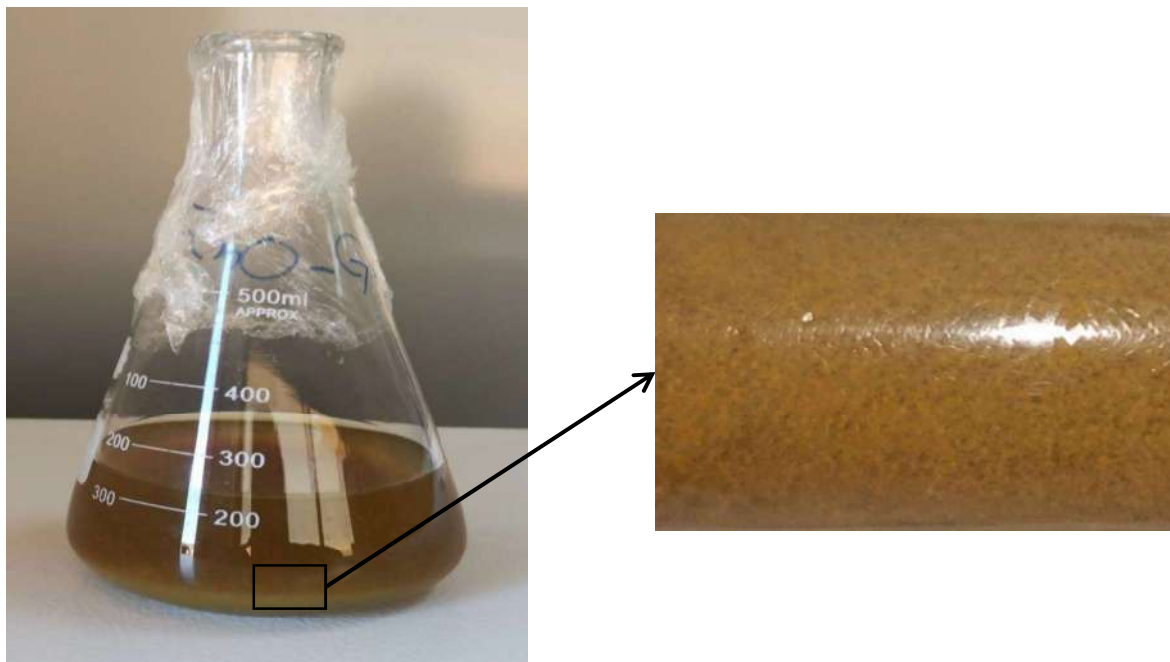


Figure III.8: Visual observation of precipitate formation post green synthesis of ZnO NPs.

The formation of visible precipitate at the bottom of the reaction flask is shown in (Figure III.8) Suggest the first indicator of the occurrence of chemical reactions between zinc ions and the bioactive compounds present in the plant extract, resulting in the formation of zinc containing particles.

This observation is considered a preliminary indication of NPs formation consequent to the conversion of zinc precursors into ZnO solid particles because of the pomegranate-derived phytochemicals, potentially phenolic compounds or other reducing agents, present in the peel extract. At this stage we cannot determine which compounds reacted. Also, this visual observation alone is insufficient to confirm NPs formation and further characterization is required to ensure the success of the synthesis.

b) UV–Visible Characterization

The UV–Visible spectrum of the ZnO NPs (Figure III.9) shows a strong absorption peak at 363 nm with a secondary peak observed around 417 nm.

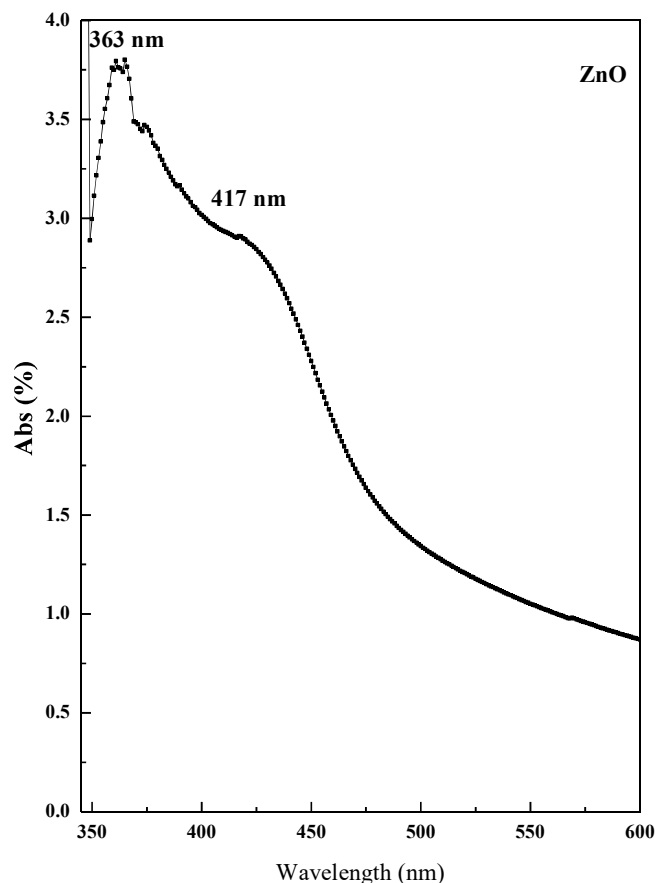


Figure III.9: UV-Visible absorption spectrum of green-synthesized ZnO NPs.

According to M.M. Almoneef *et al.* (2024) zinc oxide nanoparticles exhibit a characteristic absorption peak around 350.34 nm¹⁴⁶. The absorption peak obtained in this study is therefore in close range with the reported literature values, confirming the successful synthesis of ZnO nanoparticles.

The slight difference between the literature value and the obtained result may be attributed to experimental conditions during synthesis like concentration effects or characterization.

c) FTIR Characterization

The FTIR transmittance spectrum revealed different absorptions at specific wavelength ranges, indicating the presence of several functional groups, observed in (Figure.III.12).

A peak at 3203.09 cm^{-1} suggests the presence of carboxylic acid, (O-H) commonly found in hydroxyl groups of flavonoids and phenolic compounds. These hydroxyl-rich phytochemicals, identified during phytochemical screening of the aqueous extract of pomegranate peels, act as natural reducing agents by donating electrons to convert Zn^{2+} ions into ZnO NPs.¹⁴⁷

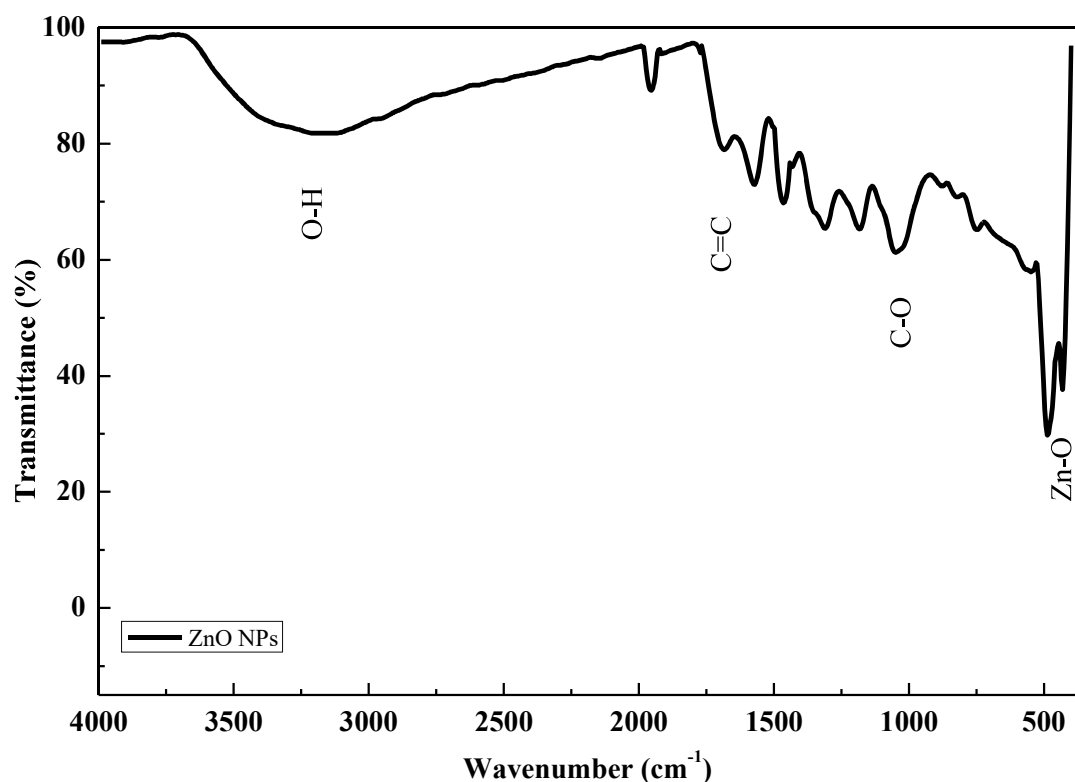


Figure III.10: FTIR spectrum of green-synthesized ZnO NPs.

A peak at 1700.85 cm^{-1} , indicates the presence of conjugated alkenes and aromatic rings. The (C—C) stretching vibration contributes to metal ion chelation and serves as a natural capping agent that enhances NPs stability.¹⁴⁸

1041.27 cm^{-1} related to carbonyl groups (C=O) and aromatic compounds from plant biomolecules.¹⁴⁹

Stretching vibrations show peaks at 500 cm^{-1} in the FTIR spectra of the synthesized Zn/ZnO NPs, confirming the production of ZnO.¹⁵⁰

d) Scanning Electron Microscopy (SEM) Characterization

The scanning electron microscopy (SEM) micrographs presented in Figure (III.13) illustrate the surface morphology of ZnO nanoparticles synthesized through a green biosynthetic route. The ZnO nanoparticles exhibit a granular and quasi-spherical

morphology, forming a dense and relatively homogeneous coating. The inset reveals an aggregated structure resulting from the assembly of primary nanocrystals.

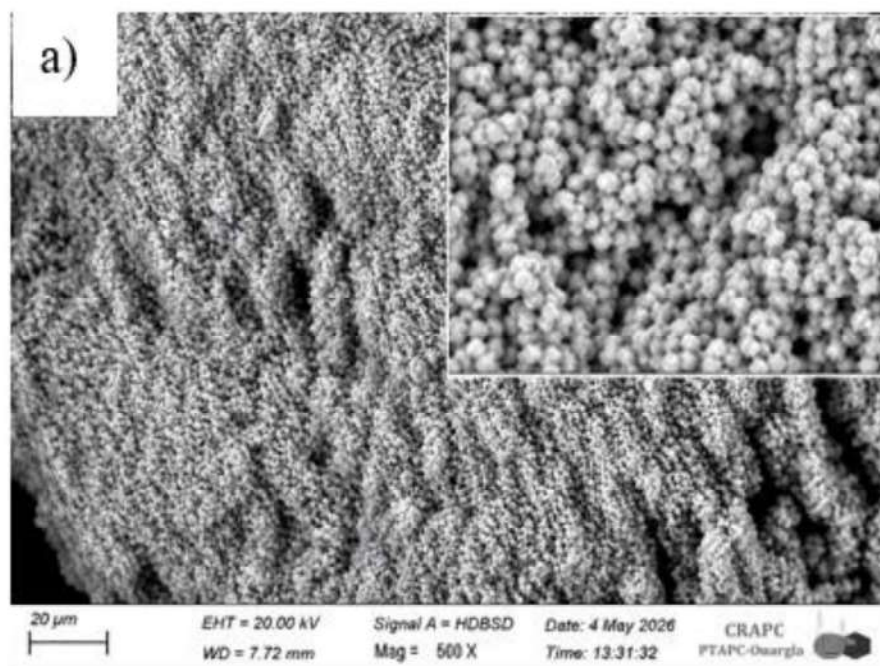


Figure III. 11: SEM image of biosynthesized ZnO NPs.

These morphological observations corroborate the spectroscopic findings and confirm the effectiveness of the biogenic synthesis approach using pomegranate waste, in which plant-derived biomolecules play a key role in the reduction of metal precursors, the control of crystal growth, and the colloidal stabilization of metal oxide nanostructures.

III.4 Biosurfactant-capped ZnO nanoparticles (Bio–Nano) Characterization

a) UV–Visible Characterization

UV–Visible absorption spectrum (Figure III.14). is a comparison of the UV–Vis spectrum of the biosurfactant alone; the biosurfactant-coated ZnO nanoparticle system shows two characteristic absorption bands corresponding to both constituents.

The absorption band at lower wavelengths, 254-259 nm, is associated with the biosurfactant, whereas the peak around 373 nm is characteristic of ZnO nanoparticles.

The presence of both bands within the same spectrum provides evidence for the successful formation of a biosurfactant–ZnO bio-nano system.

This result indicates that biosurfactant molecules were effectively adsorbed onto the nanoparticle surface, acting as capping and stabilizing agents, rather than existing as a separate phase in the dispersion.

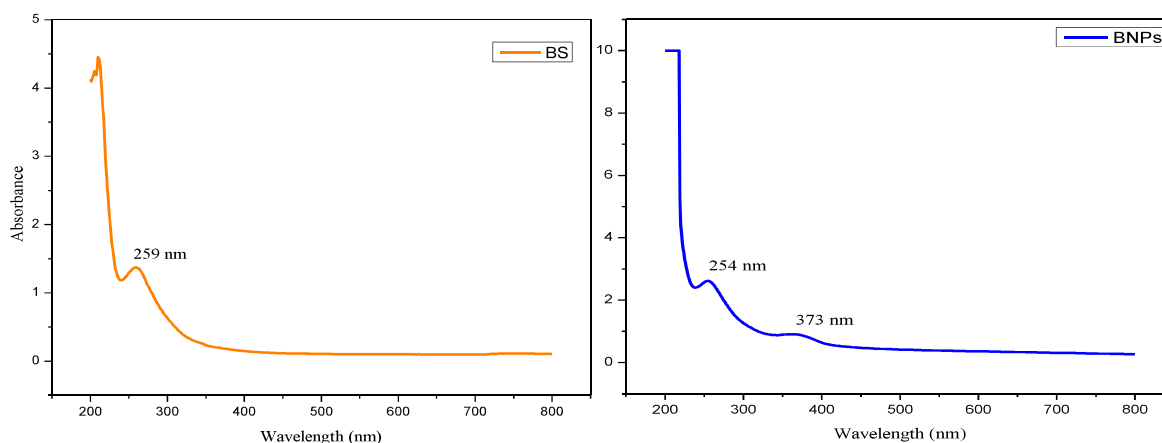


Figure III.12: UV–Visible absorption spectrum of the a) biosurfactant b) biosurfactant–ZnO nanoparticle system.

However, confirmation of coating and particle morphology should be supported by additional characterization techniques such as FTIR.

b) FTIR Characterization

The FTIR spectrum of the biosurfactant–ZnO NPs system exhibited characteristic absorption bands corresponding to both the biosurfactant and the ZnO NPs.

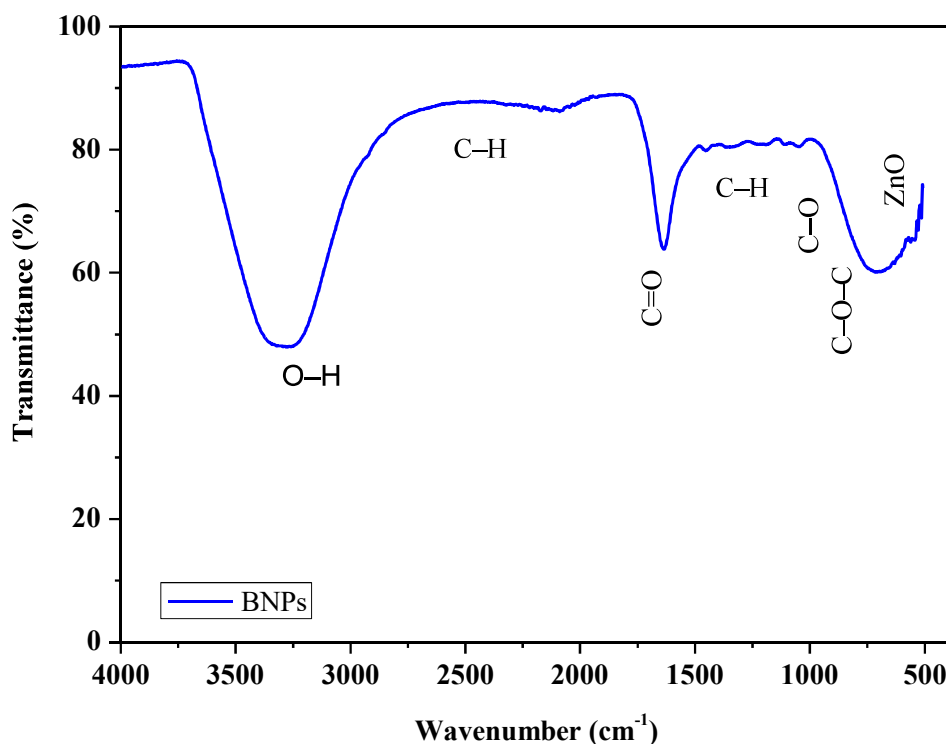


Figure III.13: FTIR spectrum of the biosurfactant–ZnO NPs hybrid system. BNPs.

A broad absorption band observed in the 3200–3400 cm^{-1} region was attributed to O–H stretching vibrations of hydroxyl groups involved in hydrogen-bonding interactions. An absorption band observed around 1600–1700 cm^{-1} may be associated with oxygen-containing functional groups, including carbonyl-related vibrations and adsorbed water molecules. Furthermore, absorption bands in the low-wavenumber region below 700 cm^{-1} are consistent with Zn–O stretching vibrations, indicating the presence of ZnO NPs. The coexistence of biosurfactant-related functional groups and ZnO vibrations suggest the formation of the biosurfactant–ZnO NPs system.

III.5 Interfacial Performance Evaluation

The measured samples in (Table III.1) are listed as following:

OB: Oil–Brine.

OBBS: Oil–Brine–Biosurfactant.

OBNPs: Oil–Brine–ZnO NPs.

OBBNPs: Oil–Brine–BNPs.

Table III.1: Interfacial Tension Measurements.

	Aged Formulation				Fresh Formulation	
	25 °C		80 °C		25°C	
System (70 :30)	FT (mN/m)	FT Reduction (%)	IFT (mN/m)	FT Reduction (%)	FT (mN/m)	FT Reduction (%)
OB	38.9	0	37.3	0	38.9	0
OBBS	34.2	12.1	3.3	0.7	42.9	-10.3
OBNPs	44.8	-15.2	38	-1.9	52.8	-35.7
OBBNPs	36.8	5.4	39	-4.6	47	-20.8

The interfacial tension results demonstrated that the biosurfactant formulation exhibited the best interfacial performance among the investigated systems from 38.9 mN/m to 34.2 mN/m at 25°C and from 37.3 mN/m to 33.3 mN/m at 80°C, confirming its effectiveness in reducing the interfacial forces between the oil and brine phases. In contrast, the ZnO nanoparticle suspension and the nano-biosurfactant system exhibited higher IFT values of 36.8 mN/m at 25°C and 39.0 mN/m at 80°C under the tested conditions. Although the hybrid system was successfully developed and characterized, it did not exceed the interfacial performance of the biosurfactant alone. This behavior may be attributed to nanoparticle agglomeration, which can reduce the effective surface area available for interfacial interactions and consequently limit the expected enhancement in IFT reduction.

The comparison between freshly prepared and aged formulations revealed a noticeable improvement in interfacial performance after approximately one week of aging. The lower IFT values obtained for the aged formulations suggest that contact time influences the behavior of the developed systems, possibly through progressive interfacial equilibration and changes in nanoparticle distribution within the suspension. This observation is particularly relevant for the nano-biosurfactant formulation, which exhibited a more pronounced improvement after aging compared to the freshly prepared sample. Safari *et al* (2023), and previous studies¹⁵¹ have reported that biosurfactant-related processes often evolve over extended periods of time¹⁵², with surface and interfacial properties improvement.

The differences observed between fresh and aged formulations indicate that aging time is an important parameter influencing system performance. Finally, this study may be considered an initial investigation highlighting the potential significance of formulation aging and providing a basis for future studies involving longer monitoring periods and further optimization of nano-biosurfactant systems for enhanced oil recovery applications.

Conclusion

This work focused on the development and evaluation of a hybrid nano-biosurfactant system for potential enhanced oil recovery (EOR) applications. The study was structured around several main stages. First, a biosurfactant was produced through microbial processes and subsequently characterized to confirm its surface-active properties. Green-synthesized ZnO nanoparticles were then prepared and characterized. The hybrid nano-biosurfactant system (BNPs) was developed through the interaction between the biosurfactant and ZnO nanoparticles, and its successful formation was confirmed through physicochemical characterization techniques.

The second stage of this work focused on evaluating the interfacial performance of the developed systems. Interfacial tension measurements were conducted on oil–brine systems containing biosurfactant, ZnO nanoparticles, and the BNPs formulation under different temperature conditions. The results demonstrated that the biosurfactant exhibited the highest interfacial activity, achieving the greatest reduction in oil–brine interfacial tension. Although the hybrid nano-biosurfactant system did not surpass the performance of the biosurfactant alone under the investigated conditions.

Furthermore, the comparison between freshly prepared and aged formulations highlighted the influence of contact time on interfacial behavior. The observed improvement in aged systems suggests that formulation aging and nanoparticle distribution may play an important role in determining the performance of nano-biosurfactant formulations. This finding represents an interesting perspective for future investigations aimed at optimizing hybrid systems for EOR applications.

Overall, the results obtained in this study demonstrate the potential of biosurfactant-based formulations as environmentally friendly alternatives for improving oil recovery processes. In addition to their biodegradability and reduced environmental impact compared with conventional chemical agents, biosurfactants offer promising interfacial properties that can contribute to enhanced oil mobilization. The present work provides a foundation for further research on nano-biosurfactant systems and highlights the importance of formulation parameters, aging time, and nanoparticle stability in the development of efficient EOR technologies.

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