

Review Article

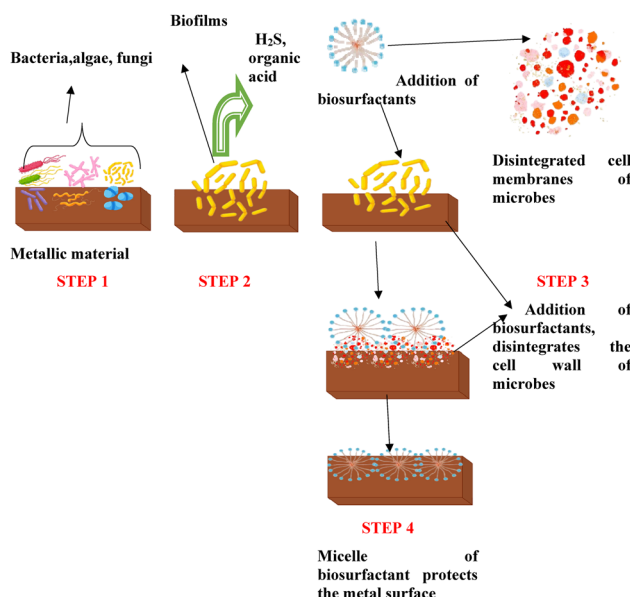
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Biosurfactants in biocorrosion and corrosion mitigation of metals: An overview

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Abstract: Biocorrosion, or microbiologically influenced corrosion, is a phenomenon where microorganisms deteriorate the metals. While corrosion is generally considered undesirable due to its negative impact on the integrity and lifespan of materials, the significance of biocorrosion is a major problem because it can cause material deterioration, financial losses, and environmental issues. Conventional corrosion protection techniques frequently use chemicals, which come with risks to human health and the environment. Biosurfactants are surface tension-reducing agents with a low molecular weight that attract many researchers and industrialists due to their excellent chemical properties and stability at extreme temperatures, pH, and under alkaline conditions. These compounds reduce the surface tension of liquids, leading to improved wetting and spreading on metal surfaces. This can help to create a more uniform and protective layer, preventing the accumulation of corrosive agents. This review



Graphical abstract

explores different types of biosurfactants, which include lipopeptides, glycolipids, phospholipids, etc., and how they work to prevent corrosion. The investigation of biosurfactants in corrosion protection not only addresses environmental concerns but also holds promise for innovation in the development of efficient and long-lasting corrosion mitigation strategies for a variety of metal substrates, given the growing demand for green and sustainable technologies.

Keywords: biosurfactants, biocorrosion, corrosion protection, rhamnolipids, glycolipids, bioremediation

1 Introduction

Surfactants are amphiphilic compounds that contain both hydrophobic and hydrophilic ends and reduce interfacial tension between any two phases. These are surface-active agents, and when added in small quantities to the liquid, they improve the ability to spread and moisten the surfaces

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[1]. These surface-active compounds are capable of acting as emulsifiers, moistening agents, dispersants, cleaners, foaming agents, anti-adhesives, anticorrosive, anti-bacterial, and anti-static agents [2–7]. According to the hydrophobic and hydrophilic ends, surfactants are classified as anionic, cationic, and amphoteric [8].

Recently, the international market has driven researchers in the synthesis of both chemical and green surfactants as they possess a vital role in the field of Science, Engineering, and Technology [9]. The main active commercially produced surfactants belong to the various classes of groups like alkylbenzene sulphonates, alcohol ethoxylates, sulphates, and ethersulphates [10]. These groups of surfactants are used in the field of detergent, households, and personal care products [11], and they are economically viable. Even though they are not expensive, chemical surfactants possess several disadvantages. The added surfactants may have a chance of being absorbed by wildlife plants and deposited in water bodies, thus causing high toxicity to aquatic life, reducing dissolved oxygen, and reducing the photosynthesis process in plants [12].

In the past few years, scientists have focused on the synthesis of bio-based surfactants to compensate for the performance of chemical surfactants and diversify the range of applications in various fields. Biosurfactants, also known as bio-based surfactants or green surfactants, are synthesized by yeast, fungi, and certain bacteria [13,14]. They exhibit a remarkable diversity of chemical structures, encompassing lipopeptides, glycolipids, phospholipids, and proteins, and are useful in many different industrial applications because of their structural variability, which contributes to a wide range of functional properties. Biosurfactants are used in various fields, such as food, agriculture, petroleum, and cosmetics, as they reduce surface and internal surface tension and possess emulsifying, stabilizing, wetting, spreading, foaming, and cleaning properties similar to chemical surfactants [15–17]. More recently, biosurfactants have

found various applications in the fields of corrosion, health-care, textiles, and bioremediation [18]. The importance of these naturally occurring compounds keeps growing as researchers continue to explore new microbial sources, optimize production processes, and learn more about the field of biosurfactants. Because of their adaptability and sustainability, biosurfactants are positioned to play a significant role in the development of green technologies and ecologically friendly solutions for a variety of industries (Figure 1).

Biosurfactants play a significant role in the corrosion inhibition of metals due to their unique properties and environmentally friendly nature. Corrosion poses a serious hazard and pulls down the economy, industry, and country. Bio-corrosion caused by aerobic and anaerobic bacteria causes severe damage to different industries and services, and it is recognized as an important category of corrosion [19,20]. To control and prevent such hazardous bio-corrosion, bio-based biosurfactants can be used. The present review focuses on the types of biosurfactants and their roles in the prevention and control of corrosion. We report a few real-world examples from the literature that use biosurfactants as intelligent and environmentally friendly biocides. This review gives some novel insights and ideas for researchers on emerging trends and future directions in using biosurfactants as corrosion inhibitors for metals. With increasing concerns about environmental pollution and sustainability, there is a growing interest in developing green corrosion inhibitors. Biosurfactants offer a sustainable alternative to traditional chemical inhibitors since they are produced from renewable resources and are biodegradable. Future research may focus on optimizing biosurfactant production processes to enhance their environmental friendliness. A better understanding of these mechanisms will facilitate the design of more effective biosurfactant-based corrosion inhibitors. As research into biosurfactant-based corrosion inhibitors progresses, there is a need for scalable production methods and commercialization

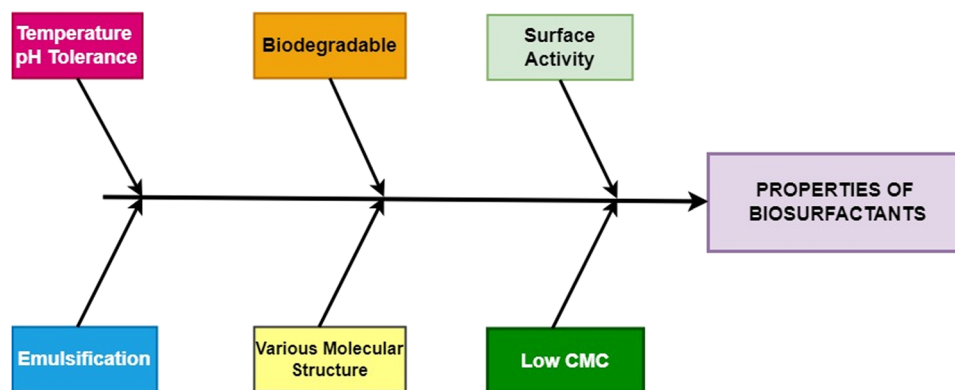


Figure 1: Properties of biosurfactants.

strategies. Future efforts may focus on scaling up biosurfactant production processes, conducting large-scale corrosion testing, and collaborating with industry partners to bring these innovative inhibitors to market.

2 Types of biosurfactants

Due to their high efficiency and biodegradability, biosurfactants have been used as effective corrosion inhibitors for metals. According to the hydrophilic and hydrophobic ends, surfactants are classified into anionic, cationic, and amphoteric surfactants [21]. Biosurfactants are usually classified by their microbial origin, polarity, and chemical composition, as represented in Figure 2. The microbial origin of biosurfactants can be glycolipids, lipoproteins and lipopeptides, surfactants, lichensysin, fatty acids, and phospholipids [22]. Biosurfactants contain hydrophobic and hydrophilic parts. The hydrophobic part is composed of a functional group of carbohydrates and amino acids, while the hydrophilic part typically contains long-chain fatty acids. The biosurfactants obtained from various microorganisms are listed in Table 1.

2.1 Glycolipids

Glycolipids are compounds that contain fatty acids and carbohydrate moieties. They correspond to the group of compounds based on the nature of lipids and carbohydrate

components [23]. According to the nature of lipids, they are categorized as rhamnolipids (RH), trehalose lipids, and sophorose lipids. They contain a hydrophobic lipid tail and one or more hydrophilic sugar groups linked by a glycosidic bond. The main structure of the glycolipids consists of a mono- or oligosaccharide group attached to a sphingolipid or glycerol group with one or two fatty acids. They are commonly found in Gram-positive microorganisms. Glycolipids are compounds containing fatty acids and carbohydrate moieties. They correspond to the group of compounds based on the nature of lipids and carbohydrate moieties [23]. Based on the nature of lipids, they are categorized as RHs, trehalose lipids, and sophorose lipids.

The other groups of compounds, like RHs, are derived from *Pseudomonas aeruginosa* and trehalose lipids and are found in various Gram-positive bacteria belonging to the mycolates group [24]. The sophorose lipids are derived from non-pathogenic yeast [25].

2.2 Lipopeptides and lipoproteins

Lipopeptides contain linear or cyclic oligopeptides acylated with fatty acids. They are commonly synthesized from *Bacillus* and *Pseudomonas* [26]. They are fatty acids linked to a peptide chain with a hydrophilic head and are linked to the lactone ring in the case of cyclic peptides. As lipopeptides are highly stable, biodegradable, and non-toxic, they play a vital role in various fields like cosmetics, healthcare, biomedical, pharmaceutical, and food industries [27].

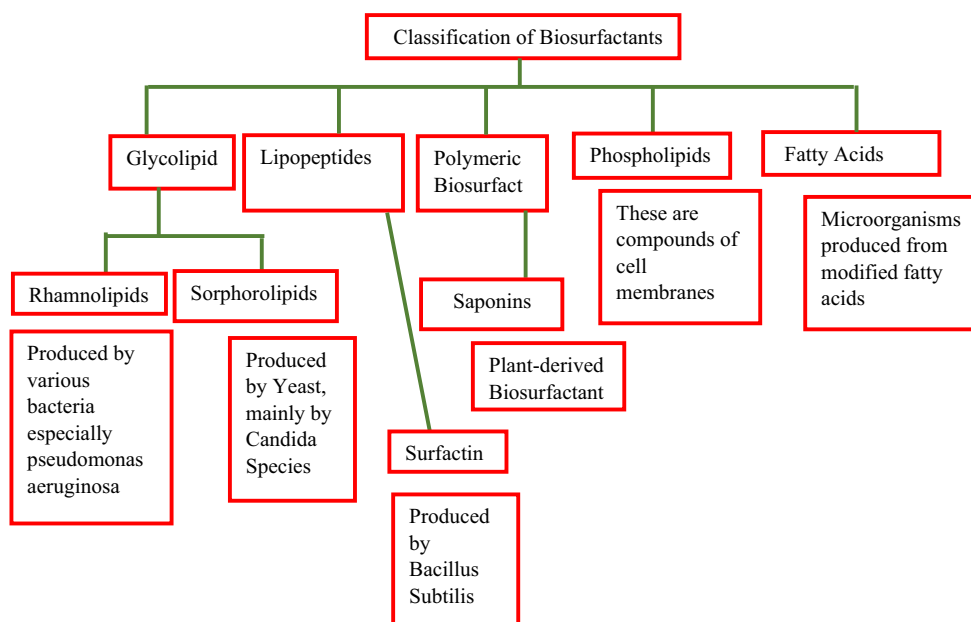


Figure 2: Classification of biosurfactants.

Table 1: Biosurfactants derived from microorganisms

Nature of biosurfactants	Class	Microorganism
Rhamnolipids, sophorolipids, trehalolipids	Glycolipid	<i>Pseudomonas aeruginosa</i> , other species of <i>Pseudomonas</i> [98], <i>Rhodococcus</i> sp., <i>Candida bombicola</i>
Surfactin	Lipopeptide	<i>Bacillus subtilis</i>
Viscosin	Lipoproteins	<i>Pseudomonas fluorescens</i>
Emulsan, lipomannan	Polymer	<i>Candida tropicalis</i> , <i>Acinetobacter radioresistens</i>
Arthrofactin	Polypeptide	<i>Arthrobacter</i> spp.

Lipoproteins are surface-active biosurfactants produced from *Bacillus subtilis*. They are complex particles that have a hydrophobic core at the centre of non-polar lipids. They are surrounded by a hydrophilic membrane surrounded by an amphipathic coat of protein, phospholipid, and cholesterol [28].

2.3 Surfactants

Surfactants are cyclic lipopeptides produced mainly by various strains of Gram-positive bacteria, specifically from the genus *B. subtilis*, and they are the most efficient biosurfactants used in various industries. The composition consists of hydroxy fatty acid and seven amino acid peptide rings [29]. These seven amino acids contain L-asparagine, glutamic acid, L-leucine, L-violin, and two D-leucines with a long hydrophobic fatty acid chain. Surfactants are found to possess many biomedical properties, including antiviral, anti-fungal, anti-mycoplasma, and anti-bacterial activities [30–32].

2.4 Lichensysin

Lichensysin is a highly effective anionic cyclic lipopeptide that is produced by *Bacillus licheniformis* using glucose as its main source. It produces several biosurfactants that act efficiently in the presence of some other biosurfactants, and they are very stable at higher temperatures and pH and under alkaline environments [33].

2.5 Fatty acids and phospholipids

Phospholipids contain hydrophobic fatty acid chains with hydrophilic moieties. In nature, phospholipids occur as several classes with different polar moieties. Because of their amphiphilic nature, they can be used as emulsifiers. The growth of n-alkanes results in the production of large

quantities of phospholipid fatty acid surfactants by several bacteria and yeast. The amphiphilic nature of these lipids depends on the length of the hydrocarbon chain in their structure [34].

3 Microbially induced corrosion or biocorrosion

Microbiologically influenced corrosion (MIC), or biocorrosion, is the term used to describe the degradation of materials, particularly metals, brought on by the actions of microorganisms [35]. Algae, bacteria, fungi, and other microorganisms all contribute to the acceleration of the corrosion process in biocorrosion. These microbes can cause corrosive byproducts or foster environments that are more conducive to corrosion [36]. These byproducts are frequently formed as a consequence of the microorganisms' metabolic processes. These microorganisms form a thin film on the surface of the metal, called biofilms, and these biofilms adhere to the metal surface, trapping the corrosive agents and leading to localized corrosion. Before looking into the process or mechanism of inhibition of corrosion by biosurfactants, we must identify how the corrosive byproducts are formed on the metal surface by microorganisms. The ways in which corrosive byproducts can be formed are explained as follows.

During the process of biocorrosion, a very low level of oxygen is present in the corrosive environment. At that time, microorganisms engage in anaerobic respiration, which in turn produces corrosive byproducts like organic acids and hydrogen sulphide. The main bacteria involved in the formation of biocorrosion are sulphate-reducing bacteria [37]. These sulphate-reducing bacteria metabolize sulphate present in the environment and produce hydrogen sulphide.

On surfaces, microorganisms have the ability to form biofilms, which produce an EPS-protective matrix. Corrosive agents can be trapped by this biofilm, which concentrates them against the material surface and encourages localized corrosion.

Some microorganisms produce organic acids as metabolic byproducts. By fostering an acidic environment, organic acids like formic or acetic acid can hasten the corrosion of metals.

On the metal surface, microorganisms might speed up electrochemical reactions. For instance, corrosive agents may be produced as a result of the microorganism and transfer electrons between microorganism and the metal surface [38]. Depending on the type of microorganisms and environmental conditions, the formation of corrosive byproducts may vary.

4 Corrosion inhibition mechanism of biosurfactants

Bio-corrosion caused by aerobic and anaerobic bacteria causes severe damage to different industries and services, and it is recognized as an important category of corrosion [39–41]. It is a complex interaction between metal surfaces and microorganisms that can induce corrosion. The degradation of metals can be accelerated by the corrosive byproducts that are produced by the metabolic activities of the microorganisms in the biofilm, such as hydrogen sulphide and organic acids [42]. Such microbially induced corrosion by microbes' forms biofilms that can be prevented by biosurfactants that are produced from some other microbes. Biosurfactants interact with biofilms and are greatly influenced by their structure and chemical properties; consequently, they disrupt the formation of biofilms via various mechanisms. These characteristics allow biosurfactants to function as agents that inhibit biofilm formation, adhesion, fouling, and corrosion.

These biosurfactants destroy the biofilms by disrupting their plasma membrane or cell wall. When the cell wall is disturbed, it is very difficult for the microorganism to combat the added biosurfactant [43,44]. Hence, the added biosurfactants attack the cell walls of corrosive bacterial cells and thus retard the movement of ions inside and outside of the bacteria, which leads to bacterial death. Thus, the lipid compounds are reported to effectively dissolve the biofilm and protect the metal surface from corrosion. Specific ways of disrupting biofilms by a few biosurfactants are shown in Figure 3.

Corrosion inhibition of metal surfaces involves complex mechanisms, and the extent of inhibition depends on the type of protective layers formed on the metal surface. The protective layers may be mono- or multidimensional. At the same time, the inhibitive nature may be attributed to the following factors: (i) interaction of inhibitor molecules on the metal surface, (ii) adsorption of the inhibitor molecules on the metal surface, (iii) chemical reactions, (iv)

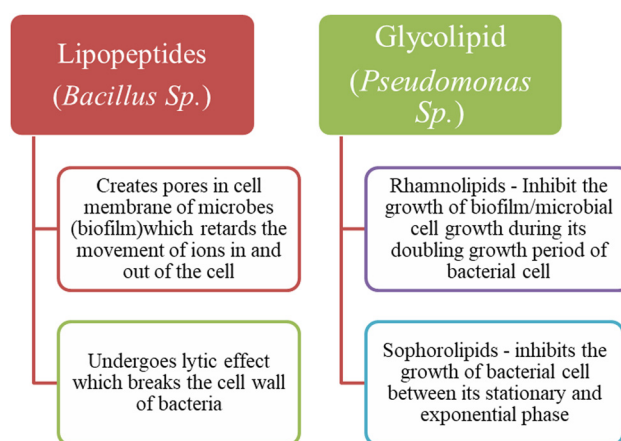


Figure 3: Action of lipopeptides and glycolipids on biofilms.

concentration of the inhibitors, (v) temperature, etc. Before discussing the mechanism of inhibition of metal surfaces by biosurfactants, we must perceive the complete structure of biosurfactants. As discussed in this review, the chemical constituents of biosurfactants can vary widely depending on the producing organism, which mainly constitutes glycolipids, lipopeptides, phospholipids, proteins, peptides, fatty acids, etc.

When these biosurfactant-containing functional groups like $>C=O$, $-OH$, $-NH$, $COOH$, and $-PO_4^{4-}$ are added to the corrosive medium containing metals, the hydrophilic head of the biosurfactant (particularly contains heteroatoms of O, N, P, etc.) strongly interacts with the metal ions found or biofilms found on the metal surface, like metal-ion-heteroatom chelation. The non-polar hydrophobic end, which is lying at the air-liquid interface, inhibits or does not allow any corrosive-producing substances near the metal surface. Thus, the biosurfactant molecules adsorb onto the metal surface and form a monolayer of protective film, which is termed surface aggregation. Also, these biosurfactants are good dispersing agents, which prevent biofilm formation as well as cause dispersal of the inhibiting molecules on the surface by scrambling the biofilm and making it soluble in the environment [45]. The functional groups present in the biosurfactants attack and inhibit several genes involved in the formation of biofilms.

When the concentration of biosurfactant increases, it tends to form a multilayer of protective film on the metal surface. In addition, the biosurfactant molecules accumulate or aggregate in a head-to-tail pattern and form a micelle. Metal surfaces are hydrophilic in nature, and consequently, the surfactant molecules are attracted to their surfaces. Thus, in turn, biosurfactants permeate and adsorb onto the interface, reducing the cohesion and thereby either preventing or promoting the attachment of biofilm-forming

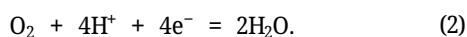
organisms. By creating a stable emulsion or protective layer on hydrophobic surfaces, biosurfactants can disrupt the bio-film due to their emulsifying and micelle-forming properties [46]. On the metal surface, they promote the development of a passivation layer that serves as a barrier between the metal and the corrosive environment, known as the passivation layer, and helps stop additional corrosion from occurring. Thus, it modifies the electrochemical reactions occurring on the metal surface and alters the kinetics of corrosion reactions by suppressing both anodic and cathodic reactions.

The hydrophilic and hydrophobic nature of biosurfactants enables them to interact with interfaces between the aqueous and non-aqueous phases of the corrosive medium. A simple mechanism of corrosion inhibition of metals by biosurfactants involves the following reactions, and the mechanism is shown in Figure 4.

An anodic reaction by which the metal is corroded is given by equation (1):



A cathodic reaction takes place as per equation (2):



The anions present in the corrosive media adsorb onto the metal surface, causing the metal to act as negatively

charged. Biosurfactants have the ability to form micelle and, in turn, emulsify the hydrophobic compounds. This property can be utilized to disperse or solubilize corrosion-inducing substances, preventing them from coming into contact with the metal surface.

Also, the heteroatoms present in the biosurfactants are assumed to protonate and produce cations. Now, the protonated biosurfactants were adsorbed on the negatively charged metal surfaces and formed a film, which acts as a protective layer.

The adsorption of biosurfactants in anodic locations occurs through heteroatoms, leading to delayed metal corrosion. Also, adsorption on the cathodic locations reduces the evolution of oxygen. Furthermore, ligand formation also occurs between heteroatoms of the biosurfactants and unoccupied d-orbital on the metal involved in the adsorption process and inhibits metal corrosion.

5 Corrosion protection of metals using various biosurfactants

Corrosion protection of metals depends on the specific type of biosurfactant, the metal being protected, and certain environmental factors. Ongoing research in this field

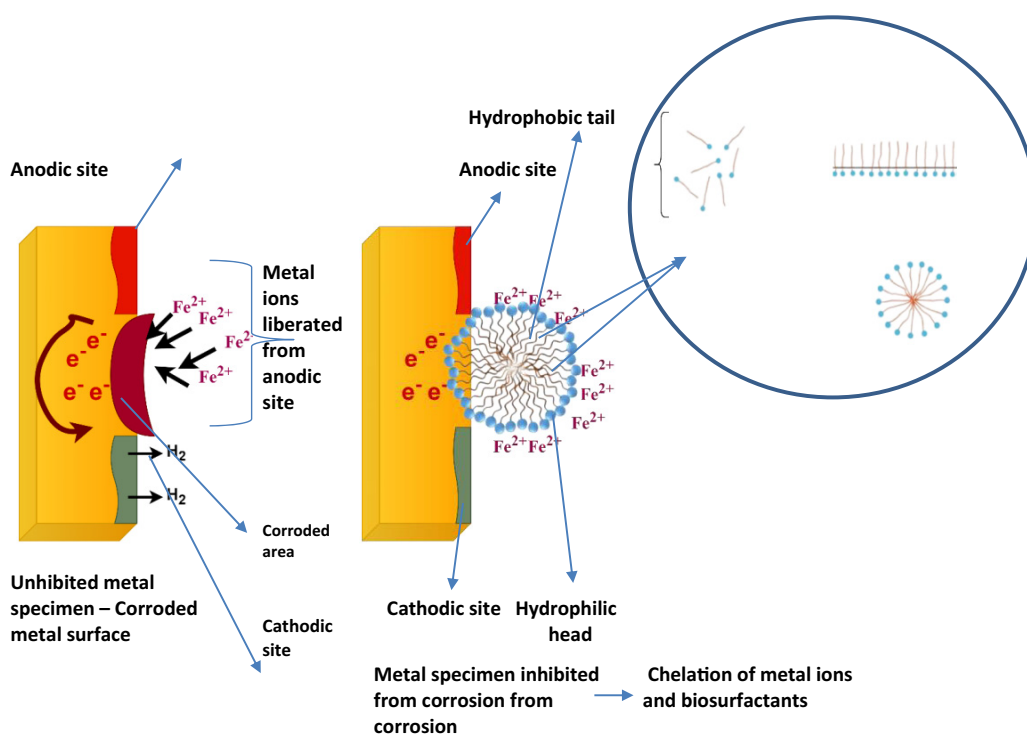


Figure 4: Mechanism of corrosion inhibition by biosurfactants.

continues to explore new ways to harness the potential of biosurfactants for corrosion control in various industrial applications.

5.1 Coco monoethanolamide (CMEA)

CMEA was investigated as a corrosion inhibitor for the protection of mild steel using 1 M HCl [47]. The inhibition efficiency of CMEA at 0.6163 mM and 60°C was found to be 99.01%. It performs as a mixed-type inhibitor, and its adsorption at the metal–acid interface follows the Langmuir isotherm. Theoretical findings from density functional theory, Monte Carlo, and molecular dynamics simulations were used to demonstrate their experimental results, and the potentiodynamic polarization studies revealed that the Tafel slopes at different inhibitor concentrations follow the same trend with reduced corrosion current density (j_{corr}). The inhibition was mainly cathodic and inhibited the hydrogen evolution reaction, as evidenced by the shift towards the cathodic direction. This shows that solution resistance was greater for the solution containing inhibitor, and corrosion resistance was also increased when the inhibitor dosage increased, which shows that the inhibitors form a protective layer on the surface of the metal. Further, they suggest that CMEA develops a defensive layer on the surface of the metal through a physiochemisorption mode. The functional groups like $>\text{C}=\text{O}$, $-\text{OH}$, and $>\text{NH}$ present in the CMEA get protonated in an acidic solution and form cationic molecules in the medium, as well as the counter ions (anions) induce the metallic surface to behave as negative. Thus, the cations formed by CMEA and anions on the metal surface form a defending layer on the metal surface. They reported that the CMEA bio-surfactant can act as a potent inhibitor for mild steel.

5.2 Asparagine and arginine

The two biosurfactants, viz. sodium *N*-dodecyl asparagine, and sodium *N*-dodecyl arginine, were employed as green corrosion inhibitors on the dissolution of mild steel (MS37-2) in aqueous sodium chloride solutions [48]. Electrochemical impedance measurements showed that sodium *N*-dodecyl asparagine and sodium *N*-dodecyl arginine surfactants were effective in inhibiting MS37-2 corrosion in NaCl solution. The polarization measurements revealed that the biosurfactants added to the sodium chloride solution altered both the anodic and cathodic branches of the polarization curves towards lower current densities. The anodic and cathodic reactions were slowed down, preventing corrosion on MS-37-2.

Electrochemical impedance studies showed that the increase in corrosion resistance and decrease in the double-layer capacitance was due to the continuous replacement of the water molecule by the adsorption of the biosurfactants, which reduces the interfacial tension and forms a protective film on the surface of MS-37-2. The study concluded that the inhibition efficiency depends on the concentration, nature, and type of the surfactant. With increasing the concentration of biosurfactants, the interfacial tension on the metal surface is minimized, thus protecting it from corrosion. The microbial-influenced corrosion by the *Pseudomonas* species on carbon steel ST37 was investigated using biosurfactants derived from the *Bacillus* species [49]. They determined the least inhibitory concentration and minimum biofilm inhibitory concentration using the broth microdilution technique, and the corrosion of carbon steel was determined by weight loss measurements. The corrosion rates were determined by antibiofilm assays and they revealed that the biofilm on the metal surface formed by aerobic microorganism *Pseudomonas* species induces the corrosion by utilizing the oxygen present in the biofilm and results in the formation of anodic sites on the surface. A thin layer of biofilm was found on carbon steel treated with a biosurfactant, and a few bacteria cells were attached to the surface of the layer. Thus, the added biosurfactant eradicated the biofilm and reduced the microbial corrosion of carbon steel.

5.3 RH (*Pseudomonas* species)

The corrosion inhibition of aluminium alloy in acidic rainwater by RH biosurfactant was investigated [50]. They synthesized RH biosurfactants from the strains of *Pseudomonas* species and carried out the corrosion test in Aluminium alloy D16T A by electrochemical studies at room temperature. They showed that the aluminium alloy in acidic rainwater was protected when it was immersed in the RH biosurfactant. After 3 h of exposure to acid rain and the addition of biosurfactants at concentrations of 0.1, 0.25, and 0.5 g L⁻¹, the impedance magnitude increases by 0.1 Hz. A similar effect was also observed after 24 h exposure to the metal alloy with a biosurfactant in rainwater. The increase in impedance magnitude represents the formation of a barrier film on the aluminium surface by the biosurfactants. As RHs contain hydroxyl, carboxyl, and carbonyl functional groups, they exist as carboxylate anions in the solution. These anions are bonded to the outer regions of the oxide film through the physical mode of adsorption. In addition, the added RHs form a low soluble complex with the aluminium alloys and are deposited at the anodic sites. They concluded that environmentally safe

corrosion inhibitors could be synthesized for aluminium alloy corrosion by using sustainable surfactants.

5.4 Glycolipid (*Pseudomonas mosselii* F01)

Parthipan *et al.* investigated the microbial corrosion inhibition using the glycolipid biosurfactant against bacterial strains of *Streptomyces parvus* B7, *B. subtilis* A1, *Acinetobacter baumannii* MN3, and *Pseudomonas stutzeri* NA3 on carbon steel. The glycolipid-based biosurfactant was synthesized from *Pseudomonas mosselii* F01 [51]. The rate of corrosion was monitored using weight loss and electrochemical studies. They reported 87% corrosion inhibition using weight loss, decreased corrosion current and potential, and high resistance capacity. The highest level of corrosion inhibition was due to the high energy interaction between the added glycolipid and carbon steel. They proved that glycolipid-based biosurfactants can act both as corrosion inhibitors and biocide. The reason for inhibition was explained by the mechanism of inhibition, as biosurfactants possess anti-bacterial activity: the active microbes present in the biosurfactant absorb onto the corrosive bacterial cell and restrict the biological reaction to take place. It was also attributed to the fact that biosurfactant molecules' adsorption on the metal surface is that their interaction energy with the metal surface is higher than that of water molecules with the metal surface. Metals in different corrosive environments protected by several microorganisms are provided in Table 2.

5.5 *Marino bacter salsuginis*

The *Bacillus marine bacteria*, *Marino bacter salsuginis*, was employed to study the corrosion behaviour of X80 pipeline steel in marine environments [52]. Electrochemical impedance spectroscopy and polarization studies were carried

out for the corrosion monitoring process. Due to the formation of the biofilm, the pipeline steel has higher polarization resistance, charge transfer resistance, and reduced corrosion current density. *Bacillus subtilis* and *Bacillus licheniformis* were employed as pitting corrosion inhibitors for aluminium 2024 by electrochemical impedance spectroscopy [53]. They reported that the secretion of 20 amino acids reduced the corrosion rate of the aluminium alloy at pH 6.5. They found that many uniform pits were found on the surface of the alloy in the uninhibited medium, whereas reduced pits in the presence of microorganisms due to the formation of biofilm and the capacitive nature of the impedance spectra were observed using electron microscopes. The presence of carboxylic acid groups decreases the corrosion rates due to the production of polyaspartate and γ -polyglutamate by *B. licheniformis*.

5.6 RH (*P. aeruginosa*)

The mechanism of inhibition was explained by the chelation of aluminium ions and carboxylic acid through Coulombic interaction, hydrogen bonds, and dipole-dipole interaction. RH produced by *P. aeruginosa* was investigated as an effective corrosion inhibitor for X70 carbon steel in seawater [54]. According to the weight loss measurements, they reported that the corrosion rate of carbon steel decreased from 18 to 0.05 mm/year with the addition of 0.1% (m/V). The increase in inhibition rate was attributed to the interaction of hydroxide molecules of RH on the metal surface.

5.7 RH

The corrosion protection efficiency of RH was studied on X65 carbon steel in CO₂-Saturated Oilfield-Produced Water [55] using the gravimetric method and electrochemical

Table 2: List of metals protected by various biosurfactant

Microorganism/biosurfactant	Metal	Medium
CMEA biosurfactant [41]	Mild steel	1 M HCl
N-Dodecyl arginine, asparagine [48]	Mild steel (MS 37-2)	Aqueous NaCl solution
Biosurfactant from <i>Bacillus</i> sp. [49]	Carbon steel ST-37	Oil
Glycolipid from, <i>Streptomyces parvus</i> B7, <i>Bacillus subtilis</i> A1, <i>Pseudomonas stutzeri</i> NA3, and <i>Acinetobacter baumannii</i> MN3 [70]	Carbon steel	Acid medium
Marine bacteria from <i>Marinobacter salsuginis</i> [47]	X80 pipeline steel	Alkaline medium
<i>Bacillus subtilis</i> and <i>Bacillus licheniformis</i>	Aluminium	Neutral
RH produced by <i>Pseudomonas aeruginosa</i> [53]	X70 carbon steel	Sea water
Rhamnolipid [54]	X65 carbon steel	CO ₂ -saturated oilfield
Phospholipids [55]	Carbon steel	15% hydrochloric acid

measurements. They found an inhibition effect of 90% on increasing the concentration of biosurfactant. From the polarization bipolar branch curves, the cathodic and anodic branches represent only one reaction process but predominate along the anodic side. They also reported that the addition of RHs decreased the corrosion current density, and they act as a mixed type of inhibitor by forming a thick protective layer on the surface of the metal. The interaction of the RHs and metal surface occurs between the rhamnopyranose ring and C=O groups and the vacant d orbitals of carbon steel.

RHs extracted from *P. aeruginosa* were used against corrosive strains of *B. subtilis* A1, *S. parvus* B7, *P. stutzeri* NA3, and *A. baumannii* MN3 on concrete rebars in 0.5 N NaCl using electrochemical studies [51]. According to their report, the biosurfactant system included in mixed consortia demonstrated an inhibition efficiency of approximately 87% in the presence of naturally occurring corrosive bacterial consortia. Also, the XRD and experiments on weight loss and electrochemical analysis validate the function of biosurfactants in the corrosion inhibition process and the biosurfactant's efficacy as a microbial corrosion inhibitor. The electrochemical studies reported that a good corrosion inhibitory effect was observed for carbon steel, which contains RHs and increased corrosion current and charge transfer resistance. Further, the interaction of RHs onto the metal surface was confirmed by the formation of a protective layer with the help of microscopic studies.

Zin et al. [56] investigated the corrosion inhibition efficiency of aluminium alloy by RH bio-complex synthesized from *Pseudomonas* sp. PS-17 strain using Tafel plots. It was found that the aluminium alloy in the presence of RH showed a pattern of frequency dependence phase angle, which indicates the possible formation of a barrier film on the surface of the metals. Finally, they concluded that an increase in the rate of re-passivation of the aluminium alloy on newly formed surfaces indicates that the RH bio-complex can act as an effective corrosion inhibitor.

5.8 Phospholipids

Phospholipids extracted from vegetable oil waste were used to prevent corrosion on the carbon steel surface in 15% hydrochloric acid. Various chemical surfactants like acetone C.70 (C12-C14 alkyltrimethylammonium chloride), cationic SAA, catapav (C16-C18 alkyl dimethylbenzylammonium chloride, cationic surfactant), oxypav (tertiary amine oxides, nonionic surfactant), CP-20 (condensation products of mono- and dialkylphenols with ethylene oxide, nonionic

surfactant), and oleylamidopropyl dimethylamine (a mixture of zwitterionic surfactant, oleylamidopropyl dimethylamine, and sodium chloride) were added as additives with the phospholipids [57]. The corrosion rate was determined using a weight loss method, and its electrochemical corrosion rate was estimated based on the corrosion current density. They reported that phospholipids were found to possess 86.5% inhibition efficiency. The combined use of surfactants and phospholipids tends to show a synergistic effect on the corrosion inhibition efficiency. Phospholipids, when combined with surfactants, tend to show a high level of corrosion protection, up to 95%.

5.9 *Penicillium citrinum* and *Trichoderma*

The biosurfactant produced from *P. citrinum* and *Trichoderma*, which were isolated from municipal dumpsite, was used as a corrosion inhibitor for mild steel bar in NaCl solution [58]. Corrosion inhibition efficiency was tested using weight loss measurements at different concentrations of the fungi. Mild steel bars were immersed in different concentrations (v/v) of 5, 7.5, and 10% of inhibitors for immersion times of 14, 28, and 100 days. To compare its efficiency, parallelly, Tween 80, a non-organic surfactant, was also used to study the corrosion inhibition property of the mild steel bar in NaCl solution. It was found that the biosurfactant with 10% concentration showed the highest inhibition efficiency of 58.01%, and also, the biosurfactant of *Penicillium citrinum* was found to be more effective in corrosion protection than the *Trichoderma* and non-organic surfactant. In addition, they reported that when mild steel bars were immersed in the corrosive media with and without inhibitors, the colour of the solution changed from clear to brownish, and some sludge formation was observed. However, the solution containing biosurfactants does not produce sludge and does not contain any colour. According to the study, biosurfactants not only prevent corrosion but are also used for the bioremediation process [59].

5.10 *Pseudomonas fluorescens*

The corrosion behaviour of AISI 304 stainless steel was investigated using Gram-negative bacteria *Pseudomonas fluorescens* in NaCl medium by electrochemical studies [60]. Hiemenz and Rajagopalan determined the surface activity and critical micelle dilution by surface tension measurements using the Wilhelmy plate method [61]. According to them, when the samples are immersed in biosurfactants, the formed

oxide layer on the steel surface is more compact, which decreases the density of pits to a higher anodic/cathodic surface area. When the corrosive medium is too aggressive, the corrosion will increase at a faster rate; the formed oxide layer does not nucleate before the biosurfactant gets adsorbed on the metal surface. Hence, they concluded that for better protection efficiency, the surface of the metal must be pre-passivated before the biosurfactant addition.

5.11 *Bacillus* sp.

Biosurfactant produced by indigenous oil reservoir bacteria *Bacillus* sp. was aimed to determine the corrosion caused by *Pseudomonas* sp. 1 and *Pseudomonas* sp. 2 on Carbon Steel ST37 using the weight loss method [62]. The authors used 15% of glutaraldehyde as a positive control. They revealed that biosurfactant decreased the corrosion rates due to the formation of biofilms, which reduces the microbial-induced corrosion, and the added *Bacillus* Sp. as an inhibitor able to inhibit the film formation of *Pseudomonas* sp. 1 and *Pseudomonas* sp. 2. The intervention effects given by their studies are summarized as follows:

- Minimum inhibitory concentration of the biosurfactant: $62.5 \mu\text{g ml}^{-1}$
- Minimum biofilm inhibitory concentration (MBIC) of the biosurfactant: $31.25 \mu\text{g ml}^{-1}$
- Minimum biofilm eradication concentration for 50% eradication (MBEC50) of the biosurfactant: $500 \mu\text{g ml}^{-1}$
- Biosurfactant is able to inhibit the attachment of *Pseudomonas* sp. 1 and *Pseudomonas* sp. 2 to Carbon Steel ST37 surface
- Biosurfactant is able to eradicate the preformed biofilm on the steel surface
- Reduction of corrosion rate in Carbon Steel ST37: from 4.56×10^{-4} to $3.31 \times 10^{-4} \text{ mm year}^{-1}$ based on the MBIC value and from $5.18 \times 10^{-5} \text{ mm year}^{-1}$ to 2.7×10^{-5} after biofilm eradication at the MBEC value.

The mechanism of inhibition was explained as follows: the biosurfactant prevented certain bacteria from adhering to the steel surface and removed the existing biofilm, which lowered the rate at which Carbon Steel ST37 corroded. This type of biosurfactant can be used as a good anti-corrosion agent in the oil industry.

5.12 Bio-MOF-1

Feng et al. [63] encapsulated benzimidazole in the micropores of bio-MOF-1 and investigated its anti-corrosion durability on

mild steel using electrochemical studies. As benzimidazole has hetero atoms with lone pair of electrons, both benzimidazole and bio-MOF-1 showed synergistic corrosion protection. They reported that the impedance arc value decreased when the immersion time increased and showed the highest inhibition efficiency of 85.36% recorded for the encapsulated inhibitor.

5.13 Surfactins and quorum quenching lactonase

MIC on steel coupons was investigated by Huang et al. using some biologically active compounds, such as surfactin, capsaicin, gramicidin, and an enzyme quorum quenching lactonase [64]. They evaluated the effectiveness of different coating additives in reducing the formation of corrosion tubercles on steel surfaces. They found that the coating additives, surfactin and the quorum quenching lactonase, significantly reduced the formation of corrosion tubercles by 31, 36, and 50%, respectively. They demonstrated the potential of highly stable quorum quenching lactonases to provide a reliable, cost-effective method to treat steel structures and prevent biocorrosion. The main intervention effects given by them are summarized as follows: surfactin: reduced the number and coverage of tubercles on steel coupon surfaces by 31 and 37%, respectively. Quorum quenching lactonase reduced the formation of corrosion tubercles by 50%. Bacterial community composition: significant differences were observed in the bacterial communities on experimental and control coupons for all treatments ($p < 0.05$). The mechanism of inhibition was attributed to the use of a silica gel matrix to encapsulate anti-corrosion biochemicals and enzymes, allowing their activity to last for several months, even after all cells were dead. The enzymatic activity of the silica gel coating, including the lactonase enzyme, was greatly reduced after 42 days of exposure to water. The decrease in the observed corrosion compared to the silica gel coating control was statistically significant for surfactin and the lactonase enzyme. These findings suggest that the encapsulated additives, particularly the lactonase enzyme, play a role in inhibiting corrosion on steel surfaces.

5.14 *Pseudomonas fragi*

The corrosion inhibition effect of some aerobic bacterium *Pseudomonas fragi*, facultative anaerobe *Escherichia coli* DH5a on SAE 1018 carbon steel was investigated by

Jayaraman et al. [65]. They reported that the presence of *P. fragi* or *E. coli* DH5a resulted in 2- to 10-fold lower mass loss compared to sterile controls. Increasing the temperature from 23 to 30°C resulted in a 2- to 5-fold decrease in corrosion inhibition with *P. fragi*, whereas the same shift in temperature resulted in a 2-fold increase in corrosion inhibition with *E. coli* DH5a. Also, in a few steel coupons, corrosion observed with non-biofilm-forming *S. lividans* TK24 was observed. The mechanism of inhibition was explained as follows: the live cells produce a protective biofilm that inhibits corrosion, resulting in a significant reduction in mass loss when compared to sterile controls. The biofilm, which is made up of both living and dead cells, is embedded in a sparse glycocalyx matrix and is essential for inhibiting corrosion.

6 Other applications of biosurfactants in various industries

6.1 Bioremediation

Bioremediation is a process that uses living organisms to remove or neutralize pollutants from a contaminated environment. Biosurfactants, which are surface-active compounds produced by microorganisms, play a crucial role in enhancing bioremediation and biodeterioration efforts [66–68]. Pollutants such as air, soil, and water are universally present in the environment. Many researchers reported the carcinogenic effects of organic pollutants on human health [69,70]. The microbial species take up an efficient role in the eradication of pollution and are involved in the formation of intermediate compounds like glycolipids. These glycolipids play an active role in the bioremediation of pollutants [71–73].

It was reported that biosurfactants play a crucial role in dispersing hydrocarbons in the medium [74]. *Pseudomonas* species produce RH with very low surface tension and alter their cell wall. Man-made activities like manufacturing, mining, and usage of electronic devices have led to the liberation of metals like Ba, Cd, Hg, Ni, Pb, and Sr in the environment [75]. These toxic metals become a major contaminant when it is mixed with water and soil. The contaminated soil sites may be converted into landfill sites in the future. In such cases, this may cause a severe impact on the environment and affect the food chain.

Recently, biosurfactants were employed to remove these pollutants from the environment in order to resolve

this issue [77]. When the biosurfactants are added to the environment, they interact with the pollutants through any one of the possible reactions like electrostatic interaction, ion exchange, counter-ion binding, or precipitation dissolution [78]. The added biosurfactants chelate with the metal ion surface and form a micelle [79]. This micelle helps to remove the metals from the contaminated environment [80].

Cadmium metal was removed from the environment by an RH-based biosurfactant [81], and it was found that it was very effective in the removal of cadmium by forming a complex between cadmium(II) and the added RH, thus reducing its toxicity. Similarly, strontium was removed by adding very low concentration (80 ppm) of RH [82]. It was reported that the biosurfactant lipopeptide was synthesized from *C. lipolytica* and was employed to remove Cu and Zn. The study found that the added lipopeptide exhibited 96% efficiency in the removal of metals [83]. Singh et al. also found that lipopeptides were also effective in reducing heavy metals like Cd, Fe, and Pb [84].

6.2 Pharmaceutical industries

The various functional groups of biosurfactants confer them to possess many potential applications in various fields. The hydrophilic and hydrophobic nature of biosurfactants is supposed to act like detergents on the cell walls of many bacteria and fungi and tend to possess antimicrobial activity [85]. Several biosurfactants have strong antibacterial, antifungal, and antiviral activity.

Das et al. reported that the biosurfactants extracted from marine *Bacillus circulans* exhibit excellent antimicrobial activity against Gram-positive and Gram-negative pathogens [86]. Fernandes et al. [87] investigated the antimicrobial properties of *Bacillus subtilis* R14 against various bacterial strains. They reported that lipopeptides were very effective against the bacterial strains. Also, it was reported that the biosurfactants were found to control the adhesion of microorganisms on the infected sites of the wound [88]. Thus, the biosurfactants were employed on the wounded surface before the application of medicine in order to prevent the colonization or grouping of microorganisms (Rivardo et al., [89]).

6.3 Nanoparticle synthesis

Nanotechnology is a wide area and attracts the attention of many researchers as it converts matter into the near-

atomic scale to produce new structures. It provides many scientific advancements in various fields, such as energy, materials, electronics, coatings, cosmetics, manufacturing, and many other daily activities. Nanomaterials synthesized through nanotechnology are unique due to their physical, chemical, and mechanical properties. Many researchers are focusing on the synthesis of the nanomaterial through various methods, like chemical reduction, co-precipitation, hydrothermal, sol-gel, and micro-emulsion. These methods involve high temperature, pressure, and energy during the synthesis, and they also generate many biologically toxic byproducts as they pollute the environment [90]. Moreover, it faces a main disadvantage of the use of chemicals and self-agglomeration in aqueous solutions [91]. Hence, the bio-fabrication of nanomaterial is a more sustainable, cheap, and eco-friendly method. Biosynthesis of nanoparticles involves the usage of natural plant extracts, polysaccharides, gum exudates, algae, fungi, yeast, etc. [92–94]. More recently, researchers have focused on the synthesis of nanomaterials using biosurfactants as they reduce environmental impacts, reduce waste, and improve the stabilization of nanomaterials using sustainable substrates [95]. Biosurfactants are surface-active compounds that possess both hydrophilic and hydrophobic properties. They are also called surface-active biomolecules, which are mainly synthesized from microorganisms, and they tend to show exceptional properties like low toxicity, specificity, and relative ease of synthesis [96]. Also, when compared with chemical surfactants, biosurfactants have several advantages, such as environmental cleaning by biodegradation and depollution of industrial effluents [97–99].

Silver nanoparticles were synthesized using a biosurfactant produced by *Bacillus cereus* UCP [100]. The synthesized nanoparticles were characterized using UV-VIs spectroscopy, scanning electron microscopy, and zeta potential methods. The study reported that the average size of their obtained nanoparticles was 20 nm. And it was found that the synthesized nanoparticles were found to possess 85% inhibition against *P. fellutanum* and *A. niger*.

Nickel oxide nanorods were synthesized using commercial RH as a stabilizer. The synthesized nanorods were found to possess a size of 22 nm in diameter [101]. Silver nanoparticles were characterized by UV-vis absorption spectroscopy. The morphology was found to be spherical by TEM and SEM.

Water-soluble RHs from *P. aeruginosa* were employed to synthesize ZnS spherical nanoparticles [102]. They obtained the nanoparticle in the size of 4.5 nm.

Polyaniline nanofibres and nanotubes were synthesized using RHs [103]. They reported that when comparing the synthesis of PAN with other additives, the PAN synthesized using RH showed uniform morphology and size.

7 Conclusions

For the past few years, biosurfactants have attracted many researchers as it possesses many versatile amphiphilic properties. These amphiphilic compounds are good anti-bacterial and anti-biofilm agents against various microbial organisms, which induce biocorrosion in different industries. Even though various biosurfactants were studied for their anti-corrosion properties, the most studied are RHs and lipopeptides, as they possess well-characterized structures. Their distinct qualities – such as their surface activity, biodegradability, and variety of molecular structures – are desirable options for applications involving corrosion prevention. Because of their biodegradability and eco-friendly nature, biosurfactants are a greener option for corrosion inhibitors than conventional ones. This quality is particularly important in industries where corrosion and environmental considerations are among the paramount problems, aligning with the growing emphasis on sustainable practices. Much interest in employing these eco-friendly sustainable compounds in the prevention of the formation of biofilms or fouls on the metal surface and corrosion protection on metals is less studied, and very few works have been reported. Even though there is a good sign in the progress of understanding the mechanism of corrosion by biosurfactants, their production costs, scalability, and optimization for specific applications remain challenging and are left for future research purposes. Ongoing research is essential to address these challenges, explore new biosurfactant formulations, and optimize their performance under various conditions. Hence, biosurfactants are emerging as important materials that have the potential to completely change the corrosion landscape as industries look for long-term, cost-effective solutions for corrosion control.

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