A review on the role of eco-friendly inhibitors for mitigation of microbial influenced corrosion of steel and its impacts

Shiv Kumar Manu\textsuperscript{1}, R Manivannan\textsuperscript{2}
\textsuperscript{1,2}Department of Chemical Engineering, National Institute of Technology Raipur, Chhattisgarh 492010, India

E-mail: \textsuperscript{1}shivkumarmunu@gmail.com, \textsuperscript{2}rmani.che@nitrr.ac.in

Abstract. Microbially induced corrosion (MIC) is a localized corrosion caused due to the presence of micro-organism. Such micro-organisms found in oil wells are responsible for localized changes in the aqueous atmosphere (e.g., modify the composition of electrolytes, materials, pH and oxygen level). Conventionally, inorganic corrosion inhibitors were used to deter the microbial corrosion. However, ecological toxicity of inorganic corrosion inhibitors has sparked the hunt for eco-friendly inhibitors because they are biologically degradable, absence of toxic elements. Plant goods are affordable, readily available and can be recycled, as well as being environmentally friendly and socially appropriate. There is an intense initiative underway to use corrosion inhibitors of plant origin for metals that are susceptible to different environmental conditions. Both efforts were inspired by a need to replace the chemical additives used in aqueous solutions to reduce the deterioration of metals and various alloys. Plants constitute a type of fascinating compound source currently being investigated for use in the safety of metal corrosion in most structures and as a potential substitute for toxic synthetic inhibitors. Research results on the use of eco-friendly phytochemicals as inhibitors of microbiologically influenced corrosion are summarized in this review article. A general introduction to the subject of inhibitor for biocorrosion mitigation is addressed accompanied by comprehensive literature review on the use of natural inhibitors in aerobic or anaerobic condition of management for corrosion of steel metals and various alloys in biotic corrosive media.

Keywords: Microbially influenced corrosion, micro-organism, sulfate reducing bacteria, Desulfovibrio desulfuricans, electrochemical polarization, scanning electron microscopy, stainless steel

1. Introduction

Corrosion is a process that occurs on the metal surfaces induced by the environment of the surrounding environment (moisture, air, soil) \cite{1}. Corrosion can inflict catastrophic damage to components of metal and alloy having economic effects in terms of restoration, reconstruction, product degradation, health and environmental contamination. Owing to these adverse effects, corrosion is an unnecessary tendency that can be avoided. Corrosion in subsea injection, storage, and well-fluid pipes may often occur under-deposit. In addition to the presence of mineral deposits, microorganisms are commonly found in pipeline integrity management systems which aggravate the problems. In real-life situations, abiotic mechanisms are difficult to be encountered due to the pervasive existence of the micro-organisms where any of them have the potential to deteriorate the metal because of their involvement or activity contributing to microbiologically influenced corrosion (MIC).

The metabolic activity of microorganisms in MIC corrosion processes results in the degradation of a metal directly or indirectly. It is believed that anaerobic sulfate reducing bacteria (SRB) is the major source of microbiological corrosion degradation and corrosion research has thus been the primary
focus. Nonetheless, it is now recognised that obligate anaerobic (Desulfovibrio sp.) species are just as important anaerobic organisms are the most corrosively damaging mixed bacterial populations in a biofilm. Obligate anaerobes do not undergo oxidative phosphorylation. In fact, they are destroyed by oxygen, lose enzymes like catalase, peroxidase, and superoxide dismutase.

Based on the oxygen requirements, bacteria can be categorized into different groups, which is schematically shown in Fig. 1 [2].

1. **Aerobes**: Bacteria grow in ambient air containing oxygen (~21%) and a minimal amount of carbon dioxide (~0.03%).
2. **Obligate aerobes**: Require absolute oxygen for growing. (Pseudomonas aeruginosa, Mycobacterium tuberculosis, Bacillus subtilis and Acidithiobacillus ferrooxidans).
3. **Obligate anaerobes**: are the bacteria which thrive under high reduction intensity conditions and oxygen is poisonous for such bacteria. (Clostridium perfringens, Bacteroides, Clostridium botulinum).
4. **Facultative anaerobes**: are skillful of growing in both anaerobic and aerobic environments. (Enterobacteriaceae group, Staphylococcus aureus, E. coli, S. aureus).
5. **Aerotolerant anaerobes**: are the bacteria which has the capacity to protect from the reactive oxygen molecules.

![Fig. 1: Schematic showing the various types of bacteria [2, 3].](image)

The main types of microorganisms linked to metal corrosion failures are:

1. Sulfate reducing bacteria
2. Metal-oxidizing bacteria
3. Sulfur oxidizing bacteria
4. Fungi, Micro-algae

Sulfate-reducing bacteria (SRB) are usually 3 to 10 micron sized single-celled species. These bacteria require an anaerobic atmosphere and might thrive in soil and potable water and in almost every circumstance that includes water and nutrients traces Desulfovibrio and Desulfotomaculum genera are gram-negative (do not retain the gram stain color). The former is usually mesophilic (live at moderate temperature) and can be halophilic (salt-lover), while the later genus species (Desulfotomaculum nigrificans) is either mesophilic or thermophilic(live at higher temperature)[4]. Desulfovibrio's most recognized species do not survive at temperatures above 48°C, and are thus mesophilic. Widdel and Pfennig [5] identified some new genera of SRB such as Desulfobacter postgatei and Desulfotomaculum acetoxidans which can use acetate for their growth [6]. The Desulfovibrio species
are the most commonly encountered sulfate-reducing bacteria which are particular interest to the field technician in the oil field.

Anaerobic SRB may live in the presence of oxygen (O\textsubscript{2}) for a significant amount of time [7] before they are trapped in a substrate and can be exceptionally small where the anaerobic states are present, such as in crevices, small holes, and indoor tuber. Some SRB strains can accept exposure to oxygen (Desulfovibrio vulgaris and Desulfovibrio desulfuricans). Growth was not happened when oxygen is used as the terminal electron acceptor [8-9]. While SRB is sometimes called strict anaerobic, in the presence of air other genera of Desulfovibrio can conduct oxidative phosphorylation by using oxygen as the acceptor of the terminal electron [10]. In the anaerobic respirations, sulfur compounds elimination is significant as it yields hydrogen sulfide (H\textsubscript{2}S) product, widely regarded as a poisonous chemicals with a distinctive odour. H\textsubscript{2}S has a profound effect on the chemistry of the atmosphere by its chemical reactivity. Table 1 shows the characteristics of some bacterial species which is responsible for bio-corrosion in metal.

**Table 1. List of bacterial species causing microbial influenced corrosion.**

| Bacteria                      | Physical appearance       | Cell wall              | References |
|-------------------------------|---------------------------|------------------------|------------|
| Desulfovibrio desulfuricans   | Vibrio                    | Gram negative bacteria | [11]       |
| Desulfovibrio vulgaris        |                           |                        |            |
| Desulfovibrio bearsil         |                           |                        |            |
| Desulfovibrio thermophilis     | Rod                       |                        |            |
| Desulfovibrio baculatus       |                           |                        |            |
| Desulfovibrio africanus       | Spirillum                 |                        |            |
| Desulfovibrio gigas           | Large spirillum           |                        |            |
| Desulfotomaculum antartium    | Rod                       | Gram positive bacteria  | [5]        |
| Desulfotomaculum acetoxidans  | Rod                       |                        |            |
| Desulfotomaculum nigrificans  | Rod                       |                        | [11]       |
| Desulfotomaculum orientis     | Curved Rod                |                        |            |
| Desulfomicrobium salsuginis   |                           | Gram negative bacteria  | [12]       |
| Desulfomicrobium aestuarii    | Rod                       |                        |            |
| Desulfomicrobium baculatum    |                           |                        | [13]       |
| Desulfobulbus propionicus     | Lemon shaped/Ovoid/Ellipsoid | Gram negative bacteria | [14]       |
| Desulfobacter hydrogenophilus | Ovoid                     | Gram negative bacteria  | [15]       |
| Desulfococcus biacutus        |                           |                        | [16]       |
| Desulfococcus multivorans     | Sphere                    | Gram negative bacteria  | [17]       |
| Desulfococcus oleovorans      |                           |                        | [18]       |
Desulfovomile tiedjei | Large rod | Gram negative bacteria | [19]

1.1. The cathodic depolarization theory

This theory explains that the SRB absorbs hydrogen by taking an enzyme (hydrogenase) to reduce sulfate, which is shown in Fig. 2[20,21].

![Cathodic depolarization diagram](image)

Fig. 2: Mechanism of steel bio-corrosion in the presence of SRB [22,23].

Fig. 2 shows the steel biocorrosion mechanism with sulfate-reducing bacteria. Metal becomes polarized when exposed to water and it loses positive metal ions (step I). Without oxygen, free electron reduce protons, which is resulted from water (step II), to produce hydrogen and occupy on the metal surface (step III). Reducing agent [H] transfer from the iron to the bacteria in the cathodic site. [H] agent is pledged for reduction of sulfate \( \text{SO}_4^{2-} \) to sulfide \( \text{H}_2\text{S} \) in the anodic site (step IV). Only 25% of the dissolved \( \text{Fe}^{2+} \) reteliate stoichiometrically with \( \text{H}_2\text{S} \) to yield \( \text{FeS} \) (step V). Remaining \( \text{Fe}^{2+} \) reteliate with hydroxyl group and yield more soluble \( \text{Fe(OH)}_2 \) as corrosion product (step VI) [22].

Stainless steel has good corrosion resistance, since it includes high amounts of chromium, molybdenum and nickel. Thus, it has broader applications in the marine world for the processing of oil and gas. However, stainless steel isn't good enough for MIC when exposed to the aquatic environment. The corrosion resistance behaviour of stainless steel is due to the formation of solid oxide film, commonly known as passivation. The slow rate of corrosion and decreased amount of corrosion products on the stainless steel surface make this metal vulnerable to biofouling. In the stainless steel, passivated surface provides the ideal location for accommodating the microbes and is thus susceptible to localized corrosion in the form of cracks, under stress or in solutions containing chloride. Green inhibitor play an important role to combat the biocorrosion of metal.

2. Corrosion inhibitor

A corrosion inhibitor is a material that reduces the corrosion rate of metal in a corrosion environment. An optimum concentration of corrosion inhibitor is required to reduce the corrosion rate, without affecting the concentration of corrosive medium. Inhibition of corrosion was accomplished by adding a chemical compound which inhibits metal oxidation. Corrosion resistance is a dynamic process,
which relies on the protective structures formed on the metal surface. Cathodic inhibitors delay the 
cathodic reaction, while, anodic inhibitors delay the anodic reaction. Some compounds are classified 
as mixed inhibitors that affect both the cathodic and anodic reactions. Corrosion inhibitors are 
classified as organic and inorganic inhibitors. Chromate is an inorganic inhibitor used to prevent the 
corrosion of iron and its alloys in aqueous media of broad pH spectrum. However, the chromate ions 
are known to be undesirable from an environmental point of view. Organic compounds with functional 
groups carrying atoms of N, O and S are commonly used corrosion inhibitors. Many of these chemical 
compounds are expensive. Efforts were therefore geared towards the production of cost-effective and 
non-toxic barriers to corrosion [24]. Corrosion inhibition happens by the adsorption of the inhibitor 
molecule and subsequently by a change in the potential deviation between the metal electrode and the 
solution due to the interface's non-uniform distribution of electrical charges [24].

A corrosion inhibitor has two ways to suppress the corrosion [24]:

1. By interacting with the corrosive material / medium, the corrosion inhibitor may turn the 
corrosive state into a non-corrosive environment.
2. The corrosion inhibitor binds to the metal surface and protects the metal from degradation.

The inhibitors have been further classified as follows [24]:

1. Cathodic inhibitors (CI)
2. Anodic inhibitors (AI)
3. Mixed type inhibitors

The CI suppress the cathodic reaction while the AI suppress the anodic reaction. CI reduce the 
diffusion hydrogen or oxygen to the metal surface. Arsenic and selenium ions are examples of 
cathodic poison, which reduce the diffusion of oxygen. The production of hydrogen in acidic solutions 
hindered by CI, or oxygen reduction in neutral or alkaline solutions [24]. AI react with oxygen 
forming a thin layer on the metal surface. Through oxidizing a surface layer which is less reactive to 
corrosive materials they reduce the material's corrosion potential. AI are usually effective in the pH 
range between 6.5 and 10.5. Oxyanions such as molybdates, chromates, sodium nitrite and tungstates 
are examples of AI. Such oxyanions play a significant role in the repair of the defects of the passive 
iron oxide film. Mixed-type inhibitors affect both anodic and cathodic regions of a polarizing curve 
region. Organic compounds, acting as mixed-type inhibitors, include organic agents adhered on the 
metal surface to create dissolution barrier at the anode and oxygen removal barrier at the cathodic 
sites. For organic mixed-type inhibitors, the defensive functional groups can be amino, carboxyl, or 
phosphonate [24].

2.1. Green corrosion inhibitor

Green corrosion inhibitors are derived from naturally occurring compounds such as plant extracts. It 
is easy to handle and not posing any interruption to the normal operation of the plants. Plant extracts 
are observed as abundant source of natural chemical compounds and they are environmentally benign. 
In many of these plant extracts, the corrosion inhibition activity may be attributed to the heterocyclic 
compounds such as flavonoids, alkaloids etc. Also, the existence of cellulose, tannins, and polycyclic 
compounds usually improves the films formation over the metal surface, thereby resist corrosion [25- 
26]. The plant extract can be extracted by low-cost and quick procedures. Previously, various type of 
natural products were used to inhibit the corrosion in different metals. Whereas, in case of synthetic 
inhibitor, it showed smart anticorrosive activity, but most of the inhibitors are toxic to individuals and 
surroundings. Table 2 show the various type of inhibitor used in steel for mitigation of microbial 
influenced corrosion.
Table 2: List of inhibitor used in steel for mitigation of MIC.

| Bacterial species | Metal          | Inhibitor                                      | Characterization techniques          | Results                                                                 | References |
|-------------------|----------------|-----------------------------------------------|--------------------------------------|--------------------------------------------------------------------------|------------|
| SRB               | X80 carbon steel | Sodium pyrithione (SPT)                       | • Weight loss study                  | Bio-corrosion inhibition is increased with the addition of SPT          | [27]       |
|                   |                |                                               | • EIS                                |                                                                          |            |
| Gram positive and gram negative bacteria with fungi | Mild steel | Alginates polymeric cationic surfactants      | • FTIR                               | Good action against some gram(+ve) and gram(−ve) bacteria with fungi    | [28]       |
|                   |                |                                               | • NMR                                |                                                                          |            |
|                   |                |                                               | • Gravimetric analysis               |                                                                          |            |
|                   |                |                                               | • Surface tension                    |                                                                          |            |
|                   |                |                                               | • EIS                                |                                                                          |            |
| SRB               | Mild steel     | Polyalthia longifolia plant extract           | • Weight loss                        |                                                                          | [29]       |
|                   |                |                                               | • TEM                                | P. longifolia extract acted as a biocide                                |            |
|                   |                |                                               | • SEM                                |                                                                          |            |
|                   |                |                                               | • XRD                                |                                                                          |            |
|                   |                |                                               | • FTIR                               |                                                                          |            |
|                   |                |                                               | • Tafel                              |                                                                          |            |
| Mixed SRB         | Pipeline steel | ZnO-interlinked chitosan nanoparticles        | • SEM                                | Formation of stable green biocide                                       | [30]       |
|                   |                |                                               | • TEM                                |                                                                          |            |
|                   |                |                                               | • XRD                                |                                                                          |            |
|                   |                |                                               | • FTIR                               |                                                                          |            |
| Bacillus thuringiensis | Mild steel | Ginger extract                              | • Electrochemical studies            | Maximum biocorrosion inhibition efficiency (BIE) as ~80%                 | [31]       |
|                   |                |                                               | • Weight loss                        |                                                                          |            |
|                   |                |                                               | • XRD                                |                                                                          |            |
|                   |                |                                               | • FTIR                               |                                                                          |            |
| Environmental sulfidogenic bacteria | Mild steel | Cationic gemini surfactant                    | • Redox potential study              | Inhibitor blocked the biofilm development                               | [32]       |
|                   |                |                                               | • Sulfide production                 |                                                                          |            |
| Sulfidogenic bacteria | Mild steel | Novel cationic gemini surfactant (NCGS)       | • Sulfide production                 | BIE of ~97% was obtained                                                | [33]       |
|                   |                |                                               | • Redox potential study              |                                                                          |            |
| SRB               | Carbon steel   | Tetra-hydroxymethylphosphonium sulfate (THPS) | • FTIR                               | Acted as mixed-type inhibitor                                           | [34]       |
|                   |                | with different fatty acids                    | • NMR                                | Increased the corrosion resistance                                     |            |
|                   |                |                                               | • Surface tension                    |                                                                          |            |
|                   |                |                                               | • Weight loss                        |                                                                          |            |
|                   |                |                                               | • EIS                                |                                                                          |            |
| Desulfovibio species | X80 steel | Citrus reticulata peels extract mediated copper nanoparticles Composite | • EIS                                | ETP-CuNPs reduce the Desulfovibio sp. population                        | [35]       |
|                   |                |                                               | • Weight loss                        |                                                                          |            |
|                   |                |                                               | • SEM/EDAX                           |                                                                          |            |
|                   |                |                                               | • TEM                                |                                                                          |            |
| SRB and TGB (total general bacteria) | L360 pipeline steel | Polyacrylamide inhibitor | srb and tgb (total general bacteria TGB) | Weight loss | SEM | CLSM | TEM | XPS | EIS | Microbial acidification lead to pitting corrosion | [36] |
|-----------------|--------------------|-------------------------|---------------------------------|------------|-----|------|-----|-----|-----|---------------------------------|-------|
| Desulfovibrio species | Steel | Acanthus montanus | Desulfovibrio species | Weight loss | Plant extract show good bio-corrosion resistant | BIE increases with inhibitor concentration | [37] |
| Desulfovibrio alaskensis | Carbon steel | Lemon grass essential oil (LEO) | Desulfovibrio alaskensis | Weight loss | TEM | Minimum inhibitory concentration | LEO showed an immediate killing effect against SRB | LEO protect the bio-corrosion of carbon steel coupons | Citral, present is LEO is responsible for inhibition | [38] |
| Desulfovibrio species | Steel | Costus afar leaves extract | Desulfovibrio species | Weight loss | Media absorbance examination techniques | Extract decreased the absorbance of the media values | Decline in weight loss and corrosion rate with extract | [39] |
| MIC | Stainless steel | Salvia officinalis | MIC | Contact angle measurements | Salvia officinalis extract modify the stainless steel surface properties | [40] |
| Mixed culture | Mild steel | Carica papaya peel extract, Musa paradisiaca peel extract and Moringa oleifera leaf extract | Mixed culture | Weight loss | EIS | Tafel | FTIR | BIE rises with rise in the extract concentration | Act as mixed type inhibitor | [41] |
SRB and IOB (iron oxidizing bacteria) | Steel | Aloe barbadensis extract | Weight loss | BIE is between 89 and 100% for IOB and 66 and 100% for SRB | [42]  
SRB | Carbon steel | Daphne gnidium | Weight loss, EIS | BIE of ~95% from weight loss study and ~91% from EIS | [43]  
Desulfovibrio desulfuricans | Stainless steel | Benzyldimethyl-dodecylammonium chloride | SEM/EDS, CLSM, Tafel | Inhibitor prevented the bio-corrosion | [44]  

EIS – Electrochemical impedance spectroscopy, SEM – Scanning electron microscopy; FTIR – Fourier transform infrared spectroscopy; CLSM – Confocal laser scanning microscopy; NMR – Nuclear magnetic resonance; TEM – Transmission electron microscopy; XPS – X-ray photoelectron spectroscopy, XRD – X-ray diffraction, EDAX – Energy dispersive X-ray.

3. Conclusion

This paper explores MIC principles, research approaches and control procedures, and addresses measures for minimizing MICs. Substantial future work is expected to fill in the holes of this research. The extensive collection of research work outlined suggests that intense study is essential to solve the metal corrosion problem. Few literature made an attempts to find green inhibitors as alternatives to toxic corrosion inhibitors of fossil origin. Corrosion inhibitor is one of the best choice for protecting metals and alloys from corrosion. As the organic corrosion inhibitors are generally toxic, the researchers has turned towards the inhibitors of green extract because they are biologically degradable and may not pose any serious threat to the environment. As well as being environmentally sustainable and widely applicable, plant materials are cheap, easily available and reusable. While significant research has been done on corrosion protection by green extracts, research on the comprehensive adsorption mechanisms and active ingredient recognition are also sparse. This analysis shows that green corrosion inhibitors are the path to future in the battle for more stable and environmentally friendly security corrosive cement. Owing to the renewability of its resources, the use of green inhibitors also has the potential to be cost effective.

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