



# A Brief Insight into Microbial Corrosion and its Mitigation with Eco-friendly Inhibitors

M. Lavanya<sup>1</sup>

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## Abstract

Corrosion results from the electrochemical reactions between the metal and its existing environment. Corrosion results in severe and expensive damage to a wide spectrum of industries. When microbes are involved in corrosion it is seldom possible to economically evaluate its impact. Microbially influenced corrosion is recognized to cause catastrophic failures contributing to approximately 20% of the annual losses. In many engineering applications, microbially influenced corrosion control is of prime importance. Expensive, toxicity and sometimes, even ineffectiveness of the current chemical strategies to mitigate microbially influenced corrosion have shifted the interest towards eco-friendly inhibitors. The present review discusses microbial induced corrosion in various metals and its inhibition through eco-friendly inhibitors. In addition, the study also reviews the morphological and electrochemical impedance results.

**Keywords** Microbially influenced corrosion · Eco-friendly inhibitors · Metal · Electrochemical impedance

## 1 Introduction

Degradation of metals by means of interaction with their associated environment is known as corrosion. Sometimes this term corrosion is also applied to deterioration of concrete, plastic and wood but often is considered with respect to metals [1]. Higher operating and maintenance costs, catastrophic failures are all consequences of corrosion [2]. World wide corrosion losses in 2015 was ~2.5 trillion dollars [3]. Out of the many techniques employed to eliminate or reduce corrosion the most practical method is the application of inhibitors [4]. Biocorrosion is one among the eight different types of corrosion. In many industries such as power generation, waste water treatment plant, oil and gas production, MIC (Microbiologically Influenced Corrosion) has been identified as most dangerous [5].

MIC contributes to approximately 20% of the annual losses [6–8]. MIC is not a new form of corrosion, but to date, it is a more serious and dangerous problem of the industry. In 1891, the scientist Garrett studied microbial corrosion, it

is the first report about microbes for corrosion [9]. MIC has significant ecologic and economic impact [10]. MIC was known to be a key factor for numerous pipeline failures. One such incident of pipeline rupture took place in New Mexico in the year 2000. MIC was also a main suspect in the pipeline leak in Alaska on March 2, 2006 which lead to a spike in oil prices world wide [11].

Biocorrosion may be prevented by reducing biofilm formation on the surface of the metal. Biocides and few dispersive agents are applied to the metal surface to reduce the formation of biofilm as a part of chemical treatment. Nevertheless these treatments have lost their applications due to the environmental concerns. Therefore development of eco-friendly inhibitors is drawing attention in the recent years [12].

This research article focused on the behavior of eco-friendly corrosion inhibitors on metals for microbial corrosion in various media.

## 2 Microbial Corrosion Mechanism

MIC is the consequence of the combination of “three M’s” (Fig. 1): microorganisms, media (chemical composition and physical parameters, e.g., temperature and flow), and metals [9].

✉ M. Lavanya  
lavanya.m@manipal.edu

<sup>1</sup> Department of Chemical Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India

**Fig. 1** Schematic representation of the effects of media, metal and microorganisms on MIC



**Table 1** Microbes involved in corrosion and its classification [18]

Bacteria	Sulphur oxidizing bacteria
	APB (inorganic Sulphur acid by Acidothiobacillus, organic by Bacillus sp.
	Sulphur reducing bacteria
	Slime producing bacteria
	Iron reducing bacteria
Fungi	Aspergillus Niger
	Penicillium cyclospium
Algae	Blue green algae

A combination of microorganisms, media and metal together lead to microbial corrosion which is shown diagrammatically in Fig. 1. Biocorrosion frequently occurs due to pitting corrosion subsequently allowing the microbes to accumulate in specific places repeatedly [13]. It is an electrochemical phenomena where microorganisms accelerate material degradation by their metabolic action on the material [14].

Bio-corrosion is connected with microbes or the metabolites resulting from their activities which include exopolymers, enzymes, acids and volatile compounds. The cathodic and the anodic reactions are affected by these metabolites leading to a variation in the metal interface electrochemistry. The main bacteria involved in the corrosion of mild steel, cast iron and stainless steel are sulphur oxidizing bacteria, SRB (Sulfate-Reducing Bacteria), manganese oxidizing bacteria, iron-oxidizing/reducing bacteria, etc. These microbes stimulate corrosion in several ways. [15, 16]. These microbes coexist in naturally arising biofilms, frequently developing synergistic consortia. During microbial corrosion, the microbes initiate, facilitate and aggravate corrosion through co-operative metabolism and then develop a biofilm on the metal surface. Material and microbe interactions cause the bacteria to adhere and form a biofilm. Biofilm consists of 95% water with Extracellular Polymeric Substance (EPS) and inorganic matter/cell suspension. The environmental factors strongly affect the development of microbial community within the biofilm. Biofilm is also responsible in transforming the properties at the metal/solution interface [17]. The microbes involved in corrosion process are listed in Table 1.

### 3 Microbial Corrosion in Metals

Microbes can directly or indirectly disturb the integrity of many metals used in industrial applications. Most of them including copper, iron, nickel, aluminum and their alloys, are more or less vulnerable to damage. Only titanium and its alloys appear to be usually resistant [19].

#### 3.1 Aluminum Magnesium Alloy

The 2024-T31 aluminum-magnesium alloy was investigated for its susceptibility to microbial corrosion in the presence of SRB. The sample was immersed in various test solutions and maintained at constant temperature of 30 °C in an incubator. As time elapsed microbial colonies and deposition of corrosion products were observed on the substrate. Biofilm and passivation film both were found to jointly control corrosion in 2024-T31 aluminum-magnesium alloy. SRB caused excessive corrosion in the alloy along with pitting on the metal surface. In the very beginning an uneven biofilm was observed on the metal surface which weakened in the mid stage along with the growth of a protective passive film therefore reducing the corrosion rate. Later localized corrosion cells were formed accelerating corrosion [20].

#### 3.2 Carbon Steel, Copper Aluminum

The growth cycle of SRB, *Desulfovibriocaledoniensis*, and the influence of SRB on the corrosion activities of Q235 and the environmental parameters during a growth cycle in the presence and absence of oxygen were studied. Culture solutions with dissolve oxygen encouraged sluggish growth and rapid decay of SRB. Conductivity, pH and sulphide anion concentration were affected by the growth process of SRB both under aerobic and anaerobic conditions. During the stationary growth phase OCP (Open Circuit Potential) shifted towards positive end. Through the exponential growth phase the Rct (charge transfer resistance) increased rapidly while it decreased after the stationary phase [21].

Corrosion behavior of carbon steel, pure aluminum and copper were studied in sea water. Epifluorescence microscopy and electrochemical techniques were applied for the investigation. Ecorr moved to the negative direction with time for carbon steel and aluminum. Corrosion causes the Ecorr to move towards the negative end. These

metals easily corrode in sea water. On the corroding metal substrates biofilms does not form easily. Bacteria hardly adhere to the copper surface and therefore Ecorr seldom changed [22].

### 3.3 Aluminum alloy

Aluminum alloys find diverse applications owing to their excellent chemical and physical properties ranging from aircraft to construction [23–25]. Aluminum and its alloys offer corrosion resistance through a thin passive layer of aluminum oxide known as Alumina naturally formed on its surface [26].

Aluminum alloy (7065-T6) was investigated for its corrosion behavior in saline environment involving *Aspergillus niger* (*A. niger*). Methods and techniques used for the study included HPLC, GC, surface analysis and electrochemical measurements. The localized corrosion increased 2.4 times in the presence of *A. Niger* as compared to its absence. The increased corrosion rate was attributed to the enhanced cathode and anode reactions due to the presence of biofilm generated by *A. Niger*. Additionally *A. Niger* secreted organic acid was found to enhance corrosion. After the early adaptation period *A. Niger* adhered to the aluminum surface easily.  $\text{Al}(\text{OH})_3$  and  $\text{AlO}(\text{OH})$  were confirmed to be present as corrosion products through XRD analysis. In the presence of *A. Niger* corrosion accelerated which was confirmed through weight loss, surface analysis and electrochemical measurements [27].

Microbes present in the corrosion products of diesel-transporting pipelines, their corrosion effects on 2024 aluminum alloy was the topic of research. Microbes under study were *Serratia marcescens* (*S. marcescens*) ACE2, a Gram-negative bacteria and *Bacillus cereus* ACE4, a Gram-positive bacteria. Aeronautical fuel storage tanks often suffer microbial growth and contamination which result in corrosion further leading to higher operating and maintenance costs. The bacteria instigated pitting in the fuel tank. Bacteria develops biofilm when exposed to the salty environment. These biofilms are responsible for pitting corrosion. As compared to *S. marcescens* ACE2 corrosion damage caused by *B. cereus* ACE4 is more intense [28].

This report aims at evaluating the risk of MIC on 6061 Aluminum alloy and pure aluminum in spent nuclear fuel. Out of the identified microbes *Bacillus cereus* (*B. cereus*) RE 10 was the most predominant. This bacteria was selected for investigating its corrosion intensity of 6061 Aluminum alloy and pure aluminum. On the surface of 6061 Aluminum alloy deeper pits were observed after exposing it to *B. cereus* RE 10 for 20 days but no such observations were found on pure aluminum. A definite correlation was noticed between, corrosion deposits, biofilm patches and pitting [29].

### 3.4 Carbon Steel

Carbon steel (CS) is a material with properties such as good electrical and thermal conductivity and excellent mechanical strength. The cost of carbon steel is cheaper as compared to few other metals. However, one of the disadvantages of using this metal is that it rusts easily resulting in environmental and economic losses [30]. CS and its alloys are used all over the world in boilers, pipelines, bridges and so on. With relatively good corrosion resistance CS is also applied in marine environments [31]. A laboratory scale test set up was employed to study the effect of SRB on carbon steel corrosion. The test medium was North Sea water. The test medium was inoculated with a bacterial species namely *Desulfovibrioalaskensis* or *Desulfovibriodesulfuricans*. Also antimicrobial treatment was given to the flow cell. Higher electrochemical activity and hence lower corrosion resistance was exhibited by the steel coupons in the presence of the bacterial species. Pit formation increased with exposure time. However, bacterial action was provisionally blocked due to the antibacterial treatment. As a consequence of long term exposure biofilm and corrosion products were developed on the carbon steel specimen [32]. The authors report the MIC of API 5L X80 by SRB. The corrosion behavior of carbon steel was analyzed by electrochemical techniques along with field emission scanning electron microscopy (FESEM). The interactions between carbon steel, biofilm and the test solution was analyzed with the equivalent circuits obtained from EIS study. The biofilm formed on the metal substrate results in excessive localized corrosion. In addition, iron sulfide layer formed also contributes to corrosion. The iron sulphide layer formed is porous in nature. Corrosion product formed included various sulphide and oxide components as revealed by the EDS study [33].

### 3.5 Zinc

Zinc is widely used in construction, automobiles and shipping industries. Zinc offers a high resistance to corrosion by forming a passive layer of  $\text{ZnO}$  and  $\text{Zn}(\text{OH})_2$  when exposed to the atmosphere [34]. It is ranked fourth among the metals that are produced and consumed worldwide [35]. In the Urban, rural and marine sites of Luthania, *Aspergillus niger* was isolated. Aluminum and Zinc were exposed to *A. Niger* for 2 years under humid conditions. A double layer corrosion product formed on the surface of zinc was detected from EIS analysis. The inner layer was thinner due to the microorganism activity but had an enhanced passivation capacity as compared to the outer layer. MIC affected the pores, microcracks present on the aluminum surface as confirmed from the decreased layer thickness and increased corrosion resistance. The study postulated that microbes assist

in preventing corrosion and therefore may be considered as corrosion inhibitors in place of toxic chemicals [36].

Few microbes are known to cause severe corrosion in some of the metals. In the present study the influence of *Desulfovibrio vulgaris* on zinc and galvanized steel was investigated. Weight loss suffered by galvanized steel and zinc was 101 times greater than carbon steel. While comparing galvanized steel and zinc potentiodynamic studies indicated that zinc was more prone to SRB induced corrosion [34].

### 3.6 Magnesium

Magnesium finds its application in the area of military and aerospace [37]. It has been further extended to storage, electronics and also orthopedic implants. It has been considered to replace the heavy metal alloys in the near future. Magnesium and its alloys have outstanding properties, such as machinability, lightweight, shock absorption and impact resistance [38]. The corrosion behavior of magnesium alloy in the presence of SRB was reported in this study. X-Ray spectroscopy and SEM analysis of the corrosion film were carried out for knowing its composition. Additionally the morphology of the corrosion product and the mechanical properties of the alloy was also investigated. The results showed that SRB played a key role in the Magnesium alloy corrosion by enhancing pitting. Therefore SRB affect the residual strength of the alloy through enhanced pitting [39]. A specially designed method was employed to study MIC in magnesium alloy. It is known as solid culture medium method. Electrochemical method was used to study the corrosion behavior along with the surface analysis with Scanning electron microscopy (SEM). Presence of SRB resulted in excessive pitting of the alloy. The results indicated the characteristic feature of MIC as pitting. The key component responsible for pitting due to SRB involved hydrogenase enzyme. Cathodic reaction was accelerated due to SRB as indicated by the electrochemical study [40].

### 3.7 Steel

Steel is extensively used in engineering applications due to its ability to form passive layer on its surface and hence resist corrosion [41]. Stainless steels are generally used in processing equipment, heat exchangers, beverage industries, food factories and biomedical industries [42]. This metal has good resistance to various environments and corrosive solutions. The resistance to corrosion is confirmed by the presence of a passive film. The passive layer on stainless steel is naturally formed in water and air with a thickness of 10–100 Å. This layer consists of both chromium and iron oxide [43]. A variety of stainless steels with different microstructures were investigated for its influence on microbial corrosion. The effect of microstructure was studied in

the presence of two species of SRB. The medium for study included Electrolyte A and Electrolyte B with different constituents. Biofilms were analyzed with the help of SEM. The metabolites of SRB caused a premature rupture of the passive films leading to formation of pits. A correlation between the pit morphology, its composition and medium composition was established [44].

This paper explores a serious microbiologically influenced failure in the elbows of a buried amine pipeline in a petrochemical plant. Out of the many different corrosion mechanisms MIC is one which the pipelines may experience. A systematic investigation has been carried out by the researchers which includes exhaustive corrosion product analysis, microstructural analysis and monitoring the presence of microorganisms. The failure of the pipeline was ascribed to the presence of SRB which is mainly responsible to MIC as indicated by other researchers. EDS spectra confirmed the existence of Sulphur indicating the role of SRB in inducing corrosion. SRB shows very good adaptability to extreme environment conditions. The damaging metabolic activities of SRB is concerned with its capacity to utilize organic compounds, aromatic and aliphatic hydrocarbons and also cause sulfate to sulfide reduction [45].

### 3.8 Titanium

Titanium is a metal which is highly resistant to corrosion. The stable oxide film formed on the surface of Titanium offers better corrosion resistance. Titanium alloys are applied in various fields ranging from automotive to biomedical industries. It offers features like excellent mechanical properties, low density and light weight making it more attractive for the marine environment [46].

The corrosion performance of a titanium alloy was studied in a solution containing SRB. Initially SRB adhered to the surface of the alloy in small amounts progressively forming colonies and increased as time elapsed as indicated by the bacterial adhesion experimental study. The amount of Sulphur increased with the elapsed immersion time. Sulphur in small amount was perceived to have a protective effect. Nevertheless higher amount of Sulphur showed a detrimental effect on the oxide film. Pitting corrosion was observed on the alloy surface. Electrochemical studies indicated a better resistance in the initial time period of immersion and later showed an increased corrosion rate. This observation is attributed to the increased Sulphur content in the medium as greater immersion period [47]. Biocorrosion is a threat to many metals. The phenomena was studied in the presence of a microbe *Pseudomonas aeruginosa*. Pure titanium was the metal under study. Electrochemical tests were conducted on the metal in the medium containing the marine bacterium. The metal was observed to be corrosion resistant up to 14 days of immersion whereas the resistance

decreased after that time period due to the biofilm developed on the surface. Severe pitting corrosion was observed with a pit depth of 1.2 m. The biofilm causes the passive film to be unstable [46].

Corrosion of titanium is the major concern when it is used for dental treatment. This study aimed to investigate the mechanism of the microbiologically induced corrosive properties of titanium. An experimental well was made of polymethyl methacrylate with pure titanium at the bottom. Viable or killed cells of *Streptococcus mutans* were packed into the well, and pH at the bacteria-titanium interface was monitored with and without glucose. The corrosion current and passive current was low and stable under killed cells while it increased under viable cells. The polarization resistance and oxygen concentration under killed cells were high and stable, while those under viable cells decreased [48].

### 4 Green Inhibitors

A substance which when added to a corrosive solution in a small concentration causes a reduction in the corrosion rate is known as an inhibitor [47]. Most frequently used corrosion inhibitors include synthetic chemicals such as inorganic and organic compounds. These synthetic chemicals are costly and harmful to the environment [49]. Due to the aforementioned characteristics of chemical corrosion inhibitors, there has been increasing search for eco-friendly corrosion inhibitors. This class of Inhibitors are environmentally friendly and are acquired from natural products [50]. The hunt of such corrosion mitigating agents for metals originated in mid of 1900s [51]. The first eco-friendly green inhibitor (Chelidoniummajus) was applied in the 1930s and it showed better performance than chemical inhibitors [52]. A variety of green organic compounds are known to show excellent properties in shielding metal surfaces against corrosion [53]. Because of the renewable nature, ease of application and availability, biodegradable, and biocompatible

nature and being least expensive, several plant extracts have been used earlier [12].

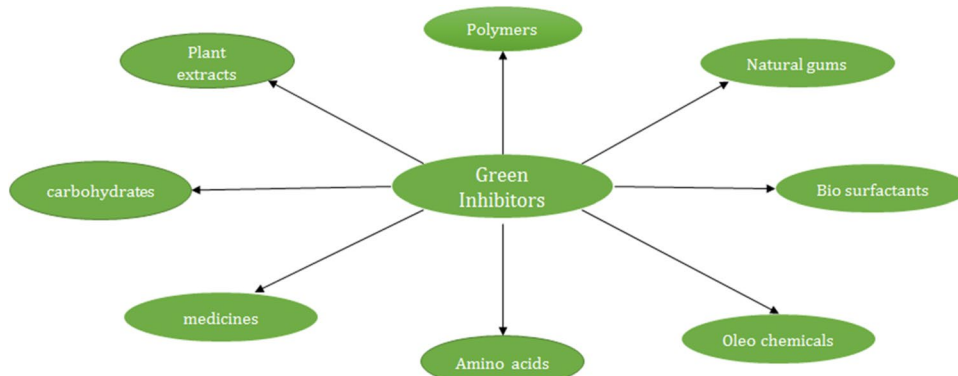
Classification of the eco-friendly green corrosion inhibitor is shown in Fig. 2 [54].

Even though, plant extracts are of biological origin regardless of the aqueous and organic nature, are treated as environmentally benevolent however usually they are accompanied by low protection efficiencies at relatively higher concentration. It is proposed to minimize the growth of microbes on the metal surface which reduces the corrosion rate. One of the greatest challenges of using organic extracts as corrosion inhibitors is their limited solubility's especially at their higher concentration. Another constraint of using plant extracts for mitigating corrosion is that extract preparation is highly tedious as it involves several steps [54].

Moreover, using of organic solvents for extraction may harm the environment. Similarly, application of complex organic molecules, such as ionic liquids and drugs as corrosion alleviating agents is also restricted because its synthesis is extremely expensive. Application of rare earth elements for protection of metals against corrosion is limited by some shortcomings. It is very difficult to separate rare earth element one from another. This discloses the limitation of applied technology. Also, the extraction procedure includes the production of a lot of waste such as ammonia, acids and some radioactive elements, which can possibly disturb the environment if not treated properly. Further the rare earth metals are unstable which may arise as a considerable problem in using those elements as corrosion inhibitors [55]. Few of the extracts have the capacity to hinder microbial growth as they are very efficient reactive oxygen scavengers [56].

Corrosion protection efficiency of organic green corrosion inhibitors (OGCIs) has been connected to the availability of organic compounds including oxygen, nitrogen, Sulphur and phosphorus which have corrosion alleviating potentials for metal attack [57]. OGCIs reveal their protective action via chemisorption or physisorption onto metal/solution interface by eliminating molecules of water on the metal surface for barrier film formation [58]. The adsorbed

Fig. 2 Broad classification of green inhibitors



film of inhibitors separates the material from the corrosive environments. Several factors including nature of metal and corrosive environment, temperature, solubility, molecular structure of the inhibitor molecule affects the adsorption behavior of organic corrosion inhibitors [12]. Corrosion alleviation with organic corrosion inhibitors involves two steps: the first consist of the transfer of the corrosion inhibitors over the metal surface and second comprises the interactions between metal and adsorbed inhibitor molecules. Adsorption of the inhibitor molecules on the metal surface is principally governed by its electronic structure and the residual charges present over the surface [59].

A few requirements for selecting the inhibitors are listed in Fig. 3 [60].

The techniques employed to monitor microbial corrosion include open circuit potential (OCP), linear polarization

resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve.

### 5 Factors Effecting the Performance of Green Inhibitors

The efficiency of corrosion inhibitors is dependent on its surface adsorption characteristics. Other factors that influence the protection efficiency include the structure of the inhibitor, its concentration, the test exposure time and most importantly temperature [61].

### 6 Factors Affecting MIC

MIC depends on metal type (host location), nutrients present in the environment and groups of organisms found in the bulk. Microorganisms alter the conditions at the interface between the metal and the substratum, modifying electrochemical reactions, which are fundamental for corrosion processes [62].

### 7 Other Applications of Green Inhibitors

Green inhibitors are used in many industries. The chief applications are listed in Fig. 4 below [63].

Across the world in many countries reinforced concrete is used in construction. Nevertheless the material suffers severe corrosion in certain environments. Corrosion inhibitors are added to the concrete mixing water to increase its corrosion resistance [64]. Nano containers are used to store corrosion inhibitors. Though they are efficient they lack structural features supporting coating dispersion. Therefore corrosion inhibitors are loaded into nanotubes. These find applications in anti-microbial food packaging [65].

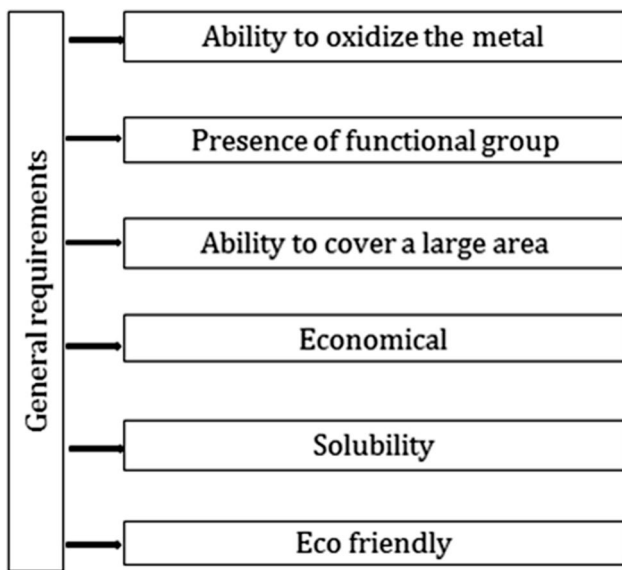
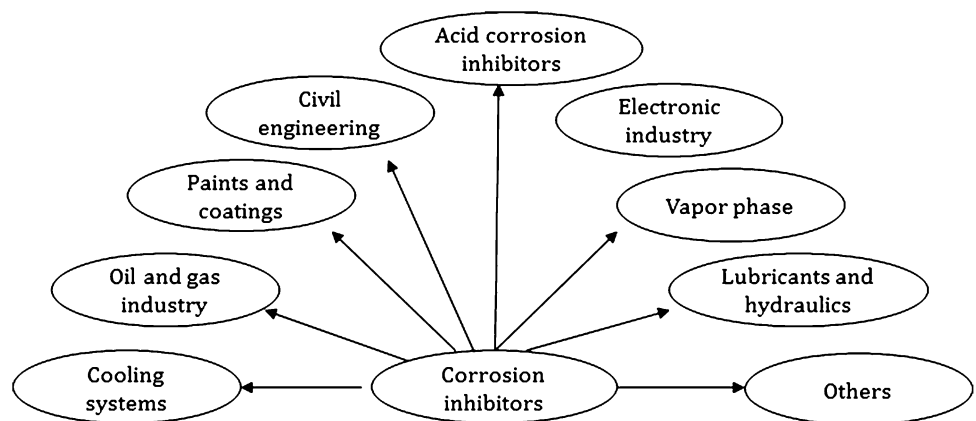


Fig. 3 Requirements for selection of inhibitors

Fig. 4 General applications of inhibitors



**Table 2** Eco-friendly inhibitors applied in various media to mitigate MIC

Metal	Medium	Inhibitor	References
Carbon steel API 5LX	Hypersaline	Neem extract	[66]
Copper	Synthetic sea water	Chitosan polymer	[67]
Aluminum	Phosphoric acid	Cassava starch	[68]
Aluminum	HCl	Exudate gum	[69]
Carbon steel	Phosphoric acid	Etoricoxib (drug)	[70]
Copper and Zinc	Artificial sea water	Tobacco	[71]
X80 steel	HCl	<i>Allium cepa</i> extract	[72]
Carbon steel	Acid and Alkaline medium	Moringa leaf	[73]
304L stainless steel	Medium based on artificial sea water consisting Pseudomonas aeruginosa	<i>Cistus ladanifer</i> leaf	[74]
Steel	Winogradsky medium	Aloevera extract	[75]
Mild steel	Cooling water	Ginger extract	[76]
st37 steel	Cooling tower water	<i>Myrtus communis</i> extract	[77]
Mild steel	1.5% NaCl	<i>Artemisia pallens</i>	[78]
Mild steel	Crude oil–water environment	<i>Moringa oleifera</i> leaves, and <i>Carica papaya</i> peels	[79]
Mild steel	Marine environment	<i>Carica papaya</i>	[80]
Carbon steel	Sulphate reducing bacteria media	Chitosan based nano composite	[81]

Few microbial induced corrosion studies carried out with various inhibitors are listed in Table 2.

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## 8 Summary and Conclusions

Corrosion inhibitors employed in the industries mostly include synthetic compounds. Although they are effective in mitigating microbial corrosion they are toxic in nature and hazardous to the environment further leading to stringent environmental regulations. Therefore there is a need to develop eco-friendly inhibitors to mitigate microbial corrosion. This publication focuses on various green inhibitors that has been and can be used to inhibit microbial induced corrosion in different metals and media.

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### Declarations

**Conflict of interest** The authors declare that they have no competing interest.

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