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Carbon steel under attack: microbial corrosion and emerging prevention techniques

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Abstract
A cascade of chemical and biological events causes the breakdown of materials due to corrosion. The intricate issue of microbiologically influenced corrosion (MIC) impacts a wide range of sectors. The majority of the corrosion in oil gearbox systems, both internal and exterior, is caused by it. Although numerous hypotheses and models have been put out to account for MIC, our comprehension of how microorganisms interact with metal surfaces and the interpretation of microbial activity leading to biocorrosion remains limited. Carbon steel (CS) can experience pitting corrosion due to bio corrosion's several pathways. Microorganisms can be either corrosive or anticorrosive, and both play an essential role in the corrosion process. Galvanization, anticorrosive microorganisms, plant and algae extracts are all viable options for MIC inhibition. Many chemicals that prevent corrosion in industrial settings are extremely harmful to human health. Green corrosion prevention methods are urgently required. Concerning this matter, scientists are concentrating on inhibitors based on metal coatings, bacterial biofilms, and natural extracts. Extracts from plants and algae have shown promise in dealing with various metals. A layer of nickel alloy on steel can prevent biocorrosion to a certain degree. CS is an essential metal with many industrial uses, and this study aims to learn more about its corrosion. Efforts to combat CS biocorrosion are scant. Approaches to managing biocorrosion in CS are the subject of this review.

Corrosion and its types

Environmental factors gradually deteriorate materials through a process known as corrosion, which is a chemical reaction that changes a metal into an oxide, hydroxide, or other substance [1]. Different types of corrosion have been described below:

- Galvanic corrosion also known as bimetallic corrosion is the degradation of one metal near a joint when two electrochemically dissimilar metals are electrically connected [2].
- Pitting is the most destructive form of corrosion that forms pits on metal surface which deep down with the passage of time to change the overall structure of metal [3].
- The most prevalent form of corrosion is uniform corrosion, often known as general corrosion. This happens when

corrosion is initiated throughout metal surface [4].

- When fluid is unable to easily reach some areas, a condition known as crevice corrosion sets up. Cracks are another name for these openings. These include under gaskets area, insulation materials, threads and clamps [5].
- Erosion is the destruction of the surface of material due to mechanical action of liquid flowing in metal pipes, *i.e.,* particles in fast flowing liquid cause erosion of materials [6].
- Corrosion that is thought to be induced by microorganisms on metal surfaces is known as microbial corrosion [7].

Microbiologically influenced corrosion (MIC)

The degradation of metal surfaces caused by the presence and metabolic activity of microbes on materials is known as microbial corrosion, also known as biological corrosion or Microbiologically Influenced Corrosion (MIC). Microbes do not start a new corrosion process instead they just intervene the already occurring corrosion at the surface by altering the conditions at metal/material surface. There are two types of microbes based upon their role in the corrosion process *i.e.,* corrosive microbes and anti-corrosive microbes. Corrosive microbes are harmful as they accelerate corrosion process through secretion of acidic/non acidic metabolites [8]. Anti-corrosive microorganisms play a major role in preventing the corrosion process through the production of biofilms on metal surface [9].

MIC was discovered in 1891, when he observed the corrosion of lead cables caused due to the interaction of cable with bacterial metabolites. Underground storage and related pipeline systems have historically been believed to experience internal corrosion issues mainly as a result of carbon dioxide, hydrogen sulphide, and oxygen. But later on, investigators reported the involvement of microbes in corrosion of underground materials [10]. MIC affects underground storage tanks [11], water distribution systems [12], rail systems [13], cooling water systems [14], medical implant devices [15], and nuclear waste storage facilities [16]. A variety of materials such as carbon steel, aluminum alloy, stainless steel (SS), duplex SS, high nitrogen SS, magnesium, copper alloys and even concrete are affected by MIC [17]. Pipelines lose over 20% of their total corrosion-related value due to MIC. Bacteria form biofilms on metal surface by secreting extracellular polymeric substances (EPS). When the upper layer of a biofilm uses up all the carbon, the organic carbon available to the sessile cells in the lower layer eventually runs out, creating a starved environment where the sessile cells on the metal surface corrode [14].

Sectors affected by MIC

The oil and gas sector frequently employs CS for pipeline and storage tank construction because of its superior mechanical strength, mild ductility, and wear resistance [18]. Developed nations'

GDP drops by almost 5% due to CS corrosion, which causes massive economic loss [19]. In the oil and gas industry, microbes are responsible for 20-30% of corrosion issues. CS pipelines are affected by internal corrosion due to the formation of biofilms by the bacteria present in the material which is being transported through the pipelines [20] and external corrosion caused by soil bacteria [21].

Techniques used to study MIC

An assortment of methodologies have been employed to investigate the microbial corrosion of CS, including but not limited to scanning electron microscopy (SEM), potentiodynamic polarization technique, Fourier transform infrared spectroscopy (FTIR), and atomic force microscopy (AFM) [22, 23].

Corrosion mitigation

To mitigate the corrosion of CS or any other metal, conventional methods rely on disinfection and cleansing. However, this approach is not dependable; therefore, inhibitors are an alternative [24]. Inhibitors against corrosion are one of the most prevalent, economical, and efficient methods of metal protection. These inhibitors include microbial biofilms, plant or algal extracts and metal coatings [25]. Galvanization is the process of coating metals like zinc, copper, nickel, cobalt, aluminum on the surface of carbon steel or any other metal or alloy to prevent corrosion. There are two approaches by which galvanization can be done *i.e.,* hot galvanization and cold galvanization [26].

Carbon steel

Steel is an alloy having different elements in different percentages. The percentage of carbon varies in different types of steel which determine its properties. Stainless steel is a type of steel having carbon around 0.08%, whereas CS has a high content of carbon compared to stainless steel. CS is of low cost, thus used extensively in industries and transport facilities. Low-cost carbon steel is preferably used in construction material across industries as it is considered to be the more economical option than the corrosion resistant alloys.

- CS typically consist of a carbon (C) content of less than 1.5%, in addition to minor amounts of manganese (Mn), silicon (Si), phosphorus (P), and sulfur (S). CS is further classified into three varieties according to the carbon percentage: low carbon steels (less than 0.25% C), medium carbon steels (0.25 to 0.70% C) and high carbon steels (0.70 to 1.05% C) [27]. Distinction in mechanical properties, including but not limited to mechanical strength, ductility, and hardness, can be attributed to variations in the C content of CS. Subsequent to its properties, CS may be further categorized into various classifications [28]:
- Grade 1008 contains 0.08% C by weight and is considered as good for forming.

- Grade 1018 contains 0.18% C by weight and is used for general application and good for welding.
- Grade 1030 contains 0.30% C by weight and has low hardenability.
- Grade 1045 contains 0.45% C by weight and used in power transmission.

Applications of carbon steel

The structural components, industrial pipe lines, and household appliances made of CS are just a few examples of its many uses. In the context of oil and gas applications, the two most common types of corrosion are sour corrosion (H_2S) and carbon dioxide (CO_2) corrosion [29].

Crude oils used in the oil and gas industry can reduce corrosion naturally because to the presence of S, aromatic resins, nitrogen (N), and other chemical species [30]. A passive protective coating formed by organic or inorganic inhibitors is the most common method of preventing corrosion on steel surfaces [31].

The oil and gas industry is among the industries where the use of CS is high, and research into how to prevent corrosion in acidic environments is an ongoing effort to enhance the performance of CS while keeping costs down in comparison to other alloys.

MIC of CS

Microbes involved in CS biocorrosion

Okoro *et al.,* (2014) identified sulphate reducing bacteria (SRB), iron reducing bacteria, and S, Fe and Mn oxidizing bacteria as the primary bacterial species linked to MIC of CS [32]. Additional microorganisms that contribute to metal MICs, are several fungal species, methanogens, and nitrate reducing bacteria [33, 34].

Mechanisms of CS biocorrosion

To comprehend biocorrosion, one must be familiar with its many processes. Nitrate, sulphate, and proton ions, among others, serve as electron acceptors in MIC produced by anaerobes [14]. This process can only take place in the presence of a biofilm of sulfate or nitrate reducing bacteria on a metal surface. The reduction of sulphate or nitrate occurs because bacterial biofilms are necessary for the transmission of electrons produced during extracellular metal oxidation [33]. According to Jia *et al.,* (2018), this specific kind of MIC is called EET-MIC [35]. Xu and Gu (2014) discovered that sessile cells are more acidic towards CS when organic carbon is scarce and the electron source for sulphate respiration is elemental iron [36].

To understand the bioenergetics of SRB-MIC against CS, one need to understand the biocatalytic cathodic sulfate reduction (BCSR) hypothesis. According to the BCSR hypothesis, the SRB cell wall is responsible for transporting the electrons that are produced during iron oxidation.

$$\text{Anodic reaction: } Fe \rightarrow Fe^{2+} + 2e^{-} \text{ (iron dissolution)}$$

$$\text{Cathodic reaction: } SO_4^{2-} + 9H^{+} + 8e^{-} \rightarrow HS^{-} + 4H_2O \text{ (BCSR)}$$

Like BCSR, bio catalytic cathodic nitrate reduction (BCNR) can be used to explain bioenergetics mechanism behind NRB-MIC.

Remedies to overcome CS biocorrosion

A less dependable approach of reducing corrosion of CS and other metals is to utilize inhibitors, nevertheless, this strategy relies on frequent cleaning and disinfection [24]. One of the most prevalent, efficient, and cost-effective ways to safeguard metals is through the use of inhibitors to reduce corrosion [25].

Microbial biofilm based inhibition

One of the three potential methods that Zuo (2007) outlined for preventing biofilm-induced metal corrosion is the (1) Microbial degradation of corrosive chemicals. (2) The generation of antimicrobials by non-corrosive bacteria, which inhibits the growth of germs that cause corrosion [37]. (3) The overproduction of EPS by non-damaging microbes, which might lead to the construction of a protective layer.

An electrodeposited Zn-Ni-Chitosan coating on steel was tested by Zhai *et al.,* (2019) for its ability to inhibit the growth of SRB and *Escherichia coli*. Researchers discovered that Zn-Ni-chitosan coatings significantly reduced corrosion rates and inhibited SRB when compared to Zn-Ni alloy coatings [38].

They also compared the *E.coli* attachment to coated material and found that chitosan enhances antibacterial properties. Carbon mild steel corrosion inhibition by *Bacillus subtilis* biofilm was investigated. Based on the previous studies, it is concluded that beneficial bacterial biofilm secretes gramicidin S that inhibits the growth of SRB and reduces the corrosion rate of mild steel [1].

Plant and algal extract based inhibition

Many of the chemicals employed as corrosion inhibitors in modern manufacturing processes are extremely harmful to both people and the environment. Enzyme processes can be disrupted and certain vital organs like kidneys and liver can be damaged by these inhibitors. Paul and Koley (2016) discovered that papaya seeds, a vegetable waste product, effectively inhibits acid corrosion of low-carbon structural steel [39].

CS can have its acid corrosion reduced by using synthetic organic inhibitors such as phenylthiourea, pyridine, and quinolone. According to a research, certain heterocyclic chemicals can effectively prevent corrosion [40]. It has also been found that proteins from animals and plant extracts can reduce corrosion [41]. An earlier study looked at how a handful of environment friendly inhibitors like garlic, yeast, pepper, and coffee could prevent CS from corrosion. Researchers have shown that these environment friendly inhibitors may significantly reduce acid corrosion on mild steel, with surface adsorption rates ranging from 70 to 90% [42].

The anti-corrosion properties of watermelon extract against mild steel in HCl and H_2SO_4 solutions have been studied. Watermelon extract has an inhibitory effect that grows as its concentration rises [43].

A composite of zinc oxide and copper oxide nanoparticles on a CS surface was created by Sadek *et al.,* (2019) using brown algae extract [44]. The anti-biofilm and anti-adherence capabilities of these nanoparticle polymers were examined against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Pseudomonas mirabilis*. The use of nanoparticles to inhibit biofilm formation on CS coupons significantly reduced biofilm formation, according to SEM surface examination. According to the findings, the environment friendly nanocomposite might be utilized for several purposes, including preventing biofilm formation, inhibiting biocorrosion, and preventing corrosion.

Metal coating-based inhibition

Galvanization is a corrosion prevention technique that involves coating CS or any other metal or alloy with metals such as zinc, copper, nickel, cobalt, or aluminum. There are two methods for galvanization: hot galvanization and cold galvanization. It was the first study to examine the corrosion behavior of mild steel using the newly developed cold galvanizing process. Research by Chavan *et al.,* (2013) indicated that cold sprayed zinc coatings are thick and dense, effectively protecting mild steel substrates against corrosion [45].

According to earlier research, chitosan's amino groups are able to compromise bacterial membrane integrity, leading to bacterial mortality [46]. Chitosan exhibits biocidal properties, which have led to its use as a composite material in various coatings [47, 48]. Chemical deposition and electrodeposition can be used to create coatings that have antibacterial characteristics, as previously described [49].

In addition, Li *et al.,* (2013) found that phosphate, hydroxyapatite, Ag or ZnO nanoparticles, and chitosan may be combined to create coatings with enhanced antibacterial characteristics[33]. Under microbiological corrosive circumstances, the Zn-Ni alloy coating on stainless steel was shown to be more susceptible to damage. Electrodeposition of Zn-Ni alloy onto chitosan resulted in Zn-Ni-chitosan coatings, which effectively addressed this issue.

Conclusion

Over time, research has enabled the development of advanced, nature-inspired, economical, and efficient remedies for MIC. Approaches like metal coating, biofilm-based inhibition, and natural extracts offer promising solutions. These methods provide balanced control of biocorrosion without the harmful side effects of earlier techniques. Preventing MIC is crucial to avoid significant industrial and economic losses. Natural antimicrobial extracts and protective metal coatings show strong potential for future applications. Their reliability makes them suitable candidates for effective corrosion control strategies. In coming years, more accurate solutions to biocorrosion are anticipated. Researchers suggest cold galvanization of CS as an effective method. This approach has already shown success in reducing corrosion in stainless steel. If proven effective, CS could replace costly metals in industries due to its affordability.

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