

Microorganisms in Structural Materials Biodegradation and Microbiological Corrosion

Subjects: Engineering, Marine

Contributor: M. Saleem Khan, Ke Yang, Zifan Liu, Lujun Zhou, Wenle Liu, Siwei Lin, Xuelin Wang, Chengjia Shang

Microbiologically influenced corrosion (MIC) is the process of material degradation in the presence of microorganisms and their biofilms. This is an environmentally assisted type of corrosion, which is highly complex and challenging to fully understand. Different metallic materials, such as steel alloys, magnesium alloys, aluminium alloys, and titanium alloys, have been reported to have adverse effects of MIC on their applications. Though many researchers have reported bacteria as the primary culprit of microbial corrosion, several other microorganisms, including fungi, algae, archaea, and lichen, have been found to cause MIC on metal and non-metal surfaces. However, less attention is given to the MIC caused by fungi, algae, archaea, and lichens.

Keywords: microorganisms ; microbial degradation ; microbiologically influenced corrosion and biofilms ; structural materials

1. Introduction

The process of material deterioration by the direct or indirect involvement of various microscopic microorganisms is called microbiologically influenced corrosion (MIC). MIC is also termed as microbial corrosion, bio-corrosion, and microbially induced corrosion. In 1891, Garret, for the first time, discussed MIC when he found degradation of lead-covered cables by microorganisms ^[1]. Later on, in 1910, Gaines reported the corrosive activities of microorganisms by relating the sulphur present in the corrosion product with the activities of microbes ^[2]. However, more attention was paid to this problem in the middle of the last century, and intensive research was conducted, reporting the involvement of microorganisms in the deterioration of various materials ^[3].

MIC is the main cause of localized corrosion, including pitting corrosion, crevice corrosion, and stress corrosion cracking. Microorganisms become attached to the material surface, secrete extracellular polymeric substances (EPS), and form a biofilm, usually growing in the shape of a continuous sheet, sludge, or tubercle ^[4]. The name biofilm was coined in 1978 and defined as a matrix enclosing bacterial cells adherent to each other or to surfaces and interfaces ^{[5][6]}. Biofilms formed by corrosive microbes have been considered a topic of interest since 1943 ^[7]. Different factors, such as the type of microorganisms, surface morphology, chemical composition of the medium, and hydrodynamics, affect biofilm formation on material surfaces ^{[8][9]}.

EPS is a highly important component of a biofilm, performing the function of glue, keeping microorganisms together in a safe sheath where they can securely grow and proliferate in different shapes. MIC cooperates in the process of wear, cavitation, and erosion, triggering the peeling of the material surface. Since microorganisms usually colonize the material surface, they are more aggressive in producing pits on the surface, which is a worse form of corrosion compared to uniform corrosion ^{[10][11]}. Pits are usually initiated beneath the biofilm, attributed to the secretion of corrosive metabolites and the formation of concentrated cells.

2. Bacteria

Most bacteria are unicellular microorganisms and are frequently present in various environments ranging from soil to water, acidic hot springs, and radioactive waste products ^[12]. This group of microorganisms can survive at temperatures ranging from -10 °C to 100 °C and pHs from 0 to 10.5. The oxygen concentration needed for their growth is 0 to saturated medium, and the pressure required is from vacuum to 31 MPa. Some bacteria are extremely halophilic, living in a salt concentration of 30% (parts per billion). Bacteria that increase the corrosion process are observed to have good growth at a temperature range of 15 °C to 45 °C and pHs of 6–8 ^[13].

Bacteria have the ability to accumulate on a metal surface and establish a biofilm, which contains live and dead bacterial cells, extracellular polymeric substances (EPS), corrosion products, as well as organic and inorganic debris. The percentage of the corrosion products and EPS in a biofilm is about 75%–95%, while 5%–25% of a biofilm is made up of bacterial cells [14][15]. Biofilm formation leads to gradients of pH and oxygen concentration at the metal/biofilm interface, resulting in severe localized corrosion attacks, such as pitting, crevices, and stress corrosion cracking [16][17].

Based on oxygen use, bacteria are further divided into aerobic bacteria, anaerobic bacteria, facultative anaerobe, and micro-aerophilic bacteria. According to the published research, bacteria live both in aerobic and anaerobic environments and have the ability to enhance the bio-deterioration of metallic and non-metallic materials; however, it has been reported that anaerobic corrosion is more destructive compared to aerobic corrosion [18]. Anaerobic bacteria, including iron-reducing bacteria (IRB), acid-producing bacteria (APB), iron- and manganese-oxidizing bacteria (IOB, MOB), and sulphate-reducing bacteria (SRB), are reported to have detrimental effects on the properties of metals. Among them, SRB have been considered to play a key role in the process of corrosion [19][20]. SRB usually use SO_4^{2-} as a terminal electron acceptor for energy generation in their metabolism, which indirectly contributes to the accumulation of corrosive sulphide and organic acid end-products, causing localized pitting corrosion of metals. Different steel alloys have been reported with severe corrosion rates in the presence of SRB [14][21].

The iron sulphide (FeS) formed during this process works as a catalyst, promoting the reduction of protons on the material surface, which increases electron transfer, resulting in fast dissolution of the metal. Gu et al. proposed another theory called the bio-catalytic cathodic sulphate reduction (BCSR) theory [22]. The BCSR theory postulates that in MIC caused by SRB, sulphate works as a cathode while iron works as an anode. With the help of a biocatalyst, sulphate consumes the electrons released during iron oxidation and becomes reduced [22][23].

3. Fungi

Fungi are eukaryotic organisms, such as yeast, moulds, and some well-known mushrooms. Contrary to bacteria, fungi are heterotrophs that secrete digestive enzymes into the surrounding environment and absorb dissolved molecules for their nutrition. Fungi can survive and grow in an environment highly deficient in water. Two species of this group, *Aspergillus* and *Penicillium*, have been found to tolerate very high and low pHs (above 12 and below 2) in their environment [24].

The involvement of fungi in MIC has been reported. Alekhova et al. found degradation of aluminium alloys by fungi-induced MIC on the Mir Space Station [25]. Carbon steel and aluminium alloys exposed to hydrocarbon fuel have been found to have an increased corrosion rate caused by fungi [26]. Videla et al. clarified the MIC mechanism in a fuel/water system as follows: (1) organic acidic metabolites locally increase the proton concentration, (2) metabolites of microorganisms decrease the surface energy of the interface passive oxides film to electrolytes, (3) the presence of microorganisms increases the oxidizing properties of the medium, thus increasing the chances of pitting corrosion, (4) microorganisms utilize corrosion inhibitors from the medium, and (5) adhesion of microbes speeds up the dissolution of metals [26].

Metabolically, fungi are highly diverse microorganisms that are able to obtain nutrition from the degradation of various organic materials, such as polymeric organic compounds and hydrocarbons. Some fungi produce organic compounds, including organic acids and complexants, which affect the properties of metals [27][28]. Fungus-induced degradation of the coatings and underlying metals has been reported in several studies [29][30].

It has been stated that fungal-induced corrosion of metallic materials and coatings is associated with the production of organic acids [31]. Fungal degradation of aluminium has attracted more attention from researchers due to its impact on the integrity of aircraft [32]. Damage to aircraft integrity caused by fungal biofilms has been reported on several occasions [32]. Fungi degrade organic materials, such as lubricants, cladding, and jet fuel, and generate organic acids [32][33][34][35].

4. Algae

Algae are unicellular aquatic microorganisms and are able to produce their own food by the process of photosynthesis. Algae are not closely related to each other in an evolutionary sense. For instance, they can live as single-cell microscopic algae or can be found in macroscopic and multicellular forms, which exist in the form of a colony.

Besides their adverse effects on water quality, these microorganisms considerably influence the corrosion process of engineering materials in marine environments [36]. The attachment of single-cell algae (diatoms) to stainless steel surfaces has been observed by different researchers [37][38][39][40][41]. It was found that the colonization of diatoms on a stainless

steel surface was more active and fast in the light compared to the dark ^[42]. The process of photosynthesis plays a key role in enhancing corrosion by changing the surface state (such as dissolved oxygen and pH) of metallic materials ^{[43][44]}. Degradation due to algal biofilms has been reported for metallic materials.

Furthermore, through ecological studies, it has been specified that algae and bacteria living together in a fouled part of the material maintain an extremely close association with each other ^{[45][46]}. A study on symbiosis-induced biofouling in a marine micro-fouling system, where bacterial biofilms form the underlying layer and microalgae work as the elementary biofouling layer, has been reported ^[47]. It was found that the corrosion rate of carbon steel (Q235) immersed in a culture medium inoculated with the bacterium *Bacillus altitudinis* was 2.2 times higher than that in a sterile medium. Meanwhile, the corrosion rate of Q235 steel in the presence of both *Phaeodactylum tricornutum* and its symbiotic bacterium *B. altitudinis* was about 7 times higher compared to the effects of the individual bacterial strain.

Microalgae have been found to secrete EPS, which further triggers the corrosion process by complexation with metals ^[36]. Multispecies biofilms are able to form stable micro-consortia that strengthen the three-dimensional structure of the adhesive layer and accelerate biofouling.

5. Archaea

Archaea are a group of microorganisms originally believed to be bacteria and called archaebacteria owing to their physical similarities. But later, through genetic analysis, it was found that archaea are different organisms from bacteria and eukaryotes. This analysis earned them their own domain in the three domain classification originally proposed by Woese in 1977, alongside the eukaryotes and the bacteria ^[48]. In addition to bacteria, archaea are also an important part of the microbial system ^[49].

Archaea are broadly distributed in the world. The majority of archaea have the ability to inhabit and thrive in some extreme environments, such as those with enormously low oxygen levels, high acidity, high salinity, and very high temperatures, which provide archaea with distinctive cell structures and metabolic characteristics ^[50].

Archaea have been found to cause MIC of metallic materials ^{[51][52]}. For instance, the presence of methanogenic and thermophilic archaea has been reported in high-temperature, anaerobic oil production fluids collected from the North Sea and North Slope of Alaskan oil fields ^[53]. Both the methanogenic and thermophilic archaea found in the above-mentioned locations were reported to have corrosion triggering effects ^{[54][55]}. It was stated that the methanogenic archaea (*Methanothermobacter* sp.) used carbon steel as an energy source and accelerated its corrosion process, while the thermophilic archaea (*Thermococcales* sp.) enhanced carbon steel degradation through its iron reduction ability as well as the secretion of fatty acid metabolites. Furthermore, Usher et al. observed the colonization and corrosive effects of methanogenic archaeal communities on a carbon steel surface ^[56].

Methane-producing microbes trigger the corrosion process of iron-containing metals. H₂ has been considered as an electron shuttle between Fe(0) and methanogens. Some of the methanogens, such as the *Methanosarcina acetivorans*, catalyse direct electron transfer from metal-to-microbe to support methane production ^[57]. In *M. acetivorans*, deletion of the gene for multiheme eliminated methane production from Fe(0) by the outer-surface c-type cytochrome *MmcA*, which is consistent with the basic role of *MmcA* in other forms of extracellular electron transfer.

6. Lichens

A lichen is actually two organisms working as a single stable unit. Lichens are plant-like organisms that consist of a symbiotic association of algae or cyanobacteria and fungi. Lichens have about 20,000 known species worldwide that have been found surviving in different environmental conditions. This is a diverse group of organisms, having the ability to colonize a wide range of surfaces, including tree bark, exposed rock, biological soil crust, and other metallic and non-metallic materials in various environments. Through metabolism, lichens discharge different kinds of organic molecules, such as oxalic acid and polyphenolic acids, indicated as "lichen acids", that have been confirmed to play a vital role in weathering and neogenesis ^[58].

The deterioration caused by lichens occurs at the interface between the lichen and metal substrate. This interface has been considered a place of significant physical and chemical activities, presenting a very complex heterogeneity in which both primary and secondary minerals, organic acids, and compounds, as well as all kinds of organisms, including lichens, free-living fungi, free-living algae, and bacteria, are involved ^[59].

The deterioration of ceramics due to lichen development on their surfaces has been reported [60]. It has been stated that the oxalic acid released by lichens was the main reason for ceramic deterioration and aging [60]. The deteriorating effects of lichens on natural rocks and building stones have been recognized long before [61][62]. The mycobiont of lichens, which is always in close contact with the substrate, makes them able to cause deterioration. Bio-deterioration by lichens is, in general, attributed to a combination of physical mechanisms (such as the pressure exerted by the expansion and contraction of thalli, rhizine adhesion, and hyphal penetration) and chemical factors, which include the interaction of carbon dioxide, organic acids, and lichen substances with complex properties [63].

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