

Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences

Available online at www.jcbps.org

Section B: Biological Sciences

CODEN (USA): JCBPAT

Review Article

Mechanism of Microbial Corrosion: A Review

¹Imo, E.O.*, ²Ihejirika, C.E., ¹Orji, J.C., ¹Nweke, C.O., ¹Adieze, I.E.,

¹Department of Microbiology, Federal University of Technology, P.M.B. 1526, Owerri, Imo State Nigeria.

²Department of Environmental Technology, Federal University of Technology, P.M.B. 1526, Owerri, Imo State, Nigeria.

Received: 08August2016; **Revised:** 21 August 2016; **Accepted:** 29 August 2016

Abstract: The role of microorganisms in microbial corrosion is to constantly create surface conditions that favor the maintenance of cathodic and/ or anodic reactions. There is no generally accepted mechanism of microbiologically influenced corrosion (MIC). Instead various mechanisms of MIC that reflects the variety of physiological activities carried out by different microorganisms have been reported and some have been analyzed better than others. Studies have shown that corrosion of metals in the presence of microorganisms is as a result of the microbial modifications of the environment near the metal surfaces. Microorganisms can influence corrosion processes through their direct actions on anodic and cathodic reactions, formation of biofilms, corrosive media in the form of metabolic by-products and modifications on resistance films on metal surfaces among others.

Key words: biocorrosion, microorganisms, biofilms, mechanism

INTRODUCTION

An important aspect of quantifying mechanism of MIC is to demonstrate how the microbial reactions interfere with the corrosion processes¹. There is no universal mechanism of MIC¹⁻³. Many mechanisms exist and some of them have been described and quantified better than others¹. Beech and Gayland,

2observed that mechanical and structural factors all play a role, both biotic and abiotic in nature, and these may all work in concert to cause and sustain MIC.

One of the first proposed mechanism for MIC, the cathodic depolarization theory- also known as the classical theory –was put forth in 1934 by Kuehr *et al.*⁴, in order to explain the unexpected high rate of corrosion failure encountered on buried cast iron pipelines in the Dutch countryside^{5,6}. Beech and Gaylarde² stated that in anaerobic conditions where sulfate-reducing bacteria (SRB) thrive, hydrogen ions typically serve as the terminal electron acceptor at the cathode in a corrosion reaction. The reduced hydrogen would then adsorb onto the metal surface, polarizing it. According to the classical theory, the role of SRB was to consume this cathodic hydrogen by means of enzyme hydrogenase, catalyzing the recombination of the adsorbed atomic hydrogen gas, thus depolarizing the cathode⁵.

According to Beech and Gaylarde², various mechanisms of biocorrosion, which reflect the variety of physiological activities carried out by different types of microorganisms, have been identified. And the diversity of these mechanisms is such that it is difficult to expect that a single unified concept can be conceived to bring them all together¹. Studies show that accelerated corrosion of metals in the presence of microorganisms stems from the microbial modifications to chemical environment near metal surfaces⁷⁻¹⁰. Such modifications depend, of course, on the properties of the corroding metal and on the microbial community structure of the biofilm deposited on the metal surface^{3, 11-14}.

The conclusion that there are many mechanisms of MIC, rather than a single one, is generally accepted in the literature and was exemplified by the paper by Starosvetsky *et al.*¹⁵ who concluded that to uncover MIC in technological equipment failures require an individual approach to each case, and that an assessment of the destructive role of the microorganisms present in the surrounding medium is possible only by analyzing and stimulating the corrosion parameters found in the field¹⁶.

Quite concisely, Beech *et al.*⁷ described MIC as a consequence of coupled biological and abiotic electron-transfer reactions i.e. redox reactions of metals enabled by microbial ecology. According to Lewandowski and Beyenal¹, an important aspect of quantifying mechanism of MIC is to demonstrate how the microbial reactions interfere with the corrosion processes and, based on this, identify products of these reactions on the surfaces of corroding metals using appropriate analytical techniques. The existence of these products, associated with the increasing corrosion rate, can then be used as evidence that the specific mechanism of MIC is active. The action of microorganisms in the processes of corrosion can occur through one or more of the following: 1.direct influence on the speed of anodic and cathodic reactions 2.formation of biofilms that enable the emergence of differential aeration cells 3.formation of corrosive media due to the acids generation 4.modification on the resistance of films existing on the metal surfaces caused by products of microbial metabolism.

Direct influence on the speed of cathodic and anodic reactions: The existence of a biofilm can impede the diffusion of chemical species-both into and out of the biofilm-thus producing localized chemical environments that are significantly different from the bulk³. These localized environments can in turn, greatly affect the underlying corrosion and also directly influence the speed of cathodic and anodic reactions. By inhibiting the diffusion of the corrosive chemicals away from the metal surface, the biofilm can effectively act as a concentration multiplier¹⁷. The H₂S generated by SRB in anaerobic region is potentially made more potent when encapsulated beneath a biofilm than otherwise.

In addition to concentrating the H_2S , the biofilm can also concentrate the corroded ferrous ions, a key factor in MIC. Past studies by Lee and Characklis¹⁸ have shown that the presence of ferrous ions is a major factor for MIC to occur on iron or steel in an aqueous environment. They grew a pure culture of SRB in the absence of ferrous ions and little to no corrosion was observed despite a high level of microbial activity.

Formation of biofilms that enables the emergence of aeration cells: Microbial biofilms of different composition and thickness develop on all surfaces in contact with aqueous environment¹⁹. According to Lewandowski and Beyenal¹ metal corrosion can be brought about by the formation of differential aeration cells resulting from different concentrations of oxygen occurring at different locations on the metal surface. The effect of different concentrations of oxygen at different locations on the metal surface can be caused by the active consumption of oxygen by microorganisms in biofilms not uniformly distributed on the metal surface. It can also be caused by passive mechanism in which oxygen access to some areas is physically obstructed. For example, as the growth of microorganisms continues on the metal surface and the depth of the biofilm layer increases, there will be little penetration of oxygen in the biofilm layer against the metal surface. Anaerobic bacteria like SRB can thrive in the deep layers of the biofilm where there is limited oxygen. Some of these anaerobic organisms are capable of metabolizing carbon from stainless steel and some produce nitric, sulfuric, or other organic acids that may further accelerate corrosion processes.

According to Lewandowski and Beyenal¹ if the oxygen concentrations at two adjacent locations on a metal surface are different, then the cell potentials at these locations will be different as well. The location where the oxygen concentration is higher will have a higher potential (more cathodic) than the location where the oxygen concentration is lower (more anodic). The different in potential will give rise to current flow from the anodic locations to cathodic locations and to the establishment of corrosion cell and all these can be caused by the presence of biofilms. This is the mechanism of differential aeration cells, and the prerequisite to this mechanism is that the concentration of oxygen vary among location^{20,16,21}. Many measurements using oxygen microsensors have demonstrated that oxygen concentrations in biofilms can vary from one location to another²².

Formation of corrosive media due to acids generation: This mechanism of MIC is closely related to the type of microorganisms active in the biofilm and to their metabolic reactions^{2,23,24}. Most heterotrophic organism including bacteria and fungi secrete organic acids during fermentation of organic substrates and as metabolic by products. Little *et al.*¹⁹ reviewed that organic acids may force a shift in the tendency for corrosion to occur. They observed that the impact of organic acid is also intensified when they are trapped at the biofilm/ metal interface. For example, acetic acid from *Clostridium aceticum* and sulfuric acid produced by sulfur oxidizing bacteria (SOB) such as *Thiobacillus thiooxidans*, are known contributors to corrosion. Another example is sulfate-reducing bacteria (SRB) corrosion^{25, 26}. According to Javaherdashti²⁷, the corrosion of mild steel caused by SRB is probably the most celebrated case of MIC because it provides a direct, and easy to understand link between microbial reactions and electrochemistry. He noted that despite the progress in research and understanding of the process, little has been done to prevent or stop this type of corrosion once initiated, and SRB corrosion is still considered the main type of MIC. For example, Bolwell in²⁸ demonstrated that engine failures in gas turbines were caused by SRB growing in the seawater lubricating oil coolers and contaminating it²⁸.

Sulfate-reducing bacteria produce hydrogen sulfide H_2S by reducing sulfate ions²³. According to the mechanism that was proposed by Von Wohlzogen Kuhr in 1934, SRB oxidize cathodically generated hydrogen to reduce sulfate ions to H_2S , thereby removing the product of cathodic reaction and stimulating the progress of the reaction²⁹.

Modification on the resistance of films existing on the metal surfaces: Biofilms facilitate the modifications of the protective films on metal surfaces²³. For example, copper-nickel alloys in seawater can be colonized by bacteria and other organisms after extended periods of exposure despite their perceived anti-fouling properties. Videla³⁰, explained that in such a situation, biofilm formation is conditioned by the chemical nature and distribution of inorganic passive layers and by the elemental composition of the substratum³¹. Studies also showed that, after several months of exposure, bacteria can be found entrapped between layers of corrosion products and EPS in a layered structure. Biofilm detachment might facilitate the removal of inorganic passive layers, resulting in formation of crevices and patchy distribution of the biofilm.

Videla and Herrera²³ observed that stalked ciliates, seen sometimes as the predominant biofouling species, can facilitate passive layer detachment through adhesive effects developed at the fixation points of pseudopodia and assisted by water flow velocity. According to Hamilton³², the formation of FeS on metal surface can bring about a local decrease in pH that enhances the breakdown of passive film, which can lead to the activation of corrosion cells between the metal surface as anode and FeS as cathode.

CONCLUSION

The capacity of some microorganisms to produce corrosive metabolic by-products makes them a real threat to the stability of metals. Despite the increased recognition and documentation of corrosion of metals and industrial materials as a result of MIC, the establishment of a specific mechanism of biocorrosion has remained elusive to researchers. This can be attributed to the complexity of the metal/microbe interaction. Studies have shown that biotic and abiotic factors including chemical, mechanical, structural and microbial enzymes and metabolites may all work in concert to cause and sustain MIC. Hence it must be emphasized that environmental conditions and the microbial species present may dictate the predominant mechanism. It is therefore important that a multi-disciplinary approach comprising metallurgists and microbiologists should be involved in designing and developing models that will facilitate better understanding of microbial interactions with metal surfaces and corrosion processes.

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Corresponding author: Imo, E. O.

Department of Microbiology, Federal University of Technology, P.M.B. 1526, Owerri,
Imo State Nigeria.