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Role of Microorganisms in Corrosion Induction and Prevention

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Authors' contributions

This work was carried out in collaboration between both authors. They designed the study, wrote the protocol, wrote the first draft of the manuscript and managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Microbiologically-influenced corrosion (MIC) is defined as the deterioration of metals as a result of metabolic activities of microbes. The biological harmful activities modify local chemistry and render it more corrosive to the metal. The aerobic iron and manganese bacteria are mainly responsible about the accelerated pitting attacks of stainless steel, however the anaerobic sulfate reducing bacteria (SRB) are responsible for most highly corrosion damages to offshore steel structures. Most MIC takes the form of pits that form below the colonies of living organic matter and mineral and the deposits of biological origin. Stainless and carbon steel tanks, pipelines, heat exchangers, fuel storage tanks are mainly affected by MIC. On the other hand, other beneficial microorganisms play a major role for protecting these surfaces from corrosion via different mechanisms including biofilms formation. The aim of this review is to present a spotlight on the history and the role of microorganisms on the induction and prevention of corrosion. This includes corrosion inhibition mechanisms employing beneficial microorganisms with special reference to microbial biofilms to avoid the dramatic economic loss due to corrosion. On the contrary, different types of harmful microorganisms included in corrosion are also discussed including iron and sulfur reducing bacteria.

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1. INTRODUCTION

Corrosion is a natural process, which converts a refined metal to its oxide or hydroxide or another compound which is a more stable form, or can be generally defined as the gradual destruction of materials by microorganisms or by chemical and electrochemical reactions with their environment. Different types of corrosion were reported such as galvanic [1], pitting [2], uniform [3], erosion [4], lamellar [5], crevice [6] and microbial corrosions [7]. Microbial corrosion is also called microbiologically-influenced corrosion (MIC) or biological corrosion. MIC is defined as this type of corrosion that is caused by the presence and activities of microorganisms or the deterioration of metals as a result of metabolic activities of microbes. Both harmful (corrosive) [8-10] and beneficial (potentially anti-corrosive) [11-13] microorganisms play a major role in inducing and preventing microbial corrosion respectively. Many investigators reported the invention of a sol-gel that could be used as a coat on metal surfaces and that could contain protective organisms; these organisms secrete antibacterial and antifungal substances able to fight aggressive agents. Microbiologically induced corrosion (MIC) is the most misunderstood of all corrosion processes. In the past, internal corrosion problems in underground storage and associated pipeline systems were primarily thought to be due to oxygen, hydrogen sulfide, and carbon dioxide. Microbial corrosion was almost completely ignored. Recently many investigators reported the antagonistic effect of beneficial bacteria against MIC. Gana et al. [14] indicated the antagonistic potential of nonpathogenic Bacillus strain B21 against sulfate-reducing bacteria (SRB) consortium, as a biocontrol agent to fight corrosion in the oil industry. Growth of SRB in co-culture with bacteria strain B21 antagonist exhibited decline in SRBgrowth, reduction in production of sulfides, with consumption of sulfate. In this connection, Bano and Qazi [15] reported an independent bacterial secretion of substances expressing protective role against MIC. Antagonistic activity of non-corrosive *Bacillus* isolates designated as SN-8 and SS-14 was evaluated against mild steel corrosion influencing, *Bacillus cereus*-SNB-4 and *Bacillus coagulans*-SS-5, respectively. Their results indicated that this activity resulted to the reduction of the intensity of MIC besides the protection of mild steel from abiotic corrosion indicating that the selection of microbial strain activities serve as bio-control strategies for protecting metals from corrosion. The aim of this review is to present a spotlight on the role exerted by harmful and beneficial microorganisms in induction and prevention of corrosion.

2. HISTORY OF MICROBIAL CORROSION

The first observation in corrosion was reported by Austin (1788), who noticed that neutral water become alkaline when it acts on iron, followed by a published paper by Thenard (1819) in which he suggested that corrosion is an electrochemical phenomenon. Davy (1824) proposed a method for sacrificial protection of iron by zinc. In 1829, Hall established that iron does not rust in the absence of oxygen. De la Rive (1830) suggested the existence of microcells on the surface of zinc. Later Faraday made many investigations between the period from 1834 to 1840 which are the most important contributions, he indicated evidence of the connection between chemical action and the generation of electric currents and his two famous laws of electrochemical action are the basis for calculation of corrosion rates of metals [16]. The first reported suggestion that microorganisms might be involved in corrosion was made by Garrett (1891), in which he suggested that the interaction of bacterial metabolites and products with a lead cable led to corrosion of cable material. Whitney (1903) provided a scientific basis for corrosion control based on electrochemical observation. Previous studies of investigators led Evans (1923) to provide a modern understanding of the causes and control of corrosion based on his classical electrochemical theory.

In 1934 Von Wolzogen Kuhr and Vander Klugt identified the sulfur reducing bacteria (SRB) for the first time responsible for metal corrosion under anaerobic conditions and proposed the mechanism of anaerobic corrosion which is referred as the cathodic depolarization theory. They reported that this cathodic depolarization mechanism is achieved by the metabolic oxidation of hydrogen from the metal surfaces by the SRB with the formation of FeS as the main product. This theory was supported by many investigators [17-20]. Booth and his coworkers were able to show a direct relationship between the hydrogenase activity and the cathodic depolarization activity and weight loss of mild steel coupons.

Later, many investigators suggested that hydrogen sulphides and iron sulphides produced from the activity of SRB [21,22] were also directly involved in the cathodic depolarization [23]. However, others reported that the conversion of sulphides to the highly corrosive elemental sulphur might be the main cause of high corrosion rates [24-27]. On the contrary, Iverson [28,29] has introduced another explanation for the anaerobic corrosion process by the sulfur reducing bacteria through the production of highly corrosive phosphide instead of sulphides. Many hypothesis were reported to elucidate the mechanism through which SRB can cause corrosion, however none can explain the high corrosion rates observed in the field. Hamilton [30,31,32] reported that corrosion in general and microbial corrosion in particular are complex phenomena and he summarized the relationship between microbial corrosion and SRB.

Many investigators interested in hydrogen metabolism and hydrogenase in SRB reintroduced the cathodic depolarization theory [33-36]. After few years Pankhania [37,38] reported that *Desulfovibrio vulgaris* is unable to grow in acetate plus sulfate medium unless hydrogen is provided as an energy source. The demonstration of the growth of *D. vulgaris* in acetate medium was clarified later, where the only source of hydrogen is that from a mild steel electrode. Recent contributions of the three pioneers Evans [39], Uhlig [40] and Fontana [41] and their published books led to considerable progress towards the modern understanding of corrosion. Nowadays the subject of corrosion is interdisciplinary and involves all basic sciences, such as chemistry, physics, biology and all disciplines of engineering, such as electrical, civil, mechanical, and metallurgical engineering.

3. MECHANISM OF BIOCORROSION ACTION

Generally, one of the possible mechanism to elucidate biological corrosion processes, is that microorganisms can produce electron flow, or modify the local environment changing it to a corrosive one. The inert deposits produced by microorganisms below the surface of a metal shield this area form electrolyte and initiate a differential aeration cell. The area under microbial colonies becomes the anode and the metallic area around this area encourages the reduction of oxygen and become the cathode. By this procedure the metal is dissolved under the area of microbial deposits producing a pit. The pit area resulted depending mainly on the microbial colony density. In case of sulfur reducing bacteria (SRB) and under anaerobic condition they reduce sulfate producing sulfide and oxygen. Then the sulfide ions combine with ferrous ions to form iron sulfide and the metal surface is dissolved. The produced oxygen reacts with hydrogen to form a water molecule.

The initial process of microbial corrosion process starts by the combination of a metal atom (M) with hydroxyl negative ions (OH^-) of water forming metal hydroxide (MOH) leaving proton (H^+) ions. This ties up the oxygen and renders the local area more concentrated with H^+ (acid) ions. If chloride or other similar ions are around, the process is accelerated [42,43].

4. CORROSION INHIBITION EMPLOYING BENEFICIAL MICROORGANISMS

The dramatic economic loss due to corrosion encourages scientists to search for a way to stop and prevent corrosion using beneficial microorganisms biofilms. Three mechanisms were proposed for the action of these microorganisms, the first includes the removal of corrosive oxygen by bacterial activities through aerobic respiration, the second mechanism initiates by the growth inhibition of corrosion-causing bacteria, such as sulfate reducing bacteria (SRB) by producing some antimicrobials within biofilms. The third proposed mechanism is made by generation of a protective layer from some specified bacteria, such as *Bacillus lichiniformis* which produce a sticky protective layer of γ-poly-glutamate on aluminum surface [44]. Zuo et al. [45], reported that biofilms were used to produce gramicidin S, a cyclic decapeptide in order to inhibit corrosion-causing. The growth of two Gram positive and Gram negative bacteria namely *Desulfosporosinus orientis* and *Desulfovibrio vulgaris* respectively was shown to be inhibited by supernatants of the gramicidin-S-producing bacteria and also by purified gramicidin-S. Mass loss measurements and Electrochemical impedance spectroscopy showed that the protective beneficial biofilms decreased the corrosion rate of mild steel by 2- to 10-fold when challenged with the natural SRB. Scanning electron microscope and reactor images revealed that SRB attack was inhibited by protective biofilms that secrete gramicidin S.

Wadood et al. [46] reported that *Bacillus subtilis* strain S1X and *Pseudomonas aeruginosa* strain ZK have the ability to inhibit corrosion of stainless steel 304 surface in a minimal salt medium with 1.5% NaCl as a corrosive agent. They illustrated this effect by the development of a protective biofilm on the metal surface. In this connection, Rajasekar and Ting [47] demonstrated that the corrosion potential (E_{corr}) and pitting potential (E_{pit}) were lower in the presence of the previously mentioned bacteria in an organic medium when compared to an organic one. They also added that many salts such as nitrates, phosphates were found to accelerate the formation of bacterial metabolites and consequently led to the enhancement of corrosion resistance.

Generally biofilm contains a large number of communities of microorganisms attached to a surface or interface. The initiation of biofilm formation starts by some bacterial strains in response to the presence of oxygen or nutrients or both. This stage followed by transition of biofilm from free-living microorganisms to firmly attached biofilm cells with the production of secondary metabolites and significant increase in resistant from chemical, biological or biological attack. The most unique bacterium industrially is *Bacillus subtilis* in forming a rough biofilms at the air-liquid interface rather than on the surface of a solid phase in a liquid, due to the movement of the cell toward or away from O_2. The formation of biofilms by *Bacillus subtilis* and related other bacterial species permit the control of infection by plant pathogens and reduction of mild steel corrosion. Morikawa [48]) supports these findings for using biofilms of *Bacillus subtilis* as a starting step that may lead to a new biotechnology to control harmful biofilms. Other investigators reported another bacterium *Bacillus brevis* 18-3 biofilm capable to reduce corrosion rates of mild steel by inhibiting both the sulfate-reducing bacterium *Desulfosporosinus orientis* and the iron-oxidizing bacterium *Leptothrix discophora* SP-6. When these two bacterial genera were introduced to a non-antimicrobial-producing biofilm control, *Paenibacillus polymyxa* ATCC 10401, a corrosive synergy was created and mild steel coupons underwent more severe corrosion than when only *D. orientis* was present, showing an increase via electrochemical impedance spectroscopy (EIS) (2.3-fold) and a difference via mass-loss measurements (1.8-fold). However, when a gramicidin-S-producing, protective *B. brevis 18-3* biofilm was established on mild steel, a decrease in the corrosion rate by about 20-fold compared with the non-gramicidin-producing *P. polymyxa ATCC 10401* biofilm control. In addition, mass loss for the protected mild steel coupons was (4-fold decrease) which is significantly lower than that for the unprotected ones [49]. In this connection, many other applications of beneficial biofilms are studied including their use in microbial fuel cells [50] and protection of higher organisms against undesirable microorganisms [51]. The following table describes some differences between beneficial and harmful microorganisms (Table 1).

5. TYPES OF MICROORGANISMS INCLUDED IN CORROSION

Two types of single-celled bacteria namely aerobic and anaerobic bacteria. The aerobic bacteria have the ability to use and detoxify oxygen, whereas anaerobic bacteria can survive without the presence of oxygen. Acid producing bacteria [52,53], sulfate reducing bacteria (SRB) [54-58], sulfur oxidizing bacteria [59,60] and iron precipitating bacteria [61] are among those groups of bacteria involved in the bio-corrosion process [62]. In this connection SBR was found to be the most aggressive bacteria in bio-corrosion induction due to the release of corrosive H_2S [63,64]. SBR cause detrimental effect by producing harmful biofilms on metal surfaces in many industrial sectors [65,66]. Many investigators reported that biofilms formation affect anodic and cathodic reactions causing proper conditions for microbial corrosion induction [67,68].

Most of the internal corrosion problems in oil pipelines and storage tanks are mainly due to the role of corrosive bacteria and also to the factors influencing misuse of inhibitors and biocides in pipe line industry [69]. Electrochemical measurements and surface analysis indicated that SRB adhere onto copper surface resulting to the formation of cuprous sulfide. This product besides EPS is very helpful for bacterial adhesion on copper by providing a barrier against copper toxicity. Chen et al. [70] indicated that SRB metabolic activity decreases the anodic area and starts localized corrosion of copper during stationary and exponential phases.

Table 1. Differences between beneficial and harmful microorganisms

Harmful microorganisms	Beneficial microorganisms
Their presence and activities cause the induction of Microbiologically-influenced corrosion (MIC).	Their presence play a major role in preventing and protecting metal surfaces from corrosion.
Aerobic and anaerobic harmful bacteria cause deterioration of carbon steel, stainless steel, aluminum alloys and copper alloys.	Some specified beneficial bacteria exert their protective effect against corrosion through the formation of biofilms or producing a sticky protective layer.
Examples of these harmful bacteria are Sulfate reducing bacteria (SRB), Ferrobacillus ferrooxidans, Acidithiobacillus thiooxidans, Thiobacillus thioparus, T.concretivorus, Leptothrix sp, Desulfovibrio sp., Desulfomonas sp. Gallionella sp., Mariprofundus sp., Pseudomonas sp., and *Shewanella* sp.,	Examples of these beneficial bacteria are *Bacillus subtilis*, *Bacillus lichiniformis*, and *Desulfosporosinus orientis*.
Bacterial corrosion may appear in the form of pitting corrosion.	Beneficial bacteria appear in the form of biofilms or a protective layer.
The highly corrosive effects of some of these bacteria are induced by the production of sulphuric acid, sulfate and H_2S to oxidize iron to iron oxide.	The highly protective effects of these beneficial microorganisms are induced by the secretion of antibiotics (such as gramicidin-S) within the biofilm layer as secondary metabolites of microorganisms.
The possible mechanism to elucidate biological corrosion processes, is that microorganisms can produce electron flow, or modify the local environment changing it to a corrosive one. In case of sulfur reducing bacteria (SRB) and under anaerobic condition they reduce sulfate producing sulfide and oxygen.	The mechanism for microbial corrosion control include formation of protective layers through biofilms, growth inhibition of corrosion causing bacteria by antimicrobials produced within biofilms and finally removal of corrosive agents by microbial physiological activities.

6. BACTERIA RESPONSIBLE FOR IRON CORROSION

Corrosion of iron takes place in both aerobic and anaerobic conditions. The enzymes of filamentous bacteria (sidirophilic) are able to use dissolved iron and reduce insoluble ferric oxide to soluble ferrous hydroxide. The energy obtained by oxidizing soluble ferrous iron are used to produce the insoluble brown ferric iron (rust). *Thiobacillus ferroxidans*, *Gallionella*, *Crenothrix*, *Leptothrix* and *Sphaerotilus* are examples of this type of bacteria [71]. The name of the Genus *Thiobacillus* emerges from its ability also to oxidize inorganic sulfur compounds besides iron. Many other bacteria can corrode iron unaerobically including sulphate reducing bacteria such as *Desuphovibrio* and *Desuphofotomaculum*. The highly corrosive effect of these bacteria can be explained by their production of sulphuric acid, sulfate and H_2S to oxidize iron to iron oxide. *Ferrobacillus ferroxidans* also produces H_2SO_4 and oxidizes iron into iron oxides and hydroxides rust. Locally corrosion usually started by pitting at some points of steel surfaces [72,73].

7. PROTECTION AND PREVENTION OF MIC

MIC can be prevented by regular mechanical cleaning of surfaces, dry storage and treatment with biocides to control the propagations of microorganisms. Protection of steel or concrete against microbial corrosion has become very important task in sewage treatment, municipal pipeline and storage industries. The best solution for protection is by providing a barrier between wastewater and steel or concrete. Coal tar epoxy, ceramic epoxy, solids polyurethane and polyethylene are the most using coatings systems [74]. On the other hand PVC (Polyvinyl Chloride) and coal tar epoxy have been used mainly for concrete substrates. Nowadays there is a great challenge to provide a more reliable and economical coating for the previously mentioned two substrates [75]. Another approach have been also made to eliminate or reduce the source of MIC which include proper design of pipelines and structures, cathodic protection, environment alteration and the use of effective antimicrobial agents [76]. Some of the same techniques are also applied for the prevention of electrochemical corrosion either by cathodic protection using an external voltage source or by breaking the metallic circuit and insulate electrode from electrolyte by means of coating, painting and tapes. The cathodic depolarization is a corrosion control method where the potential of the anode or cathode or both is changed resulting to corrosion protection and minimizing the potential difference. Corrosion protection is achieved when the potential difference is reduced to a minimum. Depolarization is an electrochemical phenomenon that involves the removal or prevention of polarization in a substance or of polarization arising from the field due to the charges induced on the surface of a dielectric when an external field is applied [17,19,77].

Rajasekar and Ting [78] reported the presence of a corrosive bacterial consortium in water samples. The corrosive bacterial effect is due to biosurfactant which contributes to an increase of cell surface hydrophobicity of bacteria and consequently enhanced bacterial adhesion on the copper metal surface in the form of microcolonies due to the accumulation of extracellular polymeric substances (EPS). They also reported that this inhibition can be effectively controlled by the treatment of copper metal surface with bronopol biocide. Other investigators confirmed the adhesion of microorganisms responsible for MIC to copper surface by the excretion of bacterial EPS to form a slime layer (Li et al. [79]). The effect of SRB on corrosion behavior of copper was investigated using electrochemical measurements and surface analysis in seawater (Chen et al. [70]). Results obtained indicate that SRB adhere onto copper surface to form biofilm. This effect of corrosion resulted to the production of cuprous sulfide. Cu_2S and EPS are helpful for SRB by providing a barrier against copper toxicity. The corrosion rate mainly dependant on the bacterial metabolic activity especially during exponential and stationary phases of growth.

8. TYPES OF PROTECTION

8.1 Protection Using Epoxy and Polyurethane Coating

Many investigators reported the utilization of polyurethane coating for protection against microbiologically influenced corrosion (MIC) to achieve continuous protective coating barrier to resist the highly aggressive chemicals such as sufuric acid [80-84]. Diniz et al. [85] investigated organic coatings based on epoxy and polyurethane matrices containing polyaniline doped with dodecyl benzene sulfonic acid (Pani-DBSA). Their results indicated that a decrease in the electrical resistance, increase in capacitance and decrease in open circuit potential. According to these results epoxy based coatings had improved performance when Pani-DBSA was used as pigment; whereas for the polyurethane coatings, Pani-DBSA seems to play an adverse effect. Raman spectroscopy indicated a possible chlorination of the epoxy matrix after 30 days exposure to salt spray chamber.

8.2 Cathodic Protection

This method depends on making the metal surface as a cathode of an electrochemical cell in order to control the corrosion of a metal by maintaining a continual electrical charge on the metal and consequently its dissolution as positive ions is inhibited. The name is introduced to explain the entire metal surface is forced toward the cathodic condition. This method is generally used to protect metal buried structures and other oil pipelines. Many investigators reported another treatment by the use of the corrosion of another active metal such as a piece of aluminum or zinc buried besides the metal to be protected [86-88].

8.3 Sacrificial Coatings

In this procedure, application of a coating of a more active metal to supply negative charge was made. The most common way to protect steel is through coating with a thin layer of zinc, this method is well known as galvanizing. Zinc coating being less noble than iron, so it tends to corrode selectivity. The dissolution of this sacrifying zinc coating produces electrons which concentrate in the iron making it cathodic and consequently preventing its dissolution [89,90].

9. ECONOMIC COST OF MIC

No definite official figure for the economic cost of MIC, but some indication of its importance can be gained from individual companies or sectors of industry. However the costs associated with repairs and replacements are millions of dollars annually (Bibb [91]). Jack et al. [92] estimated that 34% of the corrosion damage experienced by one oil company was related to microorganisms and MIC-related costs of repair and replacement of piping material used in different types of service in the USA were estimated to be around $ 0.5-2 Billion per annum. Booth [93] suggested that 50% of corrosion failures in pipelines involved MIC, while Flemming [94] proposed that approximately 20% of all corrosion damage to metallic materials is microbially influenced.

10. CONCLUSIONS

This review deals with the main role of microorganisms in corrosion induction and prevention. The microorganisms that take place in MIC induce many unique features, the most important being the formation of beneficial biofilms between metal surfaces and the liquid environment leading to many modifications between the metal and solution interface. As a result of these modifications a microbial inhibition of corrosion can be attained by changing the electrochemical behavior of the metal from active to passive. On the contrary different roles of harmful biofilms in enhancing microbial corrosion were mentioned including a) biofilms accumulation form a diffusion barrier for certain chemical species. b) Patchy distribution of biofilms induce differential aeration effects. c) Biofilms facilitate the removal of protecting films when biofilms separated from the surfaces. d) Biofilms interfering with oxidation-reduction conditions at the metal-solution interface. e) Biofilms change the structure of inorganic passive layers by increasing their dissolution and removal from the metal surface.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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