An Outline to Corrosive Bacteria

Maiara C. Moura[*1], **Emmanuel V. Pontual**[1], **Patrícia M. G. Paiva**[1] and **Luana C. B. B. Coelho**[1]

[1]Departamento de Bioquímica, Centro de Ciências Biológicas, Avenida Professor Moraes Rego, s/n, 50670-420, Universidade Federal de Pernambuco, Recife, Brazil.

The metallic corrosion is a spontaneous process that causes damage in almost all sectors of human activity. Among the most affected structures stand out the pipes for oil transportation. The biocorrosion occurs due to the fixation of bacteria, release of metabolites and formation of biofilms that induce or accelerate the corrosion process. Among the groups of bacteria involved in the corrosion process are included: I- EPS-producing bacteria, II- acid-producing bacteria, III- sulfur-oxidizing bacteria; IV- iron-precipitating bacteria and V- sulfate-reducing bacteria (SRB). The main methods used in industry to prevent the spread of corrosive bacteria include biocides, protective coatings (antifouling) and corrosion inhibitors. This article provides an overview of biofilm formation process and biocorrosion discussing the main groups of corrosive bacteria, as well as the current methods and alternative techniques to control these environmentally harmful processes. In addition, the review throws the idea that plant compounds may be employed to control biocorrosion.

Keywords corrosion; biocorrosion; biofilms, corrosive bacteria; corrosion inhibitors; natural products

1. Introduction

Corrosion is the deterioration of a material, especially metal, as a result of chemical or electrochemical reactions on the metal/solution interface [1, 2]. The electrochemical process is the most common in nature and consists of oxidation-reduction irreversible reactions which results in the formation of a corrosion cell [3]. The metallic corrosion is a spontaneous process (AG <0) which consists of the inverse of metallurgical processes, where the processed metals revert to their natural state of lower free energy, i.e. chemical compounds or minerals [1]. The metallic corrosion represents an economic burden for many industry sectors [4, 5]. According to the World Corrosion Organization [6], the annual cost of corrosion is greater than 3% of global GDP (Gross Domestic Product); however, governments and industries pay little attention to corrosion, except in high-risk areas, like aircrafts and pipelines.

The corrosion influenced by microorganisms is called biocorrosion, presenting the same electrochemical nature of the traditional corrosion [7, 2]. The attachment of bacteria, release of metabolites and formation of biofilms change the electrochemical conditions at the metal/solution interface inducing or accelerating the corrosion process [8-10]. The bioaccumulation, accumulation of organic material on the metal surface, results in the formation of biofilms, which is a basic characteristic of the process of microbial influenced corrosion [11, 12]. The unwanted growth of biofilms has negative impact on various activities and represents significant losses for industries [13]. It is estimated that about 20% of all damages caused by corrosion are influenced by microorganisms; corrosion is the main cause of problems in the pipes of oil industry, affecting the costs of production and storage [10, 14].

The groups of bacteria involved directly and indirectly in the process of biocorrosion are: I- exopolysaccharide or extracellular polymeric substances (EPS)-producing bacteria; II- acid-producing bacteria, III- sulfur-oxidizing bacteria; IV- iron-precipitating bacteria; V- sulfate-reducing bacteria (SRB) [15]. The major responsibility for biocorrosion is attributed to SRB, since there is H_2S release during its metabolism, a reactive, toxic and corrosive agent [16, 17]. The SRB cause serious damage to the petrochemical industry resulting from the formation of biofilms on the metal surface [18, 19].

The methods used to prevent biocorrosion act by inhibiting the growth or metabolic activity of the microorganisms and changing the environment in which the corrosion process occurs [20]. Among the main methods used in the industries are included: I- physical processes [7, 20]; II- biocides [21], III- protective coatings [20] and; IV- corrosion inhibitors [22]. These methods are used generally combined in order to decrease or eradicate the metal exposure to the action of biocorrosion [20, 21, 23]. However, the use of biocides is associated with development of bacterial resistance [24]. Moreover, antifouling coatings and corrosion inhibitors can have their effectiveness diminished due to the metabolization by certain bacteria species [22, 25], in addition to being highly toxic [14].

Plant compounds have been described as potential tools to control the growth of several microorganisms involved in biocorrosion [26-35]. This review suggests the idea that these compounds may be employed in biocorrosion control. Also, the current scenario of corrosion influenced by microorganisms, the major groups of corrosive bacteria, and the methods used to control biocorrosion are discussed.

2. Corrosion

Corrosion is a spontaneous deterioration process of a material, metallic or non-metallic (plastic, concrete and ceramics), by chemical or electrochemical action of the environment, allied or not to mechanical strains [1, 2]. These reactions

occur on the surface of separation between the material and corrosive medium resulting in undesirable changes, such as wear, chemical variations or structural changes, making the material unsuitable for use [1, 36].

The chemical process occurs without water, corresponding to the direct attack of a chemical agent on the material without electron transfers [1]. The electrochemical process consists of spontaneous and irreversible reaction, being most common in nature, necessarily involving the presence of water and electrons transfer [3].

The metal corrosion is the transformation of a metal or metal alloy by its interaction with a particular means of exposure resulting in the formation of corrosion products and the release of energy, i.e. consisting of the natural tendency of processed metals to revert to their native state (AG <0), as chemical or mineral compounds of lower free energy (Figure 1) [1].
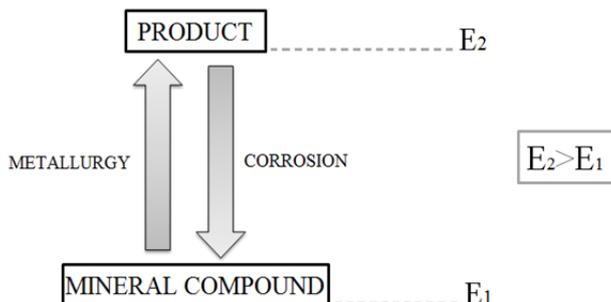
Fig. 1 Transformation of a mineral substance into metal products as performed in the metallurgical industries which occurs with absorption of energy ($E_2 > E_1$). On the other hand, the corrosion corresponds to the inverse of metallurgical process and thus occurs spontaneously with decreasing energy ($E_2 < E_1$).

The electrochemical process of metal corrosion occurs due to the difference in chemical potential between metal and environment, involving the reaction of these materials with non-metallic substances present in the medium (O_2, H_2S, CO_2, etc.), i.e. there is the metal oxidation (anodic reaction) (Figure 2A) and the reduction of an oxidizing agent (cathodic reaction) (Figure 2B) leading to the formation of a corrosion cell [1, 3].

$$A \quad \boxed{A \rightarrow A^{n+} + ne}$$

$$B \quad \boxed{B^{n+} + ne \rightarrow B}$$
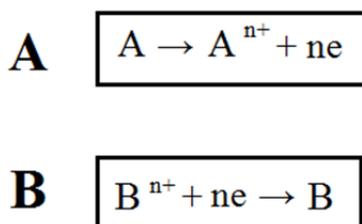
Fig. 2 Electrochemical process of corrosion. (A) Anodic reaction representing the oxidation of a metal by a non-metallic substance (eg. O_2, H_2S or CO_2) releasing a number (n) of electrons (e). (B) Cathodic reaction where an oxidizing agent is reduced.

2.1. Economic importance of metallic corrosion

The metallic corrosion can have a major impact on the economy of each country, since high financial costs are required to avoid this process; in 2010, costs related to corrosion were the equivalent of US$ 500 billion for the United States and US$ 76 billion for Brazil [5, 37]. Economic losses caused by corrosion have been the subject of several studies [37].

The wear of storage tanks and pipelines for oil caused by corrosion may result in micro-leaks causing environmental contamination [5, 37]. In addition, leakage of products such as gas, oil or multiphase cause environmental disasters predicted as crime by the Brazilian law of environmental crimes.

2.2. Biocorrosion, bioaccumulation and biofilms

The biocorrosion is the deterioration of a metal influenced by microorganisms that influence corrosion by modifying the electrochemical conditions on the metal/solution interface [2, 7, 38, 39]. This change occurs by the attachment of bacteria to the metal through the release of metabolites on the material surface or biofilm formation that influence the anodic and cathodic reactions, creating conditions for corrosion [8-10].

The process of bioaccumulation or biofouling, which occurs due to accumulation of organic material on the metal surface including cellular debris, EPS and microorganisms, results in the formation of biofilms [12]. According to Videla [23], most of the microorganisms studied so far are related to the process of bioaccumulation and biocorrosion.

The biofilm that occurs after the adsorption of organic and inorganic molecules on the material surface is formed by adherent sessile bacteria that will grow and produce EPS. The latter, once formed, allow new reactions taking place or that the existing kinetic reactions being altered, accelerating the metal wear [8, 40]. In biofilms, microbial populations exhibit functional interdependence and collectively promote microbial activity that would not be likely to occur for only one of the species of composing the biofilm [41, 42].

The formation of a biofilm comprises the following stages: I - formation of a film, through the adsorption of organic and inorganic molecules on the metal, which modifies the load distribution on the metallic surface and, also serves as a nutritional source for bacteria, facilitating the adherence of free-floating microorganisms present in the liquid; II - adhesion and multiplication of aerobic bacteria forming microcolonies; III - production of EPS by some sessile bacteria; IV - colonization by aerobic free-floating microbial cells, that will consume the oxygen by respiration, creating a local anaerobic environment in the biofilm as required by strict anaerobic bacteria and ; V - increase of biofilm thickness, which may favour the shedding of the outer layers [8, 43-46].

The EPS produced by the bacteria adhered to the biofilm capture essential ions to their growth, they are used as a means of attachment, protect bacteria against biocides interfere with the mechanisms of corrosion by favoring creation of differential aeration areas, besides serving as a nutritional source in case of low nutrient availability [12]. The process of corrosion by differential aeration occurs due to uneven distribution of the biofilm on the metal with aerated regions (surrounding the biofilm) and non-aerated regions (below the biofilm) [1]. The biofilm formation on the metal surface is a basic feature of microbial corrosion process and its presence decreases the oxygen content, reaching levels of almost total anaerobiosis [11].

It is known that 40% of pipe corrosion for oil industry is attributed to microbiological corrosion and it causes havoc from the order of US$100 million in production, transportation and storage of oil every year in the U.S. [14, 47]. Pipe biofilms can cause from the reduction in the fluid velocity due to the process of incrustation on the duct walls to the lost through leaks of products generated by corrosion, with consequent impacts on the environment [5].

Environmental problems are associated with biocorrosion including the use of biocides (disinfectants or antiseptics), antimicrobial substances or preparations capable of preventing, inhibiting or eliminating microorganisms, and the use of antifouling coatings (antifouling) and corrosion inhibitors, which are toxic and often cause pollution [7]. Among the most widely used biocides there are chlorine, ozone, bromine, aldehydes, acrolein and phosphonic tetrakis sulfate (hydroxymethyl) (THPS) [21, 48, 49].

3. Corrosive bacteria

Bacteria are simpler prokaryotic organisms from the structural point of view but complex from the biochemical and metabolic point of view, allowing the adaptation to the most varied types of habitat [15]. These microorganisms live and reproduce in pH between 0.5 and 13, temperatures ranging from -12 °C to 110 °C and under pressures of up to 1400 bar [15]. About 98% of the microorganisms making up biofilms are bacteria [50].

Most bacteria related to the corrosion process are part of the sulfur cycle in nature [51]. This cycle consists of microorganisms capable of metabolizing sulfur compounds in two ways: I- chemo-autotrophic: bacteria use electrons of inorganic compounds (H_2S, S and Fe^{2+}) as an energy source, using the CO_2 as their main carbon source [52], and II- chemo-heterotrophic: bacteria utilize electrons specifically from hydrogen atoms of organic compounds as energy source. This category of microorganisms can utilize various compounds as final acceptors of the respiratory chain such as nitrate, nitrite, sulfate, Fe^{3+}, sulfur, fumarate and pyruvate [53].

According to Gentil [1], the action of microorganisms in the processes of corrosion can occur through one or more of the following factors: A- direct influence on the speed of anodic and cathodic reactions; B- modification on the resistance of films existing on the metal surfaces caused by products of microbial metabolism; C- formation of corrosive media due to the acids generation. D- formation of tubers that enable the emergence of differential aeration cells, E- combined action of bacteria.

The EPS-producing bacteria, acid-producing bacteria, sulfur oxidizing bacteria, iron precipitating bacteria and sulfate reducing bacteria (SRB) are involved in the process of biocorrosion [15]. The latter group is responsible for much of the damage caused by microbial corrosion, thus most studies related to biocorrosion is focused on the SRB [22]. The microorganisms associated with biocorrosion are widely distributed (freshwater, sea water, industrial systems and storage tanks, among others) and may influence the spread of all types of metal corrosion [2]. Table 1 shows some bacteria causing corrosion as well as their damage and Figure 3 summarizes the biocorrosion process promoted by some types of corrosive bacteria which are discussed below.

Table 1 Bacteria associated with biocorrosion and their respective local of isolation and damaging actions.

Species	Local of isolation	Damaging actions
Serratia marcescens	• Products of corrosion of diesel and naphtha pipelines.	• Degrades petroleum products due to the release of the enzyme aryl hydrocarbon hydroxylase (AHH) that acts on the corrosion of metals.
Gallionella sp.	• Products of corrosion of petroleum and naphtha pipelines; • Metal surfaces immersed in fresh water and sea water.	• Promotes biomineralization due to deposition of iron hydroxides on the metal surface, modifying the electrochemical processes at the interface metal/solution, inducing corrosion.
Pseudomonas sp.	• Products of corrosion of diesel pipelines; • Metal surfaces immersed in fresh water and sea water.	• Production of EPS that favors the formation of biofilm.
Bacillus sp.	• Products of corrosion of diesel pipelines; • Metal surfaces immersed in fresh water and sea water.	• Degrades petroleum products due to the release of the enzyme aryl hydrocarbon hydroxylase (AHH) that acts on the corrosion of metals; • Production of EPS that favors the formation of biofilm.
Thiobacillus sp.	• Products of corrosion of naphtha pipelines.	• Promotes biomineralization due to deposition of iron hydroxides on the metal surface, modifying the electrochemical processes at the interface metal/solution, inducing corrosion; • Production of sulfuric acid, which increases the corrosion process.
Sulfolobus sp.	• Products of corrosion of naphtha pipelines.	• Promotes biomineralization due to deposition of iron hydroxides on the metal surface, modifying the electrochemical processes at the interface metal/solution, inducing corrosion; • Production of sulfuric acid, which increases the corrosion process; • They may also oxidize sulfur.

References [2, 14, 54-59]

3.1. EPS-producing bacteria

EPS-producing bacteria are initial colonizers due to aerobic and facultative anaerobic metabolism, with the ability of EPS excretion [60]. They alter electrochemical characteristics of metal surface creating a favourable environment for adhesion by other microorganisms, thus stimulating biofilm formation and favouring biocorrosion [11, 61-63]. Due to the aerobic metabolism, they provide ideal conditions for anaerobic bacteria by consuming the oxygen over time [63]. EPS, formed by proteins, polysaccharides, lipids and nucleic acids, protects microbial cells against metal ions, biocidal action and helps to trap other microbial species, thereby contributing to increased thickness of biofilm [12, 64]. *Pseudomonas* is the main genus of EPS producer [60, 65].

3.2. Acid-producing bacteria

Aerobic bacteria are able to produce short-chain organic acids such as acetic, formic, lactic, propionic and butyric acids as products of their metabolism from the fermentative metabolism of organic materials [66]. They are also initial colonizers due to aerobic metabolism [67]. These microorganisms are present in a variety of environments, including gas stands and oils [68]. Organic acids serve as substrates for the SRB, accelerating the corrosion process, besides reducing the pH of the medium [66, 69, 70]. Furthermore, the large amount of organic acid produced acts by metal depolarization starting the local corrosive process [67].
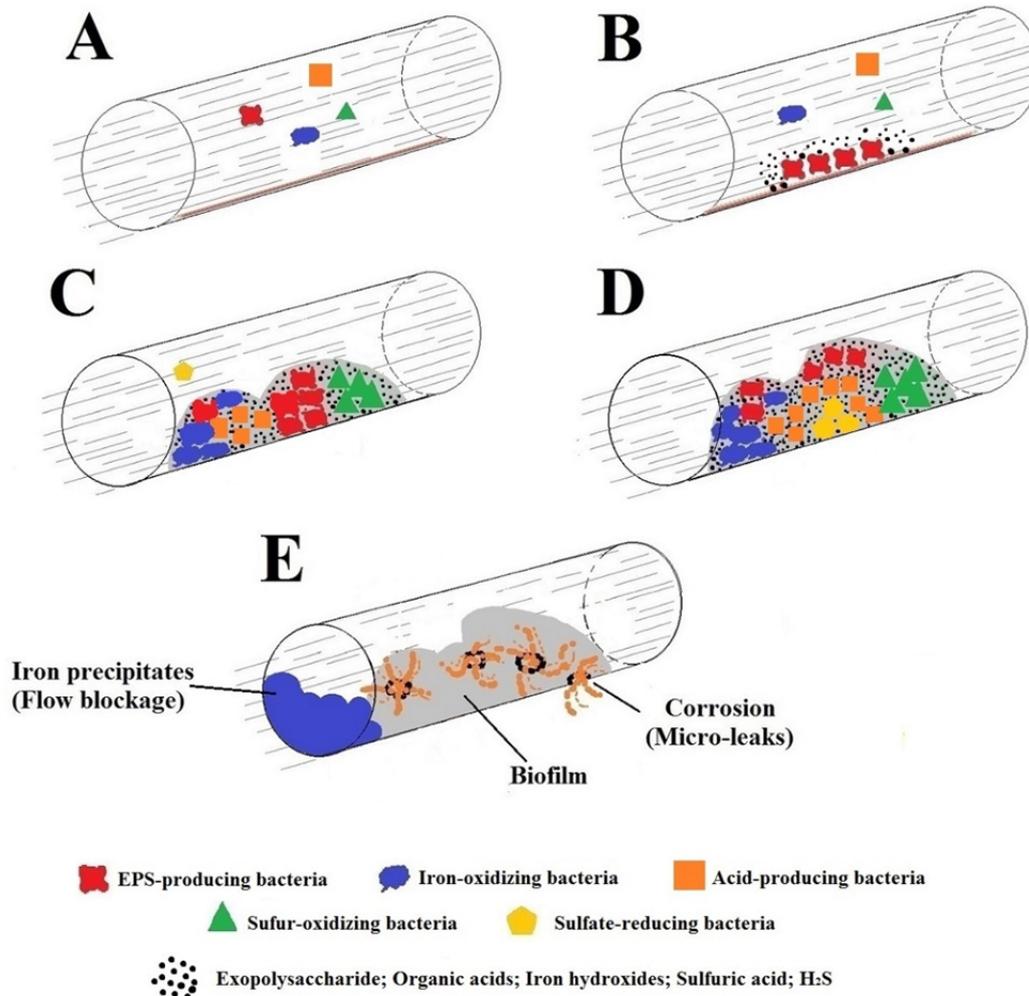
Fig. 3 Biocorrosion process promoted by some types of corrosive bacteria. (A) Aerobic corrosive bacteria from freshwater, sea water, industrial systems or storage tanks reach out the pipeline, that have a conditioning organic and inorganic film on the surface. (B) EPS-producing bacteria are attached to pipeline walls and produce exopolysaccharides, which creates a favourable environment for adhesion by other microorganisms. (C) Adhesion of other groups of corrosive bacteria to pipeline walls, which will release their metabolites, developing into a microcolony through cell division, consuming oxygen available. Action of iron oxidizing bacteria results in large accumulation of ferric precipitation leading to blockage in pipeline; sulfuric acid released by sulfur oxidizing bacteria promotes the acidification of the environment. (D) The low oxygen concentration and organic acids released by acid-producing bacteria favour attach and development of sulfate-reducing bacteria producing hydrogen sulfide (H_2S) accelerating corrosion process and reducing the pH. (E) A corroded pipeline partially blocked by iron precipitates with micro-leaks and containing bacterial biofilm.

3.3. Sulfur-oxidizing bacteria

The sulfur oxidizing bacteria are aerobic and facultative anaerobic microorganisms which obtain the energy necessary for growth from the oxidation of inorganic sulfur compounds such as sulfide, sulfite, thiosulfate and, in some cases the sulfur [56]. Oxidative metabolism results in the production of sulfuric acid which promotes the environment acidification; this high acidity provides great aggressiveness to the environment [71].

Regarding sources of carbon and energy, sulfur oxidizing bacteria may be divided into four groups [56]: I-mandatory chemolithotrophic: grows from CO_2 and inorganic compounds, II- facultative chemolithotrophic: may grow chemolithotrophically (CO_2 and inorganic compounds), heterotrophically (organic compounds as energy and carbon source) or mixotrophically (using both paths simultaneously); III- chemolithoheterotrophic: the energy is generated from the oxidation of inorganic sulfur, but they are unable to fix CO_2; IV- n chemorganoheterotrophic: oxidize inorganic sulfur compounds but do not derive the energy from this reaction.

This group encompasses many genera, being the *Acidithiobacillus* species the most studied; they are gram-negative, rod-shaped, strict aerobic and use CO_2 as the sole carbon source [72]. This group also include bacterial species from the genera *Sulfolobus*, *Thiomicrospira*, *Beggiatoa*, *Acidithiobacillus*, and *Thiothrix* as well as the species *Thiosphaera pantotropha* and *Paracoccus denitrificans* [56].

3.4. Iron-oxidizing bacteria

Iron oxidizing bacteria are aerobic microorganisms, belonging to a large and diverse group, that get energy necessary for their metabolism from iron oxidation [23, 52]. Consequently, there is the formation of iron hydroxides that generally form insoluble precipitate on the surfaces, promoting regions with different oxygen levels [73, 74]. They are characteristically difficult to be isolated and cultured in the laboratory, being widely found in water from rivers, lakes and oil production [23]. They have mostly a locomotor sheath and their presence can be detected by a large accumulation of ferric precipitated as corrosion product [23]. This accumulation or inorganic fouling leads to problems to industrial equipment such as blockages in oil pipelines [23, 52]. Among the most common iron bacteria are highlighted: the species *Thiobacillus ferrooxidans* and the genera *Crenothrix*, *Gallionella*, *Leptothrix* and *Spherotillus*.

3.5. Sulfate-reducing bacteria (SRB)

The SRB form a morphological- and phylogenetically heterogenous group that includes bacteria and restricted anaerobic archaebacteria, although some species have significant tolerance to oxygen [75, 76]. They are mainly gram-negative bacteria, mesophilic and some thermophilic generally spore-forming [77]. These microorganisms are capable of oxidizing various organic compounds of low molecular weight, including mono- or dicarboxylic aliphatic acids, alcohols, hydrocarbons and aromatic compounds, using sulfate ion or other sulfur compounds (thiosulfate, sulfite, etc.) as electron acceptors [36, 76, 78]. Acetate, lactate, pyruvate and ethanol are among the most commonly used substrates by SRB [78]. The stimulation of SRB growth is due to the existing anaerobic conditions in the biofilm explained by the deposition of corrosion products combined with microorganisms and, during the secondary of oil recovery, where there is injection of sea water, rich in sulfate [18, 19, 79, 80].

The ability to utilize sulfate as the final electron acceptor is a reduction process restricted to SRB, whose H_2S formed in the assimilative reduction of sulfate is immediately converted to organic sulfur, while H_2S is secreted in the dissimilative reduction and acts as oxidizing agent to metabolize the organic matter. Large amounts of biogenic hydrogen sulfide can be produced (above 1,100 kg day^{-1}) [80]. Although also being chemically produced by the dissolution of rock's metal sulfides in the reservoir, most of the H_2S formed in pipelines originates from the metabolic activity of sulfate-reducing bacteria [81].

Considering the numerous economic losses related to metabolic activity of SRB in the petrochemical industry, much research has been directed towards prevention and control of corrosion caused by this group of bacteria [56]. These studies are directed to the use of metabolic inhibitors such as molybdate, nitrate and nitrite, and application of biocides, which help the control of metabolic activity of SRB and subsequent inhibition of biogenic H_2S production [56, 82-84].

Several mechanisms contribute to contain the formation process of biogenic H_2S by using metabolic inhibitors: I- competition between SRB and heterotrophic bacteria reducer of nitrite or nitrate by ordinary electron donors, resulting in competitive SRB exclusion [85]; II- increased redox potential due to the presence of intermediaries of nitrate reduction (nitrous oxide and nitric oxide), since the biological production of H_2S occurs only at low redox potential (below -100 mV) [86]; III- Change of energy metabolism of some SRB, reducing nitrate instead of sulfate [18]; IV- sulfide oxidizing bacteria and nitrate or nitrite reducing use the nitrate or nitrite to re-oxidizing H_2S, resulting in the H_2S removal [87]; V- inhibition of the dissimilatory sulfite reductase by nitrite that performs final enzymatic step via sulfate reduction by SRB [86].

The use of metabolic inhibitors widely used in oil industry has been associated with increased risk of metal corrosion [18, 48, 84, 85]; explained by the formation of polysulfide, inorganic sulfur (S (aq)) and thiosulfate through simultaneous oxidation of sulfide by sulfide oxidizing bacteria and nitrate reduction by nitrate-reducing bacteria [48].

Some research has been conducted to study the mechanisms responsible for biofilm formation and biocorrosion processes by SRB [88, 89]. SRB are responsible for much of the damage caused by microbial corrosion [14, 51, 90, 91]. Another economic impact on the oil industry is related to the acidification of oil and gas by H_2S [47, 79, 92, 93]; furthermore, this gas is toxic to humans [94]. These bacteria have been found in storage tanks and transport of oil and gas; their presence is associated with problems of biofouling and biocorrosion [14]. The genera *Desulfovibrio* and *Desulfotomaculum* are the most abundant among SRB associated with biofilms and corrosion in pipelines of petrochemical industries [19, 95, 96].

4. Biocorrosion control

The biocorrosion reaches different industries, especially petrochemical and oil areas in their various systems, such as: cooling circuits, storage tanks, water injection lines, among others [23]. The detection and monitoring of biocorrosion are ways to prevent and control this type of corrosion and investments for this purpose have increased in recent times due to the increasing damage caused in various industries [21]. In most industrial systems, bioincrustations are associated with abiotic fouling [20]. Thus, the study on the control and prevention of biocorrosion cannot be focused only on the activity and growth of microorganisms, but on the physicochemical properties of the metal/solution interface [20].

The methods employed to prevent biocorrosion act by inhibiting the growth or metabolic activity of microorganisms changing the environment in which the corrosion process occurs in order to avoid the adaptation of these bacteria [20]. Physical (cleaning procedures) and chemical methods (sanitization through the use of biocides and antifouling coatings such as inks or corrosion inhibitors) are used generally combined in order to improve the procedure [20, 21]. These methods intend to reduce or eliminate metal exposure to the action of biocorrosion, either by direct elimination of microorganisms or reduced effect of their metabolites on the material [23]. However, inefficient cleaning and monitoring strategies for systems and lack of skilled professionals in the area of microbiological corrosion provide increased corrosion losses [23, 97]. Below is Table 2 of the main control methods of biocorrosion used worldwide, as well as the action and problems associated with use.

Table 2 Methods employed to control biocorrosion and their respective mode of action and associated problems.

Method	Examples	Mode of action	Associated problems
Physical	• Washing with brushes; • Injection of air or gas; • Manual cleaning.	Removes physical deposits.	• Abrasive method that may damage protective films; • Not effective in removing thick biofilms.
Biocides	• Chlorine; • Ozone; • Bromine; • Aldehydes; • Acrolein; • THPS	Prevention, inhibition or elimination of microorganisms.	• High toxicity.
Protective or antifouling coatings	• Silicones; • Resins; • Antifouling paints.	Formation of a protective film.	• They are used as nutritional source by some bacteria. • High toxicity.
Corrosion inhibitors	• Amines; • Fatty acids; • Phosphate esters; • Ammonium nitrate.	Formation of a protective film.	• They are metabolized by some bacteria, causing increased microbial growth and increased rate of corrosion; • High toxicity.

References [7, 20-22, 25, 49, 54, 98]

The physical method comprises mechanical cleaning which matches any method capable of promoting physical removal of the material deposited on the surface and includes the use of brushing, water jets, among others [23]. Furthermore, the chemical cleaning is summarized in the use of various chemical substances, being used after mechanical cleaning [7, 20]. According to Videla [23], biocides stands among the most commonly used effective control methods. Biocides, a heterogeneous group of agents, are widely used in the petroleum industry for internal protection of oil and gas pipelines in the refining area, water injection, secondary recoveries, drilling fluids and the oil production itself for control of planktonic microorganisms and mainly for biofilm generators, possessing antibacterial, antifungal and algaecide activities [24]. However, some biocides may not have activity against certain types of microorganisms within the same group, due to the development of bacterial resistance [24].

Protective or antifouling coatings and corrosion inhibitors form a protective film adsorbed on the metal/solution interface [22, 98]. They are widely used in industrial systems, however their use is associated with increased bacterial growth, since they are nutrient source for some bacteria species [22, 25] in addition of being highly toxic to humans and other non-target organisms [22, 34]. The continuous use of these inhibitors can result in reversible (temporary) or irreversible (permanent) damages to organs such as kidneys and liver, or disrupt a set of biochemical processes [34]. In this scenario, the use of these compounds has been limited on the basis of environmental regulations [34].

Natural products are pointed as corrosion inhibitors, and among them plant compounds have attracted interest since they are inexpensive and ecologically acceptable [29, 30, 32, 34, 35, 99, 100]. Tannins, organic acids, alkaloids, pigments and proteins from plants are known to inhibit metal corrosion [34, 101]. Extracts of *Zenthoxylum alatum* were active on the corrosion of carbon steel in phosphoric acid [29]. Li et al. [32] investigated the inhibitory effect of berberine extracted from *Coptis chinensis* in soft steel which was active against corrosion in 1 M sulfuric acid. Molecules present in aqueous extract for Fenugreek leaves were spontaneously adsorbed on mild steel surface and were capable of inhibiting corrosion on steel in a dose-dependent manner in the presence of HCl and H_2SO_4 [102]. Aqueous extract of *Rosmarinus officinalis* leaves [99], *Lawsonia inermis* leaves [30], *Allium sativum* [8], *Chamaemelum mixtum* [100], *Cymbopogon proximus* [100], *Nigella sativa* [100] and *Phaseolus vulgaris* [100] inhibited metal corrosion. The adhesive protein from the marine mussel *Mytilus edulis* and the bovine serum albumin (BSA) were both adsorbed on

carbon steel and were able to inhibit corrosion [103]. BSA addition in buffered saline significantly decreased the corrosion rate of titanium [104] and molybdenum [105].

Plant products have showed antibacterial activity and the studies have focused in the use of extracts or isolated compounds to combat human-pathogenic and/or phytopathogenic bacteria [26, 27, 106, 107]. As noted earlier, several of these bacteria species are involved in biocorrosion arising from natural biofilms that develop in industrial facilities [23, 108].

Serratia marcescens, *Klebsiella oxytoca*, *Pseudomonas aeruginosa*, *P. stutzeri*, *Bacillus sp.*, *B. subtilis*, *B. cereus*, *B. pumilus* and *B. megaterium* were isolated from diesel and naphtha-transporting pipelines located in the northwest and southwest regions in India; the association with localized corrosion of the pipeline steel in the presence of these consortia was corroborated [108]. A joint project of different european aircraft manufacturers confirmed the involvement of isolates from genera *Micrococcus*, *Enterococcus*, *Staphylococcus* and *Bacillus* in strong corrosion damage in aluminium alloy, commonly used in aircraft construction [109]. These bacteria may create a microacidic environment (acid producing bacteria), which favors the development of other bacteria, or produce EPS, favoring the formation of biofilm (EPS-producing bacteria) [108, 109]. The arguments presented here point to the importance of investigating plant compounds as potential agents in control of biocorrosion (Table 3).

Table 3 Plant compounds active against pathogenic bacteria that are involved in biocorrosion.

Plant product	Bacteria
Protein preparations of *Moringa oleifera* flowers (MoE and MoPFT)	• *B. subtilis* • *S. aureus* • *E. faecalis*
Seed lectin from *Eugenia uniflora* (EuniSL)	• *S. Aureus* • *P. aeruginosa* • *Klebsiella* sp. • *B. subtilis*, • *Enterococcus* sp.
Volatile oil of black pepper (*Piper nigrum*)	• *M. luteus* • *B. subtilis* • *S. marcescens* • *E. faecalis*
Volatile oil of oregano (*Origanum vulgare*)	• *M. luteus* • *B. subtilis* • *S. marcescens* • *E. faecalis*
Root of liquorice (*Glycyrrhiza glabra*)	• *B. cereus* • *B. megaterium* • *B. subtilis* • *E. faecalis* • *K. pneumoniae* • *M. luteus* • *P. aeruginosa* • *S. aureus*
Extract of pomegranate peel (*Punica granatum*)	• *P. stutzeri*

References [27, 110-113].

5. Conclusion

Agents currently used to control biocorrosion are strongly toxic and may induce the development of bacterial resistance. In this sense, natural compounds such as extracts and products isolated from plants comprise promising alternatives due to its large spectrum of biological properties, low environmental risk and low cost. This review, motivated by an ecological awareness and based on the success of plant compounds as anticorrosive and antimicrobial agents intends to stimulate the search for new agents able to avoid biocorrosion in an environmental friendly way.

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