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Geobacter sulfurreducens: An iron reducing bacterium that can protect carbon steel against corrosion?

Claudia Cote *, Omar Rosas, Régine Basseguy *

Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, BP 84234, 4 allée Emile Monso, F-31432 Toulouse cedex 4, France
CNRS, Laboratoire de Génie Chimique, F-31432 Toulouse, France

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ABSTRACT

The effect of *Geobacter sulfurreducens* on the electrochemical behaviour of carbon steel in anaerobic phosphate solution is studied here. In natural environments, *G. sulfurreducens* is able to reduce Fe(III) to Fe(II) during the oxidation of acetate. High availability of Fe(II) promoted the formation of an iron (II) phosphate layer on the steel. It is assumed that this phosphate layer, formed only when bacteria were present, is responsible for maintaining the corrosion potential stable even after intrusion of air. In contrast, the corrosion potential in the abiotic experiments suffered an increase of 450 mV after few hours of exposure to air.

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1. Introduction

Microbial development occurs in almost all environments through biofilm formation and may be responsible for microbiologically-influenced corrosion (MIC), also known as microbial corrosion or biocorrosion, which can be defined as the enhancement or acceleration of corrosion by the presence of bacteria [1]. However, many authors have questioned the harmfulness of biofilms on metal surfaces and even argued that some of them may reduce corrosion rates by various mechanisms [2–5]. One of these mechanisms is a surface reaction leading to the formation of a corrosion-inhibiting layer of phosphate such as the iron phosphate named vivianite.

Vivianite is an iron (II) phosphate, $Fe_3(PO_4)_2{\cdot}8H_2O$, which may be used as a corrosion inhibiting agent of iron because of its low solubility: it forms a film of poorly soluble and non-oxidising corrosion product on the metal surface [4–7]. Corrosion inhibition is the slowing down of the corrosion reaction usually performed by substances (corrosion inhibitors) which, when added to an environment in small amounts, decrease the rate of attack by this environment on a metal [8]. A protection method against corrosion used by some industries is acid phosphating with phosphates of zinc, iron or manganese, which leads to vivianite production [4]. This procedure is carried out at temperatures of up to 95 °C and pH values between 2 and 3.5.

One of the most studied mechanisms of corrosion inhibition promoted by microorganisms, or microbially influenced corrosion inhibition (MICI), is corrosion control using beneficial biofilms [7–10]. These benefits can be linked either to physical characteristics of the biofilm or to biochemical characteristics involving metabolites. A biofilm is a highly organised bacterial community with cells entrapped in a matrix of extracellular polymer substances (EPS). On the one hand, the bacteria may form a persistent film adhering to the metal/solution interface and reducing the corrosion rate by forming a transport barrier, which may prevent the penetration of corrosive agents (such as oxygen, and chloride), decreasing their contact with the metal surface and thus reducing corrosion [7,8]. However, some studies have shown that this protection is not effective and that biofilms could instead promote corrosion by the formation of a non-uniform patch which, in the presence of aerobic respiration, results in the formation of a differential aeration cell, thus accelerating the corrosion rate [7,11]. On the other hand, corrosion inhibition is sometimes explained by the biochemical characteristics of the microorganisms themselves and/or their enzymes. For instance, a vivianite deposit was observed on mild steel electrodes placed in a galvanic cell in presence of hydrogenase from *Clostridium acetobutylicum* (an iron reducing bacterium – IRB) [12,13]. The consequence of this catalysed deposit was a delay in pitting corrosion or a reduced corrosion rate. Other authors [9,10,14,15], have claimed that different species of bacteria (most of them belonging to the IRB-group) induce a reduction of corrosion rates, the prevention of pitting

* Corresponding authors at: CNRS, Laboratoire de Génie Chimique, F-31432 Toulouse, France. Tel.: +33 5 34 32 36 17; fax: +33 5 34 32 27 00.
E-mail addresses: ccote@jouy.inra.fr (C. Cote), regine.basseguy@ensiacet.fr (R. Basseguy).

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corrosion and a reduction of both cathodic and anodic reaction rates for materials such as stainless steel [16], mild steel and aluminium brass [9,10]. Little et al. [16] and Eashwar et al. [17] have claimed that corrosion inhibition on stainless steel is due to a mechanism in which siderophores (iron chelators) produced by microorganisms within biofilms at neutral pH act as inhibitors and enhance the passivity of stainless steel by reducing the passivation current (i_p). Other mechanisms most frequently cited for MICI are resumed by Little and Ray [18] in a critical review. These mechanisms are: formation of a diffusion barrier to corrosion products that stifle metal dissolution, consumption of oxygen by respiring aerobic microorganisms within the biofilm causing a diminution of that reactant at the metal surface, production of metabolic products that act as corrosion inhibitors (e.g. siderophores, vivianite), production of specific antibiotics that prevent proliferation of corrosion-causing organisms (e.g., sulphate-reducing bacteria (SRB)), formation of passive layers that are due to the presence of microorganisms [18], reduction of ferric ions to ferrous ions (in presence of IRB) and increase consumption of oxygen [15,19]. Moreover, Herrera and Videla [20] claim that the introduction of IRB in industrial water systems that contain SRB and other corrosion-inducing bacteria causes not only the exfoliation of corrosion products but also the protection of the metal surfaces from further corrosion. In general, the main mechanisms of corrosion inhibition by bacteria are linked to a marked modification of the environmental conditions at the metal/solution interface by biological activity [20].

Moreover, IRB have been reported to biologically produce vivianite at laboratory scale under aerobic conditions with a few bacterial strains such as *Pseudomonas* sp. [2] and *Rhodococcus* sp., using a metal coupon and 20 mM of phosphate buffer [4,5,21]. Islam et al. [22] reported vivianite formation under anaerobic conditions by *Geobacter sulfurreducens* using soluble Fe (III) (iron citrate) as electron acceptor. When the organism was grown using insoluble crystalline Fe (III) and oxy-hydroxide as electron acceptor, Fe (III) reduction resulted in the formation of magnetite instead of vivianite. These same results were also observed by Lovley and Phillips [23].

G. sulfurreducens is a dissimilatory IRB thanks to its electron exchange capabilities with solid substrate [24]. However, its role in corrosion is still uncertain. Recent studies with *G. sulfurreducens* have shown that these bacteria can exert two different effects on 304L stainless steel: just after inoculation, G. *sulfurreducens* cells create a cathodic reaction on the material, which leads to a fast increase in its open circuit potential (OCP), heightening the corrosion risk. In contrast, after a few days, well established biofilms shift the pitting potential towards positive values, which may be interpreted as a protective effect [3]. This research concluded that *G. sulfurreducens* played a role in the corrosion behaviour of 304L, which depends on medium composition. In the absence of acetate (lack of electron donor), *G. sulfurreducens* biofilms promote the propagation of pitting whereas, in the absence of fumarate (lack of electron acceptor), *G. sulfurreducens* cells were able to delay pit occurrence, thus protecting the metal.

The controversy about enhancement of corrosion and/or protection against corrosion promoted by microorganisms is still unresolved regarding this bacterial group. According to some reports, IRB are able to induce protection of carbon steel [3,16,20] while others suggest a considerable increase of corrosion through the reduction and removal of passive films of ferric compounds on the metal surface [3,19,20].

On the other hand, iron reducers can have a major effect on the availability of iron ions through the solubilisation of insoluble iron compounds and the resulting formation of biominerals [25]. Biologically induced mineralisation is a process where bacteria produce biominerals, commonly as a secondary event from interactions between the activity of the microorganisms and their surrounding environments [26]. The formation of phosphate minerals has frequently been observed in sedimentary environments where biological productivity is high [27]. Since *G. sulfurreducens* is a ubiquitous species in sediments and soils, it can have a relevant effect on corrosion and the corrosion protection of buried industrial equipment such as off-shore and harbour structures, oil and gas pipes and buried storage tanks [28]. Nevertheless, this bacterial genus has mainly been studied in the context of microbial fuel cells rather than that of corrosion.

Although *Geobacter metallireducens* and *Shewanella oneidensis* have been equally studied concerning their role in biomineralisation and their use of Fe (III) as terminal electron acceptor in anaerobic respiration processes, only *Shewanella* has been studied in relation to corrosion processes [19,29,30].

Corrosion studies involving iron reducing bacteria such as *G. sulfurreducens* have been reported only by Mehanna et al. [3,13,28]. Other studies have dealt with the behaviour and characteristics of these bacteria, such as their electroactivity, their environmental role concerning iron sources and bio-mineralisation, and their metabolism [22–24,31,32]. Moreover, little work has been done to examine which iron reducing microbial species are prevalent within bacterial communities that lead to corrosion [20]. Considering the lack of knowledge about the influence of these bacteria in corrosion, the objective of the present study is to find out whether *G. sulfurreducens* is able to protect carbon steel against corrosion and, if so, what the mechanism of inhibition is.

In the present work, the concentrations of electron donor (acetate) and electron acceptor (fumarate) were considerably reduced for the electrochemical experiments with the aim of diminishing the likelihood of biofilm formation through the scarcity of carbon source. Thus the interference of EPS and of the complex biofilm itself in the electrochemical behaviour was reduced. Furthermore, lowering the acetate concentration would unbalance the redox state of the bacterial cells, forcing them to search for a new source of electrons on the material surface. All these altered conditions (electron acceptor and donor and phosphate concentration) would make it possible to see the response of the bacteria on carbon steel in conditions much closer to those of the environments where this type of bacteria may live. The final objective was to determine whether *G. sulfurreducens* enhances or inhibits the corrosion of carbon steel in these conditions.

2. Experimental procedure

2.1. Bacteria and media

The *G. sulfurreducens* ATCC 51573 strain used for the experiments was obtained from DSMZ (Deutsche Sammlung von Mikroorganismen und Zellkulturen). The media and solutions were prepared following the DSMZ protocol [33]. The culture growth medium contained 28 mM NH_4Cl, 5 mM NaH_2PO_4, 1.3 mM KCl, 29.7 mM $NaHCO_3$ and 10 mM sodium acetate (electron donor). The medium was sterilised by autoclaving at 121 °C for 15 min. Once the medium had cooled down, a sodium fumarate solution (electron acceptor) filtered with a 0.2 μm pore filter was added to obtain a final concentration of 50 mM of fumarate in the medium. 10 mL/L of vitamins (ATCC MD-VS) and 10 mL/L of minerals solution (ATCC MD-TMS) were also added.

The *G. sulfurreducens* culture was performed in anaerobic glass vials with 50 mL of growth medium. The vials were sealed with butyl rubber septa and de-aerated by injecting N_2/CO_2 (80:20, v/v) at least 30 min before the injection of bacteria (10% of bacterial initial suspension). This first incubation lasted for 3–5 days at 30 °C for optimum bacterial growth. The culture was ready for inocula-

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