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Control of microbiological corrosion on carbon steel with sodium hypochlorite and biopolymer

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ABSTRACT

In the present work, the interaction of a mixture of a biocide, sodium hypochlorite (NaClO), and a biopolymer, xanthan, with carbon steel coupons exposed to seawater in a turbulent flow regime was studied. The cell concentrations, corrosion rates, biomasses, and exopolysaccharides (EPSs) produced on the coupon surfaces with the various treatments were quantified. The corrosion products were evaluated using X-ray diffraction (XRD), and the surfaces of steels were analysed by scanning electron microscopy (SEM). The results indicated that xanthan and the hypochlorite-xanthan mixture reduced the corrosion rate of steel.

1. Introduction

Microbiologically induced corrosion (MIC) is used to designate the corrosion caused by the presence and activities of microorganisms. Microorganisms can accelerate the reaction rate of the corrosion process or modify the corrosion mechanism. The corrosion mechanism of steel depends essentially on the presence or absence of oxygen. In the presence of oxygen, aqueous corrosion is governed by the formation of different Fe(III) oxides and oxyhydroxides, depending on their stability. Lepidocrocite (γ-FeOOH), goethite (α-FeOOH), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) are therefore likely to form [1,2]. In the absence of oxygen, the reduction of water governs the corrosion process and produces hydrogen and a hydroxyl [1,3]. The iron reacts with the hydroxyl to form Fe(II) hydroxide and then magnetite Fe_3O_4, water, and molecular hydrogen [4]. When microorganisms are present in the medium, corrosion products such as iron sulphide (FeS) can be found consequent to reactions between sulphur anions (S^{2-}) and steel [5,6]. These sulphur anions are derived from the reduction of sulphate $(SO4)^{2-}$ by sulphate-reducing bacteria (SRBs) [5,6]. When the steel is exposed to the sulphur anions, it initially forms a film of mackinawite ($Fe_{(1+x)}S$), an iron-rich monosulphide phase, but with poor protection for the surface. This film is converted into more stable iron sulphide films such as greigite (Fe_3S_4), smythite ($Fe_{(3+x)}S_4$), or pyrrhotite ($Fe_{(1-x)}S$), as a result of biological and electrochemical reactions [7]. Pyrite (FeS_2) is the most thermodynamically stable type of iron sulphide [7]. According to Little and Lee [8], during steel corrosion in the presence of SRBs, an adherent thin layer of mackinawite is formed. When the thickness increases, the layer becomes less adherent. If the concentration of ferrous ion in the electrolyte is low, mackinawite turns into greigite. This change is not observed in non-biological systems. If the concentration of ferrous ion is high, mackinawite is formed together with a complex of iron oxyhydroxide. According to Lee and Characklis [9], low concentrations of iron dissolved in the medium form thin and adherent protective films with low corrosion rates. By contrast, high concentrations of dissolved iron in the medium cause the loss of adherent sulphide precipitates from the steel, with a marked increase in the corrosion current [10].

El Hajj et al. [1] reports that iron sulphide protection depends on the uniformity of sulphide deposits, its crystalline state, the nature of the steel, and defects on steel surfaces, among other factors. In the corrosion of steel in seawater are also found compounds formed by the presence of iron-precipitating bacteria, which produce orange-

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red iron oxide $Fe_2O_3{\cdot}H_2O$ tubercular corrosion products and iron hydroxide $Fe(OH)_3$ by oxidising either ferrous ions present in the medium liquid or in the substrate [8]. The tubercular corrosion products include the compounds $Fe(OH)_2$ or Fe_3O_4 and corrosion products from the development of SRBs, such as the aforementioned iron sulphides.

The effects of biofilms on metal marine corrosion may be the opposite, causing either acceleration or inhibition of the corrosion process [7]. The decreased corrosion rate is usually due to the effect of the "barrier" of biofilm deposits that uniformly cover the metal surface. However, because biofilms are not used to uniformly cover the metal surface, accelerated corrosion is most common. This acceleration is a consequence of the permanent separation of anodic and cathodic areas, the breakdown of corrosion product protective films, and the stimulation of anodic or cathodic reactions, or both.

The colonisation of surfaces, with subsequent biofilm formation, begins as soon as a metallic surface is submerged in water [11]. Biofouling is an undesired phenomenon of adherence and biofilm accumulation on a surface that is submerged or in contact with seawater. This accumulation consists of an organic film composed of microorganisms incorporated into a polymeric matrix, retained particles, and dissolved and adsorbed substances (salts and/or corrosion products) [12]. The process by which biofilms accumulate on a surface stems from physical, chemical, and biological processes [13]. In industrial equipment such as heat exchangers, which can use seawater as a coolant, biofouling can become the primary cause of the decrease in efficiency. In heat exchangers, biofouling increases the fluid frictional resistance, reduces the efficiency of the heat transfer, and increases maintenance and operational costs. Therefore, the reduction, prevention, and elimination of biofouling are goals of the utmost priority for industrial plants [12]. Various methods have been used to minimise the accumulation of biofouling on surfaces: (a) chemical treatments such as the addition of biocides in fluids, aimed to eliminate organisms that gain entrance into the system or to reduce the growth rate of microorganisms within the biofilm and (b) mechanical methods such as the use of pigs to remove biofilms from the systems [8]. The choice of the technique used depends on numerous factors [14]: (a) accessibility, (b) the nature of the microorganisms, (c) the thermal hydraulic conditions of the process, (d) treatment costs, (e) safety standards, and (f) environmental impacts. The most important antifouling chemical methods are chlorination, bromochlorination, ozonisation, hydrogen peroxide addition, non-oxidising biocides, synergetic chemical products, antifouling paints, and non-toxic coatings [15,12].

Chlorination is a common method of controlling the formation of biofilms on utilities and in the process industry [11,8]. Because the transport of chlorine through the biofilm occurs by controlled diffusion, the rate of this process depends on the concentration of chlorine in the fluid (chlorine demand) and on the turbulence of the system [8]. The chlorine in the system can inactivate microbial cells and oxidise nutrients [16]. Chlorine reacts with organic and inorganic components within the biofilm, restraining the cell material and inactivating the cells. In a mature biofilm, chlorine can also react with the exopolysaccharides (EPSs) responsible for the biofilm's integrity [8]. It is well known that it is more difficult to eliminate sessile bacteria with biocides than to kill these microorganisms in circulation due to the difficulty of biocide penetration into the biofilms [8,17,18]. Biofilms formed by microorganisms rich in EPSs require a higher chlorine concentration relative to those formed by cells with lower EPS contents [8]. The hypochlorite oxidises EPSs within the biofilm, resulting in EPS depolymerisation, dissolution, and separation [8]. Because higher doses of biocides culminate in higher corrosion rates in the majority of cases, the combination of a biocide with a biopolymer is an alternative approach to the control of biofilms and, consequently, MIC [19–21]. This study analysed the effects of the biocide sodium hypochlorite, the biopolymer xanthan, and the combined effect of both sodium hypochlorite and xanthan on the formation of biofilms on carbon steel coupons.

Table 1
Chemical products used in the process.

Chemical Agents	Concentration/time ppm/day
NaClO	1.0/1.0
Xanthan	1.0/14
NaClO and Xanthan	1.0 NaClO/1.0 + 1.0 xanthan/14

2. Experimental methods

2.1. Specimens

Rectangular carbon steel SAE 1010 coupons with dimensions of $100 \times 10 \times 3$ mm and an area of ca. 2796 mm^2 were used.

2.2. Process fluid

The fluid used was seawater collected in the region of the SUAPE port complex, Ipojuca-PE-Brazil. Seawater samples were always collected at the same place, submitted to a microbiological analysis, and then placed in a closed dynamic (*looping*) system. The volume of seawater used in each experiment was 13 L.

2.3. Chemical agents

An oxidising biocide (sodium hypochlorite—NaClO), a biopolymer produced by microorganisms (xanthan), and the biocide combined with the biopolymer were tested. In all cases, additions were carried out intermittently. The chemical agents and concentrations used are listed in Table 1.

The NaClO used was supplied by the Vetec Company and had the following characteristics: 4–6% chlorine content and 1.1 g/mL specific mass. Xanthan was imported from China via Quimitêxtil LTDA and had the following characteristics: a pH of 7.5 and a viscosity of 1544 mPa s (solution 1% KCl).

2.4. Equipment

The experiments were undertaken in a closed looping dynamic system made of polyvinyl chloride (PVC), with a diameter of 38.1 mm, connected to a cooling system with a fluid capacity of 20 L. The carbon steel coupons were attached to plastic rods with plastic screws to avoid any interference in the study from other materials that could facilitate the galvanic corrosion process. The coupons were then placed along the inner side of the PVC tubes so that they were equally exposed to the circulating water flow (Fig. 1). Water circulation was achieved with a 372.6 W pump, a flow of 0.0022 m^3/s, and a rate of 2.7 m/s to simulate a turbulent regime ($Re > 4000$) that would be experienced in the field. All tests were performed under the same flow rate to allow comparisons of the action of different fluids, using a naturally aerated environment and a process temperature of $33 \pm 3\,^{\circ}C$.

2.5. Description of the experiments

The carbon steel coupons were treated prior to each experiment by blasting them with glass beads and then washing them with isopropanol followed by acetone to remove organic matter. The coupons were subsequently dried in an oven at 70 °C for 30 min, placed in a desiccator for another 20 min, and weighed before being exposed to the systems [22]. The process time was 28 days for