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RESEARCH ARTICLE

ELECTROCHEMICAL BEHAVIOR OF STAINLESS STEEL IN *OXONIA-ACTIVE* WITH *GEOTRICHUM CANDIDUM*

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Abstract

In this study the corrosion effect of AISI 316L Stainless Steel treated by *Oxonia-Active* (consisting of dihydrogen dioxide and ethaneperoxoic acid solution) and in a mixture consisting of *Oxonia-Active* and *Geotrichum candidum* suspension was investigated. The electrochemical behavior made by Linear Polarization indicated that the stainless steel shows a higher corrosion rate in mixture consisting of *Oxonia-Active* and *Geotrichum candidum* suspension than in that only *Oxonia-Active*. The polarization curves obtained at different times after immersion of samples confirm that the mixture of biocide and fungal suspension is more destructive for metallic surface than pure biocide.

Keywords: metallic surface, biocide, fungi, corrosion

Introduction

Fungi are important in food biotechnology as they are starter cultures with the ability of modifying food characteristics (Maier *et al.* 2009). Also fungi are important in industrial biotechnology on antibiotics production (Deacon, 1997) and other beneficial by-products, such as enzymes (Gautam *et al.* 2011), vitamins (Szentirmai, 1999), organic acids (Schuster *et al.* 2002) etc. On the other hand, the food spoilage create an economical issue (Muñoz *et al.* 2010) and it is annually estimated that between 5 and 10% of the world's food production is lost due to biodeterioration through fungal actions (Pitt et Hocking, 1997). The risk of health problems can appear due to mycotoxins produced as secondary metabolites of fungi during the stationary phase of growth in specific physico-chemical conditions (Garcia *et al.* 2009). Therefore, the control of fungal spoilage is essential and decisive in the preventing different biological risks. The metallic surfaces of bioprocessing equipments interact with the exposed electrolytic environment (washing and disinfecting solutions, disinfecting solutions with microorganisms etc.) through electrochemical mechanism (Landoulsi *et al.* 2008; Osarolube *et al.* 2008). Electrochemical behavior of stainless steels is studied intensively and the synergic effect of biocide and fungi is a challenging research area (Bellezze *et al.* 2005; Hiromoto and Hanawa, 2006; Osarolube *et al.* 2008; Stoica *et al.* 2010b). Some results show that the AISI 304 stainless steel

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presents a higher corrosion rate in mixtures of biocide and fungi than biocide alone (Stoica *et al.* 2010a, b). In this study the corrosion effect of AISI 316L stainless steel treated by *Oxonia-Active* biocide and in a mixture consisting of *Oxonia-Active* and *Geotrichum candidum* suspension was investigated. The corrosion behavior of stainless steel was evaluated through Linear Polarization Technique (LP) which offers very fast measurements on surface corrosion rate process.

Materials and methods

AISI 316L stainless steel

Tests were performed using AISI 316L stainless steel (SS) samples. The SS was prepared in rectangular samples (40mm×10mm×2mm) and pretreated by mechanically polishing with abrasive paper of increasingly finer grit from between 800 and 2000 µm and finally chemical cleaning (Stoica *et al.* 2010a). The samples as working electrode was covered with a tetrafluoroethylene-perfluoroalkylvinylether copolymer (PFA) foil sample except an exposed test area of 1 cm^2. The working electrode was embedded horizontally in the electrochemical cell for polarization measurements.

Biocide solution

The biocide (*Oxonia-Active*) is a commercially disinfectant, effective against all types of microorganisms in food industry manufactured by Ecolab (GmbH & Co), based on H_2O_2 (dihydrogen dioxide – 27.5% wt) and $C_2H_4O_3$ (ethaneperoxoic acid 8% wt). Fresh solutions of *Oxonia-Active* were prepared by dilution of commercially *Oxonia-Active* biocide. The concentration of *Oxonia-Active* was 0.2% performed at 15°C and it lasts for 1800 s.

Fungi strains

The *Geotrichum candidum* fungal suspension with a spore's concentration of 1.3x10^6 cells/mL was prepared. An aliquot volume of fungal suspension (20 mL) was used in the electrochemical experiments (100 mL as total volume) and final concentration of fungal suspension was of 20/100*1.3x10^6 cells/mL.

Electrochemical study

Tests on the corrosion behavior of SS samples were performed in *Oxonia-Active* biocide solution with and without *Geotrichum candidum* fungal suspension. The electrochemical measurements were carried out in a glass electrochemical-cell equipped with three electrodes, at 15±1ºC temperature. The working electrode (WE) was the AISI 316L stainless steel, the counter electrode (CE) was a Platinum foil (2 cm^2) and the reference electrode (RE) was saturated calomel electrode (SCE). The entire three-electrode assembly was placed in a Faraday cage to limit the noise disturbance and then connected to potentiostat-galvanostat Bio-Logic SP-150 - France, using EC-Lab® Express v 9.46 software. The electrochemical measurements were carried out using the Linear Polarization Technique. The potential range was between -1 V to +1 V (vs. SCE) with a scan rate of 50 mV/s and the triplicate polarization measurements were initiated after 30 seconds from immersion.

Results and discussions

Electrochemical behavior of AISI 316L stainless steel immersed in biocide *Oxonia-Active* solution and respectively in mixture consisting of biocide *Oxonia-Active* solution with *Geotrichum candidum* suspension was investigated at 15±1ºC, by Linear Polarization Technique. The polarization curves obtained at different times from immersion (40 s and 1800 s) are showed in Figure 1. It was possible to determinate the electrochemical parameters like corrosion potential (E_{corr}), current density (j_{corr}) and corrosion rate (V_{corr}) using *Tafel fit. Analysis Tools* and results are presented in Tables 1 and 2.

The electrochemical system contains the metallic surfaces immersed in mixture consisting of biocide *Oxonia-Active* solution and *Geotrichum candidum* suspensions was compared with the electrochemical system immersed only in the biocide and fungi. The electrochemical behavior was studied by potentiodinamic method. There were compared firstly the polarization curves of SS immersed only in biocide *Oxonia-Active* solution (curves number 1 and 2) with the polarization curves of SS immersed in the mixture consisting of biocide *Oxonia-Active* solution and *Geotrichum candidum* suspension (curves number 3 and 4). Finally a comparison of electrochemical fitted parameters from experimental data was very efficiently.

Figure 1 presents the polarization curve of *SS* immersed in *Oxonia-Active* biocide only and the polarization curves of *SS* immersed in the mixture consisting of biocide with *Geotrichum candidum* suspension at 40 s and 1800 s.

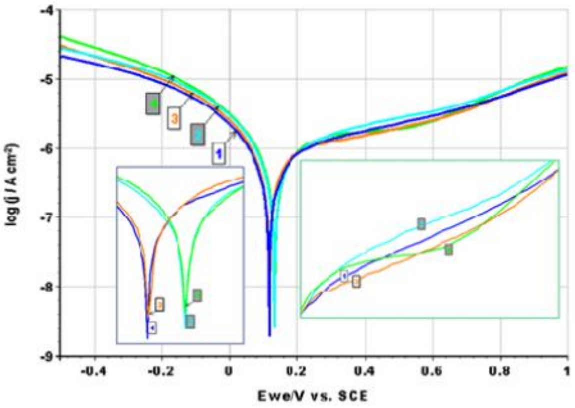

Figure 1: *Polarization curves of SS immersed in biocide Oxonia-Active biocide at 40 s (1) and 1800 s (2) and in mixture consisting of biocide with Geotrichum candidum suspension at 40 s (3) and 1800 s (4).*

From the polarization curves, it can be observed a lower shift of E_{corr} value to the positive direction for *SS* immersed in *Oxonia-Active* biocide with and without *Geotrichum candidum* suspension at 1800 s (Fig. 1, curves 2 and 4). The absence of the parallelism of cathodic and anodic branches between the curves 1 and 2 which correspond to the biocide and curves 3 and 4 which correspond with the mixture suggests that the processes on *SS* immersed in mixture are different from that on *SS* immersed in *Oxonia-Active* biocide only.

Table 1 presents the electrochemical parameters of AISI 316L stainless steel surfaces at action of *Oxonia-Active* biocide with and without *Geotrichum candidum* suspension at 40 s.

As it can be observed from the Table 1 the E_{corr} is +133 mV (SCE) and j_{corr} is 0.627 µA/cm^2 for *SS* immersed in only *Oxonia-Active* biocide. The *SS* immersed just in *Geotrichum candidum* suspension indicated E_{corr} of -208 mV (SCE) respectively j_{corr} of 0.115 µA/cm^2. In case of mixture consisting of *Oxonia-Active* biocide with *Geotrichum candidum* suspension the E_{corr} value is of +129 mV (SCE) at 40 s, but the presence of *Geotrichum candidum* suspension in biocide is characterized by a significantly increasing of current density from 0.627 µA/cm^2 to 0.705 µA/cm^2.

Table 1. *Tafel parameters of AISI 316L stainless steel surfaces at action of Oxonia-Active biocide with and without Geotrichum candidum suspension at 40 s.*

Solution	**Time (s)**	E_{corr} **(mV)**	j_{corr} **(µA/cm^2)**	**βc (mV/dec.)**	**βa (mV/dec.)**	V_{corr} **(mm/y)**
Oxonia-Active	40	133±4.24	0.627±0.0200	230±7.78	453±41.50	0.0065±0.0001
G. candidum	40	-208±14.85	0.115±0.0113	260	386±12.73	0.0001±0.0001
Oxonia-Active with G. candidum	40	129±5.35	0.705±0.0007	238±6.36	655±33.23	0.0073±0.0001

Table 2 presents the electrochemical parameters of AISI 316L stainless steel surfaces at action of *Oxonia-Active* biocide with and without *Geotrichum candidum* suspension at 1800 s.

As it can be observed from the Table 2 at 1800 s the E_{corr} is shifted to +137 mV (SCE) and j_{corr} is 0.684 µA/cm^2 for *SS* immersed in only *Oxonia-Active* biocide.

Table 2. *Tafel parameters the electrochemical parameters of AISI 316L stainless steel surfaces at action of Oxonia-Active biocide with and without Geotrichum candidum suspension at 1800* **s.**

Solution	**Time (s)**	E_{corr} **(mV)**	j_{corr} **(μA/cm^2)**	βc **(mV/dec.)**	βa **(mV/dec.)**	V_{corr} **(mm/y)**
Oxonia-Active	1800	137±7.78	0.684±0.0050	221±9.90	493±42.00	0.0071± 0.0001
G. candidum	1800	-205±20.00	0.147±0.0180	280±27.03	368±35.00	0.0015± 0.0001
Oxonia-Active with G. candidum	1800	134±2.83	0.782±0.0004	229±6.36	587±2.12	0.0081± 0.0000

The SS immersed just in *Geotrichum candidum* suspension indicated E_{corr} of almost same value of -205 mV (SCE) but increasing of j_{corr} of 0.147 μA/cm^2. In case of mixture consisting of *Oxonia-Active* biocide with *Geotrichum candidum* suspension the E_{corr} values is of +134 mV (SCE) and presence of *Geotrichum candidum* suspension in biocide indicate also an increasing of current density with about 0.1 μA/cm^2.

The shift of E_{corr} suggests that the *Geotrichum candidum* suspension added in the biocide *Oxonia-Active* solution is a depolarization agent for ASI 316L stainless steel surfaces, confirmed by the shifts in the cathodic (β_c) and anodic (β_a) Tafel slopes (Burstein, 2005; Elsener, 2005; McCafferty, 2005). This process is predominant anodic, as it can be seen from the Table 1. The mixture at 40 s after immersion shifts the cathodic (β_c) slope from 230 mV/decade to 238 mV/decade and anodic slope (β_a) from 453 mV/decade to 655 mV/decade (Table 1). At 1800 s the cathodic (β_c) slope shits from 221 mV/decade to 229 mV/decade and anodic slope (β_a) from 493 mV/decade to 587 mV/decade (Table 2). The shift of the Tafel slopes reveals that the *Geotrichum candidum* suspension induces a corrosion mechanism on metallic surface (Muhamath et Kulanthai, 2009). These results suggest that the mixture consisting of *Oxonia-Active* biocide with *Geotrichum candidum* suspension controlling predominantly the anodic reactions. The shift of E_{corr} and the increase of j_{corr} values indicated a synergic effect from mixture with *Geotrichum candidum* suspension and *Oxonia-Active* biocide. This fact can substantially accelerate the corrosion process of metallic surfaces immersed in the mixture consisting of biocide and fungal suspension. The predominant anodic parameters could be an answer of degradation metallic surfaces and this phenomenon is in good agreement with data previously reported in literature (Stoica *et al,* 2010a).

Biocide-Fungi Synergic Effect

The corrosion behavior on *SS* surfaces was tested in the biocide solution with and without fungal suspension. All electrochemical parameters indicated a shifting of E_{corr} potential and an increasing of j_{corr} values for the surfaces immersed in mixture consisting of biocide with fungal suspension compared with data obtained when metallic surfaces were immersed only in biocide and respectively in fungal suspension. The corrosion behavior of AISI 316L stainless steel samples is reflected also through V_{corr} (corrosion rate). Figure 2 presents the V_{corr} values of *SS* immersed in *Oxonia-Active* biocide, in *Geotrichum candidum* suspension and respectively V_{corr} values obtained when *SS* sample were immersed in the mixture consisting of biocide with *Geotrichum candidum* suspension after 40 s and respectively 1800 s as contact period between metallic surface and environment.

In case of biocide *Oxonia-Active* solution without fungal suspension it can be observed that the *SS* present a low-moderate rate of corrosion during the contact time (Fig. 2, series 1).

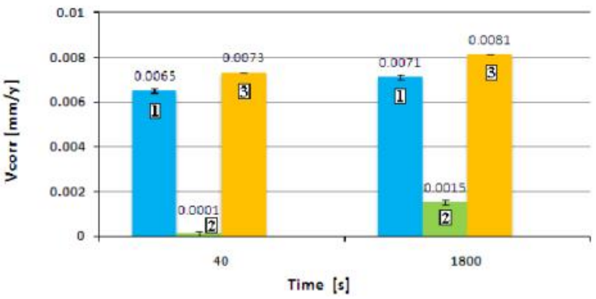

Figure 2. *V_{corr} values of SS immersed in Oxonia-Active biocide (series 1), in Geotrichum candidum suspension (series 2) and immersed in the mixture consisting of biocide with Geotrichum candidum suspension (series 3), at contact time of 40 s and 1800 s.*

It is observed that the V_{corr} values increase more at the mixture consisting of biocide with *Geotrichum candidum* suspension (Fig. 2, series 3). In this case it can be observed that the V_{corr} values increase more during the experiment (Fig. 2, series 1 and 3) compared with the results when the surfaces were exposed only at the biocide solution. Thus, the AISI 316L stainless steel surfaces are more corrosive in electrochemical system containing by *Oxonia-Active* biocide with *Geotrichum candidum* suspension, at the different exposure time. As a conclusion data presented in Figure 2 indicates an increasing of surfaces corrosion immersed in mixture of biocide with fungal suspension compared with biocide only. The values reported already in literature shows that the *SS* surfaces present an increasing a corrosion rate by immersion in biocides with different fungal suspension (Stoica *et al.* 2010a). The mixture of biocide with fungi alters on metallic surfaces and it can transform them into a new surface which has reducing functions: corrosion resistance, abrasive resistance or might possibly encourage more biofilm adhesion and biofilm resistance to detachment (Pringle *et al.* 1983; Fontana, 1986; Holah and Thorpe 1990).

Conclusions

There were studied the electrochemical behavior of AISI 316L Stainless Steel on the action of biocide with and without fungal suspension, through Linear Polarization Technique. The mixture consisting of *Oxonia-Active* biocide and *Geotrichum candidum* suspension is more destructive for metallic surface than *Oxonia-Active* only. This mixture decreases the corrosion resistance of the metallic surfaces, the abrasive resistance and may possibly favor the biofilm adhesion on the biotechnological equipments. The synergic effect of the mixture consisting of *Oxonia-Active* biocide and fungal suspension can be ignored at macroscopic level, but at nanoscopic level should be taken into account because it can have a negative influence on obtained products quality.

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