Electrochemical study of stainless steel surfaces in biodegradable biocides

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The aim of this study is to evaluate the electrochemical behaviour of Stainless Steel (SS) surfaces in biocide solutions used in food contact surface. The action of three disinfectants was studied: Neoseptal, Actisept and Anasept. The samples of AISI 304 SS were exposed to the disinfectant solutions and after this treatment were examined by Scanning Electron Microscopy (SEM). The electrochemical behaviour of AISI 304 SS in the solutions was put in evidence by linear polarisation measurements. SEM analysis demonstrated that damages depend on the chemical nature of the disinfectant. The voltammetry measurements have shown a strong influence of biocide solution in the electrochemical behaviour of SS.

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1. Introduction

Product quality, health and sanitation issues are major concerns in the food-processing industry. This industry cannot tolerate corrosion deposits in the manufactured product, corrosion products are not acceptable in the food product due to health reasons; therefore, almost all processing equipment are fabricated from corrosion-resistant material. In many food industries, production lines are daily cleaned and disinfected [1]. These processes are essential steps in preventing food contamination with pathogenic and spoilage microorganisms [2]. The most efficient method to maintain effective sanitation is use of cleaning-in-place (C.I.P.) systems used with closed equipment. Disinfection is the process of applying a disinfectant against unwanted microbial contaminants [3]. A disinfection protocol usually ends with the elimination of the disinfectant traces by rinse, but, there are authors who consider that disinfectant application is the last step of a disinfection protocol and rinsing with water is not necessary [4]. Also, some biocide producers support the idea that as long as the remaining disinfectant in the processing food lines does not exceed the legal limits [5], it does not represent a chemical risk for the consumers' health and it may reduce the general food contamination. In other words, the remaining disinfectant serves as a sentinel against microorganisms. But the residual disinfectant can potentially lead to a significant degradation of equipments' materials *via* corrosion that, in turn, can increase the adhering of soil [6,7,8]. Some authors [8] have emphasized the importance of the chemical nature and finishing of materials in relation to the surface cleaning ability. Material texture and topography are also influencing surface cleanability. Impurities attachment in pits and crevices would not receive the same cleaning shear forces as dirt attached to a smooth surface, the rough surfaces being much difficult to clean comparing to smooth surfaces. Numerous factors affect disinfection efficacy in food line products, such as: pH, concentration of the disinfectant, contact time [9]. Generally, low pH values cause high corrosion; acidic environments can cause a breach in protective layer of metallic surfaces, whereas high pH can decrease metal solubility. Stainless steels (SS) are widely used in food and beverage manufacturing and processing industries for manufacture, bulk storage and transportation, preparation and presentation applications. Alloys of 304 AISI SS are the most familiar materials used in food applications because are easy to clean, durable, inert and sanitary.

The aim of this work was to evaluate the electrochemical behaviour of AISI 304 SS in different disinfectant solutions, by linear polarization. Using SEM could be evaluating the influence of disinfectants on the metallic surfaces.

2. Experimental

2.1. Pre-treatment of stainless steel substrate

Tests were performed on AISI 304 SS. The coupons were mechanically polished with abrasive paper of increasingly finer grit between 80 and 1200 μm and chemically cleaned [10]. The substrate was adapted as working electrode. The exposed area of the working electrode was 12 cm^2.

Disinfectant solutions. The action of three commercially disinfectants on AISI 304 SS, at the maximum concentration, was studied in this investigation.

a) First disinfectant with Neoseptal namely (2% sln. of H_2O_2 30%) was examined. The pH of the working disinfectant solution was 2.67. The biocide pH has an important influence in the redox process that takes place at SS interface and the importance of chemical electroactive substances in the corrosion process.

b) The second disinfectant with Actisept namely (0.25% sln. of sodium dichloroisocyanurate - source of chlorine) was studied. The pH of the working disinfectant solution was 5.85.

c) The last disinfectant with Anasept namely (0.5% sln. of mixture of active substances: Hexamethylenediamine, Polyhexamethylene biguanide, Quaternary ammonium compounds, Propylenglicol) was examined. The pH of the working disinfectant solution was 6.80.

All disinfectants are approved by the Romanian National Register of Biocide Products [11] to be used in processing areas. The measurements were made using the WTW INOLAB 720 pH-meter.

2.2 Electrochemical study of samples

The electrochemical investigations were performed in a glass typical cell with a capacity of 50 mL (Metrohm, Switzerland) with three electrodes: platinum plate as counter electrode (CE), saturated calomel (SCE) as reference electrode (RE) and AISI 304 SS as working electrode (WE). Tests were performed at room temperature. These three-electrodes form an assembly which was placed into a Faraday cage to limit external noise. Then the assembly was connected to a potentiostat/galvanostat model SP-150 (Bio-Logic SAS, France). The investigations are carried out by means of VMP3 and EC-LAB Express 9.46 software. The electrochemical behaviour of AISI 304 SS in each disinfectant was emphasized by linear polarization method. The polarization curves and Stern–Geary relationship [12] were used to determine the corrosion current (I_{corr}), the corrosion potential (E_{corr}). Using Tafel fit and polarization resistance (R_p) fit analysis may cause corrosion rate (V_{corr}) and R_p parameters. These parameters were measured at the initial moment and after 3 days of contact between SS coupons and disinfectants solutions.

2.3. Microscopically characterization of the surface

The morphological characteristics of AISI 304 SS surfaces were examined by means of scanning electron microscopy (SEM). The micrographs were recorded by means of Quanta 200 Philips FEI device before and after the electrochemical investigations in 20 fields with area 100 μm^2 for each sample [13].

3. Results and discussion

3.1. Potentiodynamic polarization

The WE were carefully cleaned and rinsed with bidistilled water before their immersion in the electrochemical cell with biocide solution. Each measurement started after 60 s to access an equilibrium potential between SS coupons and biocide solution, because of electronic interactions at interface [14,15]. The point of intersection between the anodic and cathodic reactions establishes the corrosion potential (E_{corr}) of the metal and indicates the magnitude of corrosion current (I_{corr}). Fig. 1-4 present the electrochemical behaviour of SS coupons tested in three disinfectants. The electrochemical parameters are shown in Tables 1-3.

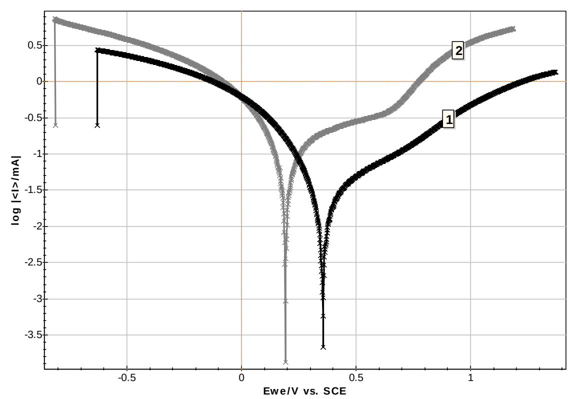


Fig. 1. Polarization curves of AISI 304 SS coupons at Neoseptal solution action at different contact time: 1) initial; 2) after 3 days.

Table 1. Electrochemical parameters of SS coupons at Neoseptal solution action.

Time	AISI 304 SS			
	E_{corr} (mV)	I_{corr} (µA)	R_p (Ω)	V_{corr} (µmpy)
initial	364.09	22.83	1920.93	19.54
after three days	198.78	94.62	499.84	81.62

Fig. 1 shown polarization curves in case of AISI 304 SS coupons immersed in Neoseptal (which contains hydrogen peroxide with pH 2.67). The potential E_{corr} was shifted less positive values after three days and I_{corr} increased almost four times, in microamperes range. The experimental R_p indicates lower resistance of SS at Neoseptal action after three days. At longer contact time between SS coupons and biocide, R_p value decreased with 1500 Ω (Table 1), thus confirming the increasing of corrosion rate values. The Neoseptal solution is the most aggressive medium.

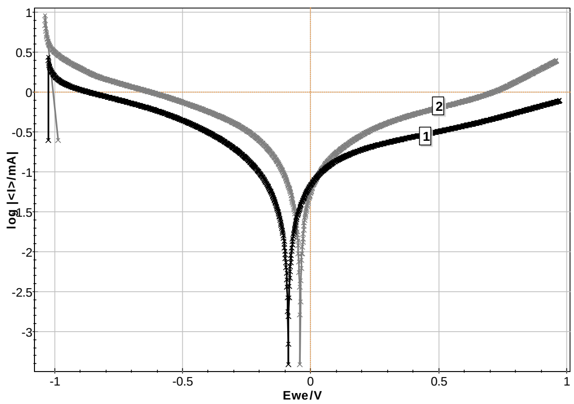


Fig. 2. Polarization curves of AISI 304 SS coupons at Actisept solution action at different contact time: 1) initial; 2) after 3 days.

Table 2. Electrochemical parameters of SS coupons at Actisept solution action.

Time	AISI 304 SS			
	E_{corr} (mV)	I_{corr} (μA)	R_p (Ω)	V_{corr} (μmpy)
initial	-88.16	54.56	1221.40	34.07
after three days	-36.65	68.55	684.84	59.14

Fig. 2 has shown the resistance of SS at Actisept (which contains sodium dichloroisocyanurate of pH 5.85) action after three days. The potential E_{corr} was shifted in less negative range and decreased after three days, but I_{corr} increased a little. The experimental R_p indicates a decreasing from 1221.4 Ω at initial contact to 684.84 Ω after three days, thus confirming the slow increasing of corrosion rate value (Table 2).

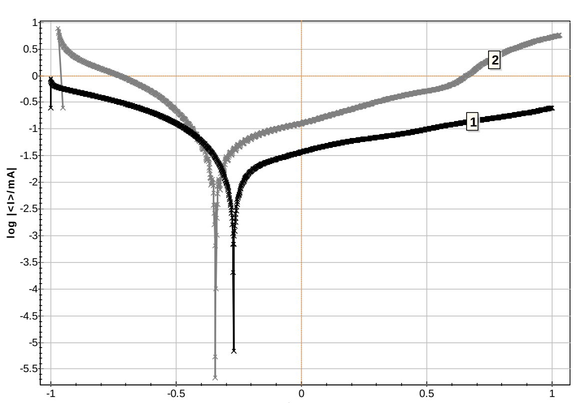


Fig. 3. Polarization curves of AISI 304 SS coupons at Anasept solution action at different contact time: 1) initial; 2) after 3 days.

Table 3. Electrochemical parameters of SS coupons at Anasept solution action.

Time	AISI 304 SS			
	E_{corr} (mV)	I_{corr} (μA)	R_p (Ω)	V_{corr} (μmpy)
initial	-269.41	23.71	3094.04	12.69
after three days	-328.71	31.52	1366.9	27.19

Fig. 3 has shown the resistance of SS at Anasept action after three days. This disinfectant is recommend for surfaces cleaning because contains additive against corrosion. The potential E_{corr} was shifted in less negative range (-60 mV) and I_{corr} increased a little. The experimental R_p indicates a pronounced decreasing from 3094.04 Ω at initial contact of 1366.9 Ω after three days, thus confirming the increasing of corrosion rate value two times (Table 3). At this disinfectant the SS coupons indicate better corrosion resistance compared with Neoseptal and Actisept biocide. But however it is not indicated in disinfection of C.I.P. because this disinfectant produces foam.

The relevant behaviour of SS coupons in tested disinfectant solutions is presented in Fig. 4. The range values for E_{corr} after three days of immersion can observe.

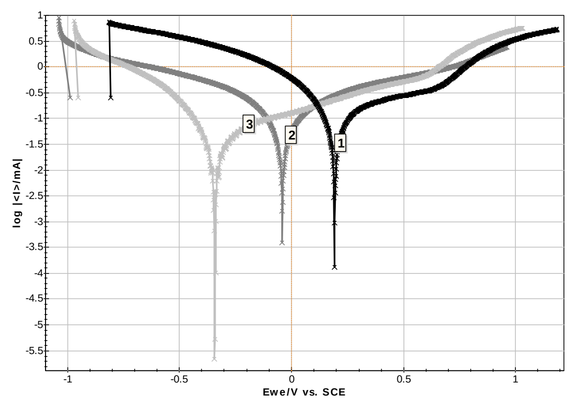


Fig. 4. Polarization curves of AISI 304 SS in disinfectant solutions at after three days immersion: 1) Neoseptal; 2) Actisept; 3) Anasept

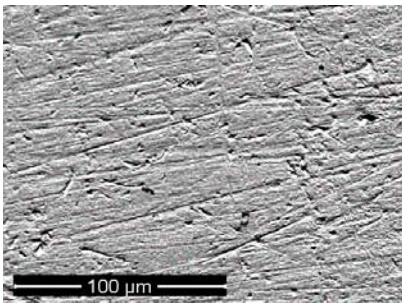
3.2 Microstructure characterization

It is widely accepted in the literature that the disinfectant residuals increase corrosion of materials [16]. To characterize the morphology of surface four coupons were chosen to compare all samples immersed in all disinfectant solution with a control sample. For AISI 304 SS surfaces the susceptibility to crevice corrosion is dependent on the surface finishing. The aspects of the surfaces exposed to the various media are shown in Fig. 5.

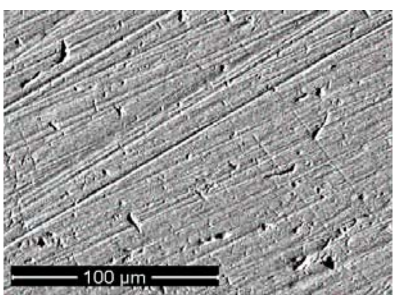
The Neoseptal disinfectant produces some imperfections on the surface (Fig. 5a). Usually, low value of pH enhances the corrosion process; the acidic environment can produce some breaches in the protective layer [17].

For Actisept disinfectant a reduced destruction of AISI 304 SS surface was observed (Fig. 5b), but Anasept disinfectant shows a lower destruction surface (Fig. 5c), that can be related with basic pH of the biocide solution. At initial time from the contact, the corrosion rate for Anasept disinfectant is less than 0.02 mm per year (mmpy) and is considered outstanding.

The corrosion rate is excellent in the range between 0.02 and 0.1 mm per year (mmpy) for all studied disinfectants at any time of contact in agreement with Fontana [18].



a)



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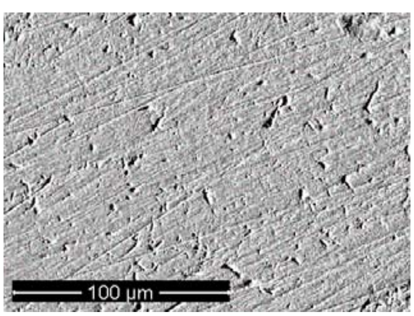

c)

Fig. 5. SEM micrograph of AISI 304 SS in disinfectant: a) Neoseptal; b) Actisept; c) Anasept

4. Conclusions

The corrosion behaviour of AISI 304 SS surface in active substance like as Neoseptal, Actisept and Anasept disinfectants were evaluated and the electrochemical parameters were calculated. The E_{corr} and I_{corr} values have shown a difference between the behaviour of SS surface to the disinfectants action. The V_{corr} decreases at the initial contact time between the SS coupons and biocide solutions in the following order: Actisept<Neoseptal<Anasept. The order was changed after three days from immersion of the coupons in the following order: Neoseptal<Actisept<Anasept. The corrosion rates of AISI 304 SS surface immersed in active substances like as Neoseptal, Actisept and Anasept disinfectants are excellent (high).

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