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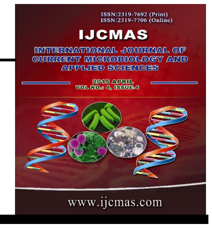

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Original Research Article

Study of the Effect of Lactic Acid Fermentation End Products on the Speed of the Corrosion Process

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A B S T R A C T

Corrosion is the result of a series of chemical, physical and (micro) biological processes leading to the deterioration of materials such as steel and stone. It is a world-wide problem with great societal and economic consequences. Prevention of, or reduction in the rate of corrosion may be accomplished by the use of a biological, environmentally friendly anti-corrosive layer at the metal interface. In this paper, we show the effect of lactic acid fermentation end products on the low-carbon steel corrosion process. The study of the corrosive stability of steel samples was conducted with the gravimetrique method. The duration of the procedure was 120 hours at 18ºC. After the treatment the steel samples were washed with water and dried to constant weight. The structure of layer over steel plates was analised by Scanning electron microscopy (SEM) JSM 5510. *Parameters of corrosion* After retrieval, the corrosion products were removed when washed with water. They were dried in an oven. After the removal of corrosion, steel plates were cleaned and reweighed as above to estimate weight loss. The rate of corrosion, the degree of protection, and coefficient of protection were calculated. The corrosion rates K ($g/cm^2.h$) presented as follows: $K = \Delta G / S.\tau$, $g/cm^2.h$; Where: K is the corrosion rate; ΔG – losses of mass consequence of corrosion, g; S- is the area of plates, m^2; τ- is duration of the corrosion, h.In order to track out the inhibitor properties of EPS synthesized in media, the degree of protection (Z) and coefficient of protection (γ) have been calculated using the formulas: $Z = (K_0 - K\,i) / K_0$ x100,%; $\gamma = K_0/Ki$; Where: K_0 is the corrosion rate in control media; K_i – the corrosion rate in test media. Key Results: The cover formed on the steel sample when treated with acetic acid shows there is no protection from corrosion, table 1 and figure 1A. The cover is probably due to the synthesis of ferrous acetate. Figure 1B shows a picture of a steel surface sample treated directly with lactic acid. The cover here probably consists of ferrous lactate crystals. When the steel plate was treated with ethyl alcohol, the highest coefficient of protection was registered, 86.21% (table 1). Carbon dioxide causes corrosion of the steel sample, too, because of the fact that it forms weak carbon acid in water. It can be seen from table 1 that the speed of corrosion ($K.10^{-5}$, $g/cm^2.h$) in the carbon acid is slightly higher than the one in the lactic acid and about four times lower than the one in the acetic acid. Microscope techniques provide information about the morphology of microbial cells and colonies, their distribution on the surface and the nature of corrosion products (crystalline or amorphous). They can also reveal the type of attack (e.g. pitting or uniform corrosion) by visualizing changes in microstructure and surface features after removal of the covering and corrosion products (Fig. 1). In literature there is no information about the effect of the fermentation end products on the corrosion process. The results we have obtained let us conclude that some of the end products possess a certain extent of protection against corrosion, but EPS have better protecting properties (Ignatova-Ivanova and Ivanov, 2014). From this, it is evident that some microorganisms and/or their polysaccharides or products from the fermentation process can act as strong corrosion inhibitors.

Keywords

Corrosion,
Corrosion rate,
Coefficient of protection

Introduction

Corrosion is the result of a series of chemical, physical and (micro) biological processes leading to the deterioration of materials such as steel and stone. It is a world-wide problem with great societal and economic consequences (Kip and van Veen, 2015). Prevention of, or reduction in the rate of corrosion may be accomplished by the use of a biological, environmentally friendly anti-corrosive layer at the metal interface. In the vast majority of ecosystems, be they associated with industrial plant (Costerton and Lashen, 1984), the natural environment (Allison and Sutherland, 1984), or animal and plant infections (Costerton *et al.,* 1987), microbial cells grow in association with surfaces. Surface-associated growth leads to the formation of biofilms, which can be defined as a consortium of microorganisms which are immobilized at a substratum surface and embedded in an organic polymer matrix of microbial origin (Marshall, 1992). Attachment to a surface is thought to initiate a cascade of physiological changes in the cells which leads, in part, to the overproduction of exopolymers (Allison and Sutherland, 1987; Davies and Geesey, 1995). These exopolymers not only immobilise the cells on the colonised surface, but also facilitate the spatial arrangement of different species within a biofilm (Costerton *et al.,* 1994). Such interactions give the biofilm community metabolic and physiological capabilities which are not possible for the individual, unattached cells (Gilbert *et al.*, 1997). Very often biofilms are composed of mixed communities of microorganisms and their metabolic products (Allison, 1998). In our previous studies (Ignatova-Ivanova *et al.,* 2009; Ignatova-Ivanova *et al.,* 2011; Ignatova-Ivanova and Ivanov, 2013) was shown that at the presence of high concentration of lactose (5 to 15 %), high concentration of sucrose 4%, and concentration sucrose 4% and 2% maltose the strains *Lactobacillus delbrueckii B5*, *L. delbrueckii K27, L. delbrueckii B8, L. delbrueckii O43, L. delbrueckii K3, L. delbrueckii K17, and L. delbrueckii K15* synthesized exopolysaccharides which have inhibitory properties. Moreover, mixture of 5% sucrose mixed with 5% maltose, or with 5% lactose stimulated the formation of microbial biofilm inhibiting the corrosion of steel (Tsveteslava Veselinova Ignatova-Ivanova and Radoslav Iliev Ivanov, 2014).

In this paper, we show the effect of lactic acid fermentation end products on the low-carbon steel corrosion process.

Materials and Methods

The study of the corrosive stability of steel samples was conducted with the gravimetrique method (Raychev *et al.*, 2002). Before use, steel panels (10 x 4 x 0,2 mm) were treated with 70% C_2H_5OH, washed with water and dried in an oven, cooled in a desiccator, weighed on a balance and kept in a desiccator unit used. The weight of the samples was measured using analytical balances. The dimensions of the samples were measured with micrometer. The steel plates are placed directly in the end products of the heterofermentative lactic acid fermentation, namely lactic acid, acetic acid, carbon dioxide (water saturated with carbon dioxide), and ethyl alcohol.

The duration of the procedure was 120 hours at 18ºC. After the treatment the steel samples were washed with water and dried to constant weight.

The structure of layer over steel plates was analised by Scanning electron microscopy (SEM) JSM 5510.

Parameters of corrosion After retrieval, the corrosion products were removed when washed with water. They were dried in an oven. After the removal of corrosion, steel plates were cleaned and reweighed as above to estimate weight loss.

The rate of corrosion, the degree of protection, and coefficient of protection were calculated.
The corrosion rates K ($g/cm^2.h$) presented as follows:

$K = \Delta G / S.\tau, g/cm^2.h;$

Where: K is the corrosion rate; ΔG – losses of mass consequence of corrosion, g; S- is the area of plates, m^2; τ- is duration of the corrosion, h.

In order to track out the inhibitor properties of EPS synthesized in media, the degree of protection (Z) and coefficient of protection (γ) have been calculated using the formulas:

$Z = (K_0 – K i) / K_0 x100,\%;$
$\gamma = K_0/Ki;$

Where: K_0 is the corrosion rate in control media; K_i – the corrosion rate in test media

Result and Discussion

The steel samples are placed directly in solutions of lactic acid 80%, acetic acid concentrated, carbon dioxide (water saturated with carbon dioxide), and ethyl alcohol 96%. A steel plate put in freshly distilled water is used as a control. The received results are presented in table 1. The structure of the layer over the steel plates was analyzed by Scanning electron copy.

The results from this procedure are shown in figure 1. The cover formed on the steel sample when treated with acetic acid shows there is no protection from corrosion (Table 1 and Figure 1A). The cover is probably due to the synthesis of ferrous acetate. Figure 1B shows a picture of a steel surface sample treated directly with lactic acid. The cover here probably consists of ferrous lactate crystals. When the steel plate was treated with ethyl alcohol, the highest coefficient of protection was registered, 86.21% (Table 1). Carbon dioxide causes corrosion of the steel sample, too, because of the fact that it forms weak carbon acid in water. It can be seen from table 1 that the speed of corrosion ($K.10^{-5}$, $g/cm^2.h$) in the carbon acid is slightly higher than the one in the lactic acid and about four times lower than the one in the acetic acid.

Microscope techniques provide information about the morphology of microbial cells and colonies, their distribution on the surface and the nature of corrosion products (crystalline or amorphous). They can also reveal the type of attack (e.g. pitting or uniform corrosion) by visualizing changes in microstructure and surface features after removal of the covering and corrosion products (Fig. 1).

In previous experiments we have shown the effect of the biofilm created by lactic acid bacteria on the speed of the corrosion process (quotation). We have also shown that LAB synthesize EPS which possess protector properties, too (Tsveteslava Veselinova Ignatova-Ivanova and Radoslav Iliev Ivanov, 2014; Ignatova-Ivanova and Ivanov). A study similar to ours has shown that of a polysaccharide producing culture Delta marina was found to act as a strong corrosion inhibitor with almost complete passivation of mild steel, reducing the corrosion rate by 95% (Ford *et al.*, 1988).

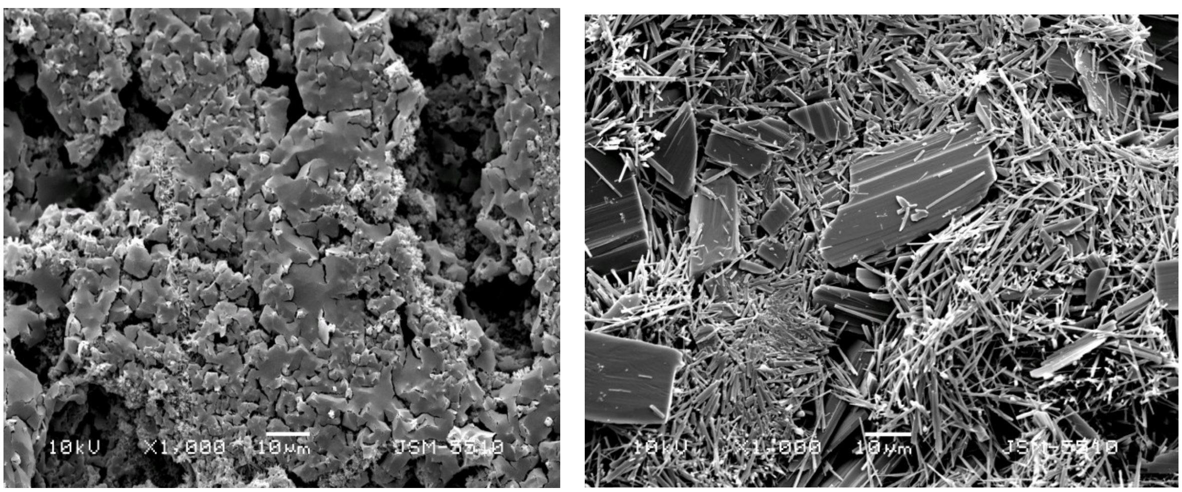
In literature there is no information about the effect of the fermentation end products on the corrosion process. The results we have obtained let us conclude that some of the end products possess a certain extent of protection against corrosion, but EPS have better protecting properties (Ignatova-Ivanova and Ignatova-Ivanova, 2014). From this, it is evident that some microorganisms and/or their polysaccharides or products from the fermentation process can act as a strong corrosion inhibitors.

Table.1 Indicators of corrosion

№ sample	Solution	K.10^{-5}, g/cm^2.h	Z, %	γ
1.	*Lactic acid	0.50	13.80	1.16
2.	*Acetic acid	2.03	0	0.28
3.	Carbon dioxide	0.53	8.62	1.09
4.	*Ethyl alcohol	0.08	86.21	7.25
5.	control	0.58	-	-

*The steel plates were photographed after washing; Results are mean ± SEM of three separate trails.

Fig.2 Biofilm formed by the fermentation end products on the surface of mild steel, visualized using SEM. A) Acetic acid B) Lactic acid



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Author contributions

All the authors have read the final manuscript and approved for submission.

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