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INVESTIGATION OF BEE POLLEN AS AN ECO-FRIENDLY CORROSION INHIBITOR FOR BRONZE IN A SIMULATED ACIDIC RAIN SOLUTION

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ABSTRACT: *Bee pollen was tested as potential green corrosion inhibitor of bronze in simulated acid rain in a weakly acidic solution containing Na2SO4 and NaHCO3 (pH 5), simulating an acid rain in the urban environment. Potentiodynamic polarization, scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) techniques were used to evaluate the inhibitive performance of bee pollen against bronze corrosion. Potentiodynamic polarization revealed that the bee pollen acts as a mixed-type corrosion inhibitor; its inhibiting efficiency increases with increasing the pollen concentration attaining the maximum value of 74.7% in the presence of 100 ppm pollen. SEM-EDX analysis confirmed that bee pollen is able to retard the bronze corrosion in a simulated acidic rain solution.*

Keywords*: bronze; corrosion; inhibitor; bee polen;*

1. Introduction

In the last 50 years, the ancient and modern bronzes exposed in urban atmosphere have been subjected to advanced degradation processes, due to the significant intensification of the air pollution, which caused the increase of the rainfall acidity [1]. Although the bronzes suffer a spontaneous oxidation when exposed to humid air, forming an oxide layer (called patina) which further protects their surface from corrosion, the acidic rainfall might lead to the dissolution of the patina layer, leaving the bare metal exposed to the aggressive environment [2]. In these conditions, the bronze-made objects start corroding and additional protection treatments are needed to save them from the complete degradation. One of the most inexpensive and effective method to mitigate the bronze corrosion in aggressive media is the use of corrosion inhibitors. Up to now, various synthetic organic compounds have been used as bronze corrosion inhibitors [3], i.e. azoles, in particular benzotriazole and its derivatives [4], imidazoles [5], triazoles [6], thiadiazoles [7], phenothiazine derivatives [8], amino acids [9]. In spite of their excellent anticorrosive properties, many of these synthetic organic inhibitors have undesirable side properties, even in very small concentrations, due to their toxicity to humans, harmful effects on the environment, and high cost [11]. Due to increasing the awareness for human health and environmental protection, the research in the field has been orientated toward the goal of finding cheap and effective corrosion inhibitors at low or ''zero'' environmental impact.

Therefore, in the last years, considerable attention has been paid on the use of green corrosion inhibitors, i.e. substances naturally occurring in nature, such as plants extracts, plants oils, bee products, which are environmentally acceptable, biodegradable, inexpensive, readily available and renewable sources of materials [12]. Several recent studies have already attested the good anticorrosive effectiveness of propolis [13-16] and honey [17-22] on the metal corrosion. Moreover, the pollen extract has been proved as an eco-friendly corrosion inhibitor for pure copper in hydrochloric acid [23] and for aluminum alloy in bicarbonate buffer at pH 11 [24].

Bee pollen is a natural product with well-known antioxidant and antimicrobial properties from beehives; it has a complex composition and contains amino acids, flavonoids, phenolic compounds, alkaloids, proteins, carbohydrates, lipids, nucleic acids, mineral elements (Al, K, Ca, Cu, Fe etc.), enzymes/coenzymes, carotenoids, volatile oils, vitamins [25].

The present research focuses on the application of the bee pollen as a potential green corrosion inhibitor for bronze in a weakly acidic solution containing Na2SO4 and NaHCO3 (pH 5), simulating an acid rain in the urban environment. Potentiodynamic polarization and and scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) techniques were used to evaluate the inhibitive performance of bee pollen against bronze corrosion.

2. Experimental

The corrosive blank electrolyte was an aqueous solution of 0.2 g/L Na2SO4 + 0.2 g/L NaHCO3, acidified to pH=5 by addition of dilute H2SO4. The concentration of the pollen in the corrosive solution was ranging from 50 to 200 ppm

For the corrosion tests, an electrode made of bronze with the following chemical composition (wt. %): Cu-94.03; Sn-3.31; Pb-0.24; Zn-1.44; Ni-0.25; Fe-0.22 and S-0.51 was used as working electrode. The bronze specimen was first embedded in an epoxy resin (Buhler, EpoxycureTM), leaving a working area of 0.28 cm2. A calomel electrode was used as reference electrode, while the counter-electrode was made of a large platinum grid.

A three-electrode cell was used for the electrochemical experiments. The electrochemical measurements were performed using a PAR model 2273 potentiostat, after 1-h stabilization of the bronze electrode at the open circuit potential (OCP) in the corrosive solution.

Before the electrochemical measurements, the bronze electrode was abraded using successive grade of silicon carbide paper grit (from 800 up to 2400), washed thoroughly with distilled water and with ethanol.

Polarization curves were recorded at constant sweep rate of 10 mV/min, in a wide potential range of ± 200 mV vs. open-circuit potential (OCP), from the cathodic to the anodic direction. On this wide potential window, Tafel extrapolation method was applied.

For morphological studies, the bronze surface was prepared by keeping the electrodes during 48 hours in the corrosive solution in the absence and in the presence of the optimum concentration of pollen. Then, the specimens were washed gently with water, carefully dried and analysed without any further treatment by scanning electron microscopy (SEM) using a JEOL JSM 5600 LV microscope, equipped with EDX spectrometer - Oxford Instruments (INCA 200 software). The energy of the acceleration beam employed was 15 kV and the given results are 250× magnitudes.

3. Results and discussions

3.1. Potentiodynamic polarization measurements

Tafel polarization curves of the bronze electrode exposed to the simulating acidic rain solution in the absence and in the presence of different concentrations of pollen are displayed in Fig. 1.

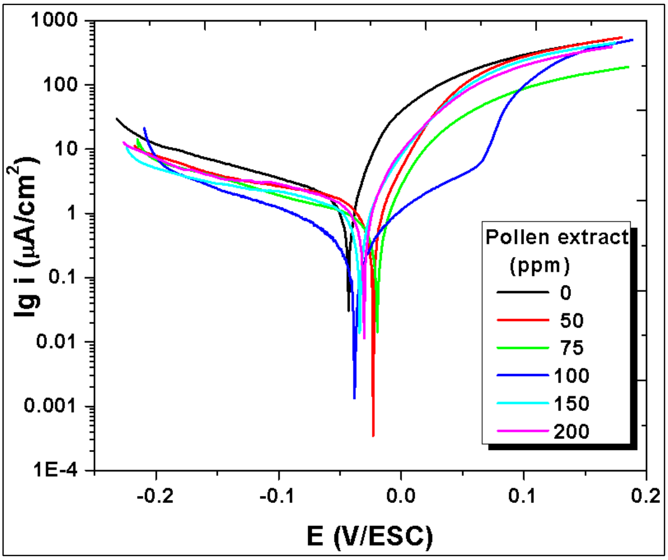

Fig. 1. Polarization curves for bronze in 0.2g/L Na2SO4 + 0.2g/L NaHCO3 (pH=5) with and without the different concentrations of pollen

As seen in Fig. 1, both the cathodic and anodic branches of the polarization curves are displaced towards lower current densities in the presence of all investigated pollen concentrations as compared to the blank solution. This decrease of the current density values could be explained by the inhibitive effect exerted by pollen on both, cathodic oxygen reduction and anodic bronze dissolution reactions, which is an indicator of the corrosion rate diminution.

The electrochemical corrosion parameters, including corrosion potential (Ecorr), corrosion current density (icorr), cathodic Tafel slope (βc), and anodic Tafel slope (βa), were determined from the polarization curves by Tafel interpretation, according to the following equation:

$$i=i_{corr}\{\exp(\beta_a(E-E_{corr})]-\exp(\beta_c(E-E_{corr})]\} \quad (1)$$

The obtained values of the electrochemical corrosion parameters and the corrosion rates calculated from the icorr values, according to Faraday's law are presented in Table 1.

The inhibition efficiency (z) values of the pollen extract are also included in Table 1 and were calculated using the following

Table 1. Corrosion kinetic parameters for bronze corrosion in simulated acidic rain (pH=5) in the absence and in the presence of pollen at different concentrations

Pollen conc. (ppm)	E_{corr} (mV/ESC)	i_{corr} (μA/cm²)	v_{cor} (mp/year)	$-\beta_c$ (mV/dec)	β_a (mV/dec)	z (%)
0	-42.3	2.89	1.34	384.4	36.4	-
50	-22.1	1.48	0.69	224.4	37.9	48.8
75	-19.6	1.16	0.54	287.7	36.4	59.9
100	-38.3	0.73	0.34	241.8	56.0	74.7
150	-33.94	1.12	0.52	267.8	40.9	61.2
200	-30.84	1.27	0.60	203.6	37.0	56.1

equation:

$$z(\%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \cdot 100 \qquad (2)$$

where i^0_{coor} and i_{corr} are the values of the corrosion current densities in absence and in presence of the pollen extract, respectively.

As shown in Table 1, the corrosion potential values, Ecorr are slightly shifted towards more positive values in the presence of the pollen extract. However, this shift is lower than ± 85 mV, suggesting that the pollen could be regarded as a mixed-type inhibitor, acting to a higher extent on the bronze dissolution process.

The decreases of the current density values, icorr observed in the presence of all investigated pollen concentrations suggest that this natural product is able to inhibit to some extent the bronze corrosion, most likely due to the adsorption of its components on the bronze surface, which form a protective barrier film which isolate the bronze from the aggressive solution and reduce its corrosion rate.

As illustrated in Table 1, the inhibiting efficiency of the pollen on bronze corrosion increases with its concentration from z = 48.8% at 50 ppm inhibitor to the maximum value of 74.7% obtained in the presence of 100 ppm pollen. Further increases in the pollen concentration led to a slight decrease of its inhibiting efficiency, most probably due to a deterioration of the adsorbed inhibitor film. A similar behavior was formerly noticed in the case of copper corrosion in the presence of Tantum Rosa [26, 27]

The corrosion rate of the bronze in the simulated acidic rain solution (pH=5) is about four times lower in the presence of 100 ppm pollen as compared to its absence. Therefore, this concentration was stated as the 'optimum' concentration in the investigated experimental conditions.

3.2. SEM-EDX investigations

The surface morphology of the copper after 48 hours of immersion in the corrosive solution in the absence and presence of the inhibitor determined by SEM is observed in Figure 2.

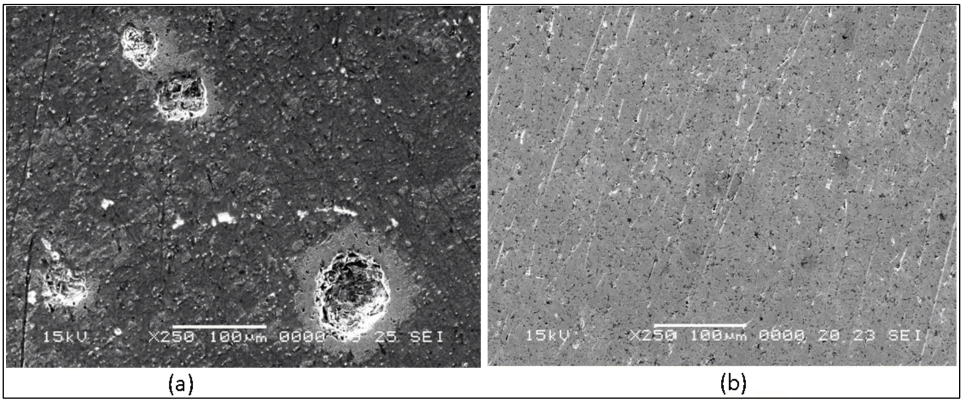

Fig. 2. SEM micrographs of the bronze sample after 48 hours of exposure to 0.2 g/L Na_2SO_4+0.2 g/L $NaHCO_3$ (pH 5)
solution in the absence a) and in the presence of 100 ppm pollen (b)

SEM micrographs obtained in the absence of the inhibitor (fig. 2a) show that the bronze surface was strongly corroded in the simulated acid rain solution. In the presence of 100 ppm bee pollen (fig. 2b), the bronze surface has a smooth appearance, without corrosion marks, while the surface defects that appeared during mechanical grinding.

These images suggest that pollen plays a protective role against bronze corrosion immersed in 0.2 g/L Na2SO4+0.2 g/L NaHCO3 (pH 5).

EDX spectra of bronze surface exposed to the corrosive environment in the presence of pollen (fig. 3b) show a decrease in the intensity of peaks corresponding to O, Sn and Cu compared to those determined on the surface exposed in the solution without inhibitor (fig. 3a).

4. Conclusions

In the present work, the inhibitive behaviour of pollen on bronze corrosion in a weakly acidic aqueous environment simulating an acidic rain (0.2 g L-1 Na2SO4 + 0.2 g L-1 NaHCO3, pH 5) was evaluated using potentiodynamic polarization, scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) techniques. Potentiodynamic polarization measurements

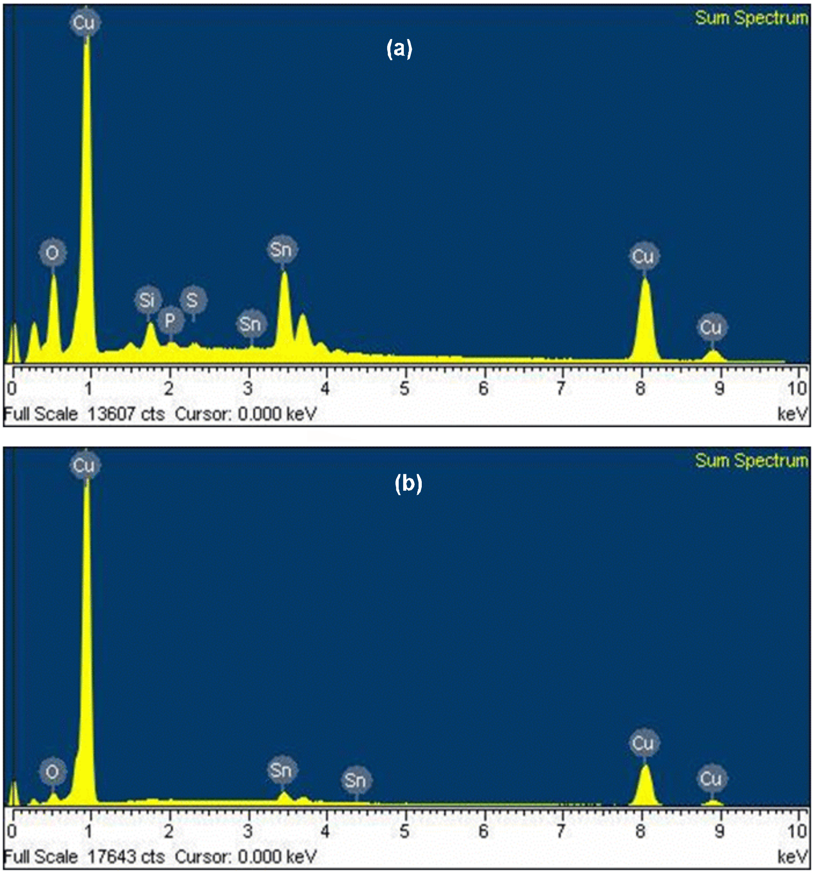

Fig. 3. EDX analysis of the corrosion products formed on the bronze surface after 48 hours of exposure to 0.2 g/L Na_2SO_4+0.2 g/L $NaHCO_3$ (pH 5) solution in the absence (a) and in the presence of 100 ppm pollen (b)

The reduction of the O content when pollen is added to the corrosive solution shows its inhibitory effect, in accordance with the results of the electrochemical measurements.

indicated that bee pollen behavse as a mixed-type inhibitors affecting both, the cathodic oxygen evolution, and the anodic metal dissolution.

The inhibiting efficiency of the bee pollen on bronze corrosion increases with its concentration, from 48.8% at 50 ppm inhibitor to the maximum value of 74.7% obtained in the presence of 100 ppm pollen, which was then stated as the 'optimum' concentration in the investigated experimental conditions.

SEM-EDX analysis revealed that the bronze corrosion process was significantly reduced in the presence of the bee pollen and the bronze surface had a smooth appearance, without visible traces of corrosion.

Concluding, it might be assessed that the bee pollen is able to protect to some extent the bronze surface from corrosion in a simulated acidic rain solution (pH=5).

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