Antifouling effect of two saturated copper coatings applied on carbon steel structures[(·)]

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Abstract

Biofouling is the colonization of man-made substrata by sessile organisms. The aim of this paper is to evaluate the performance of two antifouling saturated copper coating. Bioassays were carried out at a harbor in Argentine (38°02'S-57°32'W). During six months, one series of pipes and panels were removed monthly to estimate the recruitment of macro and microfouling species and immediately replaced by clean ones. Another series was removed from the beginning of exposure to monitor the development of the established community (accumulative pipes and panels along six months). Data obtained from control (without a saturated copper coating) and saturated-copper coated pipes and panels were compared in order to estimate performance of the coating. One of two saturated copper coating demonstrated a good effect antifouling.

Keywords

Antifouling; Biofilms; Biofouling; Coating copper; Mild steel.

Efecto *antifouling* de dos cubiertas saturadas de cobre aplicadas sobre estructuras de acero al carbono

Resumen

El biofouling es la colonización por organismos sésiles en sistemas de sustratos hechos por el hombre. El objetivo fue evaluar el efecto antifouling de dos cubiertas saturadas de cobre. Los estudios se llevaron a cabo en un puerto de la Argentina (38°02'S-57°32'W). Durante seis meses, una serie de caños y paneles fueron removidos mensualmente para estimar el reclutamiento de las especies del macro y microfouling, y fueron sustituidos inmediatamente por caños y paneles limpios. La otra serie de caños y paneles fueron removidas desde el inicio de la exposición en forma acumulativa durante los seis meses, para seguir el desarrollo de la comunidad. Los datos obtenidos de los controles sin cubierta y de los caños y paneles con las cubiertas saturadas de cobre fueron comparados para estimar el comportamiento antifouling de las mismas. Una de las dos cubiertas saturadas de cobre demostró un buen efecto antifouling.

Palabras clave

Antifouling; *Biofilms*; *Biofouling*; Cubierta de cobre; Acero al carbono.

1. INTRODUCTION

Metal surfaces immersed in natural or industrial waters undergo a sequence of biological and inorganic changes as a consequence of accumulation process in the metal/solution interface that is not necessarily uniform in time or space[1]; in turn, these changes lead to the establishment of biofouling. An intensive control program to inhibit biofouling development in offshore platforms and piping is very important to prevent future problems[2]. The increase in off-shore oil extraction has created a special awareness about biocorrosion processes, as attested by several specialized publications and conferences[3 and 4].

One of the most significant problems encountered in these systems is the growth of biofilms of heterotrophic aerobic bacteria and sulfate reducing bacteria (BRS) [5]. These are ubiquitous in our environment and occur in waterlogged soils, marine sediments, beneath macrofouling layers, etc., flourishing under anaerobic conditions[6]. Fungi, yeast, microalgae, protozoa[7] and macrofouling are also present[8 and 9]. Biofilms promote interfacial physicochemical reactions

that are not normally favored under abiotic conditions[10].

Abiotic factors, characteristics of the seawater, the amount of organic matter and pH, influence the distribution of colonizing microbial species in the resultant biofilm.

According to[11], sessile bacteria monitored through bioprobe devices provide an experimental means of verifying the formation of microbial biofilm.

These industrial problems can be treated by different methods, including: cleaning the system, controlling the levels of planktonic and sessile bacteria, avoiding biofilm formation, using oxidizing biocides, soluble and natural biocides[12 and 13], and antifouling saturated copper coating.

Different authors have studied the biofouling of stainless steel and copper alloys immersed in polluted seawater[14-17].

The use of appropriate sampling and monitoring strategies complemented with field and laboratory microbiological techniques is necessary to achieve a proper understanding of the effects derived from microbial activity and the role of biofilms in the corrosion reaction, in order to apply effective control and prevention countermeasures[18].

The goal of this work was to evaluate the performance of two antifouling saturated copper coatings. Bioassays were carried out in a harbor in Argentine (38°02'S-57°32'W).

Microbiological techniques were applied, abiotic factors were studied, and light microscope and scanning electron microscope (SEM) observations of biological communities were made.

2. MATERIALS AND METHODS

Bioassays were carried out in Mar del Plata harbor (38°02'S-57°32'W). The series consisted of: i) control pipes (without copper) and pipes covered with saturated copper coating (A). A seamless carbon steel pipe of the kind habitually use in the oil industry was coated with 250-micron thick epoxy after heating at 200 °C, a second 300- micron thick layer of a polypropylene copolymer to function as adhesive between the epoxy and the third layer, which was about 60 mm thick and made of polypropylene with hollow glass microspheres. A 300- micron thick polypropylene film with necessary stabilizers was extruded onto this isolated pipe, and covered with 100 % copper powder (grain size 45-63 microns) on its entire surface, wich would be in contact with the sea water. The copper powder was thus strongly adhered to polypropylene to avoid its rubbing off due to abrasion. The second series included ii) control panels (without copper) and panels covered with saturated copper coatings (B). Coating (B) was similar to (A) in composition; however, it was not extruded but hand-spread onto the panel surfaces for the bioassays, (Figs.1 and 2). The samples were vertically hung from a floating dock, about 0.3 and 1.5 m below the water surface to allow colonization by fouling organisms. Every month one series (pipes and panels) was removed to estimate the recruitment of micro and macrofouling species, and was immediately replaced by a clean one. The other series were checked monthly (during six months) to assess and record the development of the biofouling community from the beginning of the exposition (accumulative panels). Table I show the sampling schedule used in this study.

2.1. Laboratory analyses

2.1.1. Microbiological studies

The samples were collected directly from the sampling site, refrigerated and sent to the laboratory immersed in seawater. Biofilm was removed from the sampling
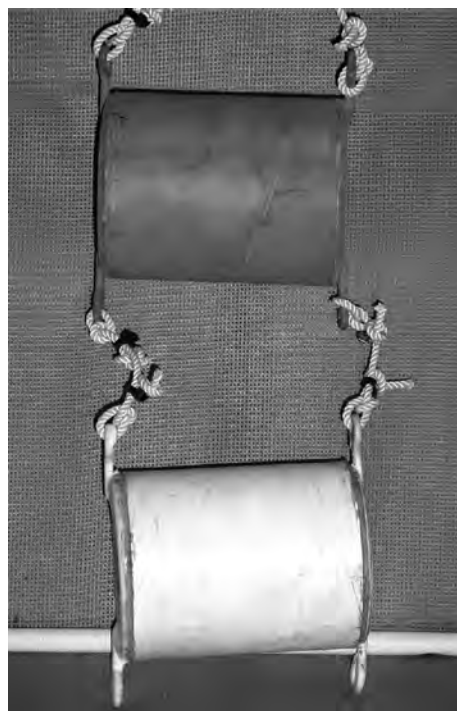

Figure 1. General view of the series of pipes before immersion. Top, pipe covered by saturated copper coating (A); Bottom, control pipe (without copper).

Figura 1. Vista general de las series de tubos antes de la inmersión. Arriba, tubo cubierto por una capa de cobre saturado (A); Abajo, tubo control (sin cobre).

Figure 2. General view of the series of panels before immersion. Top, panel covered by saturated copper coating (B); Bottom, control panel (without copper).

Figura 2. Vista general de la serie de paneles antes de la inmersión. Arriba, panel cubierto con una capa de cobre saturado (B); Abajo, panel control (sin cobre).

Table I. Sampling schedule.
Month (M) Accumulative samples (AS)
Monthly samples (MS)

*Tabla I. Cronograma de muestreos.
Meses (M), Muestras Acumulativas (AS),
Muestras Mensuales (MS)*

Month		
1st	Placement of samples	
2nd	Remove MS and AS	Restore MS
3rd	Remove two MS and AS	Restore MS
4th	Remove two MS and AS	Restore MS
5th	Remove two MS and AS	Restore MS
6th	Remove two MS and AS	Restore MS
7th	Remove two MS and AS	

surface by scraping and suspended in physiological solution. Viable microorganisms were counted by standard techniques[6 and 19] and different culture media were used[20]. Gram stains and biochemical test were performed on the samples.

2.1.2. Microfouling and macrofouling studies

The abundance of sessile species was estimated by recording their presence in the square cells or quadrates of a grid placed over the entire panel; sets of 10 random cells were considered statistically representative of the whole panel. New sets of random quadrates were used for each pipe and panel per month. Once the abundance for each species was estimated and recorded, it was expressed in a percentage scale. Five abundance categories were used: rare 1-25 %; scarce 25.1-50 %; frequent 50.1-75 %; abundant 75.1-100 % [21].

2.1.3. Microscopic and scanning electron microscope (SEM) studies

Observations of biological communities were made. Samples were observed under a JEOL JSM-T 100 Scanning Electron Microscope using conventional techniques[22]. Microfouling was observed under optical microscope (100x and 200x).

2.2. Field studies

Abiotic factors were recorded in the study area at the time of first immersion and at subsequent monthly intervals.

3. RESULTS AND DISCUSSION

Abundant fixation (approx. 80 %) was recorded on the pipe with copper coating (A). Macrofouling was represented by the sandy tubes of *Corophium*, ascidians both colonial, genus *Botryllus*, and solitary, genus *Ciona*, and algae of the species *Enteromorpha intestinalis* (Chlorophyta) and *Polysiphonia* (Rhodophyta). In terms of microfouling colonization, diatoms were the predominant adhesive organisms. Microbiological counts were high in both cases[23].

The coating (A) was not effective to prevent fixation of organisms in the six months (Fig.3); however, it was effective to prevent fixation of

Figure 3. Pipe covered by saturated copper coating (A), after six month of immersion.

Figure 3. Caño cubierto por una capa saturada de cobre (A) después de seis meses de inmersión.

Figure 4. Pipe covered by saturated Coating (A) after a month of immersion. Can be observed the loss of cupper coating.

Figure 4. Caño cubierto por una capa saturada de cobre (A) ldespués de un mes de inmersión. Puede observarse el desprendimiento de la capa de cobre.

organisms on a month-to-month basis, as shown by the analysis of monthly controls. In a chloride containing medium such as seawater a complex anodic layer structure that involves an inner Cu_2O and an outer $Cu(OH)_2$ layer is built. The structure of these anodic layers can be represented by a poorly hydrous inner Cu_2O non-homogeneously covered by $Cu(OH)_2$. Chloride ions absorbed on the copper surface and Cu(I) and Cu(II) soluble species are formed in the presence of oxygen. These ions have a marked biocidal effect[24].

The coating (A) did not perform well for longer-term control of adhesion (Fig. 4). It is due that copper had high leaching speed, due to a fault in the technique aplication (extruded) so that the pipes were unprotected after 30 days of immersion., the performance might have been affected by the method used to apply the coating. The extrusion process like that coating A produces defects such as surface or internal cracking when the surface of extrusion splits or when the centre develops cracks or voids. The cracks are attributed to a state of tensile stress at the deformation zone. Therefore, defects due to incorrect stress distribution are frequently found after extrusion processes. Such tensile stress are absent in the panels with coating B which was not extruded but hand spread on to the panel[25]. This fault can be serious economic loss in the industry oil petroleum and offshore in its different processes of extraction, processing, distribution and storage is affected by serious problem derived from microorganisms and biofoluling processes.

Tables II and III show the counts of sessile bacteria from the monthly sampled series and the accumulative series (immersed during six months) of control panels and saturated copper coating panels (B), respectively.

The control panels subject to both monthly and accumulative exposition presented high microbial densities corresponding to the biofilm. Heterotrophic bacteria were observed in 10^{12} CFU/cm^2 orders of magnitude, acid producing bacteria and anaerobic sulfate-reducing bacteria (SRB) were detected in orders of 10^5 mo/cm^2 (Tables II and III).

In the case of panels covered by the copper coating, only high levels of aerobic heterotrophic bacteria biofilm were detected for both monthly and accumulative six month exposure (Tables II and III). The presence of this biofilm could favor the adhesion of macofouling organisms in a period longer than six month. Neither fungi nor yeast were detected in either cases. After the six-month immersion, numerous macrofouling and microfouling species were observed in the control panel. This panel was dominated by solitary ascidians, which in turn provided suitable substrate for the settlement of other organisms such as algae (*Enteromorpha* sp. and *Ectocarpus* sp.), bryozoans, and tubeworms, as well as facilitating sediment deposition. Some barnacles, other bryozoans, and sand tube building worms were also recorded on the surface of the panel (Fig. 5).

With respect to the establishment of microfouling, a large amount of microfouling was observed

Table II. Amounts of sessile bacteria recorded. Monthly sampling.
MC: monthly control - MCu: monthly with copper coating (B)
CFU cm-2: colony forming unit cm-2
mo: microorganisms
WG: without growth

Tabla II. Valores de bacterias sésiles registrados. Muestreo mensual.
MC: control mensual- MCu: mensual con cubierta de cobre (B)
CFU cm-2: Unidades formadoras de colonias por cm-2
Mo: microorganismos. WG: sin crecimiento

Microorganisms Sampling	Heterotrophic aerobic bacteria (CFU cm^{-2})		Acidifying activity bacteria (Mo cm^{-2})		SRB (Mo cm^{-2})	
	MC	MCu	MC	MCu	MC	MCu
February/March	300×10^6	160×10^5	100	WG	100	WG
March/April	244×10^8	60×10^8	100,000	WG	1,000	WG
April/May	100×10^{12}	245×10^8	10,000	WG	1,000	WG
May/June	33×10^{10}	30×10^7	1,000	WG	10,000	WG
June/July	69×10^{10}	97×10^9	1,000	WG	100,000	WG
July/August	168×10^{10}	74×10^7	100	WG	WG	WG

Table III. Amounts of sessile bacteria recorded. Accumulative sampling (six-month immersion).
AC: accumulative control - ACu: accumulative with copper coating (B).
CFU cm-2: colony forming unit cm-2
Mo: microorganisms. WG: without growth

Tabla III. Valores de bacterias sésiles registrados. Muestreo acumulativo
(seis meses de inmersión).
AC: control acumulativo- ACu: acumulativo con cubierta de cobre (B)
CFU cm-2: Unidades formadoras de colonias por cm–2
Mo: microorganismos. WG: sin crecimiento

Microorganisms Sampling	Heterotrophic aerobic bacteria (CFUcm^{-2})		Acidifying activity bacteria(Mo cm^{-2})		SRB (Mo cm^{-2})	
	AC	Acu	AC	Acu	AC	ACu
February/March	300×10^6	160×10^5	100	WG	100	WG
February/April	240×10^{10}	240×10^8	10,000	WG	1,000	WG
February/May	86×10^{12}	38×10^8	10,000	WG	1,000	WG
February/June	38×10^{10}	74×10^8	1,000	WG	10,000	WG
February/July	58×10^{10}	180×10^{10}	1,000	100	10,000	WG
February/August	65×10^{10}	97×10^7	10,000	WG	100,0000	WG

including different species of diatoms, as corroborated by SEM (Fig. 6).

The panel covered with copper coating (B) did not show macrofouling. Microscopic examination showed only a thin film dominated by a few diatom species on the lower half of the panel (Figs. 5 and 7). Although this cover is similar to (A), its good performance was due to the fact that it was hand-exspread and no copper leaching was observed.

The water of harbour presenting scarce removal and high pollution levels (low DO values 0,8 ml/l to 6.0 ml/l, pH 7,56 to 8,30, salinity 32 % to 35 % high content of suspended organic matter and sulfide).
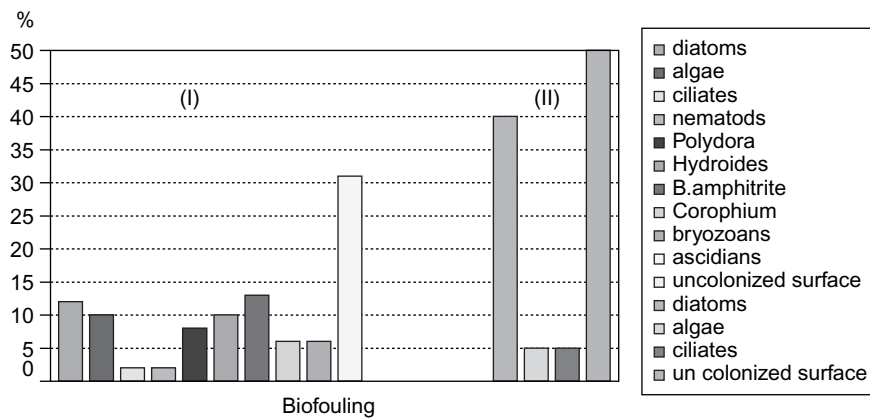
Figure 5. Cover percentage on control panel (I) and panel covered by saturated copper coating (B) (II) (6 months of immersion).

Figura 5. Porcentaje de cobertura en el panel control (I) y panel cubierto con una cubierta saturada de cobre (B) (II). (6 meses de inmersión).
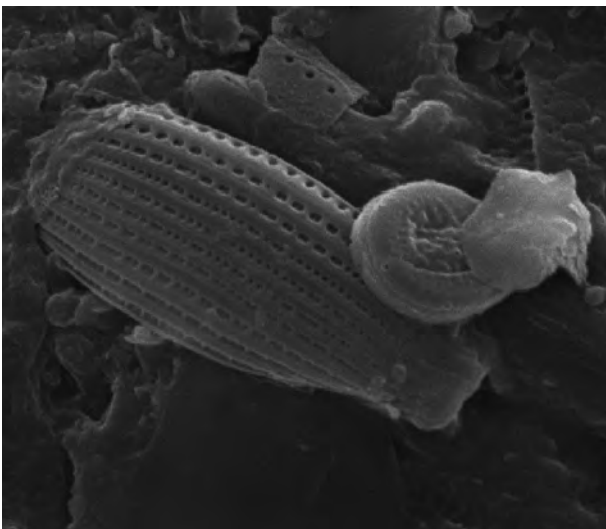

Figure 6. SEM micrograph showing diatoms corresponding to a panel with copper layer (B). (third month of immersion) X 3500. Image wide 18.08 μm.

Figura 6. Fotografía de MEB mostrando diatomeas correspondientes al panel cubierto por la capa de cobre saturado (B). (tres meses de inmersión) X 3500. Ancho de la imagen 18,08 μm.

Figure 7. Panel covered by saturated copper coating (B) after six month of immersion.

Figura 7. Panel cubierto por la capa de cobre saturado (B) después de seis meses de inmersión.

Abiotic factors (water and air temperature) varied during the course of this study. Water and air temperature was lower during the winter months. Air temperature was higher during the warm months principally February. The variations in microbial counts could be related to these conditions. The amount of heterotrophic bacteria was high, and even more so during the warmer months (Tables II and III). However, favorable conditions for microbial development in seawater can allow bacterial colonization to occur during longer periods (Table IV).

Tabla IV. Factores Abióticos

Table IV. Abiotic factors

	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.
Water temperature	19.0 °C	22.8 °C	21.0 °C	14.7 °C	11.4 °C	8.9 °C	9.3 °C
Air temperature	27.7 °C	26.8 °C	21.8 °C	17.6 °C	9.4 °C	7.6 °C	13.0 °C
Conductivity	47.8 mS	55.3 mS	47.6 mS	45.1 mS	43.8 mS	40.6 mS	42.7 mS
pH	8.00	8.30	7.94	8.03	7.56	7.63	7.80

4. CONCLUSIONS

The panel covered with saturated copper coating (A) showed low antifouling performance after 6 months of accumulative exposure, in contrast with the panels exposed monthly during a period of six months. This was probably due to the loss of Cu, which could be explained by either a high rate of leaching, or defective adhesion of the coating to the pipes determined by the type of treatment applied.

The panel covered with saturated copper coating (B) showed good antifouling performance after six months of immersion. This is evidenced by comparing the heavy fouling registered on the control panel vs. the thin film of microfouling organisms registered on this copper-coated panel. Nevertheless, both the samples with saturated copper coating (B) and the control showed important adherence of heterotrophic aerobic bacteria. This could favor the adhesion of macrofouling organisms in a period superior to the 6 months of this study. Future investigations will assess the progress of colonization during longer periods.

Acknowledgements

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