Chapter

Reducing Emerging Contaminants Ensuing from Rusting of Marine Steel Installations

Karima Hanini, Sameh Boudiba and Merzoug Benahmed

Abstract

Marine steel installations are usually subject to biocorrosion due to their immersing in seawater. Biocorrosion-causing microorganisms, such as bacteria and fungi, often form biofilms on materials, inducing chemical changes in these materials and in the surrounding liquid medium. The formed biofilms resulting from this phenomenon are considered as emerging contaminants. In this work, in addition to the realization of the electrodeposition of zinc on a steel in chloride bath with various concentrations of *Taxus baccata* extracts as additives using a direct courant supply, the study of the corrosion of the obtained substrates was performed in seawater as an aggressive environment. The efficiency against corrosion was evaluated by potentiodynamic polarizations and weight loss measurements. The coated surface morphology was analyzed using brightness meter, thickness meter and adhesion tests. The experimental results showed that all tested extracts performed the quality of the zinc deposits and their efficiency against corrosion indicating that coated samples in the presence of the extracts were more resistant minimizing the emerging contaminants in seawater.

Keywords: *Taxus baccata*, biocorrosion, emerging contaminant, inhibition, electrodeposition

1. Introduction

Emerging contaminants (ECs), also known as emerging organic contaminants [1] and contaminants of emerging concerns (CECs) [2], are a group of natural and synthetic chemicals with their transformation products occurring in water bodies throughout the globe. Actually, these materials, which are also considered as microorganisms (e.i. biofilm) present in the environment, are not monitored and have a high potential of causing environmental damage in addition to be suspected of detrimental effects on ecosystems and human health. It should be noted that as reported in the literature, the exposure to environmental relevant concentrations of ECs caused significant alterations in the microbial community composition and function [3].

The biocorrosion, or microbiologically influenced corrosion (C.I.M), which represent one of the biofilms source is an electrochemical phenomenon of dissolution of a metal affecting all industries, where microorganisms (in particular bacteria) can develop [4]. To minimize the biocorrosion and therefore the emerging contaminants, electrodeposition of zinc is usually used for marine steel installations

protection, it is a suitable, fast and cost-effective way to improve the surface hardness, anti-corrosion properties and wear resistance...etc. [5]. The electrodeposition consists principally in the immersion of a steel as an electrode in a container containing an electrolyte and a zinc as a counter electrode. The electrodeposition electrolytes usually contain metal salts, species to increase electrolyte conductivity and additives, added to improve leveling metal and to optimize the properties of the deposited metal (hardness, brightness, corrosion resistance, roughness, porosity, grains size .....) [6]. The clear problem with these additives is that they are all synthetic, toxic, high cost and they have a significant negative impact on the environment, such as furfurale and thiourea [7–11]. To resolve this problem, the new trend in the current research is focused on replacing synthetic additives with less expensive, biodegradable and effective natural products such as extracts obtained from natural products as *Manihot esculenta* [12], *Saccharum officinarum*, *Ananas comosus* [13], *Taxus baccata* [14] and *Daphne gnidium* L. [15].

In this work, two main objectives are targeted. Firstly, we are focused on the use of plant extracts obtained from a plant belonging to Algerian flora (*Taxus baccata*), as additives in chloride baths for the zinc plating of a mild steel (E24–2). Secondly, we will evaluate the effect of the addition of the investigated extracts as additives, namely on the quality of the zinc deposit, on one hand and on the other hand, on the resistance of the deposit against corrosion, therefore the decrease of the emerging contaminants effect.

2. Emerging contaminants

Emerging contaminants are synthetic or naturally occurring chemicals or any microorganisms that are not commonly monitored in the environment but have the potential to penetrate in the environment and thereby causing known or suspected adverse ecological and/or human health effects. These contaminants consist of pesticides, pharmaceuticals, personal care compounds, industrial additives by-products, food additives, water treatment by-products and nanomaterials including metal oxides, zero-valent metals, quantum dots, dendrimers, composites and nanosilver [16].

According to the previous definitions, the products resulting from steel corrosion in marine environment such as biofilms and iron oxides are considered as emerging contaminants.

3. Corrosion

Corrosion is the spontaneous destruction of metals and alloys caused by chemical, biochemical and electrochemical interactions between materials and their environments. These environments can be humidity, oxygen, inorganic and organic acids, high pressures, temperature, chlorides, etc. During corrosion, metals tend to convert to more thermodynamically stable compounds [17].

4. Zinc electroplating

Zinc electroplating provides corrosion resistance by acting as a barrier and sacrificial coating. Because zinc is more reactive that steel, the zinc coating corrodes first, protecting the steel substrate. The rate of corrosion of zinc is at least 10 times slower than that of steel, thus a thin coating of zinc can protect steel for long time.

Electroplating is an electrochemical process, which takes place according to a certain number of elementary stages of electrolytic crystallization leading to the reduction of the dissolved species M^{+n} into metal atoms M, and to the incorporation of these atoms into the crystal lattice of the substrate. In general, for a coating, we have to make the cathode the object to be coated, the anode is then made of the metal, which we want to coat and the electrolyte will contain a solution of a salt of this metal. Species to increase electrolyte conductivity and additives are added to improve leveling metal and to optimize the properties of the deposited metal [11].

5. Additives

The development of coatings requires when using a direct current, the addition in small quantities of certain organic or inorganic additives to the electrolysis bath. These additives will modify the mechanisms of electrodeposition by selectively affecting the rate of germination and/or growth of deposited species. The use of additives in electrolysis baths is expressed by a reduction in surface roughness, an increase in hardness and an improvement in both deposits gloss and morphology [6].

6. Experimental

6.1 Plant extracts

The stems and leaves of *Taxus baccata* were harvested in April 2016 in Babor (altitude 2000 m), in little kabylia (northern end of the wilaya of Sétif, in Algeria). The aerial parts were cut into small pieces, they were then subjected to an extraction procedure by maceration in a lukewarm methanol–water mixture (7/3:V/V) for 24 hours. This operation was repeated three times. The various recovered fractions were then combined and evaporated under reduced pressure at a temperature below 70° C until a syrupy residue was obtained. The latter phase was taken up by boiling water, decanting for one nights to eliminate the chlorophyll. The filtered mixture was subjected to liquid–liquid extraction using several solvents separately in a sequence of increasing polarity, starting from dichloromethane (MDE), ethyl acetate (EAE) and n-butanol (BE), where the organic phase was recovered for each solvent. The latter solutions were evaporated to dryness using a rotary evaporator to obtain the desired extracts [18].

6.2 Materials

The tests were carried out on a mild steel of grade E24–2, having a chemical composition in % by weight (C, 0.17; Mn, 0.6; P, 0.035; S, 0.035; Si, 0.04; Al, 0.02 to 0.05; N, 0.01; Fe remaining). Plates of 2 cm x 6 cm x 0.1 cm in dimension were coated with epoxy resin leaving a single exposure surface. The substrates were plated with a pure zinc (99.91%). Prior to each experiment, the surfaces of all samples were mechanically abraded using different types of silicon carbide emery paper, cleaned with acetone, rinsed with distilled water then dried with air.

6.3 Electrodeposition bath

The chloride solution for the coating was a mixture of $ZnCl_2$ (65 g/l), KCl (200 g/l), H_3BO_3 (20 g/l) and different concentrations of *Taxus baccata* extracts (1 g/l to 1.6 g/l) [19].

6.4 Experimental conditions

All experiments were carried out in an aerated medium, pH = 5 and current of 0.04 A. The steel sample represents the anode of the electrochemical cell, while the zinc plate represents the cathode leaving a distance of 1 cm between them. The zinc plating of the steel was carried out for 30 min, with gentle stirring, by partially immersing the steel sample and the zinc electrode in the chloride bath. To determine the weight of deposited zinc on surfaces, all substrates were weighed before and after electroplating. At the end of the process, the samples were removed from the bath, cleaned with distilled water and air dried [14].

6.5 Quality of the deposited zinc layer

The thickness of the deposited zinc layer was measured with an Elektro-Physik (eXacto) apparatus and the adhesion of the coated zinc to the substrate was examined by the ASTM D3359 method [20]. For the adhesion test, an "X" was etched on the film and an attached adhesive tape was applied to the samples, and then removed strongly. This test is macroscopic and more qualitative. The gloss of the zinc deposits was measured using a Poly Gloss meter with a large beam of white light at a measuring angles of 20°, 60° and 85°. Calibration was performed automatically using a highly polished black standard built into the gloss meter. The final gloss values were the average of three measurements taken for each coating.

6.6 Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were performed in seawater with the coated samples as working electrode, a platinum rod as counter electrode and a saturated calomel electrode (SCE) as a reference electrode. A controlled computer (Voltalab PGZ 301) instrument with Voltamaster 4 software was employed for this purpose. The measurements were applied in the potential range of ±1500 mV at a sweep rate of 1 mV/s.

6.7 Gravimetric measurements

To evaluate the corrosion resistance of the electrodeposited substrates, weight loss measurements were made. Each sample coated in chloride baths containing different concentrations of the extracts was partially immersed in seawater (corrosive medium). Measurements were collected every five days for a month and the Eq. (1) was used to determine the corrosion rate [21]:

$$CR = \frac{w}{At} \tag{1}$$

w: average weight loss.
A: total area of one mild steel specimen.
t: immersion time.

7. Results and discussion

7.1 Quality of electrodeposited zinc

The quality of the electrodeposited zinc was observed through the deposit parameters as the brightness, the strength adhesion and the thickness. The obtained

results are presented in **Table 1** for MDE, **Table 2** for EAE and **Table 3** for BE. Where: + adhesion is strong, ++ adhesion is very strong.

Via **Tables 1–3** we noted that there is an increase in the deposited mass, thickness and adhesion when increasing the concentration of MDE (1.6 g/l). However, for EAE and BE, these parameters reached a maximum value at 1.2 g/l and then decreased, indicating that the better deposit (nucleation and growth) is found in these concentrations. The obtained results may be related to two considerations: the first one is that the adsorption of additives on the surface, leads to a partial coating of the steel, thus blocking the active sites and causing a decrease in the nucleation rate. The second consideration is that the additive will complex with one of the electroactive species in the solution, therefore the step of dissociation of the complex introduces a new kinetic constant before the redox reaction of the electroactive species at the electrode surface [22]. Furthermore, and according to ASTM D 523 [23] regulations, we observed that the deposits obtained with the addition of the extracts were matt. However, when adding different concentrations (1.2; 1.4 and 1.6 g/l) of BE, the deposits were semi-gloss. In addition, all measured thicknesses were in agreement with ASTM A879 and ASTM B633 [24].

7.2 Potentiodynamic polarization measurement

The corrosion resistance of the electrodeposited mild steel was tested in seawater at 298 K to evaluate the effect of adding extracts to the chloride baths. The electrochemical parameters such as E_{corr}, i_{corr} and CR are collected in **Table 4** for MDE, **Table 5** for EAE and **Table 6** for BE.

From **Tables 4–6**, it can be seen that the addition of the investigated extracts as additives gave rise to significant decreases in current densities as well as the corrosion rate compared to the sample obtained without extracts addition. This indicates that the studied extracts strongly modified the quality of the deposit producing coatings more resistant to corrosion and therefore lessening the formation of biofilms, which represent one of emerging contaminants. It is also noted that the dependence of the

C (g/l)	Mass deposited (g)	Thickness (μm)	Adhesion	Brightness (GU)
Without extracts	0.0423	15	+	Matt 05.30
1	0.0248	8.67	+	Matt 14.15
1.2	0.0395	13.92	+	Matt 02.30
1.4	0.0424	15.12	++	Matt 01.75
1.6	0.0481	17.15	++	Matt 19.10

Table 1.
Mass, thickness, brightness and strength adhesion of the deposited zinc layer in the presence of MDE.

C (g/l)	Mass deposited (g)	Thickness (μm)	Adhesion	Brightness (GU)
Without extracts	0.0423	15	+	Matt 05.30
1	0.0450	15.99	++	Matt 08.60
1.2	0.0551	19.60	++	Matt 14.65
1.4	0.0477	16.20	++	Matt 19.40
1.6	0.0366	12.11	+	Matt 09.70

Table 2.
Mass, thickness, brightness and strength adhesion of the deposited zinc layer in the presence of EAE.

Cencentration (g/l)	Mass deposited (g)	Thickness (μm)	Adhesion	Brightness (GU)
Without extracts	0.0423	15	+	Matt 05.30
1	0.0467	16.10	++	Matt 13.40
1.2	0.0685	24.83	++	Semi bright 32.85
1.4	0.0405	14.36	++	Semi bright 31.45
1.6	0.0393	13.40	+	Semi bright 31.75

Table 3.
Mass, thickness, brightness and strength adhesion of the deposited zinc layer in the presence of BE.

MDE extract	C (g/l)	$-E_{corr}$ (V/SCE)	i_{corr} ($mAcm^{-2}$)	CR (mm/y)
Without extract	/	923.8	0.6514	9.791
With extract	1	1064.4	0.4653	5.442
	1.2	1176.4	0.3220	4.840
	1.4	1095.3	0.1427	2.145
	1.6	1136.4	0.1411	1.650

Table 4.
Polarization parameters for corrosion of electroplated mild steel without and with different concentrations of MDE at 293 K.

EAE extract	C (g/l)	$-E_{corr}$ (V/SCE)	i_{corr} ($mAcm^{-2}$)	CR (mm/y)
Without extract	/	923.8	0.6514	9.791
With extract	1	787.8	0.000967	0.01131
	1.2	159.2	0.000184	0.002158
	1.4	699.2	0.000347	0.005219
	1.6	618	0.005706	0.06674

Table 5.
Polarization parameters for corrosion of electroplated mild steel without and with different concentrations of EAE at 293 K.

density of the corrosion current and the additive concentration in the electroplating bath was not linear, probably due to the fact that in each electroplating process there is an optimum additive concentration, whereby the deposit quality is the best [25].

7.3 Gravimetric measurements

Figure 1 shows the corrosion rate curves of the mild steel in the absence and in the presence of optimal concentrations of *Taxue baccata* extracts used as additives during their immersion in seawater for one month.

Table 7 gathers the values of the corrosion rate in the absence and in the presence of optimal concentrations of *Taxue baccata* extracts tested separately as additives in zinc baths.

The examination of **Table 7** and **Figure 1** displayed a better corrosion resistance for all plated samples in the presence of optimal concentration of extracts as additives than those plated in their absences. Furthermore, the plated sample without additives recorded a corrosion rate value of 0.0052 (mg cm^{-2} h^{-1}) during one month of immersion time in seawater. In contrary, the corrosion rate values for plated specimens with additives were in the range of 0.0025 and 0.0018 mg cm^{-2} h^{-1}.

BE extract	C (g/l)	$-E_{corr}$ (V/SCE)	i_{corr} ($mAcm^{-2}$)	CR (mm/y)
Without extract	/	923.8	0.6514	9.791
With extract	1	1107.6	0.2283	3.431
	1.2	1076.4	0.1287	1.933
	1.4	1143.6	0.2631	3.955
	1.6	1124	0.3574	5.371

Table 6.
Polarization parameters for corrosion of electroplated mild steel without and with different concentrations of BE at 293 K.

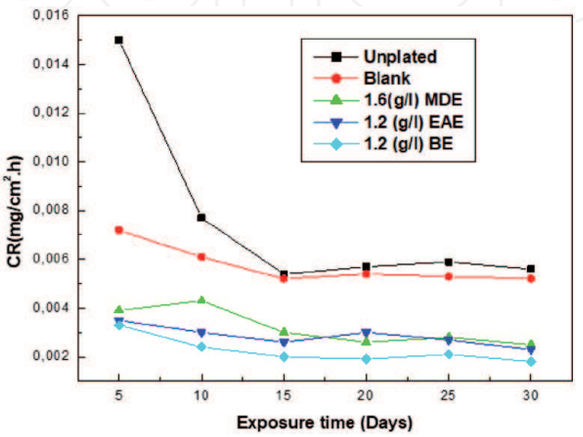

Figure 1.
Variation of the corrosion rate versus exposure time for unplated and zinc plated mild steel samples without and with optimal concentration of MDE, EAE and BE.

Substrate	C (g/l)	Time (Days)	5	10	15	20	25	30
Unplated	/	CR (mg/cm^2.h)	0.015	0.0077	0.0054	0.0057	0.0059	0.0056
Blank	/		0.0072	0.0061	0.0052	0.0054	0.0053	0.0052
Plated with MDE	1.6		0.0039	0.0043	0.003	0.0026	0.0028	0.0025
Plated with EAE	1.2		0.0035	0.003	0.0026	0.003	0.0027	0.0023
Plated with BE	1.2		0.0033	0.0024	0.002	0.0019	0.0021	0.0018

Table 7.
Corrosion parameters obtained from weight loss measurements of the electroplated mild steel using optimal concentrations of MDE, EAE and BE.

The obtained values of corrosion rate for the specimen plated in the presence of 1.6 g/l of MDE and 1.2 g/l of EAE and BE were lower than the others. This ascertainment is in good agreement with that obtained from potential polarization.

8. Conclusion

As part of the challenge against emerging contaminants, the use of three extracts obtained from *Taxus baccata* as additives in electrdeposition of zinc was evaluated. The obtained results leads to the following points:

1. Electroplating results showed that all extracts can be used as wetting and leveling additives.

2. In addition to being wetting and leveling the BE can also be regarded as brighteners at a well-defined concentration.

3. Samples coated in the presence of different concentrations of *Taxus baccata* extracts, in particular the EAE, exhibited a higher corrosion resistance than that coated in their absence, and therefore they can minimize the emerging contaminants in seawater.

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References

[1] Jurado, A., et al., *Emerging organic contaminants in groundwater in Spain: a review of sources, recent occurrence and fate in a European context.* Science of the total environment, 2012. **440**: p. 82-94.

[2] Dulio, V., et al., *Emerging pollutants in the EU: 10 years of NORMAN in support of environmental policies and regulations.* Environmental Sciences Europe, 2018. **30**(1): p. 1-13.

[3] Geissen, V., et al., *Emerging pollutants in the environment: a challenge for water resource management.* International soil and water conservation research, 2015. **3**(1): p. 57-65.

[4] Feugeas, F., et al., *Corrosion influencée par les micro-organismes: influence du biofilm sur la corrosion des aciers, techniques et résultats récents.* Journal de physique III, 1997. **7**(3): p. 631-663.

[5] Alizadeh, M. and H. Safaei, *Characterization of Ni-Cu matrix, Al2O3 reinforced nano-composite coatings prepared by electrodeposition.* Applied Surface Science, 2018. **456**: p. 195-203.

[6] Kanani, N., *Electroplating: basic principles, processes and practice*. 2004: Elsevier.

[7] Arts, J.H., et al., *Subacute (28-day) toxicity of furfural in Fischer 344 rats: a comparison of the oral and inhalation route.* Food and chemical toxicology, 2004. **42**(9): p. 1389-1399.

[8] Gupta, G.D., A. Misra, and D.K. Agarwal, *Inhalation toxicity of furfural vapours: an assessment of biochemical response in rat lungs.* Journal of applied toxicology, 1991. **11**(5): p. 343-347.

[9] Smith, P.B. and C. Crespi, *Thiourea toxicity in mouse C3H/10T12 cells expressing human flavin-dependent monooxygenase 3.* Biochemical pharmacology, 2002. **63**(11): p. 1941-1948.

[10] DIEKE, S.H. and C.P. RICHTER, *Acute toxicity of thiourea to rats in relation to age, diet, strain and species variation.* Journal of Pharmacology and Experimental Therapeutics, 1945. **83**(3): p. 195-202.

[11] Gamburg, Y.D. and G. Zangari, *Theory and practice of metal electrodeposition*. 2011: Springer Science & Business Media.

[12] Loto, C., A. Olofinjana, and R. Loto, *Effect of Manihot esculenta c. leaf extract additive on the zinc electroplating on mild steel in acid chloride solution.* International Journal of Electrochemical Science, 2014. **9**: p. 3746-3759.

[13] Loto, C.A., *Synergism of Saccharum officinarum and Ananas comosus extract additives on the quality of electroplated zinc on mild steel.* Research on Chemical Intermediates, 2014. **40**(5): p. 1799-1813.

[14] Hanini, K., et al., *Influence of different polyphenol extracts of Taxus baccata on the corrosion process and their effect as additives in electrodeposition.* Sustainable Chemistry and Pharmacy, 2019. **14**: p. 100189.

[15] Belbah, H., et al., *Effect of a Natural Brightener, Daphne gnidium L. on the Quality of Nickel Electroplating from Watts Bath.* Journal of New Materials for Electrochemical Systems, 2016. **19**(2).

[16] Naidu, R., et al., *Emerging contaminants in the environment: risk-based analysis for better management.* Chemosphere, 2016. **154**: p. 350-357.

[17] Fontana, M.G. and N.D. Greene, *Corrosion engineering*. 2018: McGraw-hill.

[18] S. Boudiba, K. Hanini, I. Selatnia, A. Saouane, S. Hioun, and M. Benahmed, "Experimental, theoretical and mathematical studies of *Echium italicum* L. extract as a corrosion inhibitor for carbon steel in acidic medium," *Materials Research Express*, vol. 6, p. 086546, 2019.

[19] Loto, C., et al., *Effect of Allium Cepa (onion) extract additive on the morphology of zinc electroplated mild steel in acid chloride solution.* Can. J. Pure Appl. Sci, 2015. **9**(1): p. 3267-3277.

[20] Astm, D., *3359-02: standard test methods for measuring adhesion by tape test.* ASTM International, West Conshohocken, PA, 2002.

[21] Loto, C. and R. Loto, *Effects of Nicotiana tobaccum extract additive on the quality of electroplating of zinc on mild steel.* Polish Journal of Chemical Technology, 2013. **15**(1): p. 38-45.

[22] Youssef, K.M., C. Koch, and P. Fedkiw, *Influence of additives and pulse electrodeposition parameters on production of nanocrystalline zinc from zinc chloride electrolytes.* Journal of the Electrochemical Society, 2004. **151**(2): p. C103.

[23] ASTM, D., *523-89, Standard Test Method for Specular Gloss.* ASTM International, 1999.

[24] Anchors, H.E., *Anchor bolt and sleeve assembly of material indicated below with capability to sustain, without failure, a load equal to 6 times the load imposed when installed in unit masonry assemblies and equal to 4 times the load imposed when installed in concrete as determined by testing per ASTM E 488 conducted by a qualified independent testing and inspecting agency. 1.* Material: Carbon-steel components, zinc plated to comply with ASTM B, 2010. **633**: p. 061053-6.

[25] Muresan, L.M. and S.C. Varvara, *Leveling and brightening mechanisms in metal electrodeposition.* M. Nunez, Nova Science Publishers, Inc. New York, 2005.