

Article

Environmental Behavior of Novel “Smart” Anti-Corrosion Nanomaterials in a Global Change Scenario

Mariana Bruni ^{1,2} , Joana Figueiredo ¹ , Fernando C. Perina ¹ , Denis M. S. Abessa ²  and Roberto Martins ^{1,*} ¹ CESAM-Centre for Environmental and Marine Studies, Department of Biology, University of Aveiro, 3810-193 Aveiro, Portugal; marianabruni@ua.pt (M.B.); jrmf@ua.pt (J.F.); perinafc@ua.pt (F.C.P.)² Biosciences Institute, São Paulo State University (UNESP), São Vicente 11300-000, Brazil; denis.abessa@unesp.br

* Correspondence: roberto@ua.pt

Abstract

Maritime corrosion is a global problem often retarded through protective coatings containing corrosion inhibitors (CIs). ZnAl layered double hydroxides (LDH) have been used to immobilize CIs, which can reduce their early leaching and, thus, foster long-term corrosion protection. However, the environmental behavior of these nanomaterials remains largely unknown, particularly in the context of global changes. The present study aims to assess the environmental behavior of four anti-corrosion nanomaterials in an ocean acidification scenario (IPCC SSP3-7.0). Three different concentrations of the nanostructured CIs (1.23, 11.11, and 100 mg L⁻¹) were prepared and maintained at 20 °C and 30 °C in artificial salt water (ASW) at two pH values, with and without the presence of organic matter. The nanomaterials' particle size and the release profiles of Al³⁺, Zn²⁺, and anions were monitored over time. In all conditions, the hydrodynamic size of the dispersed nanomaterials confirmed that the high ionic strength favors their aggregation/agglomeration. In the presence of organic matter, dissolved Al³⁺ increased, while Zn²⁺ decreased, and increased in the ocean acidification scenario at both temperatures. CIs were more released in the presence of humic acid. These findings demonstrate the influence of the tested parameters in the nanomaterials' environmental behavior, leading to the release of metals and CIs.

Keywords: corrosion inhibitors; layered double hydroxides; leaching; climate change; ocean acidification; organic matter



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1. Introduction

Metallic corrosion is a severe technical, environmental, and economic problem that annually costs between 1% and 5% of the global gross domestic product [1]. The most effective preventive methods for dealing with corrosion include combining cathodic protection with coatings containing corrosion inhibitors (CIs) [1,2]. CIs are molecules that block the anodic and/or cathodic reaction between the metal and the surrounding corrosive agents (e.g., chlorides, present in high concentrations in seawater) by adsorbing them, thus reducing the corrosion rate [3].

Hexavalent chromium-based protection systems were extensively used across various industries worldwide but have been increasingly phased out or heavily restricted in regions such as the European Union, California, Canada, Japan, South Korea, and China due to their high (eco)toxicity and carcinogenicity [4]. Cr-free popular alternatives for maritime applications include the salts 2-mercaptobenzothiazole (MBT), benzotriazole (BTA), and

derivatives, phosphates, and vanadates [5,6]. Despite their efficiency in preventing or postponing metallic surface corrosion, these inorganic or organic CIs exert toxic effects on the biota when released into the environment [7–10]. In response to the demand for eco-friendly solutions, many alternative CIs have been proposed in the last two decades. Recent studies highlighted the potential use of bio-based molecules as eco-friendly CIs due to their biodegradability and no/low bioaccumulation potential, with a particular focus on sodium gluconate (SG) [11], glutamic acid, other amino acids [12,13], chitosan [14], plant extracts and aromatic acid lignin derivatives [15], natural polymers, and gums, among others [13]. However, despite the urgency of replacing the current generation of toxic CIs with greener and more efficient products, the truth is that most of the alternative molecules are not as cost-effective as state-of-the-art CIs, and, when highly soluble, such molecules can easily be leached from polymeric coatings, posing a threat to ecosystems [13].

Recent studies have proposed the use of layered double hydroxides (LDH), a class of stimuli-responsive engineered nanomaterials to immobilize nitrites (NO_2^-) [16–18], MBT, BTA, phosphates, vanadates, molybdates [6,19–23], the bio-based sodium gluconate (SG) [24], among other CIs. LDHs are anionic-exchange clays with a side size of 20 to 40 nm, consisting of positively charged mixed metal hydroxide layers stabilized by anions and water molecules in the interlayer space [6]. They have a general formula $[\text{M}^{2+}_{(1-x)} + \text{M}^{3+}_x(\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n}^{x-} \cdot y\text{H}_2\text{O}$, where x is generally lower than 0.33, M^{2+} is the divalent cation (e.g., Zn^{2+}), M^{3+} is the trivalent cation (e.g., Al^{3+}) and A^{n-} represents the anion (e.g., nitrates or any CI in the anionic form), which compensate the positive charge of the metallic layers, interconnected through a combination of electrostatic forces and hydrogen bonds [22]. LDHs offer a controlled release of entrapped CIs upon specific environmental triggers (e.g., chlorides, abrupt changes in pH, or temperature) and prevent the interaction between the active ingredient and other coating components, which minimizes undesired reactions and protective losses [6,19–21,23,24]. Anti-corrosion LDHs also offer gradual self-healing properties to damaged coatings [6,19,20,24]. Due to these features, several studies have shown the benefits of the immobilization of such CIs into LDHs in terms of enhanced anti-corrosion protection across various metallic substrates, such as carbon steel (e.g., SG, BTA, or nitrites) [22,24], galvanized steel (e.g., BTA) [21,23] or aluminum alloys (e.g., MBT, or vanadates) [19,20] for several coatings, including maritime applications.

Leal et al. (2023) [24] studied the intercalation of gluconate in ZnAl LDH nanocontainers and their exposure to a NaCl solution over 30 days, demonstrating that it is possible to intercalate this anion in LDH and its efficacy in preventing corrosion in carbon steel. The chlorides in the medium triggered the release of gluconate, which decreased the chloride concentration, as observed due to its intercalation in the LDH, as monitored by UV-Vis absorption spectroscopy [24]. Amanian et al. (2023) investigated the intercalation of BTA in LDH and confirmed the intercalation of BTA through Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), and Thermogravimetric Analysis (TGA) measurements [23]. Another study by Deip et al. (2020) analyzed the corrosion inhibition performance of LDH-BTA in carbon steel exposed to NaCl 3.5% solution; the Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) showed an inhibition efficiency of 77% [25]. Tedim et al. (2010) demonstrated the high corrosion inhibition efficiency of LDH loaded with MBT in an aluminum alloy, primarily in neutral pH, in a 3.5% NaCl solution [6]. Seniski et al. (2020) [26] investigated the intercalation of NO_2^- into ZnAl LDH. The intercalation of LDH- NO_2 was characterized by XRD analysis, which revealed very sharp and symmetric peaks, indicating well-crystallized samples. The NO_2^- intercalation was confirmed by FTIR analysis [26]. The possibility of NO_2^- intercalation into LDH was also studied and confirmed by Xu et al. (2017) [27]. Both studies demonstrated better corrosion performance compared to the tested reference.

In addition, the LDHs controlled-release technology also reduces the ecotoxicity and/or hazard of the soluble CIs (e.g., MBT, BTA, Gluconate) to marine organisms [7–9]. However, the environmental behavior and fate of these innovative anti-corrosion nanoadditives remain poorly understood, particularly in the context of global change.

The Intergovernmental Panel on Climate Change (IPCC) projects that under the SSP3-7.0 scenario, the mean global ocean surface pH could decline by approximately 0.4 units. At the same time, the temperature is expected to rise by 2.7 °C compared to preindustrial levels by 2100 [28]. It is recognized that these environmental changes, together with co-contaminant stress, can alter the fate and behavior of nanomaterials in the water column, thereby affecting their bioavailability and ecotoxicity to marine organisms [29]. For example, silver nanoparticles and nanoforms of copper dissolve faster in high temperatures of freshwater [30,31], while in seawater, low pH promotes the aggregation of titanium oxide nanoparticles [32] and the opposite for carbon nanotubes [33], highlighting the difficulty of finding a typical pattern for all nanomaterials. Understanding how predicted environmental changes in the marine compartment interact with nanomaterials, particularly with the understudied LDHs, is essential for assessing their effective environmental risk and for defining long-term management strategies associated with coatings containing nanoadditives.

Therefore, the present study aims to assess and compare the environmental behavior of four recently developed anti-corrosion “smart” nanomaterials (LDHs loaded with the anionic forms of BTA[−], MBT[−], NO₂[−], and the bio-based SG[−]) in an ocean acidification scenario at different water temperatures simulating temperate and tropical marine ecosystems and under the presence and absence of organic matter. This approach enables the study of how multiple environmental stressors, such as increased temperature, acidification, and organic matter, may impact the long-term stability, degradation, and release dynamics of these materials. To the best of the author’s knowledge, this is the first study to evaluate the environmental behavior of these four LDH-based nanoadditives under combined global change conditions. This novel assessment associates different environmental triggers with the release of anions, within a global change context, to better understand the potential environmental risks of these compounds. Specifically, it is hypothesized that the layered double hydroxides (LDHs) will undergo higher dissolution and release more anions under acidified and warmer conditions, which are expected to accelerate material degradation and affect their environmental fate.

2. Materials and Methods

2.1. Materials

Zn-Al layered double hydroxides (LDH) intercalated with benzotriazole (abbreviated as LDH-BTA), 2-mercaptobenzothiazole (abbreviated as LDH-MBT), nitrites (abbreviated as LDH-NO₂) and sodium gluconate (abbreviated as LDH-SG) were supplied by Smallmatek, Lda. (Aveiro, Portugal). The materials were synthesized as described by Tedim et al. (2010) [6]. All tested materials (LDH-BTA, LDH-MBT, LDH-NO₂, and LDH-SG) were recently morphologically, texturally, and chemically fully characterized by Pellanda et al. (2021) [22], Martins et al. (2017) [7], and Leal et al. (2023) [24], respectively. Humic acid (HA; CAS nr. 1415-93-6), hydrochloric acid (CAS nr. 7647-01-0; ACS grade reagent, 37%), salt Pro Reef, cellulose acetate filters (0.45 µm), and sterile syringe filters (0.22 µm) were purchased from FlukaTM (Buchs, Switzerland), Sigma-AldrichTM (St. Louis, MO, USA), Tropic Marin[®] (Hünenberg, Switzerland), Prat Dumas[®] (Couze-et-Saint-Front, France), and Frilabo[®] (Porto, Portugal), respectively.

Preparation of Dispersions and Experimental Design

A stock dispersion (500 mL) of LDH-BTA, LDH-MBT, LDH-NO₂, and LDH-SG with a concentration of 200 mg CI L⁻¹ (i.e., expressed considering the loading content of the active ingredient) for each condition was prepared using artificial saltwater (ASW; salinity 35; pH 8.0). ASW was prepared by dissolving Pro Reef sea salt in reverse osmosis water, filtered through a 0.45 µm pore size filter, and sterilized at 120 °C for 20 min in an autoclave, to prevent the influence of organic matter or microorganisms, which could otherwise introduce uncontrolled variables and affect the reproducibility of the results.

The following conditions were defined: “temperate seawater” (T = 20 °C, pH = 8.0, without humic acid—HA); “tropical seawater” (T = 30 °C, pH = 8.0, without HA); “acidified temperate seawater” (T = 20 °C, pH = 7.6, without HA); “acidified tropical seawater” (T = 30 °C, pH 7.6, without HA); “temperate seawater enriched with natural organic matter (NOM)” (T = 20 °C, pH = 8.0, with HA); and “tropical seawater enriched NOM” (T = 30 °C, pH = 8.0, with HA). Stock dispersions enriched with NOM were prepared by adding 1 g L⁻¹ of humic acid (following the procedure by Bazrafshan et al., 2012) [34]. Acidified stock dispersions (pH = 7.6) were prepared by adding 500 µL of 0.1 M HCl into 1 L of dispersion to decrease the pH by 0.4 to simulate the SSP3-7.0 scenario [28]; in this treatment, pH remained between 7.6 and 7.8 during the 96 h experiments.

Stock dispersions were then placed in an ultrasonic bath for 15 min and diluted to obtain the concentrations used in the present study: 1.23, 11.1, and 100 mg CI L⁻¹. During ultrasonication, dispersions were maintained in 200 mL capped flasks to prevent pH reduction due to gas exchange with the external atmosphere, including CO₂, which could contribute to this process. Each set was then placed in rooms with controlled temperatures (T = 20 ± 0.3 °C; T = 30 ± 0.9 °C). Aliquots of 2 mL were taken every two days (0, 48, and 96 h) for immediate dynamic light scattering (DLS) analysis. To determine released corrosion inhibitors, aliquots of 2 mL were taken at times 0 and 96 h after dispersion preparation; apart from SG for each, a volume of 8 mL was sampled. For metal quantification, aliquots of 8 mL were taken immediately after dispersion preparation and after 96 h. For the chemical measurements, collected aliquots were filtered using a 0.22 µm syringe filter to retain the LDH particles and prevent further dissolution and/or anion-exchange processes [7–9]. Filtrated samples for BTA, MBT, and NO₂⁻ quantification were analyzed immediately after filtration, SG samples were refrigerated at 4 °C until analysis, and samples for elemental analysis were acidified (2% HCl final concentration).

2.2. Environmental BEHAVIOR

2.2.1. Nanomaterials Hydrodynamic Size

The hydrodynamic radius of the nanomaterials at the highest tested concentration (100 mg CI L⁻¹) under the different environmental conditions was monitored over time through DLS using a Zetasizer Nano-ZS (Malvern Instruments, Malvern, UK) to check the highest radius size nanostructures could achieve since the highest concentration tends to form more agglomerates. DLS was measured in triplicate at 0, 48, and 96 h using an aliquot of 2 mL, with the solution vigorously agitated for 5 s before each measurement to resuspend the sedimented particles.

2.2.2. Release of Corrosion Inhibitors

The concentration of corrosion inhibitors released through the anionic exchange mechanism to the media was quantified over time. Filtered samples (n = 4 per condition; volume = 0.3 mL; ASW used as a blank) were placed in a 96-well microplate and read in a UV-Vis spectrophotometer (λ_{BTA} = 275 nm; λ_{MBT} = 310 nm; λ_{NO₂} = 220 nm; Biotek®, model: Synergy HT, Winooski, VT, USA). Calibration curves for the analyzed chemicals

were built from 10 known concentrations of each analyte of interest in ASW, ranging from 100 to 0.195 mg L⁻¹, following a dilution factor of 2 [7]. The following equations were then determined and used to estimate the concentrations of BTA, $y = 0.0326x + 0.0608$ ($R^2 = 0.98$), MBT, $y = 0.0365x + 0.0786$ ($R^2 = 0.97$), and NO₂⁻, $y = 0.0188x + 0.1106$ ($R^2 = 0.90$). The detection limits were 0.0053 mg L⁻¹ for BTA, 0.0100 mg L⁻¹ for MBT, and 0.1059 mg L⁻¹ for NO₂⁻. Gluconate was determined through high-performance liquid chromatography (HPLC; Dionex, model ICS3000) at the NOVA Lisbon University at the LAQV-REQUIMTE certified facilities (Costa da Caparica, Portugal). The limit of detection was set at 2.01 mg/L.

2.2.3. Release of Metallic Elements

Zn and Al, metals structurally present in the LDH layers, were determined in the filtered and acidified water samples ($n = 1$) under different conditions, including the negative control (only ASW) as a proxy for LDHs partial dissolution over time (0 and 96 h). Samples were analyzed through Inductively Coupled Plasma Optical Emission Spectrometry (HORIBA Jobin-Yvon, model Ultima, Glasgow, UK). Quantifications were run at the LAQV-REQUIMTE certified facilities. Detection limits were 0.01 and 0.02 mg L⁻¹ for Al and Zn, respectively. The squared correlation coefficient (R^2) of the calibration curves obtained for Al ($y = 84,506x + 33,116$) and Zn ($y = 2,998,701x + 47,010$) standard solutions was 0.99 and 1.0, respectively.

2.3. Data Analysis

The data obtained were checked for normality and homoscedasticity using Shapiro–Wilk and Bartlett tests ($p < 0.05$). Statistical differences between the negative control and the treatments were analyzed by two-way ANOVA, followed by Bonferroni's post-test to compare each condition among all the others ($p < 0.05$), ensuring control over type I error in multiple comparisons, and Dunnett's post-test to compare the treatments against the negative control ($p < 0.05$).

3. Results

3.1. ZnAl LDH-BTA

Figure 1 shows the different endpoints measured on ZnAl LDH-BTA dispersions exposed to the environmental conditions over time. DLS measurements (A) in the highest tested concentration (at 0, 48 and 96 h) and chemical quantifications in the lowest, intermediate and highest tested concentration of the nanomaterial (1.23, 11.11 and 100 mg BTA L⁻¹) after 96 h of preparation, namely the concentration of dissolved BTA (B), Al³⁺ (C) and Zn²⁺ (D) present in the aqueous media.

The DLS results show that LDH suspensions exhibited heterogeneity in particle size, possibly due to the presence of large aggregates or agglomerates (Figure 1A). The hydrodynamic size of the suspended nanomaterials was then based on the average of peak 1 values (intensity distribution). Particle size tended to decrease over time at 20 °C and 30 °C, and was slightly reduced at 30 °C with an acidified pH. In contrast, it increased at 20 °C with an acidified pH and slightly in the presence of organic matter at both temperatures (Figure 1A).

The release of the anionic form of BTA from the ZnAl LDH-BTA was significantly higher in all treatments at the concentration of 100 mg L⁻¹ compared to the control. Among the treatments, at 11.1 mg L⁻¹, the presence of HA and acidification, together with a high temperature, significantly enhanced the release of BTA (3.8 mg L⁻¹) compared to the other conditions. At 100 mg L⁻¹, the presence of HA in both temperatures increased the release

of the anion compared to the other conditions, presenting a concentration of 3.4 mg L^{-1} at 20°C with HA and 4.2 mg L^{-1} at 30°C with HA (Figure 1B).

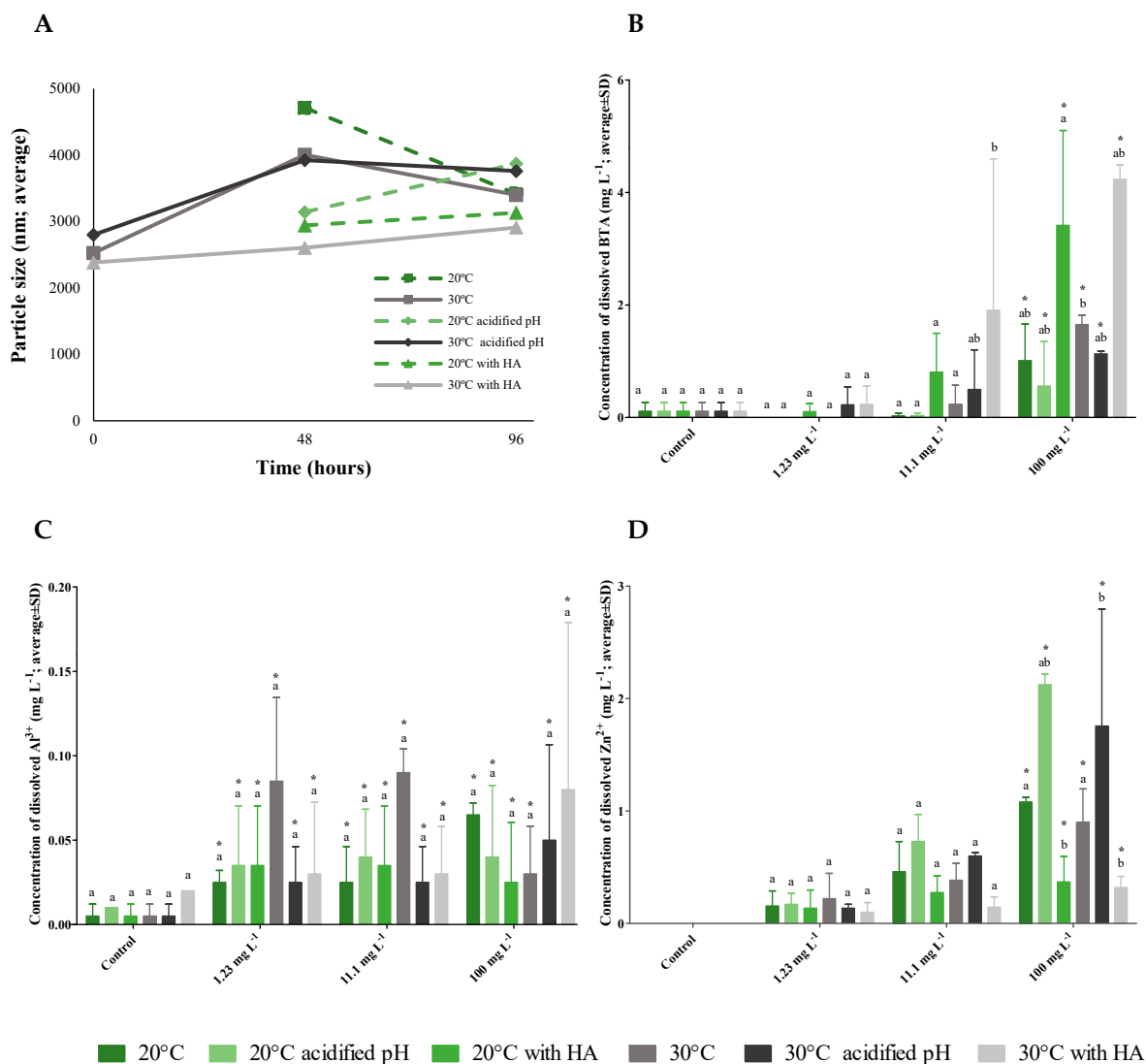


Figure 1. (A) Dynamic light scattering of ZnAl LDH-BTA dispersions ($100 \text{ mg BTA L}^{-1}$) measured at 0, 48, and 96 h after the preparation of dispersions ($n = 3$), and quantification of (B) benzotriazole (BTA), (C) Al^{3+} , and (D) Zn^{2+} , in ZnAl LDH-BTA dispersions ($n = 4$) at three concentrations (1.23 , 11.11 , and $100 \text{ mg BTA L}^{-1}$ 96 h after dispersions preparation), plus a negative control without nanomaterial. All dispersions were prepared in artificial saltwater and were submitted to six environmental conditions: 20°C (normal pH, without humic acid (HA)), 20°C and the ocean acidification scenario (-0.4 units; without HA), 20°C with HA (normal pH), 30°C (normal pH, without HA), 30°C and the ocean acidification scenario (without HA), and 30°C with HA (normal pH). Different letters indicate significant differences between conditions ($p < 0.05$, Bonferroni's test), an asterisk (*) indicates a significant difference between the treatment and the negative control ($p < 0.05$, Dunnett's test, and the bars indicate the difference between the released concentrations in the two timepoints (0 h and 96 h).

The release of Al^{3+} presented no significant differences among treatments. However, the concentration of this metal was significantly higher compared to the control, with a maximum concentration of 0.08 mg L^{-1} (Figure 1C).

Released Zn^{2+} was significantly higher at 100 mg L^{-1} in the acidified tropical scenario. At the same time, the presence of HA decreased its release in both temperature regimes when compared with the treatment at 20°C without HA (Figure 1D). Compared with the

negative control, the levels of dissolved Zn^{2+} were significantly higher in the highest tested concentration in all tested conditions.

3.2. ZnAl LDH-MBT

Figure 2 presents the endpoints measured on ZnAl LDH-MBT dispersions exposed to the six tested environmental conditions over time: DLS measurements (A) in the highest tested concentration (at 0, 48 and 96 h) and chemical quantifications in the lowest, intermediate and highest tested concentration of the ZnAl LDH-MBT (1.23, 11.11 and 100 mg MBT L^{-1}) after 96 h of preparation, namely the concentration of MBT (B), Al (C) and Zn (D) present in the aqueous media.

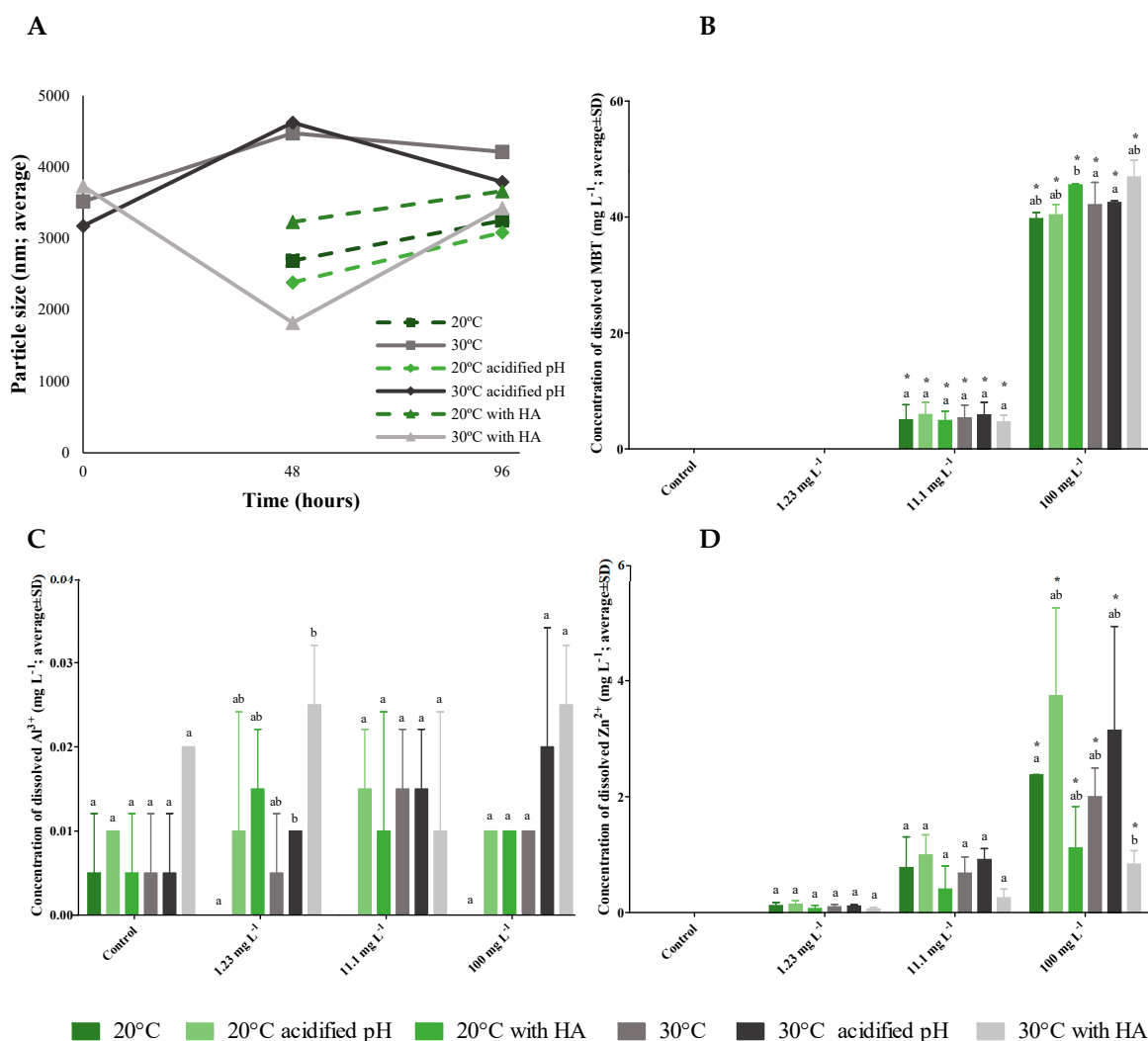


Figure 2. (A) Dynamic light scattering of ZnAl LDH-MBT dispersions (100 mg MBT L^{-1}) measured at 0, 48, and 96 h after the preparation of dispersions ($n = 3$), and quantification of (B) 2-mercaptobenzothiazole (MBT), (C) Al^{3+} , and (D) Zn^{2+} , in ZnAl LDH-MBT dispersions ($n = 4$) at three concentrations (1.23, 11.11 and 100 mg MBT L^{-1} 96 h after dispersion preparation), plus a negative control without nanomaterial. All dispersions were prepared in artificial saltwater and were submitted to six environmental conditions: 20 °C (normal pH, without humic acid (HA)), 20 °C and the ocean acidification scenario (−0.4 units; without HA), 20 °C with HA (normal pH), 30 °C (normal pH, without HA), 30 °C and the ocean acidification scenario (without HA) and 30 °C with HA (normal pH). Different letters indicate significant differences between conditions ($p < 0.05$, Bonferroni's test), an asterisk (*) indicates a significant difference between the treatment and the negative control ($p < 0.05$, Dunnett's test), and the bars indicate the difference between the released concentrations in the two timepoints (0 h and 96 h).

DLS data demonstrated that the presence of HA in the ZnAl LDH-MBT dispersion at high temperatures resulted in a reduction in particle size, particularly noticeable at 48 h (Figure 2A). However, nanomaterials dispersed at 30 °C tended to aggregate or agglomerate over time at both pH conditions (Figure 2A). At 20 °C, DLS in all treatments exhibited a similar behavior, with a tendency for aggregation or agglomeration from 48 to 96 h (Figure 2A).

Dissolved MBT was significantly enhanced in the intermediate and highest tested concentrations on all tested environmental conditions compared to the control. At the highest concentration tested, almost half of the immobilized MBT was released into the ASW; this phenomenon was significantly higher in the presence of HA at both tested temperatures (45.6 and 48.9 mg MBT L⁻¹ at 20 °C and 30 °C, respectively).

There were no significant differences in Al³⁺ concentrations in any dispersions compared with the negative control. Among the treatments, there were also no significant differences in dissolved Al³⁺. However, some exceptions were recorded, notably at the lowest tested concentration subjected to the ocean acidification scenario and in the presence of organic matter (Figure 2C). Remarkably, these levels are lower compared to those of the other tested nanomaterials, particularly at the highest tested concentration (Figure 2C).

Overall, the higher the tested concentration, the higher the concentration of dissolved Zn²⁺ (Figure 2D). Zn²⁺ levels were notably higher in all dispersions at the highest concentration tested compared to the negative control. Additionally, at 100 mg L⁻¹, Zn²⁺ release was significantly greater in the ocean acidification scenario across both temperatures (Figure 2D).

3.3. ZnAl LDH-Gluconate

Figure 3 illustrates the endpoints measured on ZnAl LDH-Gluconate dispersions exposed to the six environmental conditions over time, namely the DLS data (A) in the highest tested concentration (at 0, 48 and 96 h) and chemical quantifications at three tested concentrations of ZnAl LDH-Gluconate (1.23, 11.11 and 100 mg Gluconate L⁻¹) after 96 h, namely the concentrations of dissolved BTA (B), Al³⁺ (C) and Zn²⁺ (D).

Regarding DLS data, the most noticeable pattern is the decrease in the size of ZnAl LDH-Gluconate aggregates/agglomerates over time when exposed to 30 °C in the three scenarios. This trend was also observed at 20 °C in regular pH conditions and without HA (Figure 3A).

Similarly to the other anions, gluconate release was significantly enhanced at the highest (~60%) and intermediate (~40%) concentrations tested compared with the control. Comparing gluconate concentrations among treatments at 100 mg L⁻¹, it is noticeable that gluconate release is significantly lower under acidification and in the presence of HA scenarios at both temperatures (Figure 3B).

Overall, the higher the tested concentration, the higher the release of Al³⁺, as the concentrations of dissolved Al³⁺ were significantly higher in all scenarios at 100 mg L⁻¹ compared to the control. Differences among treatments were also recorded: (a) the dispersion of 1.23 mg L⁻¹, kept at 30 °C together with acidification, presented a significant increase of Al³⁺ (0.07 mg L⁻¹); (b) at 100 mg L⁻¹, the presence of HA significantly induced the release of Al³⁺ (0.09 ± 0.07 mg L⁻¹ in average; Figure 3C).

The Zn²⁺ release pattern observed in the other nanomaterials was also seen in ZnAl LDH-Gluconate dispersions: the higher the tested concentration, the higher the concentration of dissolved Zn²⁺. At 100 mg L⁻¹, the acidified condition at both temperatures induced a higher Zn²⁺ release compared with the remaining treatments. However, it is noticeable that the measured dissolved Zn²⁺ concentrations were significantly higher at the

highest tested CI concentration compared to the negative control, regardless of the tested environmental condition (Figure 3D).

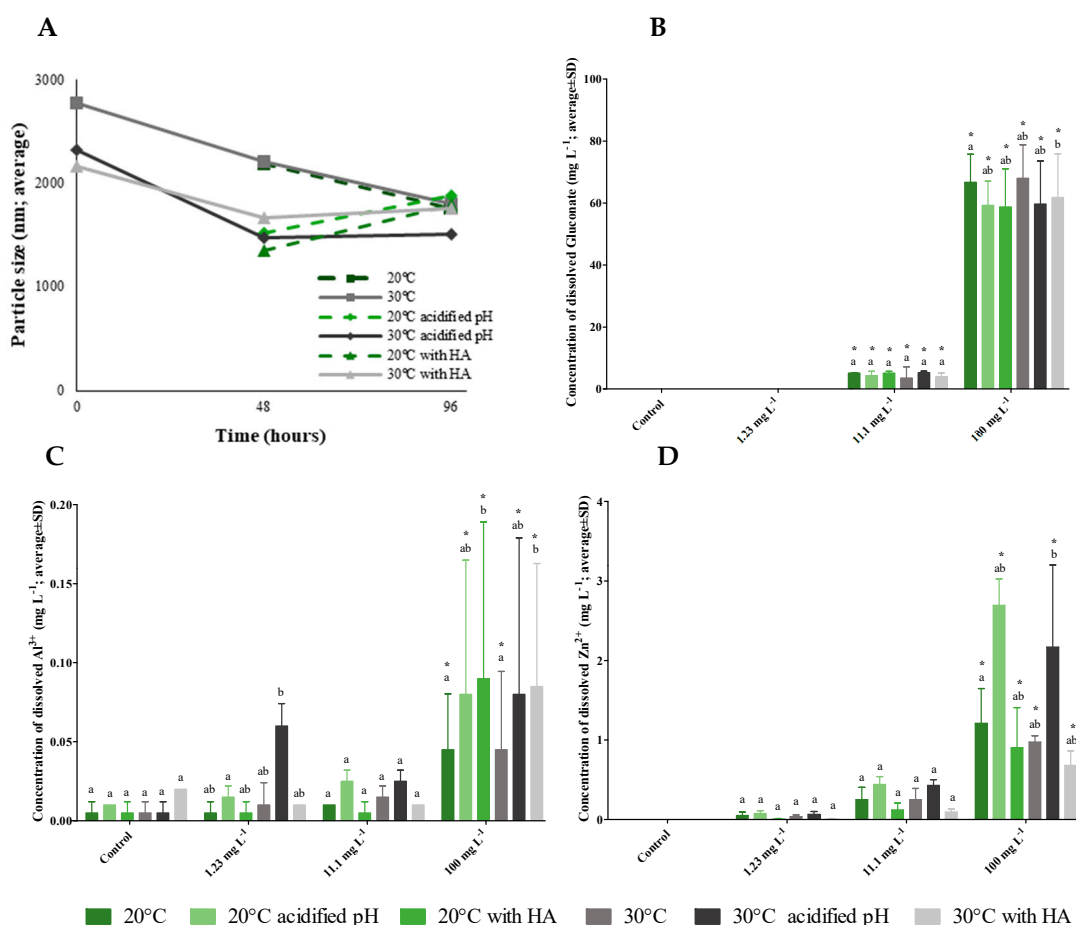


Figure 3. (A) Dynamic light scattering of ZnAl LDH-Gluconate dispersions (100 mg SG L⁻¹) measured at 0, 48, and 96 h after the preparation of dispersions (n = 3), and quantification of (B) gluconate (SG), (C) Al³⁺, and (D) Zn²⁺, in ZnAl LDH-Gluconate dispersions (n = 4) at three concentrations (1.23, 11.11 and 100 mg SG L⁻¹, 96 h after dispersion preparation), plus a negative control without nanomaterial. All dispersions were prepared in artificial saltwater and were submitted to six environmental conditions: 20 °C (normal pH, without humic acid (HA)), 20 °C and the ocean acidification scenario (−0.4 units; without HA), 20 °C with HA (normal pH), 30 °C (normal pH, without HA), 30 °C and the ocean acidification scenario (without HA) and 30 °C with HA (normal pH). Different letters indicate significant differences between conditions ($p < 0.05$, Bonferroni's test), an asterisk (*) indicates a significant difference between the treatment and the negative control ($p < 0.05$, Dunnett's test), and the bars indicate the difference between the released concentrations in the two timepoints (0 h and 96 h).

3.4. ZnAl-LDH-NO₂

Figure 4 exhibits the endpoints measured on ZnAl LDH-NO₂ dispersions exposed to the six tested environmental conditions over time: DLS measurements (A) in the highest tested concentration (at 0, 48, and 96 h) and chemical quantifications in the three tested concentrations of the ZnAl LDH-NO₂ (1.23, 11.11, and 100 mg NO₂ L⁻¹ respectively) after 96 h, namely the concentration of NO₂⁻ (B), Al (C), and Zn (D) present in the aqueous media.

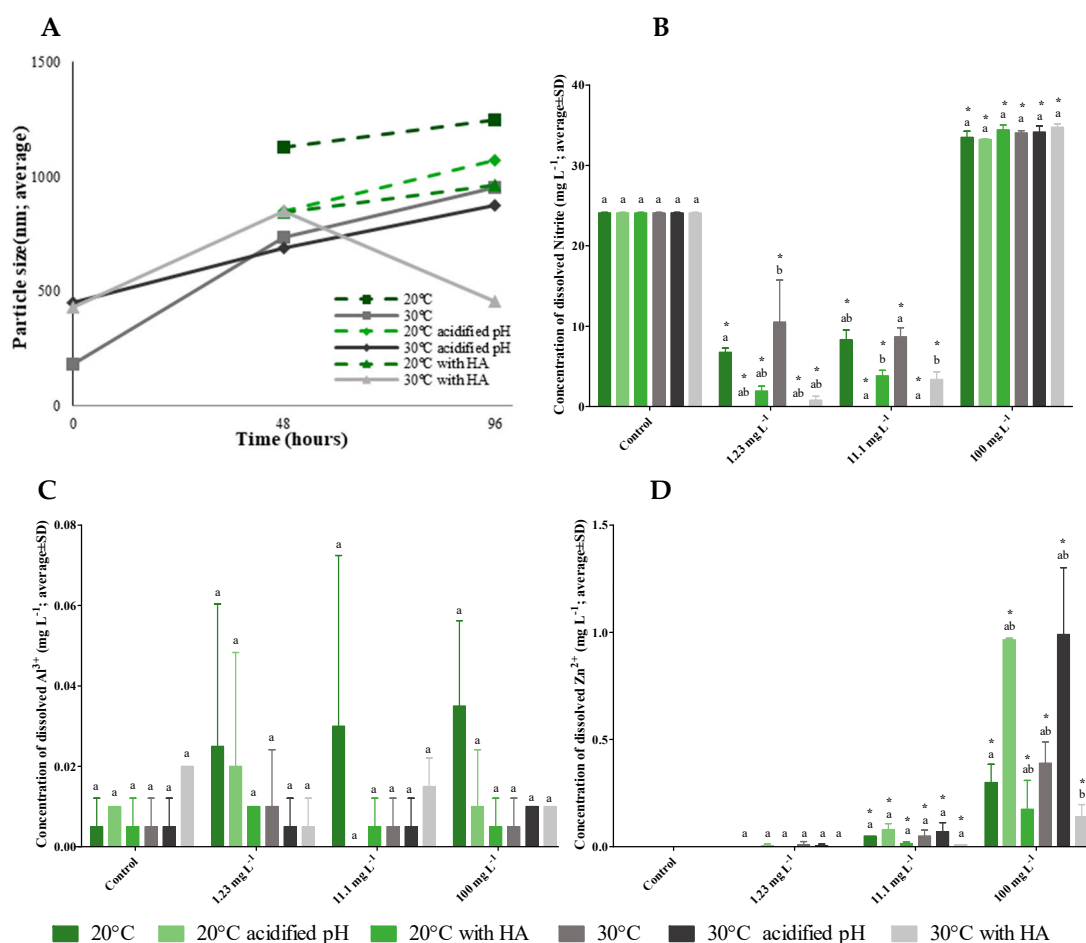


Figure 4. (A) Dynamic light scattering of ZnAl LDH-NO₂ dispersions (100 mg NO₂[−] L^{−1}) measured at 0, 48, and 96 h after the preparation of dispersions (n = 3), and quantification of (B) nitrites (NO₂[−]), (C) Al³⁺, (D) and Zn²⁺, in ZnAl LDH-NO₂ dispersions (n = 4) at three concentrations (1.23, 11.11 and 100 mg NO₂[−] L^{−1}, 96 h after dispersions preparation), plus a negative control without nanomaterial. All dispersions were prepared in artificial saltwater and were submitted to six environmental conditions: 20 °C (normal pH, without humic acid (HA)), 20 °C and the ocean acidification scenario (−0.4 units; without HA), 20 °C with HA (normal pH), 30 °C (normal pH, without HA), 30 °C and the ocean acidification scenario (without HA) and 30 °C with HA (normal pH). Different letters indicate significant differences between conditions (*p* < 0.05, Bonferroni's test), an asterisk (*) indicates a significant difference between the treatment and the negative control (*p* < 0.05, Dunnett's test), and the bars indicate the difference between the released concentrations in the two timepoints (0 h and 96 h).

DLS data showed that ZnAl LDH-NO₂ dispersions contained the particles with the lowest hydrodynamic radius among the four tested nanomaterials. Except at 30 °C with HA, particle size increased in the first 48 h, followed by a decrease between 48 and 96 h; all the remaining conditions promoted the aggregation/agglomeration of the nanomaterials over time (Figure 4A).

NO₂[−] concentrations were significantly higher in the highest tested concentration than the negative control, which already had high levels, while in the lowest and intermediate concentrations, NO₂[−] levels were significantly lower (Figure 4B).

No significant differences were observed in dissolved Al³⁺ concentrations across all treatments compared with the negative control and the various conditions. Globally, concentrations of dissolved Al³⁺ were amongst the lowest across the four tested nanomaterials (Figure 4C).

Detected levels of Zn^{2+} were significantly higher in all dispersions at the highest tested concentration compared to the negative control. Similarly to the LDH-BTA and LDH-MBT, the condition “30 °C with HA” promoted a significantly lower release of Zn^{2+} compared with the remaining 100 mg L^{−1} dispersions submitted to the other treatments (Figure 4D).

4. Discussion

This study provides the first comprehensive assessment of the environmental behavior of four innovative anti-corrosion nanomaterials, namely layered double hydroxides (LDHs) loaded with benzotriazole (BTA), 2-mercaptobenzothiazole (MBT), nitrites (NO_2^-), and gluconate (SG). It was investigated how these materials behaved when dispersed in artificial saltwater under different environmental conditions, including variations in temperature, pH, and the presence of organic matter, specifically humic acid (HA), by examining their aggregation/agglomeration and sedimentation behavior and the release of embedded active agents (corrosion inhibitors) alongside metal ions as a result of anionic exchange and partial dissolution of the LDH structure. Even though the release and dissolution processes of these materials, when incorporated into the coatings, would occur in a large system at a slower rate, minimizing the aggregation/agglomeration phenomena, these mechanisms are a key feature of LDHs, regarded as “smart” nanomaterials due to their capacity to respond to stimuli, namely the presence of water, organic matter, or anions in the surrounding environment, such as chlorides, and a decrease in pH locally [7–9,35–37]. In this study, “release” refers to the controlled liberation of corrosion inhibitors from the LDH interlayers via anion exchange, while “dissolution” refers to the partial breakdown of the LDH structure itself, leading to the release of Zn^{2+} and Al^{3+} ions. These are distinct but potentially concurrent processes, especially under acidified or high-temperature conditions.

The presence of chlorides acts as a trigger, fostering the release of the active ingredient that is weakly bonded to the inner galleries of the ZnAl LDHs and entrapping the aggressive anions [19,38]. This is an advanced feature when nanomaterials are used as coating additives since they can sense the presence of such aggressive anions and actively protect the coated surfaces [21,23,24].

The present study observed that the release of BTA, MBT, NO_2^- , and SG increased with the nanomaterial concentration, particularly in the presence of humic acid. The higher rates of anion release observed in dispersions containing humic acid suggest that natural organic matter plays a crucial role in influencing the release of active ingredients from LDHs when these materials are dispersed in seawater under different environmental conditions. The presence of HA can modify the stability and aggregation behavior of LDHs, allowing the release of intercalated active agents, which may impact the potential environmental effects of nanomaterials in the marine environment.

It is widely known that ZnAl LDH nanomaterials have good adsorption properties, removing pollutants and NOM, particularly humic acid, which naturally changes the nanomaterial’s behavior in aqueous media [39]. The presence of HA in the dispersions can cause electrostatic attraction, the reduction in surface charge of the metals present in the LDH, leading to an increase in the aggregation rates, as observed by comparing the particle’s hydrodynamic size of day 0 and day 4 in both temperature regimes containing HA [40].

Furthermore, the concentration of dissolved Zn^{2+} was systematically higher in the acidified dispersions compared to the other treatments and lower in all dispersions exposed to HA compared to the other treatments, signifying a possible interaction between Zn^{2+} and HA. It is well-documented that LDH can partially dissolve in aqueous media at neutral pH, releasing less than 10% of Zn^{2+} and Al^{3+} ions in low ionic strength media at neutral pH and temperatures of 23 °C [41] and 27 °C [42]. However, Martins et al.

(2017) [7] demonstrated that both metals were undetectable in ZnAl LDH-NO₃ dispersions prepared in high-ionic-strength media. This was not the case in the present study, where dissolved Zn²⁺ and Al³⁺ were detected in all dispersions [7–9]. Several studies evaluating the aquatic toxicity of Zn²⁺ are summarized in the review conducted by Bordin et al. (2024) [43], where reported exposure concentrations in seawater systems range from 0.006 to 810 mg L^{−1}. The most sensitive endpoint identified was an EC₅₀ of 0.03 mg L^{−1} for echinoderms. These findings underscore the potential environmental concern associated with Zn²⁺ release, especially considering that nearly all treatments in the present study resulted in dissolved zinc concentrations exceeding this threshold [43]. This suggests that even partial dissolution of LDH-based nanomaterials under acidified or warmer conditions could pose ecotoxicological risks to sensitive marine organisms. Therefore, understanding the bioavailability and toxicity of Zn²⁺ under varying environmental conditions is essential for evaluating the safety of these materials in marine applications.

In the worst tested scenarios—namely, ocean acidification for Zn and high temperature and/or presence of HA for Al—LDHs released to the media no more than 4% of the total elemental composition of their positively charged layers (28% and 5% of the total weight of LDHs correspond to Zn and Al, respectively). The average concentration of Al in each dispersion did not exceed the maximum measured environmental concentrations (MEC) in coastal waters (0.5 mg L^{−1}) [44]; however, dissolved Zn exceeded the maximum MEC (0.025 mg L^{−1}) [45] in most dispersions. Therefore, the availability of dissolved cations could favor different chemical reactions. Following the speciation of dissolved cations in seawater, it is expected that Al is present mainly in its dissolved form, as was the case in the present study. Therefore, the comparative increase in dissolved Al³⁺ can be explained by the speciation of this cation that favors dissolution rather than complexation or precipitation [44].

On the other hand, Zn²⁺ can react with chlorides [46], interact with LDHs being removed through isomorphic substitution, complexation, and electrostatic interactions [47], or complexate with natural organic matter [48,49], as already documented for bimetallic cations, namely Zn²⁺, Mg²⁺, or Fe²⁺, affecting the physicochemical properties and behavior of LDHs in different media. Yang et al. (2009) [50] investigated the complex stability of copper, zinc, cobalt, and aluminum in the presence of humic acid. They concluded that Cu and Zn had the highest stability constants, while Al formed less stable complexes with HA [50]. Additionally, the ability of HA to mediate electron transfer may also explain the increased release of ions from LDHs [51,52]. Thus, in the LDH dispersions containing natural organic matter, the complexation of Zn²⁺ with HA can be regarded as the most likely explanation for the decrease in dissolved Zn²⁺ compared to the other treatments at the same nanomaterial concentration. Instead, the Zn²⁺ increase in the ocean acidification scenarios, regardless of the tested temperature, is likely due to the higher dissolution rate of the LDH provoked by the decrease of 0.4 units, alongside the speciation of the metal that favors the formation of Zn²⁺ as pH decreases [53]. A similar pH-dependent behavior has been observed in other engineered nanomaterials [54], including in the sibling MgAl LDH dispersed in PBS over a pH gradient [55]. Li and collaborators demonstrated that the concentration of dissolved Mg (the divalent cation) increased threefold in the dispersion at pH = 5.2 compared to pH = 7.4. In contrast, Al (the trivalent cation) was not detected (detection limit of 0.05 mg L^{−1}) in any scenario. However, the release of the entrapped anion, which acts as the active ingredient (methylene orange), was also pH- and time-dependent [54], though this is unlikely in the present study. Here, no significant differences were observed in the concentration of the four corrosion inhibitors (the entrapped anions) in acidified dispersions compared with other environmental conditions. This may be due

to the subtle pH change (only -0.4 units), and future studies should investigate whether acidic conditions ($\text{pH} < 7$) also promote the release of BTA, MBT, NO_2^- , and/or SG.

Although the present study focused on short-term assays, it is essential to consider that the tested materials are intended for use as nanoadditives in high-performance coatings, where long-term direct release into the environment is not expected under normal use conditions. However, accidental release or degradation over time may occur; future studies should investigate how these materials behave under prolonged exposure and more extreme environmental conditions. In particular, the presence of natural organic matter may influence the long-term stability and mobility of LDHs by altering their surface charge, aggregation behavior, and ion exchange capacity. These interactions could affect the kinetics of anion release and the formation of secondary products. Although not addressed experimentally in this study, the importance of investigating these mechanisms in future work is recognized. Moreover, the potential for adverse environmental reactions involving the released anions (e.g., BTA^- and MBT^-) should be further assessed, particularly regarding their transformation products, persistence, and bioavailability, as these anions are known to cause ecotoxicity on certain marine species [7–10].

Additionally, natural seawater is a more complex and dynamic system, and future studies should investigate how microbial activity, additional ions, and natural organic matter may influence the environmental behavior of these materials under realistic conditions. This study also acknowledges the importance of further research on the behavior and fate of these nanomaterials under more realistic environmental conditions, especially when added into maritime coatings, where the release of anions and cations is expected to decrease sharply due to their immobilization in the polymeric matrix. Anionic exchange will only occur in response to environmental triggers. Conversely, partial dissolution and cation release may happen in harsh conditions, potentially leading to polymer degradation and affecting its components. It is crucial to note that the environmental evaluation of the four innovative anti-corrosion nanoadditives was initially focused on realistic scenarios to better assess ecotoxicological risks related to the direct discharge of nanomaterials into seawater and the bioavailability of their main components. Currently, an environmental risk assessment of these nanomaterials in temperate and tropical marine environments is underway.

As previously discussed, the literature has generally focused on one type of nanomaterial or limited environmental factors [55]. In contrast, the comprehensive approach of the present study enables a comparison and a deeper understanding of how these innovative nanomaterials behave in real-world environmental scenarios, particularly in the context of the current global climate change awareness. It addresses both academic and industrial needs concerning the environmental implications of nanotechnology and opens pathways for optimizing polymeric formulations tailored to more specific, regional, current, and/or future conditions. This study also contributes to the growing database on the behavior of industrially relevant engineered nanomaterials under environmental stressors, providing open-access data that is valuable for academia, industry, and stakeholders. In fact, R&D companies can now utilize this information to adapt their nano-based products and develop safe and sustainable-by-design nanomaterials that minimize chemical release (e.g., Zn) and adverse environmental impacts, while maintaining their anti-corrosion performance. This is crucial for the transition towards a zero-net pollution world [56].

5. Conclusions

This is the first comprehensive study to simultaneously assess the environmental behavior of four innovative LDH-based anti-corrosion nanomaterials under multiple global change stressors. The results show that even minor acidification significantly enhances

the partial dissolution of layered double hydroxides, releasing high levels of Zn that may pose an environmental hazard. Conversely, dissolved organic matter increases Al levels and encourages the release of anions, such as corrosion inhibitors. This work highlights the knowledge gaps regarding chemical behavior in the context of global change. Understanding the chemical bioavailability under different conditions is crucial for assessing the toxic effects on marine life in temperate and tropical regions, as well as for developing eco-friendly alternatives that do not compromise anti-corrosion performance. Our findings support the need for improved frameworks to assess nanomaterial behavior in diverse environments and under future ocean conditions, thereby promoting responsible management and disposal that align with environmental protection standards.

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Abbreviations

The following abbreviations are used in this manuscript:

CIs	Corrosion Inhibitors
LDH	Layered Double Hydroxides
ASW	Artificial Salt Water
MBT	2-mercaptobenzothiazole
BTA	Benzotriazole
SG	Sodium Gluconate
NO ₂ [−]	Nitrite
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
OCP	Open Circuit Potential
EIS	Electrochemical Impedance Spectroscopy

I.E.	Inhibition Efficiency
IPCC	Intergovernmental Panel on Climate Change
HA	Humic Acid
NOM	Natural Organic Matter
DLS	Dynamic Light Scattering
HPLC	High-Performance Liquid Chromatography
MEC	Measured Environmental Concentrations

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