



Ecological assessment and corrosion inhibition potential of novel double-chain arginine-based cationic surfactants

M. Teresa García^{a,*}, Ana de la Fuente^a, Lourdes Pérez^a, Elena Bautista^a, Sergio Vázquez^a, Olga Kaczerewska^{b,c}, Roberto Martins^c, João Tedim^b

^a Surfactants and Nanobiotechnology Department, Institute for Advanced Chemistry of Catalonia, IQAC-CSIC, Jordi Girona 18-26, Barcelona 08034, Spain

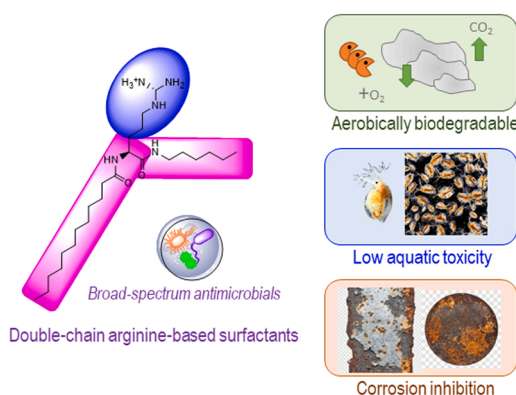
^b CICECO-Aveiro Institute of Materials and Department of Materials and Ceramic Engineering, University of Aveiro, Aveiro 3810-193, Portugal

^c CESAM - Centre for Environmental and Marine Studies and Department of Biology, University of Aveiro, Aveiro 3810-193, Portugal

HIGHLIGHTS

- Double-chain arginine-based surfactants are aerobically biodegradable.
- Alkyl chain length significantly affects biodegradation rate.
- Aquatic toxicity significantly lower than conventional quaternary ammonium compounds.
- LANHC₆ effectively inhibits carbon steel corrosion under neutral conditions.
- Sustainable green alternatives to conventional QACs with reduced ecological footprint.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Double-chain arginine surfactants
Biodegradation
Aquatic toxicity
Corrosion inhibition

ABSTRACT

This study investigates the environmental impact and corrosion inhibition of novel double-chain arginine-based cationic surfactants developed as antimicrobial agents. The research focuses on asymmetric double-chain surfactants (LANHC_x) with a 12-carbon alkyl chain and a second chain of 3–10 carbons, linked to the amino acid polar head group via amide bonds. The study assessed how alkyl chain length affects the ecological properties. Aerobic biodegradability (CO₂ headspace test) and aquatic toxicity (short-term exposure on *Daphnia magna*, *Aliivibrio fischeri*, *Tetraselmis chuii*, and *Phaeodactylum tricornutum*) were evaluated. Corrosion inhibition efficiency was determined using electrochemical impedance spectroscopy (EIS). Alkyl chain length significantly influenced biodegradation rates (1–63 % at 12 mg C/L), with the C6 homologue showing minimal degradation, though it improved at lower concentrations. Biodegradation correlated with antimicrobial potency. These compounds exhibited over one order of magnitude lower aquatic toxicity than conventional quaternary ammonium surfactants (QACs). The arginine-based surfactant LANHC₆ effectively inhibited carbon steel

* Corresponding author.

E-mail addresses: teresa.garcia@iqac.csic.es (M.T. García), anam.fuente.96@gmail.com (A. de la Fuente), lourdes.perez@iqac.csic.es (L. Pérez), elena.bautista@iqac.csic.es (E. Bautista), sergio.vazquez@iqac.csic.es (S. Vázquez), olga.kaczerewska@wp.pl (O. Kaczerewska), roberto@ua.pt (R. Martins), joao.tedim@ua.pt (J. Tedim).

<https://doi.org/10.1016/j.jhazmat.2025.139611>

Received 16 May 2025; Received in revised form 15 August 2025; Accepted 18 August 2025

Available online 19 August 2025

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corrosion in neutral conditions (80 % at 0.5 mM), outperforming conventional DTAC at a 32-fold lower concentration. Overall, these new amino acid-derived antimicrobial agents demonstrate higher biodegradation rates and lower toxicity compared to conventional QACs, making them promising alternatives as environmentally preferable corrosion inhibitors.

1. Introduction

Cationic surfactants, particularly quaternary ammonium compounds (QACs), find wide application in various industries due to their excellent properties as emulsifiers, dispersants, antimicrobials, and corrosion inhibitors [1–4]. Corrosion presents a significant challenge in numerous industries, leading to material degradation and substantial economic losses [4]. To address this issue, several solutions have been identified, with corrosion inhibitors being particularly effective. Surfactants have emerged as an especially promising class of corrosion inhibitors [5].

In recent years, dimeric quaternary ammonium surfactants have attracted considerable academic and industrial interest due to their unique properties, such as enhanced surface activity and superior antimicrobial and anticorrosive properties compared to their monomeric counterparts [4,6–10]. These attributes make them suitable for a wide range of applications [11–18]. They form protective layers on metal surfaces, reducing the interaction between the metal and corrosive agents. Their unique structure, featuring two hydrophobic chains and a hydrophilic head group, enhances their adsorption on metal surfaces, providing superior corrosion inhibition. Recent studies have demonstrated their low interfacial tension and promising corrosion inhibition effects [19,20].

This enhanced efficiency allows the utilization of reduced quantities of surfactant to achieve comparable surface or biocidal results. However, despite being more effective than their monomeric counterparts [21,22], dimeric quaternary ammonium surfactants show limited degradation in standard biodegradability tests [22,23]. In addition, quaternary ammonium surfactants have been shown to be toxic to aquatic organisms [22–25].

The discharge of these compounds into wastewater treatment plants and subsequent presence in aquatic environments has raised concerns regarding their environmental impact [3,26–35]. These concerns have been further intensified by the increased consumption of quaternary ammonium surfactants during the SARS-CoV-2 pandemic [36–38]. The negative environmental impacts of QACs include disruption of wastewater treatment plant operations, toxicity towards aquatic species, and alteration of surface water ecosystems [39]. These drawbacks have led to restrictions on the use of quaternary ammonium surfactants in Europe, particularly in food products and consumer hand and body washes [40].

Addressing these environmental concerns necessitates the development of novel, biocompatible, and efficient surfactants derived from natural resources. Among these, amino acid-based surfactants are particularly promising for creating new biodegradable molecules as environmentally responsible alternatives to conventional quaternary ammonium surfactants.

Recently, our research group has developed a novel series of asymmetric double-chain arginine-based cationic surfactants. In these compounds, two hydrocarbon tails are linked via amide bonds to an arginine polar head group. These surfactants, with one chain of 12 carbon atoms and a second chain varying from 3–10 carbon atoms, exhibit high surface activity and excellent antimicrobial properties.

The present study focuses on evaluating the biodegradability and aquatic toxicity of these novel arginine-based surfactants, as well as their potential as corrosion inhibitors. In addition, we examine how the length of the second alkyl chain influences their ecotoxicological properties, providing a comprehensive assessment of their environmental impact and potential applications.

This research contributes to the understanding of structural

parameters influencing the fate and effects of double-chain amino acid-based cationic surfactants in aquatic environments. The findings can be applied to the design of efficient and sustainable surface-active agents, addressing the need for environmentally friendly alternatives to traditional quaternary ammonium surfactants.

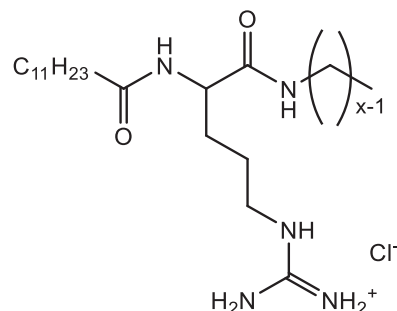
2. Materials and methods

2.1. Materials

Double-chain arginine-based surfactants (LANHC_x) were synthesised in accordance with the methodology previously outlined in the literature [41]. The chemical structure of these compounds is illustrated in Fig. 1. Benzalkonium chloride (BAC) (≥95 %) was purchased from Sigma-Aldrich.

2.2. Biodegradation testing

The aerobic biodegradability of the double-chain arginine-based cationic surfactants was evaluated through the CO₂ headspace test (OECD 310) [42]. This standard method assesses the ultimate biodegradability of an organic compound in aqueous solution through the analysis of the inorganic carbon (CO₂ production). The biodegradation kinetics of the double-chain arginine-based surfactants were determined by measuring the CO₂ production resulting from the breakdown of the surfactant molecules by microbial population at regular intervals. Each cationic surfactant was introduced as the sole source of carbon and energy at concentrations of 10 or 12 mg C/L into a buffered aqueous medium with a pH of 7.4 ± 0.2. Sodium benzoate (NaBz) at a concentration of 20 mg C/L was employed as a reference substance. The solutions were inoculated with activated sludge collected from a wastewater treatment plant (Manresa, Barcelona) and incubated in sealed vessels at 20 °C. Sampling was conducted on a weekly basis in order to ascertain the extent of the increase in the inorganic carbon concentration that occurred during the incubation period. The tests were conducted for a period of 28 days. In addition, inhibition tests were conducted with binary mixtures of NaBz and cationic surfactant at 20 and 10–15 mg C/L, respectively. The biodegradation of the substances was evaluated by measuring the net increase in the concentration of inorganic carbon, that is, the difference between the CO₂ production in the vessels containing surfactant and the endogenous CO₂ production, which was determined using a carbon analyser (Shimadzu TOC-V_{CSH}).



LANHC_x, x = 3, 4, 6, 8 and 10

Fig. 1. Chemical structure of the studied double-chain arginine-based cationic surfactants: N^ω-lauroyl-arginine-N-alkylamide hydrochlorides (LANHC_x).

The extent of biodegradation was expressed as a fraction of the theoretical amount of inorganic carbon based on the initial concentration of the test compound. The pass level for this method is established in 60 %, thus a compound exceeding this biodegradation threshold is regarded as readily biodegradable.

2.3. Ecotoxicity testing

2.3.1. *Daphnia magna* acute toxicity test

Daphnia magna acute immobilization tests [43] were conducted to assess the potential harmful effects of the synthesized surfactants on freshwater organisms. This standardized bioassay is among the most commonly used methods for evaluating chemical compound toxicity, owing to the widespread distribution of daphnids across diverse habitats and their relatively brief life cycle.

s after gentle agitation. The pH of the medium was 8.0 and the total hardness was 250 mg/L (as CaCO_3), with a Ca/Mg ratio of 4/1. The experiments were conducted in the absence of light at a temperature of 20 °C. For each surfactant, ten concentrations in a geometric series were tested. Twenty *daphnia* were employed at each test concentrations, with the animals divided into four batches of five. The percentage of immobility at 48 h was plotted against concentration on probability-logarithmic scale. A probit analysis was used with the SPSS statistics software package (IBM SPSS Statistics 29.0) to estimate the concentration required to immobilize 50 % of the daphnia after the exposure period (IC_{50}) and to determine the associated confidence limits ($p = 0.95$).

2.3.2. *Aliivibrio fischeri* bioluminescent bacteria inhibition assay (Microtox® Test)

The acute toxicity of the cationic surfactants was evaluated by measuring the luminescence inhibition of the marine Gram-negative bacterium *Aliivibrio fischeri* (strain NRRL B-11177), following exposure to varying concentrations of the surfactants. The bacterium was obtained in a freeze-dried form from Modern Water Ltd. (York, UK) and activated by rehydration with a reconstitution solution (specially prepared, non-toxic, ultra-pure water) to provide a ready-to-use suspension of organisms. The osmolarity of all standard and sample solutions was adjusted to 2 % NaCl in order to ensure optimal performance. A dilution series of the samples to be analysed was prepared in a 2 % NaCl solution. A fixed quantity of bacteria was introduced to the dilution vials. Light emission from the bacteria in contact with different samples was measured at various exposure times using the Microtox® 500 analyser.

When exposed to toxic chemicals, bacteria exhibit reduced light output proportional to the sample's toxicity. In the Microtox® bioassay [44] the concentration of a chemical causing 50 % reduction in bacterial light emission (EC_{50}) is determined from a concentration–response curve using regression analysis. The data were processed using the Microtox Omni Software. The effective concentration (EC_{50}) is defined as the sample concentration producing a 50 % decrease in light after exposure for 30 min of exposure.

2.3.3. Microalgae growth inhibition tests

Growth inhibition effects of the cationic surfactant LANCH₆ were evaluated on two marine microalgae species, the diatom *Phaeodactylum tricornutum* (Heterokontophyta: Naviculales) and the green microalgae *Tetraselmis chuii* (Chlorophyta: Chlorodendrales) following the standard protocol ISO 10253 (2016) [45] miniaturized for 24-well microplates [25].

Both photosynthetic species are cultivated in the University of Aveiro's own facilities (Department of Biology and CESAM), and no field collection was involved. Cultures were prepared using sterile 0.45 µm-filtered artificial seawater (ASW; prepared with Tropic Marin® Pro Reef pharmaceutical-grade salt; salinity 35), enriched with culture medium "Optimedium" purchased from Aqualgae SL. They were maintained in vials with approximately 150 mL of culture medium to allow gas

exchange at a temperature of $19 \pm 1^\circ\text{C}$, under continuous light (24:0 h light: dark photoperiod), with daily agitation.

Tests were run with 0.45 µm filtered artificial seawater (ASW). Exposure tests included one negative control (ASW) and five exposure concentrations of the cationic surfactant LANCH₆, namely 1, 3.33, 10, 33.3 and 100 mg/L for *P. tricornutum* and 20, 40, 60, 80 and 100 mg/L for *T. chuii* with an initial cell density of approximately 10^4 cells/mL. Microalgae growth was monitored for 72 h through daily fluorescence measurements. The regression equation between cell density (Y) and fluorescence intensity (X) was calculated as:

$$Y = 34.885X - 19681 \quad (r^2 = 0.993), \text{ for } T. \text{ chuii};$$

$$Y = 291.89X - 315415 \quad (r^2 = 0.999), \text{ for } P. \text{ tricornutum}$$

Growth inhibition was then estimated following the equation $I(\%) = (\mu_C - \mu_T) / \mu_C \times 100$, where $I(\%)$ stands for the growth inhibition percentage and μ_C and μ_T for the mean values of the average specific growth rate (μ) in the control (C) and the treatment (T) groups, respectively. The median growth inhibition concentration (IC_{50}) for each species was determined through a non-linear regression model (4-parameter logistic) with the software *GraphPad Prism* v.6.0, based on the best curve-fitting analysis in terms of the sum of squares and R^2 .

2.4. Corrosion tests

Corrosion measurements were carried out using a conventional three-electrode cell (placed in a Faraday cage) with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode and the carbon steel DC01 ($1 \times 1 \text{ cm}^2$ embedded in epoxy mold) as a working electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Gamry FAS2 Femtostat with a PCI4 Controller. Impedance spectra were obtained over a frequency range of $1 \times 10^5 \text{ Hz}$ to $1 \times 10^{-2} \text{ Hz}$ with a sinusoidal amplitude (RMS) of 10 mV and 7 points per decade, at open circuit potential. Fittings of EIS spectra were done using ZView software using a simplified Randles circuit.

Individual anodic and cathodic potentiodynamic polarization measurements were obtained by sweeping the electrode potential automatically from -0.02 V to $+0.7 \text{ V}$ vs OCP and from $+0.02 \text{ V}$ to -0.7 V vs OCP with a scan rate of 1 mV/s . A carbon steel electrode immersed in 50 mM NaCl solution (without addition of the inhibitor) was used as a blank sample.

3. Results and discussion

3.1. Aerobic biodegradability

The aerobic biodegradation of the double-chain arginine-based cationic surfactants was evaluated using the CO_2 Headspace test (OECD 310) [42], which is the reference method established by the European Commission for the assessment of surfactant biodegradation. The ultimate biodegradation of the cationic surfactants was determined by measuring the biogenically produced inorganic carbon. Given the antimicrobial properties of the cationic surfactants under investigation, biodegradation tests for these compounds were conducted at an initial concentration of 12 mg C/L, rather than the concentration typically employed in this standardized test (20 mg C/L). The biodegradation curves obtained for the double-chained arginine-based cationic surfactants (LANHCx), benzalkonium chloride (BAC)—a conventional quaternary ammonium surfactant—and the reference substance (NaBz) are displayed in Fig. 2. Table 1 presents the biodegradation percentages measured at the conclusion of the test period.

The biodegradation extent of double-chain arginine-based cationic surfactants ranged from 1 % to 63 % at the conclusion of the test period. In contrast, the quaternary ammonium surfactant exhibited null biodegradation during the same period (Fig. 2, Table 1). The extent of aerobic biodegradation of these double-chain cationic surfactants, which bear an alkyl chain of 12 carbon atoms and another shorter one of

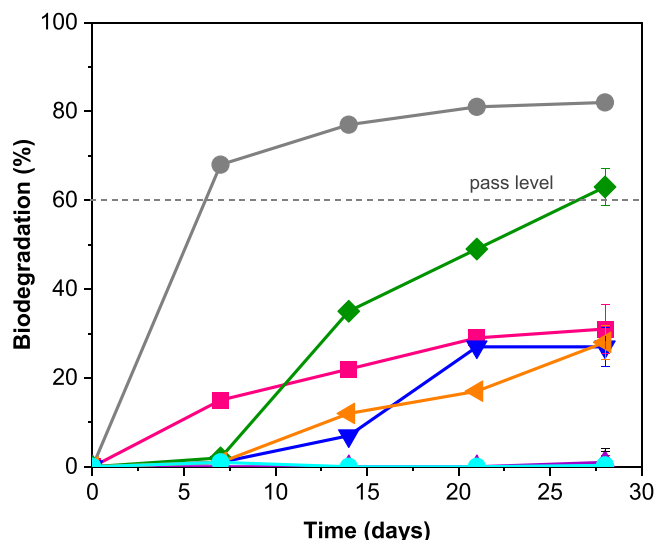


Fig. 2. Biodegradation curves for double-chain arginine-based cationic surfactants: LANHC₃ (■); LANHC₄ (▼); LANHC₆ (▲); LANHC₈ (◆) and LANHC₁₀ (◀); quaternary ammonium surfactant: BAC (●); and reference substance: NaBz (●). Surfactants and reference substance were tested at 12 and 20 mg C/L, respectively. Threshold level for ready biodegradability test: 60 % of theoretical CO₂ production.

Table 1

Biodegradation percentages of double-chain arginine-based cationic surfactants (LANHCx), benzalkonium chloride (BAC) and reference substance (NaBz) after 28 days. The 95 % confidence interval of the 28-day biodegradation percentage was calculated from four replicates.

Compound	Biodegradation (%)
NaBz	82 ± 1.4
LANHC ₃	31 ± 5.6
LANHC ₄	27 ± 4.4
LANHC ₆	1 ± 1.6
LANHC ₈	63 ± 4.1
LANHC ₁₀	28 ± 3.8
BAC	0 ± 0.3

variable length, is dependent upon the number of carbons of the second hydrophobic tail linked to the arginine polar head group. However, the extent of biodegradation does not show a linear variation with the increase in the length of the second hydrophobic chain. Firstly, biodegradation decreases with increasing the alkyl chain length reaching a minimum value for the LANHC₆ homologue. Subsequently, mineralization increases with the elongation of the hydrocarbon tail. All double-chain arginine-based cationic surfactants investigated, with the exception of LANHC₆, underwent a significant extent of mineralization (28–63 %) under the test conditions. Indeed, one of them, LANHC₈, exceeded the extent of ultimate biodegradation required to be classified as easily biodegradable.

Given the antimicrobial properties of cationic surfactants [46] and, in particular, those of this new family of double-chain arginine-based surfactants [41], their biocidal nature can negatively affect the biodegradation process [23,47]. Although such nonlinear relationships with chain length are often attributed to cut-off effects related to bioavailability, the biodegradation profile of the double-chain cationic surfactants under investigation exhibits a strong correlation with their effectiveness as antimicrobial agents [41]. Nonlinear trends in biodegradation are also commonly associated with micelle formation or reduced aqueous solubility of longer-chain homologs, which can limit bioavailability. However, in our system, inhibition data suggest that

microbial toxicity is the main driver of the observed biodegradation pattern. Accordingly, the homologue with the highest antimicrobial activity, LANHC₆ [41], is the compound that underwent the lowest degree of biotransformation in the biodegradation test (Fig. 2, Table 1). It is essential to consider the potential impact of the investigated surfactants on bacterial growth and the subsequent effect on the biological activity of the inoculum when analyzing the obtained biodegradation data. To ascertain the potential toxicity of the cationic surfactants on the microorganisms responsible for aerobic biodegradation, inhibitory checks were incorporated into the design of the biodegradation tests. Binary mixtures of the test surfactant and the reference substance at the same concentration used in the biodegradation tests were examined for the inhibition of the biodegradation of the reference substance. It is generally assumed that, if at the end of the test, the inhibition value is higher than 25 %, the compound inhibits the activity of the inoculum (OECD 310 [42]). The results of the inhibitory checks are shown in Table 2.

With the exception of LANHC₆, none of the cationic surfactants tested exhibited significant inhibitory effects on the microbial consortium responsible for aerobic degradation. The results demonstrate that LANHC₆ exhibits toxicity towards microbial populations, as evidenced by the significant reduction in the extent of biodegradation of the reference substance (> 25 %). Therefore, the limited biodegradation of the LANHC₆ homologue under the specific test conditions may be attributed to the inhibition of the inoculum activity. In contrast, the lack of biodegradation observed for the quaternary ammonium surfactant (BAC) can be attributed mainly to its resistance to microbial attack under the specified test conditions.

Further tests were conducted to determine the optimal conditions for examining the LANHC₆ homologue with regard to biodegradability. Biodegradation tests with inhibition checks were conducted at initial concentrations of surfactant of 10, 12 and 15 mg C/L. Inhibition checks for binary mixtures of the NaBz+LANHC₆ at concentrations of 20 + 10 mg C/L, 20 + 12 mg C/L and 20 + 15 mg C/L demonstrated inhibition values of 4, 26 and 90 %, respectively. In a narrow concentration range (10–15 mg C/L), the LANHC₆ homologue exerts inhibitory effects on microbial populations, with the extent of inhibition varying from negligible (less than 5 %) to severe (90 %). The results demonstrated that the initial surfactant concentration is a critical factor influencing the extent of biodegradation. Biodegradation tests for LANHC₆ were conducted at a concentration of 10 mg C/L, which exhibited no toxic effects on the inoculum. Furthermore, the concentration was sufficiently high to prevent any impairment to measurement precision. The resulting biodegradation curves are presented in Fig. 3.

A significant biodegradation degree (45 %) was obtained for the surfactant at the end of the test by reducing the LANHC₆ initial concentration to 10 mg C/L. This finding corroborates the assertion that the initial concentration is a critical parameter for assessing the biodegradation of antimicrobial surfactants. All the double-chain cationic surfactants subjected to scrutiny underwent substantial biological oxidation under the stringent conditions for ready biodegradability testing when the initial surfactant concentration was maintained at a level that did not hinder biological activity.

It can be reasonably assumed that after use, these compounds will be released and diluted in wastewater, reducing their concentration and

Table 2

Effect of cationic surfactants on biodegradation of the reference substance (NaBz).

Compounds	Concentration (mg C/L)	Inhibition (%)
NaBz + LANHC ₃	20 + 12	0
NaBz + LANHC ₄	20 + 12	7
NaBz + LANHC ₆	20 + 12	26
NaBz + LANHC ₈	20 + 12	0
NaBz + LANHC ₁₀	20 + 12	0
NaBz + BAC	20 + 12	5

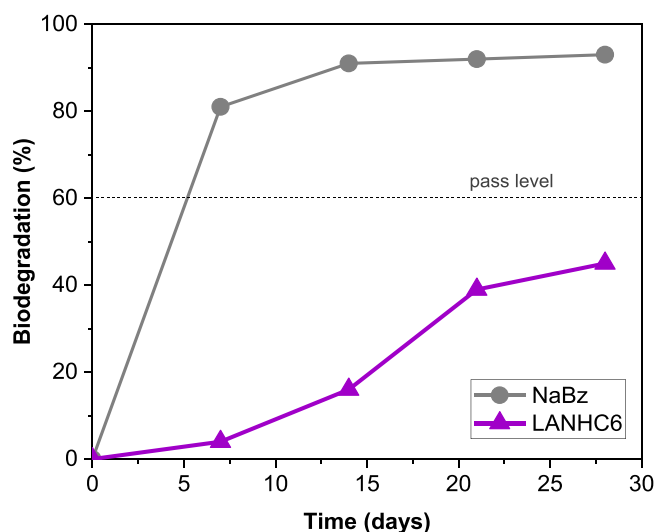


Fig. 3. Biodegradation of LANHC₆ (▲) and NaBz (●) in the CO₂ headspace test. LANHC₆ and NaBz were tested at concentrations of 10 and 20 mg C/L, respectively.

consequently their toxicity to microbial populations. It is therefore anticipated that these compounds will not impact the wastewater treatment process and will undergo biological oxidation, facilitating their removal in the biological treatment of wastewater treatment plants (WWTPs). The effective biodegradation of these compounds in WWTPs will prevent their accumulation in the environment, addressing one of the key concerns regarding the current widespread use of quaternary ammonium salts [38].

Single-chain arginine-based cationic surfactant, N^α-lauroyl-arginine methyl ester (LAM), achieved 90 % of ultimate biodegradation [48] as measured by the OECD Modified Screening Test (OECD 301E). This is a larger biodegradation extent than that of double-chain arginine-based surfactants (Figs. 2 and 3). This finding indicates that the biodegradation rate of arginine-based cationic surfactants is influenced by the number of alkyl substituents. The biodegradation of single-chain arginine surfactants [48] is observed to be higher than that of double-chain ones (Figs. 2 and 3), which is consistent with the observations made by van Ginkel and Kolvenbach regarding the transformation of quaternary ammonium surfactants [49].

3.2. Aquatic toxicity

The aquatic toxicity of all double-chain arginine-based cationic surfactants under investigation was evaluated using two acute toxicity tests: the *Daphnia magna* bioassay and the *Aliivibrio fischeri* luminescence reduction test (Microtox).

3.2.1. *Daphnia magna* test

The *Daphnia magna* test is a sensitive, robust, and widely used bioassay for the evaluation of the toxicity of surface-active agents [50–52]. The acute toxicity of the surfactants to *Daphnia magna* was determined by taking the swimming inability of this planktonic crustacean as endpoint after exposure to increasing concentrations of surfactant. Fig. 4 displays the percentage of *Daphnia magna* immobilization versus surfactant concentration for the LANHC₆ homologue whereas Table 3 shows the results of *Daphnia magna* acute toxicity tests for all the homologues.

The acute toxicity of double-chain arginine-based cationic surfactants (LANHCx) to *Daphnia magna* demonstrated clear time-dependent effects, with 48 h IC₅₀ values consistently lower than 24 h values (Table 3), indicating increased toxicity with longer exposure periods. Within the LANHCx series, toxicity progressively increased with

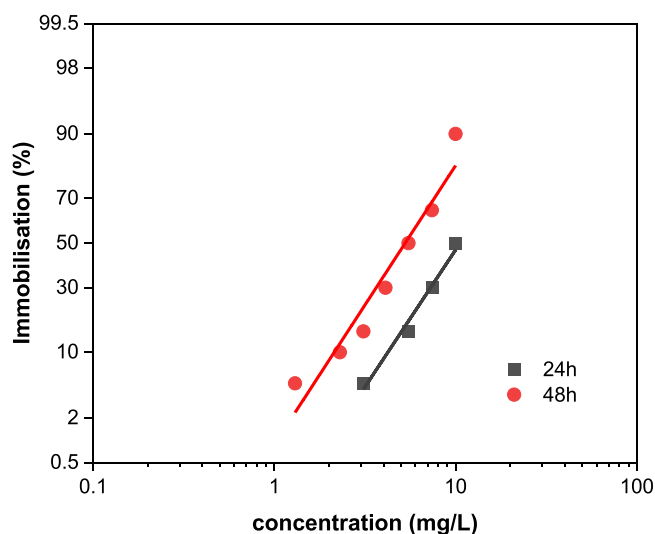


Fig. 4. Percentage of immobilized *Daphnia magna* as a function of LANHC₆ surfactant concentration after 24- and 48-hour exposure periods.

Table 3

Acute aquatic toxicity (IC₅₀ values) of novel arginine-based surfactants and conventional reference surfactants towards freshwater crustacean *Daphnia magna*.

Surfactant	24 h IC ₅₀ (95 % CI) (mg/L)	48 h IC ₅₀ (95 % CI) (mg/L)
Novel arginine-based surfactants		
LANHC ₃	12.2 (10.7–14.1)	7.8 (6.8–8.7)
LANHC ₄	11.2 (9.8–12.9)	7.7 (7.0–8.3)
LANHC ₆	10.1 (8.8–12.3)	6.0 (5.4–6.9)
LANHC ₈	–	4.1 (3.3–5.8)
LANHC ₁₀	*	*
Reference surfactants		
Arginine-based surfactants^a		
LAM	15.0	–
C ₂ (LA) ₂	4.4	–
C ₃ (LA) ₂	2.1	–
C ₄ (LA) ₂	4.6	–
C ₆ (LA) ₂	2.4	–
C ₉ (LA) ₂	2.2	–
Quaternary ammonium surfactants^b		
DTAB	0.38	–
TTAB	0.14	–
HTAB	0.13	–
BDD	0.13	–
BDT	0.13	–
BDH	0.22	–

Abbreviations: LANHCx: double-chain arginine-based surfactants; LAM: Lauroyl arginine methyl ester, Cn(LA)₂: N^αN^ω-bis (N^α-lauroylarginine)α,ω-alkylendiamides; DTAB: Dodecyl trimethylammonium bromide, TTAB: Tetradecyl trimethylammonium bromide, HTAB: hexadecyl trimethylammonium bromide, BDD: Dodecyl dimethyl benzyl ammonium bromide, BDT: Tetradecyl dimethyl benzyl ammonium bromide, BDH: Hexadecyl dimethyl benzyl ammonium bromide (BDH).

Notes: *Not soluble in the test medium, – Data not available ^(a) Data from [48] ^(b) Data from [34]

increasing alkyl chain length from C3 to C8, as evidenced by decreasing IC₅₀ values. This inverse relationship between alkyl chain length and IC₅₀ was particularly evident in the 48 h results, where values decreased from 7.8 mg/L (LANHC₃) to 4.1 mg/L (LANHC₈) in a generally linear fashion. These findings suggest that greater hydrophobicity, resulting from longer alkyl chains, corresponds to higher toxicity toward *Daphnia magna*. The absence of data for LANHC₁₀ is due to its poor solubility in the test medium.

Comparing the double-chain arginine-based surfactants with other surfactant types (Table 3) it is noteworthy that the toxicity of the double-

chain arginine-based surfactants is only slightly higher than that of the single-chain surfactant lauroyl arginine methyl ester, LAM (Table 3) whereas it is significantly lower than that of the gemini surfactants $N^{\alpha}N^{\omega}$ -bis (N^{α} -lauroylarginine) α,ω -alkylendiamides, $C_n(LA)_2$ (Table 3). Most importantly, the arginine-based surfactants investigated showed IC_{50} values that were more than one order of magnitude higher than those of the quaternary ammonium surfactants, indicating that they were significantly less toxic to *Daphnia magna*.

3.2.2. Luminescent bacterial bioassay

The luminescent bacterial bioassay (Microtox® test) has also been used to assess the aquatic toxicity of double-chain arginine-based cationic surfactants. The reduction in the light intensity emitted by the bacteria following a 30-minute exposure to the action of surfactants was taken as the test criterion. The results of the Microtox tests are presented in Table 4.

The Microtox test revealed that double-chain arginine-based cationic surfactants exhibited IC_{50} values that ranged from 1.5 to 4.5 mg/L (Table 4). Notably, toxicity initially increased with increasing alkyl chain length, reaching maximum toxicity for LANHC₆ (lowest IC_{50} of 1.5 mg/L), followed by a slight decrease in toxicity for LANHC₈. This non-monotonic relationship can be attributed to the reduced water solubility of the longer homologues in the test medium, which limits their bioavailability.

Compared to other arginine-based surfactants, the double-chain surfactants exhibited moderately higher toxicity than the single-chain surfactant LAM (IC_{50} =12 mg/L), while showing toxicity profiles similar to those of dimeric surfactants $C_3(LA)_2$, $C_4(LA)_2$, and $C_6(LA)_2$ (IC_{50} = 2.4, 5.8, and 3.0 mg/L, respectively). When compared with conventional quaternary ammonium compounds, the double-chain arginine-based surfactants were significantly less toxic to luminescent bacteria than DTAB, TTAB, HTAB (IC_{50} = 0.24, 0.28, and 0.63 mg/L, respectively) and BDD, BDT, and BDH (IC_{50} = 0.18, 0.15, and 0.55 mg/L, respectively) [34].

Based on the acute toxicity values obtained for both *Daphnia magna* and luminescent bacteria, and according to the Ecotoxicity Hazard categories defined in the OECD Guidelines, the double-chain arginine-based cationic surfactants investigated can be categorized as "Toxic to aquatic life" ($1 < IC_{50} \leq 10$ mg/L, Acute toxicity II). However, these novel surfactants exhibit a notably better ecotoxicological profile than common quaternary ammonium surfactants [34], presenting an intermediate ecotoxicity position between single-chain arginine-based surfactants (less toxic) and dimeric arginine-based surfactants (more toxic) [48].

Antimicrobial activity is a crucial attribute for surfactants used as corrosion inhibitors, particularly in aquatic environments. These multifunctional surfactants work synergistically by forming protective adsorption films on metal surfaces while simultaneously disrupting microbial cell membranes. This dual action effectively prevents biofilm formation and mitigates microbiologically influenced corrosion. LANHC₆ was selected for further investigation due to its superior antimicrobial properties compared to the other double-chain surfactant homologues [41] and its susceptibility to aerobic biodegradation (Fig. 3). This selection represents a strategic balance between

antimicrobial efficacy, biodegradability, and physicochemical properties.

Since potential applications of these surfactants in marine and aquatic environments raise concerns about their ecological impact, we first evaluated the ecotoxicity of LANHC₆ towards two marine microalgae species. The specific chain length appears to offer an optimal compromise between the bioactivity required for antimicrobial function and the environmental compatibility provided by biodegradability and moderate aquatic toxicity, while also maintaining adequate solubility for practical applications.

Following the environmental assessment, we investigated the corrosion inhibition potential of LANHC₆. This selection strategy aligns with existing literature on gemini surfactants, which indicates that compounds with intermediate chain lengths often exhibit superior performance as corrosion inhibitors, especially at concentrations approaching near their critical micelle concentration (CMC) values [53]. To evaluate its potential as a corrosion inhibitor, anticorrosion tests were conducted on carbon steel in salty media

3.2.3. Microalgae growth inhibition tests

To assess the environmental impact of LANHC₆ in marine environments, its ecotoxicity was assessed towards two marine microalgae. Dose-response curves for the green microalgae *T. chuii* and the diatom *P. tricornutum* are presented in Fig. 5, with corresponding IC_{50} values summarized in Table 5. LANHC₆ exhibits moderate toxicity toward *P. tricornutum* (IC_{50} = 11.3 mg/L), classifying it under Aquatic Chronic Category 3 (H412: Harmful to aquatic life with long-lasting effects) according to EU CLP and REACH criteria. In contrast, LANHC₆ demonstrates negligible growth inhibition in *T. chuii* (IC_{50} > 100 mg/L). This compound shows significantly reduced toxicity compared to conventional cationic surfactants, such as N-cetyl-N,N,N-trimethylammonium bromide (CTAB) with IC_{50} values of 0.55 and 1.50 mg/L for *P. tricornutum* and *T. chuii*, respectively, and N-dodecyl-N,N,N-trimethylammonium chloride (DTAC) with IC_{50} values of 4.29 and 10.6 mg/L for the same species [25]. LANHC₆ also demonstrates lower toxicity than recently developed gemini cationic surfactants, including N,N'-(oxybis(ethane-2,1-diyl))bis(N,N-dimethyldodecan-1-aminium) dichloride (12-O-12), N,N'-(oxybis(ethane-2,1-diyl))bis(N-(2-hydroxyethyl)-N-methyldodecan-1-aminium) dichloride (MOH-12), and 1,4-bis[(N,N-dimethyldodecan-1-aminium)methyl]benzene dibromide (QSB2-12), which exhibit IC_{50} values ranging from 1.14 to 9.79 mg/L for *P. tricornutum* and 1.74–6.02 mg/L for *T. chuii* [25]. Given its reduced aquatic toxicity profile, LANHC₆ represents a promising candidate for replacing conventional toxic quaternary ammonium surfactants.

To our knowledge, this is the first study to provide comprehensive ecotoxicological data for arginine-based double-chain surfactants across multiple aquatic species [54]. Previous research has primarily focused on single-chain analogues, such as *Nα*-lauroyl-L-arginine methyl ester (LAM), and gemini arginine-based surfactants (e.g., $C_n(LA)_2$), mainly assessing their antimicrobial, hemolytic, cytotoxic, and enzymatic activities [55,56]. Some of these studies have also addressed aspects of aquatic toxicity and biodegradability in freshwater systems [48], but they did not evaluate marine ecotoxicity or corrosion inhibition. A recent study by Jørgensen et al. (2023) reported the synthesis and evaluation of biodegradable arginine-based steroidal surfactants, including acute toxicity tests on *Daphnia magna* and biodegradability assessments using the OECD 301D closed bottle test [57]. Although their findings demonstrated low toxicity and favorable biodegradability, the study focussed on steroidal structures and did not include an assessment of their marine ecotoxicity or anti-corrosion performance. In contrast, our study expands the environmental assessment by including marine microalgae and bacteria, and links these results to corrosion inhibition efficiency. This broader scope highlights the multifunctional potential of LANHC_x surfactants as environmentally safer alternatives to conventional QACs.

Table 4

Acute toxicity of *Vibrio fischeri* after a 30-minute exposure period (IC_{50}) with 95 % confidence limits for double-chain arginine-based surfactants.

Surfactant	IC_{50} (95 % CI) (mg/L)
LANHC ₃	4.5 (2.1–9.7)
LANHC ₄	2.1 (0.6–6.9)
LANHC ₆	1.5 (0.6–3.2)
LANHC ₈	2.5 (1.2–5.5)
LANHC ₁₀	*

* Not soluble in the test medium,

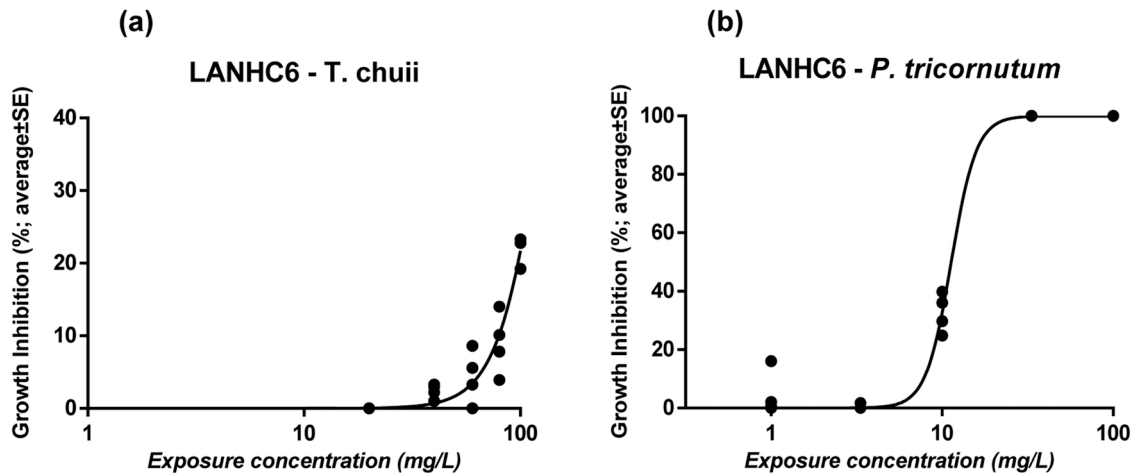


Fig. 5. Dose-response curves of the microalgae *Tetraselmis chuii* (a) and the diatom *Phaeodactylum tricornutum* (b) exposed to LANHC₆ cationic surfactant.

Table 5
Median growth inhibition concentration (IC₅₀) for the marine microalgae *Tetraselmis chuii* and the diatom *Phaeodactylum tricornutum* exposed to LANHC₆ for 72 h.

Tested species	IC ₅₀ (mg/L)	CI ₉₅ % (mg/L)
<i>Tetraselmis chuii</i>	138	124–153
<i>Phaeodactylum tricornutum</i>	11.3	7.5–17.2

3.3. Corrosion inhibition tests

The corrosion inhibition performance of LANHC₆ was evaluated using electrochemical impedance spectroscopy (EIS). The results are illustrated in Figs. 6 and 7 and summarized in Table 6.

The Nyquist plots presented in Fig. 6 show the impedance behaviour of the carbon steel electrode in NaCl solution with different concentrations of LANHC₆. The largest semicircle diameters were observed in the

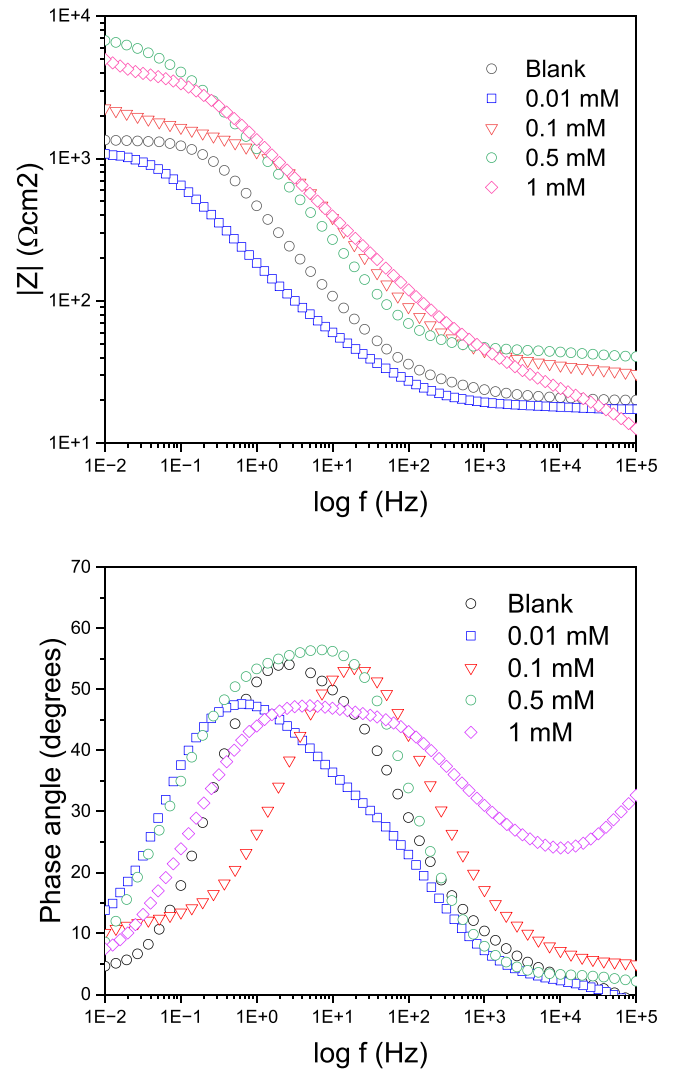


Fig. 7. Electrochemical behaviour of carbon steel after 24 h of immersion in 50 mM NaCl without (blank) and with addition of LANHC₆.

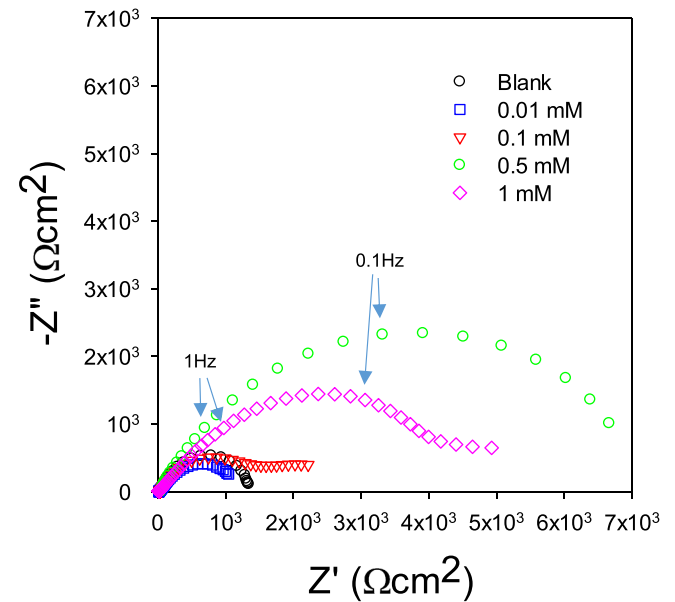


Fig. 6. Nyquist plots of carbon steel in the presence of LANHC₆ at varying concentrations, where Z' and Z'' represent the real and imaginary parts of impedance, respectively. The increased semicircle diameter, maximal at 0.5 mM, indicates enhanced charge transfer resistance and improved corrosion inhibition efficiency.

Table 6

Electrochemical parameters for carbon steel corrosion in 50 mM NaCl solution in the absence (blank) and presence of LANHC₆ after 24 h of immersion.

	Concentration (mM)	OCP vs SCE (mV)	R _{ct} (Ωcm ²)	IE (%)
Blank	-	-605	1503	-
LANHC ₆	0.01	-702	1588	5
	0.1	-600	1906	21
	0.5	-609	7538	80
	1	-607	6644	77

OCP – open circuit potential

immersion in NaCl solution for 24 h, shows two overlapping time constants in the intermediate range of frequency (10^{-1} – 10^1 Hz). Similar behaviour was observed for the lowest amount of surfactant tested (0.01 mM). With an increase in concentration of surfactant to 0.1 and 0.5 mM only one time constant at intermediate frequency (~ 10 Hz) occurs and the overall impedance increases, with this increase being more extensive for the 0.5 mM surfactant concentration. Further increase in surfactant concentration to 1 mM led to a decrease in the overall impedance magnitude, meaning that under the conditions tested, the intermediate concentration provides optimal inhibition performance. When the substrate is exposed to NaCl with 1 mM of LANHC₆, the impedance spectrum becomes more complicated, as one additional time constant at higher frequencies ($\sim 10^5$ Hz) and another one at low frequencies occur ($\sim 10^{-2}$ Hz). However, attempts to adjust these additional time constants were not successful due to the very low impedance associated with the high frequency time constant, and a lack of enough points at low frequency to define the low frequency time constant. In the end, all the EIS spectra were fitted with a simplified Randles circuit, where the capacitor associated with double layer response was replaced by a constant phase element to account for the non-ideality of the system.

The charge transfer resistance values obtained are depicted in Table 6. These values were used to estimate the inhibition efficiency, according to the following equation [58]:

$$IE = ((R_{ct} - R_{ct}^0) / R_{ct}) * 100\%$$

where R_{ct} and R_{ct}^0 represent the charge transfer resistance values with and without corrosion inhibitor, respectively, for carbon steel in 50 mM NaCl solution.

The inhibition efficiency exhibits a clear concentration-dependent trend, increasing from 5 % at 0.01 mM to 80 % at 0.5 mM. Beyond this threshold concentration, further increase in the surfactant concentration produces no significant improvement in inhibition efficiency. This behaviour is consistent with adsorption saturation near the critical micelle concentration (CMC) of LANHC₆ (1.5 mM) [41]. As the concentration approaches and exceeds the CMC, additional inhibitor molecules tend to form micelles in solution rather than contributing to the protective film on the carbon steel surface, thus not significantly decreasing the corrosion rate [58]. The maximum efficiency observed at approximately one-third of the CMC indicates that this concentration promotes optimal adsorption without significant micelle formation.

Below the CMC, LANHC₆ molecules adsorb at the metal/solution interface through a multi-step mechanism involving: (i) initial electrostatic attraction between the cationic quaternary ammonium head group and the negatively charged steel surface at the corrosion potential, (ii) displacement of water molecules from the metal surface, and (iii) formation of a compact protective layer through van der Waals interactions between hydrocarbon chains. The adsorption process involves both physical interactions (electrostatic forces between cationic nitrogen groups and the negatively charged steel surface) and chemical interactions (donor–acceptor bonding between nitrogen lone pairs and unoccupied metal d-orbitals). The presence of heteroatoms (N, O) and the extended π -electron system in the arginine residue facilitate electron donation to the metal surface, strengthening the adsorption bond and

enhancing the stability of the protective layer [59–61].

The electrochemical data provide strong evidence for this proposed adsorption-based mechanism and reveal the progressive nature of surface coverage. At 0.01 mM, the impedance spectra closely resemble the blank solution, indicating minimal surface coverage with only isolated inhibitor molecules adsorbed at the most active sites, resulting in modest 5 % inhibition efficiency. The persistence of two time constants at this concentration suggests incomplete surface coverage with heterogeneous corrosion processes still occurring. At 0.1 and 0.5 mM, the transition to a single time constant at intermediate frequency (~ 10 Hz) and the substantial increase in R_{ct} values (from 1503 to 7538 Ωcm² at 0.5 mM) indicate the formation of a more uniform and compact protective layer with enhanced barrier properties. This electrochemical signature is characteristic of monolayer formation, where inhibitor molecules organize into a well-ordered protective film that effectively blocks both anodic and cathodic sites.

The proposed inhibition mechanism is consistent with previous reports where surface analysis techniques, such as SEM, have revealed morphological evidence of film formation on steel surfaces treated with cationic surfactants [62–64]. Although SEM and XPS characterizations were not conducted in the present study, the electrochemical data obtained for LANHC₆, particularly the significant increase in charge transfer resistance and the mixed-type inhibition behavior, support the formation of an adsorbed protective layer. Incorporating surface analysis techniques in future studies will be essential to confirm the nature and composition of this film and to further explore the applicability of these surfactants in corrosion-resistant formulations.

The potentiodynamic polarization measurements shown in Fig. 8 reveal that both anodic and cathodic current densities (i) are reduced in the presence of LANHC₆. The polarization curves shift toward more positive potentials (E), indicating also enhanced corrosion resistance. Since suppression of both anodic and cathodic reactions occur, LANHC₆ acts as a mixed-type inhibitor, though the suppression of the metal dissolution appears more extensive than the oxygen reduction reaction. This more pronounced effect on the anodic reaction suggests preferential adsorption at anodic sites, which is consistent with the electrostatic attraction between the cationic surfactant and the negatively charged steel surface at the corrosion potential.

Electrochemical measurements revealed that LANHC₆ achieves a corrosion inhibition efficiency of 80 % for carbon steel. Although this level of protection is moderate when compared to highly efficient commercial inhibitors such as nitrites or benzotriazole (BTA), the performance of LANHC₆ becomes particularly significant when concentration efficiency is considered. Under identical experimental conditions,

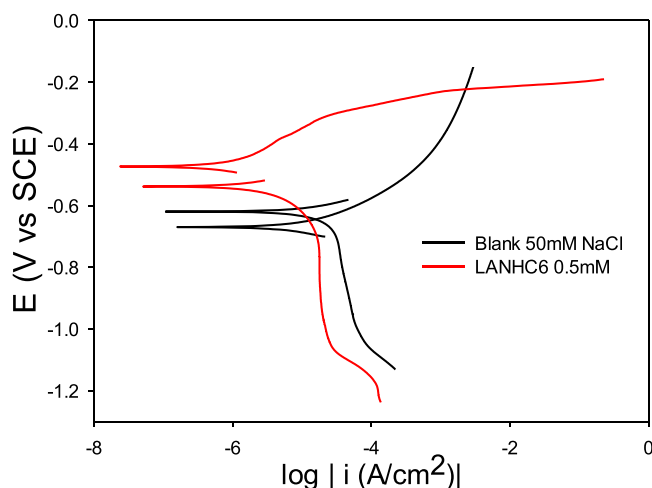


Fig. 8. Potentiodynamic curves for carbon steel after 24 h of immersion in blank solution (50 mM NaCl) and 50 mM NaCl containing LANHC₆ at its optimal concentration (0.5 mM).

DTAC, a conventional single-chain quaternary ammonium surfactant, provided no measurable inhibition at its critical micelle concentration (CMC, 16 mM) [65] in 50 mM NaCl solution [66]. In contrast, LANHC₆ achieved 80 % inhibition at only 0.5 mM, representing a 32-fold reduction in required concentration. This highlights the remarkable efficiency of LANHC₆ at low concentrations.

The superior performance of LANHC₆ can be attributed to its unique molecular architecture, which enables a multi-site adsorption mechanism. The quaternary ammonium group provides strong electrostatic interaction with the metal surface, the arginine residue offers additional nitrogen atoms capable of coordination bonding, and the two hydrocarbon chains increase the hydrophobic character of the adsorbed layer, thereby enhancing its barrier properties. This synergistic combination of electrostatic, coordination, and hydrophobic interactions explains the enhanced protective behavior compared to simpler surfactants like DTAC. Furthermore, amino acid-based surfactants such as LANHC₆ offer additional advantages, including improved biodegradability and reduced toxicity, making them more environmentally benign. These multifunctional attributes position LANHC₆ as a strong candidate for sustainable corrosion inhibition applications.

In the context of amino acid-based surfactants, LANHC₆ also shows competitive performance. To our knowledge, there are very few published studies on the use of amino acid-derived surfactants as corrosion inhibitors, and none specifically on arginine-based derivatives. While direct comparison is limited due to differences in metal substrates and experimental conditions, single-chain amino acid surfactants such as *n*-dodecyl asparagine, histidine, or tryptophan have been reported to reach inhibition efficiencies between 80–88 % at concentrations of 1.3–1.6 mM on copper surfaces [19] (Fawzy et al., 2023). In contrast, LANHC₆ achieves similar inhibition (80 %) on carbon steel at only 0.5 mM. This suggests that its double-chain architecture and arginine-based headgroup contribute to high efficiency at lower concentrations, highlighting the novelty and promise of this molecular design.

4. Conclusions

Double-chain arginine-based cationic surfactants (LANHC_x) demonstrated significantly greater biodegradability than conventional quaternary ammonium surfactants (QACs) in standard ready biodegradability assays. Alkyl chain length plays a critical role in biodegradation, with values ranging from 1 % to 63 % in a non-linear relationship. LANHC₆ exhibited minimal degradation at higher concentrations but improved significantly upon dilution, increasing from 1 % to 45 % when concentration was reduced from 12 to 10 mg C/L. This indicates a strong likelihood of biodegradation upon dilution in wastewater, suggesting a reduced environmental persistence. The partial oxidation observed is likely a result of microbial activity inhibition, an effect not expected at typical environmental concentrations, thus minimizing potential adverse impacts on wastewater treatment plants. LANHC_x surfactants exhibited significantly lower toxicity (over one order of magnitude) to aquatic organisms compared to conventional QACs, with IC₅₀ values ranging from 4.1 to 7.8 mg/L for *Daphnia magna* and 1.5–4.5 mg/L for *Aliivibrio fischeri*. When tested on marine microalgae, LANHC₆ showed moderate toxicity toward *Phaeodactylum tricornutum* (IC₅₀ = 11.3 mg/L) but negligible toxicity toward *Tetraselmis chuii* (IC₅₀ > 100 mg/L), indicating a reduced environmental impact compared to conventional cationic surfactants. The arginine-based surfactant LANHC₆ exhibits corrosion inhibition for carbon steel in neutral conditions, functioning as a mixed inhibitor that reduces both anodic and cathodic reactions. It achieves a maximum efficiency of 80 % at the optimal concentration of 0.5 mM. Higher concentrations lead to micelle formation without improving protection. Notably, LANHC₆ significantly outperforms the conventional quaternary ammonium salt DTAC, providing substantial corrosion inhibition at a concentration 32 times lower, where DTAC showed no effect under identical conditions.

Combining superior biodegradability, lower ecotoxicity, and effective corrosion inhibition, LANHC_x surfactants represent promising and sustainable alternatives to conventional QACs across multiple industrial applications. These compounds show particular promise for environmentally sensitive sectors including wastewater treatment facilities, where conventional QACs may disrupt microbial communities; marine industries such as ballast water management and aquaculture, where environmental release is inevitable; and regulated applications like textile finishing and cooling systems, where biodegradable alternatives are increasingly favored.

LANHC_x surfactants also demonstrate strong potential in healthcare disinfection, agricultural antimicrobial treatments, personal care formulations, and food processing sanitation, where their rapid biodegradation reduces environmental impact and the risk of antimicrobial resistance development. While conventional QACs may be preferred in applications requiring long-lasting antimicrobial activity (e.g., durable surface coatings), this same persistence contributes to environmental accumulation and resistance selection.

The primary barrier to widespread adoption remains the higher production cost of amino acid-based surfactants compared to conventional QACs. Synthetic route optimization therefore represents a critical priority to enhance economic viability for both industrial and domestic applications. Furthermore, their shorter environmental persistence, while beneficial for ecological applications, may limit their effectiveness in scenarios requiring long-term antimicrobial protection.

Future research should address key knowledge gaps to ensure safe and sustainable implementation, with priority given to: (1) including chronic and multigenerational toxicity effects, (2) comprehensive bioaccumulation assessment across trophic levels, and (3) environmental fate of degradation metabolites. Life cycle assessments comparing LANHC_x to conventional QACs will be essential to provide the robust safety data necessary for regulatory approval and support broader industrial adoption.

In conclusion, LANHC_x surfactants offer a balanced profile of efficacy and environmental compatibility, aligning with current regulatory trends and sustainability goals, while addressing the growing demand for environmentally responsible industrial chemicals.

Environmental implication

The growing concern over the environmental persistence and potential harm of quaternary ammonium compounds (QACs) emphasises the urgent need for sustainable alternatives. Amino acid-based surfactants, including the novel double-chain arginine-based compounds that have been the focus of this investigation, offer a promising solution. These surfactants demonstrate a superior ecotoxicological profile compared to conventional QACs, exhibiting higher biodegradation rates and lower toxicity. The inherent environmental friendliness of these compounds, coupled with their effectiveness as antimicrobial agents and even corrosion inhibitors, positions them as a potentially safer replacement for QACs in various industrial applications. This would serve to mitigate the adverse environmental impacts associated with traditional QAC surfactants. As research advances and regulations tighten, the transition towards these biodegradable and less toxic amino acid-based options could be vital for a more sustainable future.

CRedit authorship contribution statement

Ana de la Fuente: Investigation, Data curation. **García Maria Teresa:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Olga Kaczerewska:** Writing – original draft, Investigation, Data curation, Conceptualization. **Sergio Vázquez:** Investigation, Data curation. **Elena Bautista:** Investigation, Data curation. **Lourdes Pérez:** Resources, Funding acquisition. **João Tedim:** Writing – review & editing, Supervision, Funding acquisition. **Roberto Martins:** Writing –

review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Grant PID2022–136354NB-I00 funded by MCIN/AEI/10.13039/501100011033 and by “ERDF A way of making Europe”. Grant PTA 2020–018511-I funded by MCIU/AEI/10.13039/501100011033. Grant PRE2022–000837 funded by MCIN/AEI/10.13039/501100011033 and “ESF Investing in your future”. AGAUR 2021-SGR-00507. Project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). CESAM-Centre for Environmental and Marine Studies (UID/04035/2023; UID CESAM + LA/P/0094/2020), to the NEXTGENCOAT project (COMPETE2030-FEDER-00782900) and to R. Martins (DOI:10.54499/2021.00386. CEECIND/CP1659/CT0011) through State Budget funds.

The Biodegradation and Ecotoxicity service of the IQAC-CSIC is acknowledged for the assistance and support related to the biodegradation and ecotoxicity tests. The authors are grateful to Anna Lupon (EDAR Manresa, Barcelona) for supplying the WWTP samples.

Data availability

Data will be made available on request.

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