INFORMATICS JOURNALS
The Journal of Electrochemical Society of India, *Volume 74, Issue (1&2), January – March 2025; pp. 22-39*
ISSN (Print) : 0013-466X
ISSN (Online) : xxxx-xxxx
DOI: 10.18311/JESCI/2025/51176

Marine Biopolymers as Green Corrosion Inhibitors: A Roadmap to Sustainability and Circular Blue Bioeconomy

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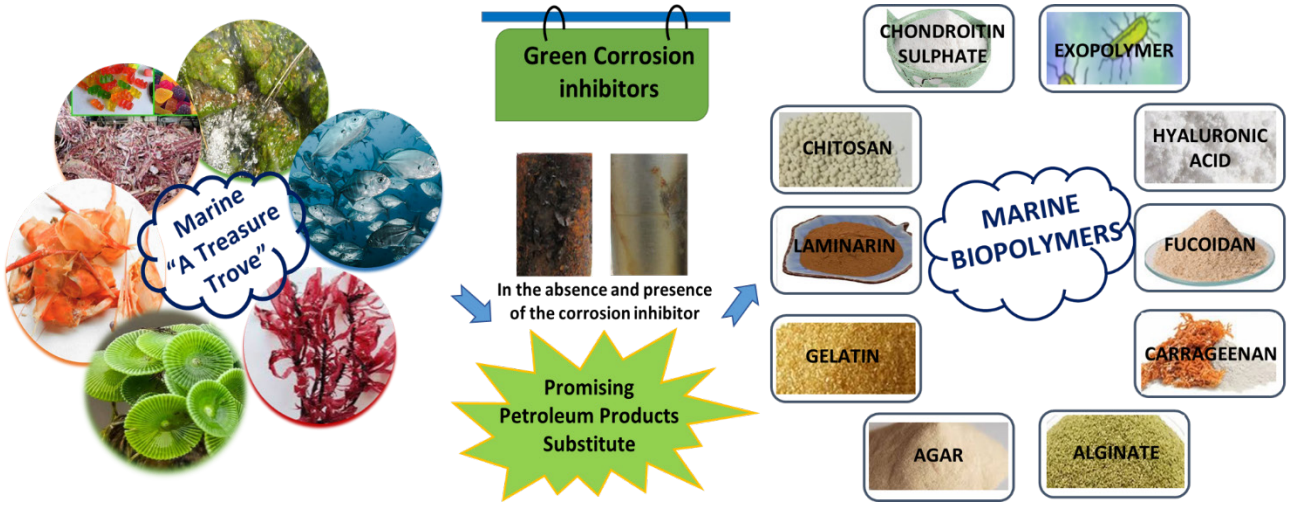
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Abstract

Synthetic polymers lost their lustre and attraction when the world woke up to new and sustainable alternatives. Marine biopolymers are a tangible asset that meets the pressing industrial and environmental needs. They challenge petroleum-derived products through their biodegradability, renewability, and low or zero carbon emissions, especially as potential substitutes for plastics and coatings. Using these abundant resources efficiently and repurposing the marine waste to valuable resources will pave the path for a sustainable future. The review focuses on the applications of these biomaterials derived from seaweed, aquatic animals, and marine microorganisms as efficient, green corrosion inhibitors for different metals in diverse corrosive environments. The paper also discusses the significance of the molecular architecture and diverse functional groups in these biomaterials, which enable them to bind effectively with the metal surfaces and inhibit corrosion.

Keywords: Corrosion Inhibitors, Marine Biopolymers, Petroleum Products Substitutes, Seaweed, Chitosan

Graphical Abstract



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1. Introduction

The red alert on the serious environmental issues, such as global warming, climate change, depletion of natural resources, and vast pollution, has given a wake-up call to redirect the research path towards sustainability and circular blue bioeconomy[1]. The dependence on fossil-based resources in versatile applications has resulted in an irreversible environmental impact. Reports of significant demand for petroleum oil in the next few decades have raised the market prices of fossil-based chemicals. The non-biodegradability of the synthetic polymers and the plethora of toxic substances generated from various industrial activities prove detrimental to the environment and human health. These impacts have drawn severe criticism from the environmental safety regulatory bodies.. Legislation under the REACH framework (Registration, Evaluation, Authorisation, and Restriction of Chemicals) has accelerated efforts to find safe, sustainable alternatives to toxic and environmentally harmful corrosion inhibitors[2]. Hence, the time has come to consciously decide on efficiently utilising the available resources for maximum productivity and minimum waste. In addition, it is necessary to promote waste utilisation to minimise its environmental impact. Biomass-derived chemical products and biomass waste utilisation can be suitable solutions for the present situation. The biomass waste from different sources, such as wood, agriculture, forestry, and seafood processing industries, is generated in abundance annually and globally. Marine biomass encompasses a broad spectrum of life forms from microorganisms like bacteria and algae to larger marine life such as fish, crustaceans, and sea mammals. The components of the marine biomass produce biopolymers that have potential worldwide applications. They make novel bioactive compounds with the highest human utility and can capture and utilise CO_2, N_2, and phosphorus, thus being a suitable candidate for sustainable applications[3]. Seafood and aquaculture industries generate large volumes of biopolymer-rich waste, which can be valorised into corrosion inhibitors, reducing environmental burden and enabling the production of value-added materials[4]. Marine food waste is a rich source of chitin and chitosan, known for their enormous economic value due to their flexible biological properties[5]. These marine resources are rich reserves of biopolymers that can be tailored to different value-added products through modifications and can play a versatile role in food industries, biomedical fields, water treatment, pharmaceuticals, cosmetics, corrosion protection, nanoparticle, and biofuel production[6,7]. Incorporating marine biopolymers into coating formulations improves corrosion resistance and lowers the environmental footprint compared to conventional chemical inhibitors[8]. They offer the dual benefit of being readily available as waste and possessing strong adhesion to metal surfaces. However, these resources are said to be underutilised compared to the terrestrial biomass and need to be explored[9]. As depicted in Figure 1, marine biopolymers possess inherent advantages that can make them effective green corrosion inhibitors. The review paper focuses on the applications of these biomaterials as green corrosion inhibitors, promoting sustainability and circular blue bioeconomy.

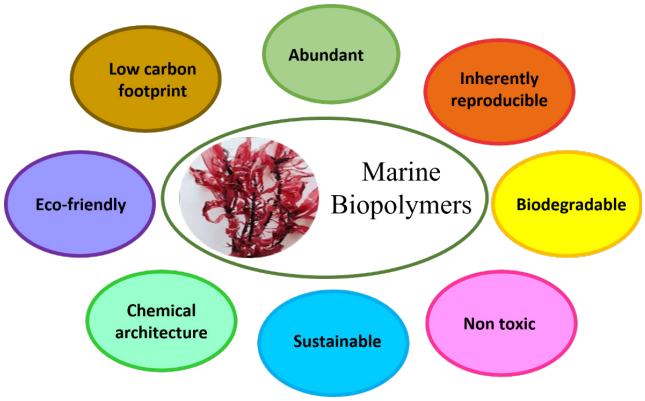


Figure 1. Advantages of using marine biopolymers as corrosion inhibitors.

Rapid industrialisation, the need to protect automotive components, and the expansion of water treatment applications have fueled rising global demand for corrosion inhibitors, which may reach USD 14 billion by 2035. Corrosion inhibitors are additives added to pipelines and containers holding corrosive liquids or gases, employed in aqueous or solvent-borne metal coatings and primer formulations. Corrosion inhibitors are frequently studied corrosion mitigation techniques as they have simple solutions against corrosion, are cost-effective, versatile, and can inhibit corrosion of metals in different environments, whether deep sea, polar, or another environment[10]. Corrosion inhibitors protect metal assets across various industries such as petroleum, oil and gas, water treatment plants, manufacturing and automotive plants, construction, and other sectors to protect metal equipment and electronic components.

These inhibitors use their active sites to be adsorbed on the metal surface through physical or chemical interactions, creating a barrier between the metal surface and the corrosive materials. Otherwise, they can form protective films on the metal surfaces and inhibit corrosion[11]. The oil and gas industries use acids in drilling, acidising, and regeneration processes. The acid pickling process is essential in steel production and acid-cleaning processes in electroplating industries for better adhesion. These processes involve intense acid usage, such as hydrochloric acid, sulphuric acid, and organic acids, namely citric acid, acetic acid, and formic acid, to remove rust and scales. However, once the metal surface is clean, the bare metal is further exposed to aggressive acid, resulting in the wearing of the metal and shortening the efficacy of the acid used. Acid inhibitors are employed to prevent the metal etching and to keep the acid effective longer[12]. Similarly, marine and offshore steel structures require regular maintenance due to constant exposure to seawater and humidity, accelerating corrosion and raising protection and repair costs[13]. Though effective, traditional corrosion inhibitors like inorganic chromates, phosphates, molybdates, and synthetic organic inhibitors face increasing restrictions due to their toxicity and environmental persistence[14,15]. Biopolymers from seaweed extracts and seafood waste are gaining popularity as anticorrosive materials due to their rich chemical structure and abundant active sites (e.g., hydroxyls, esters, sulfonates, and carboxylates), which promote functionalization and composite formation. These materials also offer the benefits of being nontoxic, eco-friendly, and biodegradable[16,17]. These abundant, biodiverse resources can be converted into corrosion inhibitors, nanocomposites, coatings, and self-healing materials, offering a sustainable pathway for corrosion protection and enhanced material durability[18-21]. Table 1 displays the corrosion inhibition potential of seaweed extracts for different metals in various aggressive environments.

2. Marine Biopolymers As Corrosion Inhibitors

Marine organisms, namely seaweed, fish, microorganisms, and seafood waste, are rich sources of biopolymers. Chemically, they may be polysaccharides, proteins, or lipids based on their structure and origin. Figure 2 depicts the structure of polysaccharides, namely alginates, carrageenans, fucoidan, agar, laminarin, derived from seaweeds, and chitin, chitosan, chondroitin sulfates, and hyaluronic acid from marine animals[7]. Marine gelatin, collagen and microorganisms secreted adhesives fall under protein-rich sources. Earlier, seaweeds were exploited for fuels, proteins, lipids, cellulose, and various chemicals[39,40]. It is gaining attention as a renewable and eco-friendly source of corrosion inhibitors. Also, their cultivation is simple, sustainable, and produces a large amount[41]. Hence, they are suitable, sustainable alternatives to synthetic corrosion inhibitors as they are an abundant reserve of bioactive polysaccharides[30,36,42-45]. Seaweeds are called red, green, or brown algae based on their pigmentation. Carrageenan and agar from red algae, ulvan from green algae, fucoidan, and laminarin from brown algae are sulfated polysaccharides[46,47]. Alginates in brown algae may be sulfated or chemically sulfated to enhance their bioactivity[48]. Marine algal polysaccharides are promising as corrosion inhibitors, self-healing coatings, and antifouling agents. Their heteroatoms adsorb onto metal surfaces, form complexes with metal ions, and offer broad surface coverage, thereby protecting the metal from aggressive environments and dissolution[49]. Marine animal food waste generates several million tons annually and globally is an attractive source of the amino polysaccharides, namely chitin and chitosan[50]. The reactive hydroxyl groups and the free amine group in chitosan aid in effective interaction with the metal surface, and their excellent film-forming nature makes it a potential green corrosion inhibitor[51].

Marine-derived polymers, rich in proteins, such as gelatin, collagen, and adhesives, can serve as barrier coatings and biocompatible layers on metallic surfaces[52,53]. Novel Extracellular Polymeric Substances (EPS) are composed of exopolysaccharides, proteins, nucleic acids, lipids, and humic substances secreted by microorganisms and their use can be extended to the environment beyond the microbial cells themselves[54,55]. EPS from marine microbes show strong potential as eco-friendly corrosion inhibitors by forming biofilms, adsorbing onto metal surfaces, and establishing protective barriers[56]. Marine proteins, such as Mussel adhesive protein, particularly containing 3,4-dihydroxyphenylalanine, can be employed in the corrosion protection of carbon steel[57]. Research shows that the recombinant protein rMrCP20 derived from the barnacle *Megabalanus rosa* adhesive cement, a common marine biofouler that can self-assemble into films on metal surfaces, exhibits significant

Table 1. Corrosion inhibition efficiency was evaluated for seaweed extracts for various metals in various corrosive media

S No	Seaweed	Metal / corrosive medium	Inhibition efficiency% / conc. / temp.	Ref
1	*Sargassum latifolium C Agardh 1820*	Mild steel / natural seawater	98.33/ 0.1g in 250 ml	22
2	*Enteromorpha prolifera* (green algae)	Carbon steel/ 1 M HCl	95	23
3	*Codium tomentosum*	Copper/ 1 M H_2SO_4	82 1g/L	24
4	*i) Pandia povanica* *ii) Sargassum tenerrimum*	Mild Steel 1010 against SKR4 strain from the cooling tower water environment	i) 66 / 25 ppm ii) 63 / 25 ppm	25
5	Alcoholic extract of *Sargassum muticum*	Mild steel / 1 M HCl	84 /500 ppm	26
6	*Gelidium* red algae	Copper / 1 M H_2SO_4	93.75	27
7	*Halopitys incurvus* (H1 Fraction)	Carbon steel / H_2SO_4	96 / 100 ppm	28
8	*Eucheuma* (red algae)	API5L steel / 0.1 M HCl	90 / 500 ppm 96.4 / 50°C	29
9	Methanolic extract of i) *Padina pavonica* (brown algae) or coral reefs ii) *Sargasun tenerrimum*	Mild steel / NaCl against bacteria *B. megaterium* SKR7 (Bioinhibitor)	i)75 / 25 ppm ii) 73 / 25 ppm	30
10	*Sargassum*	API-5L steel / 0.1 M HCl	95 / 500 ppm	31
11	*Sargassum muticum*	Mild steel / 0.5 HCl	99 / 500 ppm	32
12	*i) Ulva compressa* *ii) Pterocladiella capillacea*	Steel / $CaCl_2$ brine solution	i)63.2 / 300 ppm ii)62.3 / 300 ppm	33
13	*Gymnogongrus crenulatus*	API 5L X60 Carbon steel/injection water contaminated with sulfato-reducing bacteria	99.69 / 5 ppm	34
14	*Cystoseira baccata* (brown algae)	Carbon steel / 1 M HCl	86.5 / 700 mg/l	35
15	*Turbinaria ornata*	Mild steel / Conc.HCl against 16S rDNA	100 / 25g/L	36
16	*Halopitys incurvus*	Carbon steel / 1 M HCl	81.86/ 600 mg/L / 298K	37
17	Seaweed extract	Mild carbon steel pipelines/saline formation water	93 / 298 K declined to 85 / 328 K 1.2% (v/v)	38
18	*Caulerpin racemosa*	Mild steel / 1 M HCl	85 / 25 ppm	19

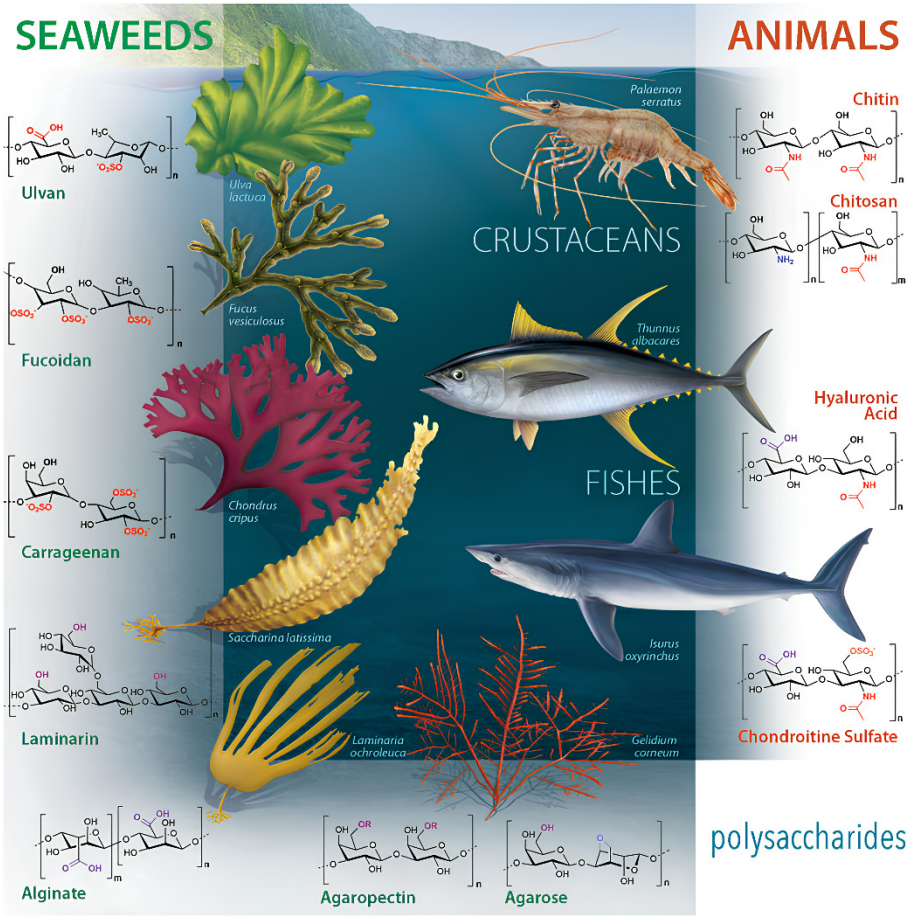


Figure 2. Marine polymers are derived from seaweed and marine animal waste.
Adopted from the Frontiers in Bioengineering and Biotechnology journal. DOI 10.3389/fbioe.. 2022.1041102

anticorrosive performance[58]. Also, the metabolites of marine Streptomyces species are effective against sulfate-reducing bacteria and serious corrosive microorganisms in marine sludge and oil field-produced water[59].

2.1 Seaweed-Derived Biopolymers As Corrosion Inhibitors

2.1.1 Alginates

Alginate, the most studied bioactive compound in aquaculture, is an anionic linear polysaccharide predominantly extracted from the cell walls of algae and some bacteria, such as *Ascophyllum* nodosum and *Pseudomonas* spp. Respectively[60]. They are alginic acid in seaweed, containing α-L-mannuronic acid and β-D-guluronic acid connected by 1,4-glycosidic bonds. The seaweed extracts give sodium alginate on immersion in an acid solution, followed by alkali neutralization[61]. The presence of free functional moieties, namely hydroxyl and carboxyl groups distributed along the backbone of alginates, provides opportunities for their modification with desired properties[62]. Sodium alginate is a promising green corrosion inhibitor for different metals in acidic, basic, and neutral corrosive media. I. Zaafarany evaluated the corrosion inhibition efficiency of water-soluble sodium alginate and sodium pectate for aluminium in an aqueous alkaline solution and reported an inhibition efficiency of 86.88% and 88.67 % respectively, for 1.6 % inhibitor concentration using the gasometric technique and weight loss method[63]. Sodium alginate showed an inhibition efficiency of 90% at 500 ppm concentration for AZ31 magnesium alloy in 3.5% NaCl aggressive medium[64]. Similarly, when deployed for copper at 25°C in 1M HCl, potentiodynamic polarisation studies revealed a corrosion inhibition efficiency of 83% at 0.1 mg/litre inhibitor concentration has been reported[65]. When tested for APIX60 high-strength carbon steel in 3.5% NaCl by the EFM method, sodium alginate of 1000 ppm

concentration exhibited an efficiency of 81.52% at 25°C[66]. When deployed for AZ91D magnesium alloy in 3.5% NaCl solution, the alginate inhibitor showed an excellent inhibition performance of 98% for 0.03 mol/L[67]. The high efficiency is due to its ability to form complexes with metal ions and block active corrosion sites. The comparative study on the corrosion inhibition effect of alginate and the other biopolymer chitosan reveals that chitosan showed a better performance than alginate for copper in 1 M HCl solution. Electrochemical studies revealed 82% and 87% efficiency for 0.1 ppm of alginate and chitosan, respectively. The better performance of chitosan is related to the better binding energy of the adsorbed chitosan inhibitor layer on the metal surface, influenced by the amine group compared to the oxygen hetero atom of the alginate inhibitor[68]. Similarly, the inhibition efficiency of sodium alginate and an inorganic sodium chromate for aluminium in a 0.1 mM acetic acid solution was studied. High-voltage direct transmission systems use aluminium in converter valves of radiators. The corrosion occurs at the inner walls of aluminium by the cooling water, and the dissolved ions form a scale on the surface of the platinum electrode, leading to product failure. The application of corrosion inhibitors will be cost-effective and more convenient. The potentiometric curves are useful in exploring both inhibitors' inhibition mechanisms. The results show that sodium chromate inhibits corrosion by forming a passive film of Al_2O_3 and Cr_2O_3 on the surface due to the chemical reaction between the metal and the inhibitor. On the other hand, the biopolymer shows a diffusion-type of inhibition where it slowly diffuses into the solution and then covers the metal surface, increasing the resistance and reducing corrosion current. The diffusion type of inhibition by the biopolymer reveals a strong cohesive film on the surface, exhibiting better inhibition than the surface-modified inhibition exhibited by the sodium chromate inhibitor. The hydrophobicity of the biopolymer reduced the exposure to corrosive solution, and the low electrical conductivity increased the resistance of the micro battery, slowing down the corrosion. This comparative study on the inhibition mechanism provided a theoretical basis for selecting better corrosion inhibitors[69]. Rather than direct injection of the inhibitors into reservoirs, newer strategies use slow-release formulations that gradually dispense inhibitors and provide long-term protection in harsh environments. To protect the underground equipment in oil wells which experienced difficulty in penetration was found by using two imidazoles were loaded into cross-linked sodium alginate gel, forming a solid inhibitor sphere. The alginate gel released rapidly in 10 h and continuously for 60 h, independent of environmental temperature and pH, enabling corrosion inhibitors to protect metallic wellbores over longer distances[70]. The efficiency of various combinations of sodium alginate inhibitors for different metals in different corrosive environments is portrayed in Table 2

WL- Weight Loss Studies, PDP- Potentiodynamic Polarisation Studies, EIS- Electrochemical Impedance Studies

2.1.2 Carrageenans

Carrageenans are mucopolysaccharides extracted from the cell walls of the red algae. It has no nutritive value but can act as additives such as thickeners, emulsifiers, and preservatives. This polysaccharide's structural unit comprises a partially sulfated linear backbone of β-D-galactose and 3,6-anhydro-α-D-galactose. Based on the degree of sulfation, carrageenan can be iota i-(mono-sulfate), kappa ƙ-(di-sulfate), and lambda ƛ-(three-sulfate)[80]. The negatively charged sulfate groups and the –O- and -OH functional groups on the structure act as active sites for adsorption. I. Zaafarany tested the inhibition efficiency of kappa, iota, and lambda carrageenans against iron in a 1 M HCl solution at 500 ppm. The results were 72%, 76% and 80% respectively, at a 500 ppm concentration. All three carrageenans were anodic inhibitors, and the adsorption obeys the Langmuir isotherm[81]. Weight loss, Tafel, and impedance studies evaluated Iota Carrageenan biopolymers as corrosion inhibitors for mild steel in 0.5 M sulphuric acid solution. Weight loss study shows excellent performance of 96.62% inhibition at 1000 ppm inhibitor concentration, and the efficiency increases at higher temperature to 97.40% at 333 K. Tafel curves show an inhibition efficiency of 82.39%. The inhibitor's excellent performance endorses the inhibitor's adsorption onto the metal surface, forming a protective layer by chemisorption through sulfate oxygen[82]. Iota carrageenan was further evaluated for aluminium in 2 M HCl in the presence of the zwitterion mediator pefloxacin. There was a substantial increase in inhibition from 66.7 % when the mediator was absent to 91.8 % in the presence of the pefloxacin mediator. This performance results from the coherent, well-ordered arrangement of the physisorbed layer on the metal surface[83]. Similarly, corrosion inhibition was

Table 2. Corrosion inhibition potential of sodium alginate for different metals in different corrosive environments

S No	Inhibitor	Metal/ corrosive medium	Inhibition efficiency in %/ conc./temp	Studies Detail	Ref.
1	sodium alginate + sodium phosphate blend	AZ31 Magnesium alloy / 3.5% NaCl	98.8 0.05 alginate +0.15 phosphate	EIS	[71]
2	sodium alginate + sodium silicate blend	S235 carbon steel / dynamic saltwater environment + 3 wt % NaCl	99 25°C / constant rotation of 0.5m/s	Electro chemical studies	[72]
3	sodium alginate + zinc acetate	D16T aluminium alloy / neutral chloride environment	89-98	PDP	[73]
4	sodium alginate + sodium silicate + sodium alginate surfactant copper complex	carbon steel in 1M HCl	96.27 5x 10^{-3} M	WL	[74]
5	alginate polymeric cationic surfactants of varying alkyl chain lengths, namely octyl, dodecyl, and hexadecyl, carbon chain length	mild steel in 1 M HCl	92.6 / 70°C (hexa decyl)	WL	[75]
6	sodium alginate, polymethylmethacrylate-based titanium dioxide, and iron oxide nanocomposite	mild steel / 15% HCl	97.28 (titania) 96.82 (magnetite)	WL	[76]
7	sodium alginate grafted 5-methyl-8-hydroxy quinoline	mild steel / 1 M HCl	89/ 10×10^{-3} g/L	EIS	[77]
8	sodium alginate grafted polyacrylamide	mild steel / 0.1 M H_2SO_4	86 / 240 mg/ 100ml	EIS	[78]
9	sodium alginate + KI + date palm seed oil formulations	AZ31Mg alloy / 3.5 wt % NaCl	80	PDP	[79]

studied for aluminium in 2 M HCl using various amino acids in place of pefloxacin. The results show that in the absence of the amino acid, the inhibition efficiency was 56.25%, which was enhanced to 73.12% and 79.06% in the presence of the amino acids at a concentration of 150 ppm. Cysteine, serine, and isoleucine demonstrate better corrosion inhibition among amino acids. Cysteine and serine contain heteroatoms such as sulfur, oxygen, and nitrogen, which enhance their interaction with the metal surface. Isoleucine's long alkyl chain strengthens surface bonding[80].

2.1.3 Fucoidan

Fucoidan is a natural sulfated polysaccharide isolated from brown algae and marine invertebrates. Chemically, it comprises galactose, glucose, mannose, xylose, fucose, and uronic acid units. Structurally, fucoidan comprises repeating disaccharide units of α-1,3 and α-1,4-linked fucose residues with the sulfate group attached to O-2, O-3, and O-4 positions of fucose residues[84]. The applications of fucoidans include anti-coagulant, anti-viral, anti-inflammatory, selective cytotoxic, and anti-tumour uses. They can also be employed in cosmeceutical, pharmaceutical, diagnostic, and synergistic therapeutic applications[85]. When tested for its potential as a corrosion inhibitor for zinc metal in natural water, fucoidan showed an excellent efficiency of 92.94% at 25°C, studied through potentiodynamic polarisation studies for 120 ppm inhibitor concentration[86]. Studies on fucoidan reveal that it is a suitable solution for the corrosion mitigation of zinc anode in aqueous zinc ion batteries for a minimum inhibitor concentration of 25 mM. Fucoidan utilises

the lone pair of electrons present on its heteroatoms to interact with the empty d orbitals present in zinc, forming a robust, covalently bonded ultrathin layer on the zinc surface that does not affect the ion transfer but can shield the surface from the corrosive electrolytes. Using fucoidan as an inhibitor enhances the effective working of the aqueous zinc batteries[87]. The Tafel studies on the corrosion mitigation of 304 stainless steel in 3.5 % NaCl by fucoidan polysaccharide revealed an inhibition efficiency of 81.7% at 200 ppm inhibitor concentration, and it was a mixed inhibitor influencing both cathodic and anodic reactions[84].

2.1.4 Agar

Agar is a seaweed polysaccharide made of agarose and agarose pectin polysaccharides. Agarose accounts for the gelling properties of agar. The unique properties of agar, such as biocompatibility, high gelling ability, and film-forming properties, are exploited in food and beverage, biomedical, and packaging applications, etc[88]. The structure of agar reveals the presence of α (1–4)-3, 6-anhydro-L-galactose and β 9(1–3)-D-galactose units. Electrochemical studies reveal that large molecules like proteins, such as gelatin or agar, polysaccharides, such as dextrin, or compounds containing long hydrocarbon chains form an adsorbed film on the metal surface, thereby preventing the diffusion of ions or molecules to or from the metal surface retard corrosion. These molecules form surface films that lead to resistance and concentration polarisation, affecting both anodic and cathodic reactions and acting as mixed inhibitors[89]. Agar demonstrates excellent corrosion inhibition as listed in Table 3 due to its hydrophilic nature and capacity to form a stable barrier film.

2.1.5 Laminarin

Laminarin is a low molecular weight storage polysaccharide and structurally β-(1-3)-glucan with β-(1-6) linkages of 20–25 units. The potential of laminarin as a corrosion inhibitor was evaluated along with sodium molybdate for Q235 steel in sodium chloride solution. The synergistic blend showed an inhibition efficiency of 92.75 % when sodium molybdate and laminarin concentrations were 0.7 g/L and 0.3 g/L, respectively. On the other hand, laminarin could show an inhibition potential of only 72.68%.

2.2 Marine Animal-Derived Polymers

2.2.1 Chitosan

Chitosan is the deacetylated product of chitin and is the only positively charged polysaccharide in nature, comprising randomly distributed β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units[95]. Chitosan has the credit of being a highly studied biopolymer, as reflected in the increased number of publications and patents annually. The chitosan structure contains electron-rich, reactive hydroxyl groups and the free amino group that provides avenues for modification through chemical reactions even under mild conditions. The hydroxyl group at the C-6 position and -NH_2 at the

Table 3. Details of the corrosion inhibition efficiency of agar for different metals

S No	Details of the Agar inhibitor	Metal/ corrosive medium	Inhibition Efficiency	%
1	Agar	mild steel / 1 M HCl	92-98 / 1000 ppm (40-60° C)	90
2	Agar	aluminium alloy/aluminium primary cell	2g/litre rate of corrosion: 0.008 mg cm-2 h−1 (short term) 0.005 mg cm−2 h−1 (long term).	91
3	Agar grafted Polyacrylamide	carbon steel / CO2- saturated 3.5 wt% NaCl solution	85 / 500 mg/L at 25°C	92
4	Agar	aluminum-air Batteries Al electrode in 4 M NaOH	62.8 Battery efficiency increases by 35.95	93
5	i) 10mM thiourea ii) 10mM thiourea +1000 ppm agar	mild steel / 0.5 M H_2SO_4	i)82 ii)96	94

C-2 position are highly susceptible to modification[96]. Besides, these functional groups can interact efficiently with the metal surface as effective adsorption centres and can serve as potential corrosion inhibitors[97]. The demand for green and sustainable materials has thrown light on using abundantly available, highly biodegradable, nontoxic chitosan and derivatives as corrosion inhibitors. Several studies reveal the efficiency of chitosan and its derivatives in inhibiting the corrosion of metals in aggressive environments. Table 4 displays the results of the most recent studies on the inhibition potential of chitosan derivatives.

Table 4. Corrosion inhibition potential of chitosan and its derivatives for different metals in different corrosive environments

S No	Corrosion inhibitor	Metal/ Corrosive medium	Inhibitor Conc.	Exposure period/ temp.	Inhibition efficiency (%)	Corrosion studies	Ref.
1	dendritic chitosan derivatives	carbon steel/ 1 M HCl	500 ppm	7 days / 60 ° C	>80 >80	WL PDP	98
2	chitosan-5-HMF3 (5-Hydroxy methyl furfural)	mild steel/1 M HCl	200 ppm	48 hrs / 30 ° C	97.56 97.01	WL PDP	99
3	chitosan and heterocyclic composite	mild steel 1 M HCl	100 ppm.	24 hrs/ room temp	98.03 98.25	WL PDP	100
4	furfural-chitosan Schiff Base integrated with nanocopper particles	N80 steel/ 1 M HCl	500 ppm	24 hrs/ room temp	95.01	WL	101
5	natural chitosan-based carbon dots	mild steel/ 1 M HCl	40 ppm		97.4		102
6	chitosan grafted with gallic acid and cerium dioxide hybrid nanocomposites	mild steel / 3.5 % NaCl	200 ppm	Room temp	93.58	Electro chemical studies	103
7	Isatin/chitosan Schiff base	Q235 carbon steel / 1M HCl	250 ppm	25 °C	88.4 %	WL	104
8	copolymeric modified chitosan Core-Shell Nanocomposite	mild steel / 0.1 M HCl	1000 ppm	298 K	96.87	PDP	105
9	chitosan ionic liquid Schiff base +3-carboxybenzenesulfonic acid	N80 steel /15% HCl	400	24 h	93%	WL	106
10	Disodium EDTA functionalized chitosan	mild steel / 1 M HCl	500 ppm	30 ° C	96.6	WL	107
11	2-((1H-Benzo[d]imdazole-2yl) thio)1(4-chlorophenyl) ethan-1-one modified chitosan	carbon steel /1 M HCl	5 ppm	25 °C.	93	WL	108
12	benzaldehyde and m-nitrobenzaldehyde modified Chitosan resin	mild steel / 0.24 M HCl	1000 ppm	298 K	>94	PDP	109
13	natural chitosan-based carbon dots	mild steel/ 1 M HCl	40 ppm		97.4		110
14	novel chitosan-oligosaccharide derivatives + fluorane	P110 steel / 3.5 wt% NaCl			91.19		110
15	chitosan methionine derivative	carbon steel/ 1 M HCl	100 ppm		99.8	PDP	111
16	zwitterion-modified chitosan	1 M HCl	400 ppm	24 h / 25 °C	97.6	PDP	112

2.2.2 Marine Collagen

Marine gelatin and collagen are present in marine invertebrates, fish, and sea mammals. Captured fish are primarily processed as skinned and deboned meat, producing protein-rich marine food waste. These by-products, especially fish skin, contain high amounts of collagen, a structural protein[113]. However, the anticorrosive behaviour of proteins is less studied than that of amino acids and may be due to the proteins' greater affordability, stability, and environmental friendliness[114].

2.2.3 Marine Gelatin

Gelatin, a macromolecular biodegradable proteinous polymer, has versatile industrial applications. Collagen is usually converted to gelatin through precipitation and thermal solubilization during a pH shift[115]. Collagen-based materials have attracted researchers to their applications in biomedical devices, maritime structures, automotive and aerospace components, infrastructure and building, and energy and power generation. Also, collagen-based materials can be evaluated for their potential as corrosion inhibitors, as the search for green, sustainable inhibitors is the need of the hour[116]. Gelatin extracted from the bone of the fish Mackerel was evaluated for its anticorrosion efficiency for iron coupons in 3.5 wt% % NaCl solution for 6 days. The results of weight loss studies show that at 400 ppm of the gelatin concentration, a maximum efficiency of 58.69%. The inhibition effect was due to the metal-gelatin complex formed on the metal surface due to the interaction between the heteroatoms, namely N and O of gelatin, with the metal[117]. Gelatin, extracted from Squid, was deployed to study its inhibition potential for carbon steel in 0.5 M H_2SO_4. It showed inhibition efficiency of 92.3% at 60 ppm inhibitor concentration[118]. When gelatin was employed for aluminium silicon alloys (I and II) in sodium hydroxide solution as corrosion inhibitor, impedance studies revealed an inhibition efficiency of 59.15 % and 49.75 % respectively, for a very high concentration of 2000 ppm[119].

2.2.4 Hyaluronic Acid

Hyaluronic acid is a glycosaminoglycan heteropolysaccharide composed of repeating disaccharide units of N-acetyl-D-glucosamine and D-glucuronic acid linked by β-(1→3) and β-(1→4) glycosidic bonds. They are a major extracellular matrix component in the synovial fluid, vitreous humour, and cartilage tissue[7]. This material shows promise as a corrosion inhibitor due to its active functional groups. Sodium hyaluronate, an expired drug tested for the corrosion inhibition of mild steel in 0.5 % HCl solution, showed a maximum inhibition efficiency of 91 % for an inhibitor concentration of 0.04g/L using polarisation studies at 303 K[120]. The corrosion behaviour of 316L austenitic stainless steel in sodium chloride solution in the presence of hyaluronic acid showed an enhanced corrosion resistance due to the formation of the passive film of chromium oxide, hydroxide, and MoO_2 formed on the metal surface, as was supported by the XPS studies. Hyaluronic acid plays a significant role in metal implants without compromising biocompatibility[121]. Magnesium, an innovative biomaterial employed in orthopaedics, suffers from the disadvantage of rapid degradation in the human body. Hyaluronic acid with multilayer cerium films on the metal implant prevented corrosion during local damage and biodegradation[122].

2.2.5 Chondroitin Sulfates

Chondroitin sulfate, an essential cartilage structural component, is a *glycosaminoglycan* polysaccharide composed of alternating N-acetylgalactosamine and glucuronic acid. This biopolymer is a promising green anticorrosive agent for mild steel in 1 M HCl, showing a maximum efficiency of 95.4 % at 500 ppm concentration at 333 K[123]. Similarly, when a blend of chondroitin sulfate and sodium alginate was employed, it showed a synergistic effect of enhanced inhibition efficiency of 95.18% against 72.78 % when used individually, for mild steel in 1M HCl[124]. When tested for zinc metal in ammonium chloride solution, it showed an inhibition efficiency of 98.9 % with an optimum concentration of 200 ppm at 308 K[125]. The chondroitin sulfate inhibitor showed an inhibition efficiency of 64% at 30 °C when evaluated for aluminium metal in an acidic solution via the weight loss studies[126].

2.3 Marine Microorganisms-Derived Biopolymers

Microbial extracellular polymeric substances have been studied for corrosion protection because of their capacity to form biofilms and bind metal ions[127]. Numerous studies have demonstrated that exopolysaccharides, bacterial biofilms, and microbial surfactants can be effective corrosion inhibitors. These substances, known as exopolymers, are primary components of biofilms that

Table 5. Sources of extracellular polymeric substances and their tendency to inhibit or accelerate corrosion

S No	Source of EPS	Metals / corrosive medium	Inhibitory or acceleratory effect	Ref
1	Iron-oxidising bacterium culture i) 7-day-old EPS ii) 14-day-old EPS & 28-day-old EPS	Q235 mild carbon steel / 3.5 wt% NaCl solutions	i) 240 ppm inhibited corrosion <240 ppm and >240 ppm accelerated corrosion ii) 240 ppm both promoted corrosion	134
2	Waste Activated Sludge	carbon steel / 3.64% NaCl saturated with CO_2	80/ 1000 ppm	135
3	*Tenacibaculum mesophilum* D-6, *Tenacibaculum litoreum* W-4, and *Bacillus* sp. Y-6,	X80 carbon steel.	The inhibitory effect is closely related to their biofilm-forming abilities.	133
4	i) Pseudomonas putida ii) Bacillus megaterium	A3 carbon steel in circulating cooling water	Inhibition of corrosion rate i) 8.86 ii)6.39	136
5	Marine *Vibrio* spp.	X80 carbon steel/ 3.5 wt% % NaCl	80/ 3 ppm	56
6	Aspergillus terreus	aluminium alloy AA 7075	accelerated corrosion	137
7	F1rA and F1hG genes of *Shewanella putrefaciens* regulated EPS	Carbon steel in artificial seawater	75% increase of EPS: 26 % increase in inhibition decrease of EPS: 1.7 times increase in the corrosion rate	138
8	*Streptococcus mutans* blended with sodium molybdate	X70 steel in 3.5 wt% NaCl solution	synergic parameter of 5.6 for 10 to 40 ppm of EPS + 50 ppm of sodium molybdate	139
9	Aspergillus terreus	316L stainless steel in seawater	enhanced uniform and pitting corrosion	140
10	*Pseudomonas aeruginosa* i) soluble EPS ii) bound EPS	EH40 steel in simulated seawater	i) inhibited corrosion ii) accelerate corrosion	141
11	i) Lactobacillus reuteri ii) Pseudomonas fluorescens iii) Escherichia coli	Q235 low carbon steel / NaCl	i) 28.25 / 300 ppm ii) 23.87 / 400 ppm iii) 21.72 / 400 ppm	142

facilitate metal surface passivation and act as diffusion barriers against corrosive agents[128]. They comprise proteins, polysaccharides, nucleic acids, and humic acids, providing plenty of functional groups for their bioactivities[129]. The exopolymers significantly play an oxymoronic role in accelerating corrosion and corrosion inhibition, depending on the microorganism and the metal[130,131]. Exopolymers inhibit corrosion primarily by forming protective films through complexation with metal ions. Additionally, excess exopolymer production can induce biomineralisation on the metal surface. Hydroxyl groups in the exopolymers may also interact with metal ions or their chelates to enhance film formation and corrosion resistance[132]. Moreover, using biofilms from local environments can aid in developing environment-specific, self-sustaining anticorrosive coatings[133]. Table 5 displays the microorganisms secreting the exopolymers and their inhibition efficiency for different metals in various corrosive media.

3. Conclusion and Future Perspectives

The marine system, a treasure trove of biodiversity with a broad spectrum of living organisms and chemodiversity with a wide variety of bioactive molecules of great significance, is undoubtedly an arena for versatile applications. In ancient days, it served as a food and

medicine stock pot, exploited as food additives and an elixir of life. The biodegradability, biocompatibility, nontoxic nature, environment friendliness, abundance, and renewability have drawn the attention of researchers to navigate in the direction of sustainability. The marine resources, namely seaweed, marine animal waste, and secretion from marine microorganisms, are rich reserves of biopolymers that show excellent potential as corrosion inhibitors that can increase the life span of the various metals employed in corrosive and harsh media. The presence of numerous functional groups in marine biopolymers enhances the bioactivity and opens new avenues for modification to tailor their properties to advance applications. Advances in biotechnology offer a valuable opportunity to develop eco-friendly, marine-based corrosion inhibitors that are sustainable, nontoxic, biodegradable, and adaptable through functionalization with specific groups and nanomaterials. The use of marine biopolymers in corrosion inhibition has thrown light on the formulations of bioinspired and biomimetic novel inhibitors with better performance and environmental compatibility. However, it is vital to remember that these marine biopolymers play pertinent roles in the sustenance of the ecosystem and are not just available for human exploitation. Unsustainable cultivation/ harvesting of marine biomass can lead to ecological damage to the marine system. With the increasing demand for green corrosion inhibitors, the sustainable management practice of cultivating and harvesting marine forests with minimum impact on the marine environment is crucial.

4. References

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