Performanceof Some Natural Carbohydrate as Corrosion Inhibitor: A Comprehensive Review

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ABSTRACT

This review describes the application of Carbohydrate biopolymers as green inhibitors for inhibition of metal corrosion. The protective capacity and precise mechanisms of these green inhibitors depend heavily on their molecular weight, chemical composition and unique electronic configurations. For instance, cellulose and chitosan possess free amine and hydroxyl groups. These groups contain heteroatoms (nitrogen and oxygen) with lone pairs of electrons. These lone pairs are shared with the vacant d-orbitals of the metal, forming coordinate bonds that create a protective molecular film over the metal surface. A detailed analysis is provided for various carbohydrate biopolymers including gums, alginates, starch, carboxymethyl cellulose, and hydroxyethyl cellulose—alongside an evaluation of how halide additives synergistically improve their anti-corrosion efficiency is discussed.

INTRODUCTION

Application of suitable inorganic and organic inhibitors is one of the most effective remedialmeasures in the field of corrosion inhibition. Use of many inorganic inhibitors, particularly those containing phosphate, chromate and other heavy metals are now being gradually restricted by various environmental regulations. Many organic inhibitors are also been reported as toxic and environmentally harmful having human health impact also. Their usage is against modern safety regulation for the industrial chemicals with severe criticism. Currently, there is an increasing quest for limiting field applications involving toxic compounds, hence the search for greener alternatives such as plant extract, amino acids, proteins and bio-polymers have been reported to have the potentiality of efficient corrosion inhibitors [1].In recent years, some polysaccharides, including gums, chitosan, starch etc have found a new role as corrosion inhibitors for metals in acidic,alkaline, as well as in saline environment [2–3].

Greenness: A prerequisite requirement for selection of inhibitor compounds

General Requirements	Greenness Criteria
Ability to oxidize the metal thereby forming a passive/protective layer on the metal surface	Non-toxic to man and nature: environmental friendliness
Presence of functional groups containing hetero-atoms (N, O, S etc.)	Cost effectiveness, especially when quantity is a factor of choice
Organic molecules should possess a large structure	Solubility of the inhibitor

Scheme 1. General pre-requisite requirements for the selection of inhibitor compounds.

DISCUSSION

Carbohydrate biopolymers are widely used as protective coatings. In corrosion inhibition, they represent a set of chemically stable, biodegradable and eco friendly macromolecules with unique inhibiting strengths and mechanistic approaches to metal surface and bulk protection with those extracted from natural sourcesregarded

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as low cost, renewable and readily available alternatives with essential and active ingredients responsible for the corrosion inhibition. The efficacy of carbohydrate biopolymers as inhibitors varies with their class depending on their molecular weights, cyclic rings as well as the availability of bond-forming groups (e.g. sulphonic acid groups) and abundance of centers of adsorption (e.g. heteroatoms).

Possible mechanisms of inhibition :

- Adsorption of the molecules or its ions on anodic and/or cathodic sites.
- Increase in cathodic and/or anodic over voltage.
- Formation of a protective barrier film.

This unique class of polymers has been widely reported as corrosion inhibitors due to their enormous functional groups and their ability to complex with ions of metals at surfaces. The presence of non-bonded/lone pairs of electrons (as well as pi electrons) on the molecules of these polymeric compounds allows for inhibitor-metal electron transfer with formation of bond whose strength is a function of the polarizability of the electron-donating group [4-5].

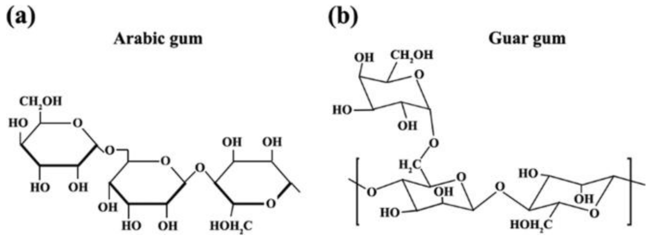
Natural Gums

Gums obtained from plants are solids consisting of mixtures of polysaccharides (carbohydrates). Because of their unique chemical composition, gums from natural sources are effective corrosion inhibitors and their evolution has greatly attracted attention considerably in the corrosion field.

The oldest and most widely utilized natural gum, Gum Arabic (GA) is highly valued as an eco-friendly corrosion inhibitor. Naturally harvested as a sticky, water-soluble sap from the Acacia tree (Leguminosae), GA consists of a complex blend of polysaccharides, sucrose, oligosaccharides, arabinogalactan, and glycoproteins—a chemical makeup that provides its strong protective capabilities [6]. The corrosion inhibition potential of Gum Arabic (GA) has been evaluated for both mild steel (MS) and aluminum (Al) in 1 M H_2SO_4 solution bythe use of weight loss and thermometric techniques. Results from weight loss and thermometric techniques revealed that both the inhibition efficiency and the degree of surface coverage proportionally increases with concentrations. It acts via physical adsorption on mild steel, whereas it undergoes chemical adsorptionon aluminum surfaces. From the results obtained, GA was concluded to be a more effective inhibitor for aluminum than for mild steel in acidic solutions [7]. In alkaline (0.1 M NaOH) medium, Umoren (2009) and Umoren et al. (2006) studied the effectiveness of GA towards the corrosion inhibition of Al with and without iodide ion (as KI) additives at 30 °C and 40 °C, using hydrogen evolution and thermometric techniques. The corrosion inhibition of GA of Al in 0.1 M NaOH was enhanced in the presence of the iodide ions due to synergistic effect. In the absence of KI, the inhibition of Al corrosion by GA is concentration and temperature dependent, a chemisorption mechanism was proposed and its adsorption on Al substrates followed Langmuir and Freundlich adsorption isotherms[8].

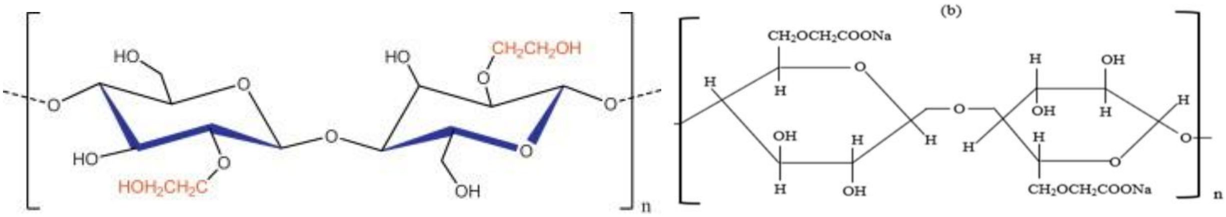
Guar gum (GG), derived from the endosperm of the guar bean seed, represents another highly documented category of natural anticorrosion polymers. Abdallah (2004) was the first to report its anti corrosion behaviour for carbon steel (L-52 grade) in 1 M H_2SO_4 containing NaCl as the corrodent using Tafel polarization and weight loss techniques. The study identified GG as a mixed-type inhibitor, suppresses both the anodic and cathodic reactions. Values of inhibition efficiency (%η) increased with its concentration for both corrosion monitoring techniques. GG adsorption on L-52 substrate followed Langmuir adsorption isotherm. The research also demonstrated that the pitting corrosion potential shifted dynamically depending on the concentration of chloride ions present in the electrolyte solution[9].

Excudated gum Raphia hookeri (RH), Universal Name is Wine Palm.It has been found to be an effective corrosion inhibitor for aluminium in HCl solution. Experimental data obtained via weight loss techniques demonstrate as the concentration of RH gum increases, the overall corrosion rate decreases which means that inhibition efficiency increases with the increase of concentration [10].



Carboxymethyl and Hydroxyethyl cellulose

Cellulose gum or simply, Carboxymethyl cellulose (CMC), is available as a sodium salt. CMC has been thoroughly evaluated as an eco-friendly corrosion inhibitor for mild steel in an aggressive 2M H_2SO_4 environment by means of chemical techniques (weight loss, hydrogen evolution and thermometric methods) at 30-60 °C. The inhibition efficiency was found to increase with increase in CMC concentration but decreased with rise in temperature. A physical adsorption (physisorption) mechanism is suggested followed by Langmuir and Dubinin Radushkevich adsorption isotherm models [11]. A comparative study on the atmospheric corrosion of mild steel and aluminum in 0.5M HCl solution by hydroxyethylcellulose (HEC) was investigated by Arukalam et al. [12] using weight loss method. From the results obtained HEC serves as a more effective inhibitor for mild steel than for aluminum in hydrochloric acid solutions. The study for the effect of halide ions (Cl^-, Br^-, I^-) additives on the performance of CMC in the acid medium has also been documented. The corrosion inhibition by CMC was enhanced in the presence of iodide ions, showing synergistic effect, Conversely, the introduction of chloride ions yields an antagonistic effect. The magnitude of %η increased with immersion time of MS in the solution of the electrolyte containing CMC and the iodide ions, and for all the other halide ions[13]. Bayol et al. (2008) have reported similar findings in 1 M HCl using chemical (weight loss method) and electrochemical (potentiodynamic polarization, linear polarization resistance and EIS) techniques. The protection of mild steel is highly concentration-dependent, classifying CMC as a mixed-type inhibitor[14]. The inhibition effect of hydroxyethylcellulose (HEC) on 1018 c-steel corrosion in 3.5% NaCl solution was investigated by using potentiodynamic polarization, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) techniques. Result identified HEC as a mixed-type inhibitors in 3.5% NaCl. Formation of a film of inhibitor on the steel surface is suggested from SEM and EDX analysis[15]. HEC has been reported to mitigate the corrosion of aluminum and mild steel in HCl solution. The corrosion rate decreased with increase in HEC concentration. The inhibition efficiencies increased with inhibitor concentration. The maximum inhibition efficiency of 69.617% and 58.145% were observed with mild steel corrosion in 1.0 M HCl and 1.5 M HCl respectively [16].



Chemical structure of hydroxyethylcellulose and Carboxymethyl cellulose repeat unit

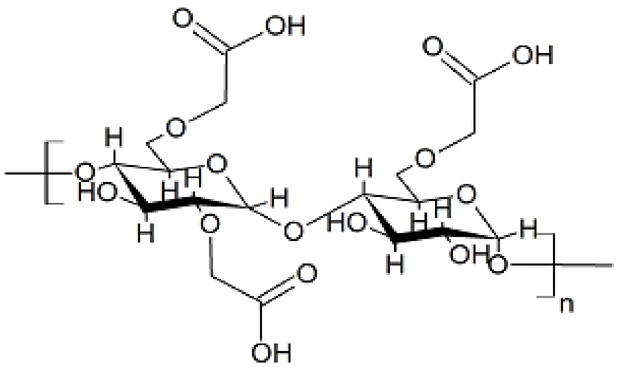
Alginates

Alginate is a group of sugars also called alginic acid due to the carboxylic acid functional group attached to their molecular structure. Alginates have also been widely reported as corrosion inhibitors for various metals in different media. The anti-corrosion behavior of sodium alginate (SA) on copper in the 1 M hydrochloric medium was carried out using weight loss and electrochemical measurements. The effect of temperature on the reactions of copper corrosion inhibition was evaluated. The thermodynamic parameters revealed that the mode of adsorption has a physical nature that follows the Langmuir isotherm. To better understand the adsorption mechanism, quantum calculations using density functional theory were performed [17]. Sodium alginatehas also been reported as corrosion inhibitor which prevent carbon steel corrosion in 0.5 M HCl by chemical and electrochemical techniques. Corrosion inhibition efficiency of sodium alginate improves significantly with increasing concentration, whereas temperature rises have an adverse effect; this was attributed to its physisorption nature at the metal-solution interface. A corrosion inhibition efficiency of 90% was obtained for

500 ppm Na alginate, and this was attributed to molecular adsorption and subsequent formation of compact film on the metal surface[18].The study of the effect of sodium alginate on anticorrosion of aluminum, magnesium, carbon steel and mild steel in various media also been studied.

Starch

The use of molecular starch as a corrosion inhibitor lacks wide application due to its reduced solubility and surface adhesion strength. Its unique molecular structures, bearing electron-rich hydroxyl group attributed to its corrosion inhibiting ability. The physical and chemical properties of cassava starch have been modified and the compounds evaluated as corrosion inhibitors of carbon steel under alkaline conditions in 200 mg/L NaCl solutions [19]. An activated starch (AS) and a carboxymethylated starch (CMS) with two different degrees of substitution were studied by means of electrochemical impedance spectroscopy and it is revealed that AS showed better inhibition efficiency than CMS [20]. Tapioca starch was examined for improvement of corrosion resistance of AA6061 alloy in sea water using electrochemical measurements. Results showed that the presence of tapioca starch significantly decreases the corrosion rates due to formation of precipitates of tapioca starch on the metal surface, hence inhibition efficiency increases [21].Native starch (NS) extract from sweet potato and alkaline modified starch (AMS) were reported as corrosion inhibitor of mild steel under acidic conditions. Addition of potassium iodide improved the inhibitive efficacy of AMS due to Synergistic effect [22].



Carboxymethyl Starch

Table 1: Summary table of different Carbohydrate as corrosion inhibitors

Carbohydrate	Metal Substrate	Corrosive Medium	Testing Methods	Key Findings / Efficiency
Gum Arabic (GA)	Mild Steel & Aluminum	1 M H_2SO_4	Weight loss, thermometric	Efficiency increases with concentration; more effective for Al than MS in acidic medium
Gum Arabic (GA)	Aluminum	0.1M $NaOH$	Hydrogen evolution, thermometric	Efficiency enhanced by iodide ions (synergistic effect); follows Langmuir and Freundlich isotherms
Guar Gum (GG)	Carbon steel	1 M H_2SO_4 + $NaCl$	Tafel polarization, weight loss	Mixed-type inhibitor; efficiency increases with concentration; follows Langmuir isotherm.

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Raphia hookeri (RH)	Aluminum	*HCl solution*	Weight loss	Corrosion rate decreases as concentration increases, leading to higher inhibition efficiency.
Carboxymethyl Cellulose (CMC)	Mild Steel	*2 M H_2SO_4*	Weight loss, hydrogen evolution, thermometric	Efficiency increases with concentration but decreases with temperature (physisorption)
Carboxymethyl Cellulose (CMC)	Mild Steel	*1 M HCl*	Weight loss, potentiodynamic polarization, LPR, EIS	Mixed-type inhibitor; highly concentration-dependent protection.
Hydroxyethyl-cellulose (HEC)	Mild Steel & Aluminum	*0.5 M HCl*	Weight loss	More effective for MS than Al in hydrochloric acid solutions.
Hydroxyethyl-cellulose (HEC)	Mild Steel	*1.0 M & 1.5 M HCl*	Weight loss	Maximum efficiencies: 69.617% (in 1.0 M HCl) and 58.145% (in 1.5 M HCl).
Hydroxyethyl-cellulose (HEC)	1018 c-steel	*3.5% NaCl*	Polarization, EFM, EIS, SEM, EDX	Mixed-type inhibitor; forms a protective film on the steel surface.
Sodium Alginate (SA)	Copper	*1 M HCl*	Weight loss, electrochemical, quantum calculations	Physisorption mode; follows Langmuir isotherm.
Sodium Alginate (SA)	Carbon Steel	*0.5 M HCl*	Chemical & electrochemical techniques	90% efficiency obtained at 500 ppm; efficiency improves with concentration but declines with temperature.
Cassava Starch (Modified)	Carbon Steel	*200 mg/L NaCl (Alkaline)*	EIS, morphology	inhibitive efficiency increases with presence of active groups
Activated Starch (AS)	Mild Steel	*Acid medium*	EIS	AS showed better inhibition efficiency than carboxymethylated starch (CMS)
Tapioca Starch	AA6061 Alloy	*Seawater*	Electrochemical measurements	Significantly decreases corrosion rates due to precipitate formation on the surface.
Sweet Potato Starch (Modified)	Mild Steel	*Acidic media*	gravimetric and potentiodynamic polarization techniques	A mixed-type inhibitor, efficiency is improved by addition of potassium iodide (synergy)

CONCLUSION

Generally, carbohydrates represent a set of chemically stable, biodegradable and eco friendly macromolecules with reliable inhibiting strengths for metal surface protection; making them effective protective coatings. This review provides an extensive overview of green corrosion inhibitors, focusing on application of some green pure carbohydrate biopolymers such as exudate gums, cellulose, alginate, and starch etc towards metallic corrosion inhibition. The effects of halide additives together with those carbohydrate was discussed. Experimental result revealed that with increasing inhibitor concentration, inhibition efficiency increases. The inhibitive properties were studied by means of different techniques such as Weight loss, potentiodynamic polarization, LPR, EIS, SEM,EDX etc. Experimental studies showed that most of the inhibition mechanism involves formation of passivation layer that prevents the passage of corrosive ions to the metal surface hence greater inhibition efficiency.

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