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Review

Application of carbohydrate polymers as corrosion inhibitors for metal substrates in different media: A review

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ABSTRACT

Naturally occurring polysaccharides are biopolymers existing as products of biochemical processes in living systems. A wide variety of them have been employed for various material applications; as binders, coatings, drug delivery, corrosion inhibitors etc. This review describes the application of some green and benign carbohydrate biopolymers and their derivatives for inhibition of metal corrosion. Their modes and mechanisms of protection have also been described as directly related to their macromolecular weights, chemical composition and their unique molecular and electronic structures. For instance, cellulose and chitosan possess free amine and hydroxyl groups capable of metal ion chelation and their lone pairs of electrons are readily utilized for coordinate bonding at the metal/solution interface. Some of the carbohydrate polymers reviewed in this work are either pure or modified forms; their grafted systems and nanoparticle composites with multitude potentials for metal protection applications have also been highlighted. Few inhibitors grafted to introduce more compact structures with polar groups capable of increasing the total energy of the surface have also been mentioned. Exudate gums, carboxymethyl and hydroxyethyl cellulose, starch, pectin and pectates, substituted/modified chitosans, carrageenan, dextrin/cyclodextrins and alginates have been elaborately reviewed, including the effects of halide additives on their anticorrosion performances. Aspects of computational/theoretical approach to corrosion monitoring have been recommended for future studies. This non-experimental approach to corrosion could foster a better understanding of the corrosion inhibition processes by correlating actual inhibition mechanisms with molecular structures of these carbohydrate polymers.

Contents

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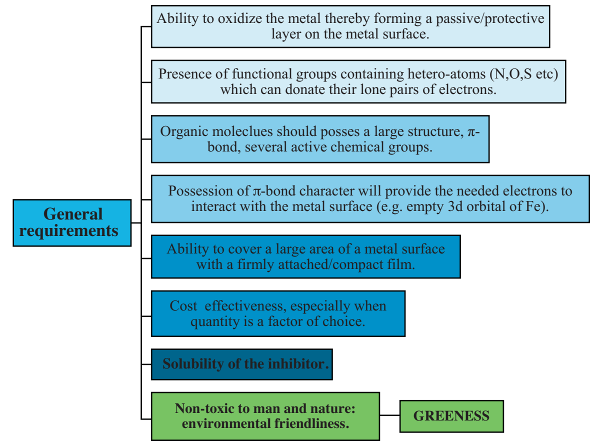
1. Introduction

Metals corrode, and this electrochemical process has huge implication on their end-use and consequently, the economics of maintenance and repairs for industrial applications. Several forms of corrosion products and all possible reactions, including stable phases, are revealed in the Pourbaix diagram of metals showing their susceptibility to corrosion depending on the pH. The rate of metal corrosion is greatly influenced by substrate and surface chemistries as well as some environmental influences (e.g. temperature, solution concentration (pH) etc.), and by understanding these factors, adequate control method can be employed to revert its degradation kinetics. By studying corrosion, researchers worldwide aim at discovering more reliable methods and strategies of preventing, or at least minimizing its spontaneous dynamics. The use of corrosion inhibitor compounds (single/multiple component, composites and blends etc.) is by far one of the most applied corrosion control strategy in oil-fields. This operation is effective if the adsorption mechanism(s) of the adsorbed inhibitor compound at the metal surface is rightly defined. Generally, a common mechanism of action of most inhibitor compounds involves the formation of passivation layer that prevents the passage of corrosive ions to the metal surface. However, the effectiveness of this layer depends on the environment to which the compound has been applied, the metal type as well as the fluid composition, quantity of water, and flow regime (Gräfen, Horn, Schlecker, & Schindler, 2002). Normally in the field, these compounds are added in small concentrations to coolants, hydraulic fluids, or any other fluid (liquid or gas) surrounding the metal substrate, like alkylaminophosphates and zinc dithiophosphates in fuel oil. Phosphates, and other inorganic substances (e.g. chromates, dichromate and arsenates) are known to have detrimental environmental effect and man health impact, as such 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 by reformulating the existing products or by identifying new chemistries for developing safer products (Killaars & Finley, 2001).

1.1. Greenness: A prerequisite requirement for selection of inhibitor compounds

The general requirements of the selection of compounds are not limited to the chemical structural pre-requite in Scheme 1, but must also include eco-friendliness and benignity (Umoren, Ogbobe, Igwe, & Ebenso, 2008a; Umoren, Obot, & Obi-Egbedi, 2009a; Umoren, Eduok, Solomon, & Udoh, 2011; Okafor et al., 2008; Obot, Obi-Egbedi, & Umoren, 2009). In recent times, owing to global interest on environment safety as well as the effect of impacting industrial activities of man's health and ecological balance, the use of toxic chemicals and operations that emit them have been minimized. On this note, the inorganic inhibitors and some of their hazardous organic counterparts, though effective for the reduction of metal corrosion at lower concentration, are gradually replaced by greener substances. Generally, eco-friendly, or simply green, corrosion formulations (inhibitors and coatings) are those chemical products that meet the required reduced level of hazardous substance generation, and the processes involving their usage are governed by sustainable chemistry without direct or indirect negative environmental or health impacts. Since



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

recommended anticorrosive coating systems are expected to be green and purely cured granules/powders with very low volatile organic compound (VOC) content and without heavy metals, their inhibitor counterparts should also meet these green label compliant standards. With the banning of chromates, corrosion control programs with greener inhibitor compounds (chromate-free inhibitor formulations) in most oil field applications are designed to effectively meet safety standards and also efficiently protect the targeted metal substrates in their service environments. Health defects of chromates ranges from mild skin allergic reactions and rashes to nasal bleeding; with arsenates, alteration of genetic material may occur at higher dosages as well as nervous breakdown and cancer. The US National Institute for Occupational safety and Health (NIOSH) have reduced the permissible exposure limit (PEL) for arsenates and chromates to 0.002 and 0.05 milligrams per cubic meter of air, respectively. (https://www.osha.gov/OshDoc/data_General_Facts/hexavalent_chromium.pdf; https://www.cdph.ca.gov/programs/hesis/Documents/arsen2.pdf).

2. Green carbohydrate polymers application for metal protection

Organic corrosion inhibitors are generally used as replacements for inorganic compounds in the control of dissolution of the metals in aqueous media. Huge interest in this class of compounds has continued to grow in the last decade as naturally occurring and some synthetic biopolymers as well as their products meet the environmental requirements for safe product application with good corrosion inhibiting potential with infinitesimally small/reduced or zero pollution risk. Carbohydrate polymers are widely used as metal linings, and protective coatings. In corrosion inhibition, they represent a set of chemically stable, biodegradable and ecofriendly macromolecules with unique inhibiting strengths and mechanistic approaches to metal surface and bulk protection (Raja et al., 2013), with those extracted from natural sources (e.g. floral) regraded as low cost, renewable and readily available alternatives with essential and active ingredients responsible for the corrosion inhibition (Rahim, Rocca, Steinmetz, & Kassim, 2008). Generally, some of these carbohydrate biopolymers are relatively high molecular mass