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Advancements in the Utilization of Chitosan and Its Derivatives for Metal Corrosion Inhibition: A Comprehensive Review

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Abstract: Chitosan is a natural, non-toxic, and environmentally friendly material with abundant sources, which has shown good effectiveness in inhibiting metal corrosion. This paper summarizes the applications of chitosan and its derivatives in corrosion inhibitors and coatings. The characteristics of different chitosan corrosion inhibitors and coatings are introduced, and the future development directions of chitosan in metal corrosion inhibition applications are discussed.

Keywords: Chitosan; Metal corrosion; Corrosion inhibitors; Anti-corrosion coatings.

1. Introduction

In chemical production processes, most pipelines and equipment are made of metallic materials, these materials are prone to corrosion when exposed to surrounding media. Corrosion involves chemical or electrochemical multiphase reactions at the interface of the metal, leading to its oxidation (ionization). This significantly reduces the mechanical properties such as strength, plasticity, and toughness of the metal, damages the geometric shape of metal components, increases wear between moving parts, deteriorates physical properties like electrical and optical characteristics, shortens equipment lifespan, and can even result in catastrophic incidents like fires or explosions. According to statistics from developed countries, losses due to metal corrosion account for 10% to 20% of annual steel production. The indirect losses caused by corrosion-related shutdowns and power outages are immeasurable. Therefore, preventing corrosion in equipment and pipelines is a crucial challenge that chemical plants must address. Common corrosion prevention methods include cathodic protection, anodic protection, corrosion inhibitor protection, and coating protection. Chitosan and its derivatives, known for their unique corrosion inhibition properties, have seen numerous applications in corrosion inhibitors and anti-corrosion coatings in recent years.

2. Utilization of Chitosan for Corrosion Inhibition.

2.1. Overview of chitosan.

Chitosan is the second largest polysaccharide in nature and is an alkaline polysaccharide. It is abundant and non-toxic to the environment, with a molecular formula of (1,4)-2-amino-2-deoxy-β-D-glucan, containing a large number of amino and hydroxyl groups. Chitosan is mainly derived from the cell walls of some algae and fungi, as well as the exoskeletons of certain arthropods such as shrimp and crabs, which contain deacetylated chitin. Hence, chitosan exhibits a broad spectrum of sourcing options, cost-effectiveness, and environmentally friendly attributes, rendering it a viable material for corrosion inhibition in academic research.

2.2. Application of chitosan materials

Chitosan possesses outstanding physical and chemical characteristics, including non-toxicity, harmlessness, favorable biocompatibility, cost-effectiveness, and a plethora of active hydroxyl and amino groups. As a result, chitosan is frequently utilized in the fabrication of microspheres, microcapsules, fibers, among other forms, showcasing remarkable efficacy in applications such as cell culture, controlled drug release, and catalyst carriers within the academic realm. Sunil A used chitosan to encapsulate the anti-cancer drug capecitabine for drug release[1], Erik Estefanliy [2]used magnetic chitosan microspheres to adsorb methyl orange in water. Sakai[3] manufactures wound dressings from hydrogel precursor inks containing phenolized chitosan (chitosan-pH) and chitosan nanofibers (chitosan-NF). Therefore, chitosan has broad prospects in drug loading and release, wastewater treatment, corrosion inhibition, and other fields.

3. Mechanism of Chitosan Corrosion Inhibition

3.1. Chitosan corrosion inhibitor

Chitosan is rich in N, O, S and other elements, in which the lone pair electrons can form coordination bonds with the empty d orbital of the metal by giving and receiving electron pairs. On the other hand, the -OH and $-NH_2$ groups in the molecule can easily protonate in acidic corrosive media, leading to electrostatic attraction with the metal surface adsorbing negative ions. They adsorb on the metal surface in the forms of chemical and physical adsorption, forming a dense protective film to inhibit the corrosion reaction between external corrosive media and the metal. Therefore, chitosan is an excellent corrosion inhibitor.

Nevertheless, chitosan demonstrates solubility solely in acids while remaining insoluble in neutral deionized water. Therefore, using chitosan directly as a corrosion inhibitor may not achieve satisfactory results. The abundance of hydroxyl and amino groups in chitosan makes it prone to alkylation, etherification, esterification, Schiff base reaction, quaternization, etc. These chemical reactions can enhance the water solubility of chitosan and increase the number of active adsorption sites on the metal surface, significantly improving the corrosion inhibition performance of chitosan [4-6].

3.2. Chitosan derivative corrosion inhibitor

3.2.1. Carboxymethyl chitosan

Chitosan can undergo various chemical modifications to yield water-soluble products. Carboxymethyl chitosan, a derivative of chitosan, contains a large number of amino and hydroxyl groups, as well as abundant carboxyl groups. In theory, carboxymethyl chitosan should exhibit excellent corrosion inhibition efficiency. Wang et al. [7]prepared an efficient carboxymethyl chitosan (CMC) corrosion inhibitor. The corrosion inhibitor showed the highest corrosion inhibition efficiency on Q235 carbon steel in a 3.5 wt% NaCl solution, reaching 91.78%.

3.2.2. Schiff base chitosan

Schiff base corrosion inhibitors contain imine groups (-CH=N-) and heteroatoms such as N and O, which can form coordination bonds with metals, allowing them to adsorb onto metal surfaces and effectively inhibit metal corrosion [8]. Most Schiff bases exhibit higher corrosion inhibition efficiency compared to their synthetic precursors, mainly due to the presence of the imine group[9]. Chitosan molecules contain numerous amino groups that can react with carbonyl groups on aldehyde substances to form stable Schiff base structures. Therefore, chitosan is widely used in the preparation of Schiff base corrosion inhibitors. Chauhan et al. [10] first synthesized a novel chitosan Schiff base - piperonal-chitosan (Pip-Cht). This chemically functionalized chitosan was applied as a corrosion inhibitor in an oil well acidizing environment for the first time. When the inhibitor dosage of Pip-Cht was 600 mg L−1, its corrosion inhibition efficiency reached 85.16%. Chauhan et al. [11] synthesized chitosan-cinnamaldehyde Schiff base (Cinn-Cht) in one step using microwave irradiation for mitigating the corrosion of carbon steel in 15% HCl. At an inhibitor dosage of 400 mg L−1, the corrosion inhibition efficiency reached 85.16%. The adsorption of the inhibitors followed the Langmuir isotherm, exhibiting a combination of physical and chemical adsorption behaviors.

3.2.3. Quaternary ammonium salt chitosan corrosion inhibitors

The nitrogen atoms on quaternary ammonium salts give them a positive charge, making them more easily adsorbed onto negatively charged metal surfaces, inhibiting the metal cation discharge reaction and thus achieving corrosion inhibition. Therefore, quaternary ammonium salts are effective metal corrosion inhibitors. Introducing quaternary ammonium salts into the chitosan chain can improve the surface properties of chitosan, enhancing its hydrophilicity. Liu et al. [12] synthesized a non-toxic, water-soluble chitosan derivative - quaternary ammonium salt vanillin oligosaccharide using chitosan, vanillin, and 2,3-epoxypropyl trimethylammonium chloride as precursors. The corrosion inhibition performance on 20# carbon steel in a saturated 3 wt% NaCl solution at 60°C indicated that the inhibitor formed a protective inhibitory film on the metal surface, achieving a maximum corrosion inhibition rate of 90.9% after 3 days. Wang et al. [13] synthesized N-vanillyl O-2’-hydroxypropyl trimethylammonium chloride chitosan (VHTC). When the VHTC concentration increased to 200 mg L-1, the inhibition efficiency reached its maximum within 24 hours, with a corrosion inhibition efficiency of 90%, comparable to traditional inhibitors such as imidazoline.

3.2.4. Chitosan is co-administered with other corrosion inhibitors.

As chitosan as a cathodic corrosion inhibitor, it has the potential to be synergistically combined with other corrosion inhibitors for enhanced effectiveness. Li et al. [14]have successfully synthesized water-soluble quaternary amine salt chitosan (QAC) and N-(4-diethylaminophenyl) quaternary ammonium chitosan (DAC) derivatives from chitosan. In a 1 M hydrochloric acid solution with chitosan, QAC, and DAC concentrations set at 10.00 mg/L, the corrosion inhibition efficiencies for X80 steel were measured at 70.28%, 93.66%, and 96.34%, respectively. These results highlight the significant enhancement in the corrosion inhibition effectiveness of chitosan on X80 steel in aggressive environments through the incorporation of quaternary ammonium salt derivatives. Wang et al. [13]synthesized N-vanillyl O-2’-hydroxypropyl trimethylammonium chloride chitosan (VHTC). When the VHTC concentration increased to 200 mg L-1, the inhibition efficiency reached its maximum within 24 hours, with a corrosion inhibition efficiency of 90%, comparable to traditional inhibitors such as imidazoline.

4. Chitosan and Its Derivatives in The Field of Anti-corrosion Coatings

4.1. Antimicrobial Corrosion-resistant Coatings

Microbiologically influenced corrosion (MIC) is one of the most common types of metal corrosion, with approximately 50% of pipeline corrosion failures attributed to MIC. Therefore, preventing MIC is crucial for inhibiting metal corrosion. The amino groups in chitosan molecules can disrupt bacterial cell mass transport, leading to bacterial death, making chitosan widely prepared as various green antimicrobial agents[15]. Incorporating chitosan materials into coatings also demonstrates good antimicrobial effects, effectively preventing microbiologically influenced corrosion. Zhai et al. [16]added 1.0 g·L−1 chitosan in sulfate electrolyte solution and prepared a smooth Zn-Ni chitosan coating using electrodeposition. After cultivating the coating in sulfate-reducing bacteria (SRB) medium for 6 days, the sterilization rate was more than 10% higher than that of the Zn-Ni coating without chitosan, showing a significant antibacterial effect. Hamid et al. [17]epared a poly(caprolactone)/chitosan/zinc oxide coating. The inhibition rates of the coating against Staphylococcus aureus and Escherichia coli both exceeded 90%. Additionally, the coating exhibited good corrosion inhibition effects.

To date, research on chitosan coatings targeting MIC in industrial settings is limited, indicating promising prospects for studying anti-MIC coatings.

4.2. Self-healing Coatings

Self-healing coatings involve incorporating micro/nanocontainers loaded with corrosion inhibitors or self-healing agents into the coating matrix. When microcracks occur in the coating, the micro/nanocontainers provide long-term corrosion protection to the substrate in the external environment. Encapsulating corrosion inhibitors or self-healing agents in micro/nanocontainers allows gradual release in the corrosive medium, enhancing the stability and uniformity of the coating compared to direct inclusion of corrosion inhibitors. Chitosan molecules contain numerous amino groups that expand upon protonation in acidic environments and contract upon deprotonation in alkaline environments, imparting pH-responsive properties to chitosan. Therefore, chitosan can serve as an excellent micro/nanocontainer for loading corrosion inhibitors or self-healing agents. Ji et al. [18]synthesized chitosan core-shell nanofibers loaded with oleic acid (OA) and 2-mercaptobenzimidazole (MBI) using electrospinning and incorporated the nanofibers into an epoxy coating to prepare a self-healing coating for corrosion protection of Q235 carbon steel. The tensile properties of the epoxy resin with chitosan nanofibers were significantly enhanced, with a load value twice that of the blank epoxy resin coating, leading to a notable improvement in mechanical performance. Through electrochemical and scratch experiments, it was demonstrated that chitosan nanofibers could form a self-healing film at the scratch site in the coating, preventing corrosion factors from entering. Song et al. [19]incorporated gelatin-chitosan microcapsules containing $La(NO_3)_3$ or $Ce(NO_3)_3$ corrosion inhibitors into cerium-based rare earth conversion coatings to prepare self-healing coatings. When the self-healing coating on magnesium alloy surfaces was damaged in 3.5 wt% NaCl, the microcapsules released their loaded corrosion inhibitors, replenishing the conversion coating and achieving coating self-healing. Liu et al. [20]prepared polyacrylic acid ester coatings loaded with sodium phytate-loaded mesoporous chitosan microspheres and applied them to copper sheets. The results showed that the corrosion inhibition effect of the chitosan microsphere-coated coating was significantly higher than that of the coating without microspheres in 3.5 wt% NaCl, transforming the water-based polyacrylic acid ester coating into a considerably corrosion-resistant coating.

In conclusion, in the field of self-healing coatings, chitosan can serve as an excellent carrier for corrosion inhibitors or self-healing agents, simultaneously enhancing the mechanical strength and corrosion resistance of coatings, offering a feasible method for strengthening coatings.

5. Conclusion

Chitosan, as a green and low-cost material, can be processed into materials that enhance the anti-microbial corrosion or self-healing properties of various corrosion inhibitors or anti-corrosion coatings due to the unique properties of its molecules. In the field of corrosion inhibitors, chitosan has been extensively studied, with many chitosan-based corrosion inhibitors demonstrating good corrosion inhibition effects, indicating broad research prospects in this area. In the realm of self-healing coatings, chitosan micro/nanocontainers have wide applications, with microfluidics serving as a convenient method for preparing microspheres/microcapsules compared to traditional methods, offering highly monodisperse microspheres/microcapsules and thus representing a feasible direction for future research on chitosan self-healing coatings. Additionally, MIC is an issue that cannot be ignored in chemical production processes. However, research on chitosan coatings for anti-MIC purposes is limited, suggesting significant research potential in this area.

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