Chapter

The Application of Chitosan-Based Compounds against Metallic Corrosion

Brahim El Ibrahimi, Lei Guo, Jéssica Verger Nardeli and Rachid Oukhrib

Abstract

Biopolymers-based compounds were used by different manners for metal protection toward corrosion phenomena, namely via inhibiting additive and coating strategies. In the last decade, the application of these compounds or their chemically modified forms as effective replacements for toxic inorganic and organic inhibitors attracts more attention. Additionally to their intrinsic chemical stability, biodegradability, eco-friendly, low cost and renewability, biopolymers set were shown the remarkable effect to control the dissolution of several metallic materials in various corrosive environments. Among a large variety of available biopolymers, chitosan and its functionalized form, as well as its nanoparticle composites, have been reported and widely used as good anti-corrosion compounds for different metal/medium systems. In this context, the current chapter aims to shed more light on this subject.

Keywords: corrosion, chitosan, chitin, inhibitor, metal, solution, coating, composite

1. Introduction

Metal corrosion is defined as a spontaneous deterioration of metallic materials caused by the adjacent environments (e.g. during the acidic cleaning process) through electrochemical and/or chemical processes. Such a phenomenon is inevitable due to its undesirable outcomes on technological and industrial applications, which leads to huge loss of natural resources, human lives and economic [1]. In this regard, researchers were compelled to perform several scientific investigations to extend the working life of these materials and to overcome the devastating impact of corrosion. Among available technical solutions, the addition of corrosion inhibitors into the aggressive environment seems to be an attractive and economic technic to effectively control corrosion [2]. Diverse organic and inorganic substances have been employed as anti-corrosion compounds for many metal-environment systems [3]. Another efficient strategy to extend the life of metallic-based materials and protect them against corrosion is the application of organic coatings [4–7].

In the present chapter, we interesting in the organic inhibitor category, which its protection ability is related to its adsorption onto the metal surface via electrostatic attraction or/and chemical bond formation, leading to the formation of a protective layer resulting in corrosion mitigation [8]. It is well known that the adsorption process of these compounds occurs via their electron-donator sites like heteroatoms (N, O, S and P) and multiple bonds (π-bonds) and aromatic rings as well. Even they are efficient, recently, the exploitation of organic substances as corrosion retarders has been limited by several strict environmental rules, and such a trend aims to limit their unsafe menace to ecology and health [9].

At this time, the use of biopolymers as promising replacement of toxic corrosion inhibitors is considered a new trend and novel strategy to omit metallic corrosion. One of the key advantages of these bio-macromolecules is their increased attachment sites to the metallic substrate, rising to good film-formation and adhesion as compared to small molecule inhibitors [10]. This capability can be further boosted by the insertion of additional adsorption sites, i.e. functional groups, within the biopolymers backbone [11]. On the other hand, these biopolymers are biodegradable, biocompatible, cheap and non-toxic. Besides, they are readily available and renewable sources of materials [12]. All these characteristics have made them ideal candidates to mitigate ecologically metallic corrosion. In this regards, a large variety of natural polymers are reported to act as anti-corrosion agents to secure the metal against dissolution such as alginate, sodium chitosan, pectin, carboxymethyl and hydroxylethyl cellulose [13, 14].

Among available biopolymers, chitosan (**Figure 1(a)**) was especially exhibited a noticeable ability to control corrosion. It is characterized by the existence of oxygen (of alcohol and ether functional groups) and nitrogen (of amine group) atoms within its backbone chain. These sites are known to act as the effective centers of adsorption to metallic substrates. Chitosan can be obtained by the deacetylation of chitin (**Figure 1(b)**), a natural polysaccharide and the main structural component of crustacean exoskeletons, and is soluble in acid media as compared to chitin, which is a highly insoluble and a non-reactive biopolymer [15]. Furthermore, chitosan exhibits a polycationic character and is non–toxic and biodegradable [16, 17].

Recently, the application of chitosan-based compound as ecofriendly corrosion inhibitor was extended to the use of its functionalized form instead of pure one. Such tendency aims to decorate chitosan backbone with particular functional motifs, generally, through the chemical modification of the amino groups. Furthermore, the enhancement of chitosan capability for protection purposes has been also attained via its combination with other chemical materials to prepare nanoparticle composites, which are served to act as the effective coatings to mitigate corrosion. In this context, it has been reported that the combination of nano-scaled organic and inorganic fillers can successfully improve mechanical, adhesion and barrier qualities of polymer coatings [18]. Among the used additives in the matrix of chitosan-based coatings, there are zinc oxide, graphene oxide and hydroxyapatite nanoparticles.

On this basis, we aimed in the present chapter to shed more light on the merits to employ different chitosan forms as sustainable compounds for corrosion controlling of metallic materials in different aggressive environments.

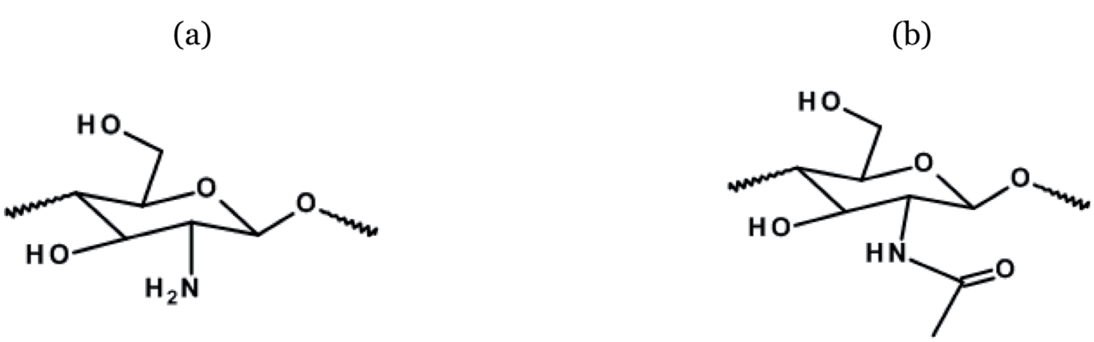

Figure 1.
Molecular structure of (a) chitosan and (b) chitin bio-macromolecules.

2. Application of pure chitosan form as corrosion inhibitor

Chitosan is a naturally occurring polymer that meets the requirements to be classified as a green corrosion inhibitor, which is a low-cost alternative of widely used inhibitors in industrial applications. The solubility of inhibitor into the target corrosive media is one of among key prerequisites that judges its utilization. For instance, such property has limited the use of chitin biopolymer as a corrosion inhibitor. In this regard, temperature, degree of deacetylation, solution's pH and molecular weight are the main factors affecting the solubilization of chitosan in the aqueous media. For instance, at the higher temperatures, with higher molecular weight (>29.2 kDa) and lower deacetylation degree, low water-solubility of pure chitosan was observed [19, 20].

As an inhibiting additive, pure chitosan has been reported to act as an effective retarder of corrosion in different aggressive environments, namely saline and acidic solutions, as well as natural ones such as seawater. Up to now, pure chitosan compound is widely applied for iron and its alloys, like mild steel and carbon steel. This particular attention owing to the fact that these metallic materials are extensively used in numerous industrial applications in which their corrosion is more intense. **Table 1** collects the obtained inhibition efficiency (IE) for pure chitosan for some metallic materials in different corrosive environments. From tabulated data, it is clear that pure chitosan can act as a potent ecofriendly corrosion inhibitor even in the most aggressive environments. This is attributed to the formation of a protective layer upon the metal surface, which prevents it attack by the aggressive species present in the solution.

Metallic material	Aggressive medium	IE(%) at [chitosan]	Ref.
mild steel	0.1 M HCl	93% at 1.8 mM	[21]
carbon steel	1.0 M HCl	93% at 5000 ppm	[22]
mild steel	3.65% NaCl	90% at 1.2 wt%	[23]
copper	1.0 M HCl	87% at 0.1 mg L^{-1}	[24]
copper	Synthetic seawater +20 ppm Na_2S	89% at 800 ppm	[25]
316 austenitic	0.1 M HCl	71% at 11 mM	[26]
mild steel	0.1 M HCl	69% at 4 μM	[27]

Table 1.
Some works on the use of pure chitosan form as corrosion inhibitor.

As mentioned above, the molecular weight of chitosan biopolymer can affect its solubility, consequently, the attained prevention efficiency. In this context, lower inhibition efficiency has been obtained for mild steel in seawater employing chitosan with higher molecular weights [28]. Furthermore, the role of exposure time to the corrosive solution on the ability of pure chitosan to reduce metallic dissolution was also evaluated. In the CO_2-saturated saline environment, the extension of immersion time has implied an improvement in the inhibitive action of chitosan [29]. In another study, the opposite behavior is outlined from which the reduction of the inhibition efficiency is attributed to the destruction of the dense adsorbed film on the metal surface at longer exposure times [30]. Concerning the influence of temperature on the inhibition process of pure chitosan, there is no commune agreement, which a favorable effect is observed by some researchers, whereas the opposite one is reported by other ones [26].

To improve the inhibition property of pure chitosan form for some metal/solution systems, the synergistic corrosion inhibiting effect was applied. In this enhancement strategy, additional compounds such as cations and anions species are added into the corrosive solution with chitosan. As result, remarkable enhancement of protection capabilities of chitosan is pointed out. For instance, the combination of pure chitosan (200 ppm) with 5 ppm of KI was led to a significant improvement of the inhibition efficiency for mild steel in acidic solution, which 90% prevention percentage was achieved instead of 74% in the case of chitosan alone [31]. In this regard, a similar tendency is noted for another steel variety, i.e. St37 steel, in concentrated sulfuric acid solution in which 92% inhibition efficiency is attained [32]. On the other hand, it was found that the adsorption mechanism of chitosan onto metal surface depends on the adopted circumstances. Chitosan can adsorb on the metal surface either via physisorption or chemisorption modes [22, 27].

3. Functionalized chitosan forms as anti-corrosion agents

The current trend in the use of chitosan-based compounds as corrosion inhibitors is its functionalization, afterward its application. This novel approach aims to increase the solubilization of these bio-compounds in almost corrosive media and to enhance their adsorption and adhesion abilities to the metallic surface. In this respect, further polar functional groups are attached to the chitosan molecular skeleton. The chemical modifications of chitosan biopolymer are often performed at amine group, which is an active site. As result, various chitosan-based derivatives with different structural compositions have been synthesized and then used to retard or suppressed metal corrosion in different aggressive environments. Even the simplest chitosan derivative, i.e. carboxymethyl chitosan (**Figure 2(a)**), an improved inhibition efficiency is attained as compared to the pure chitosan form, which is increased from 23 to 38% for steel in wastewater liquids [33].

Depending on the molecular structure, functionalized chitosan-based inhibiting additives could be classified into several categories, namely, chitosan Schiff bases, chitosan surfactants, triazole modified chitosan, chitosan polymeric salts, PEG cross-linked chitosan, carboxymethyl hydroxypropyl chitosan, chitosan thiocarbohydrazide, acid grafted chitosan, acetyl thiourea chitosan, polymer and biomaterial grafted chitosan. Here, we limit to present the inhibition activity of the three first functionalized chitosan sets.

During the last decade, Schiff bases class compounds have been attracted exceptional attention to be applied in the field of corrosion inhibition owing to the presence of imine linkage, i.e. −CH=N−. They are reported to act as potent anti-corrosion compounds for different metallic materials, especially in acidic solutions [34]. In this respect, the synthesis of chitosan Schiff bases derivatives via condensation reaction and/or under microwave irradiations are conducted. It was found that the introduction of Schiff bases functional group into the chitosan skeleton leads to a significant enhancement in the inhibition property and film adhesion of polymer on the metal surface. Generally, the achieved prevention efficiencies using those chitosan-based derivatives were higher than 80%, which outlined that chitosan Schiff base could be an appropriate candidate to employ as effective anti-corrosion agents [35]. Recently, three chitosan Schiff bases derivatives (CSB-1, −2 and − 3, **Figure 2(b)**) have been synthesized under microwave irradiations and tested as corrosion inhibitors for mild steel in acidic solution. According to the obtained experimental data, these modified chitosan compounds were exhibited significant tendencies to reduce metallic corrosion even at a lower concentration, which the supreme prevention efficiencies of 91, 87 and 85% (at 50 ppm) were attained for CSB-3, −2 and − 1, respectively [36]. Another chitosan-modified Schiff base, namely, the salicylaldeyde-chitosan Schiff base (**Figure 2(c)**), has been reported to act as a good inhibitor (IE(%) = 95.4% at

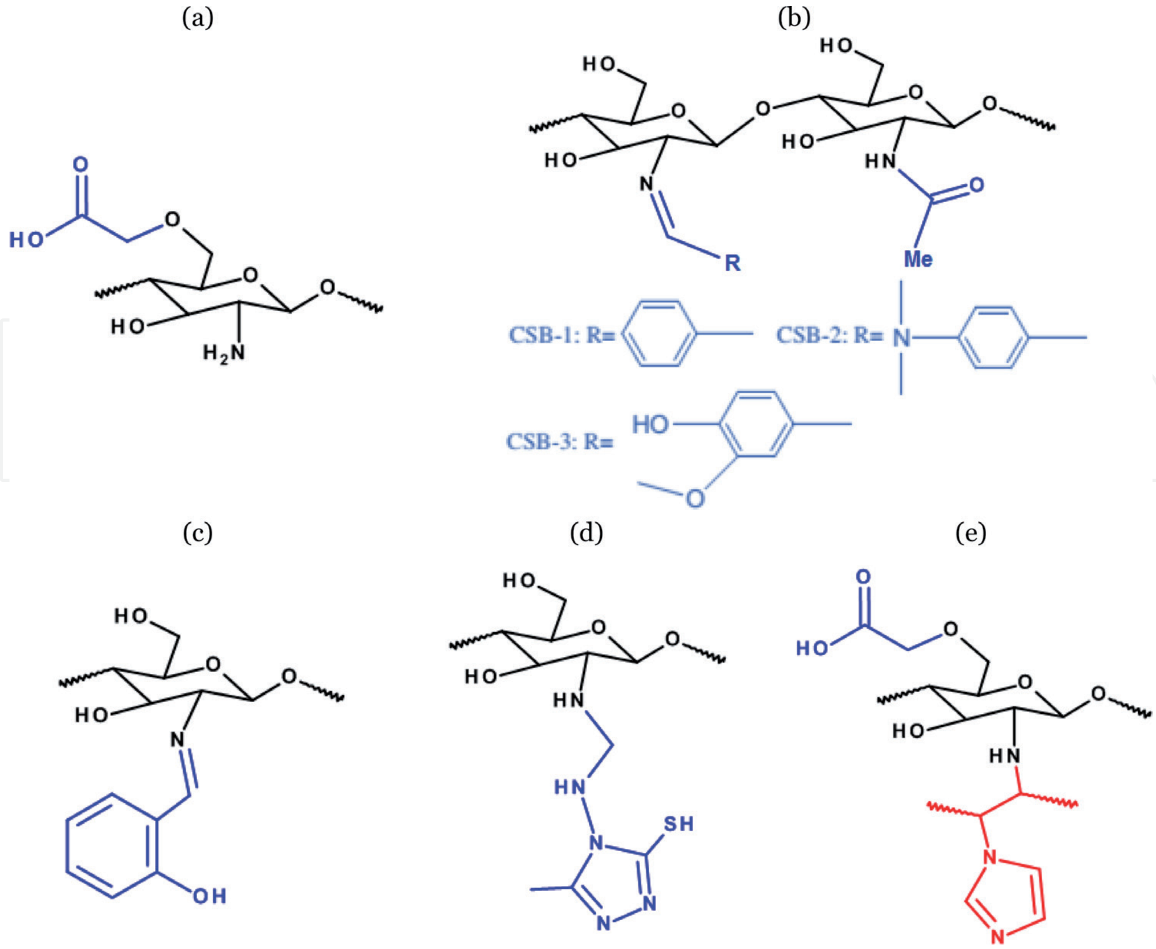

Figure 2.
Molecular structure of some chitosan derivatives used as corrosion inhibitors.

150 ppm) for J55 steel-variety in 3.5% NaCl solution saturated with carbon dioxide at elevated temperature. The merits of developed functionalized chitosan including its eco-friendly aspect, safe, simple and cheap synthesize of used Schiff base, as well as the improvement of inhibitor solubility compared to unmodified chitosan. All these listed advantages make salicylaldeyde-chitosan Schiff base as a good anti-corrosion agent for the oil and gas industries [37].

Surfactant is a surface-active agent that characterizes by the presence of hydrophilic and hydrophobic groups per molecule. These chemical compounds are largely served as effective corrosion inhibitors in the petrochemical industry dues to their affinity to be oriented at the metal/solution interface. In 2012, over 26% was the demand for surfactants as anti-corrosion components only for the petrochemical industry, as well as this request grew by 4.1% per year [38]. To combine the attractive anti-corrosion property of surfactant set with chitosan biopolymer, several chitosan-surfactants macromolecules are synthesized and then evaluated as potential retarders of corrosion. In this regard, the introduction of hydrophobic moiety into the chitosan skeleton has been led to an increase of its hydrophobic property to become surface-active polymers, which in result an enhancement of the prevention capability of chitosan. For instance, a sequence of seven modified hydrophobically chitosan surfactants were produced and their anti-corrosion property is measured for carbon steel in acid medium. As compared to the pure chitosan, good inhibition efficiencies between 93 and 74% (at 250 ppm) are achieved for those surfactants functionalized chitosan derivatives [39]. It was found that carboxymethyl chitosan thio-derivative provides the highest protection. This finding is related to its high surface activity and the presence of more active adsorption centers within its molecular skeleton as well.

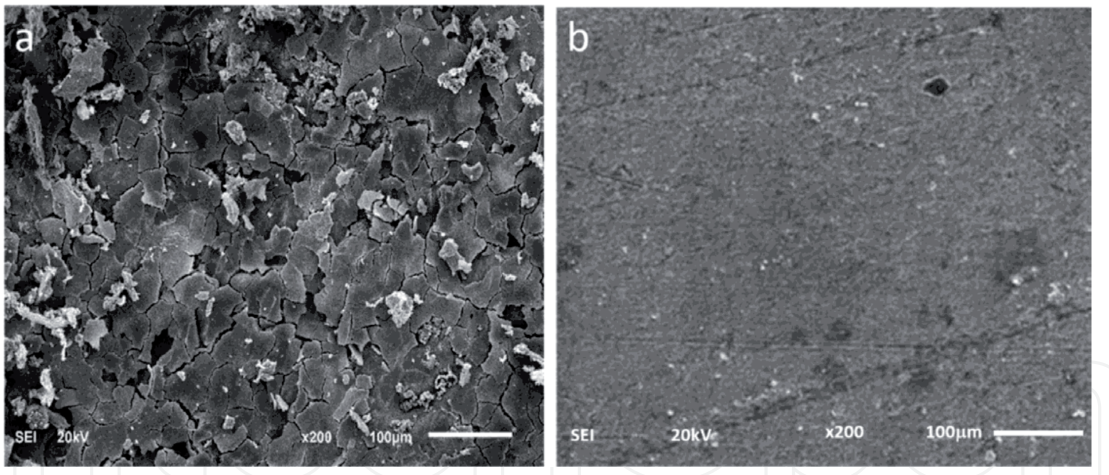

Figure 3.
SEM images of carbon steel surface (a) without and (b) with the addition of developed triazole-modified chitosan at 200 ppm [42].

A wide range of organic heterocyclic molecules has been employed to face against metallic corrosion. In this context, azole-based compounds have shown an excellent capacity to act as good anti-corrosion compounds for several metallic materials in different corrosive environments, especially in acidic ones. The latter molecule set includes N-azole, thiazole and oxazole cyclic molecules with different architectures [40]. The chemical incorporation of azole moieties or their derivatives into the chitosan backbone has shown excellent results in terms of inhibition efficiency. Recently, a novel triazole modified chitosan (**Figure 2(d)**) has been reported to act as an efficient retarder of carbon steel corrosion, which a maximum inhibition efficiency of 97% is reached using just 200 ppm of developed chitosan derivative [41]. The benefic effect of this triazole-modified chitosan biomacromolecule against corrosion can be revealed from the reported scanning electron microscopy (SEM) images as depicted in **Figure 3**. It is clear from **Figure 3(a)** that the morphology of carbon steel surface is more rough and damaged in the absence of modified chitosan inhibitor. Nevertheless, in its presence (**Figure 3(b)**) the morphology of steel surface become smoother, which supports the protection capacity of the developed chitosan derivative. In this work, it was found that the synthesized compound could block cathodic sites at the metal surface via the physical and chemical adsorption process.

In addition to the amine group, i.e. $-NH_2$, the functionalization of chitosan can be also carried out on both extra-functional groups including –OH group. This approach to amplify the inhibiting effect of chitosan has been attracting interest. We can list the example of poly (N-vinyl-imidazole) grafted carboxymethyl chitosan (**Figure 2(e)**), which is a polymer grafted chitosan. The newly synthesized chitosan derivative has exhibited interesting corrosion protection for steel metal in acid solution [43].

4. Using chitosan-nanoparticle composite form for metal protection

Chitosan composites have mainly been applied as inhibiting coatings and are used for corrosion protection purposes in different media. Some works have reported the preparation of composite coatings with chitosan to obtain protective systems to metal substrates [42, 44, 45]. To improve the anti-corrosion properties of the polymeric matrix, it is necessary to invest in improving the mechanical and adhesion properties through the incorporation of inorganic and organic fillers. It is reported that Nano-scaled fillers imply better barrier properties in the polymer coatings compared to the micron-size additives [15]. In general, a schematic for composite formation is shown in **Figure 4**.

Biopolymer chitosan-based nanocomposite coatings have been investigated for protection against copper corrosion [46]. Coatings are composed of chitosan matrix with 2-mercaptobenzothiazole and silica nanoparticles. Overall, the combination of the organic corrosion inhibitor and inorganic nanoparticles enhanced the protection efficiency of chitosan coatings, which is an important advance toward developing sustainable corrosion protection coatings for different metals.

Several researchers have reported the viability of chitosan composites films e.g. chitosan/ZnO nanoparticle composite for protection against corrosion for steel [47, 48] and bio-corrosion inhibition for S150 carbon steel [49]. All of these studies showed that the quality of the chitosan film was improved due to the addition of ZnO nanoparticles. Another study [50] evaluated and compared corrosion protection of carbon steel using two different systems of chitosan e.g. oleic acid-modified chitosan-graphene oxide composite coating and pure chitosan coating. In this case, it was observed that the corrosion protection of oleic acid-modified chitosan-graphene oxide composite coating improved by 100 folds when compared with pure chitosan coating. Thus, oleic acid-modified chitosan-graphene oxide composite is more effective in corrosion protection of carbon steel.

Another composite coating [51] consisting of graphene oxide-chitosan-silver on Cu-Ni Alloy with enhanced anti-corrosive and antibacterial properties show graphene oxide retards the diffusion of corrosive ions to the substrate and minimizes the electron transport between the electrolyte and metal, while chitosan prevents the galvanic coupling of graphene oxide with the metal surface [51].

The system chitosan/hydroxyapatite nanoparticle composites revealed that they could inhibit corrosion in steel, however, it was found that the combination of chitosan/hydroxyapatite nanoparticle with other species provides more effective protection against corrosion [52–54]. Different composites such as chitosan/hydroxyapatite-Mg [55], chitosan/hydroxyapatite-Si [56], chitosan/hydroxyapatite-multiwalled carbon nanotube [57], chitosan/hydroxyapatite-$CaSiO_3$ [58], and chitosan/hydroxyapatite-cellulose acetate [59] were synthesized and tested as corrosion protective layers. The composites chitosan/hydroxyapatite-Mg, chitosan/hydroxyapatite-Si, chitosan/hydroxyapatite-$CaSiO_3$ and chitosan/hydroxyapatite-cellulose acetate demonstrated that the insertion of the third component exhibit a representative improvement in the corrosion protection of the chitosan/hydroxyapatite nanoparticle composite, except for composite chitosan/hydroxyapatite-multiwalled carbon nanotube. Consequently, it could be expected that the presence of carbon nanotubes in any non-conductive polymer coating provides lower protection against corrosion.

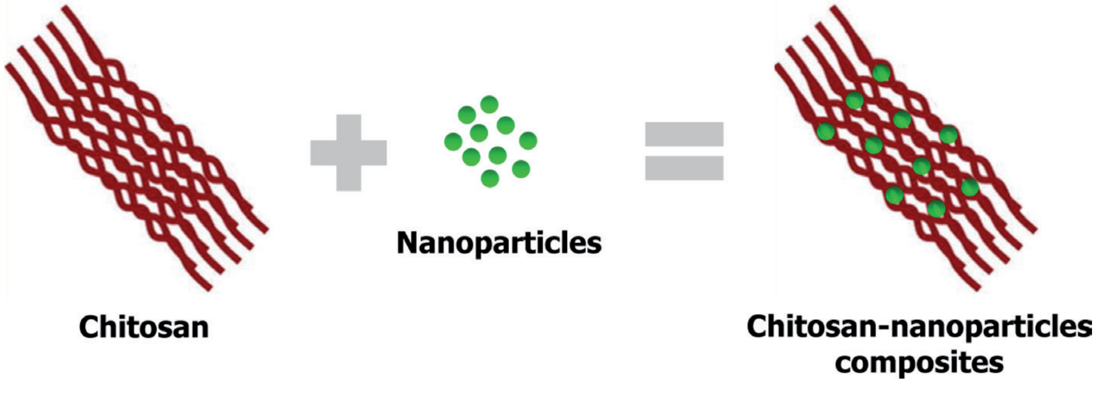

Figure 4.
Schematic presentation of chitosan-nanoparticles composites formation process.

As shown previously, the use of chitosan-nanoparticle composites led to improvements in the corrosion protection of different surfaces, i.e. copper and steel. Bahari *et al.* [46] concluded that addition of nanoparticles contributes to the reduction in swelling of chitosan coatings and crosslinked chitosan coatings are superior to the non-crosslinked ones vis-a-vis in mitigation of corrosion of copper surface. When, John *et al.* [47] concluded that mitigation of corrosion of mild steel by nanostructured chitosan/ZnO nanoparticle films was obtained based on chemical stability, oxidation control of coatings. Therefore, the process of corrosion control depends on the structure of the coating (polymeric matrix, crosslinking, adhesion, among other parameters).

5. Conclusion

Efficient inhibitors and organic coatings are able to extend the life of some metal surfaces. Chitosan is a component with a high potential for protection against corrosion of metals when exposed to corrosive media. In the first stage, the pure chitosan form is used to omit the corrosion of numerous metallic-based materials. Nevertheless, the lower water-solubility of this biopolymer was limited to its application and its utilization to a broad aggressive media range such as near-neutral solutions. Although, such weakness can overcome and the prevention performance of chitosan can be improved through different functionalization demarches. Furthermore, chitosan can be combined with the other materials to develop new chitosan-nanoparticles composites that can apply as coatings.

Author details

Brahim El Ibrahimi[1], Lei Guo[2]*, Jéssica Verger Nardeli[3] and Rachid Oukhrib[1]

1 Team of Physical Chemistry and Environment, Faculty of Science, Ibn Zohr University, Agadir, Morocco

2 School of Material and Chemical Engineering, Tongren University, Tongren, China

3 Universidade Estadual Paulista-UNESP, Instituto de Química, Araraquara, São Paulo, Brazil

*Address all correspondence to: cqglei@163.com

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