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NANOCONTAINERS FOR SELF-HEALING COATINGS ON MILD STEEL

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Abstract

Mild steel is an important material in construction, automobile, and other engineering applications. Long exposure to a corrosive environment causes damage to the material and makes it less efficient for usage. Various methodologies such as barrier coatings and self-healing coatings are employed to prevent corrosion to occur. To increase the performance of the coatings, modifications are carried out by the addition of corrosion inhibitors into the coating matrix. Direct addition leads to unwanted reactions with the coating matrix and loss of corrosion inhibitor itself. In order to prevent this problem, nanocontainers are used to encapsulate the self-healing agent/corrosion inhibitor. Therefore, recent corrosion prevention methods involve the fabrication of multifunctional coatings using different nanocontainers such as halloysite nanotubes, polymeric microcapsules, layered double hydroxide, etc. loaded with corrosion inhibitors. The release of corrosion inhibitors works on trigger mechanism arising due to change in external stimuli and thus increasing the durability of the coatings.
Key words: Corrosion protection; Nanocontainers; Self-healing; Mild steel

1. Introduction

Mild steel is regarded as one of the best industrial materials used in automobiles, construction (buildings, bridges, chemical reactors, etc.), and pipeline industries. Due to its ease of availability and cost-effectiveness, it is widely used in engineering applications. It possesses high mechanical strength, toughness, malleability, and ductility, because of which it is used in the aforementioned sectors readily [1]. Despite several applications, mild steel has poor corrosion resistance, because of which they are reactive to the outer environment when exposed for increased time duration. Corrosion is the chemical oxidation reaction leading to oxide film formation on the surface and making it less useful for extended use and vulnerable to the deterioration [2].

In order to prevent corrosion, the most common method is the use of protective coatings in the form of paints. These coatings function as a barrier between the surface of the metal and the corrosive media and hence provide protection [3]. However, paints are not adherent when directly applied on mild steel substrates, and hence hexavalent chrome based or phosphate based conversion coatings that act as adhesion promoters are used prior to painting. Due to their toxicity and carcinogenic nature, these conversion coatings have been forbidden to be used [4]. An environment friendly alternative is the use of sol-gel coatings. Since these coatings may get damaged with time leading to corrosion, corrosion inhibitors were directly added into the sol-gel matrix in order to inhibit the corrosion. The major drawback of this method was the solubility and chemical reaction of the inhibitors with the coating, which deteriorates the protection capability of the coating matrix. Recent research has shown the use of encapsulation methods to store and confine the corrosion inhibitors into nanocontainers in order to minimize excessive leaching as well as to prevent unwanted reactions between the coating and the corrosion inhibitors. These nanocontainers when embedded into the coatings provide corrosion resistance by actively releasing the corrosion inhibitor in a controlled manner [5].

Based on the extensive research investigations in this direction, different types of micro and nanocontainers proposed for corrosion protection are discussed/analyzed based on their shape, size,

and geometry. These nanocontainers are classified into nanotubes, nanofibers, nanolayers, and porous microstructures [6,7].

2. Nanocontainers based self-healing coatings

2.1 Nanotubes

Falcon et al. [8] have reported the use of halloysite nanotube (HNT) for encapsulation of dodecylamine (DOC) as an efficient corrosion inhibitor for carbon steel. The inhibitor loaded HNT was dispersed into the alkyd primer at 10% and coated on carbon steel. The electrochemical impedance spectroscopy (EIS), scanning vibrating electrode technique (SVET) and salt spray tests showed the self-healing behaviour of the coatings because of the controlled release of the corrosion inhibitor from the lumen of the HNT when subjected to change in pH. Joshi et al. [9] have used three different types of corrosion inhibitors: benzotriazole (BTA), mercaptobenzothiazole (MBT) and mercaptobenzimidazole (MBI) for loading into HNT. Tube ends were sealed using urea-formaldehyde and copper as end stoppers to achieve controlled release of the corrosion inhibitors. The loaded tubes were mixed in the alkyd paint and coated on steel panels. To observe the self-healing behaviour, the panels were dipped in 0.5 M NaCl solution and current density maps were obtained. The corrosion current scans obtained after SVET analysis shows that the mercaptobenzimidazole and benzotriazole loaded HNT with urea-formaldehyde microcapsules as end stoppers proved to be better corrosion inhibiting materials for the protection of mild steel. Xing et al [10] reported the use of HNT loaded with Na_2MoO_4 as a corrosion inhibitor and $CaMoO_4$ as end stoppers to control the release rate of the corrosion inhibitor. Different loading percentages (5, 10, and 15 wt%) of the end stoppered-inhibitor loaded halloysite nanotube was mixed with an epoxy matrix and was deposited on Q235 steel. The steel coupons were immersed in 3.5 % NaCl solution before performing electrochemical and immersion studies. The EIS and salt immersion data obtained showed that the optimized loading of 10 wt% exhibited the highest corrosion resistance and least extent of corrosion products on the surface, suggesting the controlled release of the corrosion inhibitor to obtain the self-healing behaviour. Nawaz et al. [11] have reported the use of titania nanotubes (TNT) for loading dodecylamine (DOC) as corrosion inhibitor. The encapsulated TNT was dispersed into the epoxy coating, and the properties of the coating were observed after immersing in the corrosive media at two different pH, 2.0 and 5.0. The EIS investigation showed that the coatings exhibited enhanced anti-corrosion performance at pH 2 where the active release of the corrosion inhibitor was efficient, rather than at pH 5. Abdulrahaman et al. [12] have synthesized multi-walled carbon nanotubes (MWCNTs) using acetylene and Fe-Ni/ kaolin as the catalyst. The MWCNTs were characterized using high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), differential thermogravimetry (DTG), and thermogravimetric analysis (TGA). The synthesized MWCNT was dispersed in appropriate amount of water/Arabic gum mixture using ultrasonication followed by coating on mild steel panels. The first set of samples were heated at austenitic temperature of 900 °C whereas second set of samples were heated to 950 °C for different time periods (30, 60 and 90 min) followed by soaking. The mechanical properties such as hardness, tensile strength and yield strength were found to be the best for samples heated at 950 °C with holding time of 90 min, and similar results were obtained from electrochemical measurements. The samples heated at temperature of 950 °C for 90 min possess good anti-corrosion properties suggesting that the increase in heat treatment temperature and holding time increased the corrosion protection efficiency of the coatings to a much greater extent. The schematics of different nanotubes mentioned above are shown in Fig. 1.

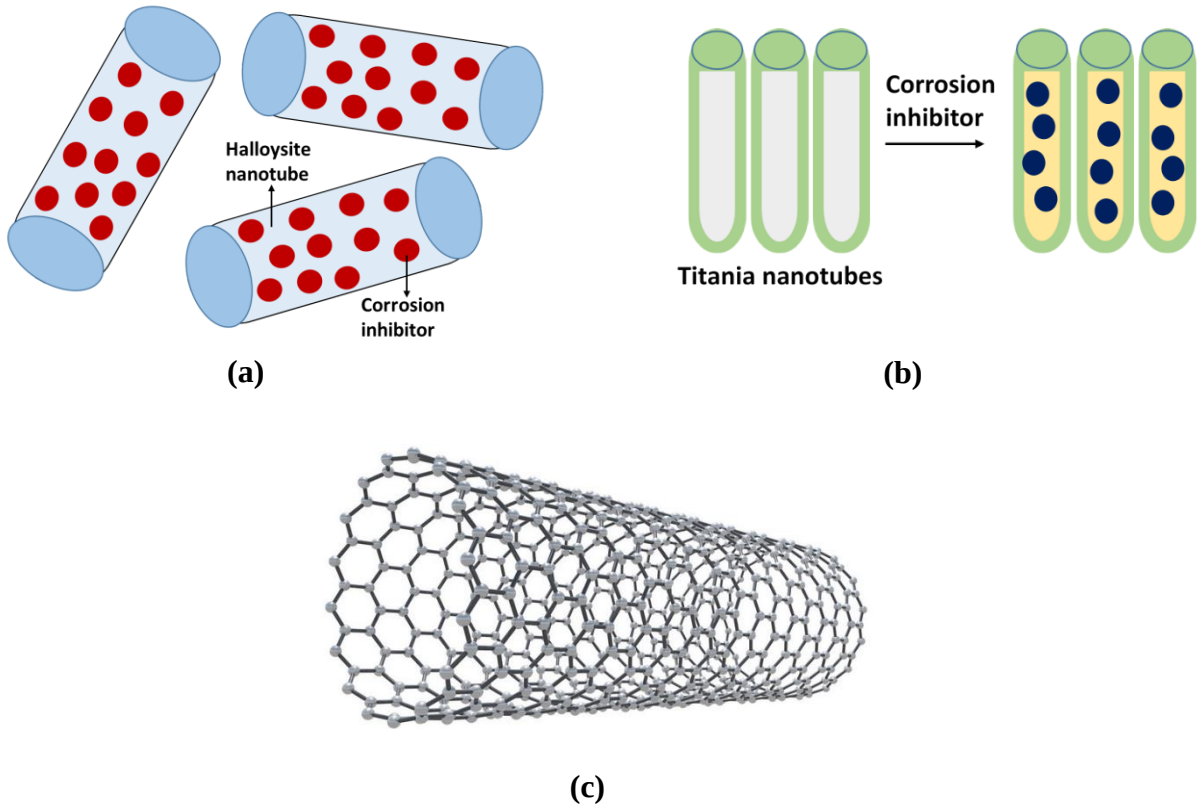

Fig. 1. Different types of nanotubes **(a)** Halloysite nanotube and **(b)** Titania nanotube loaded with corrosion inhibitor and **(c)** Carbon nanotube

2.2 Nanofibers

Yao et al. [13] have synthesized polyaniline (PANI) nanofibers using the interfacial polymerization method. To observe the anti-corrosion behaviour of the PANI nanofiber and aggregated PANI, two different coating formulations were prepared using PANI nanofibers and aggregated PANI and were deposited on carbon steel. The coated steel samples were exposed to 5 % NaCl solution to evaluate the electrochemical properties. The results showed that the PANI nanofibers have better corrosion resistance than aggregated PANI which is ascribed to the uniform and dense coating obtained using PANI nanofibers because of the excellent dispersivity in ethanol. Raman spectral analysis further confirmed the chemical composition of the passive layer formed on the surface. PANI nanofiber coated sample showed the presence of α-Fe_2O_3 and Fe_3O_4 corresponding to the formation of a thin passive film which in turn protects the mild steel from getting corroded further. Zhang et al. [14] have reported the use of epoxy microcapsules along with PANI nanofibers to incorporate into the conventional epoxy/polyamide coatings to obtain uniform and dense coating on mild steel. EIS studies were carried out after immersing the steel substrates in 12 wt% NaCl solution for 100 days at room temperature. The results obtained indicate that the controlled release of epoxy fluid from the microcapsules imparts protection and autonomous-healing properties whereas the PANI fibers form a passive film acting as a barrier to protect the metal surface from corrosion. Zhao et al. [15] in their work reported the synthesis of electrospun microfibers using a mixed solution of PANI and PMMA (polymethylmethacrylate). Different coating formulations were prepared using

different loading percentages of PANI (4, 8, 15, 25, and 35 wt%) and were coated on Q235 steel for evaluating the anti-corrosion performance. For comparative studies, PANI/PMMA coating obtained by drop-casting technique was chosen as a reference. The electrochemical results recorded after immersing the steel panels in 0.1 M H_2SO_4 solution showed that the coating obtained with 25 wt% PANI possessed better protection (η = 99.9%) among all loading percentages and drop-casting PANI/PMMA coated substrates. The obtained high protection with 25 wt% PANI can be attributed to the formation of a compact film which restricts the entry of the corrosive media. The polarization and electrochemical data reveal that the corrosion resistance increases with an increase in the dosage of PANI. The optimized loading of 25 wt% has shown superior corrosion resistance properties, and the schematic illustration of nanofibers deposited on substrate is shown in Fig. 2.

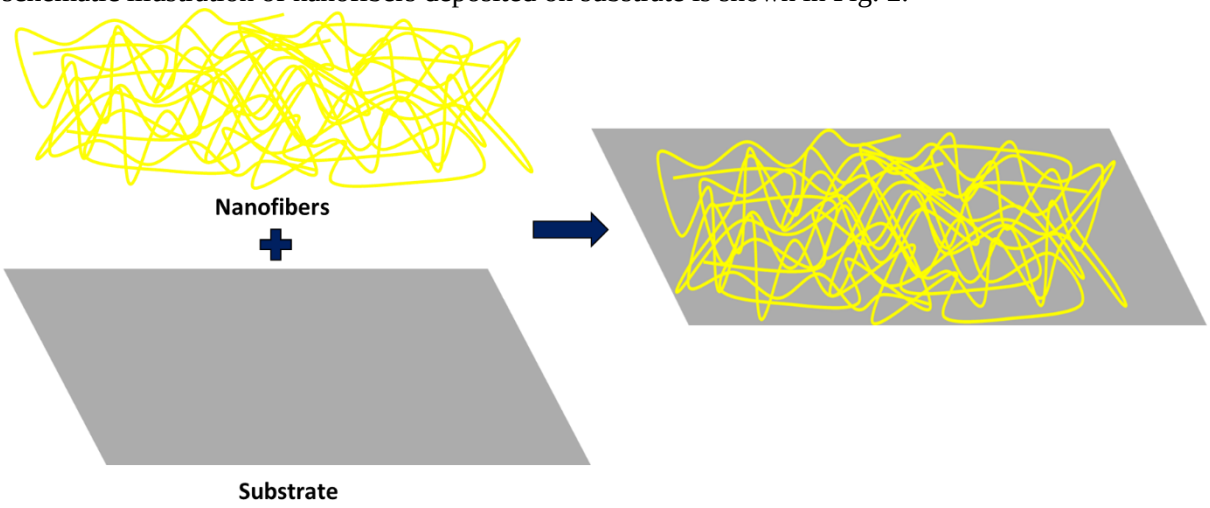

Fig. 2. Synthesized nanofibers deposited on the substrate

2.3 Nanolayers

Arora et al. [16] reported the synthesis of layer-by-layer (LbL) nanocontainers using lanthanum cerium molybdate (LCM) nanoparticles synthesized by sol-gel method. The synthesized LCM nanoparticles were used as the core onto which two different combinations of polyelectrolyte layers were deposited as the shell, and a corrosion inhibitor was sandwiched between the layers. One type of nanocontainers was made up of LCM nanoparticles/polypyrrole/benzotriazole/polyacrylic acid LbL configuration, abbreviated as LCM/PPY/BTA/PAA, and was used for mild steel substrates. The other type of nanocontainers was made up of nanoparticles/polyethyleneimine/benzotriazole/polystyrene sulfonate combination, abbreviated as LCM/PEI/BTA/PSS, and were used for magnesium alloy. The nanocontainers were then mixed into the epoxy coating and coated on the metal surface. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA) were carried in order to investigate the loading of the corrosion inhibitor into the nanocontainers, crystallinity, surface morphology, and thermal stability of the nanocontainers. Electrochemical measurements reveal that the coatings possessing nanocontainers have the highest corrosion resistance compared to only nanoparticles dispersed epoxy coated substrates. In another paper, Liu et al. [17] discuss the use of pH-responsive attapulgite (ATP) nanoparticles covered with polyelectrolyte layers of PEI and PSS with BTA layer sandwiched in between the polyelectrolyte layers. The obtained nanocontainers were added at 2 wt% to the epoxy resin and applied on Q235 carbon steel. The loading of corrosion inhibitor and surface morphology of the coatings was confirmed using transmission electron microscopy (TEM), SEM, XRD, and BET analysis. The corrosion performance and self-healing behaviour of the bare and coated substrates were evaluated using electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM), respectively. The EIS results reveal that the coating acts as a barrier because of the presence of nanocontainers in the matrix. Further, the corrosion inhibitor is released and healed the affected zone by forming a passive film on the metal surface. Edraki et al. [18] have reported different types of nanolayers based on ion exchange to protect the mild steel surface. The investigation focuses on the

use of 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzimidazole (MBI) as corrosion inhibitors which were intercalated between the layers of sodium montmorillonite clay (Na^+-MMT). XRD analysis was carried out to confirm the loading of corrosion inhibitors into MMT. The corrosion studies were performed after immersing the mild steel samples into different solutions; blank, MBT, MBI, MMT-MBT, MMT-MBI, and Na^+-MMT. The corrosion protection efficiency observed for MMT-MBT and MMT-MBI was very high when compared to only MBT, MBI, and Na^+-MMT. The SEM images obtained after immersing the samples for 24 h in the respective solutions suggest that the MMT-MBT absorbed surface has shown more uniform layer formation, hence confirming the inhibition action of the corrosion inhibitor. Duong et al. [19] reported the use of layered double hydroxides (LDH)/graphene oxide (GO) hybrid for intercalation of 2-benzothiazolylthio-succinic acid (BTSA) as an effective corrosion inhibitor. FTIR spectra, XRD profiles, and SEM images were recorded for GO, LDH-BTSA, and LDH/GO-BTSA to confirm the loading and surface morphology of the layered nanocarrier. For analyzing the corrosion protection performance, the carbon steel samples were immersed in the corrosive media (0.1 M NaCl solution) consisting of LDH/BTSA and LDH/GO-BTSA at 1 g/l concentration for 2 h. The polarization data indicate that the inhibition efficiency for LDH/GO-BTSA was 94.2 % whereas it was 85.5 % for LDH-BTSA. The high inhibition efficiency of LDH/GO-BTSA could be explained with the presence of GO, which also shows corrosion inhibitive action in addition to BTSA. Different types of nanolayer based nanocontainers are shown in Fig. 3.

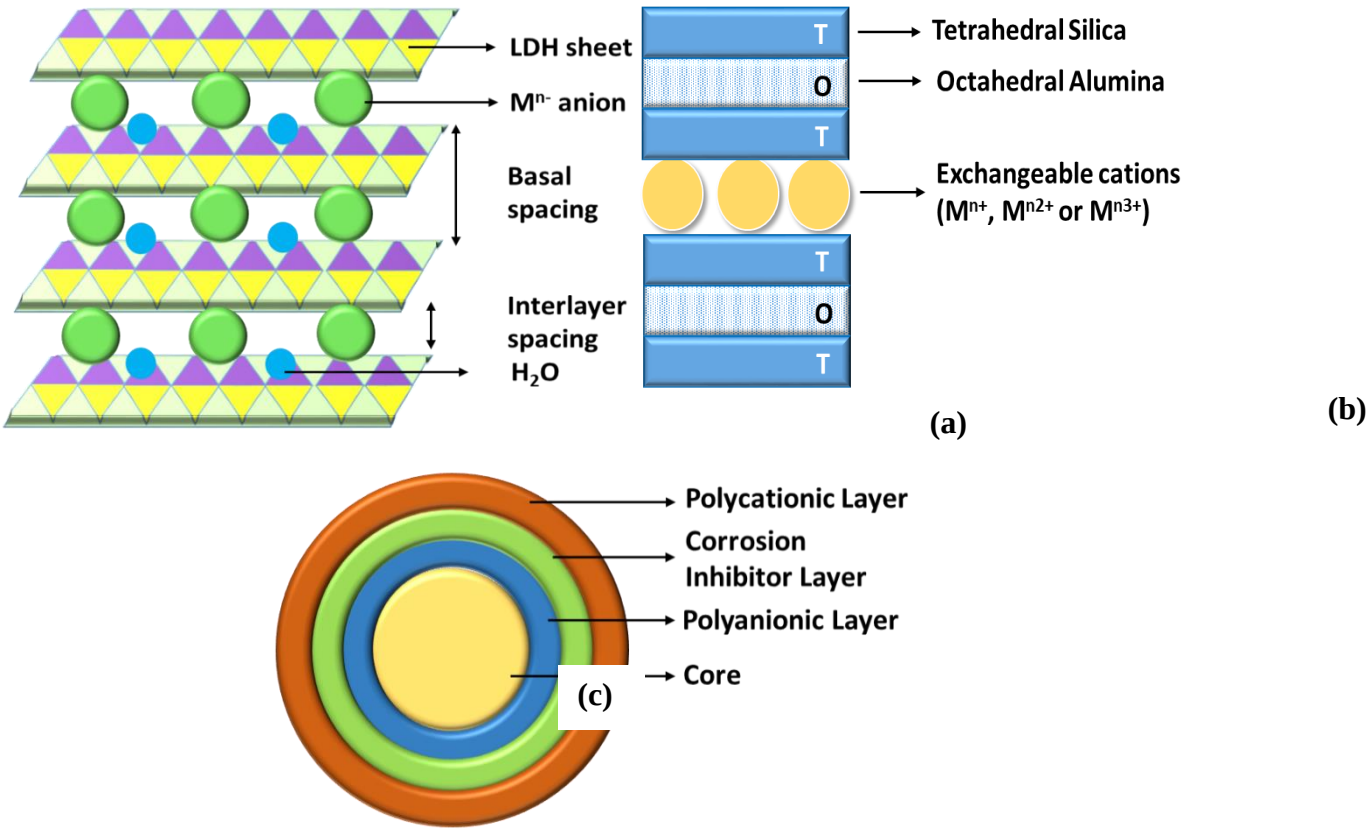

Fig. 3. Different types of nanolayer based nanocontainers: **(a)** Layered double hydroxide, **(b)** Montmorillonite clay and **(c)** Layer-by-Layer nanocontainer using polyelectrolyte layers

2.4 Porous microstructures

Roselli et al. [20] have reported the use of Cerium (Ce) ions as an effective corrosion inhibitor and loaded into the porous zeolite microstructure in order to replace the phosphate based

coatings on SAE 1010 steel panels. Two different zeolite compositions were used and were abbreviated as Z_1 and Z_2. XRD pattern obtained for both the rocks revealed that the concentration of mordenite was higher in the case of Z_1 (more than 80%) than Z_2 (50-80%). SEM images obtained for both zeolite rocks and zinc phosphate (PZ) showed that the average particle size was <10 µm. Five different coating formulations were prepared and the following nomenclature was assigned: control alkyd coating (C), Ce-Z_1/coating (1A), Ce-Z_2/coating (1B), Ce-Z_1/PZ/coating (2A), and Ce-Z_2/PZ/coating (2B). Electrochemical studies were carried out after immersing the coated steel panels in 0.5 M NaCl solution for 1, 18, and 31 days. The results suggested that the modified zeolite based coatings could effectively replace the zinc phosphate coatings partially with the use of Z_2 or totally with the use of Z_1. The corrosion protection increased for the modified zeolite based coatings because of the presence of Ce (III) ions as a corrosion inhibitor. Yeganeh et al. [21] proposed the use of mesoporous silica (MS) based nanocontainer with Na_2MoO_4 (NMO) as a corrosion inhibitor to be loaded into the nanocontainer. The composite coatings were generated by mixing Na_2MoO_4 loaded MS nanocontainers into the polypyrrole (Ppy) matrix and coated on steel substrates. FESEM images revealed that the MS powder has hexagonal pores, which was confirmed further from the observed XRD pattern relevant to the hexagonal structure of the powder. BET analysis indicated that the pore volume and diameter decreased after loading the corrosion inhibitor. The corrosion behaviour of the Ppy/MS(NMO) and Ppy/MS coated substrates was evaluated after immersing the substrates in 2 g dm^{-3} NaCl solution at pH 8. Results of the electrochemical impedance and polarization studies indicate that the incorporation of the corrosion inhibitor NMO increased the coating functionality to much higher extent as it protects the surface from corrosion attack. Further, the inhibitor restricts the formation of the corrosion products rather it helps in forming a passive layer as soon as the inhibitor is released in the vicinity of the damaged area. Figure 4 shows the schematic representation of different types of microstructures used for encapsulation.

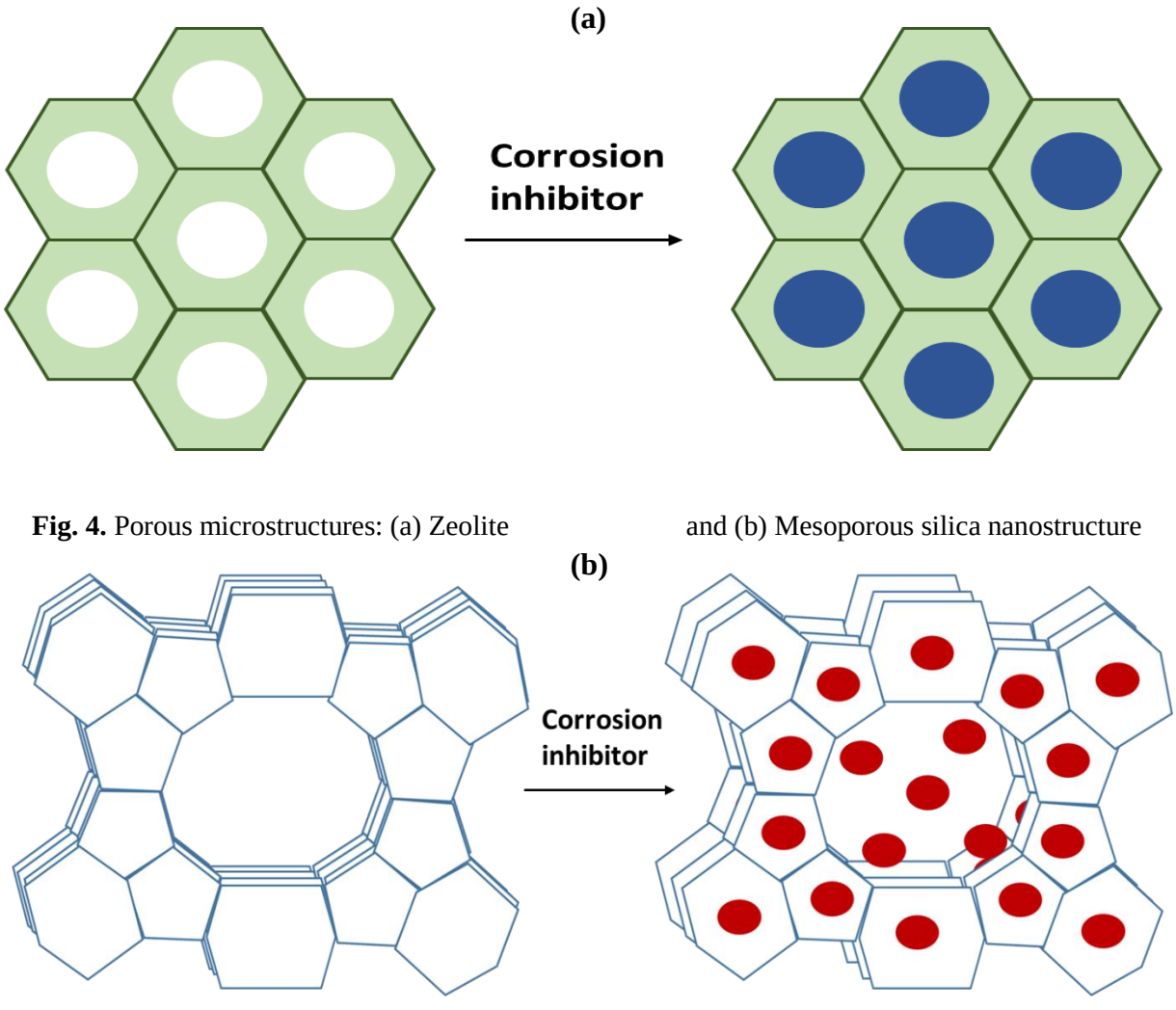

Fig. 4. Porous microstructures: (a) Zeolite and (b) Mesoporous silica nanostructure

3. Conclusions

Surface coatings obtained with the incorporation of different types of nanocontainers impart self-healing properties. This review provides insight into various types of nanocontainers used to protect mild steel on exposure to aggressive corrosive media. The nanocontainers are used as an encapsulating agent for storing and retaining the corrosion inhibitors. Nanocontainers store and seal the incorporated active corrosion inhibitors and keep them aside from leaching and/or reacting with the coating matrix, thereby enhancing the stability and durability of the surface coating. Encapsulation enables the sustained and controlled release of the corrosion inhibitors precisely at the time of the corrosion attack on demand, and thus enhanced corrosion protection efficiency would be observed with surface coatings comprising inhibitor loaded nanocotainers. With these additional functionalities, the coating properties can be enhanced to a much higher extent, and thus the durability of the mild steel substrates would be increased making it more useful for modern-day industrial applications.

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