Indian Journal of Chemical Technology
Vol. 31, March 2024, pp. 233-239
DOI: 10.56042/ijct.v31i2.3511

Synthesis of aluminium oxide nanoparticles from waste aluminium foils for corrosion inhibition of mild steel pipe

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Received 1 July 2023; accepted 31 January 2024

The driving force of Oman's economy is oil and gas industries with a fairly diversified treasure among Gulf cooperation council countries. The corrosion problems in oil pipelines would be successfully resolved by means of novel control techniques. The current study aimed to synthesize aluminium oxide (Al_2O_3) nanoparticles from waste aluminium foil and to assess its potential application in corrosion inhibition of mild steel pipe. Al_2O_3 nanoparticles have been synthesized by facile co-precipitation technique at room temperature. The synthesized Al_2O_3 nanoparticles have been used to fabricate nanocomposite thin films using a biopolymer, chitosan by dip coating technique and to carry out corrosion inhibition studies of mild steel pipe. The characterisation techniques employed are scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, energy dispersive X-ray analysis, atomic force microscopy. Atmosphere test and Wet/Dry tests are carried out to investigate the corrosion behaviour of coated specimen. From the experimental studies, it is observed that the chitosan – Al_2O_3 nano thin film could inhibit the corrosion and also to enhance the lifespan of the mild steel pipe. This novel research project is aligned with the United Nations Sustainable Development Goals (UNSDG- 9: Industry, Innovation and Infrastructure) and Oman vision 2040. The study demonstrates that the chitosan – Al_2O_3 composite thin films fabricated using dip coating technique with minimum film thickness can be a feasible solution in controlling the corrosion in oil pipelines with good film stability, high durability, with a cost effective and environmentally friendly approach.

Keywords: Aluminium oxide nanoparticles, Chitosan, Corrosion inhibition, Dip coating, Layer by layer

Introduction

Corrosion is a massive problem in the manufacturing sectors, particularly in oil and gas industries which causes damage to oil pipelines. Corrosion is the deterioration of materials due to its interaction with the surrounding environment and it affects the pipe material and accessories. Pipelines are ruptured due to corrosion, which would result in oil spillages and eventually end up in environmental pollution. Nearly 45% of Oman's Gross Domestic Product (GDP) is from oil and gas sector. Recent statistical data from the National Centre for Statistics and Information (NCSI) reports the production of crude oil will increase to 9.4% by the end of May 2023 to reach 157,462,200 barrels compared to the year 2022[1,2]. Nanotechnology helps to control corrosion problems in pipelines and also protects the metal surface from harsh environment. Nanoparticles are gaining attention due to their specific physical, chemical and physicochemical properties and hence result in improved corrosion protection compared with bulk size substances.

Corrosion in pipe material results in huge loss of money. Finding an economical and feasible solution to address the corrosion issues in oil pipe lines is important. The application of nanomaterials in the form of nanocoating will enhance the lifetime and therefore increase the profit with reduced maintenance cost. The conventional corrosion control techniques are either less efficient or more expensive with reduced durability. The thin film mediated corrosion control techniques by the combination of nanoparticles and biopolymers are the hot topic of discussion in recent times. The nano thin films can be fabricated using chemical vapour deposition (CVD), sputtering, aerosol-jet deposition, and spray pyrolysis[3]. The cheap source of Al_2O_3 is aluminium foils, which are mainly used for food wrappings and are discarded into open landfills after use. The disposal of waste aluminium foil creates environmental pollution due to the accumulation of huge quantity of the solid waste. In recent times, various processing techniques are adopted by researchers to reduce the solid waste disposal. The best method to manage the disposal of aluminium foil into the environment is recycling[4]. The currently adopted solid waste management is not very effective and produces severe environmental concerns in the form of greenhouse gas emissions[5]. The recycling process involves utilization of heavy machines that are used to shred, melt and compress the aluminium. In this study, the accumulated waste aluminium foil from open landfill was collected and effectively recycled in an environmentally friendly way. The ecofriendly approach will be beneficial to society by offering good health and also encourages value creation of the waste materials. This research focused on the utilization of green and facile method to extract Al_2O_3, since it reduces the energy requirement and also lessen the gaseous emissions. The current study attempted to synthesize and characterize Al_2O_3 nanoparticles from aluminium foil and to assess their potential applications in corrosion inhibition of oil pipelines. Recycling of aluminium waste will lead to severe environmental concerns[6]. The melting of aluminium foil results in emission of oxides of nitrogen and sulphur leading to air pollution. The noxious gases discharged from the melting process causes skin allergy, cancer, impairment of immune system, and liver damage[7,8].

The utilization of nanotechnology mediated techniques offers promising solutions to corrosion inhibition of oil pipe lines by depositing thin films in the form of protective coatings at atomic levels[9-11]. Studies show that the nanocomposites developed from TiO_2 nanoparticles and polyaniline performed well in the corrosion inhibition studies of carbon steel pipes. SiO_2 nanoparticles were also considered for the corrosion inhibition studies and to intensify the hydrophobicity[12-15]. The mechanical, antibacterial and corrosion resistance properties are improved with increased dosage of TiO_2 in the polymer composite[16,17]. The influence of varying amounts of Al_2O_3 nanoparticles on corrosion behavior of aluminum alloy in simulated vehicle coolant has been studied [18]. Layer by layer deposited thin films from polymer clay nanocomposites with nanometer thickness exhibited exceptional corrosion resistance[19]. Biopolymers are considered as environmentally friendly corrosion inhibitor; however, more studies are needed to investigate the effectiveness in acidic environment[20]. This plant extract based corrosion inhibitors are employed as alternative environmentally friendly corrosion inhibitors[21].

Regardless of the extensive research conducted during the past few decades, the surface characteristics of coating and the corrosion inhibition mechanism are not fully understood. Hence, further studies are necessary to advance the effectiveness of the coating. Therefore, here novel nanocomposite thin films were developed using a bio-polymer and Al_2O_3 nanoparticles and their performance in corrosion inhibition of mild steel specimen was assessed. The nanocomposite thin films were fabricated by dip coating technique using chitosan; a natural polymer found in crab shells. The importance of this research is the utilization of environmentally friendly polymer and Al_2O_3 nanoparticles. Al_2O_3 are preferred in this research due to their cost effectiveness, specific physical, chemical and physicochemical properties so as to improve corrosion inhibition rate.

Experimental Section

The waste aluminium foils were collected from the local landfill site and washed to remove the accumulated dusts and debris. The cleaned aluminium foils were dried in an oven at 90 °C for 4 h. Mild steel (Q235C) specimen was received as gift from Oman Qaboos Company (OQ), Oman. Al_2O_3 nanoparticles were synthesized from waste aluminium foil by green synthesis followed by co-precipitation using citric acid. The characterization techniques employed were scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray analysis (EDX) and dynamic light scattering (DLS). The surface topography was identified using atomic force microscope (AFM XE-100 model, Park Systems, Suwon, South Korea) operated in non-contact mode.

Synthesis and characterization of Al_2O_3 nanoparticles

Al_2O_3 nanoparticles were synthesized by green synthesis method by mixing 10.0 g of waste aluminium foil with 10.0 mL HCl, 76.62 g Al_2O_3, and 66.62 g citric acid under vigorous stirring at room temperature. The reaction was continued for 15 h until the colour of the solution turns to light golden colour. The resulting mixture was dried in an oven for 24 h under controlled temperature of 80 °C. Then, the dried product was ground into fine powder.

Preparation of coating solution

The chitosan solution (1% wt/v) was prepared by dissolving 1.0 g of chitosan in 100 mL of acetic acid under stirring at 50 °C for 6 h. After 6 h, the chitosan solution was mixed with 0.3 g of Al_2O_3 nanoparticles and stirred for 12 h, followed by sonication until the solution turns yellow colour to form the required nanocomposite.

Coating of mild steel specimens

The cleaned mild steel pipe was dipped in the coating solution at varying amounts of Al_2O_3 for 1 min to deposit the nanocomposite layer on the surface of pipe material. After required layer deposition, the coated specimen was dried to room temperature. The corrosion rate of the coated and uncoated specimen was tested by atmospheric and wet/dry test. The thin film stability and corrosion inhibition studies at various pH and environmental conditions were performed using coated steel pipes. The coated specimen was air dried at 60 °C for 1 h followed by corrosion studies. The weight difference method was used to gauge the corrosion rate. The corrosion rate in mils per year was calculated using the equation

$$\text{Corrosion rate (mpy)} = \frac{W \times 22300}{A \times t \times \rho}$$

Where, W is the weight loss (g), A is the area of coupon (cm^2), ρ is the density of coupon (g/cm^3) and t = time of exposure in corrosive environment (days).

Results and Discussion

The Al_2O_3 nanoparticles were successfully synthesized by green synthesis using citric acid. The SEM image shown in Fig. 1 reveals the particles are evenly distributed with some aggregation. The particle size analyses of the Al_2O_3 nanoparticles are determined using DLS and the average particle size was found to be 30 nm as shown in Fig. 2. This displays only one peak confirms the particles are more or less uniform without clustering of particles. Comparable size distribution of the nanoparticle plays a significant role in the formation of a stable thin film.

The XRD patterns of the synthesized Al_2O_3 nanoparticles were recorded using a PAN alytical XPERT PRO diffractometer operated at room temperature with a diffraction angle (2θ) ranges from 10° to 90°. The diffractogram of the Al_2O_3 particles demonstrated in Fig. 3 shows a broad peak (halo) or large bump indicates amorphous phase and the intensity

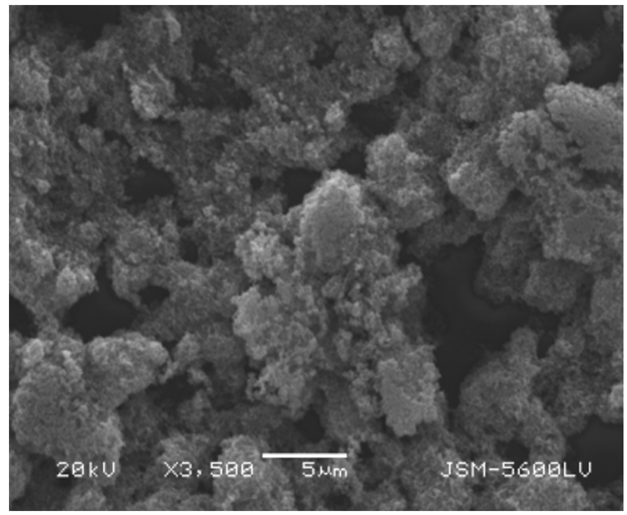

Fig. 1 — SEM image of Al_2O_3 nanoparticles

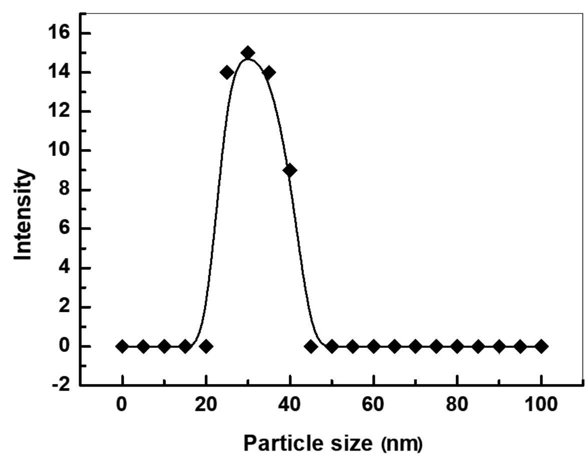

Fig. 2 — DLS of Al_2O_3 nanoparticles

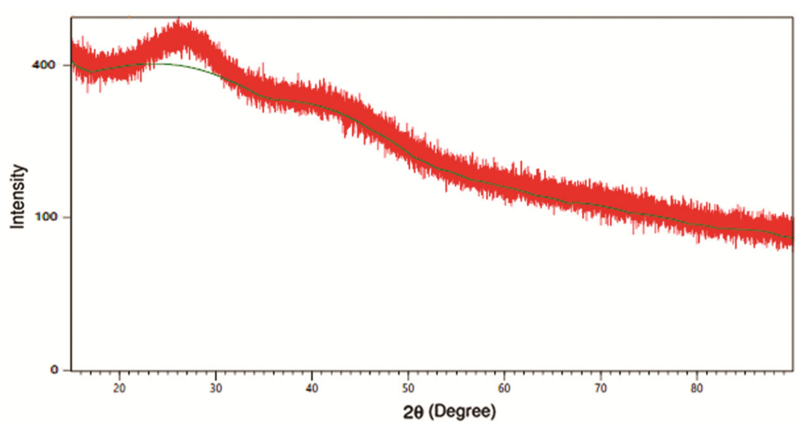

Fig. 3 — X-ray diffractogram of Al_2O_3 nanoparticles

varies with the scattering angle and hence form very broad peak. No sharp peaks are observed in the diffractogram implying the amorphous structure of the sample. The largest peak observed at angle 2θ = 29.57° reveals the successful formation of nanoparticles with high yield, which could be attributed to the presence of the Al_2O_3. The obtained diffractogram are well matched with the published results, which confirmed the amorphous phase of Al_2O_3 nanoparticles[22].

The microstructural analysis of the chitosan – Al_2O_3 nanocomposite film using SEM is shown in Fig. 4, which shows the morphology of the deposited thin films on the surface of mild steel specimen. The homogeneous distribution of layers with enhanced thickness indicates the effectiveness of coating process. SEM image reveals the formation of nanostructured thin film confirms the formation of homogenous, uniform and crack-free surface.

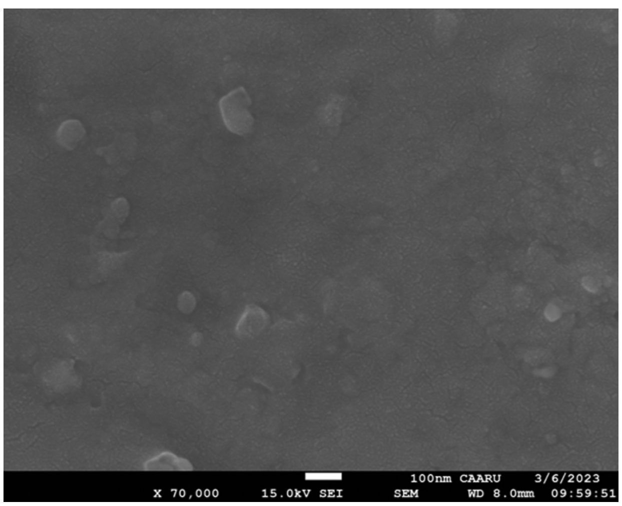

Fig. 4 — SEM image of chitosan – Al_2O_3 nanocomposite film

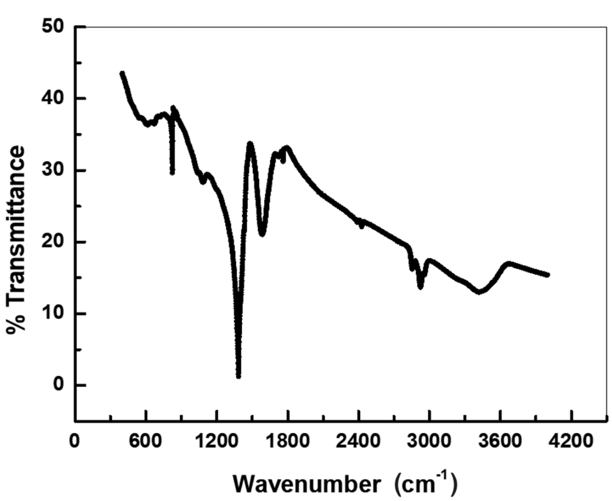

Fig. 5 — FTIR spectrum of Al_2O_3 nanoparticles

The different functional groups present in the sample are analyzed by FTIR analysis. Fig. 5 represents typical FTIR spectrum of the Al_2O_3 nanoparticles synthesized from waste aluminium foil. The FTIR spectrum displayed the main stretching modes including carbon, oxygen, hydrogen, and Al_2O_3 bands which are clearly demonstrated. The various spectra from 450 cm^{-1} to 850 cm^{-1} reveal the general features of Al_2O_3 that established the formation of Al-O bonds in the sample. The appearance of a peak at 1380 cm^{-1} is related to the chemisorbed oxygen atoms on the surface. The band observed between 3200 cm^{-1} to 3650 cm^{-1} shows the O-H stretching and band at 1640 cm^{-1} corresponds to the H_2O vibration modes [23]. The bending vibration at 1634 cm^{-1} is due to the reabsorption of water molecules from atmosphere.

The corrosion inhibition studies were carried out by exposing the coated specimen in solutions of NaCl, sea water and H_2SO_4 and the weight loss was monitored for duration of eight weeks. Fig. 6 represents the effect of various environmental conditions for imposed for eight weeks on the coated specimen. The corrosion inhibition efficiency was assessed by plotting the amount of Al_2O_3 versus corrosion rate. Fig. 6a represents the change in corrosion rate with amount of Al_2O_3 in the coating at ambient condition. The same effect was also studied in media like H_2SO_4, NaCl solution and sea water and shown in Figs 6b-d, respectively. In every case, an increase in the amount of Al_2O_3 leads to a dip in the corrosion rate and there was no effect when the amount of Al_2O_3 exceeds 1.0 g. Hence 1.0 g of Al_2O_3 can be considered to be the optimum amount required for coating.

Fig. 7 represents the 2d and 3d images of the fabricated chitosan-Al_2O_3 thin films. The AFM surface topographic image shown in Fig. 7a reveals the nanoscale deposition of the composite on the mild steel specimen. The layer deposition was monitored for a selected scan area of 20 µm × 20 µm. The globular shapes present on the surface indicate the effective layer deposition during the coating process. The non-uniformity in the coating was experienced by the variation in film thickness. This change in thickness is due to variation of the surface charge density. The corrosion inhibition studies using thin films with varying amounts of Al_2O_3 entitles the thin layer act as a barrier to safeguard the metal surface from moisture and oxygen. The corrosive environment

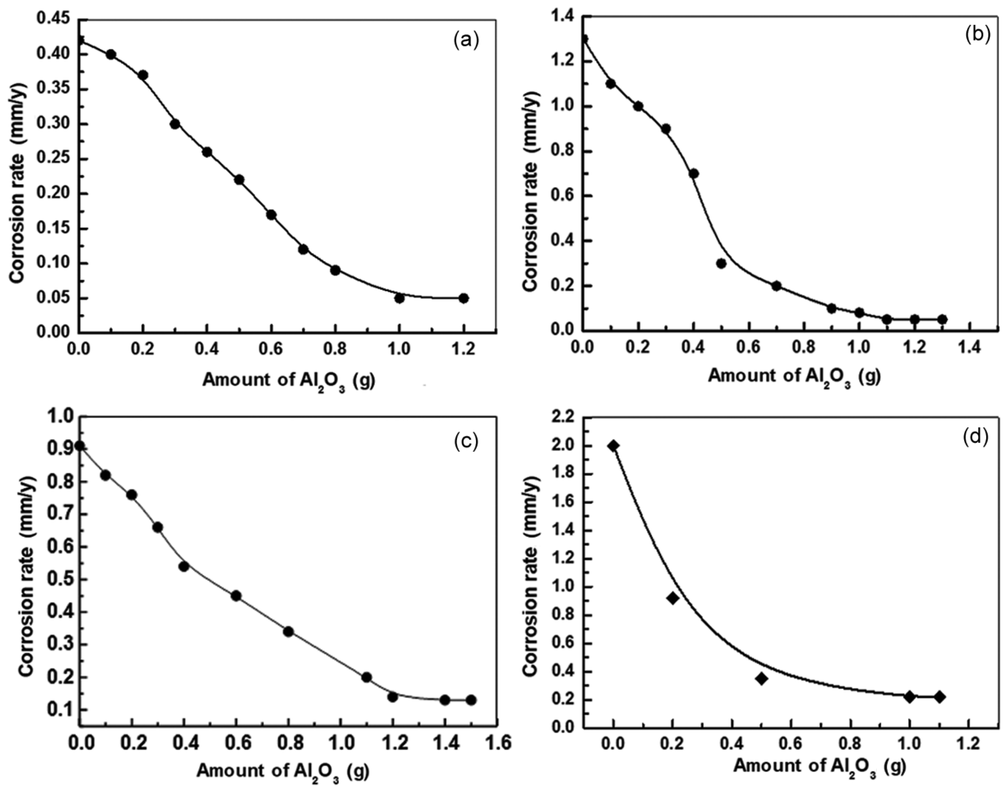

Fig.6 — Effect of amounts of Al_2O_3 on corrosion rate in coated pipe in (a) ambient condition, (b) H_2SO_4, (c) NaCl solution and (d) sea water

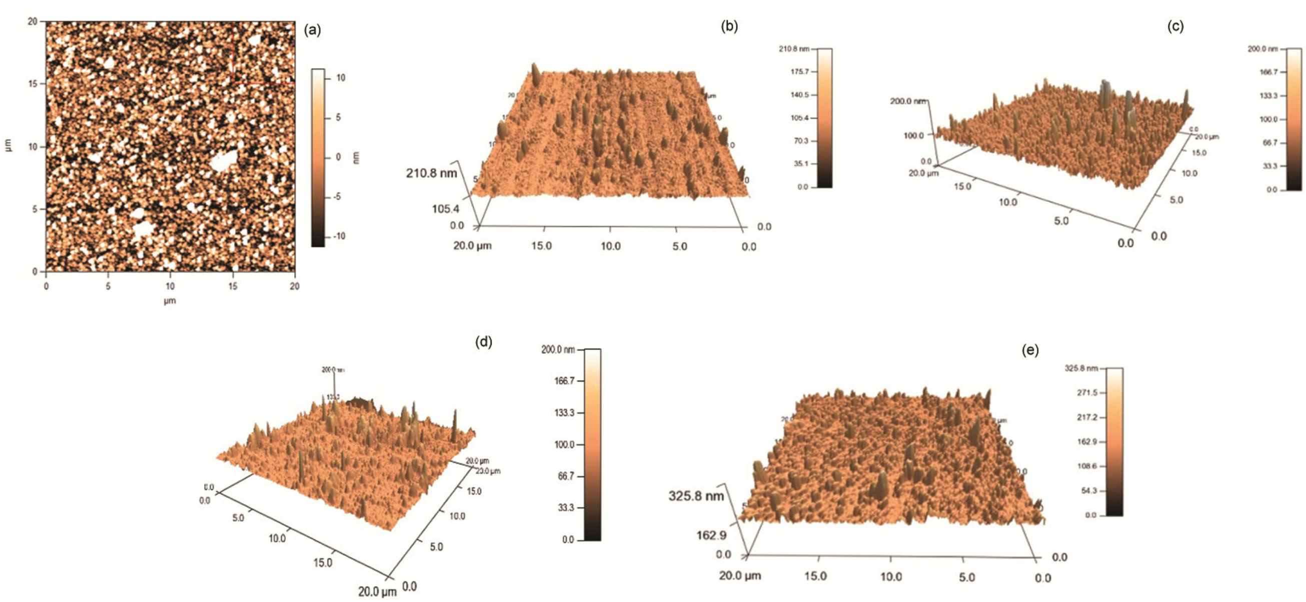

Fig. 7 — (a) 2d and (b) 3d AFM images of the fabricated chitosan – Al_2O_3 thin films; – AFM 3d images of chitosan – Al_2O_3 thin films dipped in (c) H_2SO, (d) NaCl and (e) sea water

may influence the variation of the Al_2O_3 thickness in the coating solution. The formation of passive layer may arise due to reaction with the ions in which the coated layer acts as secondary barrier to the specimen[24, 25].

The chitosan-Al_2O_3 thin film coated steel specimens were dipped in H_2SO_4, NaCl and sea water and the surface topologies are displayed in Fig. 8. The microstructural features present in Fig. 8a revealed a non-uniform coating displaying a number of peaks and valleys indicating enhanced thickness. This is because of the swelling of the coated layer due to exposure of acidic environment and hence penetrated into the substrate cavities. During the initial stages of layer deposition process, the nanocomposite layer could not spread out evenly over the mild steel surface but instead adopt a conformational change leading to the deposition of thicker layers.

Conclusion

In this research, Al_2O_3 nanoparticles were successfully synthesized from waste aluminium foil by green synthesis technique. The resulting nanoparticles were characterized and the results confirmed the successful synthesis of Al_2O_3 nanoparticles. The nanocomposite thin films were fabricated by dip coating technique using chitosan and nanoparticles. The thin films are exposed to three different environmental conditions by dipping in H_2SO_4, NaCl and sea water. The study illustrates that the nanostructured composite thin films exhibited good anticorrosive activity with extended shelf life and durability. The biocompatible and eco-friendly chitosan acted as a green corrosion inhibitor and a protective layer on the surface of mild steel. This corporate social responsibility based research would suppress the rate of corrosion and requires minimum quantity of polymer and the stability of the layer are excellent, which is one of the desirable properties in corrosion control applications.

Acknowledgement

The research team would like to thank Ms. Salha Nasser from college of pharmacy, National University of Science & Technology to perform the DLS and FTIR analysis of the samples.

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