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Effect of addition of CeO_2 nanoparticles to pectin as inhibitor of X60 steel corrosion in HCl medium

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ABSTRACT

Ceria (CeO_2) nanoparticles were synthesized and characterized using scanning electron microscopy (SEM), powder X-ray diffraction (XRD), attenuated total reflectance infrared (ATR-IR) spectroscopy and thermogravimetric analysis (TGA) techniques. The effect of addition of the synthesized CeO_2 on the corrosion inhibition effect of pectin for X60 steel in 0.5 M HCl solution was evaluated using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss techniques at 25 and 60 °C. Water contact angle measurements, scanning electron microscopy and ATR-IR techniques were employed for surface morphology characterization. Results obtained show that inhibition efficiency increased with increase in the additives concentration. Addition of CeO_2 exerted both antagonistic and synergistic effects depending on temperature, immersion time and concentration of CeO_2. Temperature was found to have profound effect on the corrosion inhibition performance of pectin without and with addition of CeO_2. The potentiodynamic polarization studies revealed that Pectin, CeO_2 and Pectin-CeO_2 mixtures functions as a mixed-type inhibitor. Results from all the surface analyses confirm the formation of protective film on the X60 steel surface.

1. Introduction

Low carbon steel of different grades is essential commodity in the chemical and petrochemical industries. They are materials of choice in the construction of storage tanks, heat exchangers, boilers, distillation towers, pipelines etc. because of its excellent physical and mechanical properties [1]. The major setback in the use of steel is that it corrodes very rapidly when it comes in contact with aggressive acid solutions if used without adequate protection. Hydrochloric acid is heavily deployed in industrial applications such as acid pickling, acid cleaning of boilers, descaling of boilers and oil well acidizing [2,3]. In order to prevent the base metal attack and reduce excessive acid consumption during these processes, corrosion inhibitors are widely employed [4]. Organic compounds containing nitrogen, sulphur and oxygen are recognized as good corrosion inhibitors [5]. However, most of the organic compounds deployed as corrosion inhibitors are not only expensive; they possess high toxicity to both humans and the environment. They are now being banned due to recent environmental legislation.

In recent times, the most important criteria in selecting corrosion inhibitors for practical application apart from efficiency is the eco-friendliness of the inhibitor because of problems of environmental pollution. In this regards, the search has been focused on the use of rare earth metals as green alternative for chromium. Cerium as one of the rare earth metals is an attractive alternative to chromium not only because of being non-toxic but also because the commercial grade salts are relatively cheap and availability (it is reported to be as plentiful as copper). Similarly biopolymers have been advocated as alternative for toxic organic inhibitors. Among the rare earth compounds, cerium salts/ions have been reported to inhibit the corrosion of steel, galvanized steel and non-ferrous alloys either by coatings or as inhibitors [6–12]. On the other hand, biopolymers are readily available as their sources are abundant; they are low cost, renewable and robust compared to their synthetic counterparts. They are also ecofriendly and benign, and possess optimal biocompatibility and biodegradability. Umoren and Eduok in their recent reviews have documented biopolymers that have been reported as corrosion inhibitors for metal substrates in different corrosive media [13]. With regards to pectin, Fiori-Bimbi et al. [14] have reported that pectin extracted from citrus peel act as a good corrosion inhibitor for mild steel in 1 M HCl investigated using gravimetric (weight loss) and electrochemical (EIS and Tafel polarization) techniques. Pectin from this source was found to inhibit corrosion of mild steel to a great extent with the highest corrosion inhibition efficiency of 94% recorded for 2 g/L concentration at 45 °C. Magnitude of inhibition efficiency was found to increase with increase in pectin concentration and temperature. Umoren et al. [15] have also investigated the anticorrosion properties of pectin extracted from apple for X60 pipeline steel in 0.5 M HCl using chemical and electrochemical techniques. Results

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obtained reveal an increase in inhibition efficiency with increase in pectin concentration and with temperature rise.

However, the use of single compound as corrosion inhibitor has the disadvantage of high amount of usage. In this regard, the combination of two or more compounds which often show a synergistic behavior is advocated. The advantage is that it leads to a reduction of the amount of inhibitor usage and also improves the corrosion inhibition effect of the inhibitor at low concentration [16]. Reports abound in the literature on the synergistic corrosion inhibition effect between organic compounds and halides ions, metal cations and so forth. Recently, Umoren and Solomon have published a review paper on the synergistic corrosion inhibition effect between organic species and halide ions for metal substrates in different corrosive environments [17]. The corrosion inhibition performance of pectin with propyl phosphonic acid (PPA) and Zn^{2+} for corrosion control of carbon steel in neutral aqueous solution has been reported [18]. Results obtained show excellent synergistic effect of pectin with other additives in the corrosion control of carbon steel. Typically, a formulation consisting of 250 ppm pectin, 50 ppm PPA and 20 ppm Zn^{2+} gave the optimum inhibition efficiency of 94%. Also the effect of addition of cerium ions on the corrosion inhibition performance of polyaniline for iron in 0.5 M H_2SO_4 has been reported by Jeyaprabha et al. [2]. It was found that addition of 1 mM cerium ions to 10 and 50 ppm polyaniline increased the inhibition efficiency from 53 and 71% to 88 and 90% respectively. The synergistic inhibition effect of polyethylene glycols (PEGs) of different molecular weight (400 and 6000 g/mol) and rare-earth Ce^{4+} ion for corrosion of carbon steel in 0.1 M sulfuric acid solution has been reported by Abd El-Lateef [19]. The synergistic effect of the rare-earth cerium (IV) ion and 3, 4-dihydroxybenzaldehye (DHBA) for steel corrosion inhibition in sulfuric acid solution was investigated by Li et al. [20]. They found that DHBA has moderate inhibitive effect and incorporation of Ce^{4+} with DHBA improves the inhibition performance significantly, and produces strong synergistic inhibition effect. Forsyth et al. [21] studied the synergistic effect of rare earth Ce^{3+} and sodium salicylate for inhibition of corrosion of mild steel in 0.1 M sodium chloride solution. The report on the synergistic inhibition effect of cerium (IV) ion and sodium molybdate for cold-rolled steel in HCl solution by Mu et al. [22] is available in the literature.

Atta et al. [23] evaluated the inhibitive ability of hybrid polymer composites based on silver nanoparticles towards line pipe steel in acid inducing corrosive environment and found that the composite could offer up to 81.16% protection to the metal surface. Atta et al. [24] had earlier found that silver nanoparticles – poly(ethylene glycol) thio composites was an effective corrosion inhibitor for carbon steel surface in HCl environment. Similarly, Sasikumar et al. [25] have reported that CeO_2 nanoparticles – polyaniline composites could serve as inhibitor for mild steel corrosion in HCl medium. In our laboratory, we have also shown that silver nanoparticles – polypropylene glycol and silver nanoparticles – poly(methacrylic acid) composites acted as corrosion inhibitors for mild steel and aluminium corrosion in H_2SO_4 medium [26–29].

There is no report to the best of our knowledge on the effect of addition of ceria nanoparticles on the corrosion inhibition performance of pectin for low carbon steel in acid media. Therefore in continuation of our quest to explore biopolymers as eco-friendly corrosion inhibitors and influence of additives on their performances, the present work reports antagonistic and synergistic corrosion inhibition effect between CeO_2 nanoparticles and pectin for a typical X60 pipeline steel in 0.5 M HCl using weight loss and electrochemical techniques; complemented by surface morphological characterization and water contact angle measurements.

2. Experimental

2.1. Chemicals and metal substrate

The chemicals used in the work were ammonium cerium (IV) nitrate ($(NH_4)_2Ce(NO_3)_6$), sodium hydroxide (NaOH), Pectin from apple having molecular weight of 75,000 g/mol and degree of esterification of 65–70% were all obtained from Sigma-Aldrich. AR grade 36% HCl was obtained from Eurostar Scientific Ltd, UK. The metal substrate was low carbon steel which conforms to API X60 material specification.

2.2. Synthesis and characterization of CeO_2 nanoparticles

The precursors such as ammonium cerium (IV) nitrate and NaOH in 1:4 M ratios were completely dissolved in de-ionized water and the pH of the solution was adjusted to 12 with addition of few drops of 1 M HCl. The prepared solution was well stirred using a magnetic stirrer for about 2 h and then, the obtained solution was placed in the microwave oven at a temperature of 60 °C for about 1 h. The formed pale-yellow precipitate was filtered and washed with de-ionized water twice. The synthesized powder was annealed at 130 °C in air for 4 h and the final product was CeO_2 nanoparticles.

IR spectra for the synthesized nanoparticles were recorded in the range of 400–4000 cm^{-1} by IR reflectance spectrophotometry (PerkinElmer, Spectrum One, with universal ATR attachment with a diamond and ZnSe crystal, The Netherlands) to confirm the formation of CeO_2 nanoparticles. The crystalline features of the synthesized product was examined by powder X-ray diffraction (XRD) using a Rigaku Corporation, Tokyo, Japan. The spectra were recorded at room temperature over a scattering angle range of $20° \leq 2\theta \leq 80°$ at a 2θ step of 0.02°. Thermal degradation of the CeO_2 nanoparticles was performed using a thermogravimetric analyzer (TA instruments, TGA 50). The thermal experiment comprised of a thermal scan at a velocity of 10 °C min^{-1} from 30 °C up to 1000 °C in nitrogen atmosphere. The surface morphology of the synthesized CeO_2 nanoparticles was analyzed using scanning electron microscope (SEM); JSM-6360 (JEOL), at an acceleration voltage of 20 kV and irradiation current of 10 μA.

2.3. Electrochemical measurements

Electrochemical measurements were performed using a Gamry Ref 3000 with Echem 6.0 operating software. A conventional three-electrode electrochemical setup was used. A X60 steel electrode with exposed surface area of 0.7855 cm^2, saturated calomel electrode (SCE) and a graphite rod were used as the working, reference and counter-electrodes, respectively. In the case of polarization and electrochemical impedance spectroscopy, prior to each measurement, a stabilization period of 30 min was allowed to establish a steady-state open-circuit potential (OCP). The potential sweep rate was 1 mV s^{-1}. The potentials were scanned primarily in the cathodic direction from the corrosion potential and subsequently in the anodic direction, that is, from −250 to +250 mV. The electrochemical impedance spectroscopy measurements were carried out at open-circuit potential (OCP) in the frequency range from 10,000 to 0.1 Hz by applying a 10-mV sine-wave alternating-current (AC) voltage. The data were collected and analyzed using E-Chem Analyst 6.0 software.

2.4. Weight loss measurements

Weight loss test was conducted in a glass reaction vessel containing 250 mL of test solution maintained at 25 and 60 °C with thermostated water bath in order to evaluate the effect of temperature on the corrosion inhibition efficacy of pectin and pectin-CeO_2 mixtures. Tests were performed under total immersion in the absence and presence of the inhibitors. In each experiment, the cleaned and weighed steel coupons were freely suspended in the different test solutions. The test coupons were retrieved after 24 h immersion, thoroughly cleaned using previously reported procedures [30], rinsed with distilled water and acetone and dried in warm air and reweighed using digital analytical balance with sensitivity of ±0.1 mg. The weight loss was taken as the difference between the weight at a given time and the initial weight of the coupon. The data of the triplicate determinations showed good reproducibility