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Interactions at the mild steel acid solution interface in the presence of O-fumaryl-chitosan: Electrochemical and surface studies

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ABSTRACT

The performance of synthesised O-fumaryl-chitosan (OFC) as corrosion inhibitor for mild steel in 1 M HCl has been evaluated through various studies. The initial screening by weight loss method revealed the good inhibition efficiency by the inhibitor. Thermodynamic and kinetic parameters have been calculated and discussed. The mode of adsorption is physical in nature and it follows Langmuir adsorption isotherm. Electrochemical measurements supported the inhibition of mild steel by the fumaryl derivative of chitosan. Polarisation studies provided the information that the inhibition is of mixed type. The formation of inhibitor film is assured by surface morphological studies with Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). The mechanism of inhibition is derived from the Fourier-transform infrared (FTIR) spectroscopy and zero charge potential measurement. The adsorbed film is characterised using FTIR and X-ray diffraction studies (XRD).

1. Introduction

The use of inhibitors for an effective mitigation of corrosion of metals and alloys in aggressive acidic condition is a common practice. Acids are more frequently used in industrial process such as pickling, descaling, cleaning and oil well acidizing (Amin, El-Rehim, El-Sherbini, & Bayoumi, 2007). Both economic and scientific considerations are involved in combating corrosion on mild steel in this environment. The effectiveness of inhibitor depends on the corrosivity of the solution, molecular structure of the inhibitor, their charge density, molecular size, mode of adsorption, temperature, etc. (Chetouani, Hammouti, Benhadda, & Daoudi, 2005).

Generally, a large number of organic compounds containing hetero atoms like, oxygen, nitrogen and sulphur have been well documented, as effective corrosion inhibitors for mild steel in acid medium (El-Rehim, Ibrahim, & Khaled, 1999; Ali, Saeed, & Rahman, 2003; Ameer, Khamis, & Al-Senani, 2000; Goel, Siddiqi, Ahmed, Khan, & Chaubey, 2010; Kissi, Bouklah, Hammouti, & Benkaddour, 2006; Mert, Yuce, Kardas, & Yazici, 2014; Noor, 2005; Obi-Egbedi, Obot, & Eseola, 2014; Saliyan & Adhikari, 2008; Yildiz, Doner, Dogan, & Dehri, 2014; Zhang, Gao, & Zhou, 2003). But their usage is limited, because of the fact that they are toxic and pose threat to human health and environment. There is a need to develop non-toxic and environmentally benign process. Hence, in the recent past, researchers focussed on the use of natural products as inhibitor (Gopal Ji, Anjum, Sundaram, & Prakash, 2015; Kamal & Sethuraman, 2012; Oguzie, 2005; Okafor, Osabor, & Ebenso, 2007; Parikh & Joshi, 2004; Ramesh, Vinod Kumar, & Sethuraman, 2001; Verma & Mehta, 1997).

In contrast to simple organic compounds, polymers exhibit superior corrosion inhibition property on mild steel (Hussain & Kumar, 2003). Polymers possess long chain carbon linkage and multiple adsorption sites, which favours better adsorption on the surface of the metal. In recent literature, wide use of natural bio polymers like polyaspartic acid (Qian, Wang, Zheng, & Hou, 2013), polycaffeic acid (De Souza & Spinelli, 2009), cellulose derivatives (Arukalam, 2014; Bayol, Gurten, Dursun, & Kayakirilmaz, 2008; Rajeswari, Kesavan, Gopiraman, & Viswanathamurthi, 2013), chitosan derivatives (Aghzzaf et al., 2012; Cheng, Chen, Liu, Chang, & Yin, 2007; Fekry & Mohamed, 2010; Sangeetha, Meenakshi, & Sairam Sundaram, 2015; Waanders, Vorster, & Geldenhuys, 2002), pectin (Fiori-Bimbi, Alvarez, Vaca, & Gervasi, 2015), etc. have been reported. These molecules occupy large surface area and isolate the metal from the aggressive ions in the solution.

Chitin is the second most abundant available material next to cellulose. Chitosan, a deacylated product from chitin has a good chelating ability with iron, due to the presence of anti corrosion effect on mild steel in hydrochloric acid solution. We have functionalised chitosan with fumaric acid. This acylated chitosan derivative is water-soluble in nature. Both chitosan and fumaric acid are

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non-toxic substances. Fumaric acid finds wide use in pharmaceutical (treating psoriasis by topical application) and food industries (acidify fruit juices). The synthesised green inhibitor O-fumaryl-chitosan (OFC) has been characterised and explored for its corrosion inhibition efficiency. Fourier-transform infrared (FTIR) technique has been utilised for determining the functional groups in the synthesised compound. The weight loss, polarisation studies and electrochemical impedance spectra were employed to study the inhibition efficiency of OFC on mild steel in acid medium. SEM and AFM depicted the nature of the adsorbed film.

2. Experimental methods

2.1. Sample preparation

Tests were performed on the mild steel with the following composition (wt%): C 0.096, Si 0.062, Mn 1.499, S 0.014, Cr 0.015, P 0.013, Cu 0.033 and Fe 98.268. Mild steel coupons of 3.5 cm × 1.5 cm × 0.04 cm sizes were prepared and used for weight loss studies. For the electrochemical studies, the specimens were covered with an epoxy resin leaving a geometrical surface area of 1 cm^2 in aqueous solution. Prior to all measurements, the specimens were abraded with emery paper from 320 grit to 1200 grit, washed with double distilled water, degreased with acetone and dried at room temperature.

2.2. Solutions

The aggressive solution, 1 M HCl was prepared from an analytical reagent grade HCl (Merck) and distilled water. Fumaric acid was supplied by Sigma–Aldrich. Chitosan (85% degree of deacetylation) was purchased from Pelican Biotech and Chemicals lab, Kerala (India). The concentration range of OFC prepared and used in this study was between 100 and 500 ppm.

2.3. Synthesis of OFC

OFC was synthesised as described here. About 1 g chitosan was suspended in 150 ml distilled water and 5 g of fumaric acid was added to the suspension. Then, 5 mL of 2 M H_2SO_4 was added drop wise at room temperature. The above mixture was heated at 80 °C for 4 h with constant stirring and cooled to room temperature. $NaHCO_3$ was added to adjust the pH to 7.0. The compound obtained was precipitated in acetone, filtered and washed with ethanol to remove the unreacted acid. Soxhlet-extraction was applied to purify the precipitant with ethanol for duration of 2 d and oven-dried at 60 °C for 12 h. The product obtained was utilised for the intended purpose (Feng & Xia, 2011). The synthesis of the proposed inhibitor is shown in Fig. 1. According to Badawy et al. (2005), this method can be considered as selective O-acylation of chitosan, as there would be formation of salt by the primary amino group of chitosan with H_2SO_4.

2.4. Weight loss measurement

A previously weighed mild steel (MS) specimen was completely immersed in a glass beaker containing 100 mL of 1 M HCl without and with addition of different concentrations of inhibitor. The coupons were withdrawn after 2 h, rinsed with distilled water, cleaned in acetone, dried at room temperature and weighed. Three such measurements were performed in each case and the mean value of the weight loss has been reported. The effect of temperature on the inhibition efficiency of OFC was studied at different temperatures (30 °C, 40 °C and 50 °C). The inhibition efficiency was calculated according to the method reported elsewhere (Sangeetha et al., 2015). The weight loss values were substituted in the Eq. (1) to calculate the surface coverage (θ).

$$\theta = (W_0 - W_1)/W_0 \quad (1)$$

where W_1 and W_0 are the weight loss with and without the addition of OFC respectively. The surface coverage values obtained from the weight loss method were fitted graphically into various isotherms and the best fit was concluded from the highest regression coefficient value.

2.5. Electrochemical experiments

The electrochemical studies were performed using a three electrode cell assembly at room temperature (Abboud et al., 2009; Fengling & Baorong, 2009). The mild steel electrode with an exposed surface area of 1 cm^2, was used as the working electrode. A platinum foil was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The polarisation and electrochemical impedance studies were carried out using CHI Electrochemical analyzer (model 760 D), Austin, USA, with an operating software CHI 760 D. The potentiodynamic polarisation was carried out from cathodic potential of −300 mV vs. OCP to an anodic potential of +300 mV vs. OCP at a sweep rate of 1 mV s^{-1}. The tafel segments of anodic and cathodic curves were extrapolated to corrosion potential. The corrosion current density (I_{corr}) was obtained from the tafel curve. The inhibition efficiency (IE %) was evaluated using the following relationship:

$$IE(\%) = \frac{I^0_{corr} - I'_{corr}}{I^0_{corr}} \times 100 \quad (2)$$

where, I^0_{corr} and I'_{corr} are the corrosion current densities without and with different concentrations of the inhibitor, respectively.

The electrochemical impedance spectroscopy (EIS) measurements were performed at measured OCP, in the frequency range 0.1–10,000 Hz and at amplitude of 5 mV peak to peak. The charge transfer resistance (R_{ct}) and capacitance of double layer (C_{dl}) were calculated from the Nyquist representation. Then the inhibition efficiency can be calculated using the following equation:

$$IE(\%) = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100 \quad (3)$$

where, R_{ct} and R'_{ct} are the charge transfer resistance values in the presence and in absence of various concentrations of the inhibitor, respectively.

The double layer capacitance (C_{dl}) was evaluated from the Eq. (4).

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (4)$$

where f_{max} is the frequency at which the imaginary component of the impedance is maximum. The potential of zero charge (E_{pzc}) was obtained using the EIS measurements. The EIS values were recorded for mild steel immersed for 1 h in 1 M HCl containing 500 ppm of OFC at an amplitude of 10 mV, by applying different potentials between −650 mV vs. SCE and −350 mV vs. SCE. The C_{dl} values were calculated at each applied potential and a plot of C_{dl} vs. potential was made.

2.6. Fourier-transform infrared (FTIR) analysis

FTIR spectrum was recorded using FT-IR JASCO 460 plus model instrument, Easton, United States, in the frequency range 4000–400 cm^{-1}. The spectra of chitosan, OFC and OFC adsorbed on mild steel were recorded and analysed according to the procedure given in the literature (Chauhan & Gunasekaran, 2007). The inhibitor was allowed to adsorb on the mild steel specimen by