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The inhibitory action of expired asthalin drug on the corrosion of mild steel in acidic media: A comparative study



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ABSTRACT

A comparative study of expired asthalin drug was studied for its inhibitive effect on mild steel in 1 M HCl and 1 M H₂SO₄ medium, using the metrics of weight loss and electrochemical techniques. The various parameters such as corrosion rate, inhibition efficiency and surface coverage were calculated. The weight loss method shows that the inhibition efficiency increases with the increase of inhibitor concentration, time and temperature. A mixed mode of inhibition mechanism was proposed for the effect of examined asthalin drug, as revealed by potentiodynamic polarization technique. Thermodynamic parameter such as free energy value was negative, that indicates spontaneous adsorption of inhibitor on mild steel surface. The nature of adsorption of the inhibitor on the mild steel surface was in conformity with Langmuir adsorption isotherm. The surface morphology of the mild steel, with and without the inhibitor, was studied using scanning electron microscopy (SEM).

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1. Introduction

Corrosion is defined as a gradual destruction of the metal by the chemical or electrochemical reaction with its environment. Mild steel has been most widely used as an alloy for structural and industrial applications since, the beginning of industrial revolution [1]. When the mild steel comes in contact with acidic medium it would be rusted. The use of acid media in the study of corrosion of mild steel has become important because of its industrial applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes [2]. Unfortunately, mild steel suffers from severe corrosion in aggressive media such as acids, used in pickling processes and descaling operations [3-5]. Hydrochloric acid and sulfuric acids are most frequently used for the pickling of mild steel [6]. Several methods were used to decrease the corrosion of metals in acidic medium, but the use of inhibitors is most commonly used. Hence, the corrosion process may be censored by the protective film of inhibitor on the metal surface.

Majority of well known inhibitors are organic compounds containing hetero atoms such as N, S, O and P atoms and multiple bonds [7]. Most of these organic compounds not only expensive but also toxic to both human beings and the environment and

therefore, their use as corrosion inhibitors are limited. Thus, efforts have been made to develop cost-effective and non-toxic corrosion inhibitors. Recently, many expired drugs have been reported to be very effective corrosion inhibitors for the protection of mild steel in acidic media [8,9]. This area of research is much important because in addition to being environmentally friendly and ecologically acceptable, expired pharmaceutical drugs are inexpensive, readily available and prevent pollution. On the other hand, deactivation of this expired drug is generally carried out with the risk of air pollution with toxic compounds containing N, S, P or halogen atoms. In most cases expired drugs can be tested as corrosion inhibitors, whereas the active substance degrades only infinitesimally. Food and Drug Administration (FDA) proved that 90% of the drugs are stable for long time after the expiration dates. On the other side, the widely used corrosion inhibitors are toxic and there are environmental regulations which control their usage and disposal. Therefore, this study was focused on inhibitory properties of expired drugs by using analytical techniques. This type of analytical chemistry research can solve two major environmental and economical problems: limitation of environmental pollution with pharmaceutically compounds and reduction of the disposal costs of expired drugs. Moreover, this research would give effective nonhazardous alternatives to toxic corrosion inhibitors [16–18].

In the present work, an attempt was made to utilize to find the chosen inhibitor (asthalin) that can be employed for inhibitive effect on the corrosion of mild steel in 1 M sulfuric acid and 1 M hydrochloric acid medium. Asthalin was a pharmaceutical compound

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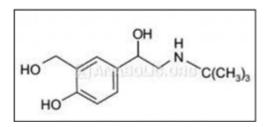


Fig. 1. Molecular structure of the inhibitor.

used as a mucolytic agent prescribed in respiratory infection like bronchitis and asthma. The structure of the asthalin is given in Fig. 1. Hence, attempts are made to utilize the expired asthalin drug acts as anticorrosion agent on mild steel in 1 M sulfuric acid and 1 M hydrochloric acid medium.

2. Materials and methods

2.1. Preparation of specimen

The rectangular mild steel strips of size $2 \times 5 \times 0.2$ cm is cut from long MS sheet and holes are drilled on the top of mild steel coupons. The percentage composition of mild steel is C (0.03), Mn (0.25), Si (0.015), P (0.003) and the remaining Fe. Each specimen was polished with different grades of emery paper, degreased with acetone, washed with distilled water and properly dried.

2.2. Preparation of the inhibitor

Expired asthalin drug collected from pharmaceutical drug house and stored. Aggressive solution of 1 M HCl and 1 M $\rm H_2SO_4$ was prepared by dilution of analytical grade HCl (36%) and $\rm H_2SO_4$ (96%) with double distilled water respectively and all experiments were carried out. The drug was obtained in pure form (does not contains any contamination) and used for this study without any further purification.

2.3. Weight loss method

The rectangular specimens with dimension of $1\times5\times0.2\,\mathrm{cm}$ were used. The pre-treated specimen's initial weights were noted accurately and were fully immersed in $100\,\mathrm{ml}$ of the experimental solution (in triplicate) of 1 M HCl and $\mathrm{H_2SO_4}$ acid with and without different concentrations $(1.0-11.0\%~(\mathrm{v/v}))$ of the inhibitor with the help of glass hooks at different time intervals (0.5, 2, 4, 6, 8 and $24\,\mathrm{h})$ and temperature (303, 313, 323, 333) and $343\,\mathrm{K})$. After the exposure period, the specimen were removed, dried and weighed. From the weight loss, the inhibition efficiency (IE), surface coverage (θ) and corrosion rate (mpy) were calculated using the following formula.

Inhibition efficiency(%) =
$$\frac{Wa - Wp}{Wa} \times 100$$
 (1)

where Wa and Wp are inhibition efficiency in the absence and presence of the inhibitor.

Corrosion rate(mpy) =
$$\frac{87.6 \text{ x weight loss (mg)}}{\text{density}(\frac{g}{cc}) \text{ x Area (cm2) x Time (h)}}$$
(2)

2.4. Electrochemical measurements

Potentiodynamic polarization experiments were carried out in a conventional three electrode set up was immersed in acid solutions in the absence and presence of inhibitor at room temperature. The working electrode was mild steel specimen with exposed area of $1 \, \mathrm{cm^2}$ and the rest being covered. A rectangular Pt foil was used as the counter electrode and saturated calomel was used as a reference electrode. The polarization was carried from a cathodic potential of $-700 \, \mathrm{mV}$ (vs. SCE) to an anodic potential of $-200 \, \mathrm{mV}$ (vs. SCE) at a sweep rate of $10 \, \mathrm{mV}$ per second. The percentage inhibition efficiency (IE %) from the polarization measurements was calculated by using the following formula

$$IE (\%) = \frac{Icorr - Icorr*}{Icorr} \times 100$$
 (3)

where I_{corr} is the corrosion current in the absence of inhibitor and I_{corr} * is the corrosion current in presence of inhibitor.

For Linear polarization study,

$$IE \ (\%) = \frac{Rpa - Rpb}{Rpa} \times 100 \tag{4}$$

where, *Rpa* and *Rpb* – resistant polarization with and without inhibitor, respectively.

2.5. Surface studies

Surface examination of mild steel sample in the absence and presence of the optimum concentration of the inhibitor immersed for 4 h in HCl medium and 6 h in sulfuric acid medium was studied using scanning electron microscope with the magnification of 20 kV x specimens.

3. Results and discussion

3.1. Weight loss studies

The inhibition efficiency (*IE*) is obtained from weight loss method in 1 M HCl and 1 M H₂SO₄ absence and presence of various concentrations of the inhibitor ranging from 1% to 11% v/v and listed in Table 1. It was found that the optimum concentration for the asthalin inhibitor was found to be 9% v/v with the maximum inhibition efficiency of 94.76% (HCl) and 95.48% (H₂SO₄) at 4 h and 6 h of immersion time, respectively. Table 2 shows the corrosion rate (*CR*) at various concentrations of the inhibitor. It is observed from the tables, the *IE* increased and the corrosion rate decreased on increasing the concentrations of the examined inhibitor. This behavior is attributed to the increase in adsorption of inhibitor to the mild steel–acid interface to increase the concentration of the inhibitor [21]. These results indicate that the examined inhibitor could act as good corrosion inhibitor [10].

3.2. Effect of temperature

To study the effects of temperature on corrosion inhibition properties, the mild steel specimens were exposed to acid solution containing different concentrations of the inhibitor at different temperature range, 303K–343 K. The influences of temperature on the inhibitor in 1 M HCl and 1 M H₂SO₄ results are presented in Fig. 2(a) and (b). It is evident from the figures, that the inhibition efficiency increased with an increase in concentrations of inhibitor at different temperature and that is decreased with increase in temperatures. This is due to the fact that, adsorption and desorption of inhibitor molecules continuously occur at the metal surface and equilibrium exists between these two processes at a particular temperature [11–13].

3.3. Activation parameters

The calculated activation parameters of the above corrosion process are listed in the Table 3. From the table, show that the addition of inhibitor leading to an abrupt decrease in the apparent activation energy (E_a). Activation energy value for blank

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