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Abstract:

Corrosion is a major economic and environmental problem in industries. Inhibitors are used to protect the metals from corrosion. At present, bio-inhibitors are widely used because they are nontoxic, biodegradable and readily available. In the present study, ten different vegetable oils were used as bio-inhibitors which are already emerged as potential biodiesel resources. Corrosion studies were carried out by using gravimetric method in mild steel specimen at 5000 ppm concentration of inhibitors in 1 N HCl medium at room temperature. The bio-inhibitors namely neem, castor, pongamia, jatropha and rubber had higher inhibition efficiency.

Key words: corrosion, bio-inhibitor, mild steel, weight loss, biodiesel

1. Introduction:

Corrosion of metal is a major industrial problem that has attracted a lot of researchers in recent years. Corrosion is defined as destruction or deterioration of metal after reacting with environment. Metals and alloys are used in automobile industries, railways, ships, petroleum industries, refineries, oil pipelines, chemical etc. [1, 2, 3]. When

these materials are exposed to the environment, great economic and environmental losses

occur. The mild steels are widely used as structural materials in various corrosive environments owing to their excellent resistance to corrosion and good mechanical properties [4, 5, 6]. Mild steels are widely used in automobile, petroleum industries and refineries and they get damaged due to internal and external corrosion when exposed to the petroleum fuels.

The use of inhibitors is one of the best options for protecting mild steel against corrosion. Many chemical inhibitors in use is either synthesized from cheap raw material or chosen from compounds having heteroatoms in their aromatic or long chain carbon system. Most of these inhibitors are toxic to the environment [7]. Among the various inhibitors, the bio-inhibitors have attracted several researchers. These bio-inhibitors are natural products which are nontoxic, biodegradable and easily available. There is a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in acid medium [8]. The first patent in corrosion inhibition was to Baldwin, British Patent 2327, for using the natural product from molasses and vegetable oils for pickling sheet steel in acids medium [9].

The corrosion rate for diesel equipments was found to be more because of the presence of certain chemical compounds in diesel fuel, especially sulfur compounds which are actively corrosive and are known as active sulfur. In the diesel engine, the fuel injection system the parts are made of high-carbon steels and they are prone to corrosion when in contact with water. If diesel fuel contains excessive water that may enter the injection system and cause irreversible damage in a very short time. Corrosion can affect

all materials in contact with the diesel, particularly engine components and storage and

handling equipment. This affects engine operability and lubricant oil properties.

During the past few decades there has been a phenomenal increase in the use of diesel engine in tractors, irrigation pumps, generators, chaff cutter, crushers, mills etc. The world is confronted with the twin crises of fossil fuel depletion and environmental problems. Due to the shortage of petroleum products, its increasing cost and environmental pollution, efforts are taken to develop alternative fuels especially, to the diesel fuel [10]. It has been found that the vegetable oils are promising alternative fuels because their properties are similar to that of diesel and are renewable, easily available and environmental friendly [11, 12, 13, 14, 15, 16, 17]. Biodiesel is nontoxic, eco-friendly and non-corrosive. Depending upon the climate and soil condition, different countries are using different types of bio-resources for the production of the alternative fuel namely the biodiesel.

In the present study, the various vegetable oils which are used as a biodiesel resources are Bassia oil (*Bassia latifolia* Linn.), Castor oil (*Ricinus communis* Linn.), Cotton seed oil (*Gossypium hirsutum* Linn.), Dillo oil (*Calophyllum inophyllum* Linn.), Jatropha oil (*Jatropha curcas* Linn.), Mustard oil (*Brassica alba* Linn.), Neem oil (*Azadirachta indica* Linn.), Palm oil (*Elaeis guineensis* Linn.), Pongamia oil (*Pongamia pinnata* Linn.), and Rubber seed oil (*Hevea brasiliensis* Muell. Arg.), were selected and analysed for their corrosion inhibition efficiency by using mild steel specimens in acid medium with and without the presence of inhibitors at 5000 ppm concentration.

2. Experimental methods

2.1. Preparation of specimen

A rectangular mild steel specimen of size 5 x 1.5cm was cut from a parent mild steel sheet. The specimens were pickled with pickling solution, washed with water, rubbed with cotton cloth and dried. After pickling, the plates were mechanically polished, degreased with trichloroethylene and kept in a desiccator for 2 hours [18]. These plates were used for the weight loss studies.

2.2. Inhibitor

In the present study, the ten different vegetable oils which are used as biodiesel resources were selected as the bio-inhibitor. The oils were as follows - Bassia oil, Castor seed oil, Cotton seed oil, Dillo oil, Jatropha oil, Mustard oil, Neem oil, Palm oil, Pongamia oil and Rubber seed oil. These oils were mechanically extracted from the seeds which were purchased from the local market. The bio-inhibitors were added to the acid medium at the concentration of 5000ppm at room temperature.

2.3. Gravimetric measurements

In the present study, the weight loss measurement was carried out for mild steel specimens in the presence and absence of inhibitors. The initial weight of the specimens was noted as w_1 . 250ml of 1 N HCl was taken in a beaker, the specimens were dipped in the solution for 24 hours, 48 hours and 72 hours with and without the presence of bio-inhibitor at the concentrations of 5000ppm at room temperature. At different intervals, the specimens were taken from the solution and dried and the final weight was noted as w_2 .

The difference between the initial weight and final weight gave the actual weight loss of

the specimens (W). The experiments were carried out in triplicates. From the weight loss,

the corrosion rate was determined using the formula

$$\text{Corrosion rate (mmpy)} = \frac{87.6 * W}{D A T}$$

where,

W is the weight loss in mg

D is the density in g/cc

A is the area of exposure in cm²

T is the exposure time in seconds

The effectiveness of the inhibitor was assessed in terms of its inhibition efficiency

(I.E %) by the following formula

$$\text{I.E (\%)} = \frac{(\text{weight loss})_{B.S} - (\text{weight loss})_{I.S} * 100}{(\text{weight loss})_{B.S}}$$

where

(weight loss)_{B.S} is the weight loss without inhibitor (blank solution)

(weight loss)_{I.S} is the weight loss with inhibitor

3. Result and Discussion

The performance of organic compounds as corrosion inhibitors can be determined by using electrochemical and chemical techniques. For the chemical methods, weight loss measurement is an ideal method suited for long term immersion test. In the present study, the weight loss of the specimens in different bio-inhibitors (biodiesel resources) with respect to the different times exposure at the concentration of 5000ppm is given in the Fig.1. The weight loss shows that the cotton and mustard oil has more weight loss and the neem oil has very less weight loss. Fig. 1 shows more weight loss for mustard, cotton and palm oil than the other seven oils. Fig. 1 clearly shows that different vegetable oils inhibited the acid induced corrosion of mild steel as evident in the least weight loss of the metal specimens in the presence of different vegetable oils when compared to the free acid solution. There is a progressive increase in weight loss of the specimens as the exposure time is increased. This signifies that the dissolution of the metals increased at higher exposure timings. Increase in weight loss with increasing exposure timing may also be due to increase in the rate of diffusion and ionization of reacting different vegetable oils in the corrosion process [19]. An increase in exposure timing may also increase the solubility of the protective films on the metals and increasing the susceptibility of the metal corrosion.

The corrosion rate of mild steel specimens for the various biodiesel resources (vegetable oil) as an bio-inhibitor at the concentration of 5000ppm in 1 N HCl are given in Table 1 and Fig. 2. The corrosion rate of mild steel in 1 N HCl was less in the presence of the bio-inhibitors when compared to the blank acid solution. The corrosion rate decrease as the exposure times of the mild steel specimen increases. The corrosion rate calculated for

the different biodiesel resources (vegetable oils) shows that the corrosion rate was higher

in cotton seed oil followed by mustard oil. The minimum corrosion rate was observed in Neem oil and Castor seed oil at different intervals of exposure times. The corrosion rate of the different vegetable oils is given in Fig.2. This clearly indicates the deviation of corrosion rate of cotton seed oil and mustard oil has a less inhibitive property. The inhibitive property of oils toward the acid corrosion of mild steel specimens can be attributed to the adsorption of the components of the oils onto the mild steel surface.

The percentage of inhibition efficiency was calculated for different biodiesel resources at the concentration of 5000ppm in 1 N HCl solution and the results are given in Table 1 and Fig. 3. The result shows that the inhibition efficiency was higher for neem oil followed by castor oil, pongamia oil, jatropha oil rubber oil and bassia oil at different exposure times of 24, 48 and 72 hrs. The inhibition efficiency was found to be low in the oils of cotton, mustard, dillio and palm. The inhibition efficiency decreases as the exposure time increases. But in the cotton seed oil, mustard oil and palm oil, the inhibition efficiency was found to increase after 24 hours of exposure.

The effect of addition different vegetable oil as the bio-inhibitor at the concentration of 5000ppm for mild steel in 1 N HCl was investigated using gravimetric (weight loss) technique at different exposure timings of 24, 48 and 72h of immersion period. The gravimetric investigation in the present work indicates that the phytochemical components of the oils are adsorbed onto the mild steel surface resulting in the blocking of the reaction sites and protection of the mild steel surface from the attack of the corrosion in the acid medium.

Corrosion inhibition is initiated by the displacement of adsorbed water molecules by the inhibitor leading to specific adsorption on the metal surface. Some of these components may have heteroatoms in their molecules [20, 21, 22]. Thus, the corrosion of mild steel may be attributed to the adsorption of some components in the oils through these atoms that are regarded as centers of adsorption onto the metal surface thereby creating a barrier for mass and charge transfer and thus isolating the metal from further attack of the corrosive anions.

In the present study, the initial weight of mild steel specimen at time, t is denoted as W_i , the weight loss is DW and the weight change at time t , $(W_i - DW)$. The plots of $\log (W_i - DW)$ against time (hours) at room temperatures was studied and it showed a linear variation which confirms a first order reaction kinetics with respect to the corrosion of mild steel corrosion in 1 N HCl solutions in the presence of different vegetable oil (Fig. 4). Fig. 4 indicates the poor corrosion inhibition property on mild steel specimens for the mustard oil and cotton seed oil than the other vegetable oils. There is a probability for a multilayer protective coverage on the entire mild steel specimen surface for the oils neem, dillio and jatropha.

4. Conclusion

Biodiesel is non-toxic, biodegradable and non-corrosive alternative fuel. In the present study, ten different vegetable oils used as biodiesel resources were analysed for the bio-inhibition efficiency for mild steel corrosion in acid medium. Among the 10 oils, the inhibition efficiency was higher for neem, castor, pongamia, jatropha and rubber oils. Low inhibition efficiency was found in mustard and cotton seed oil but their efficiency increase after 24 hours of exposure. Corrosion inhibition may be due the formation of thin oil film on the surface of the mild steel specimen which prevents corrosion. These bio-inhibitors are safe to the mild steel engines.

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Figure caption

Fig 1. Variation of weight loss (mg) of mild steel with time (hours) for different biodiesel resources at 5000ppm concentrations in 1 N HCl solution

Fig 2. Variation of corrosion rate ($\text{mg cm}^{-2}\text{h}^{-1}$) of mild steel with time (hours) for different biodiesel resources at 5000ppm concentrations in 1 N HCl solution

Fig 3. Variation of inhibition efficiency (%) of mild steel with time (hours) for different biodiesel resources at 5000ppm concentrations in 1 N HCl solution

Fig 4. Variation of Log ($W_i - DW$) of mild steel with time (hours) for different biodiesel resources at 5000ppm concentrations in 1 N HCl solution

Table 1: corrosion rate and inhibition efficiency of different biodiesel resources at 5000 ppm concentration in mild steel specimen in 1 N HCl medium

Sample	Corrosion rate ($\text{g cm}^{-2} \text{h}^{-1}$)			Inhibition Efficiency (%)		
	24 hrs	48 hrs	72 hrs	24 hrs	48 hrs	72 hrs
Control	0.017	0.018	0.013	-	-	-
Bassia oil	0.006	0.005	0.004	68.113	75.346	68.611
Castor oil	0.000	0.002	0.003	97.431	89.182	77.398
Cotton oil	0.015	0.010	0.008	11.957	48.260	40.599
Dillo oil	0.010	0.007	0.005	42.781	63.732	63.124
Jatropha oil	0.002	0.003	0.003	86.182	81.803	77.398
Mustard oil	0.014	0.010	0.009	21.169	44.235	30.430
Neem oil	0.000	0.000	0.000	98.583	99.078	99.002
Palm oil	0.009	0.007	0.006	49.956	60.252	54.106
Pongamia oil	0.002	0.002	0.003	89.725	86.751	78.434
Rubber oil	0.004	0.005	0.005	76.794	75.010	64.160

Figure 1

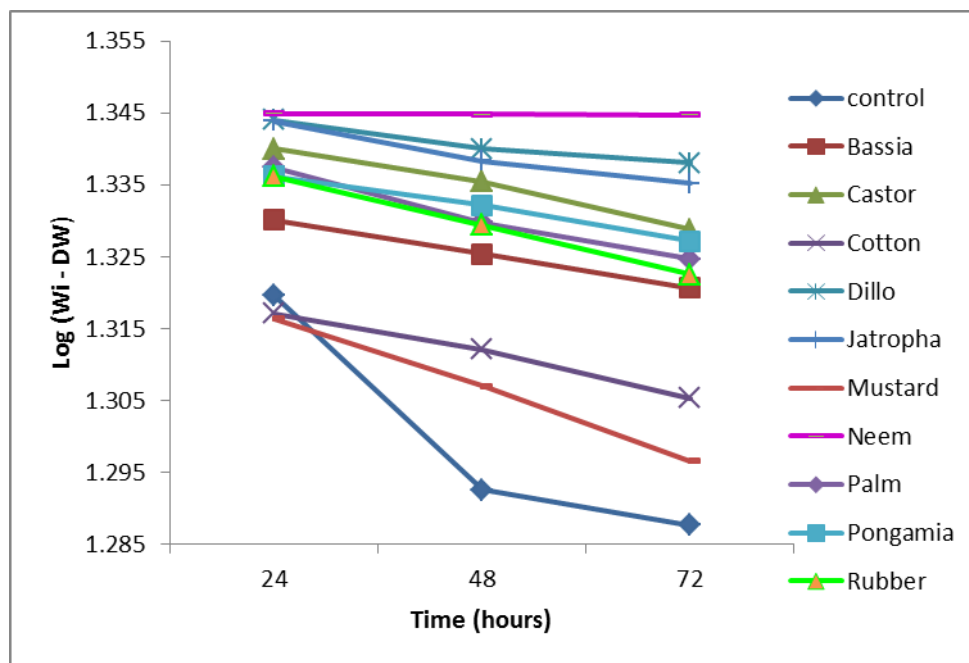


Figure 2

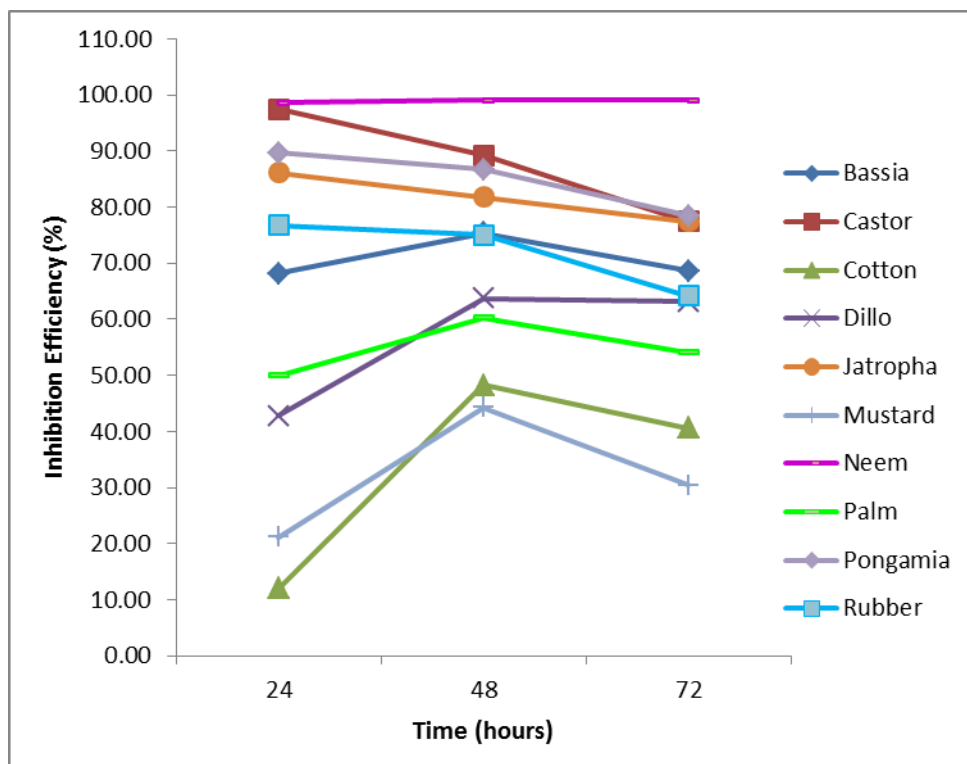


Figure 3

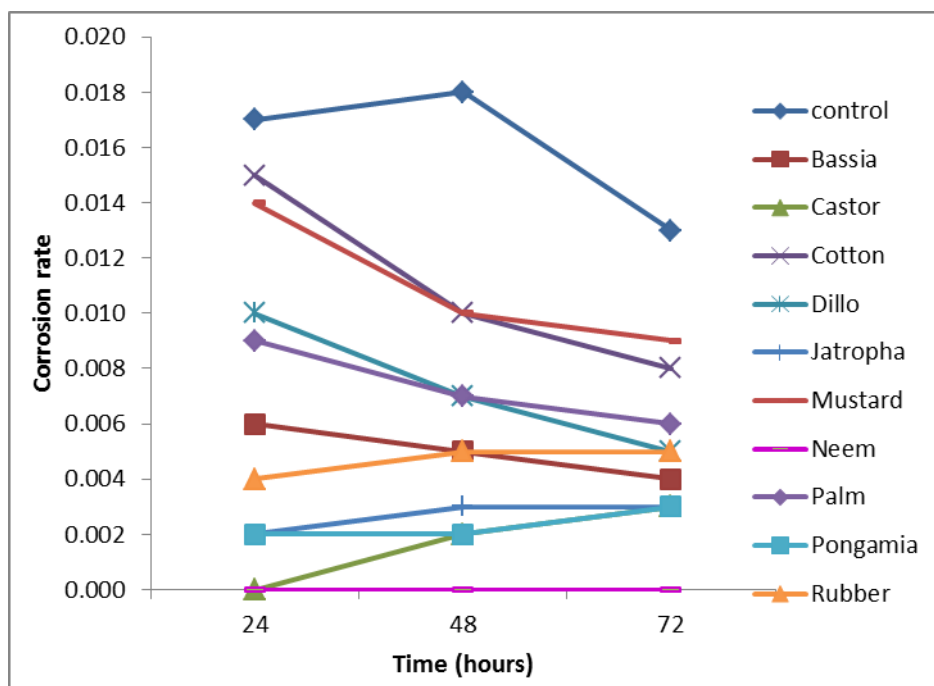


Figure 4

