

Research Article

Novel Synthesis of Vegetable Oil Derived Corrosion Inhibitors

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Two different naturally occurring vegetable oils, Cress seed oil, and Linseed oil were chemically modified via novel one pot synthesis to produce fatty acid derived amides. These were characterized by their ability to prevent corrosion of carbon steel in vigorously stirred, aerated seawater, one of the most corrosive naturally occurring environments. Corrosion inhibitor efficiencies of up to 99.6% or a corrosion rate reduction factor of 250 in this medium is reported. The one pot synthetic strategy means that the corrosion inhibitors can be made at very low cost.

1. Introduction

Carbon steel has become the preeminent construction and fabrication material for modern society. Its high strength and ease of machining and fabrication, coupled with relatively low cost, are mainly responsible for its ubiquity. However, this wonder material has a fatal flaw; in many of the natural environments it is asked to perform in, it will react with the environment and undergo spontaneous decomposition to a nonmetallic form. This *corrosion* process is well understood and has been extensively documented [1, 2]. The cost of protecting carbon steel from its service environment has been investigated by several authors over the years and a general consensus forming that the direct cost of corrosion ranges between 3 and 6% of Gross Domestic Product (GDP). The correlation between GDP and the cost of corrosion might initially be surprising, as one would not necessarily correlate the size of an economy to the cost of corrosion, but when one considers the link becomes more obvious. Carbon steel is such an integral part of society that as society becomes more industrialized, the amount of steel structures increases, and so the cost of corrosion broadly correlates to the size of an economy, and it is reasonable therefore to estimate the cost of corrosion as being a percentage of GDP. However the cost of corrosion studies, where performed, has shown some variation. This can be attributed to three principal factors, in the cost of corrosion for the economy: the industrialization

ratio of the economy, the corrosivity of the environment, and the quality of the mitigation strategies developed. Thus the United States, which, although highly industrialized, has a relatively low cost of corrosion of approximately 3.1% of GDP [3], due to high quality corrosion control, and the skills base needed to achieve good corrosion control. The United Kingdom, a similarly industrialized country, has a cost of corrosion of approximately 3.5% of GDP [4]. The differences are primarily due to the predominantly wetter and therefore more corrosive environment in the United Kingdom [5], both countries having exceptionally skilled corrosion engineers as well as mechanisms to train them. In the United States the preeminent source of corrosion engineers is NACE International, whereas in the UK there is the Institute of Corrosion. Gulf region countries tend to have costs of corrosion approaching 5.2% of GDP [6]. These countries are heavily industrialized in the oil and gas production and refining operations. The consequences of failure in these industries are not an option and so more effort is required to be invested in the prevention of corrosion, with consequently higher costs. Worldwide, the cost of corrosion has recently been assessed at \$1.8 trillion annually [7], which averages out to 3% of GDP.

Control measures to prevent corrosion are widely available and can be split into four broad approaches: design, coatings, cathodic protection, and inhibitors.

Coatings are very effective but need to be regularly applied [8]. The coating is only as good as the weakest link, so

good application is critical to performance [9, 10]. In addition the limited life of coatings means that they cannot be used for long life systems [11] nor can they be used when access for recoating is difficult. The recoating of a buried pipeline presents many challenges and is therefore not cost effective. Cathodic protection is only applicable to structures which are immersed in an electrolyte, such as underwater or submerged. This means that cathodic protection for the external side of pipelines is a successful strategy, provided that the coating chosen is compatible with the cathodic protection system [12]. Cathodic protection can also be used in the internal side of storage tanks but generally lacks the throwing power to be effective down a pipeline, without having a ribbon anode down the length of the pipeline, thus restricting flow. In practice, cathodic protection, either impressed current or sacrificial anodes, is not used to protect the internal side of pipelines from corrosion.

The internal side of transmission pipelines is a major challenge to coat with a barrier coating for several reasons. Firstly, the requirement for high quality application means that pipeline coatings have to be applied under controlled conditions (*mill applied*). The high temperatures of welding steels mean that the welding of pipe sections to produce the pipeline would therefore destroy the internal coating at the field joint. Since there are few technologies to recoat the internal side of the field joints, the field joints are usually not protected. If the field joints are not protected, then any significant corrosivity would cause rapid failure of the field joint areas. Secondly, the internal surfaces of pipelines are often subject to vigorous scouring actions by the cleaning pigs used to remove deposits. The harsh abrasive action means no coating can withstand the pigging operation. Technologies exist [13] for externally applied coatings in the trench, after welding (field joints), but no reliable system exists for the internal side of the pipeline. Thus the internal surfaces of most pipelines are left uncoated.

The uncoated internal side of pipelines means that most pipelines tend to have a limited life, typically 25–100 years [14]. The life prediction is achieved by assuming uniform corrosion rates and increasing the wall thickness with a *corrosion allowance* to provide the required life. The life of such pipelines is limited by the corrosivity of the fluid and is highly dependent upon the actual corrosion mechanisms. Problems in the early failure of pipelines can occur when localized corrosion phenomena such as pitting or crevice corrosion, which are highly localized forms of corrosion, cause premature failure of the pipeline. To extend the life of pipelines against internal corrosion, the fluids are modified to reduce the corrosivity as much as possible. This may be via drying of the fluids or the removal of corrosive gases such as carbon dioxide or hydrogen sulfide. An alternative approach is to use corrosion inhibitors to reduce the corrosivity of the fluids.

Recent developments using modern inhibitor chemicals and formulations are now providing the possibility to protect internal surfaces from corrosion by preventing the fluids from coming into contact with the steel, a dewatering of the internal surface. Many corrosion inhibitors have been developed and the reader is directed elsewhere [15] for a more comprehensive review of the subject. There are several

mechanisms by which corrosion inhibitors work: electrochemical inhibitors which interfere with the corrosion reaction, such as cathodic or anodic poisons, cathodic or anodic polarisers, or by acting as barriers, decreasing the electrical conductivity of the metal surface (dewatering) [16].

In this paper we present a novel strategy to synthesize surfactant type corrosion inhibitors. The parent chemicals are low cost vegetable oils and so are a renewable and relatively low cost source of inhibitor chemical. Being based on vegetable oils, the more natural product means it is more likely to be biodegradable and less environmentally damaging (“greener”) than some of the alternative corrosion inhibitors available. In addition we also report a novel single pot synthetic route. We feel this is most important since commercial viability will to a large part depend upon the cost of manufacture. Every chemical process which must be applied to a reaction, such as clean up and purification, significantly increases the cost and increases the production of wastes which must also be processed, at additional cost.

Characterization of the corrosion inhibitors synthesized was performed via several different methodologies. Firstly the reaction progression was followed by thin layer chromatography (TLC), the chemical changes were followed by Fourier transform Infrared Spectroscopy, (FTIR), the composition was measured by GC, and corrosion rates were quantified via linear polarization resistance measurements as well as constant immersion over time to determine corrosion rates by mass loss measurements to correlate the LPR measurements.

2. Experimental

2.1. Synthesis. The glassware for the reaction was cleaned and dried at 140°C and assembled hot. Once assembled the system was allowed to cool to room temperature under a dry nitrogen atmosphere. The reaction vessel consisted of a 3-neck 250 mL round bottomed flask equipped with dry nitrogen gas inlet bubbler, reflux condenser, and pressure equalizing separating funnel. Gas escape was through the top of the condenser. Once cool, a magnetic stirrer bar was added and the apparatus set up on a hotplate stirrer equipped with silicone oil bath. The temperature of the oil bath was monitored by external digital thermometer.

9.0 mL of dry methanol was introduced to the flask and 0.060 g of clean and dry sodium metal added. Once the sodium had completely dissolved, 20 mL of the vegetable oil was introduced and vigorous stirring commenced. The system was heated to reflux for one hour. After this time, the efficiency of the condenser was reduced by turning down the cooling water and the temperature of the system was allowed to rise to 200°C. During this time the methanol slowly escapes from the system out of the top of the now less efficient reflux condenser, allowing the temperature to rise. The reaction was held at this temperature and monitored by TLC spotting using alumina stationary phase and ethyl acetate as eluent. When the spot corresponding to the oil had disappeared, aqueous concentrated ammonia was added at the rate of 1.0 mL over ten minutes for 50 minutes (5 mL ammonia added in total). After a further 30-minute reflux the mixture was cooled under nitrogen and transferred to sample bottle.

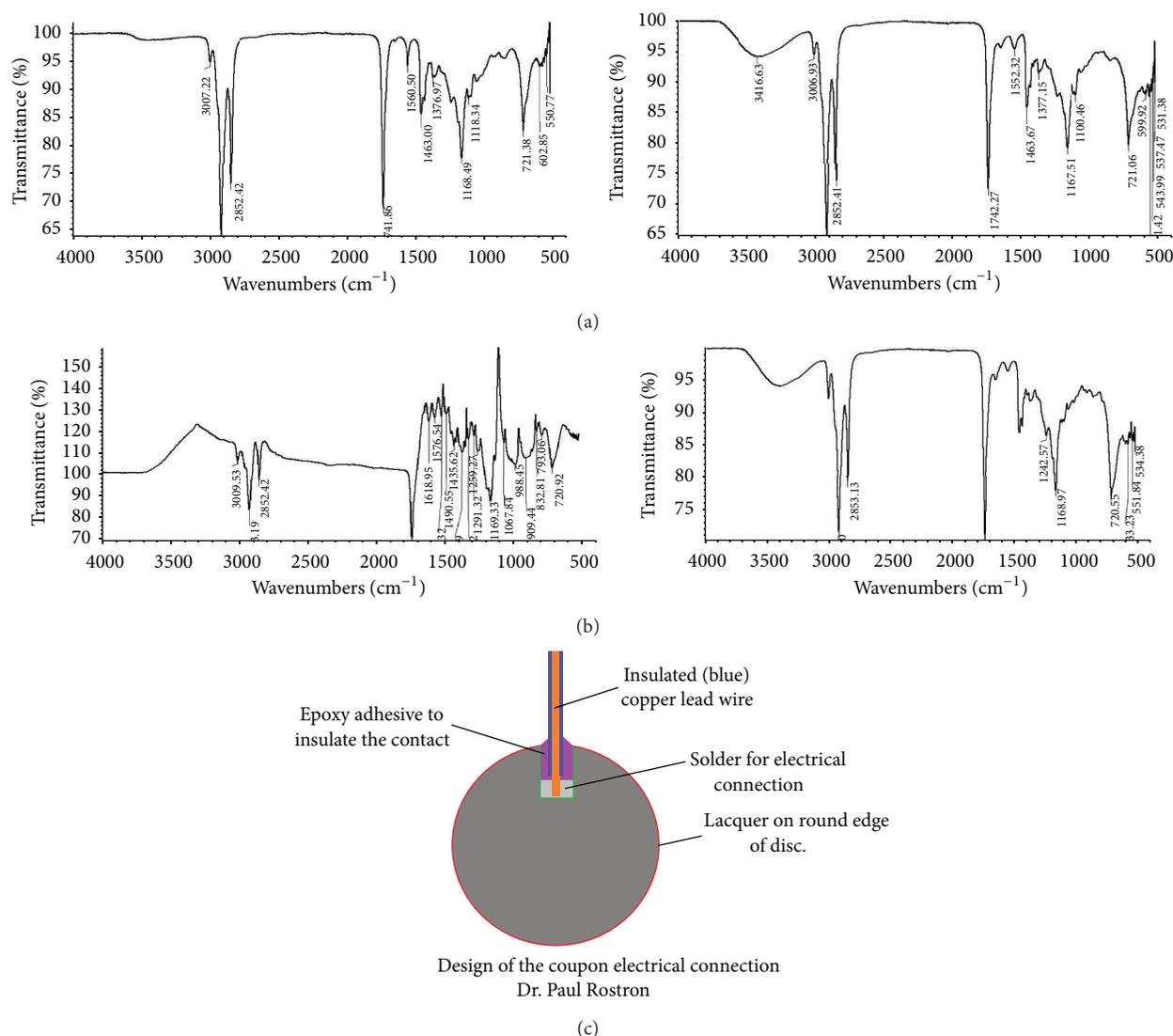


FIGURE 1: (a) FTIR spectra of the samples of Cress oil methyl ester and amide taken during the reaction. (b) FTIR spectra of the samples of Linseed oil methyl ester and amide taken during the reaction. (c) Design of the coupon electrical connection.

2.2. FTIR Characterization. The reaction progress was investigated using the Fourier Transform Infrared (FTIR) technique. Figures 1(a) and 1(b) show the spectra of Cress oil and Linseed oil methylester and amide, respectively.

2.3. Corrosion Rate by Linear Polarization Resistance (LPR) Measurement. To a 1 L flat bottomed flask equipped with two graphite counter anodes, a sample metal holder, and aerator was added 500 mL of fresh seawater. Freshly collected, natural seawater is used because studies have shown that the corrosivity of artificial seawater does not match the corrosivity of fresh seawater [17]. Fresh seawater was easily available at the test location. Carbon steel disks of approximately 25 mm diameter and 10 mm thickness, cut from round bar standard mild steel, were used as metal samples. To prevent galvanic action between the lead electrode wire and the carbon steel, the connection was designed as follows: a 5 mm diameter

radial hole was drilled into the edge. Small pieces of solder were inserted into the hole and the metal disk was heated by microblowtorch until the solder melted. An insulated copper wire was inserted into the hole (last 5 mm unsheathed) and the wire held in place until the solder freezes. The hole was then filled with epoxy adhesive. The round edge of the coupons was coated in varnish so only the flat faces were exposed to the environment. A schematic of the coupon design is shown in Figure 1(c). Finally, before each use, the faces were polished with 1200 grit emery paper. Total surface area of the samples was approximately 10 cm², although each coupon was measured individually as ± 1 mm and the accurate total surface area used.

For each experiment the linear polarization resistance was determined using a Gamry 600 potentiostat using a linear scan voltammetry program. LPR linear sweep parameters used were as follows: a scan from $E_{\text{corr}} - 50$ mV to $E_{\text{corr}} + 50$ mV,

TABLE 1: Summary of corrosion rates as measured by linear polarization resistance showing the effectiveness of the inhibitors synthesized.

Oil	Uninhibited corrosion rate	Inhibited corrosion rate	Inhibitor efficiency (%)	Corrosion rate reduction ratio
Cress seed oil amide	$2.0 \pm 0.4 \text{ mmyr}^{-1}$ $81 \pm 16 \text{ mpy}$	$8.3 \times 10^{-3} \pm 0.008 \text{ mmyr}^{-1}$ $0.2 \pm 0.01 \text{ mpy}$	99.6%	241
Linseed oil amide	$1.45 \pm 0.005 \text{ mmyr}^{-1}$ $58 \pm 0.2 \text{ mpy}$	$0.025 \pm 0.015 \text{ mmyr}^{-1}$ $1 \pm 0.6 \text{ mpy}$	98.3%	58

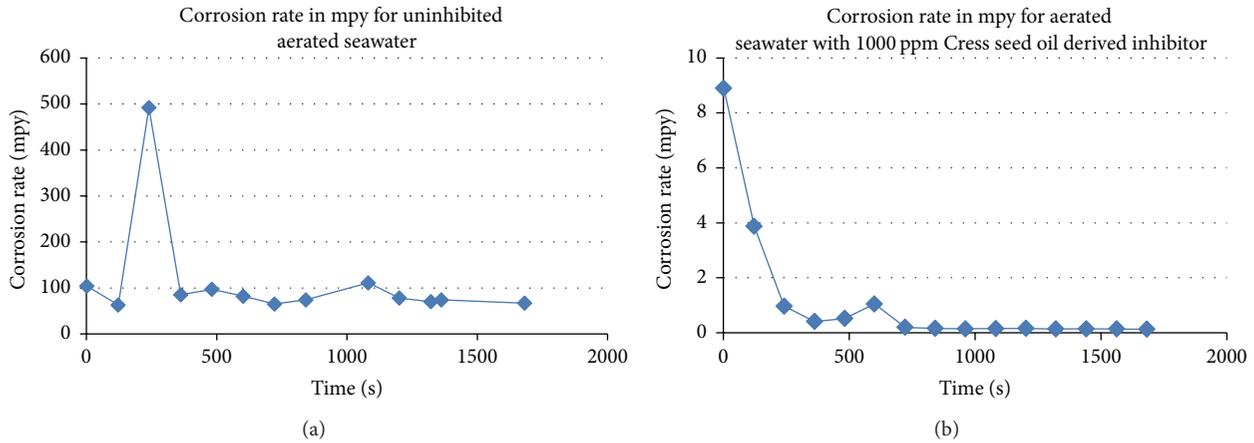


FIGURE 2: (a) Corrosion rate versus time by linear polarization measurements for uninhibited carbon steel coupon in stirred aerated seawater. (b) Corrosion rate versus time by linear polarization measurements for inhibited carbon steel coupon in stirred aerated seawater. Cress seed oil derived inhibitor at 1000 ppm concentration added.

at a scan rate of 10 mV/min. E_{corr} , or the open circuit voltage, was determined using the potentiostat and a drift voltage of <0.02 mV/min.

The seawater was vigorously stirred using magnetic stirrer and bubbled with fine air bubbles (using an aerator stone) for ten minutes to achieve a saturated aerated solution. Repeated LPR measurements were recorded for 30 minutes (approximately 15 measurements) to determine an average corrosion rate, as well as observing any time related trends. The coupon was then cleaned again to remove any corrosion from the first step and 0.5 mL of the corrosion inhibitor added, achieving an approximate concentration of $1/500 \times 1E6 = 100 \text{ ppm}$. Once uniformly mixed the coupon was returned to the apparatus and LPR measurements were recorded for a further 30 minutes (approximately 15 measurements).

The effectiveness of the inhibitors as measured by repeated linear polarization resistance measurements is shown in Figures 2 and 3. Average uninhibited corrosion rate is given in Figures 2(a) and 3(a) for the Cress oil and Linseed oil respectively. There is some slight variation, which is possibly due to the slight difference in the position of the electrodes between experiments. For this reason the effectiveness of each inhibitor is measured after the corrosion rate of uninhibited stirred seawater is measured. Thus corrosion rate reduction is a relative term and is measured individually.

The effect of added corrosion inhibitor is shown in Figure 2(b) for Cress oil and Figure 3(b) for the Linseed oil, and it shows a very substantial decrease in corrosion rate. The plots are shown to demonstrate the time average effect and also to show that whilst the uninhibited corrosion rate

is relatively uniform, the addition of the inhibitor shows a time dependency effect. This is most likely due to the establishment and build-up of the inhibitory film over time. The calculations of corrosion rate from the LPR data are summarized in Table 1.

Calculation of inhibitor efficiency is determined according to [18]

Efficiency

$$= \frac{\text{Corrosion rate}_{\text{uninhibited}} - \text{Corrosion rate}_{\text{inhibited}}}{\text{Corrosion rate}_{\text{uninhibited}}} \quad (1)$$

$$\times 100.$$

Thus for Cress seed oil efficiency = $((2.0 - 8.3 \times 10^{-3})/2.0) * 100 = 99.6\%$.

Corrosion rate reduction ratio is

$$\text{reduction ratio} = \frac{\text{Corrosion rate}_{\text{uninhibited}}}{\text{Corrosion rate}_{\text{inhibited}}} \quad (2)$$

Thus for Cress seed oil reduction ratio = $2.0/8.3 \times 10^{-3} = 240.96$.

The same calculation is done for Linseed oil.

Thus for Linseed oil average inhibitor efficiency = $((1.45 - 0.025)/1.45) * 100 = 98.3\%$.

The corrosion rate reduction ratio for linseed oil = $1.45/0.025 = 58$.

TABLE 2: Mass loss results and penetration rate in mpy and mmyr⁻¹.

(Inhibitor) (ppm)	Cress seed oil derived amide corrosion inhibitor				Linseed oil amide derived corrosion inhibitor			
	Mass loss (g/cm ⁻²)	Time (hrs)	Corrosion rate (mpy)	Corrosion rate (mmyr ⁻¹)	Mass loss (g/cm ⁻²)	Time (hrs)	Corrosion rate (mpy)	Corrosion rate (mmyr ⁻¹)
0 (control)	0.0835	240	152.5	3.86	0.0803	192	183.3	4.60
50	0.00307	240	5.59	0.142				
100	3.10 × 10 ⁻⁴	240	0.563	0.0143				
150	7.00 × 10 ⁻⁶	240	0.0128	3.24 × 10 ⁻⁴				
200	2.32 × 10 ⁻⁵	240	0.0421	0.00107	0.00208	192	4.75	0.120
400	2.94 × 10 ⁻⁵	240	0.0535	0.00136	2.90 × 10 ⁻⁵	192	0.0661	0.00168
600	7.05 × 10 ⁻⁶	240	0.0128	3.25 × 10 ⁻⁴	2.19 × 10 ⁻⁵	192	0.0854	0.00127
800	0.0000	240	0	0	7.39 × 10 ⁻⁶	192	0.0168	4.27 × 10 ⁻⁴
1000	0.0000	240	0	0	7.00 × 10 ⁻⁶	192	0.0159	4.05 × 10 ⁻⁴

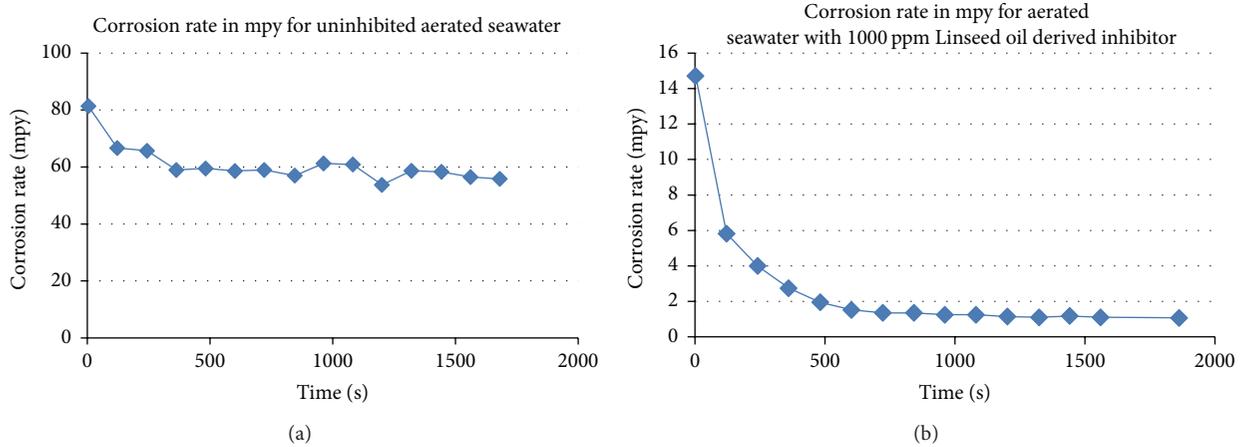


FIGURE 3: (a) Corrosion rate versus time by linear polarization measurements for uninhibited carbon steel coupon in stirred aerated seawater. (b) Corrosion rate versus time by linear polarization measurements for inhibited carbon steel coupon in stirred aerated seawater. Linseed oil derived inhibitor at 1000 ppm concentration added.

2.4. Corrosion Rate by Mass Loss. Linear polarization resistance is a very effective technique for measuring instantaneous and relative corrosion rates but is rarely performed in industry. The usual method of corrosion measurement is via mass loss. Mass loss measurements are performed by immersion of the clean, weighed samples in the corrosive environment for enough time for the corrosion process to occur. After exposure the corrosion product is removed using gentle cleaning such that only the corrosion product is removed. The samples are then weighed again and the difference in mass is recorded. The time of immersion depends upon the corrosivity expected and the quality of the balance used. In this experiment we used a 4 decimal places balance, accurate to 0.1 mg. Measurable mass loss can therefore be achieved in as little time as one week of immersion. In this experiment, the samples were exposed for 8 days.

Regular shaped rectangular samples of carbon steel plate (coupons) were cleaned to grey metal by acid etch, degreased, and dried in an oven. The dimensions were recorded using Vernier calipers and the total surface area measured. The coupons were then suspended in 1 L of freshwater containing a range of inhibitor concentration from 0

to 1000 ppm; the procedure was in accordance with ASTM G1 standard test method for corrosion rate by mass loss [19]. Images of the corrosion coupons as shown in Figures 4(a) and 4(b) show clearly the effectiveness of the inhibitors. The mass loss and resultant corrosion rate in mpy and mmyr⁻¹ are shown in Table 2.

Calculation of Mass Loss is as follows [20]:

$$\text{Mass loss} = \frac{\text{Mass}_{\text{uninhibited}} - \text{Mass}_{\text{inhibited}}}{\text{Area}} \quad (3)$$

Area was measured for each coupon as there were slight variations.

Typical calculation is as follows.

$$\text{Linseed Oil Mass Loss}_{(0 \text{ ppm})} = \frac{(18.6520 \text{ g} - 17.5458 \text{ g})}{\text{Area} = 1.1062 \text{ g}/13.77 \text{ cm}^2 = 0.803 \text{ g/cm}^2}.$$

Calculation of penetration rate is as follows:

$$\text{Corrosion rate} = \frac{K \times w}{A \times T \times D} \quad (4)$$

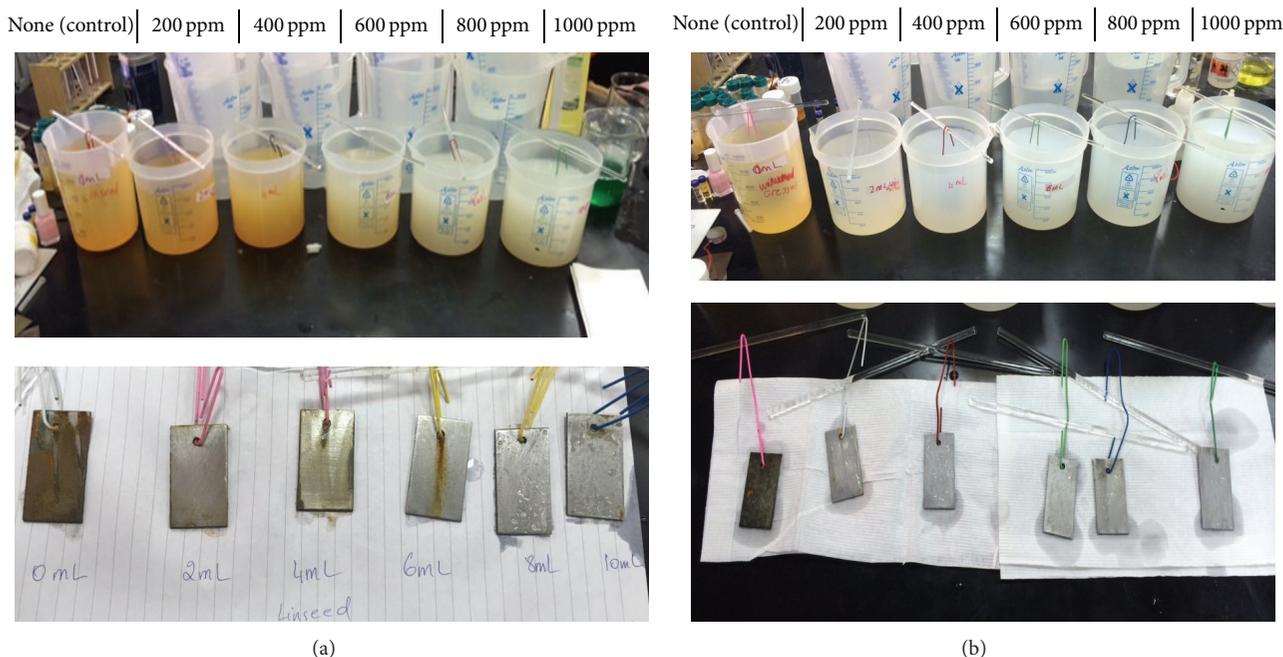


FIGURE 4: (a) Linseed oil derived CI in tap water: one-week immersion of carbon steel coupon. (b) Cress seed oil derived CI in tap water: eight-day immersion of carbon steel coupon.

K is the rate constant = $8.74 \times 10^4 \text{ mmyr}^{-1}$ or 3.45×10^6 for mpy, W is the mass in g, A is the area in cm^{-2} , and T is the time in hours; therefore 8 days = 192 hrs.

Typical calculation is as follows.

$$\text{Corrosion rate in mmyr}^{-1}_{(0 \text{ ppm})} = (8.74 \times 10^4 \times 0.0803) / (192 \times 7.87) = 4.6 \text{ mmyr}^{-1}.$$

Typical calculation is as follows.

$$\text{Corrosion rate in mpy}_{(0 \text{ ppm})} = (3.45 \times 10^6 \times 0.0803) / (192 \times 7.87) = 183.3 \text{ mpy}.$$

The same calculations are applied to all the concentrations for both Cress and Linseed oil and the results are shown in Table 2.

Figures 4(a) and 4(b) show pictures of the results of the mass loss measurements and the effect of concentration of the inhibitor on the corrosion rate.

3. Conclusions

The one pot synthesis method allows for an easy synthetic route to vegetable oil based corrosion inhibitors. The chemicals required and lack of cleanup means that the process is highly cost effective and should be a commercially viable approach to the synthesis of effective corrosion inhibitors. The corrosion rate reduction achieved was very high, with corrosion rate reduction ratios in excess of 250. This is a viable approach to reduce the corrosion of carbon steel exposed to aerated seawater.

Further work, looking at different vegetable oils as well as long term stability studies, will also be performed in the future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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