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Studies on Jasiminum grandiflorum as VCI for mild steel in marine environment

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KeyWords

Corrosion Rate-CR, Inhibition Efficiency- IE, Jasiminum Grandiflorum- JG, Mild Steel- MS, Relative Humidity- RH, Vapour phase corrosion Inhibitor- VCI, Weight Loss-WL

ABSTRACT

Corrosion inhibition behaviour of essential oil from Jasiminum grandiflorum (JG–Jasmine) on mild steel in marine environment was studied. Essential oil was obtained by hydrodistillation method and analyzed by GC and FTIR. The inhibition efficiency was ascertained by gravimetric, potentiostatic polarization methods and A C impedance measurement under controlled conditions of 100% relative humidity (RH) in NaCl environment. Antimicrobial test was carried out to evaluate the effect of inhibitor on bacteria and fungi. The FTIR and GC studies reveals that the presence of hetero atoms in the major constituents of the oil. Vapour pressure and pH ranges of this oil indicates the protecting ability of this oil from corrosion of MS. The gravimetric results confirmed that the inhibitor used in this study retards the corrosion of mild steel in NaCl environment to a good extent. The increase in the polarization of cathodic and anodic reactions of mild steel indicates that this essential oil acts as mixed type inhibitor but the cathodic protection was more predominant. The temperature effect on the corrosion behavior of steel in marine environment without and with the inhibitor at 4% was studied in the temperature range from 303 K to 323 K, the associated activation energy have been determined. From SEM studies and found to obey Temkin's adsorption isotherm reveal that the corrosion inhibition is due to adsorption of inhibitor molecules on metal surface. The inhibitor is good resistant to bacteria and fungi stains.

INTRODUCTION

Corrosion is the destruction or deterioration of metals and alloys. The damage due to corrosion is immense resulting in severe loss of money and poses material science problem. The impact of corrosion on Indian economy was around Rs. 2 lakh crores a year and at US $2.2 trillion, the annual cost of corrosion worldwide is over 3% of the world's gross domestic product (GDP) [1]. As resources are consumed in due course of time, if not immediately, conservation and recycling will become watch wards, not catch wards. Corrosion can be reduced by using inherently corrosion resistant materials like special alloys, plastics etc., or by coating on corrodable materials with corrosion resistant films and paints. It has been well established that among the corrosion protection methods, control through use of corrosion inhibitors has been found to be most cost effective [2]. Among them vapor corrosion inhibitors (VCI) are especially useful for protecting metals in cavities and other hard to reach places.

VCI are organic compounds with vapor pressure in the range 10^{-7}– 10^{-2} mm Hg [3]. They are transported by diffusion through the gas phase and adsorbed onto the metal with a thickness of a few mono layers, thereby protecting it from corrosion. Generally, VCI can be incorporated in packaging materials such as VCI treated paper, films, cardboard, foam pads, emitters, tablets and pouches which can be inserted in the packaging.

N,N-dimethylaminoethanol [4], essential oil of Salvia aucheri mesatlantica [5], Amine-based corrosion inhibitors such as morpholine [6], cyclo hexyl amine [7], ethanol amine and nitrite [8] and amine nitro benzoate [9] and combination of these [10] have been in use since the 1950’s when the United States Navy used them to protect boilers and piping systems [11]. Commercial use of VCIs (emitters, packaging products, coatings, and process applications) began in the 1970’s [12]. Though these inhibitors are used extensively they pose severe environmental problems because they are not eco-friendly.

The literature survey indicates that most of the VCIs are synthetic organic compounds. The study of VCI from natural sources is very rare. Hence essential oil from Jasmine- JG has been chosen for the present study. The advantages in favour of these oils are: eco-friendliness, easy availability from renewable sources, non-toxic nature and pleasant odour. In the present work antimicrobial activity of the oil was also studied.

MATERIALS AND METHODS

Preconditioning of metal specimen

The rectangular mild steel sheet of 0.25cm thickness was cut into strips of 5X2cm^2. The surface of the strip was smoothened by grinding in a surface grinder, polished using different grades of emery papers (1/0, 2/0, 3/0, and 4/0), degreased with trichloroethylene and stored in desiccator.

Preparation of essential oil

The essential oil was procured from M/S Encee aromatics, a perfume manufacturing company situated near Mettupalayam in Tamil Nadu, India. The company manufactures the oils by steam distillation method. The oil JG was produced from their flower. The extraction of essential oil of the flower part was conducted by steam distillation using a Clevenger type apparatus and the essential oil yield was 1.2%. The essential oil obtained was dried under anhydrous sodium sulfate and stored at 277 K in the dark before analysis.

VCI Characterization

The oil was subjected to GC analysis was performed using a Perkin-Elmer Autosystem GC apparatus (Walhton, MA, USA) equipped with a single injector and two flame ionization detectors (FID). The apparatus was used for simultaneous sampling to two fused-silica capillary columns (60 m x 0.22 mm, film thickness 0.25 lm) with different stationary phases: polydimethylsiloxane and polyethylene glycol, carrier gas: helium (1 mL/ min). Injector and detector temperatures were held at 553 K. Split injection was conducted with a ratio split of 1:80, injected volume: 0.1L. Identification of the components was based on the comparison of their GC retention indices (RI) on non-polar and polar columns, determined relative to the retention time of a series of n-alkanes with linear interpolation, with those of authentic compounds or literature data and comparison of spectra with those of literature studies.

FTIR spectrum of the oil was recorded using a Bio–Rad FTIR–65 spectro photometer to identify the functional groups present in the oil.

Vapour Pressure- The important property of the VCI is its vapour pressure, which should be high and long lasting. The vapour pressure of the VCI was measured using weight loss method and the weight loss values were substituted in the equation [1] given below [13].

$$P = \frac{W \quad [2\pi RT]^{1/2}}{AtM} \qquad [1]$$

where, P–partial vapour pressure of the essential oil, A–area of the hole in cm^2, t-time in seconds, W-weight loss in mg, T-temperature in Kelvin, R–gas constant (8.314 JK^{-1} mol^{-1}) and M–average molecular mass of the essential oil.

Preparation of VCI and VCI impregnated papers

The 0.25 **-** 2.5 mL of oil was mixed with required amount of ethanol to obtain 1-10% concentrations by volume. The total volume of solution in each case was 25ml. The pH **o**f each mixture was tested using Systronics-335 digital pH meter. The VCI mixtures prepared as above are labeled and stored in air tight containers.

The VCI impregnated papers were prepared by impregnation method [14- 15]. Kraft paper of size 30 x 30cm^2 was dipped into the VCI solution till completely wet and taken out and the excess solvent was allowed to evaporate in a dust free chamber. Then the VCI impregnated paper was cut into required size to cover the strip and stored in desiccator.

Test methods

Vapour Inhibition Ability (VIA) test

Weight loss of each specimen was found out in 0.005, 0.01, 0.05 and 0.1M NaCl environments with and without the inhibitor at 1- 10% concentration impregnated paper for 7 and 15days. 1000mL jars (10" long x 4" wide) with tight fitting rubber cork carrying a glass rod with four hooks having provisions to suspend the specimens were taken for VIA test. The bottom of the jar contained 100 ml of NaCl solution to produce 100% RH. The metal specimens were wrapped with different concentrations of VCI impregnated kraft paper suspended in these bottles by nylon tags. It is not in contact with the environmental liquid. A series of jars was kept in a thermostat water bath at 313K to allow continuous condensation of moisture on the metal specimens. The specimens were derusted, dried and reweighed and the inhibition efficiency (IE) was determined from the weight loss using the formula:

$$IE\ (\%) = \frac{WL_{\text{without Inhibitor}} - WL_{\text{with Inhibitor}}}{WL_{\text{without Inhibitor}}} \qquad [2]$$

As 4% VCI was found to give optimum protection, it was adopted for remaining tests.

Cyclic Corrosion test

For this test 4% VCI impregnated paper was used at 323K in the same set up. The tests were conducted through a temperature cycle of 16 hours in the thermostat at 323K and 8 hours at ambient temperature up to 5 cycles (5days). This method creates the conditions of cyclic evaporation and condensation of moisture on metal surface and used to evaluate the corrosion inhibiting ability in 0.005, 0.01, 0.05 and 0.1M NaCl environments[16].

Salt Spray test

This test was carried out on Chaus Corp Pine Brooke Salt spray chamber, to assess the efficiency of the VCI impregnated paper under marine environment. Metal specimens were wrapped with 4% VCI impregnated and unimpregnated Kraft papers. They were hanged in a perforated plastic container and kept inside the salt spray chamber in such a way that the wrapped specimens are exposed freely to the fog of 3.5% NaCl solution used for spraying. The spraying was carried out for 5 hours, 10 hours and 15 hours duration at 303K. The specimen was then removed from the cabinet and weight loss was determined at the end of the study [17].

Corrosion inhibition behaviour of major constituents present in the oil under VIA test

Benzyl acetate and linalool, the major constituents of the essential oil, were procured from M/S Archana agencies, Bangalore, India. As in the case of JG oil, the 4% major constituents corrosion inhibition efficiency was studied in the 0.005 M NaCl environment at 313K for 7 days in the same set up. This test was used to compare the efficiency of oil with their major constituents.

Electro chemical methods

Potentiodynamic polarization studies

For electrochemical measurements an Atmospheric Corrosion Monitor (ACM) was fabricated for mild steel as described by Mansfeld et al., (1976) [18] and used for potentiodynamic polarization and AC impedance studies. Potentiodynamic polarization studies were performed with 4% VCI paper using EG 2G PAR model 173 potentiostat. The ACM assembly consists of mild steel as a working as well as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The polarization measurements were carried out for mild steel in the presence/absence of VCI impregnated Kraft paper at a sweep rate of 1mV/sec. The open circuit potential (OCP) of the electrode with respect to SCE was noted. After a steady state was attained, the electrode potential was fixed at ± 200 mV / sec. The polarization was carried out from a cathodic potential of 750mV vs. SCE to an anodic potential of -250 mV vs. SCE at a sweep rate of 1mV per second. Graphs were drawn between potential and log I. The linear segments of the anodic and cathodic polarization were extrapolated to corrosion potential to obtain corrosion current (I_{corr}), corrosion potential (E_{corr}) and anodic (ba) and cathodic (bc) Tafel slopes. All experiments were carried out at room temperature and were conducted in duplicate to confirm the results. The inhibition efficiency was calculated using the following formula:

$$I.E\ (\%) = \frac{I_{without\ inhibitor} - I_{with\ inhibitor}}{I_{without\ inhibitor}} \times 100 \qquad [3]$$

AC impedance studies

Nyquist plots were recorded at 4% VCI impregnated and unimpregnated Kraft paper using the same experimental set up as in polarization method with PAR Impedance Electrochemical Analyzer M6310 with M398 software. Experiments were carried out at the corrosion potential for the frequency range of 10 kHz to 100 MHz by the impression of AC signals of amplitude 10 mv to the system. An AC potential of 10mV was superimposed on the steady OCP. The real part (Z') and the imaginary part (Z'') were measured at various frequencies. A plot of Z' vs. Z'' was made. The values of the charge transfer resistance (R_{ct}), double layer capacitance (C_{dI}) were obtained from the difference between low and high frequency intercept values. The charge transfer resistance values (R_{ct}) were used to calculate the percentage inhibition using the equation

$$I.E\ (\%) = \frac{R_{ct} - R^{o}_{ct}}{R_{ct}} \times 100 \qquad [4]$$

where, R_{ct} and R^{o}_{ct} are charge transfer resistance values with and without inhibitor.

Antimicrobial activity studies

The VCI coated kraft paper used for testing the ability of the oil in 100% RH, and there is a possibility for micro-organism growth. Microorganisms can also accelerate the rate of corrosion and shift the mechanism of corrosion. The detection of antibacterial and antifungal activities of oil was tested against the following listed microorganisms using well plated method [19]. Bacteria such as *Escherichia coli*, *Proteus mirabilis, Klebsiella pneumoniae, Pseudomonas flourescence*, *Klebsiella* species, *Shigella dysentriae, Micrococcus luteus*, *Bacillus subtilis*, *Enterococcus faecalis*, *Staphylococcus aureus, Salmonella typhimurium, Pseudomonas aeruginosa*, *Streptococcus pyrogens*, *Proteus vulgaris*, and *Salmonella* species were selected. Nutrient agar was prepared using beef extract (3g), peptone (5g), sodium chloride (5g), agar (15g) and distilled water (1000 mL). The 24 hour broth culture of each of the test micro organisms was aseptically introduced and 100 µL of the oil was then introduced into the wells in the plates. A control well was also filled with 100 µL of the chloromphenicol. The plates were then incubated at 37°C for 24 hours and then screened for zone of inhibition.

The procedure adopted for antifungal test is the same as mentioned in the antibacterial activities well plated method, but instead of nutrient agar, sabourauds broth was used for fungal growth. The VCI was tested against the following fungi separately. Spore suspension from the well grown and sporulating cultures of these fungi was measured [20]. Fungi such as *Aspergillus niger*, *Penicillium pinophilium*, *Phanerochaete chrysosporium, Ganoderma lucidum* and *Ischnoderma resinosum* were chosen to study the antifungal activity of the essential oils.

Free energy of adsorption

The corrosion rate is strongly influenced by temperature, concentration of environment and time of exposure. The free energy of adsorption was calculated from the results obtained from VIA test conducted at various temperatures (303, 313 and 323K using the formula [21],

$$\Delta G_{ads} = -RT \times 2.303 \times [\log 55.5\theta / c(1-\theta)] \qquad [5]$$

where, c-concentration of inhibitor in mol/liter, θ-surface coverage, R-gas constant and T- temperature in Kelvin.

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Temkin adsorption isotherm

Corrosion inhibition offered by the VCI for mild steel is confirmed from Temkin adsorption isotherms, wherein surface coverage (θ) is plotted against log C.

RESULTS AND DISCUSSION

VCI Characterization

The measured pH values of the JG oil are around 6.68 to 6.99. Literature indicates that the corrosion increases rapidly below pH-4 with hydrogen evolution. At pH 6-8.5 VCI resists corrosion [22]. The measured vapour pressure of the oil is $6.789X10^{-3}$mm Hg, which is really high to vaporize and condense after reaching the metal surface, thereby inhibit the corrosion process. FTIR spectrum for the 4% VCI impregnated papers are presented in figure 1. The C-O stretching vibration of alcoholic groups of linalool, phytol, eugenol, methyl anthranilate, sesquiterpene alcohol appeared at 1023 cm^{-1}, 1068 cm^{-1}, 1111 cm^{-1}, 1154 cm^{-1}, 1287 cm^{-1}. The absorption bands at 696 cm^{-1} and 654 cm^{-1} indicate the presence of C-C stretching and mono substituted carbon. Absorptions at around 2873 cm^{-1} corresponds to C-H stretching vibrations. The JG oil examined in this work indicate that the presence of alcoholic O-H, C=C, C-N and C-O groups [23 & 24]. GC analysis chromatogram is presented in figure 2, the retention time and the calculated peak values indicates the major chemical constituents present in JG oil is benzyl acetate-25%, d–linalool: 15.5%, benzyl benzoate: 17.5%, phytol: 12%, para cresol: 2%, methyl antharanilate: 1%, indole: 3%, eugenol: 3.5%. The GC result confirms the presence of alcoholic group and carbon-carbon double. The composition of JG oil observed in GC is similar to composition given in literature [25].

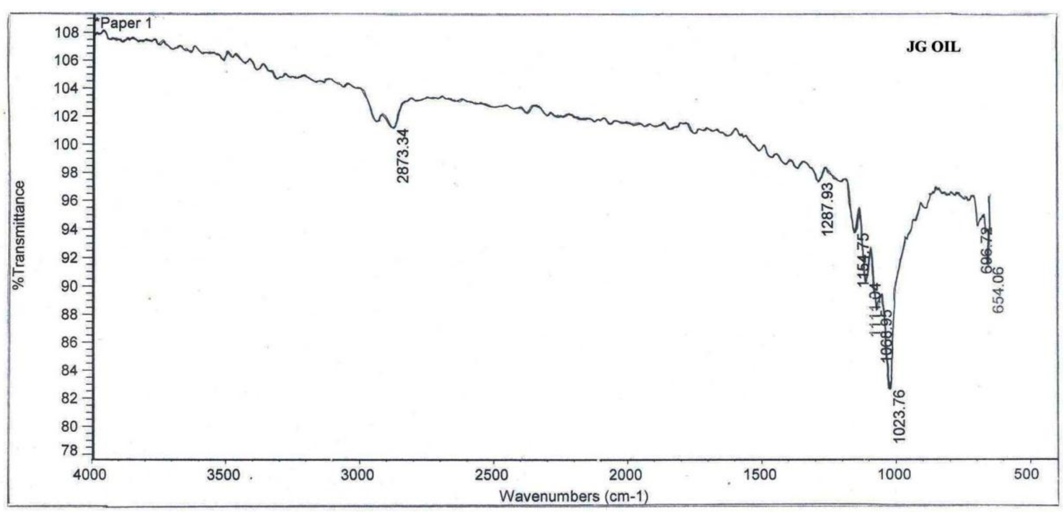


Figure 1: FTIR spectrum of JG oil

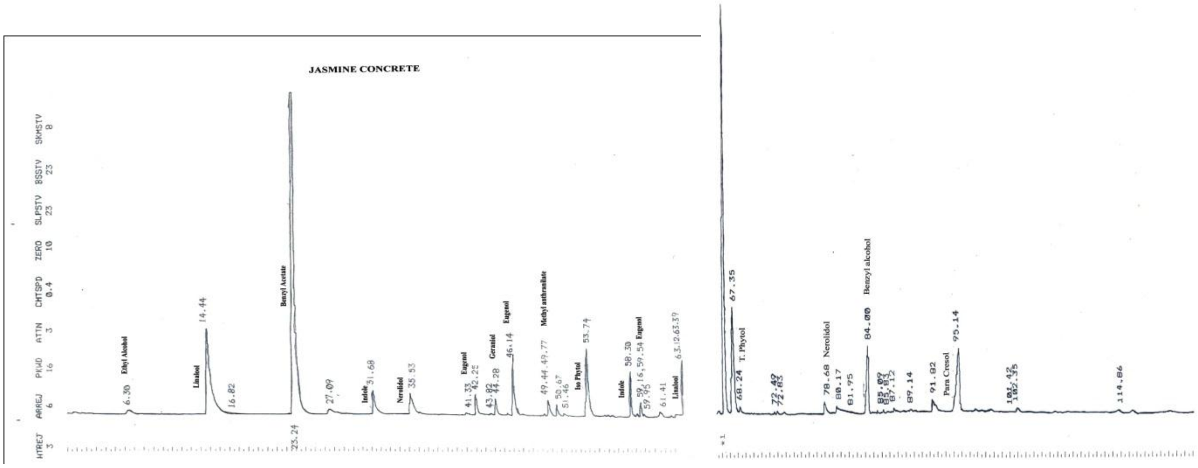


Figure 2: Gas Chromatogram of JG oil

VIA Test

The values of inhibition efficiency determined by gravimetric method at different concentrations of NaCl (0.005, 0.01, 0.05 and 0.1M) at 313K in 100% RH for 7days of exposure time are given in table 1 for mild steel. It was observed that the blank specimen has been severely corroded which is shown by the presence of brown rust all over its surface. Under the same environment in the presence of JG oil, the corrosion rate has substantially decreased. It is observed that the concentration of NaCl influence the corrosion. The efficiency of inhibition was found to be very high of the order of 90.2% for 0.005M, 89.6% for 0.01M and 81.7% for 0.1M NaCl environments. It is evident from the inhibition efficiency values that the JG oil inhibits corrosion of mild steel considerably. The weight loss increases when the concentration of NaCl increases from 0.005 M NaCl to 0.1M NaCl and inhibition efficiency values increase with increasing the concentration of VCI upto 4%, thereafter decreases due to desorption on of VCI molecules on metal surfaces. Consequently, the inhibition efficiency and surface coverage (θ) values decrease with increase in concentration of NaCl and time of exposure. Table 2 indicates the VCI ablity to protect the metal for 15days upto 70.5% in 0.1N NaCl environment effectively from rusting. From this result it is understood that in high electrolyte concentration and corrosive environment the oil is found to be most effective to protect the metal for long duration.

Table 1: Inhibition efficiency, weight loss and surface coverage of VCI for mild steel in NaCl environments based on VIA test for 7 days at 313K

VCI Conc. (%)	NaCl Environment											
	0.005M			0.01M			0.05M			0.1M		
	WL (mg)	IE (%)	Ɵ	WL (mg)	IE (%)	Ɵ	WL (mg)	IE (%)	Ɵ	WL (mg)	IE (%)	Ɵ
Blank	204	-	-	241	-	-	279	-	-	311	-	-
2	29	85.8	.86	37	84.6	.85	48	82.7	.83	62	80.0	.80
4	20	90.2	.90	25	89.6	0.90	41	85.3	.85	57	81.7	.82
6	24	88.2	.88	31	87.1	.87	46	83.5	.84	59	81.0	.81
8	26	87.2	.87	34	85.9	.86	55	80.3	.80	63	79.7	.80
10	33	83.8	.84	41	82.9	.83	59	78.8	.79	69	77.8	0.78

Table 2: Comparison of inhibition efficiency of 4% VCI based on weight loss methods in 0.005M NaCl environment

NaCl (M)	Inhibition Efficiency (%)		
	VIA Test		Cyclic Test
	7- days	15- days	5-days
0.005	90	87.0	88.0
0.01	89.6	80.6	86.5
0.05	85.3	76.2	80.9
0.1	81.7	70.5	75.0

Cyclic corrosion test

Table 2 gives the results of cyclic corrosion test as percentage of inhibiting efficiency. Under this severe corrosive environment, the oil exhibited high level inhibition efficiency. At low concentration of NaCl such as 0.005M, efficiency was around 88% and with 0.1M NaCl solution a maximum of 75% was achieved. This result proves the best performance of this oil under highly corrosive environment like cyclic condensation of moisture and dryness due to varying climatic condition.

Salt spray test

Figure 3 provides the protective ability of 4% essential oil impregnated paper on mild steel in salt spray tests for 5, 10 and 15 hours exposure with 3.5% NaCl solution. In the visual observation of the blank specimen surface showed a reddish brown film after five hour period of exposure and very thick dark brown film after 15 hours exposure. Thereafter, more rusting takes place during the longer period of exposure. On VCI protected specimens the rusting takes places after longer period of exposure only. It is applicable as VCI in marine environment. It provides upto 72% efficiency for 15 hours exposure. These results are reflects the same trend observed in the previous tests.

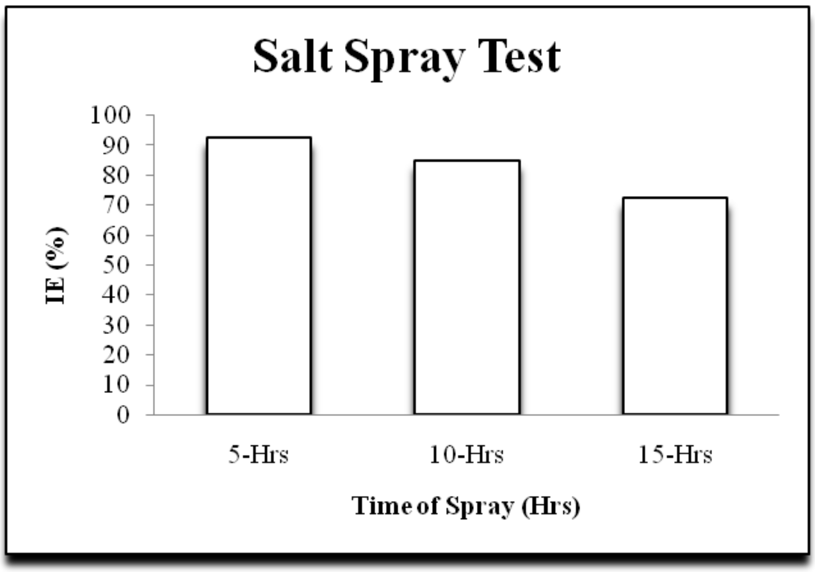


Figure 3: Inhibition efficiency for 4% concentration of VCI 3.5% NaCl environment under Salt spray test

Corrosion inhibition behaviour of major constituents present in the oil under VIA test

Corrosion inhibition behaviour of the major constituents present in the oils such as benzyl acetate and linalool on mild steel in 0.005M NaCl environment results are summarized in Figure 4. The inhibition efficiency of the major constituents is found to be 76.5% and 78.5%. The comparison of inhibition efficiency values of individual constituents with the oil under identical experimental conditions shows that the individual constituents are less efficient than the oil. This observation indicated that these constituents are not solely responsible for inhibition. In other words, these constituents present in the oil have synergetic effect towards inhibition and boost the inhibition efficiency values [26 & 27]**.**

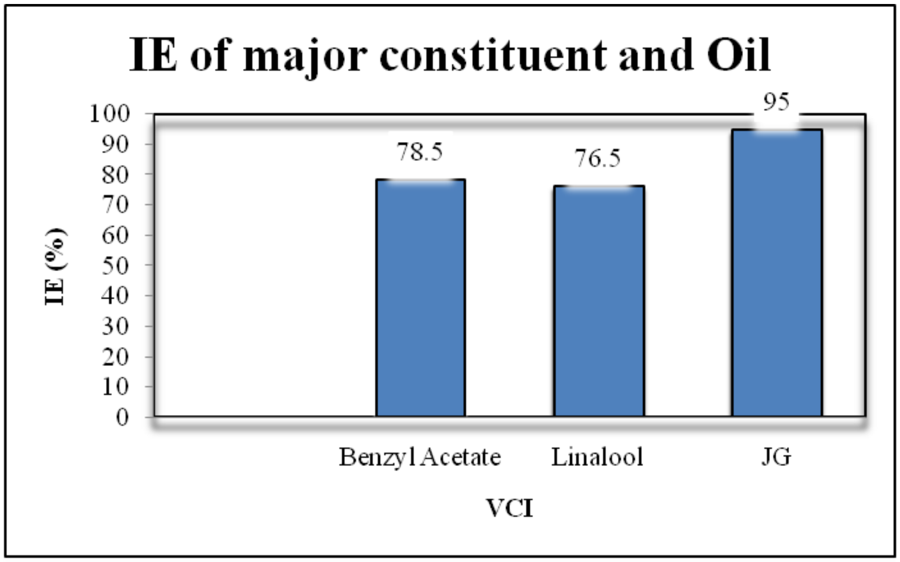
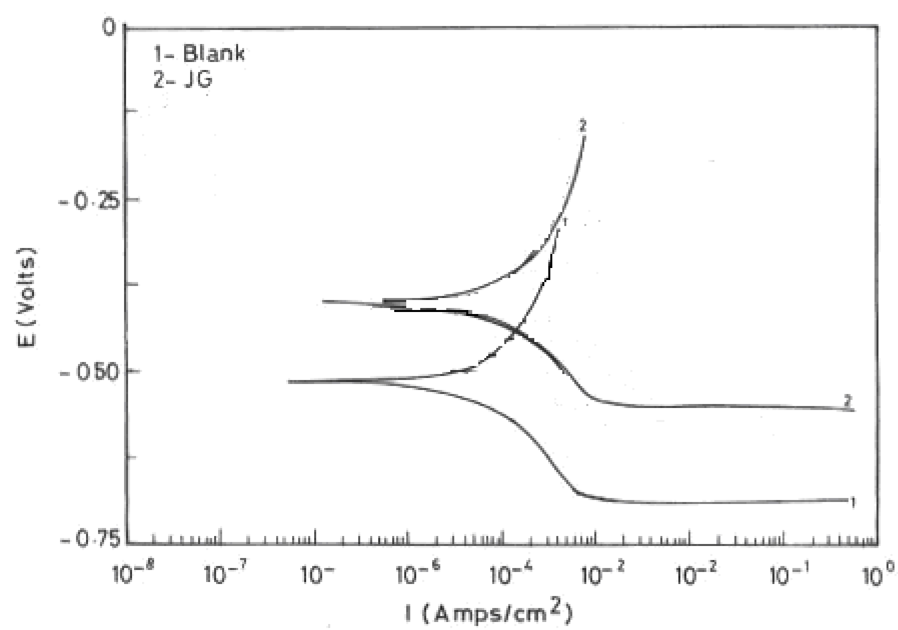


Figure 4: Inhibition efficiency for 4% concentration of major constituents based on VIA Test in 0.005 M NaCl environment

Potentiodynamic polarization studies

The results of potentiodynamic polarization behaviour of mild steel in 0.0.5 and 0.05M NaCl are shown in figures 5& 6. The corrosion kinetics parameters such as E_{corr}, I_{corr} and Tafel slopes (b_a & b_c) obtained from the anodic and cathodic polarization curves are given in Table 3**.** As the concentration of NaCl increases, the corrosivity of the electrolyte increases, resulting in increased corrosion current. The corrosion potential (E_{corr}) for the blank is



l environment. The corrosion current
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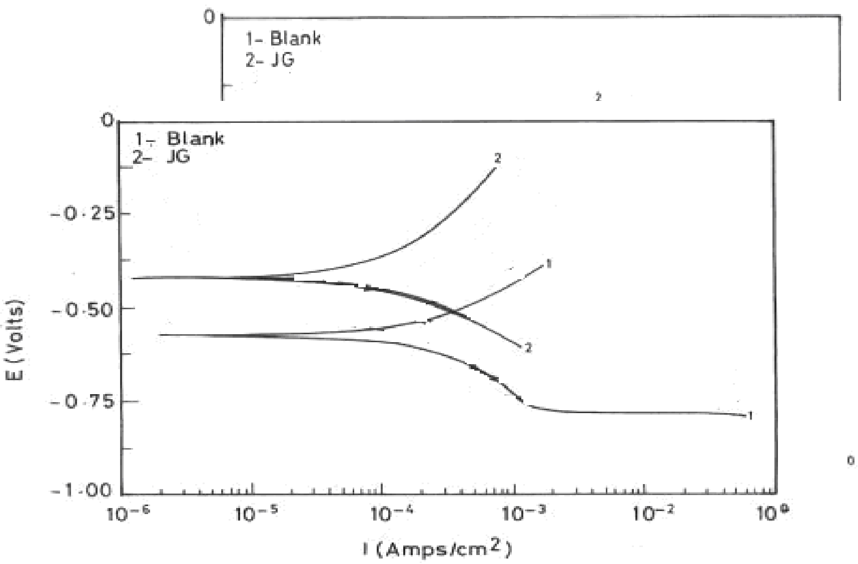
r is effective. The efficiency reaches
ion curves indicates both anodic and
ate that the cathodic protection takes

n NaCl environments

corr ($\mu A/cm^2$)		IE (%)
Blank	JG	
66.7	20.4	95.6
99.4	31.8	93.6
09.0	132.4	78.3
41.0	204	72.5



ild steel in the presence of 4% VCI in 0.005 M

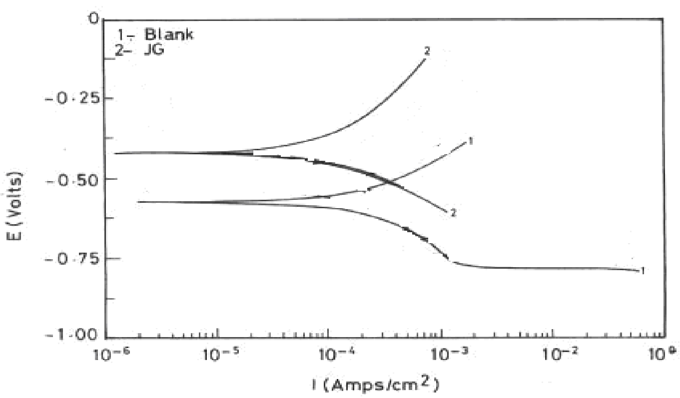


Figure 6: Potentiostatic polarization curves for the corrosion of mild steel in the presence of 4% VCI in 0.1M NaCl

AC impedance studies

The parameters derived from the Nyquist plots in figures 7 & 8 for 4% VCI paper are given in table 4. The increase in R_{ct} values of the VCI exposed specimens was observed compared to the blank. Correspondingly the double layer capacitance C_{dl} values also decreased. This decrease may be attributed to the adsorption of inhibitor on the metal specimen. The decrease in C_{dl} and increase in R_{ct} are observed for both the concentrations of 0.005 M and 0.05 M of NaCl. The appearance of semicircle in Nyquist plots indicates the adsorption of inhibitor molecules on electrode surface [29]. This adsorption is confirmed by the Temkin adsorption isotherms. The depressed semicircle is either due to the presence of pores on the electrode surface or due to the adsorption of the inhibitor molecules on the electrode surface [30].

Table 4: Inhibition efficiency based on AC impedance measurements with 4% VCI for mild steel in NaCl environments

NaCl (M)	**R_{ct} (Ω cm^2)**		**C_{dl} (μF)**		**IE (%)**
	Blank	**JG**	**Blank**	**JG**	**-**
0.005	1170	3285	$3.19 X 10^{-5}$	$1.12 X 10^{-5}$	64.4
0.05	245	600	$1.68 X 10^{-4}$	$0.67 X 10^{-4}$	59.2

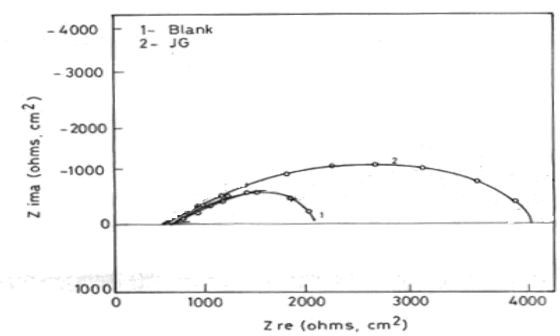


Figure 7: AC impedance diagram for mild steel in 0.005 M NaCl in the presence of 4% VCI

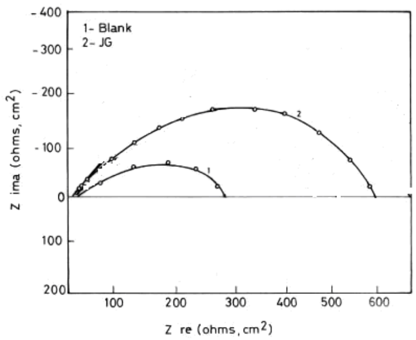


Figure 8: AC impedance diagram for mild steel in 0.05 M NaCl in the presence of 4% VCI

Antibacterial Test

The results of antibacterial test are shown in figure 9. It is clear that the JG oil inhibits the growth of microorganisms, Klebsiella pneumoniae, Staphylococcus aureus, Pseudomonas aeruginosa, Pseudomonas flourescence, Bacillus subtilis, Shigella dysentriae, Escherichia coli and Proteus mirabilis. The oil was found to be less effective in inhibiting the growth of Micrococcus luteus (20%), Streptococcus pyrogens (12%), Enterococcus fecalis (20%), Salmonella typhimurium (10%), Proteus vulgaris (5%) and Salmonella speices (20%) at 100 mg/10 μL. This oil had shown higher inhibition to the growth of Escherichia coli, Klebsiella pneumoniae, Bacillus subtilis and Staphylococcus aureus. Since the zone of inhibition against most of the micro organisms was maximum, the JG oil is considered to be more effective against bacterial stains. Hence, it can be used as a VCI impregnated paper for metals.

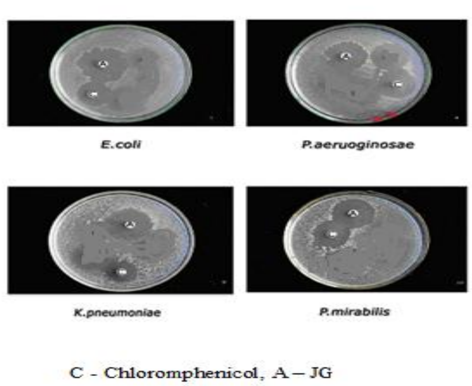


Figure 9: Antibacterial activities of 4% VCI against different bacteria

Table 5: Results of antifungal activity of VCI

VCI	Aspergillus niger	Penicillium pinophilium,	Ganoderma lucidum,	Phanerochaete chrysosporium	Ischnoderma resinosum
Blank	Rich growth with sporulation and deep purple colouration	Growth with heavy sporulation and mixed dark green-red colouration	Growth with rich sporulation and black pigmentation	Heavy sporulation and green pigmentation	Rich growth with blackish green colouration
JG	Complete inhibition growth	Complete inhibition growth	Complete inhibition growth	Partial inhibition and no pigmentation	Complete inhibition growth

1 – Control, 2 – JG oil

Figure 10: Antifungal activities of 4% VCI against *Ganoderma lucidum*

The results after 96 hours of incubation for antifungal studies are given in Table 5 and Figure 10. There were observed differences in mode and extent of inhibition by different VCI. A complete inhibition of fungal growth, sporulation and pigmentation has occurred in the action of VCI on *Aspergillus niger*. The control showed very profuse fungal growth with rich sporulation and deep purple coloration of *Aspergillus niger*. The plate exposed to VCI showed complete inhibition of fungal growth. The medium was very clear without even a speck of growth. The same result was shown by the action of oils on *Penicillium pinophilium* and *Ganoderma lucidum*. The control showed growth with heavy sporulation and dark green – red colouration. Since the zone of inhibition against most of the organism was maximum, the essential oil was found to be more effective against fungicides also. Hence, it can be used as a VCI on impregnation with Kraft paper for metals.

MECHANISM

Free energy of adsorption and Temkin adsorption isotherm

The values of surface coverage summarized in table 6 corresponding to concentration of inhibitor molecules at 303K, 313K, and 323K were used to find the free energy of adsorption. It is observed that the corrosion rate increases with increase in temperature. The higher negative values of free energy of adsorption indicate the spontaneity of adsorption process in the experimental conditions used [31]**.** Since, ΔG_{ads} values for the oil at various temperatures are found to be above 20 KJ/mol, chemisorptions should be more prevalent than physisorption [32].

Corrosion inhibition offered by the JG oil for mild steel is due to adsorption of inhibitor molecules on the metal surface. This is confirmed from Temkin adsorption isotherms given in Figure 11 and 12, wherein surface coverage (θ) is plotted against log C, a straight line graph was obtained. The plots indicate that the adsorption occurs more at lower concentration of the VCI. The surface coverage was found to increase with increase in concentration upto 4% and decrease thereafter. The plateau portion of the graph may indicate the saturation of the metal surface with adsorbed VCI molecules. At higher concentrations, surface coverage decreases showing desorption of the VCI molecules [33].

Table 6: Free energy of adsorption for 4% VCI on mild steel in 0.005 M NaCl

Temperature (K)	Surface coverage (θ)	$-\Delta G_{ads}$ (KJ/mole)
303	0.93	20.7
313	0.90	20.4
323	0.86	19.9

It is inferred from the figures 1 and 2 that the compounds present in the oil contain hetero atoms like nitrogen or oxygen or both. The lone pair of electrons on nitrogen and oxygen can facilitate the adsorption of these compounds on metal [34]. Another possibility is the interaction between the πe^{-}s of oxygen in the ring with the vacant'd' orbital of the charged metal surface [35]. **F**urther, carbon-carbon double bonds may also favour the adsorption.

A schematic representation of adsorption of VCI molecule on metal surface is represented in figure 12. An electrostatic interaction exists between N- group in the inhibitor molecule and metal surface. The carbonyl group of the inhibitor stabilizes this adsorption by an electron exchange between oxygen and the metallic surface [36].

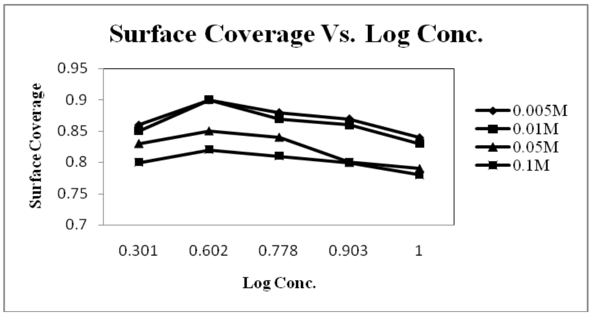


Figure 11: Temkin adsorption isotherm for 4% VCI based on VIA Test in NaCl environments for mild steel

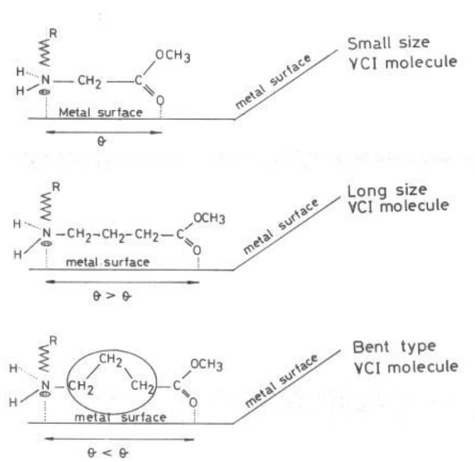


Figure 12: Schematic representation of adsorption of VCI on metal surface

Conclusion

- JG oil is non-toxic. Its pH range is almost neutral and vapour pressur is optimum to vapourise.
- The oil inhibits corrosion of mild steel at all concentration but the highest efficiency was observed in 4% con centration
- JG oil controls corrosion both anodically and cathodically.
- The control of corrosion by VCI is through adsorption.
- The adsorption of inhibitor molecules due the presence of hetero atoms in their constituents
- This inhibitor is resists to microbes. So it is safety to coat on wrapped kraft paper.

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