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INHIBITIVE ACTION OF VITIS VINIFERA (GRAPE) ON COPPER AND BRASS IN NATURAL SEA WATER ENVIRONMENT

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ABSTRACT

The present investigation deals with the dissolution behavior of pure Copper and its one of the alloy (Cu-27Zn Brass) in Natural Sea water environment at various time, temperature and various concentration of Vitis vinifera seed and skin extract. The inhibition efficiency is markedly higher in Natural sea water with addition of Vitis vinifera seed and skin extract compared with those in the inhibitor free solution. The inhibition efficiency increased with increase of inhibitor concentration but decreased with increase in temperature and exposure time. Adsorption of Vitis vinifera seed and skin extract on Copper and Brass was found to obey Langmuir and Temkin adsorption isotherm. The characterization of corrosion product on Brass in the presence of inhibitor is analyzed by UV, IR, and XRD.

Key words: Corrosion inhibition, Copper, Brass, Vitis vinifera, Natural sea water.

INTRODUCTION

Copper and its alloys are widely used in industry because of their good resistance to corrosion, in cooling water systems, for shipboard condensers, power plant condensers and petrochemical heat exchangers etc. Copper and its alloy are very interesting for many scientists, because of its great industrial importance. The dissolution behavior of Brass was studied in different environments such as sea water[1,2], NaCl [3-8], H_2SO_4[9,10], HNO_3[11,12],borate buffer[13,14,15], sodium tetraborate[16] by many investigators. The existing data shows that most of the organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors occurs through a compound containing heteroatom such as nitrogen, oxygen, and sulphur. These compounds which are adsorbed on the metallic surface block the active corrosion sites. Even though many synthetic organic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. These inhibitors may cause reversible or irreversible damage to organ system viz, Kidney, Liver, or disturb a biological process and enzyme system at some site in the body[17]. The toxicity may manifest either during the synthesis of the compound or during its application. Recently the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids as well as organic dyes has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin[18-22]. Such investigation is more important because in addition to environmentally and eco- friendly acceptable. These plants product are inexpensive, readily available and renewable sources of materials. Some investigators namely Abdel-Gaber et al., Khamis et al., Uomren and Ebenso., Okafor and Ebenso, Bendahou et al , Kliskic et al., Sanjay K. Sharma et al, and A.Sharmila et al., [23-30] have been reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. In the present study, we have chosen eco-friendly inhibitor, a green approach to prevent environmental pollution by wastage of seed and skin materials of Grape. The influence of Vitis vinifera (grape) seed and skin extract in natural sea water environment on Copper and Brass using Mass loss method with different time and temperature have been studied. The characterization of UV, IR, and XRD of Brass in the presence of inhibitor is also reported.

EXPERIMENTAL

Specimen preparation

Rectangular specimen of Copper and Brass were mechanically pressed cut to form different coupons, each of dimension exactly 5.0x2x2 Cm. Specimens containing a small hole of 2mm diameter near the upper edge were used for the determination of Corrosion rate. Each coupon was degreased by washing with Trichloroethylene then dried in acetone and preserved in a dessicator. All reagents for the present study were Analar grade and double distilled water was used for their preparation. Each specimen was suspended by a glass hook and immersed in a beaker containing exactly 50ml of the test solution and left exposed to air. Evaporational losses were made up with double distilled water. After the exposure, the test specimens were cleaned with acetone. Triplicate experiments were performed in each case and mean values of the Mass loss were calculated.

Stock solution of Vitis vinifera seed and skin extract

Wastage of Vitis vinifera seed and skin materials of about 1 Kg collected from the fresh fruit stall and dried in natural air condition for 8 to 10 days in Sunshade. Then it is grained well and finely powdered. Exactly 150g of finely powdered dried material was taken in a 500ml round bottom flask and quantity of ethyl alcohol was added to cover the powder completely. The RBF was covered with stopper and left for 48 hrs. Then the resulting paste was refluxed for 48 hrs, it was filtered. The filtrate was collected and the alcohol was removed with the help of distillation unit. The obtained paste was boiled with activated charcoal (about 1g) to remove hung and the pure plant extract is collected.

Mass Loss method

In the Mass loss measurements, Copper and Brass coupons in triplicate were completely immersed in 50ml of the test solution of Natural sea water environment in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after an hour at 303K, 313K and 333K and also measured 24, 48 and 72 hrs at room temperature. The Mass loss was taken as the difference in weight of the specimens before and after immersion determined using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6 \times \text{W}}{\text{DAT}} \qquad (1)$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),
A = Area of specimen (cm^2), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using Eq.(2) and Eq.(3), respectively.

$$\%\,\text{IE} = \frac{W_1 - W_2}{W_1} \times 100 \qquad (2)$$

$$\theta = \frac{W_1 - W_2}{W_1} \qquad (3)$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

Chemical composition of Vitis Vinifera

Vitis venifera (Grape) is one of the most widely consumed fruits in the world and is rich (90%) in water soluble bioflavonoids called Proanthocyanidins (Fig. 1)[31] and it is belong to the flavonoid family.They are also called "OPCs" for oligomeric procyanidins or "PCOs" for procyanidolic oligomers[32]. Proanthocyanidins have a strong antioxidant activity. Its anti-oxidative activities are twenty times much stronger than Vitamin C and Vitamin E[33]. The two most common sources of proanthocyanidin are grape seed (Vitis vinifera) and the white pine (Pinus maritima, P. pinaster) of southern Europe. Resveratrol (trans-3, 5, 4'-trihydroxy stilbene), belongs to a class of Polyphenolic compounds called stilbenes, found largely in the skins of red grape[34]. Fresh grape skin contains about 50-100 micrograms of Resveratrol per gram. Also it has Polyphenolic anti-oxidant properties (Fig. 2)[35].

RESULTS AND DISCUSSION

The dissolution behavior of Copper and Brass in Natural sea water environment containing different concentration of Vitis vinifera seed and skin extract with various time and temperature are investigated in the present study and their results are presented in the graphical form of Figure from 3 to 6.

Effect of time variation

In Fig. 3 and 4 shows the Corrosion rate with concentration of Vitis vinifera seed and skin extract on Copper and Brass at different time intervals 24, 48 and 72 hrs in Natural sea water environment. The corrosion rate of Copper increased with increase of exposure time in the absence of inhibitor (from 0.9293 to 2.9094mmpy). But in the presence of Vitis vinifera seed and skin extract, the dissolution rate is significantly reduced to 0.2222 mmpy, 0.4950 mmpy and 0.9429 mmpy after 24, 48, and 72 hrs respectively (Fig. 3). The inhibition efficiency is attained maximum of 76.08 percent at higher concentration (1000ppm) after 24 hrs exposure. The dissolution behavior of Copper is compared with one of its alloy (Cu-27Zn Brass) as shown in Fig. 4. The results indicate that the dissolution rate is comparatively lesser than (0.2752 to0.7552 mmpy) Copper. This is due to the presence of Zinc content in its alloy. The inhibition efficiency is achieved maximum of 92.29 percent at higher concentration (1000ppm) of inhibitor and the corrosion rate significantly reduced to 0.0212mmpy. In the case of Brass specimen the surface area is almost completely covered with thin film formation rather than Copper because the presence of Zinc content in Brass may be preferentially co-ordinated with inhibitor than Copper. The inhibitive action of Vitis vinifera seed and skin extract was due to the presence of major active compounds such as proanthocyanidin and Resveratrol. Proanthocyanidin contains ring oxygen atom and poly hydroxyl group, Resveratrol contains conjugated system of poly hydroxyl group respectively. These compounds are rich electron centre, which can serve as a good adsorption sites onto the metal surface by inhibiting the dissolution of both Copper and Brass.

Effect of Temperature

The dissolution behavior of Copper and Brass in Natural sea water containing different concentration of Vitis vinifera seed and skin extract at various Temperatures such as 303K, 313K and 333K are studied and the results are shown in Fig. 5and 6. It found that the percentage of Inhibition efficiency on Copper decreased with increase of temperature (Fig.5). The maximum of 73.68 percent of inhibition efficiency is achieved at 303K.The percentage of inhibition efficiency on Brass decreased with increase of temperature (Fig. 6). The inhibition efficiency is attained maximum of 80 percent at 303K. At rise in temperature, the reduction of inhibition efficiency is due to weak forces of physical adsorption [36, 37] on the surface of both Copper and Brass by certain specific active molecules such as Proanthocyanidin, Resveratrol in the extract may activate the corrosion inhibition in the different layers and cathodic sites on the metal surface.

Adsorption Considerations

In general, the adsorption of the inhibitor at the metal solution interface is the first step in the mechanism of inhibition in aggressive media. The surface coverage (θ) was calculated according to Eq. 3.

A direct relationship between inhibition efficiency and the degree of surface coverage (θ) can be observed at different concentrations of the inhibitor in Natural sea water environment. The mass loss measurements were tested graphically for fitting two isotherms like Langmuir and Temkin.

The Langmuir and Temkin adsorption isotherm can be expressed by the Eq. 4 and Eq. 5 given below [38, 39, 40].

$$\log C/\theta = \log C - \log K \quad (4)$$

$$\theta = K \ln C \quad (5)$$

Where θ is the surface coverage, C is the concentration of the inhibitor solution and K is an adsorption coefficient.

By plotting values of logC/θ versus logC, linear plots were generated (Fig. 7and 8) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of Vitis venifera seed and skin extract on both Copper and Brass mean that there is no interaction between the adsorbed species (i.e.; adsorbate and adsorbent). The Langmuir adsorption isotherm is better fit at 303K for both Copper (R^2 =0.99887) and Brass
(R^2 =0.99321) respectively.

A plot of θ versus logC give almost a straight line of both Copper and Brass in seed and skin extract of Vitis vinifera (Fig. 9and10). These figures indicate that the inhibitor obeyed Temkin adsorption isotherm.

Mechanism of inhibition

The inhibitive action of Vitis vinifera seed and skin extract was mainly due to the presence of rich active compounds such as Proanthocyanidin and Resveratrol respectively. These are belongs to a class of polyphenolic compound. The anodic inhibition may be due to the adsorption of principle phytochemical constituents present in the extract through ring oxygen atom and poly hydroxyl groups in proanthocyanidin or conjugated system containing poly hydroxyl groups in Resveratrol and forms a protective coating on both Copper and Brass metal surface. Thus it may prevent the contact between the metal and corrosive media in Natural sea water environment. The protonated species of the principle constituents may compete with H^+ ion reduction and may control the cathodic reaction.

UV Analysis

The UV- visible spectrum of the corrosion product on the surface of Brass in the presence of Vitis vinifera seed and skin extract are shown in Fig. 11. It shows that only one spectral absorption band around 283nm has been noticed. It may be the formation of Cu-Zn - Inhibitor complex. This band is assigned to π-π* transition and shifted to longer wavelength region i.e.; Bathochromic shift (or) Red shift. This may be conformed that the complex film formation between the Cu-Zn metal ions and the inhibitor.

IR Analysis

Fig. 12 shows the IR spectrum of the corrosion product on the Brass surface in the presence of Vitis vinifera seed and skin extract. It found that the –OH stretch was shifted from 3360 to 3440 Cm^{-1} , the –CH stretching frequency shifts from 2854.44 to 2923.87 Cm^{-1}, the –C = O stretching frequency shifts from 1604 to 1720.38 Cm^{-1}, the bend -C-OH shift from 1380 to 1411.79Cm^{-1} , the symmetric -C-O-C- stretching frequency shifts from 1026.05 to 1080.06 Cm^{-1} respectively. These results may also confirm the formation of Cu–Zn – inhibitor complex film formation on the anodic sites of the metal surface. The peak at 1319 Cm^{-1} is due to $Zn(OH)_2$ complex formed on the cathodic sites of the metal surface[41,42] and shifted from 1272.93 Cm^{-1}.

XRD analysis

The Corrosion product released from the Brass metal formed on their layer over the metal surface examined by XRD studies in the presence of inhibitor as shown in Fig. 13. It reveals that the film may be mainly combine with a rich amount of paratacamite ($Cu_2Cl(OH)_3$) and Zinc salt such as $Zn(OH)_2$, $ZnSO_4$, ZnS, $ZnCl_2$, $ZnCO_3$, etc with inhibitor.

CONCLUSION

Vitis vinifera seed and skin extract is an effective inhibitor of the corrosion of Copper and Brass in Natural sea water environment at different Temperature(303K,313K and 333K) and exposure time (24,48 and 72 hrs). Even in the presence of highly corrosive media as excisist in Natural sea water environment, the inhibition efficiency increased with increase of inhibitor concentration but decreased with temperature and time. The hetero atom such as oxygen and poly hydroxyl group in Proanthocyanidin and Resveratrol are electron rich centre and served as a good adsorption site onto the metal surface. They are responsible for the inhibitory action of Vitis vinifera seed and skin extract on Copper and Brass in Natural sea water. The inhibitor obeys Langmuir and Temkin adsorption isotherm at all temperature on Copper and Brass in Natural sea water environment. The corrosion product over the surface of Brass in the presence of Vitis vinifera seed and skin extract is characterized by FTIR, UV, and XRD studies and may conform the complex film formation on the surface of Brass.

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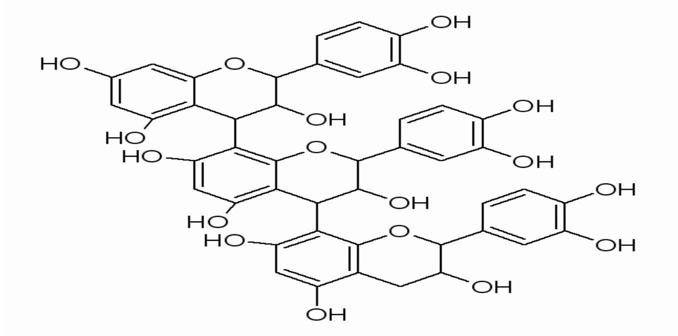

Fig.-1:The structure of Proanthocyanidin in Vitis vinifera skin extract.

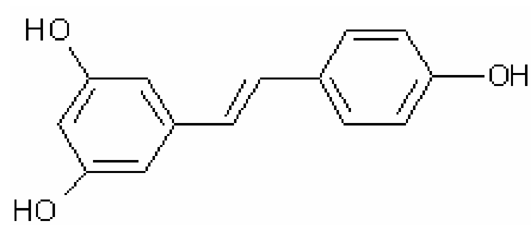

Fig.-2:The structure of Resveratrol in Vitis vinifera skin extract

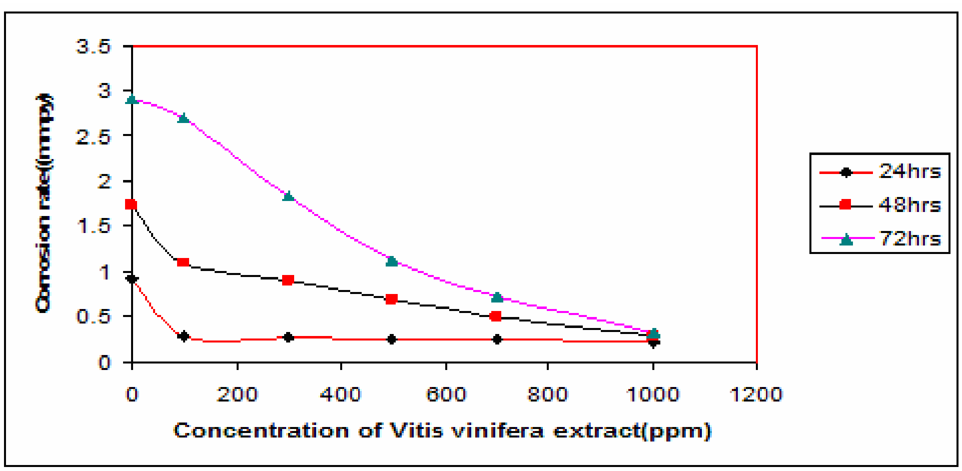

Fig.-3:Corrosion parameters of Copper containing various concentration of Vitis vinifera seed and skin extract at different time in Natural sea water.

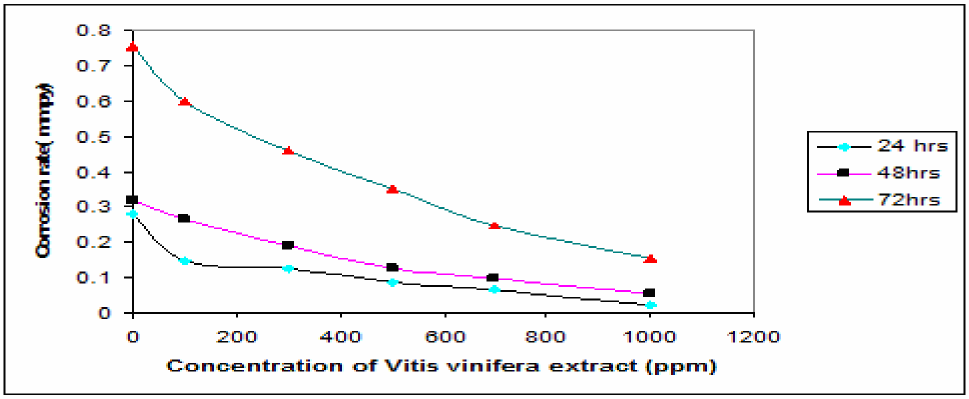

Fig.-4:Corrosion parameters of Brass containing various concentration of Vitis vinifera seed and skin extract at different time in Natural sea water.

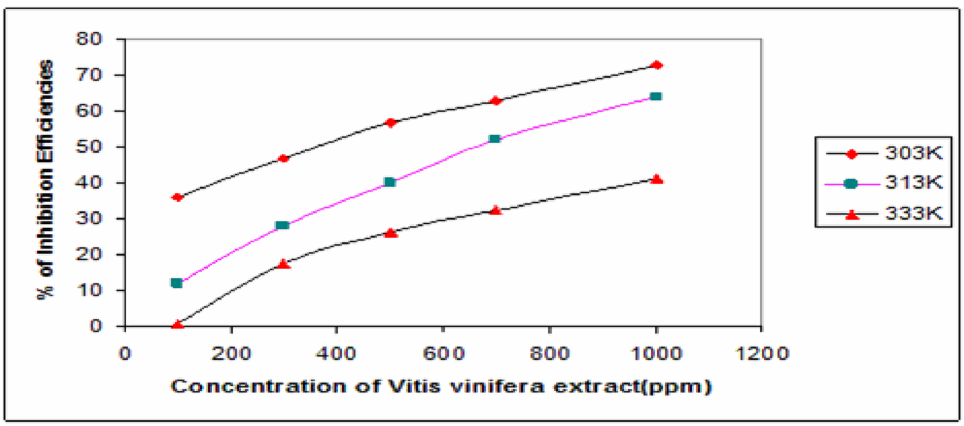

Fig.-5:Inhibition efficiencies of Copper in various concentration of Vitis vinifera seed and skin Extract at different temperature in Natural sea water.

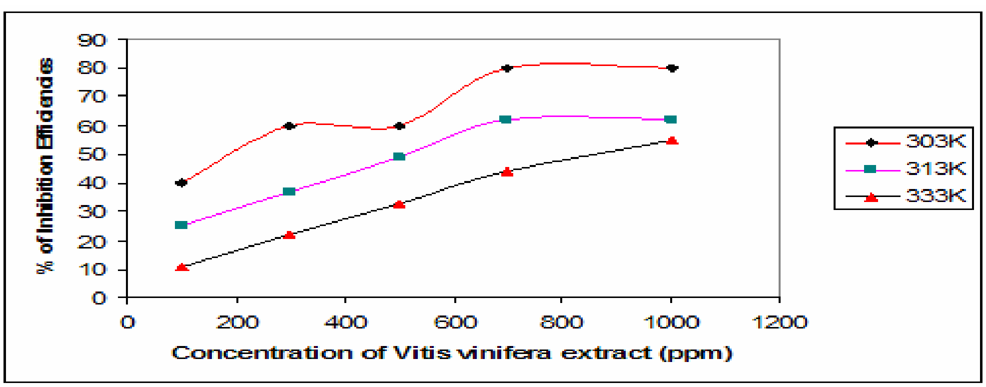

Fig.-6:Inhibition efficiencies of Brass in various concentration of Vitis vinifera seed and skin Extract at different temperature in Natural sea water.

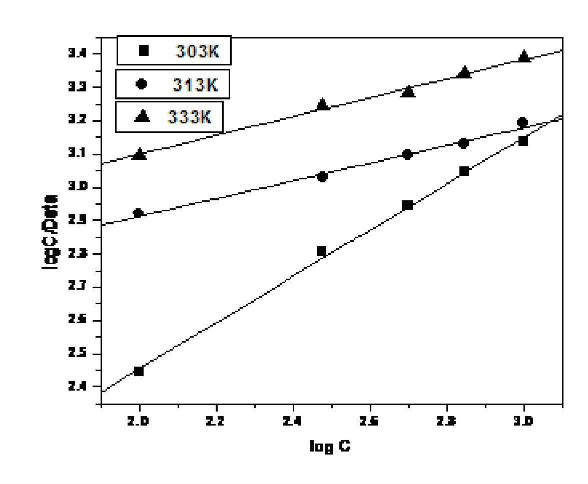

Fig.-7:Langmuir isotherm for adsorption of the Vitis venifera seed and skin extract on Copper in Natural sea water.

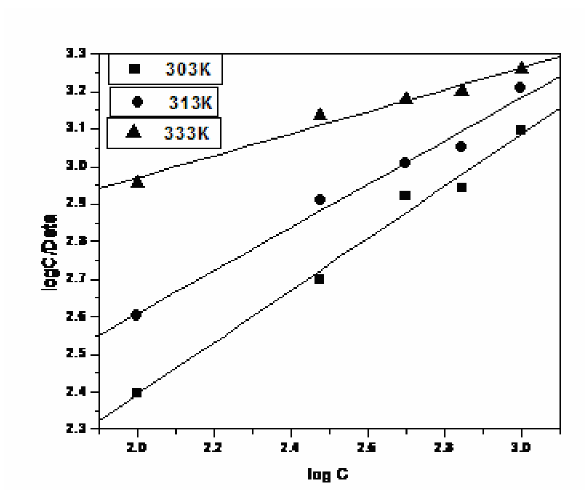

Fig.-8:Langmuir isotherm for adsorption of the Vitis venifera seed and skin extract on Brass in Natural sea water.

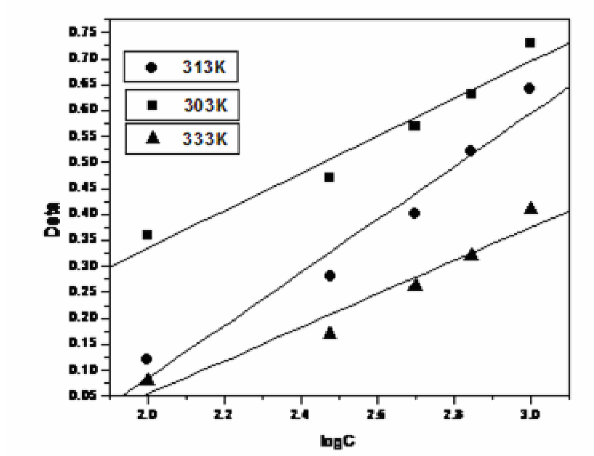

Fig.-9: Temkin isotherm for adsorption of the Vitis venifera seed and skin extract on Copper in Natural sea water.

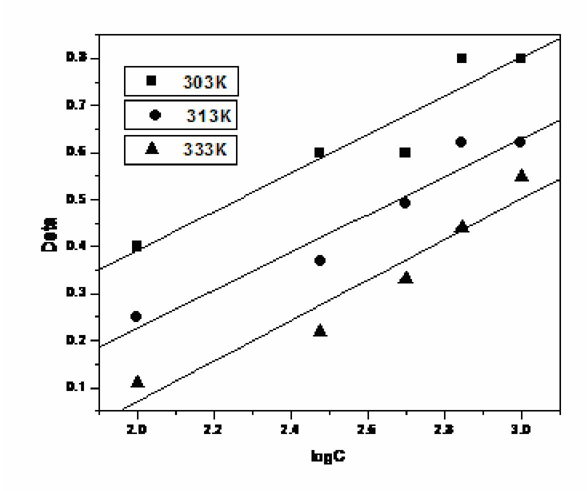

Fig.-10: Temkin isotherm for adsorption of the Vitis venifera seed and skin extract on Brass in Natural sea water.

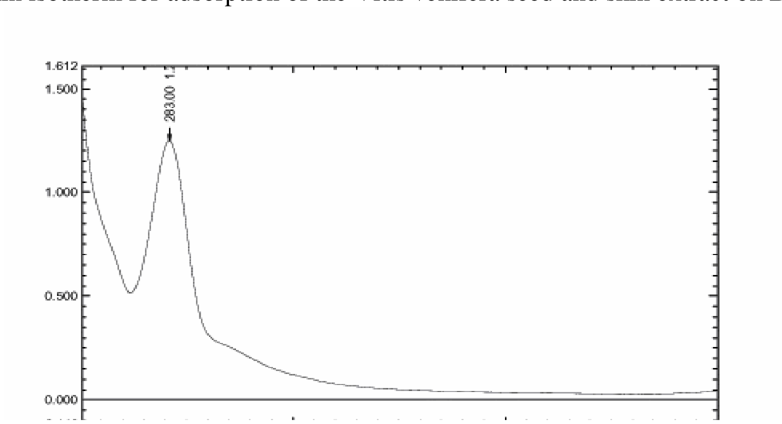

Fig.-11: UV absorption spectrum of the corrosion product of Vitis vinifera seed and skin extract on Brass in Natural sea water.

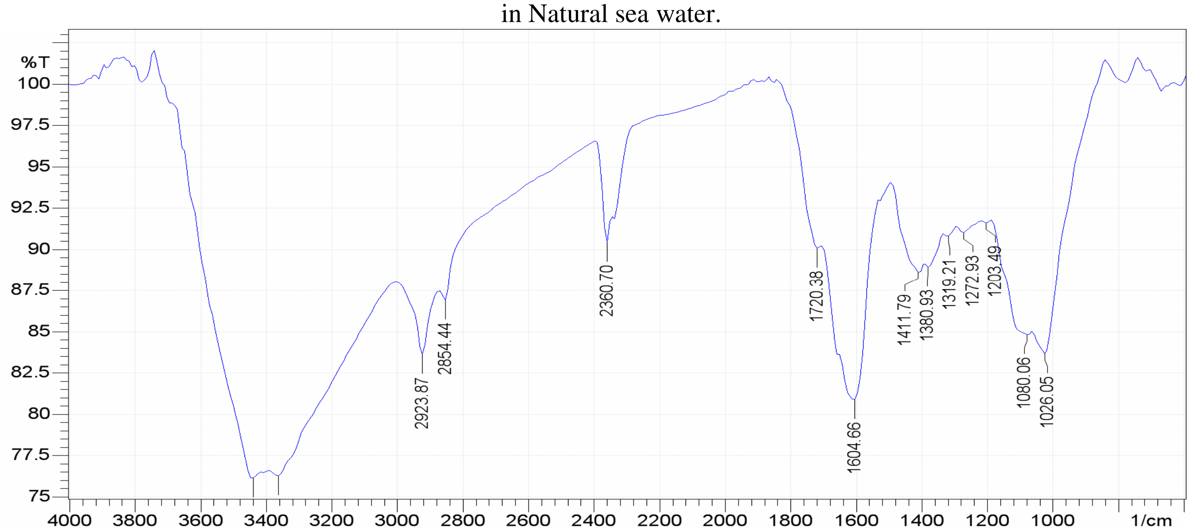

Fig.-12: IR spectrum of the corrosion product of Vitis vinifera seed and skin extract on Brass in Natural sea water.

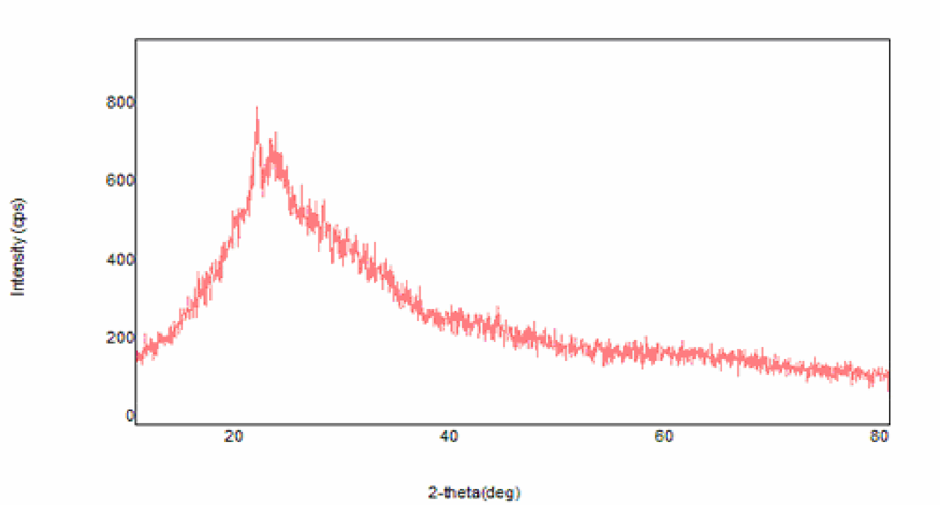

Fig.-13:XRD spectrum of the corrosion product of Vitis vinifera seed and skin extract on Brass in Natural Sea water.

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