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The Anti-corrosive Characteristics of Betalains on Cu metal

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A B S T R A C T

The use of *Betalains* Cu corrosion behavior was tested in aerated aqueous solutions of KCl for different pH values. Polarization resistance (R_p) measurements, Polarization curves and AC impedance technique were used to obtain experimental data. *Betalains* found to exhibit cationic type in acidic media solution of KCl. The impedance spectra and curves at different potentials showed that the corrosion process of metal was characterized by two distinguishable capacitance loops. The charge transfer resistance R_t and polarization resistance, R_p values calculated from the interpretation of Nyquist and Bode plots were in agreement with the results of the other techniques.

Keywords: Betalains, Polarization resistance, Nyquist and Bode plots.

A R T I C L E I N F O

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1. Introduction

H_2SO_4, HCl and gases acid is a major chemical which has mainly use in industries and cleaning product, especially in the cloth and removal of scale from boiler. Generally, acid destroys the metal and alloys, which used in tank and boiler, the data has been published about the resistance of these materials to corrosion by the H_2SO_4solution [1-4]. The most of studies were focused on the inhibition of Cu in H_2SO_4 acid using organic compounds containing nitrogen, sulphur, and oxygen atoms as corrosion inhibitors [5-6].The corrosion inhibition properties of these organic compounds

due to the *pi* electrons and molecular structure of compound.

The inhibitors and synthetic inhibitors are toxic in nature and harmful for the environment therefore it necessary to develop environmentally acceptable and low cost inhibitors in this term turmeric is best inhibitor product against the corrosion of metal because *Betalains* have tannins and dyes and other phyto-chemicals which is known for the medicinal properties like antiseptic, antibacterial, antioxidant and most likely corrosion inhibition. So, in this present study and investigation, the corrosion of Cu in 0.5N H_2SO_4solution in presence and absence of *Betalains* extract at different temperature has been studied by Electro-chemical.

The corrosion rate and inhibition efficiency of inhibitor on the metal. To resolve this problem of corrosion large amount of emulsions, and inhibiters are utilized, but these substance are harmful and non-ecofriendly substance therefore; in this present study we are trying to develop natural substance which are capable to substitute these harmful substance and with good efficiency against the corrosion inhibition similar to the non- eco-friendly substance.

Although the most effective and efficient organic inhibitors are compounds that have π bonds, the biological toxicity of these products, especially organic phosphate, is documented specifically about their environmental harmful characteristics. From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable, nowadays, which are also called eco-friendly or green corrosion inhibitors [1-4].

2. Experimental

Corrosion Analysis

Electrode materials:

The experiments were carried out with the sample of Cu. Cylindrical samples of each specimen, a approximately 1 cm in length, were cut from section of stock rod. In order to supply an electrical connection, a suitable length of copper wire was then spot-welded to one end. The cross-section surface area of each specimen metal depended, of course, on the diameter of the stock road. For the metal, this amounted to 0.506 cm^2. However, the aluminum was smaller diameter and the cross- section area in this case was 0.47cm^2. The surfaces of both the cut ends and body of metal slightly polished to remove trace of contamination and achieve a fairly surface at both the cut edges, then the cut samples were degreased in alcohol. This was carried out to improve the adhesion of the epoxy mounting resin to the so as to reduce the tendency of the metal experiencing crevice corrosion at the edge of the mounting resin, The cut section of rod was then embedded in epoxy mounting resin, with the connecting wire Protected by rigid plastic tube. The resin mixture was prepared by blending araldite with hardener in the ratio of 5:2. After hardening leaving the specimens over night, then after metal polished. Polishing of the specimens was done using SiC paper. The specimens were ground on successively smaller grades of SiC paper from P220 grit, using water as lubricant on grinding wheels. After polishing, the samples were washed in deionised water dried. Then they were kept dry.

Chemical used in the Experiments:

The two solutions were used in these tests. The first was potassium chloride of 0.5 M, which was used as it, was used as an electrolyte. This solution will encourage the pitting of substrates, due to the chloride ions. The second electrolyte was 0.5 M of potassium sulphate solution. This was used due to the replacement of chloride by sulphate here should discourage pitting corrosion.

Electrochemical Experiments:

Potentiodynamic polarization was carried out using an ACM potentiostat controlled by a PC andfor the current and resistance analysis, ANOVA instruments are used. A silver/ silver Chloride Electrode was used as a reference electrode, which was connected to the electrolytic cell using a Salt bridge and Luggin capillaries, which was placed approximately 1mm away from the working electrode. The auxiliary electrode was made of platinum and consisted of a flag shape with an area of 1 cm^2.Sample ware immersed for the 1min of time at the free corrosion potential prior to the establishment of polarization. Also, since the potentiostat controlled the voltage from the cathodic and anodic direction, the potential was held at the initial cathodic value for 1 min. before the sweep. All the measurements were performed at least twice. The temperature of the assembly was at ambient and it was open to air and not stirred. As mentioned above, the basic testing electrolyte solution used was 0.5M KCl and Sodium sulphate. Potentiodynamic polarization curves were produced using ACM Auto Tafel software at a sweep of 50-60 mV/s. the working electrode potential was measured with respect to the reference electrode and was plotted against current in external circuit. Thus giving the anodic and cathodic current curves according to the variation of the working electrode potential. As mentioned above, in order to minimize Ohamic resistance and maintain consistency. The capillary and auxiliary electrode was placed close to the working electrode and allowing formation of uniform and electric field during the anodic and cathodic polarization**.**

Preparation of Acid

The Analytical Reagent grade of H_2SO_4 was used for preparing the acid electrolyte in the present study. An aliquot of this acid was exactly diluted with double distilled water to prepare 0.5 M H_2SO_4 solutions. For each set of experiment freshly prepared 0.5 N H_2SO_4 solutions were used to avoid effect of contamination. Prepared 0.5 M H_2SO_4solutions were used to avoid effect of any contamination.

3. Results and Discussion

Result and Discussion Study of natural products

The Bougainvillea flower extract analyzed by the HPLC and IR spectroscopic methods using Yung-lin HPLC and Bruker IR instrument, the spectrograph of IR and chromatograms revealed that the nitrogenous compounds and natural dyes are present in the flower extract of pink, purple, orange and yellow flowers of Bougainvillea, after the collection these flowers were dried at room temperature

for 25days. The dried flowers of Bougainvillea grind and converted into the powder form, this powder is then analyzed into the IR and HPLC instruments and found that the extract contains the natural pigments and nitrogenous compounds, which are capable to be adsorbed over the metal surface and given good efficiency of anti-corrosion.

Extraction of Betalains

Betalains were extracted from 50 g of powdered freeze-dried Bougainvillea inflorescences, except for the purple coloured ones, of which only 1.000 g were mixed with 100 mL of purified water containing 120 mM sodium as corbate. After stirring for 30 min at room temperature, the plant material was separated from the extract. For complete extraction, the residue was rinsed with 100 mL of extractant, and the filtrate was collected in a filtering flask containing 100 mL of 100% methanol to inhibit residual enzyme activities. The precipitate formed in methanol was removed by filtering through a folded paper filter. Extracts were concentrated under reduced pressure at 30 °C and diluted to 50 mL with purified water (except for the orange-coloured extract, which had a final volume of 2 mL) and then passed through a membrane filter (0.45 µm) and stored frozen at −60 °C.

The Betalains identify and studded by the Yung-lin HPLC and Bruker IR instrument, equipped with Chem-Station software, The HPLC system was connected in series with a Bruker (Bremen, Germany) model Esquire 3000+ ion trap mass spectrometer fitted with an electro-spray ionization source operating in the positive mode. Nitrogen was used as the drying gas at a flow rate of 12 L/min and a pressure of 70 psi. The nebulizer temperature was set to 300 °C. Using helium/Ar as the collision-induced dissociation.The spectra were obtained with fragmentation amplitude of 1.8 V. An analytical-scale C18 reversed phase column with a particle size of 2-5 µm , fitted with a C18 ODS security guard column was used for pigment analysis, operating at a flow rate of 1 mL/min and a temperature of 30 °C.Betaxanthins were identified by comparison with the UV- Vis and mass spectrometric characteristics as well as the retention times of semi-synthesized reference betaxanthins obtained according to a method described previously [1]. The identities of all betaxanthin standards were checked by LC–MS analysis.

Betanin, isobetanin:

Betanidin and isobetanidin were identified by comparison with the retention times of the respective betacyanins in an extract from red beetroot prepared as described previously [2]. Lampranthin II and isolampranthin II were assigned by comparison with the corresponding retention times of the particular betacyanins in an extract from purple petals of Lampranthus sp. obtained as reported earlier [1]. No reference compounds were available for the remaining betacyanins.

For the corrosion analysis

Electrode materials:

The experiments were carried out with the sample of Cu. Cylindrical samples of each specimen, a approximately 1 cm in length, were cut from section of stock rod. In order to supply an electrical connection, a suitable length of copper wire was then spot welded to one end. The cross-section surface area of each specimen metal depended, of course, on the diameter of the stock road. For the metal this amounted to 0.506 cm^2. However, the aluminum was smaller diameter and the cross- section area in this case was 0.47cm^2.

Table 1: HPLC Data for the Bougainvillea flower (Betalains)

SN	Fractions	Betaxanthins [trivial name]	Retention Time (min)	Wawe Length	M/Z
1	B1	Histidine-bx [muscaaurin VII]	10.6	472	349
2	B2	Putrescine-bx	13.3	461	282
3	B3	Glutamine-bx [vulgaxanthin I]	15.8	470	340
4	B4	Lysine-bx	17.7	458	340
5	B5	Unknown bx	24.9	468	325
6	B6	Proline-bx [indicaxanthin]	30.8	479b	300
7	B7	Dopa-bx (I)	34.5	471	391
8	B8	Dopa-bx (II) [dopaxanthin]	35.1	472	391
9	B9	Tyrosine-bx [portulacaxanthin	42.6	471	375
10	B10	3-Methoxytyramine- bx	53.2	462	361

Table 2: IR Data for the Bougainvillea flower extract

A	2926.14	O-H str[a]
B	1653.45	C=N str and C=O str[a] (represented by shoulder)
C	1297.61	C-O str[a]
D	1100.15	C-O str[a]
E	918.38	C-H def[b] (benzene ring)

[a]str: stretch; [b]def: deformation

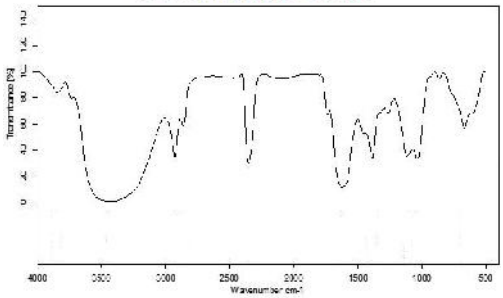

Fig 1: IR spectra of Bougainvillea flower extract

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Copper in KCl solution:

The corrosion potential of copper is about -188mV with the Ag/AgCl Electrode when immersed in KCl solution. The anodic current increases rapidly when the potential moves to a more positive direction. This behavior is likely due to the rapid dissolution attack by the chloride ions on copper surface. The cathodic current shows limiting current behavior at the value of -46µAcm^{-2} at a potential of -1150mV and below, hydrogen evolution is observed.

The addition of Betalains is mix with the solution the corrosion potential shifted to more negative value about -170 mV. In the cathodic current, the limiting current decreases significantly to less than 12µAcm^{-2}. The anodic current is inhibited significantly. Betalains extract move the corrosion potential to a negative direction at -260 mV. It also induced a region of passivity before the pitting potential. The cathodic current region shows increases in the limiting current reaching the value of -36µAcm^{-2}. This is still less than in the KCl solution showing some cathodic inhibition.

Copper in K_2SO_4 solution:

Cooper polarized in uninhibited potassium solution shows corrosion potential of -230mV with the Ag and AgCl electrode. The anodic current rises at a moderate rate prior to its increases once the potential become positive. The current (cathodic) shows limiting characteristics of about-10 µAcm^{-2}. The current moves toward the hydrogen evolution region as the potential become more negative around -1150mV.

The addition of Betalains causes the corrosion potential, which shifted to negative direction, lying corrosion potential of about -298mV. A significant reduction in the anodic current is occurs, this current rising again as the potential became more positive. In the cathodic direction, the current increases and then moves back to the value of that of the inhibition solution when the potential is -600mV and below. With the Betalains extract, induce a less reduction in anodic current.

The anodic current also rises rapidly when the potential to -10mV. The corrosion potential is negative 170mV. This inhibitor dose not has any effect on the cathodic corrosion.

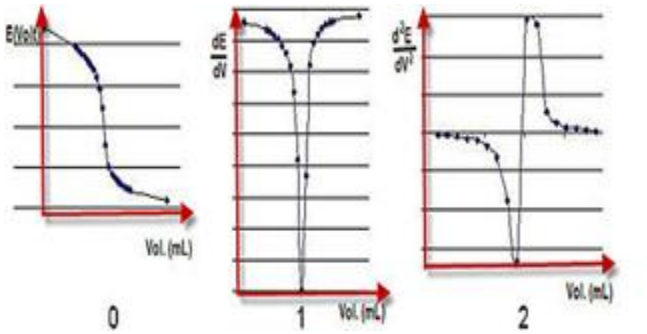

Fig 2 (A): Potentiometric analysis of Cu corrosion

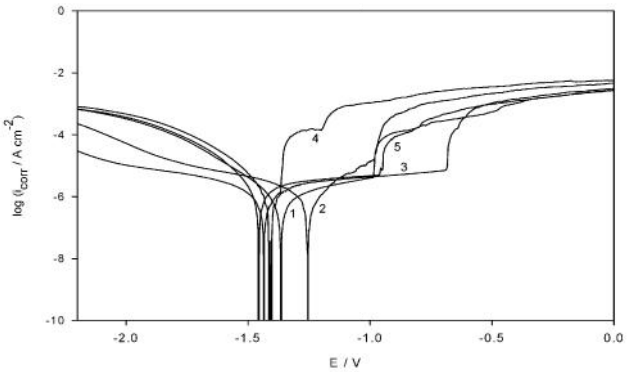

Fig 2 (B): Potentiometric analysis of Cu corrosion at different concentration of Betalains

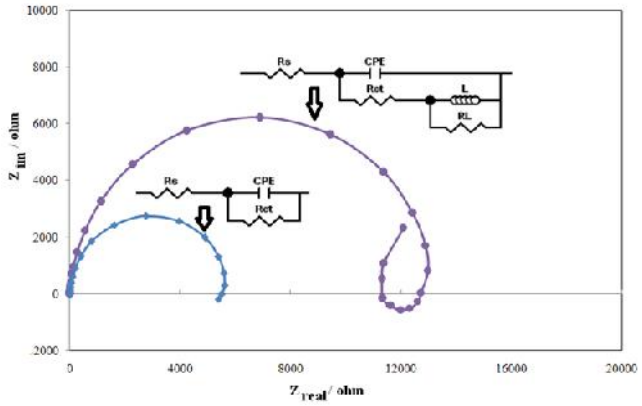

Figure 3: Nyquist and Boad plots of Cu corrosion inhibition at different concentration of Betalains

4. Conclusion

The inhibitive effect of the both used inhibitors in this method shows the good efficiency against the corrosion inhibition over the all metals and alloys. In this case, Betalains shows some inhibition but in chloride and sulphate solution Betalains given a high efficiency against the corrosion of all used metals.

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