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Electroplating using environmental friendly garlic extract - A case study

When uncoated carbon steel was immersed in an aqueous solution containing 3.5% NaCl, there was corrosion of metal. But when nickel was electro deposited on carbon steel surface, corrosion protective efficiency was observed. The corrosion protective efficiency increased for the carbon steel, electroplated with nickel and chromium. The corrosion protective efficiency decreased for the carbon steel, electroplated with nickel – chromium - garlic extract. When 1% copper sulphate solution was placed on the uncoated carbon steel surface, the red color (Cu) started appearing in 65 seconds. But in the case of nickel – chromium - garlic deposited carbon steel surface, the reddish brown color did not appear even after 1200 seconds. Polarization study leads to the conclusion that when carbon steel is electroplated with nickel and chromium the metal surface becomes corrosion resistant and the resistance decreases when electroplated with garlic extract. AC impedance study leads to the conclusion that when carbon steel is electroplated with nickel and chromium the metal surface becomes corrosion resistant and the corrosion resistant decreases when electroplated with garlic extract. The decolourization study reveals that the nickel coated carbon steel was only 40% efficient in decolourizing methyl orange solution in chloride medium whereas, carbon steel coated with nickel – chromium was 95% efficient. When electroplating was done in the presence of garlic extract the decolourizing efficiency was 85%.

Key words : Green electroplating, nickel plating, garlic extract, chromium plating

INTRODUCTION

The need for coatings with improved resistance to highly aggressive environments is high as a result of growing demand for extended safe service life of industrial objects. The corrosion and wear corrosion resistance of nitride coatings, [1] hard chromium coatings [2] and composite electrodeposited coatings of nickel and nano-crystals of silicon carbide has been studied,[3,4] Electrodeposition of silver from cyanide solutions is a long-established industrial practice [5]. Tin-zinc alloy coatings have good corrosion resistance, good frictional properties and ductility and good solderability. In view of their good properties, they have been proposed as substitutes for other industrial coatings, such as those of toxic cadmium and allugenic nickel [6]. Electrodeposition of gold and its alloys has been widely used in the production of new materials that have required specific chemical, physical and mechanical properties [7, 8], gold deposits

containing small amounts of metal ions such as nickel or cobalt have been found to yield consistently brightly alloy electrodeposits with suitable morphology, purity and hardness as well as corrosion resistance [9, 10]. Effect of α -picoline and quinoline on DC and pulse plating of nickel directly on aluminum has been investigated [11]. Characterization of electroless nickel composite coatings before and after heat treatment has been done [12]. Electrochemical deposition of nickel and nickel-thallium composite oxides films from EDTA alkaline solutions has been investigated [13]. High corrosion-resistant and long-life-span electroless nickel process has been formulated [14]. Co-deposition characteristics of nano diamond particles in electrolessly plated nickel films have been investigated [15]. Valova et al., have compared the structure and chemical composition of crystalline and amorphous electroless Ni-W-P coatings [16]. New electroless Nickel technology as an alternative to hard chromium plating has been proposed [17]. Ghosh et al., have studied the deposition of Ni/Cu multilayered coating by electroplating [18]. Ariizumi et al., have investigated the catalytic activity of Pd Ad-atoms for electroless Ni-P plating [19]. Black nickel electrodeposition from a modified watts bath has been studied [20]. Moussa, et al., have studied on induced electrodeposition of tungsten with nickel from acidic citrate electrolyte [21]. Mechanism of the chemical deposition of nickel on silicon wafers in aqueous so-

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lution has been proposed [22]. Hardening effect induced by incorporation of SiC particles in nickel electrodeposits was studied by Pavlatou et al. [23]. Nickel thin film coatings on steels with electroless plating and sputter deposition have been analysed by Mu et al [24]. Niwa et al., have studied the nickel electroless deposition process on chemically pretreated Si (100) wafers in aqueous alkaline solution [25]. Electroless Ni-P deposition through imperfections in anodic oxide films on aluminum and A15052 alloy has been done [26]. Munoz and Salinas have studied the inhibitory effects of NO₂-on Ni deposition [27]. The present work is a case study of small scale electroplating industry. The present work is undertaken.

- (i) a) To electroplate nickel on carbon steel surface, in the real situation of an electroplating unit using a bath containing nickel sulphate, nickel chloride and boric acid, using nickel anode,
- b) To electroplate nickel coated surface with chromium.
- c) To electroplate nickel coated carbon steel surface in the real situation of an electroplating unit using chromium bath containing garlic extract.
- (ii) To study the corrosion resistance behaviour of the above metal specimens
 - a) by immersing it in an aqueous solution containing 3.5% NaCl
 - b) by placing a drop of 1% CuSO₄ solution on the metal surface
 - c) by polarization, AC impedance spectroscopy and cyclic voltammetry
- (iii) To decolourise methyl orange solution using
 - a) Carbon steel
 - b) Platinised titanium
 - c) Carbon steel electroplated with nickel
 - d) Carbon steel electroplated with nickel and chromium
 - e) Carbon steel electroplated with nickel – chromium - garlic extract.

EXPERIMENTAL

Preparation of the specimen

Carbon steel (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) specimens of the dimensions 1.0 cm x 4.0 cm x 0.2 cm were used in the present study for electroplating and then measuring the corrosion resistivity of the metal surface.

Preparation of Garlic Extract

50g of garlic was crushed and boiled with distilled water. The extract was filtered and made up to 500 ml.

Electroplating

The process of electroplating of the carbon steel specimen involves the following steps.

Pickling with conc.HCl

Distilled water

Drying

Polishing (nice)

Degreasing with cleaning powder containing soda, chalk and nice emery powder.

Drying

Immersed in bath solution

Ni-Bath Solution

<Nickel Chloride	-	10 g/litre
Nickel Sulphate	-	10 g/litre
Boric Acid	-	10 g/litre
Anode	-	Pure nickel plate
Cathode	-	Carbon steel specimen
Agitation	-	Nil
Temperature	-	Room temperature
Potential	-	24 Volt
Current	-	6 amp

CHROMIUM PLATING

After nickel plating, the metal was coated with chromium solution.

Cr-Bath Solution

Chromic Oxide	-	100 parts
Sulphuric acid	-	1part
Anode	-	Pb- Sn alloy
Cathode	-	Carbon steel specimen coated with nickel
Agitation	-	Nil
Temperature	-	Room temperature
Potential	-	24 Volt
Current	-	6 amp

CHROMIUM GARLIC PLATING

100ml of Garlic extracts was added to 1 lit of the chromium plating solution.

Compositions: 100 parts chromic oxide and 1 part

ConH ₂ SO ₄	-	
Potential	-	24 Volt
Current	-	6 amp
Temperature	-	room temperature
Anode	-	Pb-Sn alloy
Cathode	-	nickel coated carbon steel surface
Time	-	5 minutes
Agitation	-	Nil

DC current was passed for 5 minutes. After electrodeposition, the specimen was washed with water and dried.

Measurement of corrosion resistance of the electroplated metal surface

The following studies were used to measure the corrosion protective nature of the film formed on the carbon steel surface after electroplating.

Immersion in chloride environment

The metal specimens in triplicate were immersed in 100 ml of an aqueous solution containing 3.5% NaCl for a period of one day. After one day the corrosion product, if formed, were cleaned with Clarke's solution [28]. The inhibition efficiency (IE) was calculated using the equation.

$$IE = 100 [(W_1 - W_2)/W_1] \%$$

Where W_1 = Corrosion rate before electroplating

W_2 = Corrosion rate after electroplating

Action of 1% Copper Sulphate Solution

One drop of 1% copper sulphate solution was placed on the surface of the metal. The time taken for the formation of a red solution of copper was determined. Cu^{2+} ion is blue in color. When an electron is transferred from Fe during the corrosion process, Cu which is red in color will be formed, Hence the time required for the formation of a red solution is an indication of the rate of electron transfer (corrosion process) from the iron to the Cu^{2+} ion on the metal surface.

Potentiodynamic Polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) were calculated.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell setup was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. From the bode plots, the impedance values [$\log(z/\text{ohm})$] were derived.

Cyclic Voltammetry

The experimental set up was the same as used in polarization and AC impedance study.

Decolourisation Process

Decolourisation of a dye such a methyl orange was attempted using various electrodes such as carbon steel, carbon steel electroplated with nickel, carbon steel electroplated with nickel and chromium, carbon steel electroplated with nickel – chromium-garlic extract and platinised titanium. The optical density of the methyl orange solution before and after decolourisation was measured by the instrument photoelectric colorimeter – 112. The electrodes were immersed in the solution containing 250 ppm of methyl orange. The solution was subjected to electrochemical decolourisation process after addition of various concentrations of NaCl. Graphite was used as cathode. Carbon steel or electroplated carbon steel or platinised titanium was used as anode. The electrolysis was carried out in an undivided cell with a stirring bar.

RESULTS AND DISCUSSION

Analysis of results of weight loss method

Corrosion rates of carbon steel (CS) samples, before and after electroplating, in an aqueous solution containing 3.5% NaCl, and the corrosion protective efficiency (CPE) obtained by weight loss method are given in Table 1. It is observed that when nickel plating was done for five minutes [Ni], the CPE was 46%. This efficiency was not sufficient. This is due to the fact that a very thin film of nickel was coated on the carbon steel surface. This film was broken by the chloride ion present in the aqueous solution. When the electroplating was done in the presence of nickel ions followed by chromium ions the CPE increased to 85%. When Ni-Cr electroplating was done in the presence of garlic extract the CPE was 68%. The inhibition efficiency decreases. This gives us a warning that Ni-Cr electroplated carbon steel vessels should not be used to presence garlic extracts, garlic pickles etc.

Table 1 - Corrosion rates of carbon steel (CS), before and after electroplating, in an aqueous solution containing 3.5% NaCl, and the corrosion protective efficiency (CPE) obtained by weight loss method

Sample	NaCl %	CR mdd	CPE %
CS	3.5	30.00	--
CS + Ni	3.5	16.20	46
CS + Ni + Cr	3.5	4.5	85
CS + Ni + Cr + garlic	3.5	9.6	68

Action of 1% copper sulphate solution on the metal surface

The time required for the appearance of reddish brown color when one drop of 1% copper sulphate solution was placed on the mild surface, before and after electroplating is given in Table 2. When a drop of 1% copper sulphate was placed on the polished carbon steel surface, a red solution started to appear at 65 seconds. The color appearance was complete after 155 seconds.

Table 2 - Time required for the appearance of reddish brown solution, when 1 drop of % copper sulphate solution was placed on the metal surface, before and after electroplating

Sample	Time of appearance of reddish brown Colour, Sec	
	Just appearance	Complete appearance
CS	65	155
CS + Ni	No appearance of reddish brown colour even after 1200 seconds	
CS + Ni + Cr	No appearance of reddish brown colour even after 1200 seconds	
CS + Ni + Cr + garlic	No appearance of reddish brown colour even after 1200 seconds	

In the case of carbon steel surface electroplated with Ni, a reddish brown color did not appear even after 1200 seconds. In the case of nickel - chromium - plated surface, and also nickel - Cr- garlic plated surface, the reddish brown color did not appear even after 1200 seconds. This indicates that the nickel

chromium and also garlic films were coated on the carbon steel surface. The formation of reddish brown solution is due to the conversion of blue Cu^{2+} ion into reddish brown Cu. This process takes place by the electron supplied by Fe, when it undergoes corrosion. After nickel plating (and also Ni-Cr, and Ni-Cr-garlic plating) the corrosion process is prevented; there is no transfer of electron from Fe to Cu^{2+} . So there is no formation of Cu. Hence reddish brown solution does not appear.

Potentiodynamic Polarization Study

The polarization curves of carbon steel surface electroplated with nickel and an aqueous extract of garlic, immersed in an aqueous solution containing 3.5% NaCl are shown in Fig 1. The corrosion parameters, namely, corrosion potential (E_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in Table 3. When carbon steel is immersed in 3.5% NaCl solution, the corrosion potential is -623 mV vs SCE. When the surface is electroplated with nickel, it shifts to the anodic side (-513 mV vs SCE); The LPR increases from 3.134×10^2 to 4.597×10^2 ohm cm^2 and corrosion current decreases from 8.366×10^{-5} to 5.846×10^{-5} A/cm². When the surface is electroplated with nickel and chromium, the corrosion potential is shifted to anodic side (-439 mV vs SCE); The LPR increases to 1.107×10^4 ohm cm^2 and the corrosion current decreases to 0.267×10^{-5} A/cm². These observations indicate that when carbon steel surface is coated with Ni, the corrosion protective nature increases. It further increases when the carbon steel surface is coated with nickel and chromium.

Table 3 - Polarization curves of carbon steel (CS) surface electroplated with chromium and an aqueous extract of garlic, immersed in 3.5% NaCl solution

Sample	E_{corr} mV vs SCE	b_c mV	b_a mV	LPR ohm cm^2	I_{corr} A/cm ²
CS	-623	287	76	3.134×10^2	8.366×10^{-5}
CS + Ni	-513	202	89	4.597×10^2	5.846×10^{-5}
CS + Ni + Cr	-439	169	114	1.107×10^4	0.267×10^{-5}
CS + Ni + Cr+ garlic extract	-507	200	87	5.229×10^3	0.5025×10^{-5}

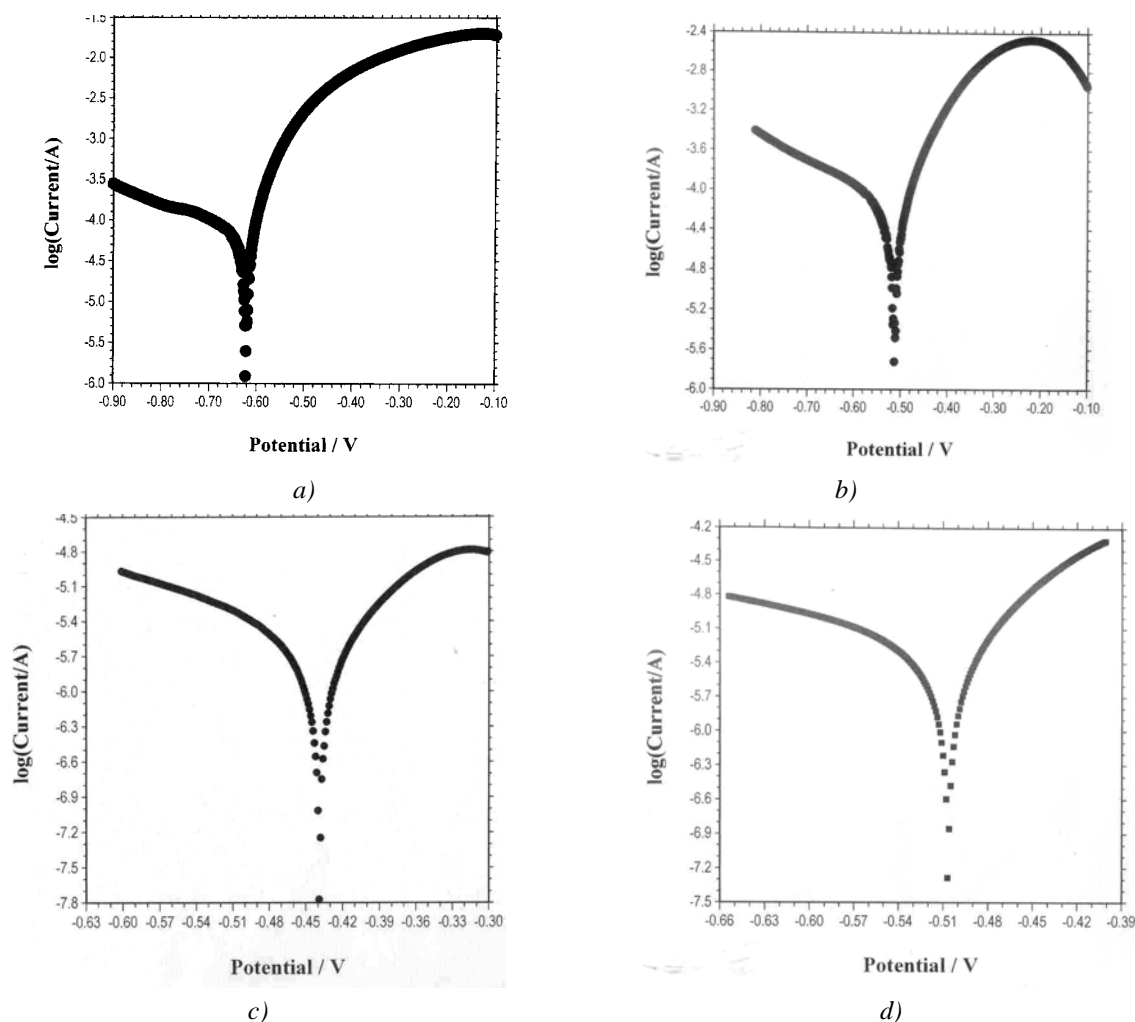


Fig.1: Polarization curves of carbon steel immersed in an aqueous solution containing 3.5% NaCl before and after electrodeposition: a) Carbon steel, b) Carbon steel + nickel, c) Carbon steel + nickel + chromium, d) Carbon steel + nickel + chromium + garlic extract

When the surface is electroplated with Ni, Cr and garlic extract, the corrosion potential is shifted to -507mV vs SCE. The LPR value changes to $5.229 \times 10^3 \text{ ohm cm}^2$; the corrosion current changes to 0.5025×10^{-5} . These observations indicate that when electroplating is done in the presence of garlic extract, the film formed on metal surface is easily broken and hence there is decrease in LPR value and increase in corrosion current.

Analysis of AC impedance spectra

The AC impedance spectra (Bode Plots) of carbon steel surface, electroplated with nickel, chromium and an aqueous extract of garlic, immersed in an aqueous solution containing 3.5% NaCl solution are shown in Fig 2. The AC impedance values [$\log(z/\text{ohm})$] are given in Table 4. When CS is electro-

plated with Ni, the impedance value [$\log(z/\text{ohm})$] increase from 0.7889 to 0.9856. When CS is coated with Ni and chromium the impedance value increases from 0.9856 to 1.574. This indicates the protective nature of the film formed on CS surface after electroplating.

Table 4 - AC impedance parameters of carbon steel (CS) surface electroplated

Sample	Impedance [$\log(z/\text{ohm})$]
CS	0.7889
CS + Ni	0.9856
CS + Ni + Cr	1.574
CS + Ni + Cr + garlic extract	0.9376

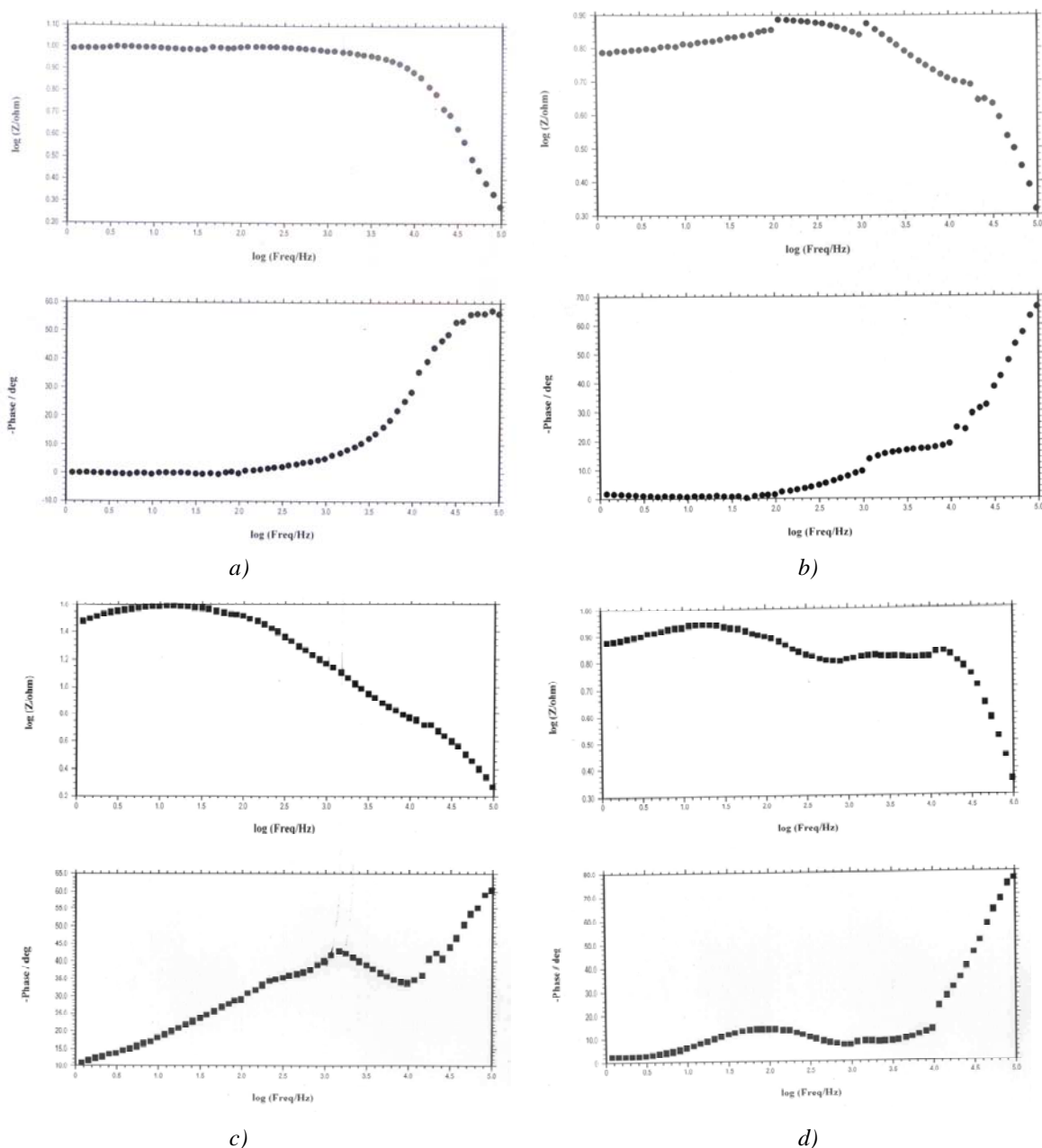


Fig.2: AC impedance spectra of carbon steel immersed in an aqueous solution containing 3.5% NaCl before and after electrodeposition: a) Carbon steel (Bode Plots), b) Carbon steel + nickel (Bode Plots), c) Carbon steel + nickel + chromium (Bode Plots), d) Carbon steel + nickel + chromium + garlic extract. (Bode Plots)

When the plating is done in the presence of garlic extract, the real impedance value [$\log(z/\text{ohm})$] slightly decreases to 0.9376. This suggests that the film formed on the metal surface, in the presence of garlic extract, is broken by the aggressive Cl^- ions present in the medium. The film is fragile. This result is in agreement with that of the polarization study.

Cyclic Voltammetry

The cyclic voltammograms of carbon steel surface electroplated with nickel, chromium and garlic extract immersed in an aqueous solution containing 3.5% NaCl are shown in Fig.3. The various parameters are given in Table 5. When carbon steel is immersed in 3.5% NaCl solution, corrosion

takes place and it is revealed by a peak at -1062 volt. It is observed that when CS surface is electroplated with nickel and also with nickel and chromium electron transfer (corrosion) does not take place. The protective film is very compact and strong. However when electroplating is done in the presence of garlic extract, corrosion takes place as revealed by the peak potential at -1.042volt.

Table 5 - Cyclic Voltammetry Parameters

Sample	Ep	Peak Ep Current $\times 10^{-3}$ A	Ah $\times 10^{-3}$ C
CS	-1.062 V	5.620	5.265
CS + Ni	-	-	-
CS + Ni + Cr	-	-	-
CS + Ni + Cr + garlic extract	-1.042V	5.854	5.247

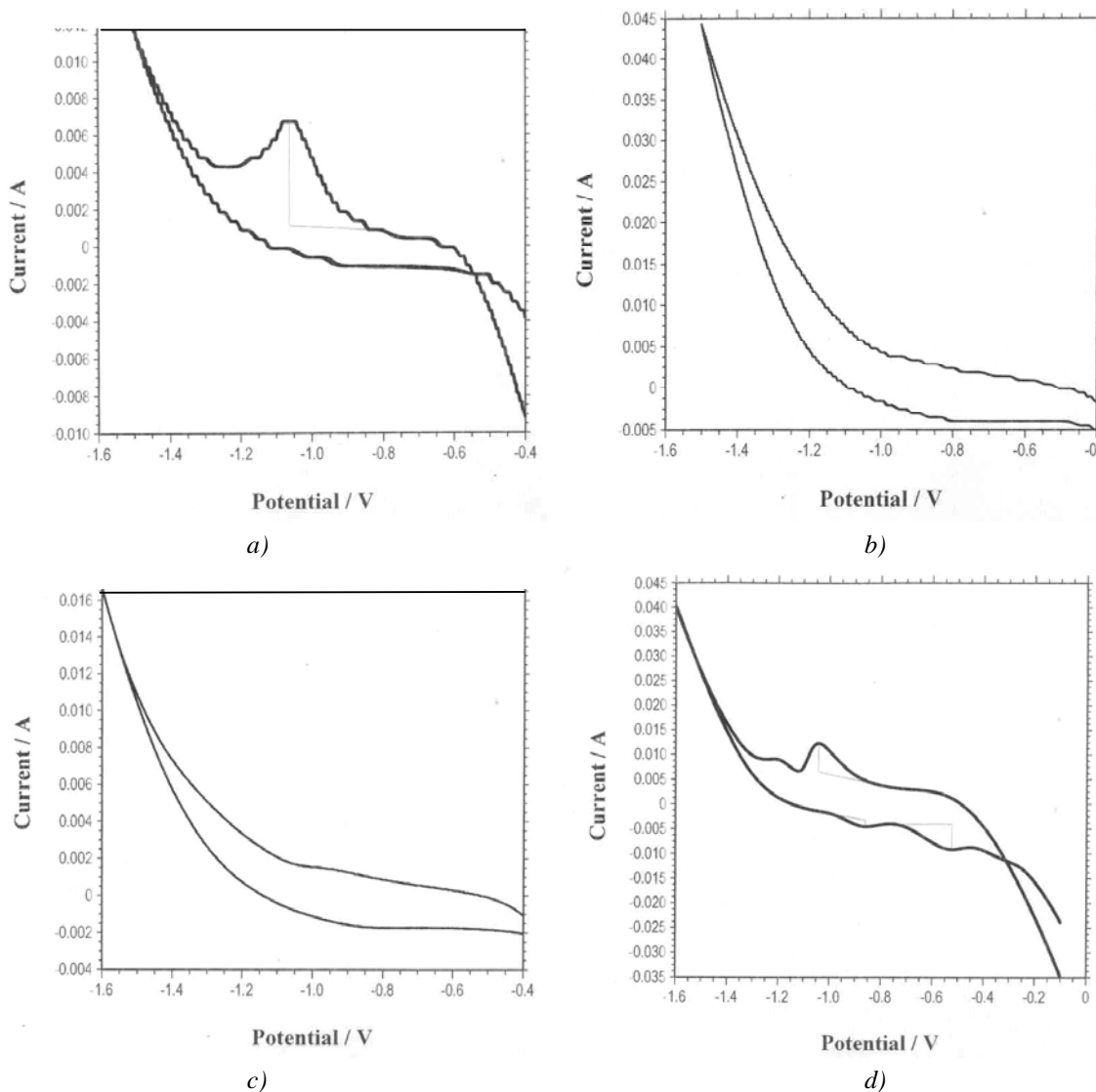


Fig.3: Cyclic Voltammogram of carbon steel. a) Carbon steel, b) Carbon steel + nickel, c) Carbon steel + Nickel +Chromium, d) Carbon steel + Nickel +Chromium +Garlic extract.

Analysis of FTIR Spectra

The structure of the active principle present in the boiled aqueous extract is shown in the Scheme-1.



Scheme - 1

It contains sulphur atom, S=O group, and two vinyl groups. A few drops of aqueous extract of garlic were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum (KBr) is shown in Fig.4. The stretching frequency due to S appears at 1264 cm^{-1} . The frequency due to S=O appears at 1044 cm^{-1} . The frequencies due to vinyl group appear at 1044 cm^{-1} and 945 cm^{-1} .

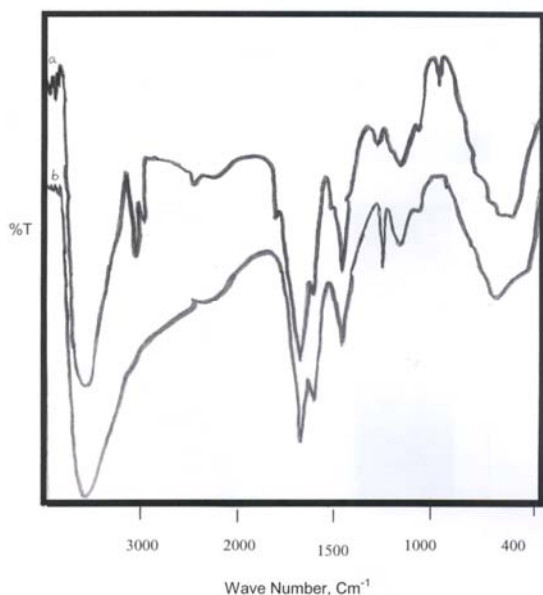


Fig.4: FTIR Spectra (KBr): a) White solid obtained by evaporation of few drops of garlic extract, b) Film formed on carbon steel Surface after electrodeposition with chromium and garlic extract.

Carbon steel was electroplated with nickel. Further this surface was electroplated in the presence of chromium bath containing an aqueous extract of garlic. A pale black film was deposited on the metal surface. It was carefully scratched, mixed with KBr and a pellet was made. Its FTIR spectrum is shown in Fig.4. It is observed that the stretching frequency due to S has shifted from 1264 cm^{-1} to 1210 cm^{-1} . The stretching frequency due to S=O has shifted from 1044 cm^{-1} to 1026 cm^{-1} . The stretching frequency due to vinyl group has shifted from 945 cm^{-1} to 912 cm^{-1} and from 1042 cm^{-1} to 1038 cm^{-1} . These observations suggest that a thin film of garlic is formed on the metal surface; the active principle of garlic has coordinated with metal ions such as Ni^{2+} , Cr^{3+} and Fe^{2+} through sulphur atom; oxygen atom of S=O group and also through the π electron of the double bonds. Thus the presence of garlic film on the electroplated metal surface is confirmed [29].

Decolourisation Process

Decolourisation using carbon steel

Uncoated carbon steel anode and graphite cathode were immersed in the solution to be decolourised (250 ppm methyl orange solution). Current was passed for 10 minutes without the addition of NaCl. There was no decolourisation. The experiment was repeated after addition of 7gms of NaCl. Current was passed. The current density was 0.4 A/cm^2 and the potential was 1.5 volt. Methyl orange solution was completely decolourised within 240 seconds. The efficiency of decolourisation was 100%. (as calculated from optical density measurement, before and after decolourisation).

Decolourisation using platinised titanium

The experiment was repeated by using platinised titanium after addition of 7gms of NaCl. Current was passed. The current density was 0.24 A/cm^2 and the potential was 5 volts. Methyl orange solution was decolourised within 240 seconds. The efficiency of decolourisation was 100%.

The supporting electrolyte plays an important role in the oxidation process. When NaCl solution is electrolysed, the active species produced is Cl^+ [30,31]. This oxidized the coloured material into colourless product.

Decolourisation using carbon steel electroplated with nickel

The experiment was repeated by using carbon steel electroplated with nickel after addition of 7gms of NaCl. Current was passed. The current density was 0.3 A/cm^2 and the potential was 2.2 volts. Methyl orange solution was decolourised within 4 minutes. The efficiency of decolourisation was only 40%. The solution turned green due to the formation of nickel chloride and also ferrous chloride. This indicates that first the nickel film dissolves in chloride medium giving Ni^{2+} ; and also iron dissolves giving Fe^{2+} .

Decolourisation using carbon steel electroplated with nickel – chromium

The experiment was repeated by using the carbon steel electroplated with nickel – chromium after addition of 7gms of NaCl. Current was passed. The current density was 0.65 A/cm^2 and the potential was 3.8 volts. Methyl orange solution was decolourised within 100 seconds. The efficiency of decolourisation was 95%. It is observed that carbon steel surface electroplated with Ni – chromium system is better than the other systems. 95% efficiency is obtained within 100 secs, where as in

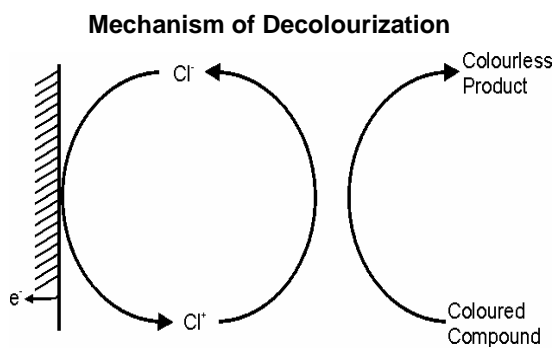
other cases, it requires more time, namely, 240 secs. The supporting electrolyte plays an important role in the oxidation process. When NaCl solution is electrolysed, the active species produced is Cl^+ [30, 31]. This oxidized the coloured material into colourless product. [Scheme 2]

Decolourisation using carbon steel electroplated with nickel – chromium – garlic

The experiment was repeated by using the carbon steel electroplated with nickel – chromium – garlic after addition of 7gms of NaCl. Current was passed. The current density was 0.58 A/cm^2 and the potential was 3.2 volts. Methyl orange solution was decolourised with in 100 seconds. The efficiency of decolourisation was 85%. It is observed that carbon steel surface electroplated with Ni – chromium – garlic system is better than the other systems. 85% efficiency is obtained within 100 secs, whereas in other cases, it requires more time, namely, 240 secs. The supporting electrolyte plays an important role in the oxidation process. When NaCl solution is electrolysed, the active species produced is Cl^+ . This oxidized the coloured material into colourless product.

Table. 6 - Decolourisation of 250 ppm methyl orange solution

System	NaCl %	Current A/cm^2	Poten tial Volt	Time s	Effici ency %
CS	7	0.4	1.5	240	100
Plati-nised Ti	7	0.24	5.0	240	100
CS + Ni	7	0.3	2.2	240	40
CS + Ni + Cr	7	0.65	3.8	100	95
CS + Ni + Cr + garlic	7	0.58	3.2	100	85



CONCLUSIONS

When uncoated carbon steel was immersed in an aqueous solution containing 3.5% NaCl, there was corrosion of metal.

But when nickel was electro deposited on carbon steel surface, corrosion protective efficiency was observed.

The corrosion protective efficiency increased for the carbon steel, electroplated with nickel – chromium.

The corrosion protective efficiency decreased for the carbon steel, electroplated with nickel – chromium- garlic extract.

When 1% copper sulphate solution was placed on the uncoated carbon steel surface, the red colour (Cu) started appearing in 65 seconds. But in the case of nickel – chromium - garlic deposited carbon steel surface, the reddish brown colour did not appear even after 1200 seconds.

Polarisation study leads to the conclusion that when carbon steel is electroplated with nickel and chromium the metal surface becomes corrosion resistant and the resistance decreases when electroplated with garlic extract.

AC impedance study leads to the conclusion that when carbon steel is electroplated with nickel and chromium the metal surface becomes corrosion resistant and the corrosion resistance decreases when electroplated with garlic extract.

The decolourisation study reveals that the nickel coated carbon steel was only 40% efficient in decolourising methyl orange solution in chloride medium whereas, carbon steel coated with nickel – chromium was 95% efficient. When electroplating was done in the presence of garlic extract the decolourising efficiency was 85%.

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