ELECTROCHEMICAL AND SURFACE ANALYSIS STUDIES ON CORROSION INHIBITION OF CARBON STEEL BY OCTANESULPHONIC ACID-BETANIN SYSTEM

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Abstract

This research aims to study the corrosion inhibition behavior of betanin a natural product in combination with Octanesulphonic acid (OS) on the corrosion of carbon steel in dam water. Results of weight loss method indicated that inhibition efficiency (IE) increases with increasing inhibitor concentration upto a particular concentration value and then it decreases. Polarization study reveals that OS-betanin system controls the anodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. The nature of the metal surface has been analysed by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and Energy dispersive x-ray detector (EDAX) measurements.

Keywords: *Corrosion; Electrochemical techniques; FTIR; SEM; EDAX.*

1. Introduction

Carbon steel has been widely employed as a construction material for pipe work in the oil and gas production, such as down hole tubulars, flow lines and transmission pipelines. Corrosion plays a very important role in diverse fields of industry and consequently, in economics. The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. Although many synthetic compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment [1] and they are often expensive and non-biodegradable. Thus, the use of natural products as corrosion inhibitors has become a key area of research [2-5], because plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that are biodegradable in nature and can be extracted by simple procedures at low cost [6]. The extracts of their peels [7], seeds [8], leaves [9] http://www.sciencedirect.com.scopeesprx.elsevier.com/science/article/pii/S0010938X10001836 - bib14#bib14 and roots [10] have been reported as effective corrosion inhibitors in different aggressive environments.

This paper reports the effect of an aqueous extracts of betanin in controlling the corrosion of carbon steel in dam water in the absence and presence of sodium octane sulphonic acid (OS), using weight loss measurements, anodic and cathodic polarization curves and electrochemical impedance measurements. The carbon steel surfaces were analyzed using (SEM) and EDAX. The medium which is dam water collected from Sothuparai dam in the state of Tamil Nadu, India.

2. Experimental method

2.1. Preparation of Plant Extract (PE)

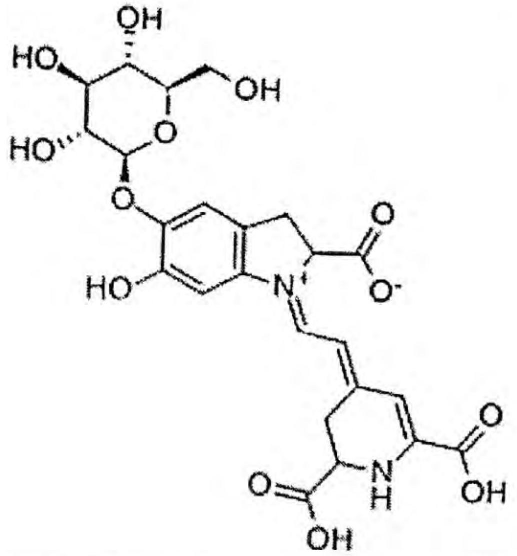
An aqueous extract of beetroot (BR) was prepared by grinding 10g of beetroot with double distilled water, filtering the suspending impurities, and making up to 100mL. The extract containing betanin was used as corrosion inhibitor in the present study.

2.2. Preparation of the specimen

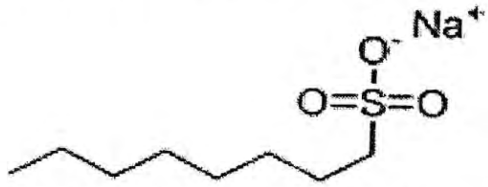
Carbon steel specimens of size 1.0cm × 4.0cm × 0.2cm, (area $10cm^2$) and chemical composition 0.026% sulphur, 0.06% phosphorous, 0.4% manganese, 0.1% carbon and the rest iron (density $7.87gm/cm^3$), were polished to a mirror finish and degreased with acetone and used for the weight loss method and surface examination studies.

2.3. Weight-loss method

Carbon steel specimens were immersed in 100mL of the water containing various concentrations of the inhibitor betanin in the absence and presence of OS for one day. The molecular structures of betanin and OS are given in scheme 1 and scheme 2.



Scheme 1: Molecular structure of betanin



Scheme 2: Molecular structure of OS

The weights of the specimens before and after immersion were determined using a Shimadzu Model AUY 220 digital balance. The corrosion products were cleaned with Clarke's solution prepared by dissolving 20g of Sb_2O_3 and 50g of $SnCl_2$ in 1L of concentrated hydrochloric acid of specific gravity 1.9 [11]. The corrosion IE was then calculated using the equation

$$IE = 100\ [1-(W_2/W_1)]\ \% \qquad (1)$$

Where W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of inhibitor. Corrosion rate (CR) was calculated in Mils penetration per year (mpy) using the formula [12] CR = 534 W/DAT............ [2]

W = weight loss in milligrams

D = density of specimen in g/cm^3

A = area of specimen in square cm

T = exposure time in hours

2.4. Potentiodynamic Polarization

Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. Saturated calomel electrode was the reference electrode. Platinum was the counter electrode. From polarisation study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = β_a and cathodic = β_c were calculated and linear polarization resistance (LPR) was also calculated.

2.5. AC impedance spectra

The instrument and cell set up used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

2.6. Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

2.6.1. Fourier Transform-Infrared Spectra

These spectra were recorded in a PerkinElmer-1600 spectrophotometer using KBr pellet. The FT-IR spectrum of the protective film was recorded by carefully removing the film formed by scratching with a clean, pointed glass rod and mixing it with KBr, and making the pellet.

2.6.2. Scanning Electron Microscopic studies (SEM) and energy dispersive x-ray detector (EDAX)

The carbon steel immersed in blank solution and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of carbon steel were examined using JEOL MODEL6390 computer controlled scanning electron microscope. The elemental analysis of the carbon steel surface at the same condition was carried out using an energy dispersive X-ray analyzer unit attached to the SEM machine.

3. Results and discussion

3.1. Weight-loss study

The physicochemical parameters of dam water are given in Table1.

Table-1: Water analysis (Sothuparai dam water, Tamilnadu, India)

Parameters	Result
Appearance	Brownish
Total dissolved solids	103ppm
Electrical conductivity	125µs/cm
PH	8.12
Total hardness	47ppm
Calcium	08ppm
Magnesium	06ppm
Iron	1.2ppm
Nitrate	10ppm
Chloride	10ppm
Sulphide	02ppm

Inhibition Efficiency (IE) and Corrosion Rate (CR)

The IE and the corresponding CR of betanin-OS system are given in Table2. It is found that the IE increases upto 4ml of betanin. Then it decreases, and this is due to the fact that when higher concentrations of betanin extract are added, the protective film (Fe^{2+}- betanin complex) formed on the metal surface goes into the solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken [13,14]. As the concentration of OS increases, IE also increases. A synergistic effect exists between betanin and OS. For example, 4ml of betanin has 10%. IE and 100ppm of OS has 40% IE. However, the formulation consisting of 4ml of betanin and 100ppm of OS has 90%.IE, i.e., a mixture of inhibitors shows better inhibition efficiency than the individual inhibitors [15,16].

Table-2: Corrosion inhibition efficiencies (IE%) and the corresponding corrosion rates (CR) in (mills per year) of betanin-OS systems

PE in ml	OS					
	0ppm		50ppm		100ppm	
	IE%	CR mpy	IE%	CR mpy	IE%	CR mpy
0	0	0.0464	-40	0.0649	40	0.0278
2	-20	0.0557	10	0.0417	60	0.0186
4	10	0.0417	80	0.0092	90	0.0046
6	-20	0.0557	20	0.0371	30	0.0325
8	-20	0.0557	50	0.0232	40	0.0278

3.2. Analysis of polarization curves

Figure 1 represents the potentiodynamic polarization curves of carbon steel in dam water in the absence and presence of inhibitor system. The cathodic branch represents the oxygen reduction reaction, while the anodic branch represents the iron dissolution reaction. The electrochemical parameter such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (β_a and β_c) linear polarization resistance (LPR) are given in Table 3. When carbon steel is immersed in dam water, the corrosion potential is -608 versus SCE. The formulation consisting of betanin (4ml)-OS (100ppm) shifts the corrosion potential to -663 versus SCE, i.e., the corrosion potential is shifted to the cathodic side. It is also observed that the shift in the anodic slope (from 204 to 163 mV/dec) is higher than the shift in the cathodic slope (from 193 to 169 mV/dec). Hence, it can be said that the same inhibitors system predominantly controls the anodic reaction [17,18]. The corrosion current value and LPR value for dam water are 9.566×10^{-7}A/cm^2 45090 Ω cm^2.

For the formulation of betanin (4ml)-OS (100ppm), the corrosion current value decreased to 6.609×10^{-7}A/cm^2 and the LPR value increased to 57238 Ω cm^2.

The fact that the LPR value increases with decrease in corrosion current indicates absorption of the inhibitor on the metal surface to block the active sides and inhibit corrosion and reduce the corrosion rate [19].

Table-3: Corrosion parameters of carbon steel immersed in dam water in the presence and absence of inhibitor obtained by polarization method

PE ml	OS ppm	E_{corr} mv vs SCE	I_{corr} A/cm²	β_a mv/dec	β_c mv/dec	LPR Ω cm²
0	0	-608	9.566×10^{-7}	204	193	45090
4	100	-663	6.609×10^{-7}	163	169	57238

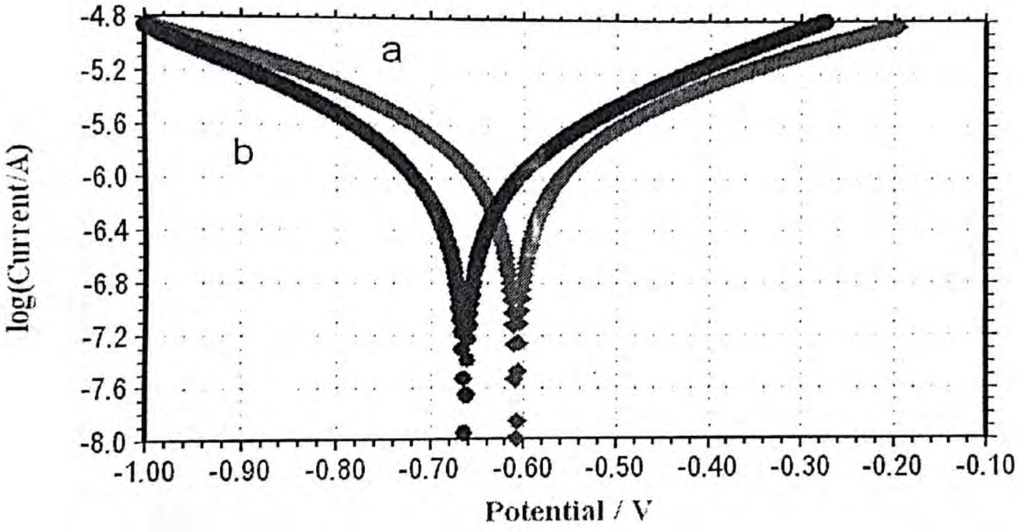


Figure 1: Polarization curves of carbon steel immersed in various test solutions a) dam water, b) dam water containing 4ml of betanin and 100ppm of OS

3.3. Analysis of AC Impedance spectra

AC impedance spectra can been used to detect the formation of film on the metal surface [20,21]. If a protective film is formed, the charge transfer resistance (R_t) increases and double-layer capacitance (C_{dl}) value decreases. Nyquist representations of carbon steel in dam water in the absence and presence of inhibitor system are shown in figure 2. The impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4. When carbon steel is immersed in dam water, R_t value is 990.3 Ω cm² and C_{dl} value is 5.1499×10^{-9} F/cm². When betanin (4ml)-OS (100ml) are added to dam water, R_t value increases from 990.3Ωcm² to 1560.6Ωcm² and the C_{dl} decreases from5.1499×10^{-9} F/cm² to 3.2679×10^{-9}F/cm². This suggests that a protective film is formed on the surface of the metal [22,23].

Table-4: Impedance parameters of carbon steel in dam water in the presence and absence of inhibitors obtained by AC impedance method

PE mL	OS ppm	R_t Ω cm²	C_{dl} F/cm²
0	0	990.3	5.1499×10^{-9}
8	100	1560.6	3.2679×10^{-9}

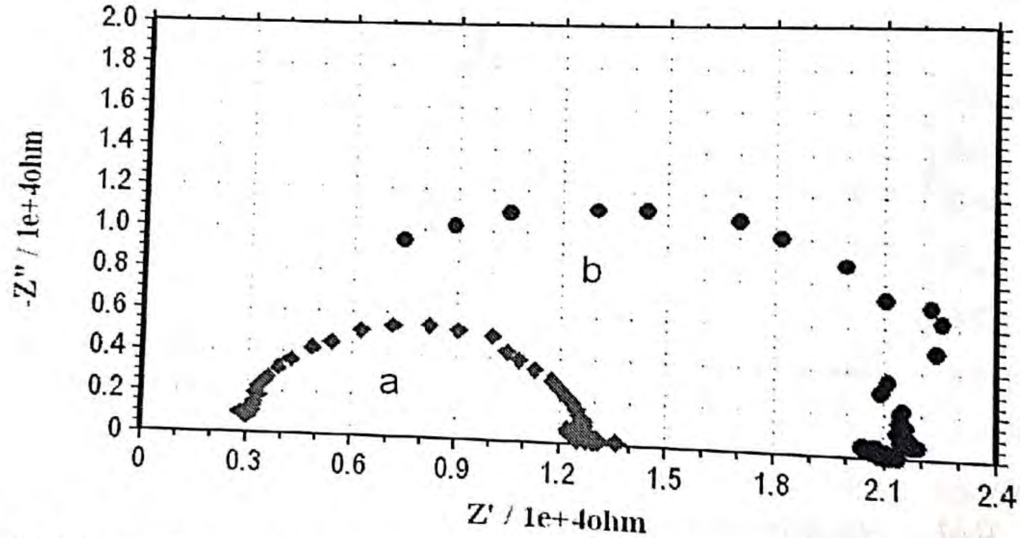


Figure 2: AC impedance spectra of carbon steel immersed in various test solutions (a) dam water, (b) dam water containing 4ml of betanin and 100ppm of OS

3.4. Analysis of FTIR spectra

FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [24]. FTIR spectra have been used to analyze the protective film formed on metal surface. The active principle in an aqueous extract of BR is betanin. The red colour of the extract is due to betanin.

A few drops of an extract of BR was dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown in figure 3 curve (a). The C=O stretching frequency appears at 1632cm^{-1}. The OH stretching frequency appears at 3437cm^{-1}. The C-N stretching frequency appears at 1111cm^{-1}. The symmetric C-O-C stretching frequency appears at 1050cm^{-1}. Thus the structure of betanin is confirmed by FTIR spectrum. The FTIR spectrum (KBr) of pure OS is given in figure 3 curve (b). The peaks at 2862cm^{-1} and 2925cm^{-1} are due to C–H stretching frequency. The S=O stretching frequency occurs at 1188cm^{-1}. The bands at 1464cm^{-1}, 1375cm^{-1} and 723cm^{-1} are due to bending C–H of methyl and methylene groups.

The FTIR spectrum of the film formed on the metal surface is shown in figure 3 curve (C). The C=O stretching frequency shifts from 1632cm^{-1} to 1625cm^{-1}. The OH stretching frequency decreases from 3437cm^{-1} to 3432cm^{-1}. The C-N stretching frequency shifts from 1111cm^{-1} to1021cm^{-1}. The symmetric C-O-C stretching frequency shifts from 1050cm^{-1} to1015cm^{-1}. The S=O stretching frequency has decreased from 1188cm^{-1} to 1105cm^{-1}. These shifts indicate that the electron clouds of C=O and S=O are shifted towards Fe^{2+} resulting in the formation of Fe^{2+}–OS and Fe^{2+}–betanin complexes on the anodic sites of the metal surface [25].

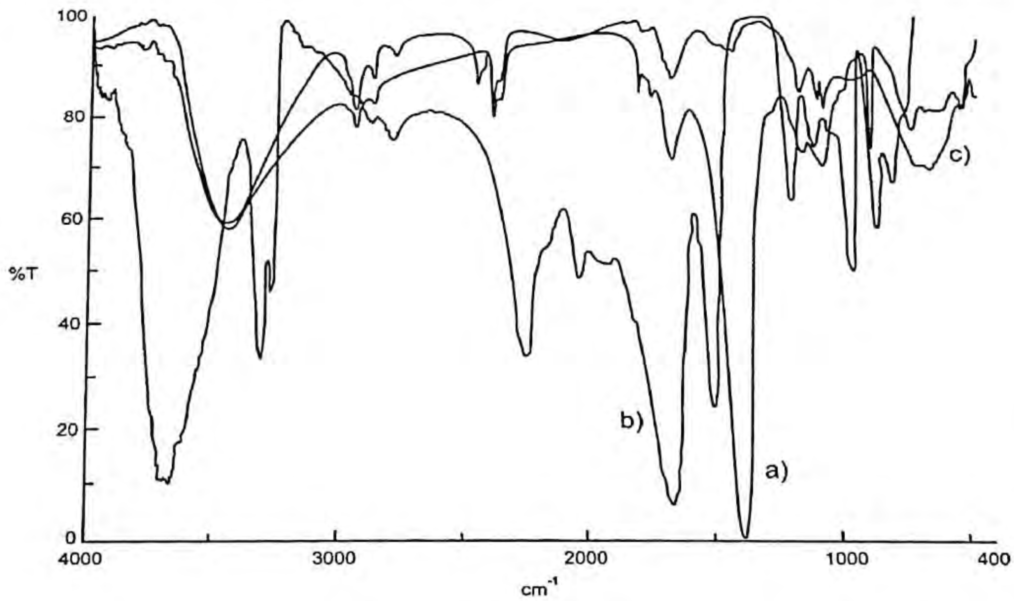


Figure 3. FTIR spectra

(a) BR extract evaporated to dryness (b) pure OS and (C) film formed on metal surface after immersion in dam water containing 4ml of betanin and 100ppm of OS

3.5. SEM Analysis of metal surfaces

SEM images of magnification X500 of carbon steel specimens immersed in dam water for 1 day in the absence and presence of inhibitors system are shown in Figure 4(b) and 4(c) respectively. The SEM micrograph of the polished carbon steel surface (control) in Figure 4(a) shows the smooth surface of the metal and the absence of any corrosion pits formed on the metal surface.

The SEM micrograph of carbon steel surface immersed in dam water in Figure 4(b) shows the roughness of the metal surface, which indicates the corrosion of carbon steel in dam water.

Figure 4(c) indicates that in the presence of 4ml of betanin and 100ppm of OS mixture in dam water, the surface coverage increases, which in turn results in the formation of insoluble complex on the surface of the metal (betanin-OS inhibitor complex). The surface is covered by a thin layer of inhibitors that control the dissolution of carbon steel [26].

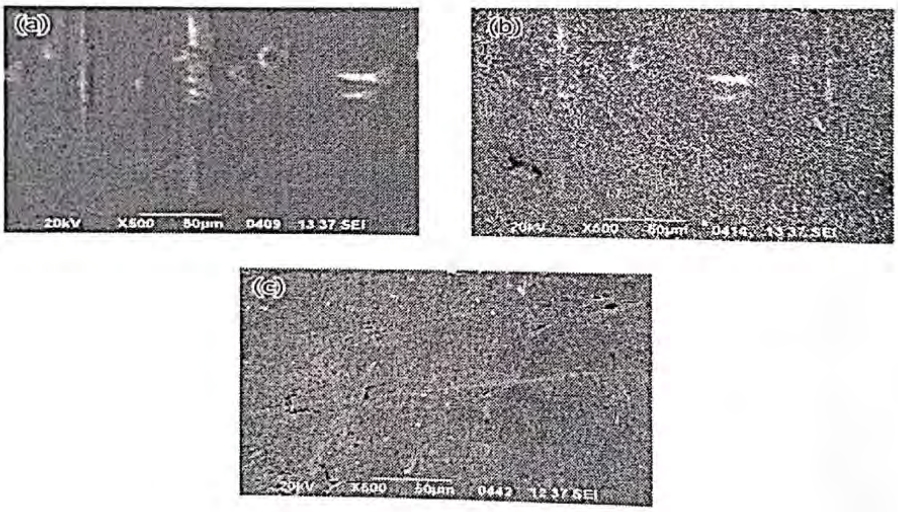


Figure 4. SEM micrographs of a) polished Carbon steel (control) – Magnification-X500 b) Carbon steel immersed in dam water – Magnification-X500 c) Carbon steel immersed in dam water containing 4ml of betanin and 100ppm of OS Magnification-X500

3.6. Surface examination by EDAX

EDAX is used to analyze corrosion films. In Figure 5 spectrum (a) shows the EDAX analysis of carbon steel surface immersed in dam water. The analysis shows the presence of corrosion products elements (Fe, O and C). In Figure 5 spectrum (b) shows the EDAX analysis of carbon steel immersed in dam water containing 4ml of betanin and 100ppm of OS. The analysis shows the presence of (N and S), which could be attributed to the presence of betanin and the organic molecule (OS) on the metal surface, forming a protective film [27,28].

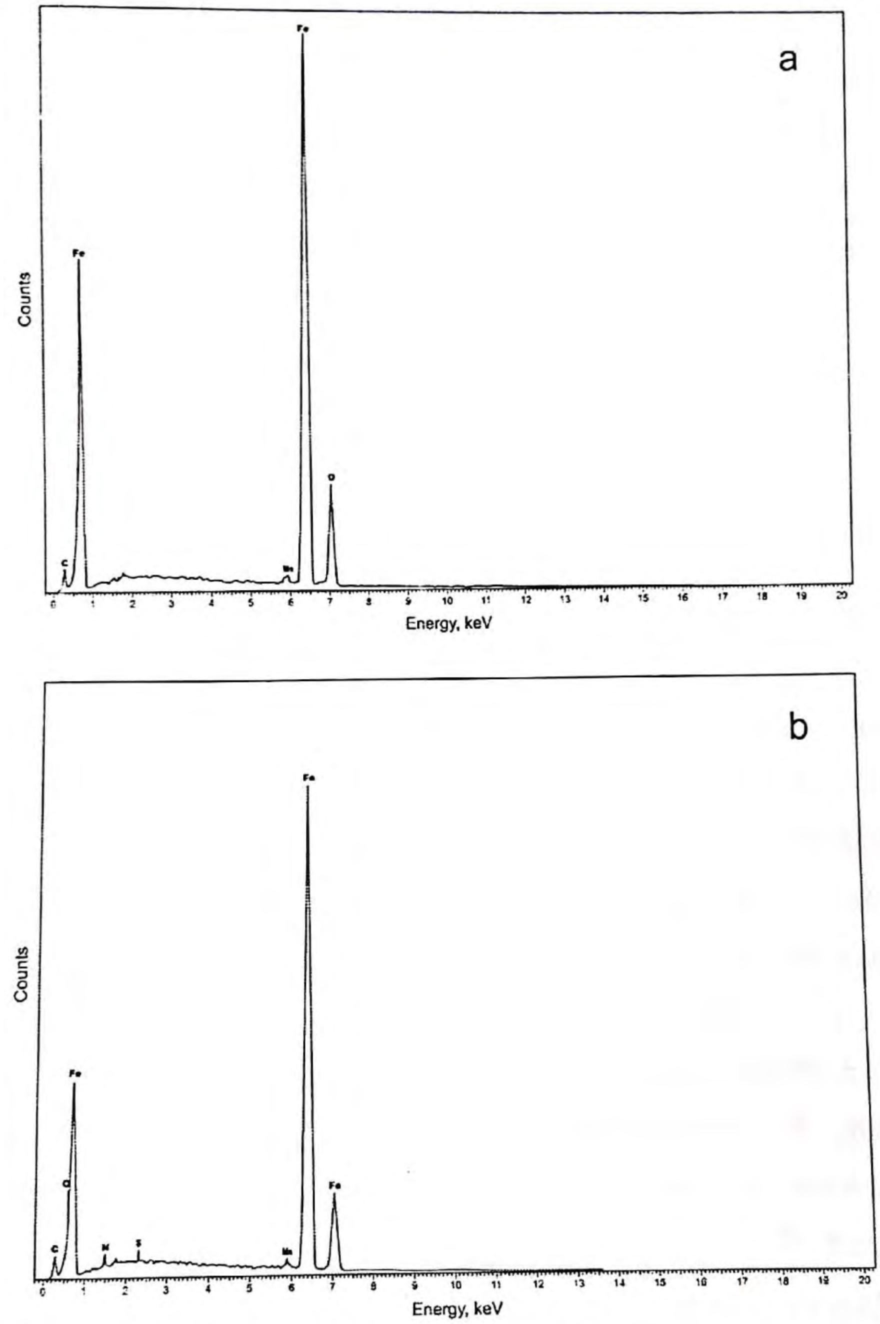


Figure 5. EDAX analysis of a) Carbon steel immersed in dam water b) Carbon steel immersed in dam water containing 4ml of betanin and 100ppm of OS

4. Conclusion

- The results of weights-loss study show that the formulation consisting of 4ml of betanin and 100ppm of OS has 90 % IE in controlling the corrosion of carbon steel in dam water.
- Polarization study reveals that the betanin-OS system predominantly controls the anodic reaction.
- AC impedance and FTIR spectra reveal that a protective film is formed on the metal surface.
- The SEM micrographs and EDAX confirm the formation of protective layers on the metal surface.

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