A Study on Anticorrosion and Antibiofouling Properties of Poly (NBA –co-AM/AMPSNa) Hydrogel

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ABSTRACT

The Hydrogel poly (N-Tertiary butyl acrylamide-co-acrylamide/2-Acrylamido-2-methyl-1-propane Sodium sulfonate) **(NBA-co-AM/AMPSNa)** –**HG47** was used as corrosion inhibitor on carbon steel in acidic medium. and as antibiofouling agent. The **anticorrosion** property of the hydrogel was determined by weight loss method, in 0.5M HCl medium. The protective film that formed on the surface of the metal which resists the corrosion was confirmed by FT-IR. The inhibitor's type of protection is determined by electrochemical studies. The film formation is also confirmed by the surface morphology SEM and EDAX and hardness analysis. This shows the complex formation between the metal cation and the hetero atoms that are present in the Hydrogel. The **antibiofouling** against the germination of zoospores of Ulva Lactuca showed a promising result.

Key words: Hydrogel, Carbon Steel, Corrosion, FT-IR, SEM, Biofouling

1. INTRODUCTION

Hydrogels, are of soft matter [1], and aggregates of water molecules and they are hydrophilic polymer networks. The have high water content, some exceed 95% by weight ratio, makes hydrogels to dissolve and transport ions and many small molecules. The polymer networks, which are often sparsely cross linked, make hydrogels being soft and elastic. They are present in nature, from muscle and cartilage in animal tissues to xylems and phloems in plants [2–4]., the development of hydrogels with new applications and enhanced mechanical fitness has attracted researchers in all fields. In industrial applications, hydrogels are relatively new compared with metals, ceramics and many other forms of polymer. The diversity of hydrogels, natural and synthetic, with different chemical compositions, makes them highly adaptive to a vast array of applications [5].

The term biofouling describes the contamination of surfaces by the adhesion of organisms and their by-products .[6] Surface biofouling of implanted medical devices is caused by the adhesion of microbial or thrombotic agents due to foreign body response [7]. Biofouling limits the lifetime of implanted medical devices, and can even result in their removal and replacement [8]. Biofouling is a complex process related to the physical and chemical properties of the target surface. The anti-biofouling properties of implanted medical devices can be enhanced by surface modifications, including controlling surface hydrophilicity and charge, biomolecule functionalization, and drug elution .For hydrophilic surfaces, resistance to the adhesion of fouling agents is ascribed to the hydration layer formed between the coating and the surrounding environment. This hydration layer serves as a physical barrier to resist the adhesion of fouling agents. Hydrogels, as well known hydrophilic materials, can substantially enhance the hydrophilicity of the coated surface

Corrosion is a natural deterioration process which can be controlled but cannot be completely prevented [9]. In past years, chemical inhibitors were used to control corrosion. Polymers are used as corrosion inhibitors because, through their functional groups they form complexes with metal ions and on the metal surface these complexes occupy a large surface area, thereby blanketing the surface and protecting the metal from corrosive

agents present in the solution The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen) that are the major active centres of adsorption.

The present determination is done,

☐ to evaluate the anticorrosion property and the inhibition efficiency of Hg-47 in resisting the corrosion on carbon steel in acidic medium.

☐ to analyse the protective film formed on the metal surface by FT-IR.

☐ to depict the coating of the inhibitor on the metal surface by SEM and hardness analysis.

☐ to identify the type of inhibitor whether anodic/ cathodic/mixed inhibitor by potentiodynamic polarization.

☐ to assess the inhibition efficiency of HG47 against the marine fouling by Ulva lactucca

2. MATERIALS AND METHODS

2.1. Preparation of poly (NBA-co-AM/AMPSNa) hydrogel -HG-47

The hydrogel,HG-47 was prepared by Free-Radical crosslinking copolymerization[10].

The three monomers N-Tertiary butyl acrylamide- NBA (0.5g), Acrylamide –AM (0.5g), 2-Acrylamido-2-methyl-1-propane Sodium sulfonate- AMPSNa (0.5g) with -cross linker -Methylene bis acrylamide- MBA (0.03g), and,-Initiator Potassium persulphate –KPS (0.05g) were addedin methanol water mixture.AMPSNa was prepared by neutralizing the 2-acrylamide-2methylpropanesulfonic acid using Sodium hydroxide. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60 ^{0}C and the polymerization was conducted for 1 day. After the reaction, the hydrogel **(HG47)** was cut into pieces 3-4 mm long. The extracted hydrogel was dried in vacuum oven at 50 ^{0}C to constant weight for further use.

2.2.Anti corrosion study

Metal Specimens

The metal specimens is carbon steel with the composition (wt%) of S-0.026 , P -0.06, Mn- 0.4, C- 0.1 and balance iron. The dimensions of the metal active surface are 1.2 X 4.1 X 0.2 cm which is used for weight loss measurements. The carbon steel specimens were polished, washed in double distilled water and degreased with acetone and used for the weight loss method.

2.2.1.Weight-Loss Method

Determination of Corrosion Rate: The specimens were immersed in beaker containing 100ml acid solutions without and with different concentration of Hg-47 using hooks. Before it was immersed, the specimens were cleaned and the weight is recorded. After 5 days, the test specimens were removed and then washed with double distilled water, dried and reweighed. The average mass loss of two parallel carbon steel specimens were obtained.

From the change in weight of specimens the corrosion rate was calculated using the following relationship,

$$\text{Corrosion Rate} = \frac{87.6 \times W}{A \times T \times D} \quad \text{(mpy)}$$

Corrosion Inhibition Efficiency (IE) was then calculated using the equation

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

Where,

W_1 = Corrosion rate in the absence of inhibitor and

W_2 = Corrosion rate in the presence of inhibitor

2.2.2.Infra Red (IR) Spectroscopy

The specimens were suspended by means of hooks in solution having with and without inhibitor for 5 days. After 5 days the specimen were taken out. Then the film formed on the metal surface was scratched off and taken for FT-IR spectral study.

2.2.3.SEM Analysis

The specimens were suspended by means of hooks in solution in the presence and in the absence of inhibitor for 72 hours. Then the specimens were taken out and the metal specimen was analyzed.by Scanning Electron Microscope (SEM)Antibiofouling effect

2.2.4.Hardness Testing

Hardness is the property of a material to resist permanent indentation. Because there are several methods of measuring hardness, the hardness of a material is always specified in terms of the particular test that was used to measure this property.

Vickers Hardness Test

It is the standard method for measuring the hardness of metals, particularly those with extremely hard surfaces:[11]. The surface is subjected to a standard pressure for a standard length of time by means of a pyramid-shaped diamond. The diagonal of the resulting indention is measured under a microscope and the Vickers Hardness value read directly. The Hardness values of polished metal, blank and with inhibitor were compared.

2.3.Anti biofouling activity

The algal zoospores were obtained by following the methods of Egan et al[12]. Briefly, mature Ulva lactuca Linn samples were collected from Kovalam Beach, Chennai, Tamil Nadu, India and examined for sporulating thalli selection. The selected thalli was cleaned using autoclaved and sterile filtered seawater. They were air dried and kept for 2 h at ambient temperature. The pieces of sporangium bearing algae were kept in a 200 mL beaker containing 100 ml sterilized seawater and left exposed to light from white light. The released zoospores were collected in a watch glass and pipette out in a known volume of filter sterilized seawater. About 100 µl of zoospores suspensions containing 2400 spores were added each well. Different concentration of hydrogel (HG43) was added as 100 µl in zoospores containing chambers. The plate was incubated at ambient temperature (24±4°C) for 2 h in complete darkness to allow the zoospores settlement. After incubation, the plates were washed gently five times with artificial seawater. The plates were examined in the inverted microscope at 100X to count the numbers of zoospores that firmly attached to the substratum. Additionally, they were kept for three more days and observed in a microscope and quantified earlier settlement data. The germination % was calculated as follows:

$$\% \text{ germination} = \frac{\text{No. of zoospores germinated}}{\text{No. of zoospores settled}} \times 100$$

3.RESULTS AND DISCUSSION
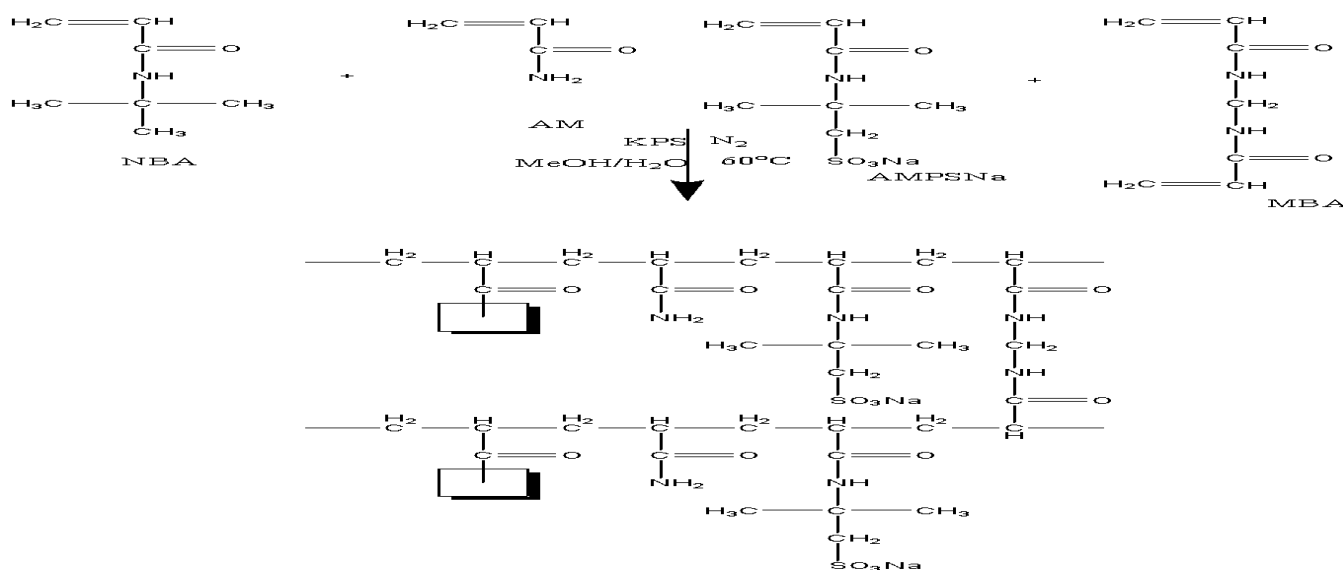
Scheme 1:Schematic representation of poly(NBA-co-AM/AMPSNa) hydrogels

3.1. IR Spectral characterization of Hydrogel

The IR analysis of the hydrogels showed that the presence of peaks corresponding to the functional groups of monomeric units present in the co polymeric hydrogel chain.(Fig.3.1) The IR spectra of HG-47 showed characteristic absorptions at 3286.11cm^{-1} corresponding to NH stretching of NBA and AM .The band at 1631.69 cm-1 is due to C=O stretching. The band for C-O stretching is observed at 1118.90 cm^{-1}. A characteristic peak around 1400 cm^{-1} corresponds to the C-H stretching in tertiary alkyl group. A peak   at 1350 cm^{-1} corresponds to S=Ostretching of SO $_3$Na of AMPSNa. . The absorptions at 2970.35 cm^{-1} is due to C-H stretching of polymer backbone. Thus the IR analysis indicates the presence of all monomeric units in the cross-linked hydrogels.
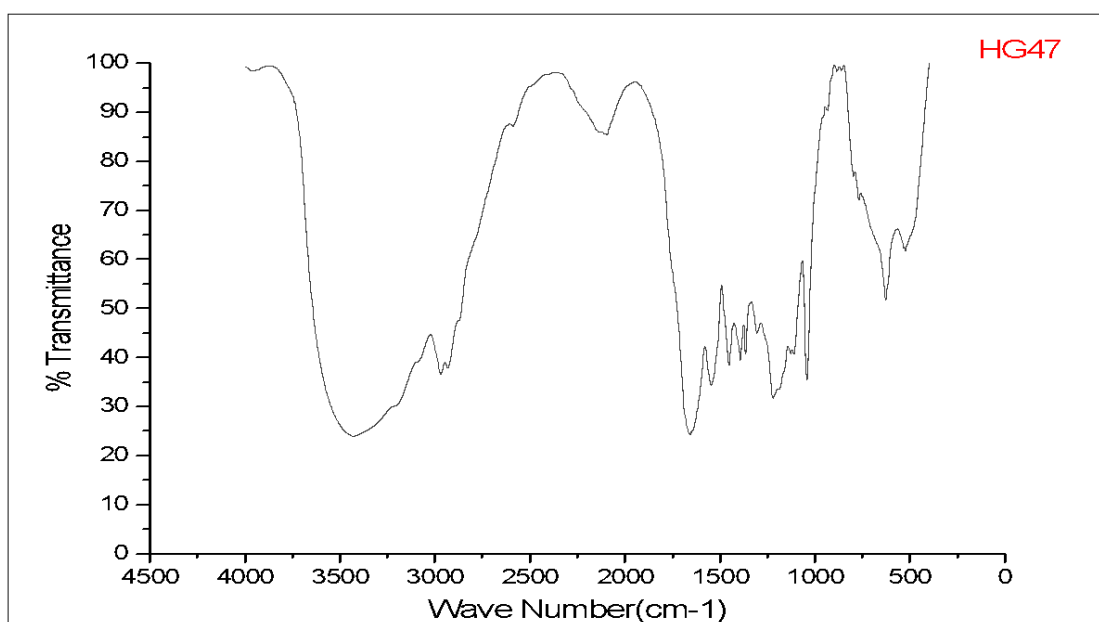

Figure 3.1.IR Spectral characterization of Hydrogel

3.2.Anti Corrosion Studies

3.2.1.Determination of corrosion rate

The corrosion rate was determined for carbon steel in 0.5M HCl by using weight loss method. Inhibition efficiency of carbon steel with various concentration of Hg-47 in 0.5M HCl at room temperature is presented in Table 3.1. .It was found that at Hg-47 at 0.5 g it has minimal inhibition efficiency 96.63 % and the corrosion rate 0.34. And the protective film is found to be stable for about 5 days and the corrosion rate has been reduced when compared in the absence of inhibitor. In the presence of Hg-47, the inhibitor combine with Fe^{2+} in the anodic sites of the metal surface. Fe^{2+}-Hg-47 controls the anodic part of the reaction.The presence of lone pair of electrons on the hetero atoms of these compounds facilitates the formation of co-ordinate bonds with the metal. Most of the effective organic inhibitors used in industry have heteroatom such as O, N and S along with multiple bonds in their molecules through which they are adsorbed on the metal surface. Thus both anodic and cathodic sites of the metal surface are protected and occurrence of corrosion is controlled. The above interpretation is in accordance with the observation reported by P.Pazhanisamy et.al[13]

Beaker No.	Wt. of polymer (g)	Immersion Period (Days)	Hg-47	
			IE (%)	CR (mpy)
1	0.5	5	96.63	0.34
2	Blank	5	-	10.07

Table 3.1.Inhibition efficiencies and corrosion rates of carbon steel in Hg-47 in 0.5M HCl

3.2.2.Analysis of FTIR

The FTIR spectrum of the film formed on the surface of the metal immersed in 0.5M HCl in the presence of the inhibitor were taken. FTIR spectroscopy has been used to analyze the protective film formed on the metal surface. The FTIR spectrum of pure Hg-47 and Hg-47- Fe^{2+} are correlated in Fig.(3.2). [14]
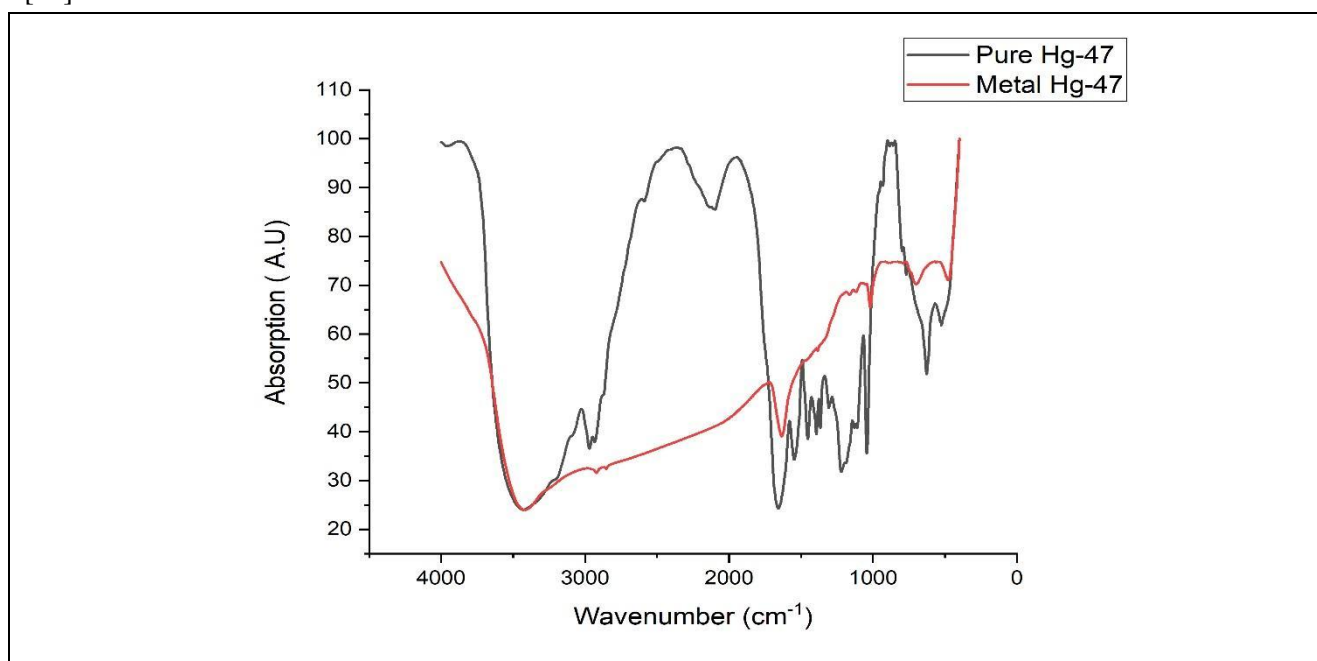

Figure 3.2. Fig.   FTIR Correlation Spectra

The N-H stretching (amide) frequencies observed for the pure Hg-47 and Hg-47 as inhibitor were 3286.11and 3416.88 cm^{-1} respectively. The shift in the band is due to the active bonding of the inhibitor with

the metal surface. The bands for C-H stretching has been observed for pure Hg-47 is 2970.35 cm^{-1}. Similarly within this range a band at 2920.54 cm^{-1} has been observed for Hg-47 as inhibitor. The band at 1631.69 cm-1 is due to C=O stretching in pure compound.The band at 1633.07 cm-1 is due to C=O stretching in the inhibitor complex.

For pure Hg-47 the band for C-O stretching is observed at 1118.90 cm^{-1}. There is a variation in the inhibitor system in which the frequency observed varied from 1118.90 cm^{-1} to 1019.79cm^{-1}. The band at 700.89 cm^{-1} in the inhibitor complex indicates the metal and hetero atom bond. The variation in the position of the band is due to the fact that the Fe^{2+}- Hg-47 complex is entailed on the metal surface. This reveals the interaction between the metal and the active hetero atoms that are present in the inhibitor. On comparing the pure compound and the compound as inhibitor there is a slight variation in the band, indicates the participation of the compound in the formation of the protective film.

3.2.3.Potentiodynamic polarization

Polarization study is an electrochemical method used to identify the formation of protective film on the metal surface. If a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and corrosion current (I_{Corr}) decreases. The polarization curves of carbon steel immersed in the presence and absence of ternary inhibitor mixture are correlated in Fig.3.3. The corrosion parameters such as corrosion potential (Ecorr), Tafel slopes (bc = cathodicba = anodic) and corrosion current (I_{corr}) [15]are given in Table 3.2.

System	E_{corr} mve vs SCE	b_c mV/ decade	b_a mV/ decade	I_{corr} A/cm^2	LPR ohm cm^2	Type of Protection
Blank	-514.19	113.404	75.326	6.0995×10^{-4}	32.2213	-
Hg-47	-562.536	191.862	62.694	2.8315×10^{-4}	72.4633	Cathodic

Table 3.2. Corrosion parameters of carbon steel immersed in 0.5M HCl in the absence and presence of HG-47systems determined from polarization method
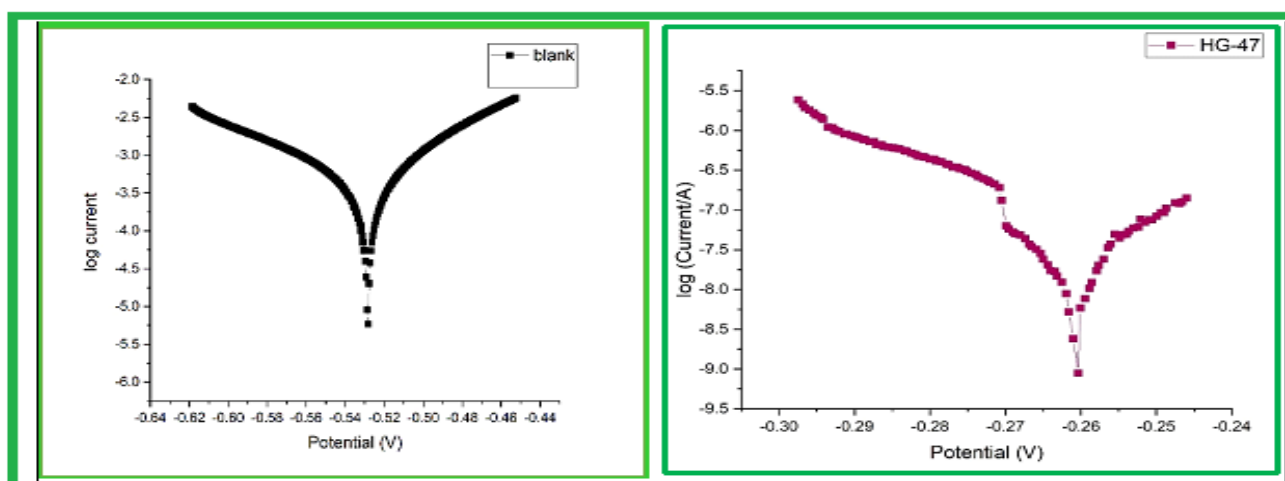

Fig.3.3. polarization curves of carbon steel immersed in HCl in the presence and absence of HG-47

3.2.4.Scanning Electron Microscope (SEM) Analysis

The texture and pore structure of the inhibited and uninhibited surface in acidic medium are shown in Fig.(10). It is confirmed that the inhibitor systems has formed a dense film over the metal surface.

The texture and pore structure of the inhibited and uninhibited surface in acidic medium are shown in Fig. (3.4). It is confirmed that the inhibitor has formed a dense film over the metal surface   The SEM images show the precipitation of the inhibitor systems on the metal surface as resistive film. The metal surface of the uninhibited system has oxides of iron (rust) which was found to be rough surface with granules and cracks at the corners of the metal specimen with few crevices on the surface as shown in Fig.(3.4.a &b.). The surface of the inhibited systems has the precipitation of Hg-47 complex. The surface was found to be smoother; the precipitation varies with the inhibitor system, without cracks and crevices than compared to that of uninhibited system The inhibitor mixture is uniformly coated on the metal surface.(3.4.c&d.) Thus the surface morphological interpretation of the uninhibited and inhibited metal surface confirms the protective film formed on the surface of the metal.[16]
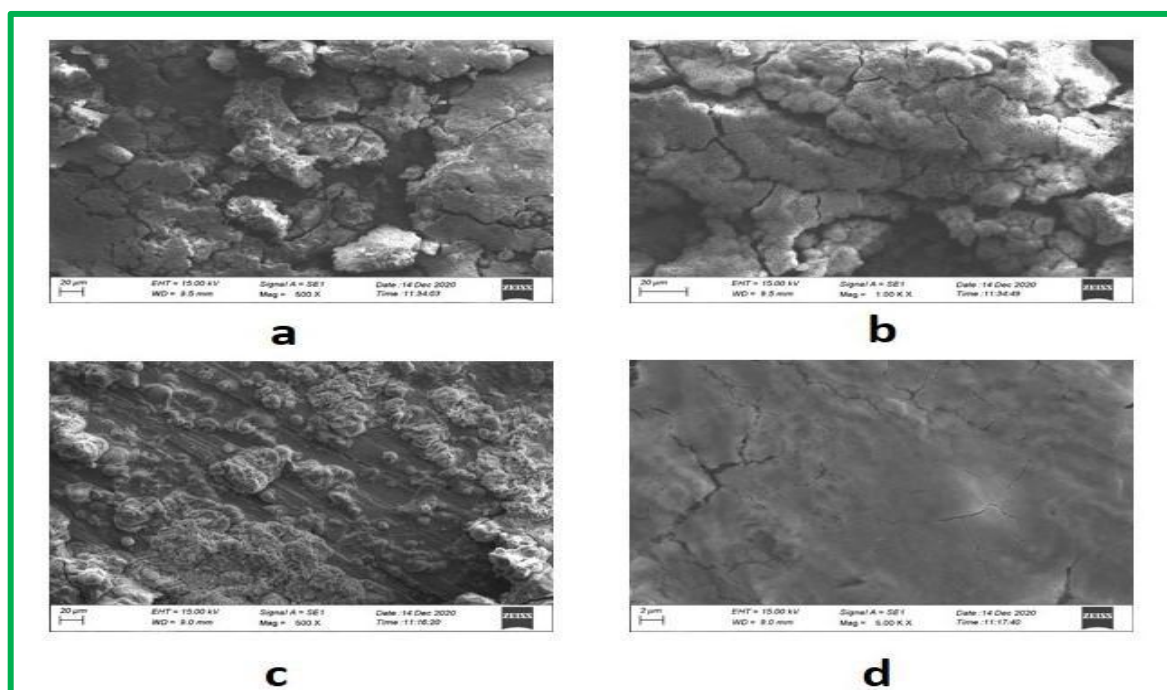
Fig.3.4.SEM images of Carbon Steel in HCl without HG-47 (a &b) and with HG-47(c&d)

3.2.5.Energy Dispersive Analysis of X-Rays (EDAX)

The EDAX survey spectra were used to determine the elements present in the resistive film formed on the metal surface. The elemental analysis EDAX of the metal surface were performed in the absence and presence of inhibitors system

The EDAX spectrum of the resistive film of the inhibitor systems formed on the metal surface shows the characteristic peaks of the elements constituting such as C, O, N, S, Fe atoms [22]. The EDAX spectrum of carbon steel immersed in 0.5M HCl containing 0.5g of Hg-47 system are shown in Fig.(3.5.b.). It shows the characteristic peak for the existence of O,C and N. These data show that metal surface is covered with C, O, S and N atoms are shown in Table- 3.3 . This layer is undoubted due to the inhibitor system. Thus the presence of O, S and N atoms in the resistive film indicates the inhibition efficiency of the inhibitor systems studied. Thus the elemental analysis confirms the complexation of Fe^{2+}-Hg-47.[17].

Table.3.3.Elemental composition

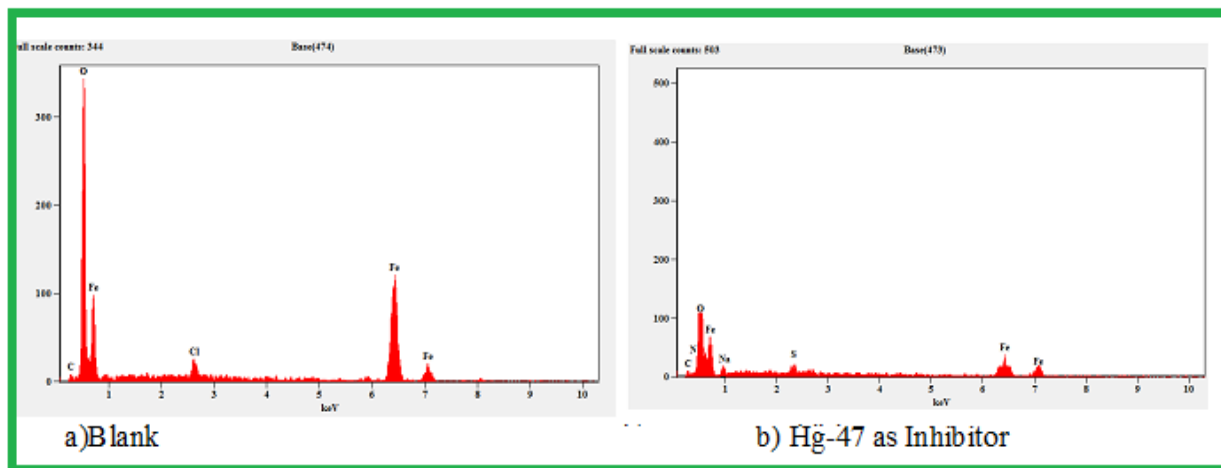| Atoms		O	Fe	C	Cl	N	S	Na
Atomic %	Blank	62.84	19.05	16.9	1.21	-	-	-
	With HG47	67.64	12.99	12.64	-	1.82	2.03	3.55

Fig.3.5.The EDAX spectrum of carbon steel immersed in a.) 0.5M HCl and b) containing 0.5g of Hg-47

3.2.6.Vicker 's Mico hardness test

Many studies showed that as corrosion resistance increases, hardness also increases [18]. From the results obtained from Vicker'stest, it is found that the hardness values are low for metal in acid (Blank) and higher and close to each other for polished metal and in presence of HG47. (Table.3.4.)This is due to the protective film layer formed by the inhibbitor

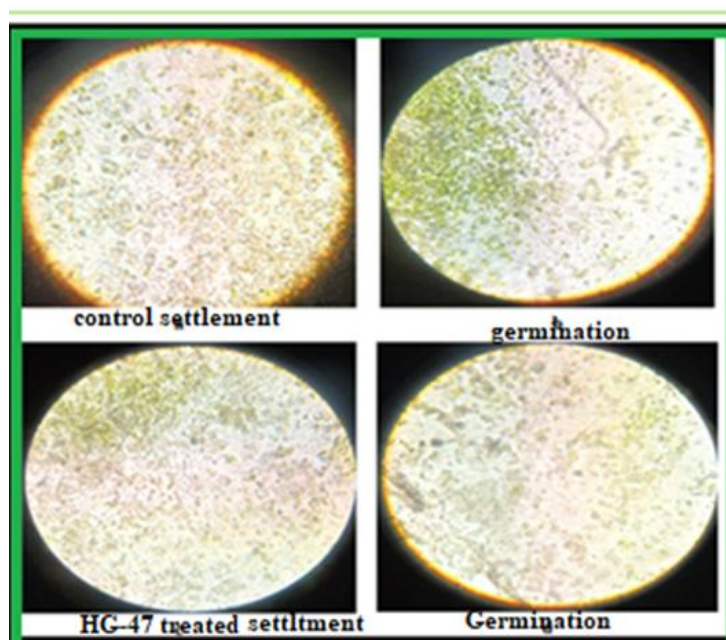| Load (gram)	Vicker's Hardness value (HV)		
	Polished metal	Blank(in 0.5 M HCl)	With HG-47 as inhibitor
25	106	95	109
50	162	113	151
100	215	155	198
200	265	205	294

Table.3.4. Vicker,s Hardness values

Fig.3.6. Vicker,s Hardness values

3.3. Anti biofouling Effect

Hydrogels inhibit adhesion of marine organisms effectively due to extensive hydration. Antibiofouling effect of poly (NBA-co-MA/AMPSNa) (HG-47) hydrogel showed a excellent Ulva lactuca zoospore inhibition given in Table 3.7.The hydrogel is a hydrophilic and anionic polymer having AMPSNa as ionic monomer. Interestingly, an anti-biofouling resistance property of the hydrogel is achieved due to the presence of sulphonate group present in hydrogel.
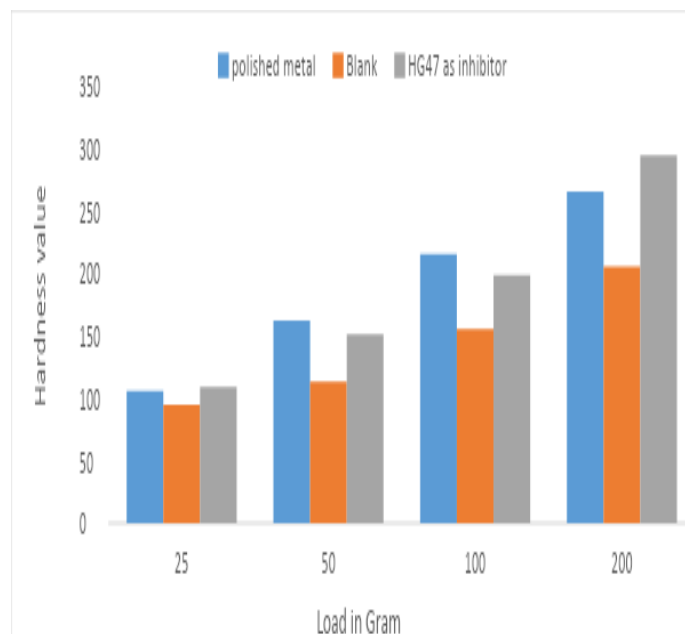

Fig.3.7.**Antibiofouling effect of poly (NBA-co-AM/AMPSNa) hydrogel**

.   As the concentration increases. Anti biofouling effect also increases. Ulva spores do not a have a cell wall, but expose naked lipoprotein membrane, which is negatively charged.[19].So the hydrophilic anionic hydrogel repels the spores thereby lowering fouling, The highest concentration of 100 µg showed a very good spectrum of inhibition of germination   60.19 % of Ulva lactuca zoospores.(Fig.3.7 and Fig.3.8)

Conc (µg/mL)	No of zoospores Initially present	No .of Zoospores settled	No .of zoospores germinated	% of settlement	% of germination	No.of zoospores inhibited.	% of inhibition
Control	2400	2254	2141	93.92	94.99	113	5.01
25	2400	1975	1422	82.29	72.00	553	28.00
50	2400	1354	863	56.42	63.74	491	36.26
75	2400	894	397	37.25	44.41	497	55.59
100	2400	412	164	17.17	39.81	248	60.19

Table.3.7.**Antibiofouling effect of poly (NBA-co-AM/AMPSNa) hydrogel**
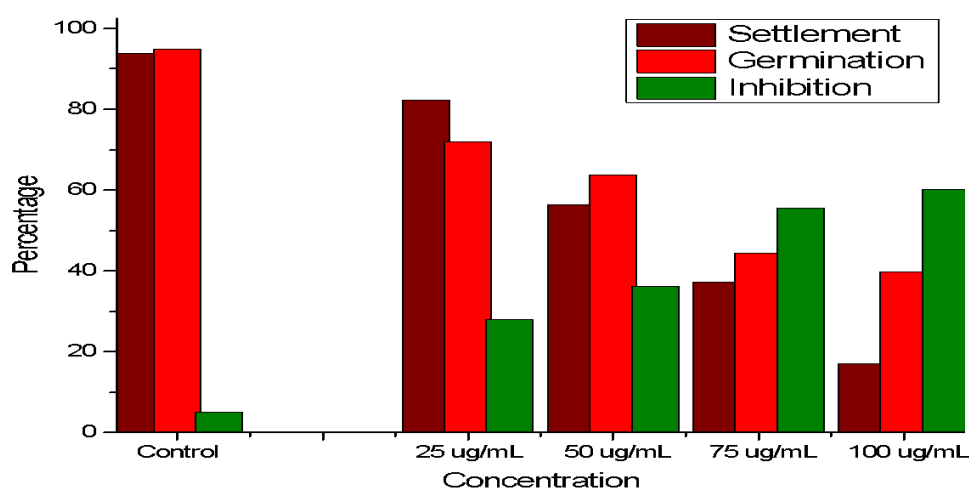
Fig.3.8.Antibiofouling effect of poly (NBA-co-AM/AMPSNa) hydrogel

3.4. CONCLUSION

From the above study it is concluded that,

- **Poly (NBA-co-AM/AMPSNa) hydrogel -Hg-47** has a good anticorrosion ability for carbon steel in 0.5 M HCl solution is due to the active heteroatoms present in it.
- The minimal efficiency was found to be 96.63% at 0.5g of Hg-47 but the stability of the protective film withstands for about 5 days.
- The shift in the bands observed in FT-IR proves the formation of the film on the surface of the metal.
- The protective film formed on the metal surface is found to be denser by the SEM analysis.
- The elements that are present in protective film formed on the metal surface is analyzed by EDAX analysis. The active hetero atoms that are responsible for the protective film are thus confirmed by the various spectral, surface morphological and elemental analysis.
- The micro hardness values on Vickers scale were comparable for polished metal and metal-inhibitor than the blank confirming the formation of protective film
- Germination of zoospores of the seaweed Ulva lactucca were reduced considerably due to high degree of hydration.

REFERENCES

1. Yang W, Wang H and Li T et al. (2019). X-mechanics—an endless frontier: Sci China-PhysMechAstron, 62 (14601).
2. Mow VC, Kuei S and Lai WM et al.(1980). Biphasic creep and stress relaxation of articular cartilage in compression: theory and experiments. J Biomech Eng,102, 73–84.
3. Zwieniecki M.A, Melcher P.J.andHolbrook .N.M. (2001). Hydrogel control of xylem hydraulic resistance in plants. Science , 291, 1059–62.
4. Bai R, Chen B and Yang J et al. Tearing a hydrogel of complex rheology (2019). J MechPhys Solids,125749–61.
5. Calo. E. and Khutoryanskiy V.V. (2015). Biomedical applications of hydrogels, a review of patents and commercial products. EurPolym J,,65, 252–67.
6. Magin C.M. Cooper S.P and Brennan A.B(2010). Non-toxic antifouling strategies. Mater Today, 13,36–44.
7. Harding J.L. and Reynolds M.M.(2014) Combating medical device fouling. Trends Biotechnol 32,140–6.

8. Yu .B, Wang. C and Ju .Y.M et al. (2008.) Use of hydrogel coating to improve the performance of implanted glucose sensors..BiosensBioelectron 23, 1278–84

9. Ahmad, Z. (2006). Principles of corrosion engineering and corrosion control. Elsevier.

10. .Brundha B.A,.Pazhanisami.P. (2010), Int. J.Chem tech Research, 2(4) 2192

11. ASM International, Hardness Testing, 2nd Edition, 06671G.

12. Egan,Suhelen,James,Sally,Holmstrom,carola,Kjelleberg,Staffan, (2001). Inhibition of algal spore germination by the marine bacterium Pseudoalteromonas, FEMS Microbiology Ecology,35 67-73.

13. Swarnalatha..V Pazhanisamy..P.(2018) Corrosion Inhibition Studies Of 3- [(Methacryloylamino) Propyl] Trimethylammonium Chloride And N-Substituted Acrylamide Ionomers RasayanJ.Chem 11,3 ,929 - 934

14. | Walzak, T. L. (1990). Electrochemical Properties Of Passive Films On440c Stainless Steel. Digitized Theses. 1942.

15. .Nagalakshmi, R., Nagarajan, L., Joseph Rathish, R., SanthanaPrabha, S., Vijaya, N., Jeyasundari, J., &Rajendran, S. (2014). Corrosion Resistance of SS316l In Artificial Urine In Presence Of D-Glucose. Int. J. Nano. Corr. Sci. Engg, 1(1), 39-49.

16. Solomon, M. M., Umoren, S. A., Obot, I. B., Sorour, A. A., &Gerengi, H. (2018). Exploration of dextran for application as corrosion inhibitor for steel in strong acid environment: effect of molecular weight, modification, and temperature on efficiency. ACS applied materials & interfaces, 10,33, 28112-28129.

17. Vengatesh, G., &Sundaravadivelu, M. (2019). Non-toxic bisacodyl as an effective corrosion inhibitor for mild steel in 1 M HCl: thermodynamic, electrochemical, SEM, EDX, AFM, FT-IR, DFT and molecular dynamics simulation studies. Journal of Molecular Liquids, 287, 110906.

18. Tamil Moli, L. Wahab. N., Gopinathan.M.,Karmegam, K.,Maniyarasi, M. (2016). Effects of gaseous nitriding AISI4140 alloy steel on corrosion and hardness properties IOP Conference Series .Materials Science and Engineering, 152, Issue 1,.012059 .

19. Zhang.X, Wang, Levänen, (2013), Superhydrophobic surfaces for the reduction of bacterial adhesion. RSC Adv.3, 12003–1202.

20. KUMAR, A. TARUN, P. LALITHA KAMESWARI, and A. Girwani. "Impact of Pusa Hydrogel incorporated growing media on floral characters and yield of pot mums (Dendranthema grandiflora L.) under various irrigation regimes." International Journal of Agricultural Science and Research (IJASR) 6.3 (2016): 195-200.

21. Mahla, Sunil Kumar, and S. S. Wanjari. "Response of Wheat to Irrigation and Hydrogel with Nutrient Management." International Journal of Agricultural Science and Research (IJASR) 7.2 (2017): 267-272.

22. AL-SOLAMI, MAZEN A. "SEAWATER DESALINATION USING SMART POLYACRYLIC ACID HYDROGEL IN HAQEL-TABUK, KINGDOM OF SAUDI ARABIA (KSA)." International Journal of Zoology and Research (IJZR) 8.2 (2018) 1-8

23. El-Shennawy, M., et al. "Effect of boron content on metallurgical and mechanical characteristics of low carbon steel." International Journal of Mechanical Engineering (IJME) 5.2 (2016) 1-14

24. El–Shennawy, M., et al. "Heat treatment effect on micro–alloyed low carbon steel with different Boron content." International Journal of Mechanical Engineering (IJME) 5.4 (2016): 9-20.

25. Selvam, R. A. J. I. V., and S. U. R. J. I. T. H. Jacob. "Experimental Investigation and Analysis of Smaw Processed Carbon Steel Pipes." International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) 8.5 (2018): 29-40.