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Comparative Study of Corrosion Behavior of SS316in Artificial Blood Plasma in the Presence of Antipyretic And Antibacterial Drugs.

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Abstract: *The Corrosion behavior of SS316in artificial blood plasma in the presence and absence of Antipyretic drug (Paracetamol) and Antibacterial drug (Bactrim) has been studied. The SS 316 alloys are used as implant metal in Orthopedics techniques. The amounts of drugs were taken in 50ppm and 100ppm amounts and they were added to the artificial blood plasma in which the metal is immersed. They were allowed to settle down for 1day and 30days batch at 37± 0.1°C. Electrochemical techniques such as Potentio dynamic polarization and AC impedance studies were carried out to investigate the corrosion behavior of SS 316 alloy.The surface analysis study, SEM technique was also used to analyze the surface of the alloys in absence of presence of the drugs.*

Keywords: *Artificial blood plasma,Bactrim, Corrosion, Paracetamol ,SS 316.*

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I. Introduction

Paracetamol, also known as Acetaminophen or APAP, is a medication used to treat pain and fever. Paracetamol is also used for more severe pain such as cancer pain and after surgery. It is typically used either by mouth or rectally but is also available intravenously. Effects last between two and four hours. Paracetamol is classified as a mild analgesic. It does not have significant anti-inflammatory activity. Paracetamol is an Antipyretic.Paracetamol consists of a benzene ring core, substituted by heterocyclic compounds such as one hydroxyl group and the nitrogen atom of an amide group in the para (1,4) pattern. The amide group is acetamide (ethanamide). The molecular formula of Paracetamol is $C_8H_9NO_2$.Bactrim also known as **Trimethoprim/sulfamethoxazole**(**TMP/SMX**) is an antibiotic used to treat a variety of bacterial infections. It consists of one part Trimethoprim to five parts sulfamethoxazole. It is an antibacterial Sulpha drug. It is used for urinary tract infections, traveler`s diarrhea, respiratory tract infections, and cholera, among others. It may be used both to treat and prevent pneumocystis pneumonia in people with HIV/AIDS. It can be given by mouth or intravenously. The molecular formula of the drug is $C_{10}H_{11}N_3O_3S$.

The first stainless steel used for implants contains ~18wt% Cr and ~8wt% Ni makes it stronger than the steel and more resistant to corrosion. Further addition of molybdenum (Mo) has improved its corrosion resistance, known as type 316 stainless steel. Afterwards, the carbon (C) content has been reduced from 0.08 to 0.03 wt% which improved its corrosion resistance to chloride solution, and named as 316L. 316L Austenitic stainless steel is the most commonly used implant material as it is cost effective [1].

1.1 Metal Implants Used for the Study

The biomedical implants chosen for the study in this particular work is **Stainless steel 316 metal implant**. Once the metal is implanted into the biological system the corrosion activity of the metal should also be studied. It is important to consider the interaction between the adjacent physiological environment and the orthopedic implant itself. More specifically, the exposed metal undergoes an electrochemical dissolution from exposure to extracellular tissue fluid at a finite rate.

1.2 Stainless Steel Metal Implant

Stainless steel finds its application in various implant procedures. But it has been predominantly used for Orthopedic implants. For years orthopedic surgeons have relied extensively upon stainless steel surgical fixation implants to treat patients with various levels of acute orthopedic injuries. The life of stainless steel surgical fixation implants is surprisingly vast. For orthopedic applications, surgical fixation implants commonly utilize stainless steel as a worthy candidate. This is largely due to its desirable structural properties, biocompatibility, and proven success in load bearing and fixation. With 316L stainless steel, a naturally corrosive biomaterial, iron, chromium and nickel ions are passively released over time –which are believed to have allergic and carcinogenic properties in-vivo. Corrosion may also lead to physical changes in an implant heightening the likelihood of mechanical failure. It is theorized that 90% of 316L stainless steel surgical implant failures are the result of pitting (cavities or "holes" produced resulting from the aggregation of localized electrochemical cells) and crevice corrosion (the loss of material at the coupling interface between a plate and a locking screw). Other methods of corrosion include inter-granular corrosion, fretting, galvanic corrosion and stress corrosion cracking. These unstable pathways, combined with the natural corrosive properties of metallic implants, potentiate the risk of implant failure or may trigger immune-mediated rejection of the implant

In terms of corrosion resistance in the human body, stainless steels or Ni-Ti super elastic whichseems to have better corrosion resistance is understood by this study. This study was designed to investigate the effect of SS316in artificial blood plasma in the presence and absence of Paracetamol and Bactrim.Paracetamol is an antipyretic drug and it is also used to lower the body temperature medical practitioners recommend this drug in cases of high body temperature during fever. Bactrim is an antibiotic. It is an antibacterial sulpha drug. The drug is used for various body ailments. This study reveals whether the implantation material SS316is affected orcorroded due to the intake of the drugs. Different concentrations of theinhibitor (Paracetamol& Bactrim) were prepared and their inhibition efficiency in artificialblood plasma has been investigated with the help of Electrochemical studies such as Potentiodynamic polarization and AC impedance spectra. The surface morphological, SEM studies was also carried out.

II. Experimental Methods

2.1 Preparation of the specimens and solution

Implant metal Stainless steel 316was purchased commercially. Drugs (inhibitor) Paracetamol and Bactrimwere purchased from pharmacy. The drugs were chosen based on their Analgesic, Anti pyretic and antibacterial property. Artificial Blood plasma was prepared in the lab, according to PN-EN ISO 10993-15 standard. The chemical composition of the artificial blood plasma (g/l distilled water) was NaCl 6.8, $CaCl_2$ 0.200, KCl 0.4,$MgSO_4$ 0.1, $NaHCO_3$ 2.2, Na_2HPO_4 0.126, NaH_2PO_4 0.026.

2.2 Potentiodynamic Polarization

Corrosion parameters namely E_{corr} (Corrosion potential), I_{corr} (Corrosion current), Tafel plots namely Anodic tafel slope (βa) &Cathodictafel slope (βb) and Linear Polarization Resistance were inferred from Polarization studies. The samples were thoroughly washed with distilled water before insertion in the cell. During the polarization study, the scan rate (V/s) was 0.01; hold time at Ef(s) was zero and quit time (s) was 2.

2.3AC Impedance Spectra

The instrument used for polarization study was also used to record AC impedance spectra. The cell setup was also the same three electrode assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (Rt) and the double layer capacitance (Cdl) were calculated from Nyquist plots, impedance log (Z/ohm) value was calculated from bode plots.

$$\mathbf{Rt = (Rs + Rt) - Rs} \qquad (1)$$

Where R_s = solution resistance

$$\mathbf{C_{dl} = ½ \pi R_t f_{max}} \qquad (2)$$

Where f_{max} = maximum frequency

2.4 Scanning Electron Microscope

A Scanning Electron Microscope (SEM) is a powerful magnification tool that utilizes focused beams of electrons to obtain information. The high-resolution, three-dimensional images produced by SEMs provide topographical, morphological and compositional information makes them invaluable in a variety of science and industry applications. Electron microscopes utilize the same basic principles as light microscopes, but focus beams of energetic electrons rather than photons, to magnify an object. A Scanning Electron Microscope provides details surface information by tracing a sample in a raster pattern with an electron beam.The electrochemical behavior and the corrosion parameters of the metal implants were studied using Potentio dynamic Polarization and AC Impedance Spectra studies. Both the studies were carried out with the help of CHI-Electrochemical workstation with impedance, Model 660A instrument. The polarization studies were carried out in a three-electrode cell assembly, in which the metal implant works as the working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

The surface morphological study was carried out by the help Scanning Electron Microscope (SEM). HITACHI-S- 3,400 N model SEM instrument was employed for the study.

III. Results And Discussion

3.1Analysis of Potentiodynamic Polarization Curve

The Potentiodynamic polarization curves of SS 316 immersed in artificial blood plasma solution in the absence and presence of 50ppm and 100ppm of Paracetamol and Bactrim are shown in Fig.1.1-1.5. Corrosion parameters namely, Corrosion potential, (E_{corr}), Corrosion current (I_{corr}), Tafel slopes (βa and βc), and Linear polarization resistance (LPR) are given in the Table 1 & 2. Polarization study has been used to confirm the formation of protective film on the metal surface during corrosion inhibition process. If a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current value (Icorr) decreases.

3.2 Corrosion behavior of SS 316 in the Artificial blood plasma

When the SS 316 is immersed in artificial blood plasma solution in the absence of Paracetamol and Bactrim the Corrosion potential (E_{corr}) was 165 mV vs SCE. The Tafel slopes values were (βc = 188 mV/decade, βa = 212 mV/decade). The LPR value was 3.26×10^5 ohm cm^2 and the Corrosion current (I_{corr}) was 8.76×10^{-8}A/cm^2. This indicates that the rate of change of corrosion current with potential is higher during the anodic polarization than during cathodic polarization.

3.3 Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 50ppm of Paracetamol

The polarization study reveals that when SS316 is immersed in Artificial blood plasma solution in presence of 50ppm of Paracetamol the corrosion potential was shifted from 165 to 104 mV vs SCE Fig.4.2. The Tafel slopes (βc = 146 mV/decade, βa = 197 mV/decade). Further the LPR value decreases from 3.26×10^5 ohm cm^2 to 1.83×10^5ohm cm^2. The Corrosion current (I_{corr}) value increases from 8.76×10^{-7}A/cm^2 to 2.41×10^{-8}A/cm^2.

3.4 Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 100ppm of Paracetamol

The polarization study reveals that when SS 316 is immersed in Artificial blood plasma solution in presence of 100ppm of Paracetamol the corrosion potential was shifted from 165 to 165 mV vs SCE Fig.4.3 The Tafel slopes (βc = 166 mV/decade, βa = 171 mV/decade). Further the LPR value decreases from 3.26×10^5 ohm cm^2 to 2.20×10^5ohm cm^2. The Corrosion current (I_{corr}) value increases from 8.76×10^{-7}A/cm^2 to 1.77×10^{-7}A/cm^2. Thus the polarization study confirms that formation of a protective film on the metal surface is not greatly seen. The polarization study reveals that the corrosion resistance of the metal is of the order,

ABP+ SS 316 < ABP+ SS 316+ 100ppm Paracetamol < ABP+ SS 316+ 50ppm Paracetamol

Table 1 Polarization results for SS 316 immersed in ABP, in the absence of Paracetamol, in the presence of 50ppm Paracetamol and in the presence of 100ppm Paracetamol

SYSTEM	E_{corr} mV Vs SCE	βc mV/decade	βa mV/decade	LPR ohm/cm^2	I_{corr} A/cm^2
ABP + SS 316	165	188	212	3.26×10^5	8.76×10^{-8}
ABP + SS 316 + 50 ppm Paracetamol	104	146	197	1.83×10^5	2.41×10^{-8}
ABP + SS 316 + 100 ppm Paracetamol	613	166	171	2.20×10^5	1.76×10^{-7}

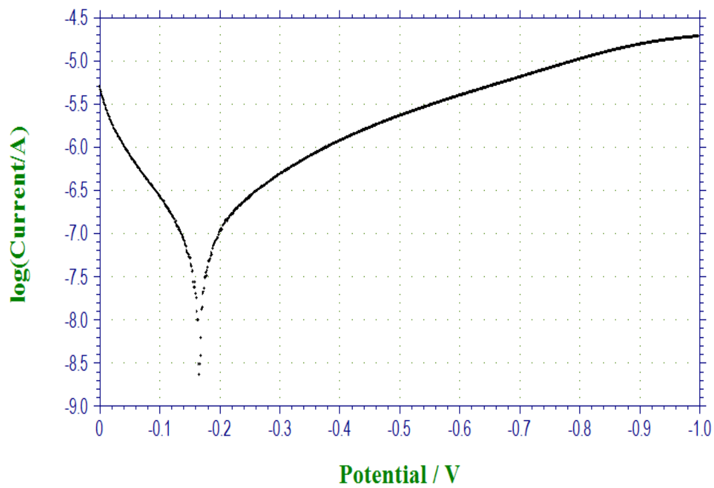


Fig 1.1 Polarization curve of SS 316 + ABP (Control)

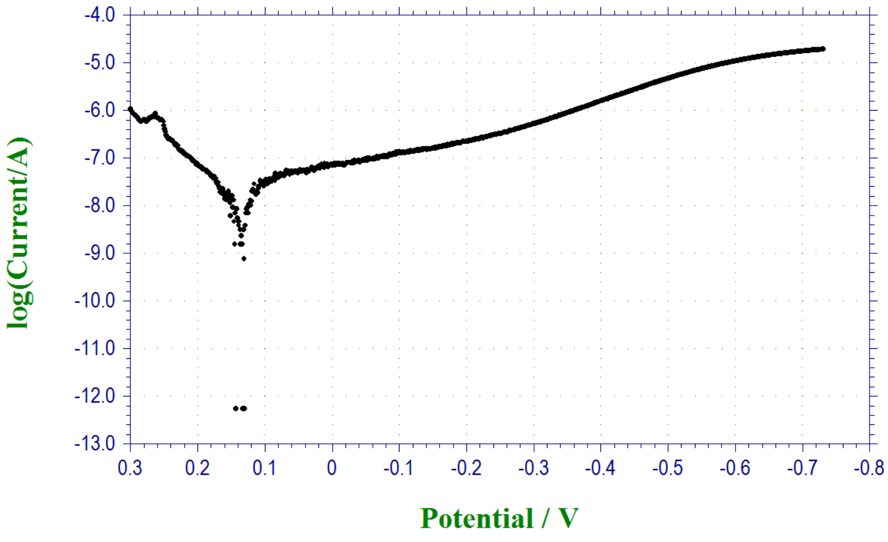


Fig 1.2 ABP + SS 316 + 50ppm of Paracetamol

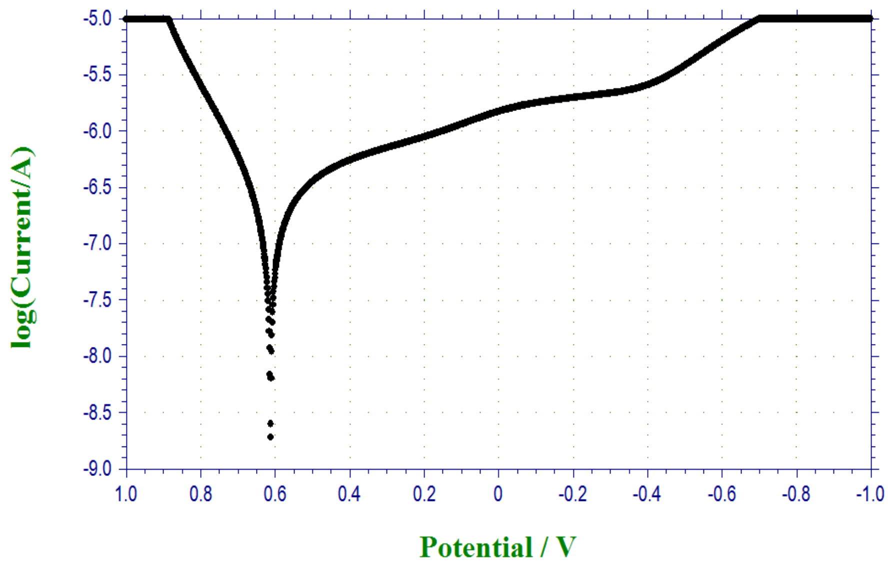


Fig 1.3 **ABP + SS 316 + 100ppm of Paracetamol**

3.5 Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 50ppm of Bactrim

The polarization study reveals that when SS 316 is immersed in Artificial blood plasma solution in presence of 50ppm of Bactrim the corrosion potential was shifted from 165 to 256 mV vs SCE Fig.4.4. The Tafel slopes (βc = 181 mV/decade, βa = 213 mV/decade). Further the LPR value increases from 3.26×10^5 ohm cm^2 to 9.42×10^4ohm cm^2. The Corrosion current (Icorr) value decreases from 8.76×10^{-7}A/cm^2 to 1.02×10^{-8}A/cm^2. Thus the polarization study confirms the formation of a protective film on the metal surface.

3.6 Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 100ppm of Bactrim

The polarization study reveals that when SS 316 is immersed in Artificial blood plasma solution in presence of 100ppm of Bactrim the corrosion potential was shifted from 165 to 316 mV vs SCE Fig.4.5. The Tafel slopes (βc = 148 mV/decade, βa = 149 mV/decade). Further the LPR value increases from 3.26×10^5 ohm cm^2 to 2.29×10^5ohm cm^2. The Corrosion current (I_{corr}) value decreases from 8.76×10^{-7}A/cm^2 to 1.19×10^{-9}A/cm^2. Thus the polarization study confirms the formation of a protective film on the metal surface. The polarization study reveals that the corrosion resistance of metal is in this order.

ABP+ SS 316+100ppm Bactrim > ABP+ SS 316 + 50ppm Bactrim > ABP+ SS 316

Table 2 Polarization results for SS 316 immersed in ABP, in the absence of Bactrim, in the presence of 50ppm Bactrim and in the presence of 100ppm Bactrim

SYSTEM	E_{corr} mV vs SCE	βc mV/decade	βa mV/decade	LPR ohm/cm^2	I_{corr} A/cm^2
ABP + SS 316	165	188	212	3.26×10^5	8.76×10^{-8}
ABP + SS 316 + 50 ppm Bactrim	256	181	213	9.42×10^4	1.02×10^{-8}
ABP + SS 316 + 100 ppm Bactrim	316	148	149	2.29×10^5	1.19×10^{-9}

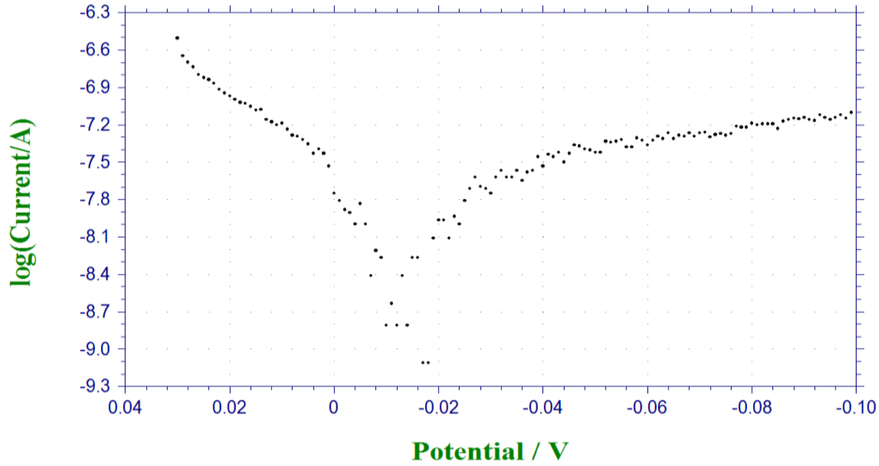


Fig 1.4 ABP + SS 316 + 50ppm of Bactrim

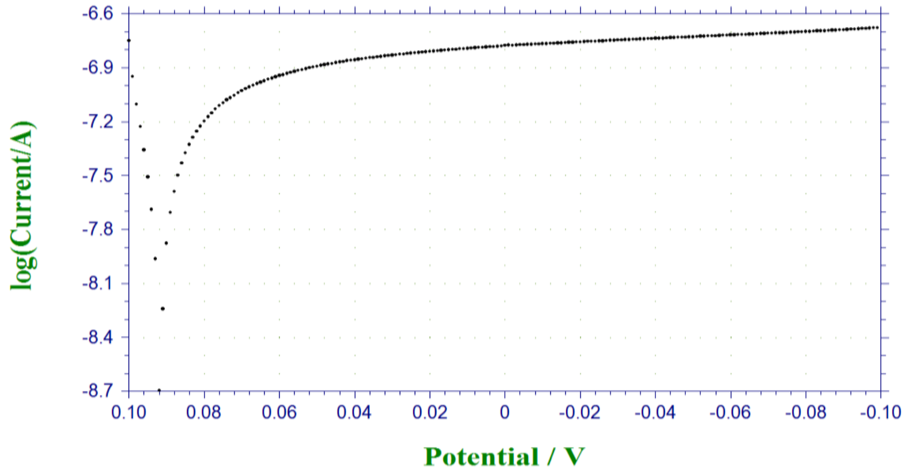


Fig 1.5 ABP + SS 316 + 100ppm of Bactrim

3.7 Analysis of AC impedance spectra:

AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) (derived from Nyquist plots) and impedance value log (z/ohm) (derived from Bode plots), of SS 316 immersed in ABP. AC impedance spectra have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (Rt) increases, double layer capacitance value (Cdl) decreases and the impedance log (z/ohm) value increases. In such a case it indicates that there exists a favorable condition for corrosion resistance.

3.8 Corrosion behavior of SS 316 in Artificial Blood plasma

When SS 316 is immersed in artificial blood plasma in the absence of Paracetamol and Bactrim, the charge transfer resistance Rt was 3798 ohm cm^2. The double layer capacitance value is 1.86×10^9 F/cm^2 (Fig 1.6). The impedance value was 3.0 (Fig 1.7)

3.8.1 Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 50ppm of Paracetamol

When SS 316 is immersed in artificial blood plasma solution containing 50 ppm Paracetamol, the charge transfer resistance Rt decreases from 3798ohm cm^2 to 3466ohm cm^2 (Fig 1.8) The Cdl value increases from 1.86×10^9 F/cm^2 to $4.21\times10^9 F/cm^{-2}$. The impedance value log (z/ohm) was 3.4.

3.8.2Corrosion behavior of SS 316 in artificial blood plasma in the Presence of 100ppm of Paracetamol

When SS 316 is immersed in artificial blood plasma solution containing 100 ppm Paracetamol, the charge transfer resistance Rt increases from 3798ohm cm^2 to 3899ohmcm^2 (Fig 1.10) The Cdl value increases from 1.86×10^9 F/cm^2 to $3.44\times10^9 F/cm^{-2}$. The impedance value log (z/ohm) was 3.4. Thus, the AC impedance spectral study reveals that the corrosion resistance of SS 316 in ABP was in the following order:
ABP+ SS 316+100ppm Paracetamol> ABP+ SS 316+ 50ppm Paracetamol + ABP+ SS 316

Table 3 AC impedance results for SS 316 immersed in ABP, in the absence of Paracetamol, in the presence of 50ppm Paracetamol and in the presence of 100ppm Paracetamol

SYSTEM	Nyquist plot		Bode plot Impedance Log(z/ohm)
	Rt ohm cm^2	Cdl F/cm^2	
ABP + SS 316	3798	1.86×10^9	3.0
ABP + SS 316 + 50ppm Paracetamol	3466	4.21×10^9	3.4
AS + SS 316 + 100ppm Paracetamol	3899	3.44×10^9	3.4

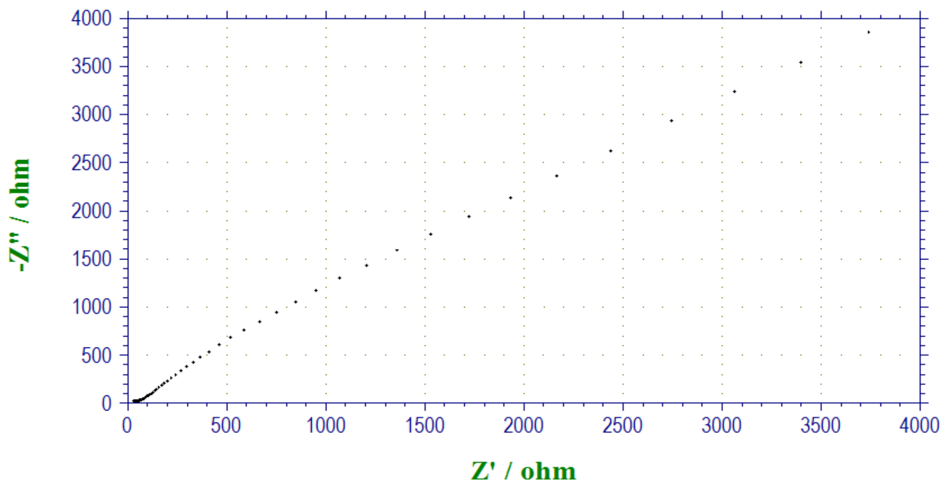


Fig 1.6 Nyquist Plot of SS 316 + ABP

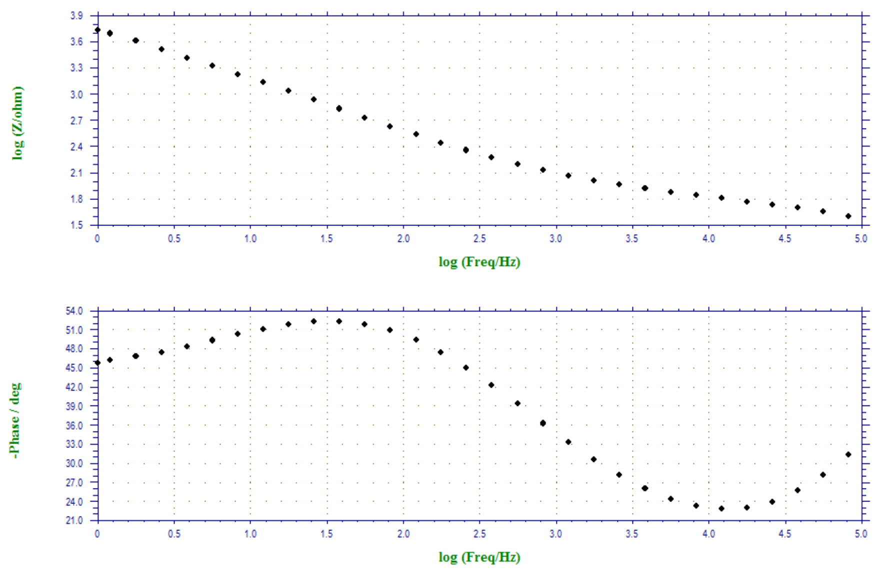


Fig 1.7 Bode Plot of SS 316 + ABP

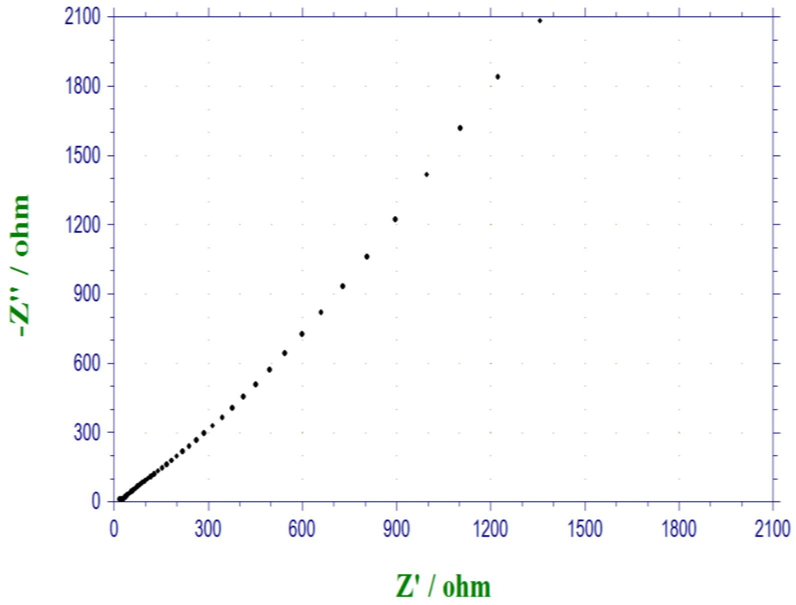


Fig 1.8 Nyquist Plot of SS 316 + ABP + 50ppm Paracetamol

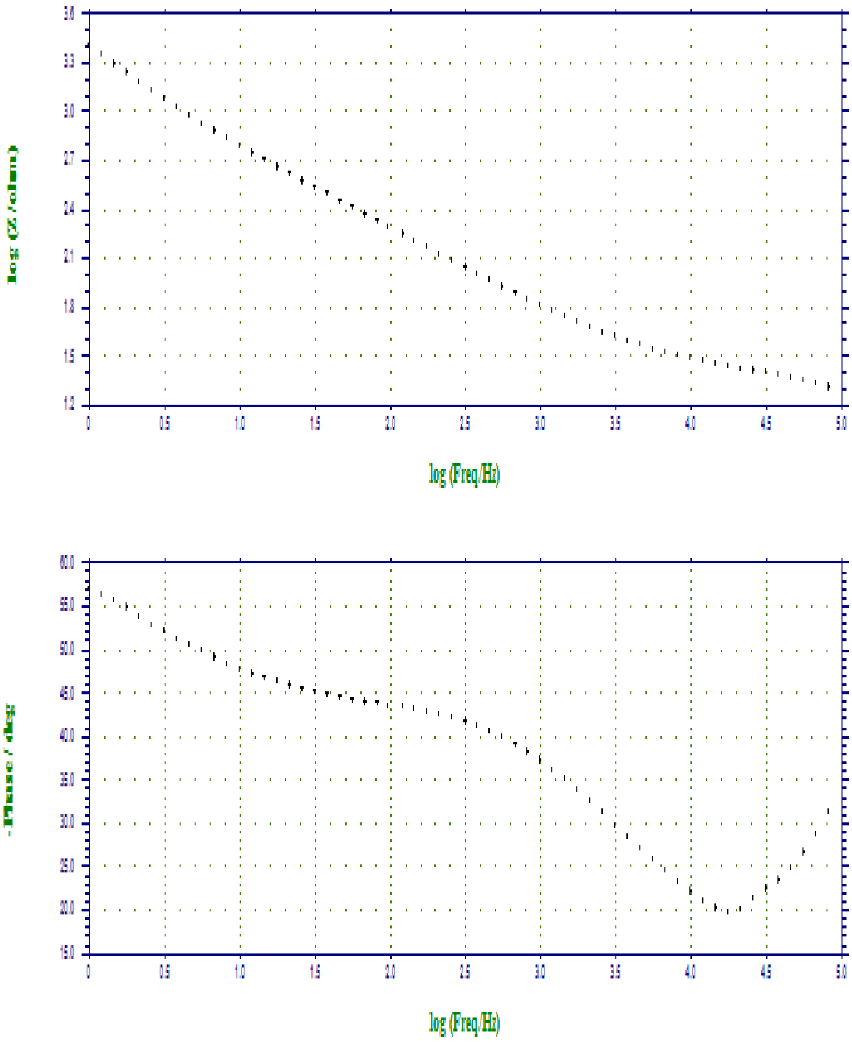


Fig 1.9 Bode Plot of SS 316 + ABP + 50ppm Paracetamol

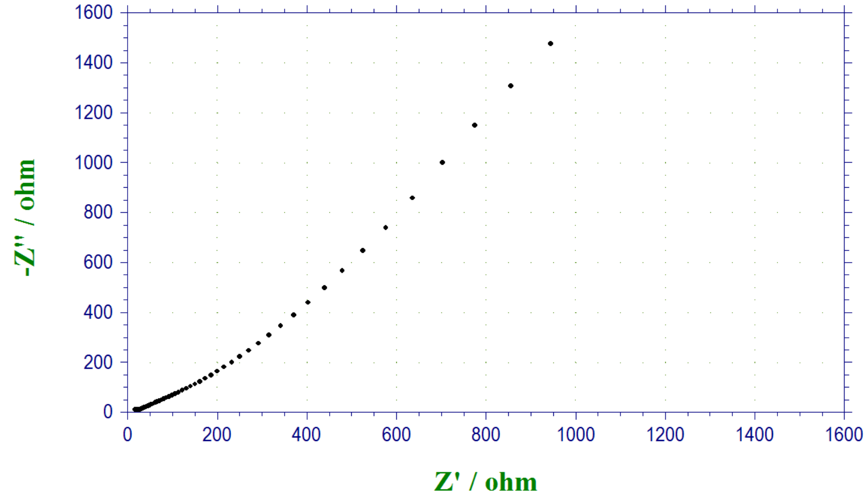


Fig 1.10 Nyquist Plot of SS 316 + ABP + 100ppm Paracetamol

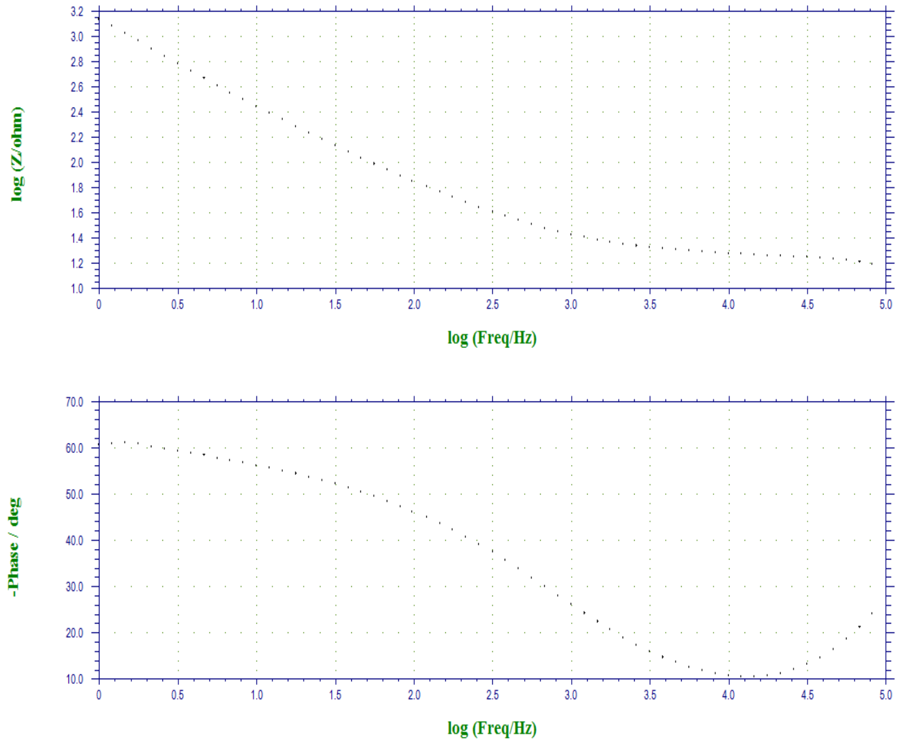


Fig 1.11 Bode Plot of SS 316 + ABP + 100ppm Paracetamol

3.8.3 Corrosion behavior of SS 316 in artificial blood plasma the Presence of 50ppm of Bactrim

When SS 316 is immersed in artificial blood plasma solution containing 50 ppm Bactrim, the charge transfer resistance Rt increases from 3798ohm cm^2 to 3876ohm cm^2 (Fig 1.12) The Cdl value decreases from 1.86×10^9 F/cm^2 to $1.90\times10^9 F/cm^{-2}$. The impedance value log (z/ohm) was 3.4.

3.8.4 Corrosion behavior of SS 316 in artificial blood plasma the Presence of 100ppm of Bactrim

When SS 316 is immersed in artificial blood plasma solution containing 100 ppm Bactrim, the charge transfer resistance Rt increases from 3798ohm cm^2 to 4727ohmcm^2 (Fig 1.14) The Cdl value decreases from 1.86×10^9 F/cm^2 to $2.31\times10^9 F/cm^{-2}$. The impedance value log (z/ohm) was 3.5.

Thus, the AC impedance spectral study reveals that the corrosion resistance of SS 316 in ABP was in the following order:

ABP+ SS 316 + 100ppm Bactrim > ABP + 50ppm Bactrim + SS 316 > ABP+ SS 316. This confirms that the formation of protective layer over the metal.

Table 4AC impedance results for SS 316 immersed in ABP, in the absence of Bactrim, in the presence of 50ppm Bactrim and in the presence of 100ppm Bactrim

SYSTEM	Nyquist plot		Bode plot Impedance Log(z/ohm)
	Rt ohm cm^2	Cdl F/cm^2	
ABP + SS 316	3798	1.86×10^9	3.0
ABP + SS 316 + 50ppm Bactrim	3678	1.90×10^9	3.4
AS + SS 316 + 100ppm Bactrim	4727	2.31×10^9	3.5

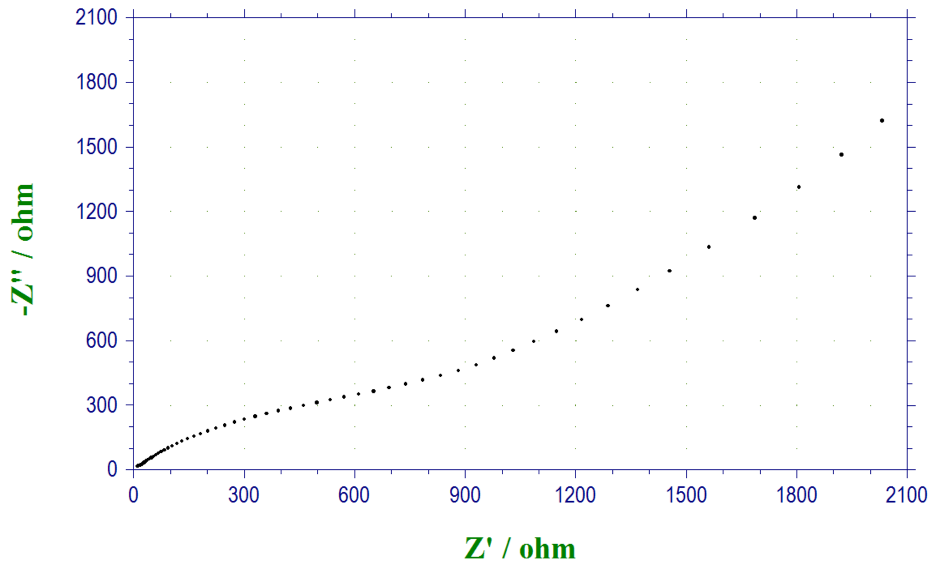


Fig 1.12 Nyquist Plot of SS 316 + ABP + 50ppm Bactrim

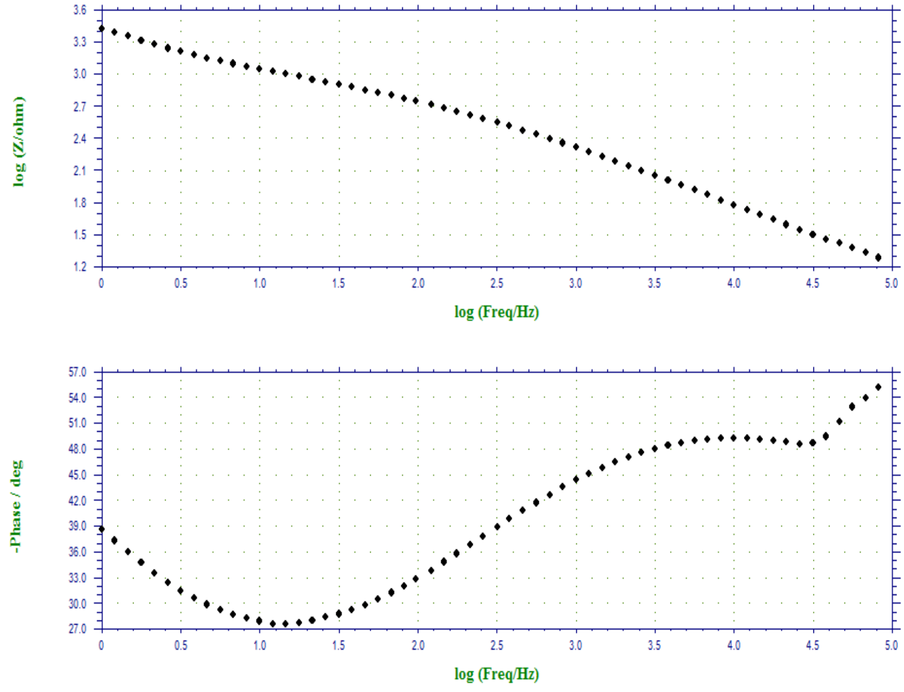


Fig 1.13 Bode Plot of SS 316 + ABP + 50ppm Bactrim

Fig 1.14Nyquist Plot of SS 316 + ABP + 100ppm Bactrim

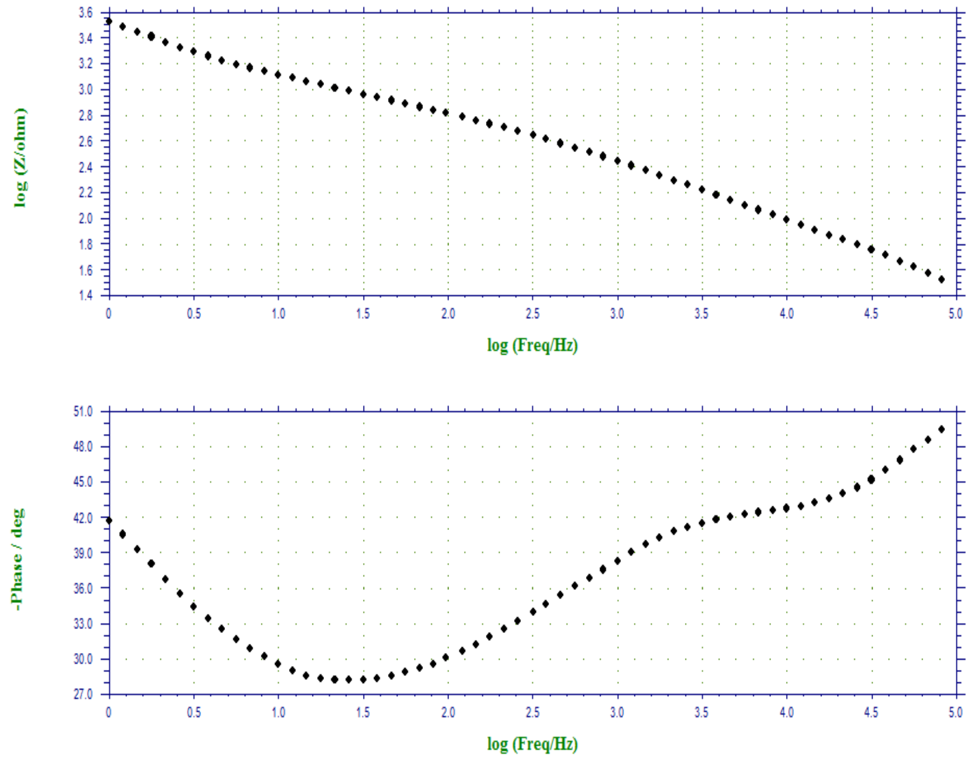


Fig 1.15 Bode Plot of SS 316 + ABP + 100ppm Bactrim

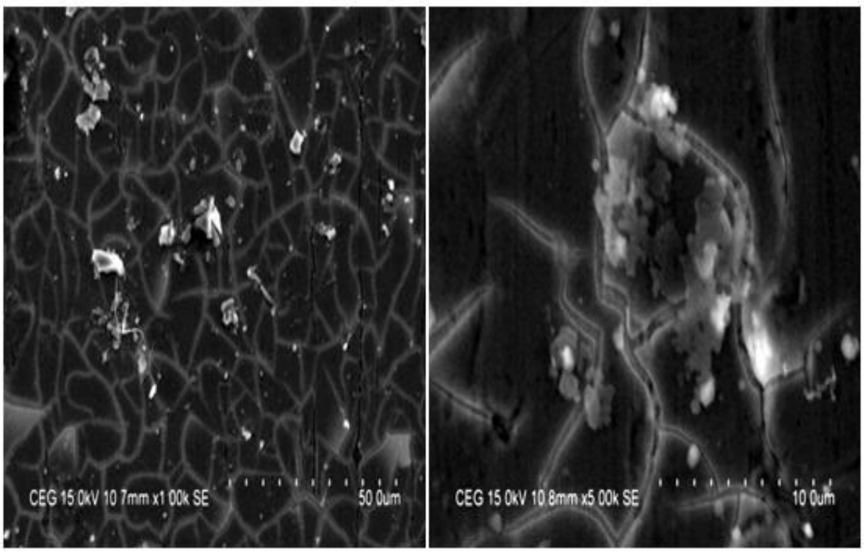
3.9Scanning Electron Microscope (SEM)

SEM provides a pictorial representation of the metal surface. To understand the nature of the surface film formed on SS 316 alloy in ABP in the presence and absence of Paracetamol and Bactrim and the extent of corrosion of metal surface can be examined by the SEM micrographs.

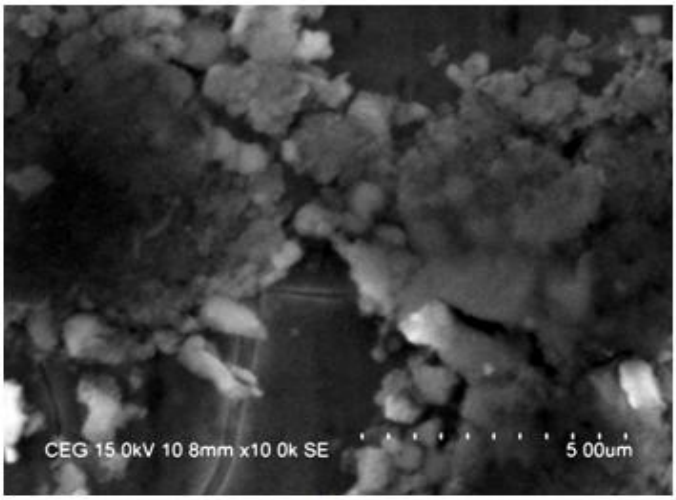
The SEM images of different magnification (10000, 5000, 1000) of SS 316 specimen immersed for 30days in the absence and presence of 100ppm Bactrim is shown in the images. (Fig 1.16 - Fig 1.17)

3.9.1SEM analysis of SS 316

The Electrochemical studies reveal that SS 316 with 100ppm of Bactrim shows good result in ABP than 50ppm of the same drug. It is more corrosion resistant than 50ppm of Bactrim with the same metal.

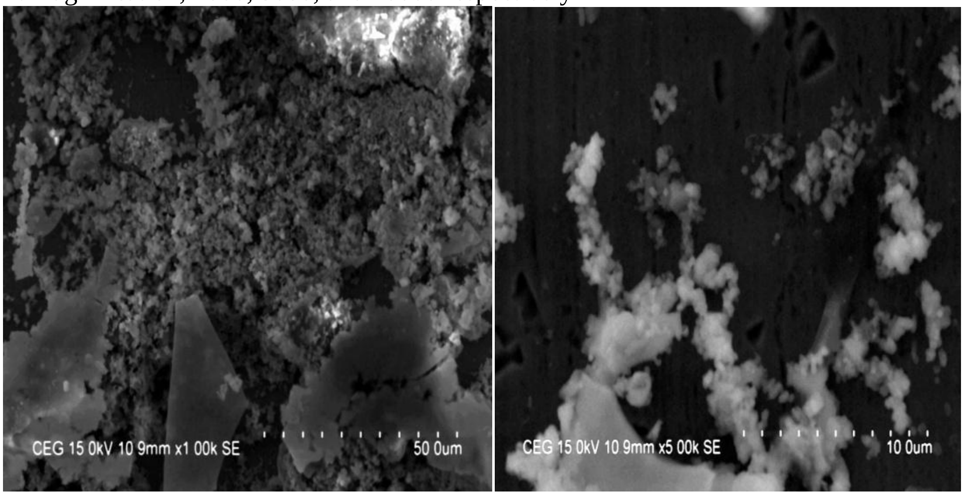


(a) (b)

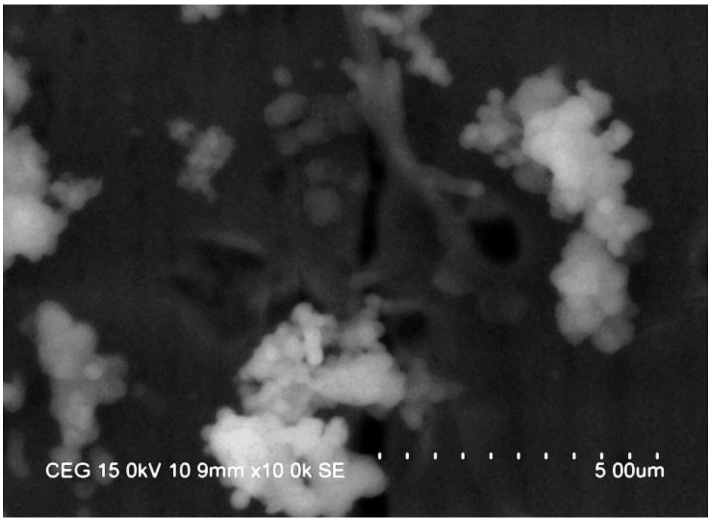


(c)

Fig 1.16 (a), (b), (c) Shows the SEM micrographs of SS 316 immersed in ABP in the absence of Bactrim (Control) under different magnification, 1000, 5000, and 10000 respectively



(a) (b)



(C)

Fig 1.17 (a), (b), (c) Shows the SEM micrographs of SS 316 immersed in ABP in the Presence of 100ppm Bactrim under different magnification, 1000, 5000, and 10000 respectively.

On comparing Fig 1.16(ABP + SS 316) with Fig 1.17 (ABP + SS316 + 100ppm Bactrim) Fig 1.17 shows the formation of Protective layer over the metal.

IV. Conclusion

4.1 Polarization Studies - Corrosion inhibition property of SS 316

From the above study we infer that the corrosion inhibition behavior of SS 316 bio implant metal was seen more with the addition of 100ppm of the drug Bactrim in artificial blood plasma rather than 50ppm of the drug. The corrosion inhibition property of the same drug with the addition of the drug Paracetamol was not appreciable. The order corrosion inhibition of the metal is given below. **ABP+ SS 316+100ppm Bactrim > ABP+ SS 316 + 50ppm Bactrim > ABP+ SS 316**

4.2 AC Impedance Studies - Corrosion inhibition property of SS 316

The AC impedance spectra show the corrosion inhibition process of SS 316 with the help Nyquist plots and Bode plots. The corrosion inhibition property of SS 316 in artificial blood plasma was seen more for 100ppm of Bactrim rather than the other drug Paracetamol. The order of corrosion inhibition of the metal is given below. **ABP+ SS 316 + 100ppm Bactrim > ABP + 50ppm Bactrim + SS 316 > ABP+ SS 316.**

4.3SEM Studies

The scanning electron microscopic study confirms the formation of protective layer over the metal in the presence of the drug Bactrim for SS 316.

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