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The influence of an eco-friendly antibiotic as anti-scalant and inhibitor for steel in gypsum solution and brine water

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ABSTRACT

The influence of sulfamerizine (SMZ) drug as anti-scalant in water containing 0.7 M Gypsum salt ($CaSO_4$) and brine water (0.7 M) has been studied by weight loss, potentiodynamic polarization and A.C impedance measurements. The formation of protective layer of SMZ was justified by chronoamperometry technique. Quantum chemical methods confirmed the absorption of anti-scalant on steel. SEM photographs evidenced the formation of stable anti-scalant film on steel in presence of gypsum salt water and brine water.

Keywords: Anti-scalants; Corrosion; Polarization; Salt water

1. Introduction

The steel components are widely used in turbine blades and also in boilers for making steam. The presence of calcium sulphate and calcium hydroxide produces a hard adhering crust on the walls of steel components. This scale prevents heat liberation of steel that leads to wastage of fuels in steam production and threatens the life of turbine blades. Numerous reports are available to prevent scale formation in boiler steel components [1–5]. However, plant extracts have not been used in steam industries as the operation process involves high temperature in industrial practice. In order to use anti-scalants at high temperature an extract-based inhibitors have been reported by Diouri et al. [6]. The in-organic compounds are toxic and hence study based on development of an eco-friendly anti-scalants is given attention. The use of antibiotics will be an alternative because of its eco-friendliness and in expensiveness. Several antibiotics [7,8] have been investigated as inhibitors for the corrosion of steel in acidic media. The detailed literature survey envisaged that no prominent reports are available for using antibiotics as anti-scalants and inhibitors. An attempt has been made to study the influence of sulfamerizine drug as anti-scalant in high saline media as this forms an indigenous report in this field of research. The present drug is used for treating fungal disease. Since, it is being used to treat bronchitis, prostatitis and urinary tract infections as oral medicine, sulfamerizine is a non toxic organic drug. When the medicine is taken orally and it exceeds the permissible limit prescribed by the medical council, the question of toxicity can be claimed for human beings. Here, the said antibiotic is added as an additive to reduce the dissolution of metal and arresting the scale

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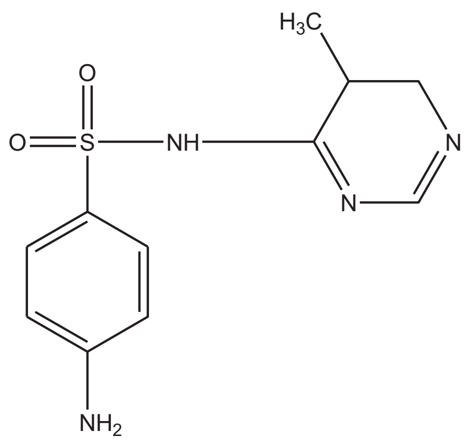

Fig. 1. Structure for Sulfamerizine.

formation. The simple molecular structure of SMZ is giving an encouraging idea as it contains sulfoxide group and imdo group in delocalized π electrons of benzene ring. The structure of sulfamerizine used as anti-scalant and inhibitor is given in Fig. 1. The better performance of anti-scalants could be due to the following:

(1) Its planar structure.
(2) The presence of absorption sites such as–NH, $–NH_2$, nitrogen atoms and benzene ring favour good anchoring through the release of electrons on metals.

2. Materials and methods

2.1. Preparation of gypsum and brine salts water samples

The mild steel specimen of the composition $C = 0.08\%$, $S = 0.04\%$, $Mn = 2.7\%$, $P = 0.03\%$, Si=Nil and Fe = remainder was used for preparing the working electrode. The steel was insulated using epoxy lacquer without affecting 1 cm^2 area to be exposed in electrolytes. Double distilled water was used for preparing 0.7 M NaCl, 0.0025 M $NaHCO_3$, 0.028 M Na_5SO_4 and 0.01 $CaCl_3$ as reported earlier [5]. The total strength of brine water was calculated as 0.74 M. For preparing 0.74 M gypsum water, accurately 127.2 g of gypsum was weighed and dissolved in 200 ml hot HCl which is then diluted to 1 l. All the chemicals used were of analytical grade. Sulfamerizine (CAS number: 127-79-7) was procured from Cipla Ltd, and required concentration was achieved by dissolving the drug in 50 ml of isopropanol and then diluted to 1 l.

2.2. Electrochemical methods

The electrochemical measurements were performed using electrochemical workstation, Sinsil Instrument, USA. 4.6 cm^2 area of platinum foil and Ag–AgCl electrode were used as auxiliary and reference electrode. The mild steel specimen of above composition with size of 1 cm^2 area was used as working electrode. 0.74 M gypsum water and 0.74 M brine water were used as corrosive environment to form scale on steel surface.

Potentiodynamic polarization was carried out by shifting the potential of mild steel ±200 mV from OCP at a scan rate of 1 mV/s in the above electrochemical analyzer involving triple electrode system. A.C impedance studies were carried out within the frequency range from 0.01 to 10,000 Hz with optimal signal amplitude of 5 mV. In order to understand the formation of scale on steel surface in gypsum and brine water media with and without the presence of sulfamerizine, chronoamperometry studies were performed by shifting the potential to −500 mV from the standard reduction potential of Fe (−440 mV) and recorded with respect to time.

2.3. Theoretical evaluation of anti-scalant

Quantum chemical analyses were done by employing Gaussian-03 software. The values of E_{HOMO}, E_{LUMO}, ΔE and μ will be useful to validate the anti-scalant behaviour of antibiotic on mild steel in gypsum and brine water.

2.4. Surface morphology

SEM images were taken for steel components exposed in gypsum and brine water samples in the presence and absence of inhibitor adopting ASTM E986-97 procedure. The magnification used was X1000 using SEM JEOL, USA.

3. Results and discussion

3.1. Weight loss studies

The results of weight loss studies are presented in Table 1. It is evident that as the concentration of inhibitor increases, the efficiency of inhibition also increases due to the effective absorption of drug molecules on the surface of mild steel. The duration of weight loss was 20 h. From the difference in weights of steel specimens immersed in gypsum and brine salts water, the inhibition efficiency was calculated as described earlier [9]. The sulfamerizine inhibits better in gypsum water than brine salt water samples. The performances

Table 1
Values of inhibition efficiency for the corrosion of mild steel in gypsum water and brine water in the presence of different concentrations of Sulfamerizine obtained from weight loss studies

	Gypsum water		Brine water	
Concentration of inhibitor	Weight loss (in g)	Inhibition efficiency (%)	Weight loss (in g)	Inhibition efficiency (%)
Blank	0.0802		0.0209	
5 ppm	0.0286	64.33	0.0104	58.23
10 ppm	0.0231	71.19	0.0081	67.46
15 ppm	0.0176	78.05	0.0069	72.28
20 ppm	0.0127	85.16	0.0051	79.51

Table 2a
Corrosion kinetic parameters of mild steel in gypsum water in the presence of different concentrations of Sulfamerizine obtained from potentiodynamic polarization studies

		Tafel slopes (mV dec^{-1})			
Concentration of Inhibitor	E_{corr} (mV)	b_a	b_c	I_{corr} (mA cm^{-2})	Inhibition efficiency (%)
Blank	−365.4	248	184	2075	
5 ppm	−364.4	223	176	712	65.6
10 ppm	−357.9	229	163	588	71.7
15 ppm	−352.1	224	172	432	79.2
20 ppm	−349.7	216	169	321	84.5

Table 2b
Corrosion kinetic parameters of mild steel in brine water in the presence of different concentrations of Sulfamerizine obtained from potentiodynamic polarization studies

		Tafel slopes (mV dec^{-1})			
Concentration of Inhibitor	E_{corr} (mV)	b_a	b_c	I_{corr} (mA cm^{-2})	Inhibition efficiency (%)
Blank	−349	873	112	873	
5 ppm	−327.6	359	108	359	58.9
10 ppm	−312.4	281	100	281	67.8
15 ppm	−298.7	253	103	253	71.1
20 ppm	−291.8	198	96	198	77.4

of SMZ molecules as anti-scalant as well as inhibitor are better in gypsum water than brine water due to the following reason:

(1) In the case of brine water, the presence of chloride ions which are having higher specific adsorption than sulphate ions. This resulted that the availability of space for the adsorption of inhibitor is less due to the strong adsorption of chlorides.
(2) In gypsum water, the existence of sulphate ions whose specific adsorption is lesser than the specific adsorption of chlorides. Thus, permitting more space for anti-scalant to get adsorbed on steel surface.

3.2. Potentiodynamic polarization

In order to assess the performance of drug molecules to be used as anti-scalants, the measurement of potential-current curves were carried out using potentiodynamic polarization technique [10] by immersing the working electrode in gypsum and brine salts water for 20 h in the presence and absence of sulfamerizine.

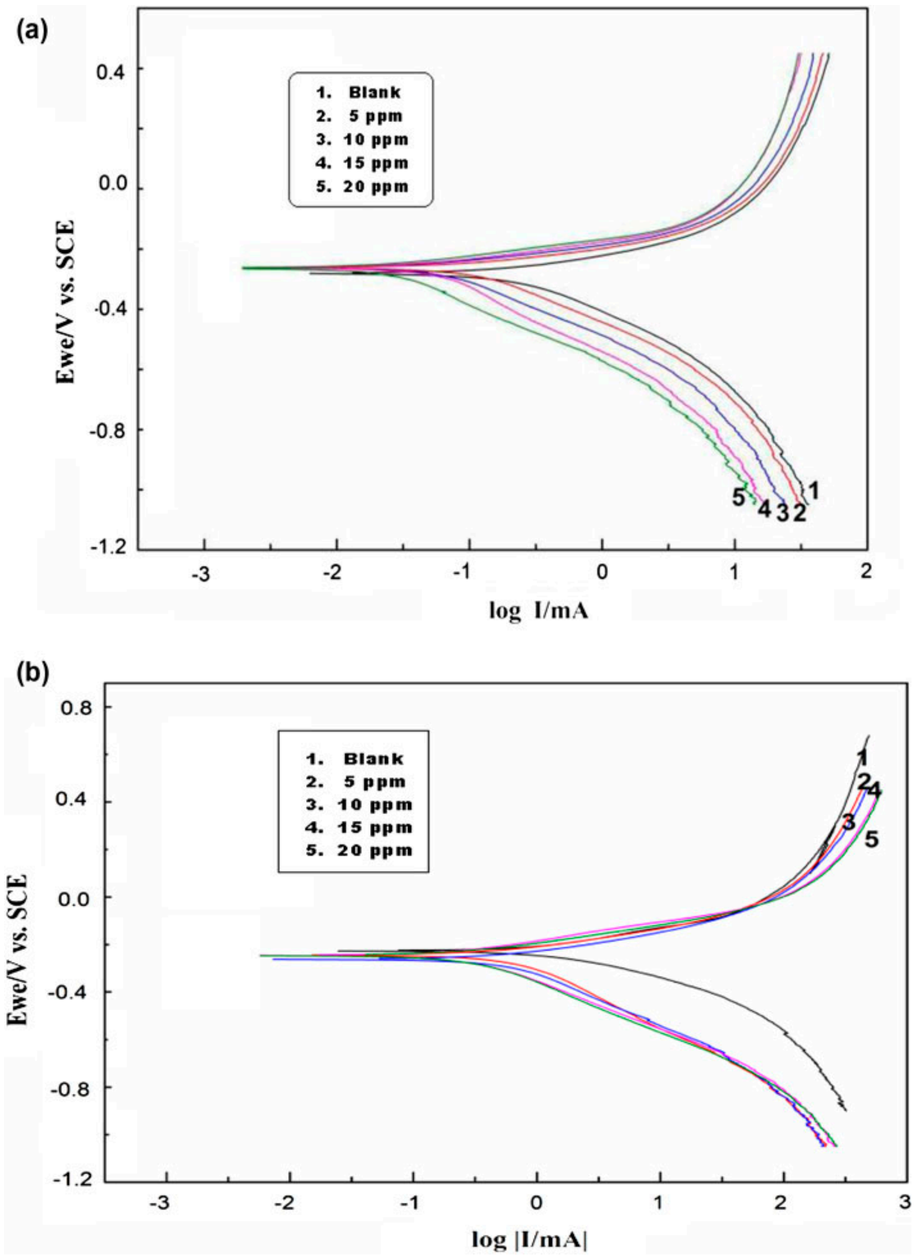

Fig. 2. (a) Polarization behaviour of Sulfamerizine in 0.7 M gypsum water and (b) Polarization behaviour of Sulfamerizine in 0.7 M brine water.

After 20 h, the OCP was noted. From which the scanning of potentials were performed from ±500 mV.

From the results of this technique (Tables 2a and 2b), it was observed that E_{corr} values were shifted to positive direction in the presence of inhibitor. I_{corr} values have also been decreased in the presence of sulfamerizine than its absence in both media. The enhancement of b_a and b_c values are not at regular implying that the performance of antibiotic in gypsum and brine water samples is under mixed control (Fig. 2(a) and (b)) From the I_{corr} values, inhibition efficiencies were calculated and the values were found to be close with results of weight loss studies.

3.3. Chronoamperometry studies

Fig. 3(a) and (b) indicate the chronoamperometry results of 1 cm^2 exposed area of mild steel in gypsum and brine salt water, respectively. During the above analysis, a calculated quantity of sulfamerizine was

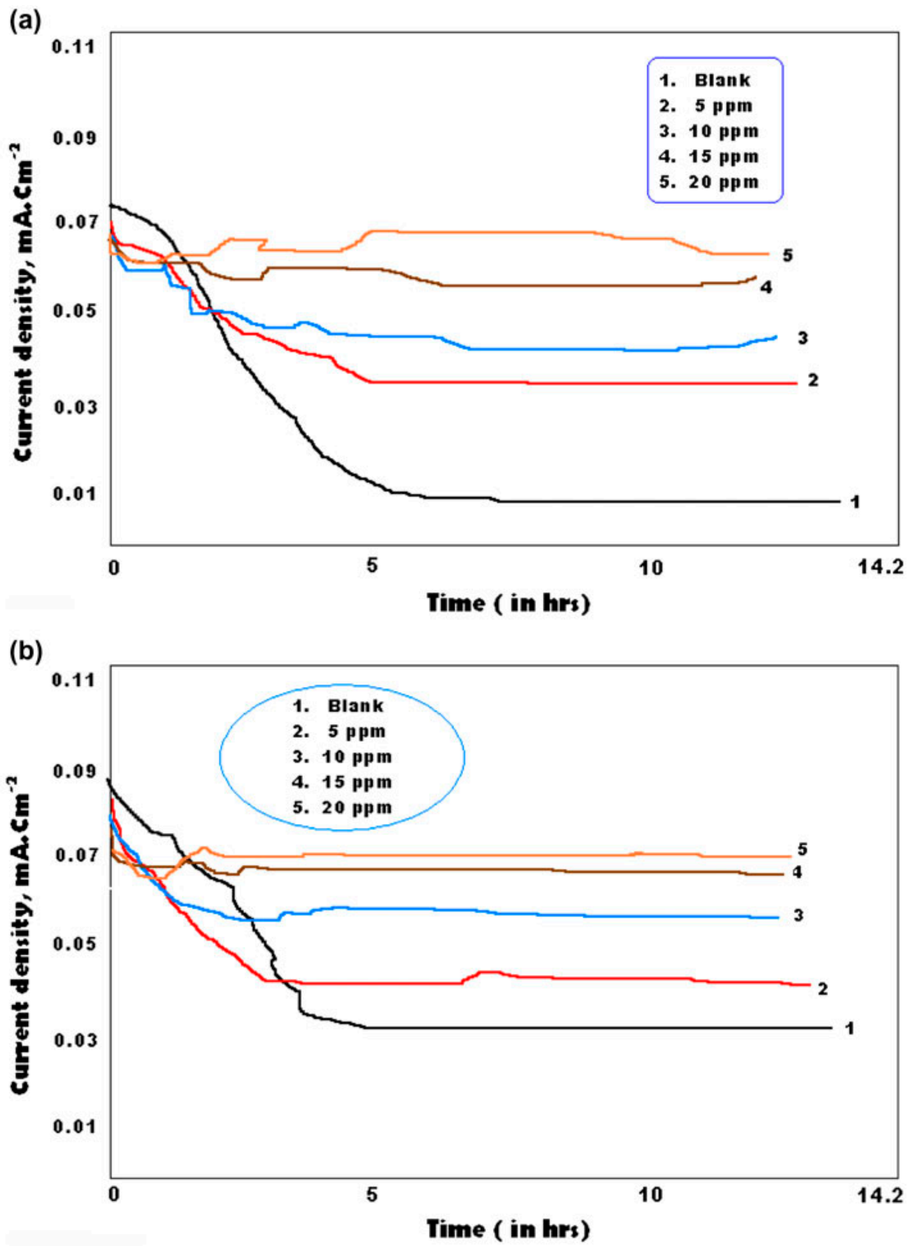

Fig. 3. (a) Chronoamperometry curves for gypsum solution and (b) Chronoamperometry curves for brine solution.

added and the temperature was maintained at 40˚C. The initiation of anti-scalant formation started at 0.068 mA cm^{-2} for 5 ppm and ended at 0.065 mA cm^{-2} for 20 ppm of sulfamerizine in gypsum water. The steady state in current density was noticed in the presence of inhibitor at timing of 2.1 h confirming that antibiotic molecules have effectively adsorbed on the steel surface and form anti-scale which inhibits the attack of sulphate ions of Ca^{2+} in gypsum water. In the absence of inhibitor, since there is no anti-scale formation the current density value was 0.072 mA cm^2 and steady state current values attained at 5 h which is 3 h delay from the presence of inhibitor establishing that in the absence of sulfamerizine molecules the adsorption of $CaSO_4$ scale took place.

In the case of brine salt water system, the decreased trend in current densities was noticed in the presence SMZ molecule due to the impressive adsorption of antibiotic as anti-scalant on steel surface. The current density values were lie-down from 0.088 to 0.08 mA cm^{-2} for 5 and 20 ppm of inhibitor in brine salt water. The current values began to be constant at the timing of 2.2 h which is higher than gypsum water. The above results confirm that SMZ molecules acted as anti-scalant and inhibitor for the corrosion of mild steel in gypsum and brine salt water.

3.4. Impedance studies

Values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist graphs are shown in Tables 3a and 3b in Fig. 4(a) and (b). It can be seen in table that the values of R_t has begun to increase with enhancement of SMZ concentrations in gypsum and brine salt water. Values of double layer capacitance are establishing that steel dissolution is high in salt water. It is found that values of C_{dl} are decreased by increasing concentrations of sulfamerizine in electrolyte. This could be due to the increased adsorption of the SMZ molecule on the surface of steel as the concentration of inhibitor increases. This is major support to corrosion inhibition by this compound, as a result of its adsorption on the metal surface [11].

3.5. Quantum chemical studies

The computed quantum chemical indices such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE) and dipole moment (μ) are summarized in Table 4. From Figs. 5 and 6, it can be observed that HOMO energy orbital's (wire frame model) were strongly distributed on pyrazinyl group and nil on benzene sulphonamide moiety. However, LUMO energy distribution showing that the electrons were strongly delocalized on benzene sulphonamide moiety alone confirming that the anchoring sites for better adsorption of inhibitor might be through pyrazinyl moiety(electron donating HOMO orbitals) than benzene sulphonamide group(electron withdrawing LUMO orbitals).

Table 3a
Impedance parameters for the corrosion of mild steel in gypsum water in the presence of different concentrations of Sulfamerizine

Concentration of inhibitor	Charge transfer resistance (R_t) Ohm cm^2	Double layer capacitance (C_{dl}) µF cm^{-2}	Inhibition efficiency (%)
Blank	14.9	80.0	–
5 ppm	74.5	67.3	67.3
10 ppm	68.3	71.8	71.8
15 ppm	63.0	78.5	78.5
20 ppm	60.0	83.0	83.0

Table 3b
Impedance parameters for the corrosion of mild steel in brine water in the presence of different concentrations of Sulfamerizine

Concentration of inhibitor	Charge transfer resistance (R_t) Ohm cm^2	Double layer capacitance (C_{dl}) µF cm^{-2}	Inhibition efficiency (%)
Blank	23.7	164.0	–
5 ppm	151.2	57.8	57.8
10 ppm	146.1	65.6	65.6
15 ppm	133.7	70.7	70.7
20 ppm	121.5	77.8	77.8

Table 4
Quantum chemical parameters for Sulfamerizine

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal Mol^{-1})	Dipole moment (Debye)
Sulfamerizine	−1.6957	−3.8339	2.1382	3.8

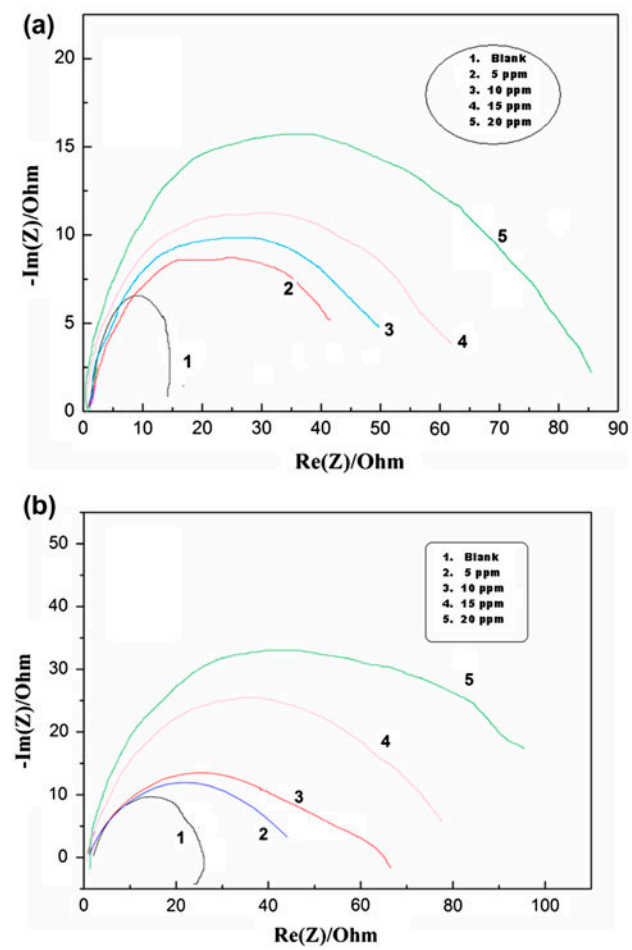

Fig. 4. (a) Nyquist plot of Sulfamerizine in 0.7 M gypsum water and (b) Nyquist plot of Sulfamerizine in 0.7 M brine water.

According to Jeeva et al. [12], when a molecule possesses similar frontier orbitals, its inhibition effectiveness can be allied to the energy levels of HOMO and LUMO and the distinction between them. It has been widely investigated that, higher the value of E_{HOMO}, better will be the adsorption of an inhibitor by virtue of releasing electrons to vacant d orbital of metal atom and higher is the inhibition efficiency. Also, lower E_{LUMO} values, associated with the acceptance of electrons from metal atom to make feedback bonds. Hence the gap between HOMO–LUMO energy levels of molecules was calculated as a vital data. Smaller value of ΔE of an inhibitor, signify the effective inhibition efficiency of organic compound. It has been reported that, large values of dipole moment will considerably enhance the corrosion inhibition [13,14].

3.6. Scanning electron microscopic images

Fig. 7(a) and (b) indicate the SEM images of steel surfaces immersed in gypsum water and brine water for 20 h. These figures confirm that in the absence of anti-scalant the dissolution of steel is more in brine water than gypsum water. The surfaces were greatly damaged which is evident from the appearance of grooves, dense and micro globules aggregation.

The addition of sulfamerizine has significantly protected surface of steel which was confirmed from Fig. 8(a) and (b). In the presence of inhibitor, the voids, grooves and island of globules were totally nullified and the formation of thin protective anti-scalant film of SMZ molecules is visible in gypsum water (Fig. 8(a)). With brine water system the performance

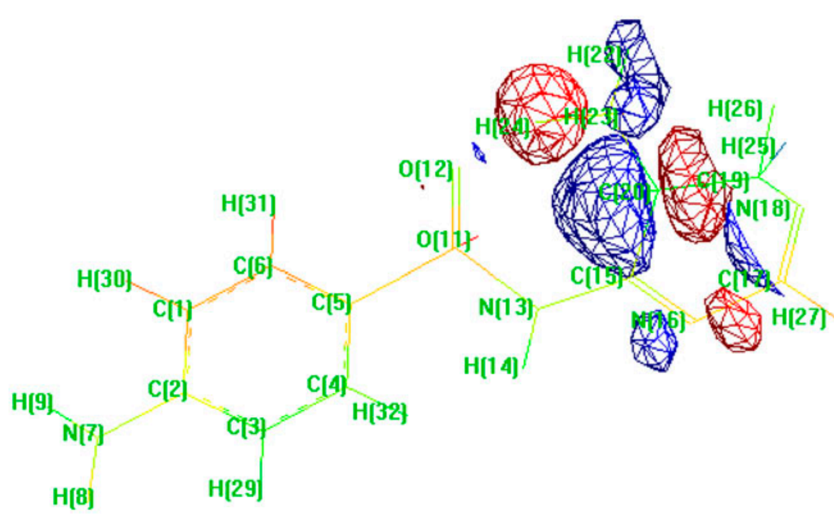

Fig. 5. HOMO wire frame model of Sulfamerizine.

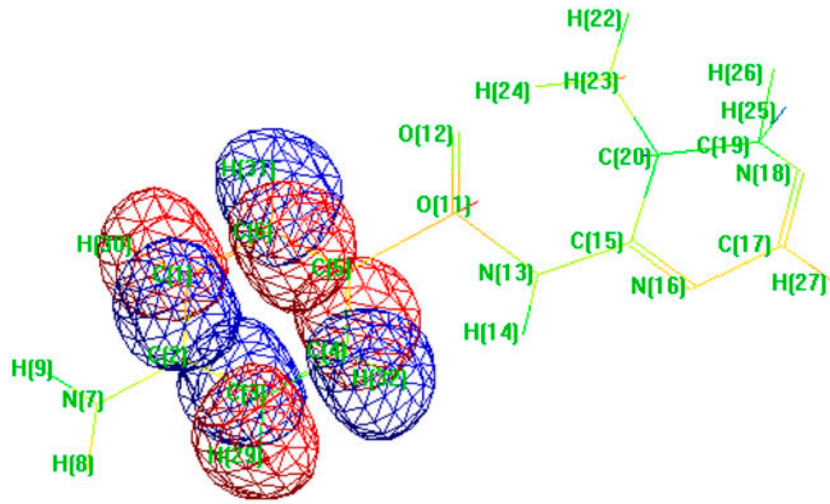

Fig. 6. LUMO wire frame model of Sulfamerizine.

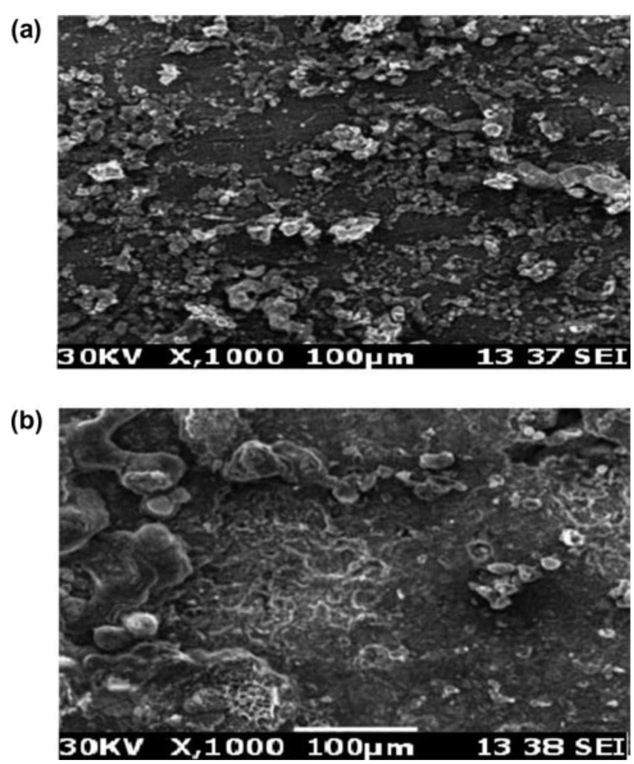

Fig. 7. (a) SEM images of steel in gypsum solution and (b) SEM images of steel in brine solution.

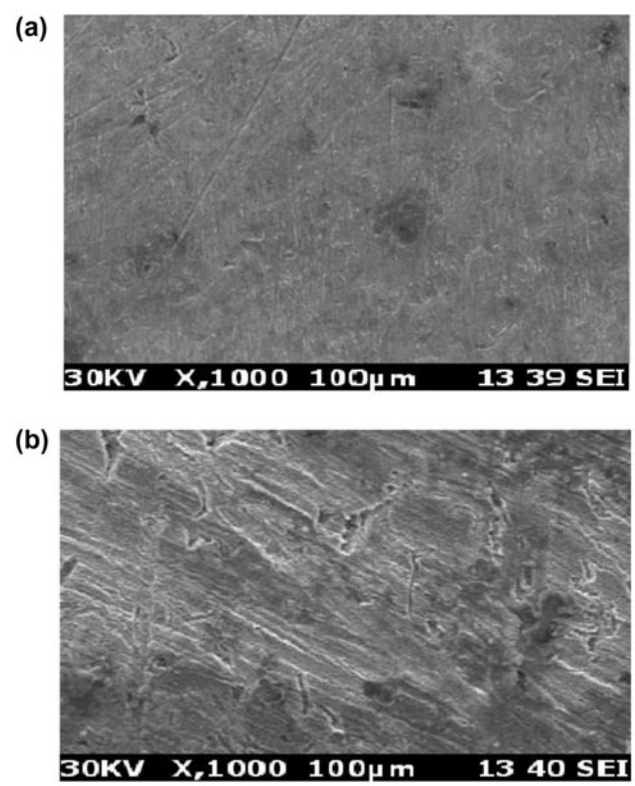

Fig. 8. (a) SEM images of steel in the presence of Sulfamerizine (20 ppm) in gypsum solution and (b) SEM images of steel in the presence of Sulfamerizine (20 ppm) in brine solution.

of SMZ is not encouraging enough owing to the appearance of crack lines along with effective blockening of voids and grooves (Fig. 8(b)).

4. Conclusions

(1) The influence of sulfamerizine on the anti-scalant and inhibition of corrosion of steel was studied by chemical and electrochemical methods. The performance of antibiotic was better in gypsum than in brine water.
(2) Sulfamerizine molecules behaved as a scale inhibitor and potentiodynamic polarization studies revealed that its performance was under mixed control.
(3) The impedance analysis clearly indicated the efficacy of inhibitor evidenced from charge transfer resistance and double layer capacitance.
(4) SEM images confirmed that the formation of scale on steel surface have been significantly reduced in corrosive media in the presence of SMZ molecules.
(5) Quantum chemical parameters validated the performance of anti-scalant in gypsum and brine waters.

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