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Improvement of corrosion resistance of anodized aluminium surfaces

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Abstract

An attempt has been made to develop a corrosion resistant anodized aluminium film using a special sealing free from rare earths based on Cellulose acetate phthalate (CAP) and Sulfamethoxazole (SM) drugs in a quantitative way.The corrosion resistance of the anodized aluminium surfaces was enhanced by the above compounds in the presence of anionic surfactant. The performance of the sealant film was screened through potentiodynamic polarization and A.C impedance analysis. The calculations of quantum mechanical descriptors such as the localization of frontier molecular orbital's, E_{HOMO}, E_{LUMO}, energy gap (ΔE) and dipole moment (μ), were used to substantiate the effective adsorption of the blended drugs on anodized surfaces. AFM studies justified the formation of protective layer on anodized metal.

Key words Anodizing, sealing, corrosion

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Introduction

The anodized aluminium is widely used in the fields of aerospace, automobile, electronic products, etc. The life of the anodized film is short due to presence micro pores in the aluminium oxide which pervades the entry of foreign materials, when it is exposed to acidic and hard water media. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of reducing metallic corrosion in aggressive media. Several substituted thiourea and drugs compounds have been investigated as corrosion retarders [1-5] for the aluminium and its alloys. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion reducers for aluminium. The so far reported sealing solution involved the utility of Nickel acetate and rare earth metals which are toxic . The present formulation is absolutely free from rare earth metals , inexpensive, versatile and eco friendly in nature. As far as we know, no systematic approach is available for the corrosion protection of anodized film by blending drugs in sealing agent. The present paper describes a preparation of special sealing agent based on cellulose acetate phthalate (CAP) and Sulfamethoxazole (SM) drugs on corrosion resistance of anodized aluminium in 1N HCl using potentiodynamic polarization and impedance methods. The quantum mechanical descriptors substantiate the performance of the blended drugs in sealing solution by virtue of forming a strong adherent layer on the metal surface.

Materials and Methods

Aluminium specimens of compositions, Cu = 0.15%, Mg = 0.5%, Mn = 0.1%, Si = 0.5%,

Zn = 0.5%, and Aluminium remainder, and of size 5 cm^2 x 0.02cm were used for anodizing and 1cm^2 x 0.02 cm for potentiodynamic polarisation , AC impedance measurements and AFM analysis.

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The aluminium specimens of the above composition was mechanically polished and then degreased with acetone. Then the panels were subjected to anodizing as per the following experimental condition. Anode: Al panels; Cathode: Lead; electrolyte: 0.47M phosphoric acid + 0.04M Acetic acid; current: 5.7 mA cm^{-2}; Time : 15 minutes. Thickness: 40- 50 microns.

Preparation of sealing agent

Exactly (1:1) ratio of A.R grade cellulose acetate phthalate (CAP) and Sulfamethoxazole (SM) drugs were dissolved in 5% sodium diacetate + 5ml of proprietary surfactant and blended well. The mixture was diluted to 500ml and then heated to 80°C. The sealing of anodized film was carried out by immersing the anodized plates into drugs impregnated solution. The duration of sealing process was varied as 10 minutes, 30 min, 45 minutes. After sealing, the plates were removed , washed , dried and characterized using electrochemical techniques. The thickness of the anodized film varies from 30-43µm.

Evaluation anodized film after sealing process

Both cathodic and anodic polarisation curves were recorded in 1NHCl potentiodynamically (sweep rate = 1 mVs^{-1}) using corrosion measurement system BAS Model : 100A , computerised electrochemical analyzer (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil of 4 cm^2 area and Hg/Hg_2Cl_2 /1NHCl were used as auxiliary and reference electrodes, respectively. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_t) were measured using AC impedance measurements (EG&G Princeton Applied research model:7310) as described in an earlier publication[6]. Quantum calculations were performed by adapting Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moment (µ) of the sealing compounds were calculated with the above given computer code package. The surface roughnesses of the anodized films before and after sealing were measured by AFM (Nanosurf easy surf 2).

Results and Discussion

Potentiodynamic polarization studies

Table 1 gives values of corrosion kinetic parameters such as Tafel slopes (ba and bc),corrosion current (Icorr) and corrosion potential (Ecorr) and resistance obtained from potentiodynamic polarization curves for anodized aluminum in 1N HCl after subjected to sealing the coatings at various time intervals. It is established that enhancing the sealing timings improve the values of both anodic and cathodic Tafel slopes to equal extent. After sealing at various time intervals, the resistance of corrosion of anodized aluminium in 1N HCl was found to follow mixed mode of reaction [7-8]. E_{corr} data have been moved to positive direction when sealing compounds were used for corrosion studies. This can be ascribed to the formation of strongly adherent sealing film on the aluminium surface. It was noticed that for anodized films which were subjected to 45 minutes sealing, I_{corr} values were decreased to considerable extent in 1N HCl due to the blocking of micro pores of coatings by sealants.

Impedance measurements

Figure 2 indicates the corrosion protection of anodized aluminium in 1N HCl solution before and after sealing observed at various timings by electrochemical impedance spectroscopy . The values of the charge transfer resistance (R_t) begin to increase with the increasing thickness of anodized film as well as the sealing timings (Table 2) ,while double layer capacitance (C_{dl}) are brought down to significant extent . This can be ascribed to increased adsorption of the sealing drugs on the micro pores of anodized film with respect to sealing intervals [9-10]. In the present study, perfect semi circles are not encountered in Nyquist plots and there is a drag is noted in the semi circles. This may be due to the fact that the corrosion resistance of sealing drugs in anodized film is partially under

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charge transfer and mass transfer control. Similar observation has been made earlier by Karthikeyan et al [11] for the electroless plating process.

AFM studies

Figure 3-6 showed the AFM results of anodized film with and without sealing at various time intervals. The average roughness values of anodized film with and without impregnation of sealants were observed at 950 nm, 350 nm(10 minutes-sealing time), 180 nm (30 minutes) and 130 nm (40 minutes) . The average roughness values of figure 6 (40 minutes) confirm that the surface is smoother than anodized metal with and without sealing at other doping intervals .This can be due to the blockening action of micro pores by sealants.

Quantum mechanical studies

Quantum mechanical calculations were performed to investigate the adsorption and inhibition mechanism of the sealing drugs. Figure 7 (A & B) shows the optimized structure of CAP and SM . The values of calculated quantum chemical parameters i.e. E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment) etc. are summarized in table-3. E_{HOMO} is related to the electron-donating ability of the molecule. In the present investigation, the adsorption of a CMA on anodized surface surface acquired on the basis of donor-acceptor interactions between the π-electrons of heterocyclic ring and carbonyl group of CMA . In the case of sulfamethoxazole, the adsorption sites were sulphoxide group, nitrogen and oxygen of hetero cyclic ring and also the vacant d-orbitals of the aluminum atom of the anodized film . The gap between HOMO–LUMO energy levels of molecules was another important factor that desires to be considered. Higher the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor. A well established fact that higher the values of the dipole interactive moment, greater is the corrosion resistance of the surfaces. Based on the values of ΔE and dipole moment, the compound SM may be firmly adsorbed on aluminum metal than CMA.

Conclusions

A special sealing process for industrial anodized aluminum parts has been formulated as a replacement of sealing solution containing rare earths. The present solution is metal free , inexpensive, versatile and eco friendly in nature. The corrosion resistance of the coatings have been systematically analyzed through electrochemical techniques.AFM studies demonstrated that the optimum sealing time for the coatings was found as 40 minutes. The quantum mechanical measurements confirmed the mere adsorption of the sealing compounds on the anodized coatings. The above investigation reveals that among the sealing compounds used, sulfamethoxazole (SM) adsorbs better than cellulose acetate phthalate (CAP).

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TABLE 1: Potentiodynamic polarization of anodized aluminium. Medium: 1N HCl

Experiment	E_{corr} (mV vs SCE)	I_{corr} ($\mu A cm^{-2}$)	βa (mV dec^{-1})	βc (mV dec^{-1})	IE (%)	θ
Pure Al	-282.14	539.47	72.0	116.4	-	-
10 min	-232.31	110.62	62.1	94.5	79.49	0.79
30 min	-210.63	81.22	51.3	86.2	84.94	0.85
45 min	-189.27	27.58	34.2	78.4	94.88	0.95

TABLE 2: Impedance data for the corrosion inhibition of anodized aluminium. Medium: 1N HCl

Operating conditions	**1N HCl solution**	
	Charge Transfer resistance (R_t) Ohm.cm^2	Double layer capacitance (C_{dl}) $\mu F.cm^{-2}$
No sealing	49	232
Sealing timing		
10 minutes (Thickness-30μm)	144	68
30 minutes (Thickness-40μm)	167	45
45 minutes (Thickness-43μm)	177	28

TABLE 3: Quantum mechanical parameters for sealants on the corrosion of anodized Al

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Cellulose acetate phthalate (CMA)	– .0.434	-7.424	6.99	4.1
Sulfamethoxazole (SM)	-1.199	-9.542	8.343	4.5

Legends for figure

1. Tafel polarisation plots for the corrosion inhibition of anodized aluminium with and without sealing.
2. .Nyquist diagram for the corrosion inhibition of anodized aluminium with and without sealing.
3. AFM images for Anodized Al (No sealing)
4. AFM images for Anodized Al (sealing timing: 10 min)
5. AFM images for Anodized Al (sealing Time :30 minutes)
6. AFM images for Anodized Al (sealing Time :40 minutes)
7. (a) Optimized structure of Cellulose acetate phthalate (CAP) , (b) HOMO view, (c) LUMO view
8. (a) Optimized structure of Sulfamethoxazole [SM] (b) HOMO view

   (c) LUMO view

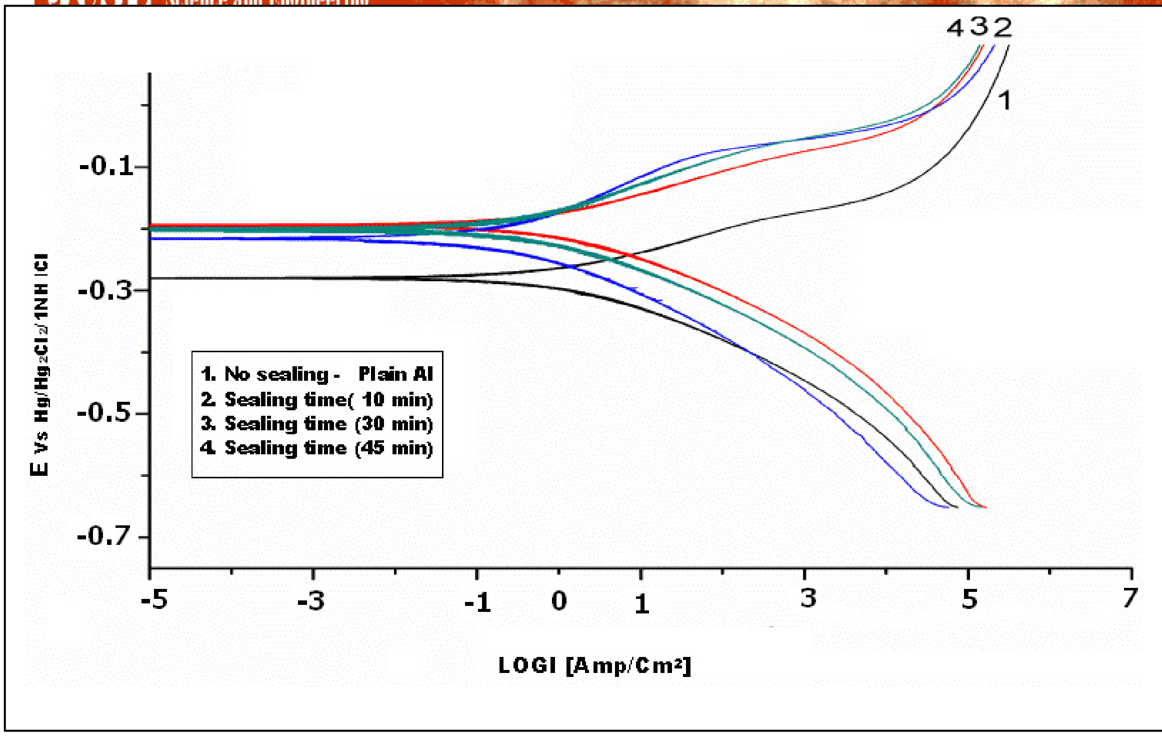


Figure 1

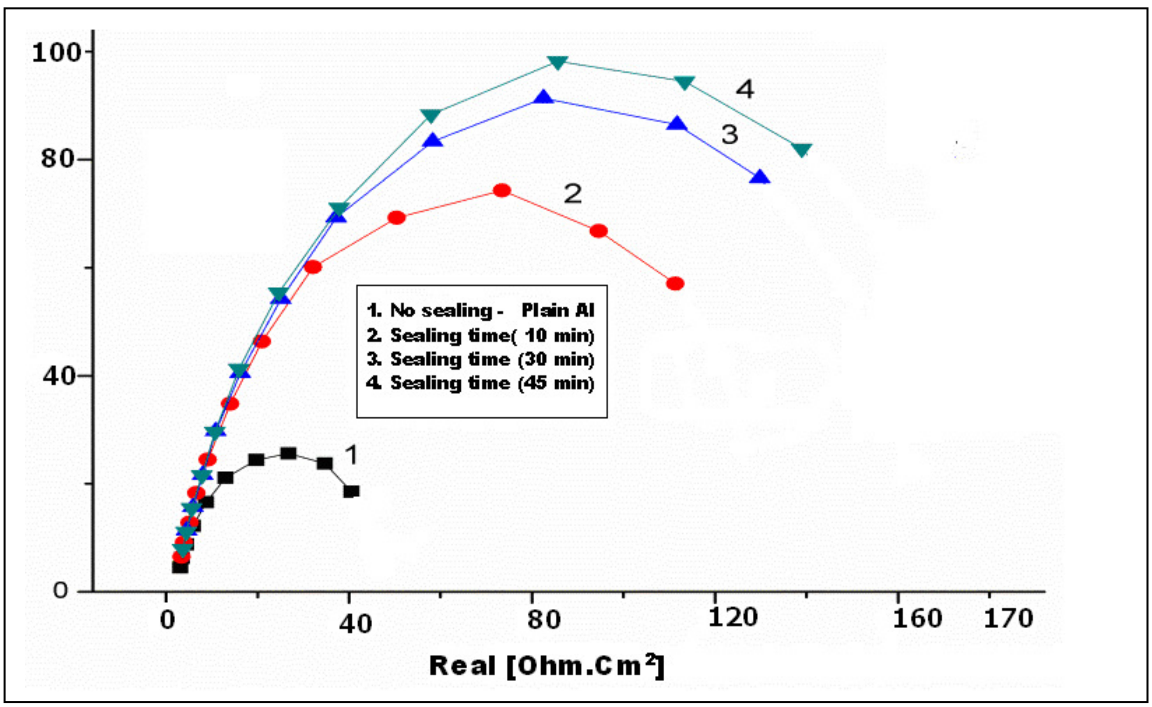


Figure 2

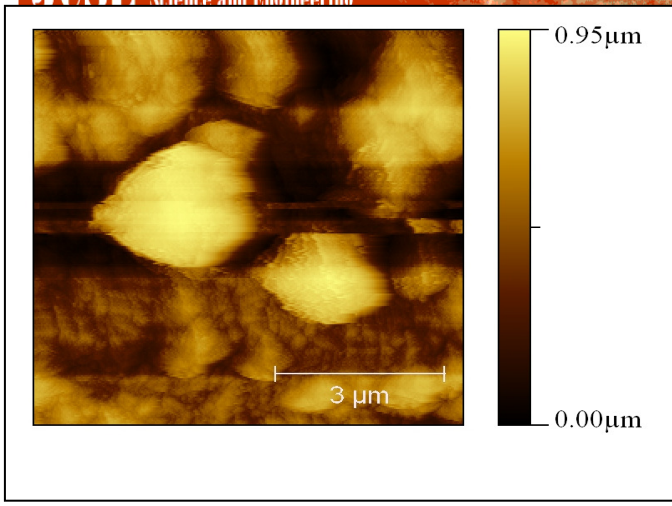


Figure 3

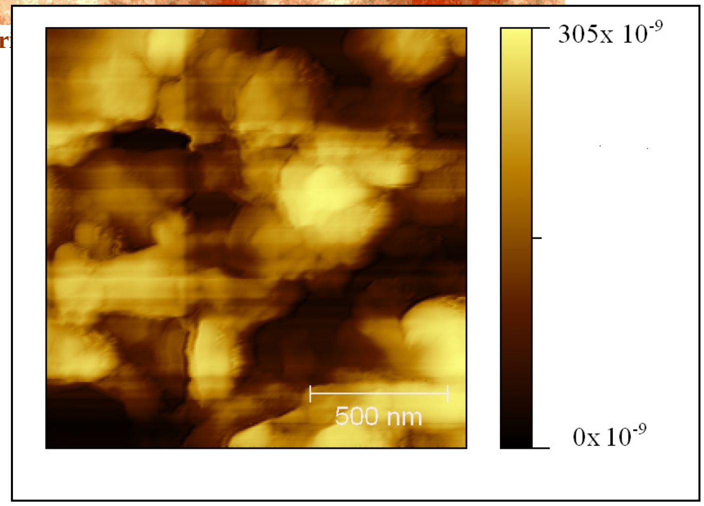
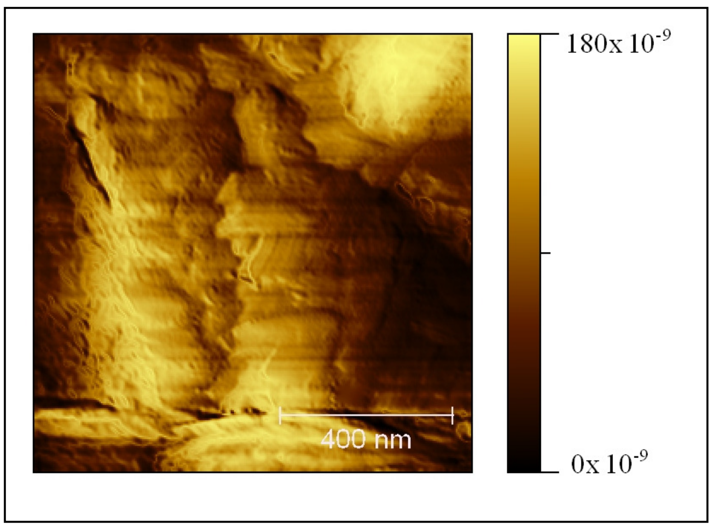


Figure 4



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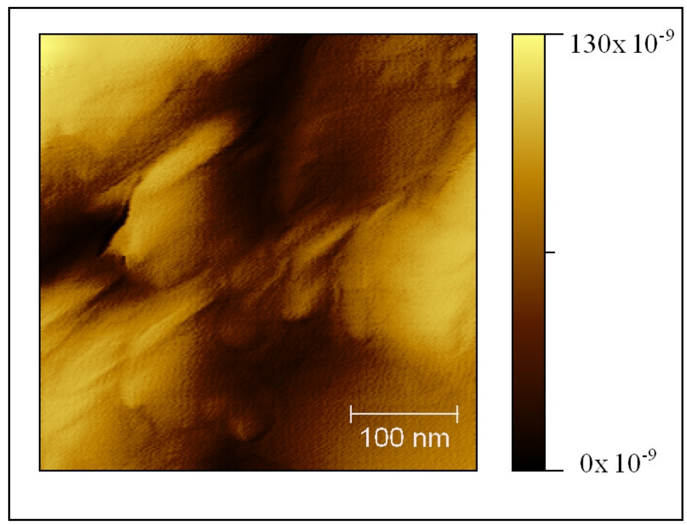

Figure 6

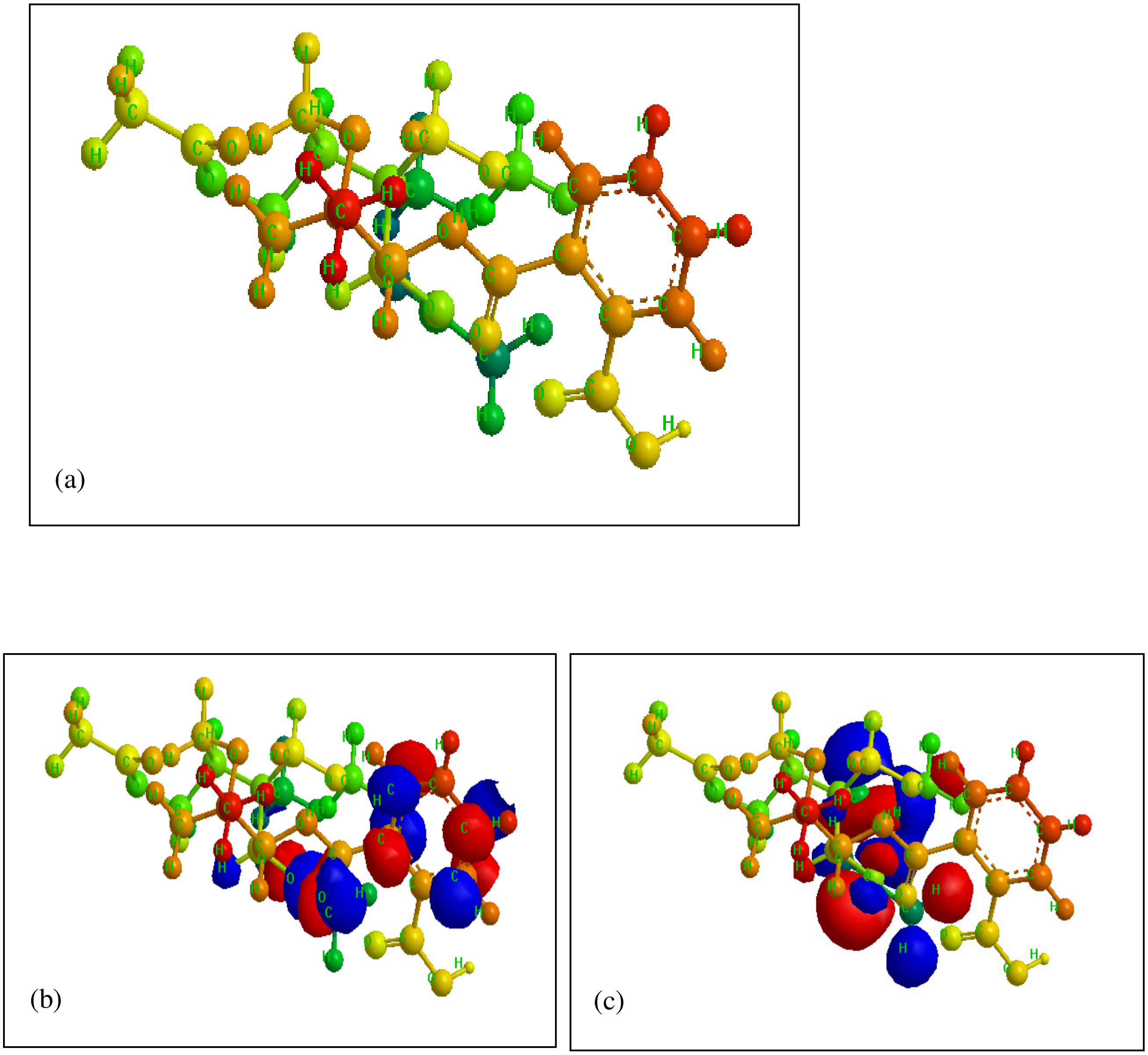

Figure 7

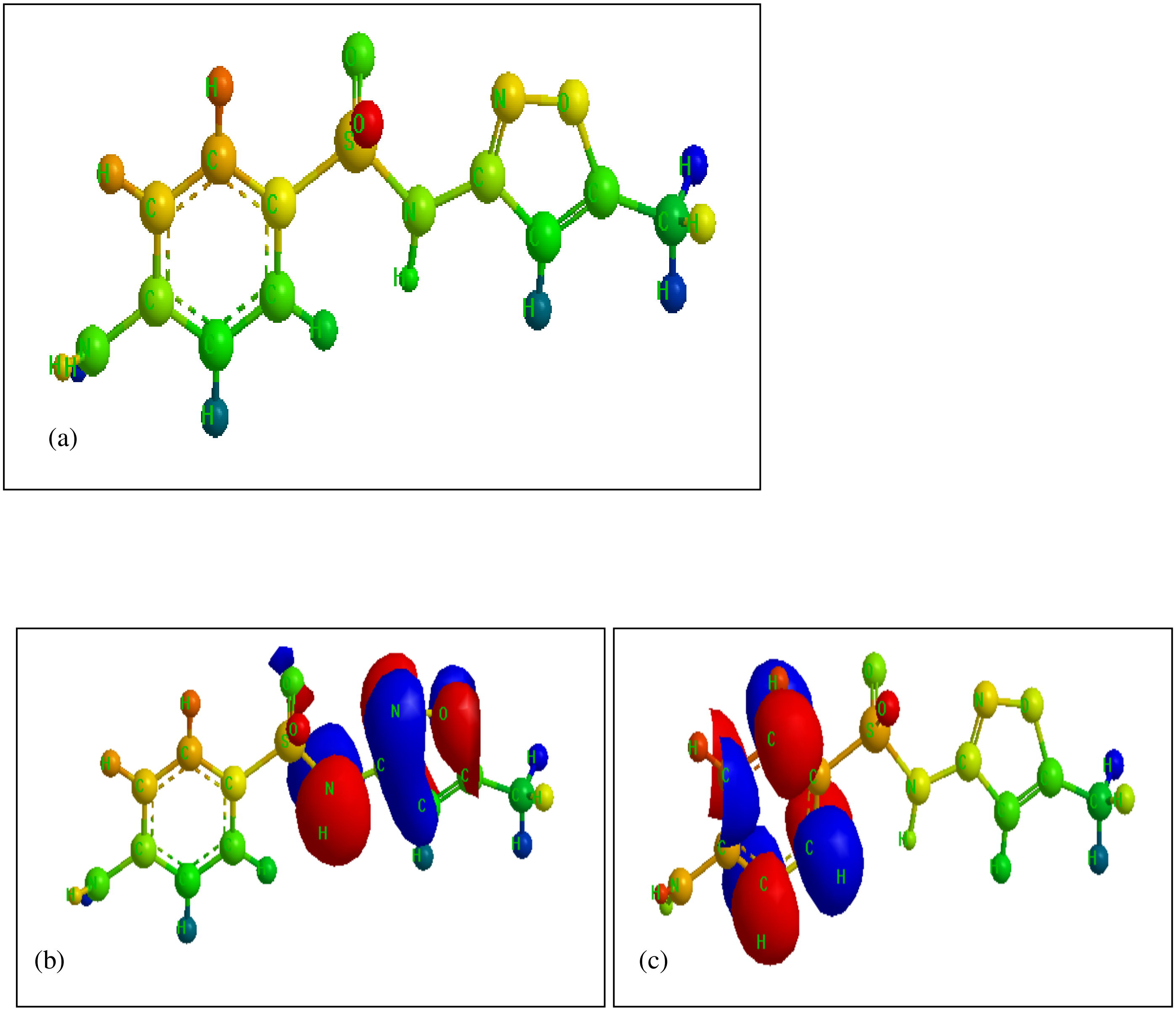

Figure 8