

Corrosion Protection of Epoxy-Coated Stainless Steel by Organic-Coating and Filler Materials

Rajesh Kumar Singh^{1*}, Sabana Latiff² and Manjay Kumar Thakur³

¹Assistant Professor, Department of Chemistry, Jagdam College, J P University Chapra – 841301, India

²Research Scholar, Department of Chemistry, Jagdam College, J P University, Chapra-841301, India

³Research Scholar, Department of Chemistry, Jagdam College, J P University, Chapra-841301, India

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*Corresponding author: Rajesh Kumar Singh, Assistant Professor, Department of Chemistry, Jagdam College, J P University Chapra – 841301, India, E-mail: rks_jpujc@yahoo.co.in

Abstract

Epoxy coating uses for the corrosion protection of stainless steel. Epoxy-coated stainless steel surface has possessed lots of porosities so pollutants and particulates materials are entered inside by osmosis and diffusion process. Pollutants like oxides of carbon, oxides of nitrogen, and oxides of sulphur form acids and they make hostile environment for base metal and epoxy polymer. These acids develop chemical reaction with epoxy-coated stainless steel. They develop corrosion cell with metal and start corrosion reaction. They can produce several forms corrosion like galvanic, pitting, stress, crevice, blistering and embrittlement. Epoxy polymer is shown swelling corrosion. Such types of pollutants are disintegrated metal and polymer and change their physical, chemical and mechanical properties. Weather changes can affect the corrosion rate of materials because the compositions of corrosive substances increase or decrease temperatures of atmosphere, concentration of pollutants, moisture, humidity and acids. They initiate the corrosion of materials. The corrosion protection of epoxy-coated stainless steel was controlled by the application of synthesized decahydrobenzo [8] annulene-5, 10-disemicarbazone and this compound was nanocoated on the surface of epoxy-coated stainless steel. Nanocoating and filler materials were formed composite a thin barrier on the surface of epoxy-coated stainless steel and studied their action in corrosion in hostile environment. Nanocoating work can be completed by the use of nozzle spray and chemical vapor deposition. Thermal parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy were used to study composite film formation. The corrosion rates of materials were calculated by gravimetric method. Surface coverage areas and coating efficiencies were obtained by the help of corrosion rate. Potentiostat used to determine corrosion potential, corrosion current and current density. Experimental observations indicated that composite film barrier was formed decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin which physical, chemical and mechanical properties did not change easily in ambient environment.

Keywords: Hostile environment; corrosion; nanocoating; filler; thermal parameters; composite film barrier;

Introduction

The corrosion of materials is a spontaneously process. It is not fully control but it can be minimized by the application of corrosion protection technique. Epoxy paint is used by automobile industries for corrosion protection. The outer bodies of transport vehicles are made of stainless steel. This metal corrodes in contact of corrosive environment, hence for their protection epoxy-coating is applied on the surface of stainless steel. But this coating cannot protect stainless steel in H₂O, O₂ (moist), CO₂, NO₂ and SO₂ environment. In these environments for the corrosion protection of epoxy-coated stainless steel was used decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin. The synthesized organic compound decahydrobenzo [8] annulene-5, 10-disemicarbazone was nanocoated on the surface of epoxy-coated stainless steel and their porosities were blocked by Tin filler.

Abrasive blasting is a common method of preparing a metal surface for application of an organic coating [1]. The performance of an organic coating/metal [2] substrate system in a corrosive environment depends on the nature of the coating, substrate,

and interface [3] between them. The properties of the interfacial region [4] are influenced by the abrasive blasting process. The corrosion behavior of coated stainless steel [5] is significantly affected by the choice of blasting abrasive and the parameters of the blasting process. They investigate the adhesion of polymer coating [6] systems of the following types: alkyd, acrylic, latex, vinyl, epoxy, coal tar epoxy [7] and a zinc-filled vinyl [8]. For every case zinc-filled vinyl, steel grit abrasive produced the lowest adhesion when compared with based abrasive. The resistance to blistering of both coal tar epoxy and urethane coatings [10] on underground steel storage tanks is more severe for tanks blasted with steel grit than for those blasted with silica sand. The effect of abrasive type on the corrosion rate and cathodic delaminating performance of bare and coated pipeline steel. They found a reduction in the corrosion rate in distilled water and delamination rate of an epoxy powder coating [11] in Cl⁻ ions solution when the steel was abrasively blasted with alumina [12] compared to steel blasted with steel grit. They interpreted the results in terms of a reduction in catalytic efficiency [13] for the operative cathodic reaction for the alumina-blasted surface, and hypothesized doping of the oxide layer on the steel with

aluminum. Cathodic delamination of organic coatings [14] on steel has been widely studied. It is generally believed that the high pH generated by the oxygen reduction reaction at the delaminating front is responsible for the loss of coating adhesion [15]. There are several techniques like metallic and nonmetallic coating, inhibitors action, polymeric coating and paint coating [16] used to control the corrosion. Metallic coating did not provide good protection in presence of atmospheric pollutants. Polymeric coating [17] used in corrosive environment but this coating did not control attack pollutants. They penetrate polymeric barrier and corrode base metal. Its bonding and bond connective disintegrate in this environment. The nitrogen, oxygen and sulphur containing alkane, alkene, alkyne, aromatic and heterocyclic organic compounds [18] applied as inhibitors against pollutants but they are not protecting materials. These corrosion protection techniques did not shave material by attack of biological micro and macroorganism [19]. Particulates are also increasing corrosion of materials for their protection [20] above mention methods is used but they do not give suitable results. Effluents and biowastes corrode materials but their protection above mentioned protection techniques used which do not mitigate corrosion. Mixed types of organic inhibitors used which work as anodic and cathodic protection in ambient environment but these inhibitors become passive in aggressive medium. The purpose of this study is to examine composite thin film formation on the surface epoxy-coated stainless steel by nanocoating compound decahydrobenzo [8] annulene-5, 10-disemicarbazone and filler Tin.

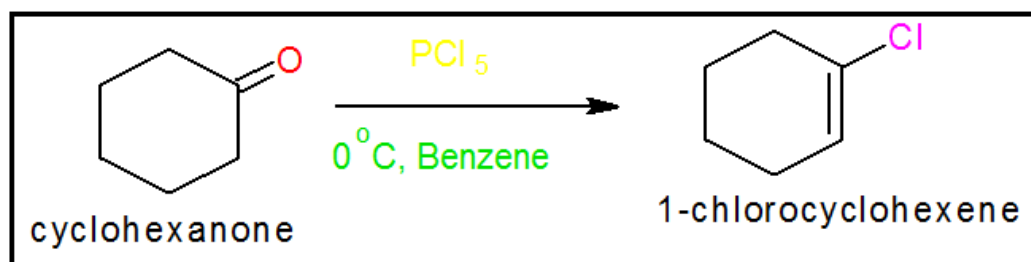
Methodology

Coupons of epoxy-coated stainless steel kept in corrosive environment and their corrosion rate determined at different temperatures, times and weathers as mentioned 2780K, 2830K,

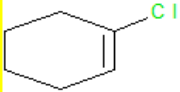
2880K, 2930K and 2980K temperature and time fixed 24, 48, 72, 96 and 120 hours. Epoxy-coated stainless steel was nanocoated with decahydrobenzo [8] annulene-5, 10- disemicarbazone and its corrosion rate calculated at above recorded temperatures and times. Tin filler used on the surface of decahydrobenzo [8] annulene-5, 10-diphenylhydrazone and corrosion rate of material determined above mentioned temperatures and times. These results were obtained by the help of weight loss experiment. Potentiostat 173 model EG & PG Princeton used to measured corrosion potential, corrosion current, current density, anodic and cathodic polarization of epoxy-coated stainless steel, decahydrobenzo [8] annulene-5,10- disemicarbazone-epoxy-coated stainless steel and Tin-decahydrobenzo [8] annulene-5, 10-diphenylhydrazone-epoxy-coated stainless steel. Plasma spray used for nanocoating purpose. The surface adherence properties studied by Arrhenius equation and Langmuir isotherm equation. The composite thin film barrier bonding formation studied by activation energy, heat of adsorption, free energy, enthalpy and entropy. The synthesis process of decahydrobenzo [8] annulene-5, 10- disemicarbazone was given as:

• Scheme1: Synthesis of 1-chlorocyclohexene

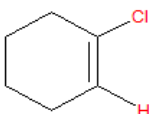
Cyclohexanone (80g) was added in dry benzene (150ml) and reaction mixture was poured drop wise into a cool solution of PCl_5 . The mixture was taken in two necks round bottle flask and stirred for further 3hours and during reaction temperature was maintained 0°C . The product was extracted from ethereal solution and was washed with 5% aqueous Na_2CO_3 then after dried with Na_2SO_4 and solvent removed by application of rotator vapor. The product was purified by column chromatograph by the use of silica gel in petroleum ether. After purification 87% of 1-chlorocyclohexene was obtained.



Physical properties of 1-chlorocyclohexene

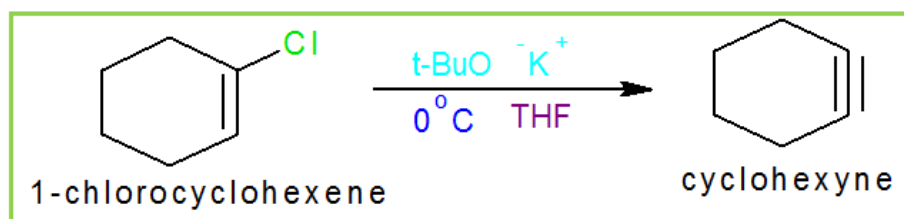
	Molecular Formula	= C ₆ H ₉ Cl
	Formula Weight	= 116.58866
	Composition	= C(61.81%) H(7.78%) Cl(30.41%)
	Molar Refractivity	= 32.29 ± 0.4 cm ³
	Molar Volume	= 113.5 ± 5.0 cm ³
	Parachor	= 263.4 ± 6.0 cm ³
	Index of Refraction	= 1.480 ± 0.03
	Surface Tension	= 29.0 ± 5.0 dyne/cm
	Density	= 1.02 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 12.80 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 116.039278 Da
	Nominal Mass	= 116 Da
	Average Mass	= 116.5887 Da
	M+	= 116.038729 Da
	M-	= 116.039827 Da
	[M+H]⁺	= 117.046554 Da
	[M+H]⁻	= 117.047652 Da
	[M-H]⁺	= 115.030904 Da
	[M-H]⁻	= 115.032002 Da

¹H NMR of 1-chlorocyclohexene


ChemNMR ¹ H Estimation		Estimation quality is indicated by color: good, medium, rough		
	Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):			
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)	
CH2	1.96	1.96	cyclohexene	
CH2	1.99	1.96	cyclohexene	
		0.03	general corrections	
CH2	1.74	1.65	cyclohexene	
		0.09	general corrections	
CH2	1.61	1.65	cyclohexene	
		-0.04	general corrections	
H	5.77	5.59	cyclohexene	
		0.18	1-Cl cis from 1-ethylene	
1H NMR Coupling Constant Prediction				
shift	atom index	coupling partner, constant and vector		
1.96	3	5	7.1	H-CH-CH-H
		8	-1.0	H-CH>C=C>H
1.99	4	8	6.2	H-CH-C(sp ²)-H
		6	7.1	H-CH-CH-H
1.74	5	3	7.1	H-CH-CH-H
		6	7.1	H-CH-CH-H
1.61	6	4	7.1	H-CH-CH-H
		5	7.1	H-CH-CH-H
5.77	8	4	6.2	H-C(sp ²)-CH-H
		3	-1.0	H>C=C>CH-H

Scheme2: Synthesis of cyclohexyne

1-Chlorocyclohexene (57g) was dissolved in THF and potassium t-butoxide (t-BuO⁻K⁺) was added (75g) at room temperature then after cyclohexene (70ml) was mixed into reaction mixture as trapping agent. After completion of reaction water was poured then it quenched with brine solution and reaction mixture was extracted from ether. Finally, the compound was dried with sodium sulphate. Solvent was removed by rotator vapor and target product was purified by silica gel column chromatograph. After purification 83% yield of 1,2,3,4,4a,5,6,7,8,8b-decahydrobipthalene was obtained.



Physical properties of cyclohexyne

	Molecular Formula	= C ₆ H ₂
	Formula Weight	= 80.12772
	Composition	= C(89.94%) H(10.06%)
	Molar Refractivity	= 25.79 ± 0.4 cm ³
	Molar Volume	= 91.7 ± 5.0 cm ³
	Parachor	= 217.9 ± 6.0 cm ³
	Index of Refraction	= 1.474 ± 0.03
	Surface Tension	= 31.8 ± 5.0 dyne/cm
	Density	= 0.87 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 10.22 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 80.0626 Da
	Nominal Mass	= 80 Da
	Average Mass	= 80.1277 Da
	M+	= 80.062052 Da
	M-	= 80.063149 Da
	[M+H] ⁺	= 81.069877 Da
	[M+H] ⁻	= 81.070974 Da
	[M-H] ⁺	= 79.054227 Da
	[M-H] ⁻	= 79.055324 Da

¹H-NMR of cyclohexyne

ChemNMR ¹H Estimation of cyclohexyne

Estimation quality is indicated by color: good, medium, rough

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

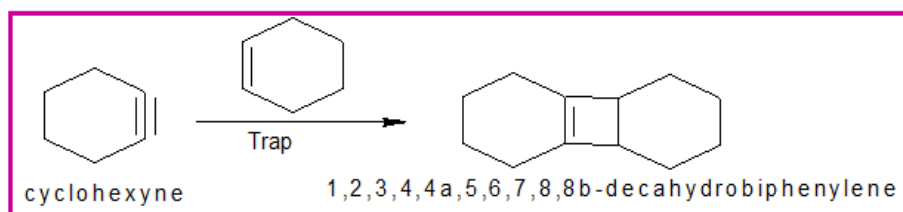
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH2 1.96	1.96	1.37	methylene
		0.65	1 alpha -C+C-C
		-0.06	1 beta -C
CH2 1.96	1.96	1.37	methylene
		0.65	1 alpha -C+C-C
		-0.06	1 beta -C
CH2 1.44	1.44	1.37	methylene
		0.13	1 beta -C+C-C
		-0.06	1 beta -C
CH2 1.44	1.44	1.37	methylene
		0.13	1 beta -C+C-C
		-0.06	1 beta -C

¹H NMR Coupling Constant Prediction

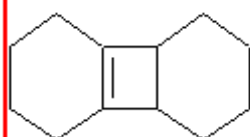
shift	atom index	coupling partner	constant and vector
1.96	3	5	7.1 H-CH-CH-H
		4	2.5 H-CH-C+C-CH-H
1.96	4	6	7.1 H-CH-CH-H
		3	2.5 H-CH-C+C-CH-H
1.44	5	3	7.1 H-CH-CH-H
		6	7.1 H-CH-CH-H
1.44	6	4	7.1 H-CH-CH-H
		5	7.1 H-CH-CH-H

Scheme3: Synthesis of decahydrobiphenylene

Cyclohexene solution poured into cyclohexyne and reaction mixture was stirred one hours then cyclohexene trapped with cyclohexyne to form an adduct of decahydrobiphenylene.

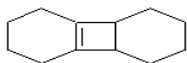


Physical properties of 1, 2, 3, 4, 4a, 5, 6, 7, 8, 8b-decahydrobiphenylene



Molecular Formula	= C ₁₂ H ₁₈
Formula Weight	= 162.27132
Composition	= C(88.82%) H(11.18%)
Molar Refractivity	= 50.88 ± 0.4 cm ³
Molar Volume	= 164.7 ± 5.0 cm ³
Parachor	= 398.2 ± 6.0 cm ³
Index of Refraction	= 1.529 ± 0.03
Surface Tension	= 34.1 ± 5.0 dyne/cm
Density	= 0.98 ± 0.1 g/cm ³
Dielectric Constant	= 2.79 ± 0.2
Polarizability	= 20.17 ± 0.5 10 ⁻²⁴ cm ³
Monoisotopic Mass	= 162.140851 Da
Nominal Mass	= 162 Da
Average Mass	= 162.2713 Da
M+	= 162.140302 Da
M-	= 162.141399 Da
[M+H] ⁺	= 163.148127 Da
[M+H] ⁻	= 163.149224 Da
[M-H] ⁺	= 161.132477 Da
[M-H] ⁻	= 161.133574 Da

¹H-NMR of 1,2,3,4,4a,5,6,7,8,8b-decahydrobiphenylene

ChemNMR ¹H Estimation

Estimation quality is indicated by color: **good**, **medium**, **rough**

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

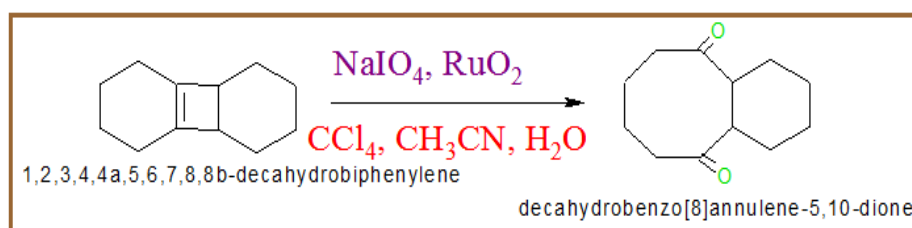
Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
CH	2.15	1.44	cyclohexane
		0.68	1 alpha -C=C from methine
		0.03	1 beta -C=C from methine
CH	2.15	1.44	cyclohexane
		0.68	1 alpha -C=C from methine
		0.03	1 beta -C=C from methine
CH2	1.99,1.890000	1.96	cyclohexene
		-0.02	general corrections
CH2	1.99,1.890000	1.96	cyclohexene
		-0.02	general corrections
CH2	1.41,1.310000	1.44	cyclohexane
		0.00	1 beta -C=C from methylene
		-0.08	general corrections
CH2	1.41,1.310000	1.44	cyclohexane
		0.00	1 beta -C=C from methylene
		-0.08	general corrections
CH2	1.65	1.65	cyclohexene
CH2	1.65	1.65	cyclohexene
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections

1H NMR Coupling Constant Prediction

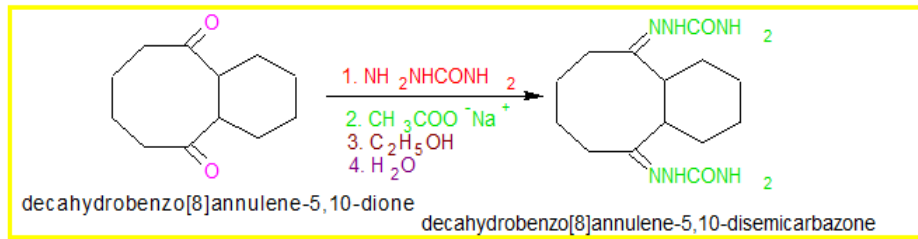
shift	atom index	coupling partner	constant and vector
2.15	7	8	7.0 H-C-C-H
		9	7.0 H-C-C-H
2.15	8	7	7.0 H-C-C-H
		12	7.0 H-C-C-H
1.94	3	5	7.1 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
1.94	4	6	7.1 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
1.36	9	7	7.0 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
1.36	12	10	7.1 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
1.65	5	3	7.1 H-C-H
		6	7.1 H-CH-CH-H
1.65	6	4	7.1 H-CH-CH-H
		5	7.1 H-CH-CH-H
1.48	10	9	7.1 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
1.48	11	11	7.1 H-C-H
		diastereotopic	-12.4 H-CH-CH-H
		12	7.1 H-C-H
		10	7.1 H-CH-CH-H

Scheme4: Synthesis of decahydrobenzo[8]annulene-5,10-dione

1,2,3,4,4a,5,6,7,8,8b-decahydrobiphenylene (78g) was taken and was dissolved with carbon tetrachloride. Sodium periodate (NaIO₄) (58g) was added into reaction mixture, then after methyl nitrile and water was added. The reaction mixture was stirred 24 hours at room temperature. The product was quenched with brine solution then adding sodium bicarbonate workup was completed with ether and ethereal solution dried with sodium sulphate. The target product was purified by silica gel column chromatograph and 76% yield of decahydrobenzo [8] annulene-5, 10-dione was obtained.

**Scheme5:** Synthesis of decahydrobenzo[8]annulene-5,10-disemicarbazone

35g of semicarbazide hydrochloride and 45g of crystallized sodium acetate in 70ml of water was dissolved then 60g of decahydrobenzo [8] annulene-5, 10-dione added and shaken. When the mixture was turbid, alcohol or water was added until clear solution is obtained and again the mixture was shaken for a few minutes and allowed standing. The mixture was warmed on a water bath for 20 minutes and then cooled in ice water. Filtered crystals were washed off with a little cold water and again recrystallized from water or from methanol and got 86% of decahydrobenzo[8] annulene-5,10-disemicarbazone.



Physical properties of decahydro [8] annulene-5, 10-disemicarbazone

Molecular Formula	= C ₁₄ H ₂₀ N ₂ O ₂
Formula Weight	= 310.39524
Composition	= C(54.17%) H(8.44%) N(27.08%) O(10.31%)
Molar Refractivity	= 79.71 ± 0.5 cm ³
Molar Volume	= 207.9 ± 7.0 cm ³
Parachor	= 590.0 ± 8.0 cm ³
Index of Refraction	= 1.692 ± 0.05
Surface Tension	= 64.7 ± 7.0 dyne/cm
Density	= 1.49 ± 0.1 g/cm ³
Dielectric Constant	= Not available
Polarizability	= 31.60 ± 0.5 10 ⁻²⁴ cm ³
Monoisotopic Mass	= 310.211724 Da
Nominal Mass	= 310 Da
Average Mass	= 310.3952 Da
M+	= 310.211176 Da
M-	= 310.212273 Da
[M+H] ⁺	= 311.219001 Da
[M+H] ⁻	= 311.220098 Da
[M+H] ⁺	= 309.20335 Da
[M-H] ⁻	= 309.204448 Da

¹H-NMR of decahydro [8] annulene-5, 10-disemicarbazone

ChemNMR ¹H Estimation

Estimation quality is indicated by color: good, medium, rough

Protocol of the H-1 NMR Prediction (Lib=SU Solvent=DMSO 300 MHz):

Node	Shift	Base + Inc.	Comment (ppm rel. to TMS)
NH	10.55	7.00	hydrazid
		5.60	1 -C=O from sec amine
		-2.05	general corrections
NH	10.55	7.00	hydrazid
		5.60	1 -C=O from sec amine
		-2.05	general corrections
NH2	6.21	6.00	urea
		0.21	general corrections
NH2	6.21	6.00	urea
		0.21	general corrections
CH	2.26	?	1.44 cyclohexane
		?	1 unknown alpha substituent(s) from methine
		?	1 unknown beta substituent(s) from methine
		0.82	general corrections
CH	2.26	?	1.44 cyclohexane
		?	1 unknown alpha substituent(s) from methine
		?	1 unknown beta substituent(s) from methine
		0.82	general corrections
CH2	1.74,1.485000	1.44	cyclohexane
		0.25	1 beta -C=N from methylene
		-0.08	general corrections
CH2	1.74,1.485000	1.44	cyclohexane
		0.25	1 beta -C=N from methylene
		-0.08	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	1.53,1.430000	1.44	cyclohexane
		0.04	general corrections
CH2	2.16,2.060000	1.37	methylene
		0.80	1 alpha -C=N
		-0.06	1 beta -C
CH2	2.16,2.060000	1.37	methylene
		0.80	1 alpha -C=N
		-0.06	1 beta -C

1H NMR Coupling Constant Prediction

shift	atom index	coupling partner	constant	and vector
10.55	14			
10.55	19			
6.21	17			
6.21	22			
2.26	7			
	8	7.0		H-C-C-H
	11	7.0		H-C-C-H
2.26	8	7.0		H-C-C-H
	12	7.0		H-C-C-H
1.61	11 diastereotopic	7.0	-12.4	H-C-H
	7	7.0		H-C-C-H
1.61	12 diastereotopic	7.1	-12.4	H-C-H
	9	7.1		H-C-C-H
1.48	9 diastereotopic	7.0	-12.4	H-C-H
	10	7.1		H-C-C-H
1.48	10 diastereotopic	7.1	-12.4	H-C-H
	11	7.1		H-C-C-H
2.11	2 diastereotopic	7.1	-12.4	H-C-H
	1	7.1		H-C-C-H
2.11	4 diastereotopic	7.1	-12.4	H-C-H
	3	7.1		H-C-C-H
1.56	1 diastereotopic	7.1	-12.4	H-C-H
	2	7.1		H-C-C-H
1.56	3 diastereotopic	7.1	-12.4	H-C-H
	4	7.1		H-C-C-H
	1	7.1		H-C-C-H

XRD of decahydrobenzo [8] annulene-5, 10-disemicarbazone

Results and Discussion

The corrosion rate of metal was calculated in the above mentioned environment in absence and presence of nanocoating and filler compounds at 2780K, 2830K, 2880K, 2930K and 2980K temperatures with help of equation $K = 13.56 W/A D t$ (where, W= weight loss of sample in kg, A= surface area of coupon in square meter, D= density in kg M-3, t= exposure time in hour). The corrosion rate of epoxy-coated stainless steel, nanocoating

and filler compounds were obtained at various 24, 48, 72, 96 and 120 hours and their values recorded in (Table1). (Figure1) indicated that corrosion rate of epoxy-coated stainless steel increased absence of coating as time enhanced but these values reduced in presence of nanocoating and filler compounds. They can be improved the quality of surface and minimized corrosion reaction. Nanocoating and filler materials were formed composite thin film barrier i.e. stopped osmosis or diffusion process of pollutants.

Table1: Nano coating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler use to protect epoxy-coated stainless steel by atmospheric pollutants

NC	Temp(OK)	2780K	2830K	2880K	2930K	2980K	C(mM)
	Times (hrs.)	24	48	72	96	120	
NC(0)	Ko	425	628	738	977	1021	0
	logKo	2.628	2.797	2.868	2.989	3.001	
NC(4)	K	148	74	49	37	27	50
	logK	2.17	1.869	1.69	1.568	1.431	
	log(K/T)	1.615	1.321	1.149	1.035	0.906	
	θ	0.65	0.88	0.93	0.96	0.97	
	log($\theta/1-\theta$)	0.268	0.865	1.12	1.38	1.509	
	%CE	65	88	93	96	97	
NC(TiN)	K	119	59	39	29	24	20
	logK	2.075	1.771	1.591	1.462	1.38	
	log(K/T)	1.52	1.223	1.051	0.929	0.855	
	θ	0.72	0.91	0.95	0.97	0.98	
	log($\theta/1-\theta$)	0.41	1.004	1.278	1.509	1.69	
	%CE	72	91	95	97	98	

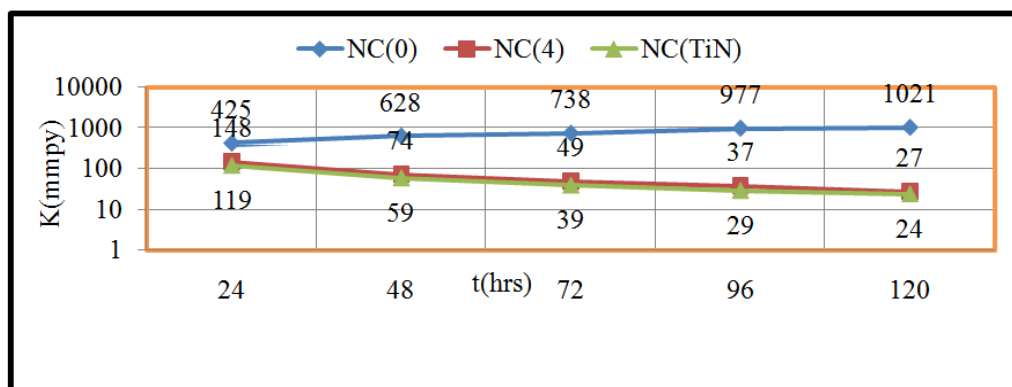


Figure 1: Plot of KVt for epoxy-coated stainless steel with nanocoating of NC (4) & TiN fillerx

The corrosion of epoxy-coated stainless steel logK versus 1/T in absence and presence of nanocoating and filler compound were plotted in (Figure2). (Figure2) reflect that corrosion rate of epoxy-coated stainless steel was higher as temperatures rising from 278 to 2980K. But nanocoating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin reduced corrosion rate as temperatures increased. Such types of trends observed clearly in (Table1). Both compounds were formed stable barrier which suppressed the corrosion of material.

(Figure3) plotted between log ($\theta/1-\theta$) versus 1/T for nanocoated decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler. The values of both the compounds log ($\theta/1-\theta$) at 278 to 2980K were mentioned in (Table1). The results of (Table1) and (Figure 3,4,5) indicate that nanocoating and filler compounds increased the values of log ($\theta/1-\theta$) at different temperatures in H₂O, O₂ (moist), CO₂, NO₂ and SO₂ environment.

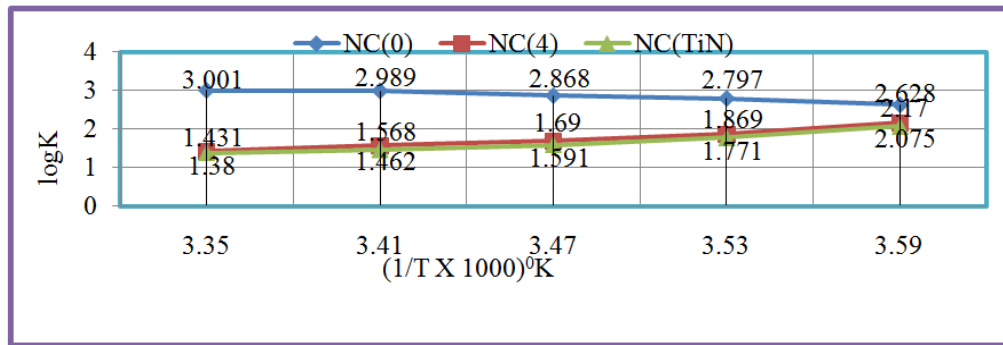


Figure 2: Plot of logK Vs 1/T for epoxy-coated stainless steel with nanocoating of NC (4) & filler TiN

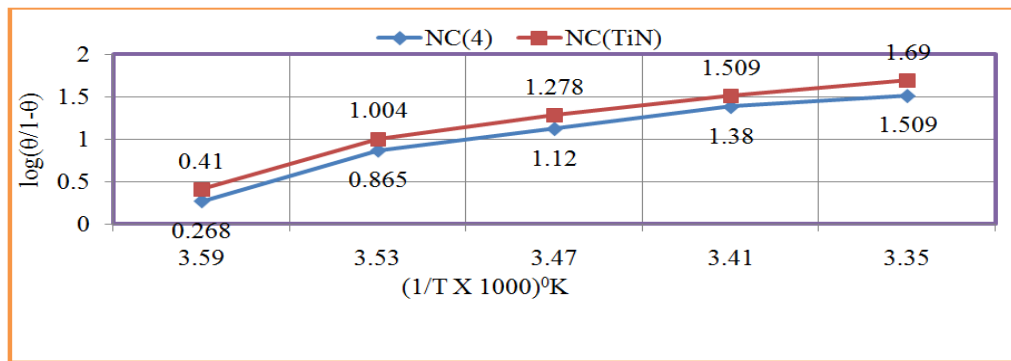


Figure 3: Plot of log(θ/1-θ) Vs 1/T for epoxy-coated stainless steel with nanocoating of NC (4) & filler TiN

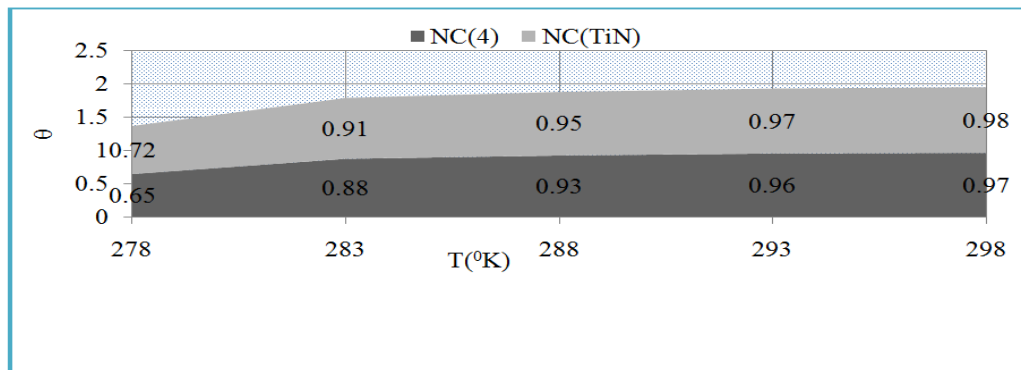


Figure 4: Plot of θ Vs T (°K) for epoxy-coated stainless steel with nanocoating of NC (4) & filler TiN

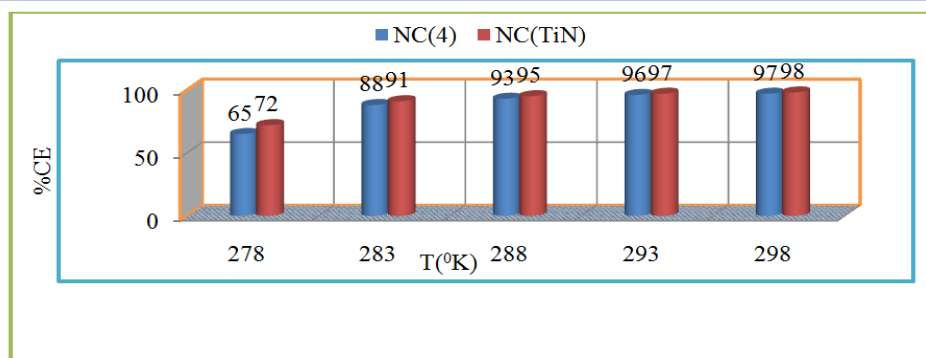


Figure 5: Plot of %CE (coating efficiency) Vs T for stainless steel with nanocoating of NC (4) & filler TiN

(Figure 4) plotted between surface coverage area (θ) versus temperature (T) exhibited surface accommodation properties of nanocoating decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler. Both compounds enhanced surface coverage area at lower to higher temperature. The surface coverage area at different temperatures calculated by equation $\theta = (1-K/K_0)$ and their values were written in (Table 1). Filler Tin increased more surface coverage area which blocked the porosities of nanocoating compound.

(Figure 5) plotted between percentages coating efficiency (%CE) versus temperature (T) at different temperatures for nanocoating and filler compounds. The nature of graph shows that nanocoating decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler rising % coating efficiency at different temperatures. The % coating efficiency at different intervals of temperatures were calculated by equation $\%CE = (1-K/K_0) \times 100$ and their values were mentioned in (Table 1).

(Figure 2) is a straight line Arrhenius plot between $\log K$ versus $1/T$ with help of this figure and Arrhenius equation $d/\ln K = A - E_a/RT$ were calculated activation energy of epoxy-coated stainless steel and nanocoating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler and their values were written in (Table 2,4,5) In all case activation energy found to be positive sign. It was observed that without coating activation energy increased but their values reduced after nanocoating and filler compounds. Both compounds occupied on the surface of epoxy-coated stainless steel by chemical bonding.

(Figure 3) indicated straight line plot between $\log (\theta/1-\theta)$ versus $1/T$ for nanocoating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler and it is a plot of Langmuir isotherm. Heat of adsorption of both nanocoating and filler compounds were determined by equation $\log (\theta/1-\theta) = \log (AC) - (q/2.303 RT)$ and (Figure 3). The values of heat of adsorption are mentioned in (Table 2). Both compounds produced negative sign of energy which confirmed that nanocoating and filler compound formed thin film on the surface of epoxy-coated stainless steel by chemical bonding.

Free energy of nanocoating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler were calculated by equation $-\Delta G = 2.303 \log RT$ and their results were expressed in (Table 2). The negative values of free energy express that nanocoating and filler compounds were adhered with base material by chemical bonding. Free energy results show that coating is an exothermic process.

Enthalpy and entropy of nanocoating of decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler were calculated by transition state equation $K = RT / N h \log (\Delta S^\ddagger / R) \times \log (-\Delta H^\ddagger / RT)$ and (Figure 6) and their values are recorded in (Table 2). These thermal parameters indicated that nanocoating and filler compounds were attached with base material by chemical bonding. Entropy of both the compounds show that nanocoating and filler compounds arranged on the surface of base material in ordered matrix. Thermal values of activation energy, heat of adsorption, free energy, enthalpy and entropy were confirmed

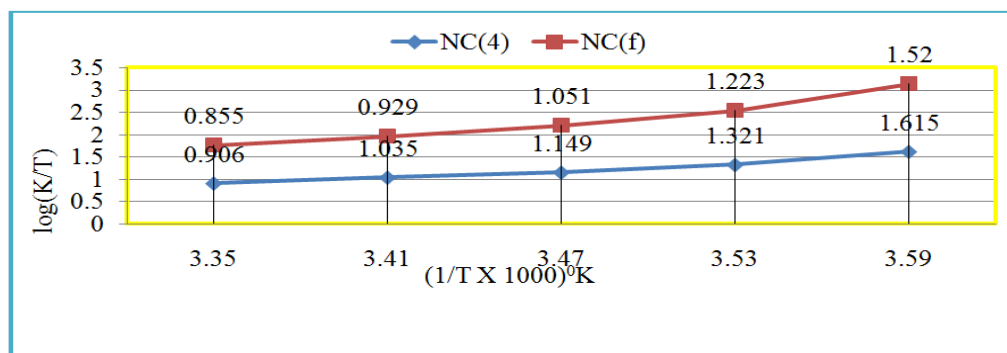


Figure 6: $\log (K/T)$ Vs $1/T$ for epoxy-coated stainless steel with nanocoating of NC (4) & TiN filler

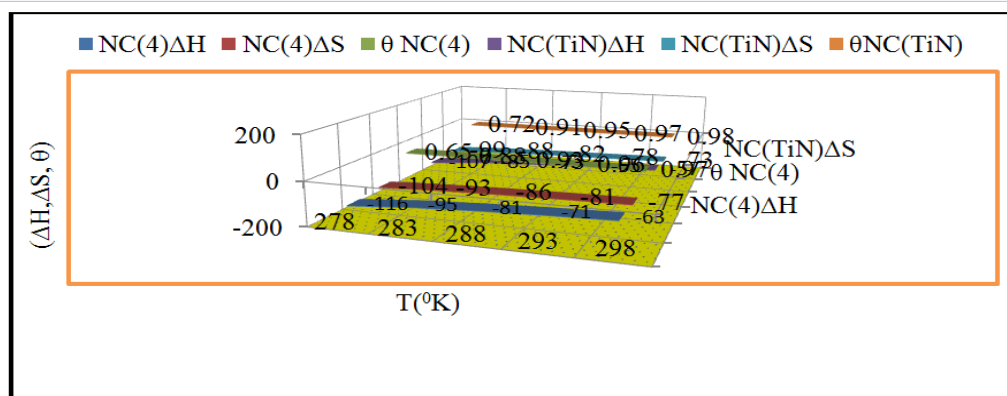


Figure 7: Plot of ΔH , ΔS , θ Vs T for epoxy-coated stainless steel with nanocoating of NC (4) & filler TiN

that decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler were adhered with epoxy-coated stainless steel by chemical bonding. These thermal parameters also noticed that nanocoating and filler compounds formed passive barrier which stable in higher temperature and corrosive medium.

(Figure 7) draws graph between enthalpy (ΔE), entropy (ΔS) and surface coverage area (θ) versus temperatures (T) for decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin in H_2O , O_2 (moist), CO_2 and SO_2 environment. The nature of plot indicate that the values of enthalpy and entropy decreased as temperatures rise which enhanced surface coverage area such results trend were observed in (Table 2).

Table 2: Thermal parameters of nano coating decahydrobenzo [8] annulene-5, 10-disemicarbazone and TiN filler for epoxy-coated stainless steel

Thermal parameters	2780K	2830K	2880K	2930K	2980K
NC(0)Ea	180	191	192	197	195
NC(4) Ea	160	137	122	112	105
NC(4)q	-10.03	-52.74	-70.96	-87.86	-95.42
NC(4) ΔG	-258	-234	-218	-205	-194
NC(4) ΔH	-116	-95	-81	-71	-63
NC(4) ΔS	-104	-93	-86	-81	-77
θ NC(4)	0.65	0.88	0.93	0.96	0.97
NC(TiN)Ea	159	135	121	111	103
NC(TiN)q	-24.79	-63.27	-79.45	-93.21	-101.38
NC(TiN) ΔG	-249	-225	-210	-201	-188
NC(TiN) ΔH	-107	-85	-73	-65	-57
NC(TiN) ΔS	-99	-88	-82	-78	-73
θ NC(TiN)	0.72	0.91	0.95	0.97	0.98

(Figure 8) was a Tafel plot which was drawn between electrode potential (ΔE) versus current density (I) for nanocoating decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler. The corrosion current and corrosion rate of epoxy-coated stainless steel and after nanocoating with decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin were calculated by equation $\Delta E/\Delta I = \beta_a \beta_c / 2.303 I_{corr} (\beta_a + \beta_c)$ and $C. R (mmpy) = 0.1288 I_{corr} (mA/cm^2) \times Eq. Wt (g) / \rho (g/cm^3)$ and their values were mentioned in (Table 3,4,5). The results of (Table 3) and (Figure 7) confirmed that epoxy-coated stainless steel exhibited

more electrode potential and corrosion current when coated with decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin their values were decreased. It was also observed that anodic current increased with epoxy-coated stainless steel whereas cathodic current decreased but nanocoating and filler compounds reduced anodic current and enhanced cathodic current. Potentiostat results show that nanocoating and filler compounds minimized corrosion rate and increased surface coverage area and coating efficiency.

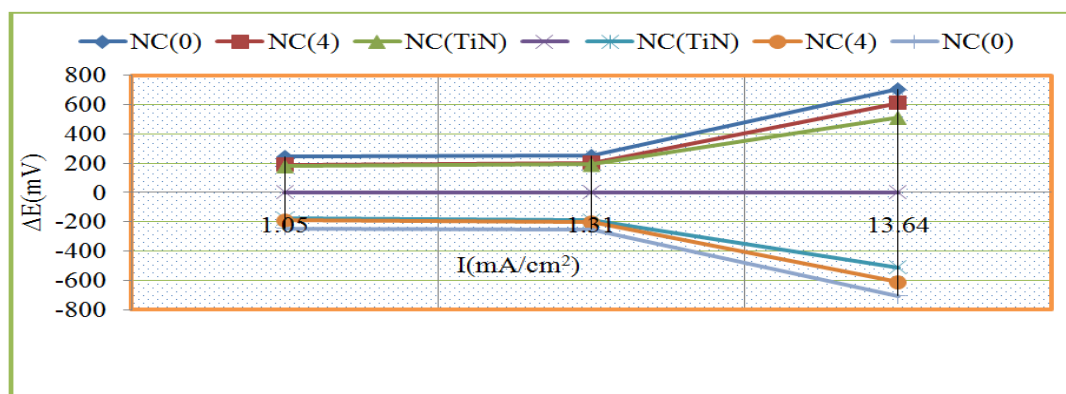


Figure 8: Plot of ΔE Vs I for epoxy-coated stainless steel with nanocoating of NC (4) & filler TiN

Table 3: Potentiostat of nanocoating decahydrobenzo [8] annulene-5, 10-disemicarbazone and TiN filler for epoxy-coated stainless steel

NC	$\Delta E(mV)$	ΔI	β_a	β_c	Icorr(mA/cm ²)	K(mmpy)	θ	%CE	C (mM)
NC(0)	-704	187	295	197	13.64	417	0	0	0
NC(4)	-251	24	35	315	1.31	39	0.91	91	50
NC(TiN)	-244	21	31	320	1.05	31	0.93	93	20

Conclusion

Nanocoating compound decahydrobenzo [8] annulene-5, 10-disemicarbazone and Tin filler were formed composite barrier on the surface of epoxy-coated stainless steel. The results of thermal parameters and coating efficiencies were indicated that composite barrier is stable in corrosive environment. All scientific observations indicate that these nanocoating and filler compounds mitigate corrosion rate. The values of thermal parameters show that they form stable barrier on the surface of base material. It is noticed that these compounds accommodate more surface coverage areas. Composite barrier stops osmosis or diffusion process of pollutants. Nanocoating and filler compounds improve the life of base material and durability.

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References

- Bhadra S, Singha N, Khastgir D. Polyaniline based anticorrosive and anti-molding coating. *Journal of Chemical Engineering and Materials Science*. 2011;2(1):1-11.
- Szabo T, Molnar-Nagy L, Telegdi J, Bognár J, Nyikos L. Self-healing microcapsules and slow release microspheres in paints. *Progress in Organic Coatings*. 2011;72(1-2):52-57.
- Wen NT, Lin CS, Bai CY, Ger MD. Structures and characteristics of Cr (III) based conversion coatings on electro galvanized steels. *Surface and Coatings Technology*. 2008;203(3-4):317-323.
- Boerio FJ, Shah P. Adhesion of injection molded PVC to steel substrates. *J of Adhesion*. 2005;81(6):645-675.
- Deveci H, Ahmetti G, Ersoz M, Kurbanli R. Modified Poly styrenes: Corrosion physico-mechanical and thermal properties evaluation. *Prog Org Coat*. 2012;73(1):1-7.
- Genzer J. Templating Surfaces with Gradient Assemblies. *J of Adhesion*. 2005;81(3-4):417-435.
- Leon-Silva U, Nicho ME. Poly (3-octylthiophene) and polystyrene blends thermally treated as coating for corrosion protection of stainless steel 304. *Journal of Solid State Electrochemistry*. 2010;14(8):1487-1497.
- Baier RE. Surface behaviour of biomaterials: the theta Surface for biocompatibility. *J Mater Sci Mater Med*. 2006;17(11):1057-1062.
- Rao BVA, Iqbal MY, Sreehar B. Electrochemical and surface analytical studies of the self assembled monolayer of 5-methoxy-2-(octadecylthiol) benzimidazole in corrosion protection of copper. *Electrochimica Acta*. 2010;55(3):620-631.
- Liu XY, Ma HY, Zhou M. Self-assembled monolayers of stearic imidazoline on copper electrodes detected using electro chemical measurement, XPS, molecular simulation and FTIR. *Chinese Sci Bull*. 2009;54(3):374-381.
- Liao QQ, Yue ZW, ZHU ZW, WANG Y, ZHANG YZ, Guo-Ding ZQ. Corrosion inhibition effect of self-assembled monolayers of ammonium pyrrolidine dithiocarbamate on copper. *Acta Phys Chin Sin*. 2009;25(8):1655-1661.
- Zhang DQ, He XM, Cai QR, Gao LX, Kim GS. Arginine self-assembled monolayers against copper corrosion and synergetic effect of iodide ion. *Journal of Applied Electrochemistry*. 2009;39(8):1193-1198.
- Sahoo RR, Biswas SK. Frictional response of fatty acids on steel. *J Colloid Interface Sci*. 2009;333(2):707-718.
- Raman A, Gawalt ES. Self-assembled monolayers of alkanolic acid on the native oxide surface of SS316L by solution deposition. *Langmuir*. 2007;23(5):2284-2288.
- Li D, Chen S, Zhao S, Ma H. The corrosion Inhibition of the self-assembled Au and Ag nanoparticles films on the surface of copper. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2006;273(1-3):16-23.
- Cristiani P, Perboni G, Debenedetti A. Effect of chlorination on the corrosion of Cu/Ni 70/30 condenser tubing. *Electrochimica Acta*. 2008;54(1):100-107.
- Cristiani P. Solutions to fouling in power station condensers. *Applied Thermal Engineering*. 2005;25(16):2630-2640.
- Videla HA, Herrera LK. Understanding microbial inhibition of corrosion. A comprehensive overview. *International Biodeterioration & Biodegradation*. 2009;63(7):896-900.
- Bibber JW. Chromium frees conversion coating for zinc and its alloys. *Journal of Applied Surface Finishing*. 2009;2(4):273-275.
- Ghareba S, Omanovic S. Interaction of 12-aminododecanoic acid with a carbon steel surface: Towards the development of 'green' corrosion inhibitors. *Corrosion Science*. 2010;52(6):2104-2113.