

**ZEOLITE/POLYANILINE BASED SELF-HEALING AND SILICON OXIDE
COATINGS FOR MICROBIALLY INDUCED CORROSION INHIBITION**

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“To my beloved ones”

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ABSTRACT

Microbially induced corrosion (MIC) occurs due to the presence of microorganisms such as bacteria, which form biofilms on the metal surface that can cause corrosion. Among the different methods that have been used to protect against MIC, coating has gained more attention because of its ease of application, low-cost and high effectiveness. Recent research has shown that self-healing coatings concept based on releasing healing agent when micro-cracks are initiated in the coating surface and hydrophobic silicon oxide based organic and inorganic coatings have great potential for use as antifouling coating. The aim of this research is to investigate the effects of self-healing and silicon oxide (SiO) coatings on inhibiting MIC in saline environment. The self-healing coating was prepared via interfacial polymerization of zeolite, polyaniline, and zeolite/polyaniline composite and then encapsulated with urea formaldehyde as a shell material to form the microcapsules and embedded in epoxy to form coating material which was applied on mild steel substrate. The SiO coating, on the other hand, was deposited on mild steel substrate using radio frequency (RF) magnetron sputtering physical vapor deposition (PVD) method with different parameters of RF power, temperature, pressure and deposition time in order to achieve optimum parameters based on minimum surface roughness and good adhesion. The surface topography and roughness were examined by atomic force microscope (AFM), while the thickness and morphology of the coatings were observed using field emission scanning electron microscope (FESEM) equipped with energy dispersive spectrometer (EDS). The adhesion test was performed using nano scratch test for SiO coating and Pull off test for self-healing coating and supported by Rockwell C test. The corrosion behavior was investigated through salt spray test for 28 days and immersion tests in nutrient rich simulated seawater (NRSS) medium with *pseudomonas aeruginosa* bacteria for 70 days. The *Tafel* electrochemical test and electrochemical impedance spectroscopy (EIS) was performed on both bare and coated steel samples. AFM results clearly revealed that by varying the sputtering parameters has a strong influence on the surface roughness of the deposited SiO coating in which its thickness varied between 30 nm to 50 nm. The thickness for self-healing coating was between 50 μm to 175 μm . From the adhesion results, both coating methods produced superior adhesion on steel substrates. Fourier transform infrared spectroscopy (FTIR) results show the successful encapsulation of the three synthesized materials. The total self-healing occurred after the release of the core material when the capsule was ruptured after 21 days left at room temperature. The specimen exposed in salt spray chamber exhibited excellent corrosion resistance for all investigated coating materials, while, the specimens immersed in NRSS medium with *pseudomonas aeruginosa* bacteria showed varying anti-corrosion properties. *Tafel* results show that the lowest corrosion rate was observed for SiO coating with a value of 0.219 mm/yr, followed by encapsulated zeolite/polyaniline composite self-healing embedded in epoxy of 0.334 mm/yr. EIS results show that among all the coatings, encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating has the highest impedance modulus (Z) at a frequency of 0.01 of 7800 ohms. In conclusion, zeolite/polyaniline composite self-healing coating is the best among all the coating materials which shows superior anticorrosive and MIC inhibition property.

ABSTRAK

Kakisan dipengaruhi mikrob (MIC) berlaku disebabkan oleh kehadiran mikroorganisma seperti bakteria, yang membentuk biofilem pada permukaan logam yang boleh menyebabkan kakisan. Terdapat kaedah berbeza yang telah digunakan untuk melindungi permukaan daripada MIC, kaedah salutan yang menjadi perhatian kerana mudah untuk digunakan, kos yang rendah dan keberkesanan yang tinggi. Kajian terkini menunjukkan bahawa konsep penyembuhan sendiri salutan melalui melepaskan ejen-ejen penyembuhan apabila retakan mikro bermula di permukaan lapisan dan silikon oksida (SiO) hidrofobik berasaskan lapisan organik dan bukan organik mempunyai potensi yang besar untuk digunakan sebagai salutan anti-cemar. Tujuan kajian ini adalah untuk mengkaji kesan salutan penyembuhan sendiri dan salutan silikon oksida (SiO) bagi menghalang kesan MIC dalam persekitaran masin. Lapisan penyembuhan sendiri telah disediakan melalui pempolimeran antara muka dengan menggunakan zeolit, polyanilina dan komposit zeolit/polianilina dan kemudian disalut dengan urea formaldehid sebagai cengkerang untuk membentuk kapsul mikro yang dimasukkan ke dalam epoksi untuk membentuk salutan yang digunakan pada permukaan keluli. Manakala lapisan SiO telah disadur pada permukaan keluli sederhana menggunakan frekuensi radio (RF) kaedah penganapan wap fizikal (PVD) permercikan magnetron dengan parameter kuasa RF, suhu, tekanan dan masa pemendapan untuk mencapai parameter optimum berdasarkan kekasaran permukaan minimum dan lekatan yang baik. Topografi permukaan dan kekasaran telah diuji dengan mikroskop daya atom (AFM), manakala ketebalan dan morfologi lapisan dianalisis menggunakan mikroskop elektron imbasan medan pancaran (FESEM) yang dilengkapi dengan spektroskopi tenaga-serakan sinar-x (EDS). Ujian rekatan dilakukan dengan menggunakan ujian calar nano untuk lapisan SiO dan ujian tarikan untuk salutan penyembuhan sendiri dan disokong dengan ujian kekerasan *Rockwell C*. Kadar kakisan ditentukan melalui ujian semburan garam selama empat minggu dan ujian rendaman di dalam larutan nutrien air laut simulasi (NRSS) dengan *Pseudomonas aeruginosa* bakteria selama 10 minggu. Ujian elektrokimia *Tafel* dan spektroskopi impedans elektrokimia (EIS) telah dilakukan ke atas kedua-dua sampel keluli dan keluli tersalut. Keputusan AFM jelas menunjukkan bahawa dengan parameter pemercikan yang berbeza-beza memberi pengaruh yang besar ke atas kekasaran permukaan salutan SiO yang dianapkan dengan tebal yang berbeza diantara 30 hingga 50 nm. Ketebalan untuk lapisan pemulihan sendiri adalah antara 50 hingga 175 mikron. Daripada keputusan ujian rekat, kedua-dua kaedah salutan telah menghasilkan rekatan yang baik pada substrak keluli. Spektroskopi Fourier penjelmaan inframerah (FTIR) menunjukkan keputusan terbaik bagi ketiga-tiga bahan mikro kapsul yang disintesis. Penyembuhan penuh terjadi selepas pembebasan bahan teras apabila kapsul pecah selepas 21 hari dibiarkan pada suhu bilik. Spesimen ujian semburan garam menunjukkan ketahanan kakisan yang sangat baik untuk semua bahan salutan manakala, spesimen ujian rendaman dalam NRSS dengan bakteria *Pseudomonas aeruginosa* menunjukkan pelbagai ciri-ciri anti-kakisan. Keputusan ujian *Tafel* menunjukkan bahawa kadar kakisan terendah telah diperhatikan untuk salutan SiO dengan nilai 0.219 mm/tahun, diikuti salutan penyembuhan sendiri komposit zeolit/ polianilina di dalam epoksi dengan nilai 0.334 mm/tahun. Keputusan EIS menunjukkan bahawa di kalangan semua salutan, salutan penyembuhan sendiri komposit zeolit/ polianilina di dalam epoksi mempunyai modulus impedans (Z) yang tertinggi pada frekuensi 0.01 daripada 7800 ohms. Sebagai kesimpulan, salutan penyembuhan sendiri komposit zeolit/ polianilina adalah yang terbaik dikalangan semua bahan salutan, iaitu menunjukkan anti-kakisan dan sifat perencatan MIC yang unggul.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xv
	LIST OF FIGURES	xvii
	LIST OF ABBREVIATIONS	xxi
	LIST OF APPENDICES	xxii
1	INTRODUCTION	1
	1.1 Research Background	1
	1.2 Problem Statement	3
	1.3 Objectives of Research	4
	1.4 Scope of Research	5
	1.5 Significance of Research	5
2	LITERATURE REVIEW	7
	2.1 Introduction	7
	2.2 Corrosion	8
	2.3 Microbial-Induced Corrosion and Biofouling	12
	2.3.1 Bacteria	15
	2.3.1.1 Gram Positive Bacteria	16

2.3.1.2	Gram Negative Bacteria	16
2.3.2	Biofilm	17
2.3.3	Differential Aeration Cell	19
2.3.4	Corrosion Causing Bacteria	19
2.4	Mechanisms of Microbial-Induced Corrosion of Steel	20
2.4.1	Microbial-induced Corrosion due to Anaerobic Bacteria	21
2.4.1.1	Sulphate Reducing Bacteria	21
2.4.1.2	Iron Reducing Bacteria	23
2.4.2	Microbial-Induced Corrosion System Resulting from Aerobic Bacteria	24
2.4.2.1	Metal Oxidizing Bacteria	24
2.4.2.2	Slime Former Bacteria	25
2.4.3	Microbial-Induced Corrosion Mechanism through Extracellular Polymeric Substances -Metal Interaction	26
2.5	Microbial-Induced Corrosion Caused by Pseudomonas aeruginosa Bacteria	27
2.5.1	Pseudomonas aeruginosa	27
2.5.1.1	The Interaction of EPS of Pseudomonas aeruginosa with Steel	28
2.5.1.2	Function of Siderophore Produced by Pseudomonas aeruginosa in Iron Reduction	29
2.5.2	Microbial-Induced Corrosion of Steels in Presence of Pseudomonas aeruginosa	30
2.6	Microbial-Induced Corrosion Inhibition Methods	38
2.6.1	Antibacterial Coatings	39
2.6.1.1	Contact-Killing Strategy	40
2.6.1.2	Adhesion-Resistance Strategy	41
2.6.1.3	Biocide-Leaching Strategy	45
2.6.2	Bi-functional Antibacterial Strategy	46
2.6.2.1	Adhesion Resistance-Biocide Leaching	47

	2.6.2.2	Biocide Leaching-Contact Killing	48
	2.6.2.3	Contact Killing -Adhesion Resistance	49
2.7		Methods of Coatings Application	49
2.8		Coatings to Inhibit Microbial-induced Corrosion in Marine Environment	52
	2.8.1	Self-healing Coatings	53
	2.8.2	Micro or Nanocapsules Embedment	53
	2.8.3	Micro or Nano-capsules Synthesis	54
	2.8.4	Self-Healing Coatings as Anti-Fouling and Corrosion Resistance Material	57
	2.8.5	Zeolite, Polyaniline and Zeolite/Polyaniline Composite for Anti-Fouling Applications	59
2.9		Physical Vapor Deposition Coatings (PVD)	63
	2.9.1	Vacuum Evaporation	64
	2.9.2	Sputter Deposition	64
	2.9.3	Ion Plating	65
	2.9.3.1	Cathodic Arc Deposition	66
	2.9.3.2	Electron Beam Physical Vapor Deposition	66
	2.9.3.3	Evaporative Deposition	67
	2.9.3.4	Pulsed Laser Deposition (PLD)	67
	2.9.3.5	Sputter Deposition	68
	2.9.4	Silicon Oxide as an Antifouling Coating	68
2.10		Summary	69
3		RESEARCH METHODOLOGY	71
	3.1	Introduction	71
	3.2	Preparation of Substrate Material	73
	3.3	Preparation of Self-Healing Coatings	73
	3.3.1	Synthesis of the Core Materials	73
	3.3.1.1	Functionalization of Zeolite	74
	3.3.1.2	Synthesis of Polyaniline	75

3.3.1.3	Synthesis of Zeolite/Polyaniline Composite	76
3.3.2	Preparation of Microcapsules Containing Core Material (Zeolite, Polyaniline or Zeolite/Polyaniline Composite)	79
3.4	Coating Process of Self-Healing Material	81
3.5	Silicon Oxide Coating by Radio Frequency (RF) Magnetron Sputtering	82
3.5.1	Physical Vapor Deposition Parameters	83
3.5.2	Deposition Process of Silicon Oxide Coating by RF Magnetron Sputtering Physical Vapor Deposition	83
3.6	Preparation of the Nutrient Rich Simulated Seawater (NRSS) Medium	85
3.7	Bacterial Inoculation in the Nutrient Rich Simulated Seawater (NRSS) Medium	86
3.8	Corrosion Test	88
3.8.1	Immersion Test	89
3.8.2	Electrochemical Test	91
3.8.3	Salt Spray Corrosion Test	93
3.9	Characterization Techniques	93
3.9.1	Analysis by Electron Microscopy (FESEM and TEM)	95
3.9.2	Analysis by X-Ray Diffractometry (XRD Analysis)	95
3.9.3	Analysis by Fourier Transform Infrared Spectroscopy (FTIR)	96
3.9.4	Differential Scanning Calorimetry (DSC)	96
3.9.5	Analysis by Atomic Force Microscopy (AFM)	97
3.10	Mechanical Testing	97
3.10.1	Rockwell C Adhesion Test for SiO ₂ Coating	97
3.10.2	Nano-Scratch Test for SiO ₂ Coating	98
3.10.3	Pull off Adhesion Test for Self-Healing Coatings	98

4	RESULTS AND DISCUSSIONS	100
4.1	Introduction	100
4.2	Microbial-Induced Corrosion Behaviour of Bare Mild Steel Substrate in NRSS Solution	101
4.2.1	Visual Inspection	105
4.2.2	Observation Using Electron Microscope	106
4.2.3	Determination of Corrosion Rate	117
4.3	Effects of Self-Healing Coatings on the Microbial-Induced Corrosion Behaviour of Mild Steel	120
4.3.1	Self-healing Coating with Zeolite Microcapsules	121
4.3.1.1	Microstructures and Properties of Encapsulated Zeolite Self-healing Embedded in Epoxy Coating	121
4.3.1.2	Adhesion Property of Encapsulated Zeolite Self-healing Embedded in Epoxy Coating	125
4.3.1.3	Performance of Encapsulated Zeolite Self-healing Embedded in Epoxy Coating	127
4.3.1.4	Corrosion Behaviour of Encapsulated Zeolite Self-healing Embedded in Epoxy Coating in 3.5% NaCl Solution	130
4.3.1.5	Microbial-Induced Corrosion Behaviour of Encapsulated Zeolite Self-healing Embedded in Epoxy Coating	136
4.3.2	Self-healing Coating with Polyaniline Microcapsules	142
4.3.2.1	Microstructures and Properties of Encapsulated Polyaniline Self-healing Embedded in Epoxy Coating	143

4.3.2.2	Adhesion Property of Encapsulated Polyaniline Self-healing Embedded in Epoxy Coating	147
4.3.2.3	Performance of Encapsulated Polyaniline Self-healing Embedded in Epoxy Coating	149
4.3.2.4	Corrosion Behaviour of Encapsulated Polyaniline Self-healing Embedded in Epoxy Coating in 3.5 % NaCl Solution	152
4.3.2.4	Microbial-Induced Corrosion Behaviour of Encapsulated Polyaniline Self healing Embedded in Epoxy Coating	158
4.3.3	Self-healing Coating with Zeolite/Polyaniline Composite Microcapsules	165
4.3.3.1	Microstructures and Properties of Encapsulated Zeolite/Polyaniline Composite Self-healing Coating	166
4.3.3.2	Adhesion Property of Encapsulated Zeolite/ Polyaniline Composite Self-healing Embedded in Epoxy Coating	170
4.3.3.3	Performance of Encapsulated Zeolite/ Polyaniline Composite Self-healing Embedded in Epoxy Coating	172
4.3.3.4	Corrosion Behaviour of Encapsulated Zeolite/ Polyaniline Composite Self-healing Embedded in Epoxy Coating in 3.5% NaCl Solution	175

4.3.3.5	Microbial-Induced Corrosion Behaviour of Encapsulated Zeolite/ Polyaniline Composite Self-healing Embedded in Epoxy Coating	181
4.4	Effects of Silicon Oxide Coating on the Microbial-Induced Corrosion Behaviour of Mild Steel	188
4.4.1	Effect of Radio Frequency (RF) on Surface Roughness and Adhesion on Silicon Oxide Coating on Mild Steel	188
4.4.1.1	Phase Analysis using X-ray Diffraction (XRD)	188
4.4.1.2	Topography and Surface Roughness	190
4.4.1.3	Top Surface Analysis by EDS and FESEM	192
4.4.1.4	Adhesion Test Result Analysis	194
4.4.2	Effect of Temperature on Surface Roughness and Adhesion on Silicon Oxide Coating on Mild Steel	198
4.4.2.1	Phase Analysis using X-ray Diffraction (XRD)	198
4.4.2.2	Topography and Surface Roughness	200
4.4.2.3	Top Surface Analysis by FESEM	202
4.4.2.4	Adhesion Test Result Analysis	203
4.4.3	Effect of Pressure on Surface Roughness and Adhesion on Silicon Oxide Coating on Mild Steel	206
4.4.3.1	Phase Analysis using X-ray Diffraction (XRD)	206
4.4.3.2	Topography and Surface Roughness	207
4.4.3.3	Top Surface Analysis by FESEM	210
4.4.3.4	Adhesion Test Result Analysis	211
4.4.4	Effect of Deposition Time on Surface Roughness and Adhesion on Silicon Oxide Coating on Mild Steel	213

4.4.4.1	Phase Analysis using X-ray Diffraction (XRD)	214
4.4.4.2	Topography and Surface Roughness	215
4.4.4.3	Top Surface Analysis by FESEM	217
4.4.4.4	Adhesion Test Result Analysis	218
4.4.5	Corrosion Behaviour of Silicon Oxide Coating in 3.5% NaCl Solution	223
4.4.6	Microbial-Induced Corrosion Behavior of Silicon Oxide Coating Using PVD	228
4.5	Summary	233
5	CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK	244
5.1	Introduction	244
5.2	Recommendations for Future	247
	REFERENCES	248
	Appendices A - C	269 - 272

LIST OF TABLES

TABLE NO	TITLE	PAGE
2.1	Industries known to be influenced by MIC	13
2.2	Occurrence of MIC in energy plants	14
2.3	Common microorganisms which caused MIC	15
2.4	Common properties of silicon oxide coating by PVD	69
3.1	Variable parameters used in the RF magnetron sputtering PVD method	83
3.2	PVD parameters with different values of RF power for silicon oxide deposition on mild steel substrate	84
3.3	PVD parameters with different values of Temperature on mild steel substrate	84
3.4	PVD parameters with different values of pressure on mild steel substrate	85
3.5	PVD parameters with different values of deposition time on mild steel substrate	85
3.6	NRSS medium components in 1 liter of distilled water	86
3.7	Types of samples used for immersion test	89
3.8	Salt spray test samples and parameters	93
4.1	Chemical composition of mild steel substrate	101
4.2	Weight loss of uncoated mild steel substrate immersed in sterile medium	117

4.3	Weight Loss of uncoated mild steel substrate immersed in bacteria-inoculated medium	117
4.4	Weight loss of bare mild steel substrate after salt spray test	119
4.5	Average surface roughness (<i>Ra</i>) for different RF values for carbon steel substrates coated with silicon oxide	192
4.6	Average surface roughness (<i>Ra</i>) for different temperature oh the PVD process for silicon oxide coating,	202
4.7	Average surface roughness (<i>Ra</i>) for different pressures for carbon steel substrates coated with SiO	210
4.8	Average surface roughness (<i>Ra</i>) for different deposition time values for carbon steel substrates coated with SiO	217

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	A schematic diagram of how coating minimizes the bacterial adhesion on the metal surface	8
2.2	A typical corrosion in pipeline system	9
2.3	Free energy curve of the metal in diverse forms	9
2.4	Refining corrosion cycle	10
2.5	Schematic of the electrochemical character of oxidization reaction in acidic environment	11
2.6	Schematic of the electrochemical character of oxidization procedure in alkyd environments	11
2.7	Diagrammatic summary of the various types of corrosion	12
2.8	Schematic of biofilm formation stages	17
2.9	Schematic demonstration of the cathode depolarization response of a ferrous substance in an oxygenated biofilm presence	18
2.10	Schematic of differential cell	19
2.11	Sulphate-reducing bacteria (anaerobic bacteria)	22
2.12	Cathodic depolarization of iron resulting from SRB	23
2.13	Schematic of corrosion reaction under tubercles created by metal-depositing bacteria	25
2.14	<i>Pseudomonas aeruginosa</i> (aerobic bacteria)	27
2.15	Chemical arrangement of pyochelin, the siderophore of <i>P. aeruginosa</i>	30

2.16	Atomic energy microscopy pictures of the presence of pits on the oxidized stainless steel surfaces 304 coupon following dissimilar exposure periods: (a) 14 days, (b) 28 days, and (c) 49 days	31
2.17	Tafel plots for the coupon 304 SS surfaces in existence of <i>Pseudomonas</i> -inoculated medium after (a) short-term exposure of 7, 14, 21, and 35 days, and (b) long-term exposure of 49, 63, and 77 days	32
2.18	SEM micrograph and EDX spectra of the pits created on the coupon 304 S surfaces in existence of <i>Pseudomonas</i> bacteria after 28 days of exposure	33
2.19	Atomic force microscopy micrographs of biofilm layer created on bare substrates of 304 SS following (a) 3 days, 7days, (c) 14 days, (d) 28 days and (e) 42 days in <i>Pseudomonas</i> medium	35
2.20	Atomic force microscopy micrographs of pits formed on 304 SS substrates (a) 14 days and (b) 49 days of exposure into <i>Pseudomonas</i> medium	36
2.21	(a) AFM micrograph of pitting damage following 49 days of exposure with microorganism NRSS inoculated matrix; (b) SEM micrograph of biofilm layer of <i>P. aeruginosa</i> created on the 304 substrate of stainless steel following 21 days of exposure in bacteria inoculated NRSS medium	38
2.22	The main strategies to combat antimicrobial surface	39
2.23	The adhesion of bacteria and biofilm formation on the metal surface	41
2.24	Schematic of Hydrophobic marine antifouling coating approach	44

2.25	Schematic of self-healing process: (a) Self-healing coating containing microencapsulated catalyst (yellow) and phase-separated healing agent droplets (blue) in a matrix (light orange) on a metallic substrate (grey); (b) Damage to the coating layer releases catalyst (green) and healing agent (blue); (c) Mixing of healing agent and catalyst in the damaged region and (d) Damage healed, protecting the substrate from the environment	54
2.26	Contrast between the dissimilar encapsulation techniques	55
2.27	Encapsulation techniques for organizing UF capsules having DCPD by means of sonication. (a) Procedure flow chart; (b) Chart illustrating the emulsion before sonication; (c) in sonication	56
2.28	Size circulation of manufactured capsules readied (a) with no sonication method, (b) having sonication method	57
2.29	Visual micrograph of cross section of microcapsules self-healing coating	58
2.30	The chemical structure for zeolite/polyaniline composite	60
2.31	Schematics of the deposition chamber for RF magnetron sputtering technique	63
2.32	Schematics of the film deposition by using magnetron sputtering technique	65
3.1	Flowchart for the research methodology	72
3.2	(a) A schematic diagram of self-healing microcapsule consists of core material and shell material and (b) A schematic of self-healing coating containing microcapsules on substrate	73

3.3	Flow of the process of producing functionalized zeolite	75
3.4	Schematic flow of the process for synthesis of polyaniline by the conventional method	76
3.5	Schematic of work process to synthesize the solution A for zeolite/polyaniline composite	77
3.6	Schematic of work process to synthesize the solution B for zeolite/polyaniline composite	78
3.7	Schematic of work process to synthesize the zeolite/polyaniline composite	78
3.8	Formation of zeolite/polyaniline composite after (a) 5 minutes, (b) 10 minutes, and (c) 15 minutes	79
3.9	Preparation of the microcapsules using the core materials	80
3.10	Self-healing coating process using a spin coater	81
3.11	Physical vapor deposition coating process using RF sputtering machine	82
3.12	Visual appearance of <i>P.aeruginosa</i> bacteria cultured on the agar plate	87
3.13	Schematic of preparation of bacteria-inoculated NRSS medium for immersion test (a) first batch and (b) second batch	88
3.14	Immersion test of steel substrate immersed in bacteria inoculated medium: (a) Schematic and (b) Actual experimental setup	90
3.15	Examples of different coated samples immersed in bacteria inoculated medium in 7 days	90
3.16	Electrochemical corrosion test set up: (a) actual and (b) schematic set up	92
3.17	The scratched samples before the salt spray test	94
3.18	The samples placed inside the chamber during the salt spray test	94
3.19	Principle of Nano-scratch Test	98

3.20	Pull off adhesion test	99
4.1	The microstructure of the mild steel substrate using optical microscope	102
4.2	Visual inspection of bare steel substrate exposed to bacteria-inoculated medium for different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days	103
4.3	Visual inspection of steel substrate exposed to sterile NRSS medium at different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	104
4.4	Visual inspection of corrosion products formed on steel substrate exposed to (a) sterile and (b) bacteria-inoculated NRSS medium for 42 days after contact with the environment	105
4.5	Visual inspection of corrosion products formed on steel substrate after salt spray test at different exposure times: (a) 3 days, (b) 7 days, (c) 14 days, (d) 21 days, and (e) 28 days	106
4.6	FESEM micrograph of mild steel substrate (a) before immersion and after exposure to <i>P. aeruginosa</i> inoculated NRSS medium for (b) 7 days, (c) 14 days, (d) 28 days, (e) 42 days, (f) 56 days and (g) 70 days	107
4.7	FESEM and EDS spectra of the a) biofilm layer formed on the bare mild steel after 70 days of immersion in bacteria-inoculated medium and b) low carbon steel before immersion test	108
4.8	SEM micrograph of mild steel substrate exposed to sterile NRSS medium at different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	110

4.9	FESEM and EDS analysis of corrosion products formed on uncoated mild steel exposed to bacteria-inoculated medium	111
4.10	FESEM image of mild steel substrate exposed to (a) sterile and (b) bacteria inoculated NRSS medium after 4 months of immersion	112
4.11	FESEM with corresponding EDS analysis of corrosion products and mineral deposits on bare mild steel substrate	113
4.12	Electrochemical Tafel extrapolation of bare substrate exposed to 3.5% NaCl solution	114
4.13	EIS result (Bode) plot for the bare substrates in 3.5 wt% NaCl solution	115
4.14	FESEM with corresponding EDS analysis of corrosion products formed on bare steel coupons during salt spray test after (a, b) 3 days (c, d) 7 days (e, f) 14 days (g, h) 21 days, and (i, j) 28 days	116
4.15	The corrosion rate trends for bare steel substrate exposed to sterile and bacteria-inoculated medium at different immersion times	118
4.16	The corrosion rate trends for the bare steel substrate exposed to salt spray test at different immersion times	120
4.17	Functionalized zeolite (a) FESEM images and (b) EDS analysis	122
4.18	Encapsulated zeolite (a) FESEM images and (b) EDS analysis	122
4.19	XRD analysis of zeolite and zeolite microcapsules	123
4.20	FTIR analysis of zeolite and zeolite microcapsules	124
4.21	DSC analysis of zeolite and zeolite microcapsules	125
4.22	Visual inspection of adhesion test for encapsulated zeolite self-healing embedded in epoxy coating (a) before and (b) after dolly removal	126

4.23	FESEM image of (a) top view surface of encapsulated zeolite self-healing embedded in epoxy coating, (b) cross section view of encapsulated zeolite self-healing coating, c) EDS of zeolite self-healing coating	127
4.24	Visual inspection of encapsulated zeolite self-healing embedded in epoxy coating after scratch and before healing	128
4.25	FESEM image of (a, e, g) top view surface of zeolite self-healing coating before healing embedded in epoxy, (c, f, h) top view surface of encapsulated zeolite self-healing embedded in epoxy coating after healing, (b) EDS of encapsulated zeolite self-healing coating before healing and (d) EDS of zeolite self-healing coating after healing	129
4.26	Cross-section view of encapsulated zeolite self-healing embedded in epoxy coating (a) FESEM micrograph and (b) EDS results	130
4.27	Electrochemical Tafel extrapolation of encapsulated zeolite self-healing embedded in epoxy coated substrate exposed to 3.5% NaCl solution	131
4.28	EIS result (Bode) plot for encapsulated zeolite self-healing embedded in epoxy coated substrates in 3.5 wt% NaCl solution	132
4.29	Visual inspection of corrosion products formed on encapsulated zeolite self-healing embedded in epoxy coated steel substrate after salt spray test at different exposure times: (a) 3 days, (b) 7 days, (c) 14 days, (d) 21 days, and (e) 28 days	133

- 4.30 FESEM with corresponding EDS analysis of corrosion products formed on encapsulated zeolite self-healing embedded in epoxy coating during salt spray test after (a, b) 3 days, (c, d) 7 days, (e, f) 14 days, (g, h) 21 days, and (i, j) 28 days 135
- 4.31 The cross-sectional area of encapsulated zeolite self-healing embedded in epoxy coating after 14 days exposure in salt spray chamber (a) FESEM micrograph and (b) EDS results 136
- 4.32 Visual inspection of encapsulated zeolite self-healing embedded in epoxy coated steel substrate exposed to sterile NRSS medium at different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days 137
- 4.33 SEM micrograph of encapsulated zeolite self-healing embedded in epoxy coated steel substrates exposed to sterile NRSS medium at various exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days 138
- 4.34 Visual inspection of encapsulated zeolite self-healing embedded in epoxy coated substrates exposed to bacteria-inoculated medium after various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days 139
- 4.35 FESEM image of encapsulated zeolite self-healing embedded in epoxy coated substrate exposed to *P. aeruginosa*-inoculated medium at various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, (f) 70 days 140
- 4.36 The ruptured microcapsules and bacteria cells on encapsulated zeolite self-healing embedded in epoxy coating after 140 days of immersion (a) FESEM micrograph, (b,c) EDS analysis 141

4.37	Schematic of contact killing behaviour of encapsulated zeolite self-healing embedded in epoxy coating layer on bacteria	142
4.38	Synthesis of polyaniline (a) FESEM micrograph and (b) EDS analysis	143
4.39	Illustration of (a) FESEM images and (b) EDS of polyaniline microcapsules	144
4.40	XRD analysis of polyaniline and polyaniline microcapsules	144
4.41	FTIR analysis of polyaniline and polyaniline microcapsules	145
4.42	DSC analysis of polyaniline and polyaniline microcapsules	146
4.43	Visual inspection of adhesion test for polyaniline self-healing coating (a) before and (b) after the test	147
4.44	FESEM images: (a) top view surface of encapsulated polyaniline self-healing embedded in epoxy coating, (b) cross-section view of encapsulated polyaniline self-healing coating and (c) EDS of polyaniline self-healing coating	148
4.45	Visual inspection of encapsulated polyaniline self-healing embedded in epoxy coating after scratching and before healing	149
4.46	FESEM micrograph of top view surface of encapsulated polyaniline self-healing embedded in epoxy coating: (a, e, g) after scratching and before healing, (f) after 7 days, (h) after 14 days, (c) 21 days, (b) EDS of encapsulated polyaniline self-healing coating after scratch and before healing and (d) EDS of encapsulated polyaniline self-healing coating after healing	151

4.47	Cross-section view of encapsulated polyaniline self-healing embedded in epoxy coating (a) FESEM micrograph and (b) EDS results	152
4.48	Electrochemical Tafel extrapolation of encapsulated polyaniline embedded in epoxy self-healing coated substrate exposed to 3.5% NaCl solution	153
4.49	EIS result (Bode) for encapsulated polyaniline self-healing embedded in epoxy coated substrates in 3.5 wt% NaCl solution	154
4.50	Visual inspection of corrosion products formed on encapsulated polyaniline self-healing embedded in epoxy coated steel substrate after salt spray test with different exposure times: (a) 3 days, (b) 7 days, (c) 14 days, (d) 21 days and (e) 28 days	155
4.51	FESEM with corresponding EDS analysis of corrosion products formed on encapsulated polyaniline self-healing embedded in epoxy coating during salt spray test after (a, b) 3 days, (c, d) 7 days, (e, f) 14 days, (g, h) 21 days, and (i, j) 28 days	157
4.52	The cross-sectional area of encapsulated polyaniline self-healing embedded in epoxy coating after 28 days exposure in salt spray chamber (a) FESEM micrograph and (b) EDS results	158
4.53	Visual inspection of encapsulated polyaniline self-healing embedded in epoxy coated steel substrate exposed to sterile NRSS medium with different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	159

4.54	SEM micrograph of encapsulated polyaniline self-healing embedded in epoxy coated steel substrates exposed to sterile NRSS medium at different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	160
4.55	Visual inspection of encapsulated polyaniline self-healing embedded in epoxy coated substrates exposed to bacteria inoculated medium after various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days	161
4.56	FESEM image of encapsulated polyaniline self-healing embedded in epoxy coated substrate exposed to <i>P. aeruginosa</i> -inoculated medium at various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, (f) 70 days	162
4.57	Ruptured microcapsules and bacteria cells on encapsulated polyaniline self-healing embedded in epoxy coating after 140 days of immersion (a) FESEM micrograph and (b,c) EDS analysis	163
4.58	Schematic of contact killing behaviour of the encapsulated polyaniline self-healing embedded in epoxy coating layer against bacteria 70 days	164
4.59	Penetration of the bacteria from beneath the coating layer towards the substrate after 140 days of immersion	165
4.60	Synthesised zeolite/polyaniline composite (a) FESEM image and (b) EDS results	166
4.61	Zeolite/polyaniline composite microcapsules (a) FESEM image and (b) EDS results	167
4.62	XRD analysis of zeolite/polyaniline composite and zeolite/polyaniline composite microcapsules	168
4.63	FTIR analysis of zeolite/polyaniline composite and zeolite/polyaniline composite microcapsules	169

4.64	DSC analysis of zeolite/polyaniline composite and zeolite/polyaniline composite microcapsules	170
4.65	Visual inspection of adhesion test for encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating (a) before and (b) after the pull-off adhesion test	171
4.66	FESEM image of (a) top view surface of encapsulated zeolite/polyaniline composite self-healing coating, (b) cross-section view of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating, and (c) EDS of zeolite/polyaniline composite self-healing coating	172
4.67	Visual inspection of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating after scratching and before healing	173
4.68	FESEM image of top view surface of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating: (a, e, g) after scratching and before healing, (f) after 7 days, (h) after 14 days, (c) 21 days, (b) EDS of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy after scratch and coating before healing and (d) EDS of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating after healing	174
4.69	Cross-section view of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating (a) Fesem images and (b,c,d,e) are the corresponding EDS analysis	175

4.70	Electrochemical Tafel extrapolation of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated substrate exposed to 3.5% NaCl solution	176
4.71	EIS result (Bode) plot for zeolite/polyaniline composite self-healing embedded in epoxy coated substrates in 3.5 wt% NaCl solution	177
4.72	Visual inspection of corrosion products formed on encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated steel substrate after salt spray test after different exposure times: (a) 3 days, (b) 7 days, (c) 14 days, (d) 21 days and (e) 28 days	178
4.73	FESEM with corresponding EDS analysis of corrosion products formed on encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating during salt spray test after (a, b) 3 days (c, d), 7 days (e, f), 14 days (g, h), 21 days and (i, j) 28 days	180
4.74	The cross-sectional area of encapsulated zeolite/polyaniline self-healing embedded in epoxy coating after 14 days exposure in salt spray chamber (a) FESEM micrograph and (b) EDS results	181
4.75	Visual inspection of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated steel substrate exposed to sterile NRSS medium with different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days	182

- 4.76 SEM micrograph of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated steel substrates exposed to sterile NRSS medium at varying exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days 183
- 4.77 Visual inspection of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated substrates exposed to bacteria-inoculated medium after various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days 184
- 4.78 FESEM image of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coated substrate exposed to *P. aeruginosa*-inoculated medium after various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days and (f) 70 days 186
- 4.79 Ruptured microcapsules and bacteria cells on encapsulated zeolite self-healing coating embedded in epoxy after 140 days of immersion (a,b) FESEM micrographs and (c,d) EDS analysis 187
- 4.80 Schematic of contact killing behaviour of encapsulated zeolite/polyaniline composite self-healing embedded in epoxy coating layer to kill the bacteria on contact with the coating 187
- 4.81 XRD patterns for SiO coating on steel substrates with different values of Radio Frequency (RF) power, (a) 150 watts, (b) 200 watts, (c) 250 watts and (d) 300 watts 189

4.82	3-D images of AFM for SiO coating on steel substrates (5 μ m x 5 μ m) with different values of Radio Frequency (RF) power, (a) 150 watts, (b) 200 watts, (c) 250 watts, and (d) 300 watts	190
4.83	AFM images analysis for SiO coated onto the carbon steel substrate with 150, 200, 250 and 300 watts of RF power (a, c, e, and g) and 2-D top view graphs for surface roughness cross section (b, d, f, and h)	191
4.84	EDS analysis at different RF power: (a) 150 watts, (b) 200 watts, (c) 250 watts, and (d) 300 watts	193
4.85	FESEM micrograph of SiO coating thin film on steel substrate with different RF power sources; (a) 150 watts, (b) 200 watts, (c) 250 watts, and (d) 300 watts	194
4.86	Images from FESEM at the surface of the steel substrates coated with SiO after the indentation test with RF power of 150, 200, 250 and 300 watts (a, c, e, and g), respectively. Indentation spot near to the surface of the substrate with 700X magnification (b, d, f and h), respectively	196
4.87	Variation of friction coefficient with scratch displacement for different RF values of SiO coating on steel substrate	197
4.88	XRD patterns for SiO coating on steel substrates at different temperatures of the PVD process (a) 150°C(b) 200 °C and (c) 250°C	199
4.89	3-D images of AFM for SiO coating on steel substrates (5 μ m x 5 μ m) with different values of temperature of the PVD process: (a) 150°C, (b) 200°C, and (c) 250°C	200

4.90	AFM images analysis for SiO coated onto the carbon steel substrate with temperatures of the PVD 150°C, 200°C, and 250°C (a, c, and e). 2-D top view graphs for surface roughness cross section (b, d, and f).	201
4.91	FESEM micrograph of SiO coating thin film on steel substrate with different temperatures of the PVD process: (a) 150°C, (b) 200°C, and (c) 250°C	203
4.92	Images from FESEM at the surface of the steel substrates coated with SiO after the indentation process with temperatures of 150°C, 200°C and 250°C(a, c, and e). Indentation spot near the surface of the substrate with 700X magnification (b, d and f)	204
4.93	Variation of friction coefficient with scratch displacement for different temperature values of SiO coating on steel substrate	205
4.94	XRD patterns for SiO coating on steel substrates with different values of Pressure (a) 20mTorr,(b) 30 mTorr, and (c) 40mTorr	207
4.95	3-D view images of AFM for SiO coating on steel substrates (5µm x 5µm) with different values of pressure. (a) 20mTorr, (b) 30mTorr, and (c) 40mTorr	208
4.96	AFM images analysis for silicon oxide coated onto the carbon steel substrate with pressures of 20 mTorr, 30 mTorr and 40 mTorr (a, c, and e). 2-D top view graphs for surface roughness cross section (b, d, and f)	209
4.97	FESEM micrograph of SiO coating thin film on steel substrate with different pressures: (a) 20mTorr, (b) 30mTorr, and (c) 40mTorr	210

4.98	Images from FESEM at the surface of the steel substrates coated with SiO after the indentation process with pressures of 20 mTorr, 30 mTorr and 40 mTorr(a, c, and e), Indentation spot on the center surface of the substrate with 700X magnification, (b, d and f) and area near the indentation spot with 700X magnification	212
4.99	Variation of friction coefficient with scratch displacement for different pressure values of SiO coating on steel substrate	213
4.100	XRD patterns for SiO coating on steel substrates with different values of Deposition Times: (a) 60 minutes and (b) 90 minutes	214
4.101	3-D images of AFM for SiO coating on steel substrates (5 μ m x 5 μ m) with different values of deposition time: (a) 60 minutes and (b) 90 minutes	215
4.102	AFM images analysis for silicon oxide coated onto the carbon steel substrate with deposition times of 60 minutes and 90 minutes (a and c), 2-D top view graphs for surface roughness cross section (b and d)	216
4.103	FESEM micrograph of silicon oxide coating thin film on steel substrate with different deposition times: (a) 60 minutes and (b) 90 minutes	217
4.104	Images from FESEM at the surface of the steel substrates coated with SiO after the indentation process with deposition times of 60 minutes and 90 minutes (a and c), Indentation spot on near to the surface of the substrate with 700X magnification (b and d)	218
4.105	Variation of friction coefficient with scratch displacement for different deposition times of SiO coating on steel substrate	219

4.106	The use of Focused Ion Beam (FIB) in TEM analysis	221
4.107	TEM micrograph of the thickness of thin film SiO coating	221
4.108	TEM images of silicon oxide coating with EDS analysis	222
4.109	High resolution TEM (HRTEM) image of silicon oxide coating showing amorphous structure	223
4.110	Electrochemical Tafel extrapolation of SiO coated substrate exposed to 3.5% NaCl solution	224
4.111	(a) Nyquist and (b) Bode plots for SiO coated substrates in 3.5 wt% NaCl solution	225
4.112	Corrosion products formed on the SiO coated steel substrate after the salt spray test for different exposure times: (a) 3 days (b) 7 days (c) 14 days (d) 21 days, and (e) 28 days	226
4.113	FESEM with corresponding EDS analysis of corrosion formed on the SiO coating during the salt spray test after: 3 days (a and b), 7 days (c and d), 14 days (e and f), 21 days (g and h), and 28 days (i and j)	227
4.114	Visual inspection of SiO coated steel substrate exposed to sterile NRSS medium within different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	228
4.115	SEM micrograph of SiO coated steel substrates exposed to sterile NRSS medium for different exposure times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	229

4.116	Visual inspection of SiO coated substrates exposed to bacteria inoculated medium after various immersion times: (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	230
4.117	FESEM image of SiO coated substrate exposed to <i>P.aeruginosa</i> inoculated medium after various immersion times (a) 7 days, (b) 14 days, (c) 28 days, (d) 42 days, (e) 56 days, and (f) 70 days	232
4.118	Schematic illustrating the detachment of the bacteria when it comes into contact with the SiO coating	233
4.119	Types of coating and synthesis/deposition methods used in the research	234
4.120	Comparison of the adhesion strength between the self-healing coated substrates	236
4.121	Comparison of the corrosion rate (mm/yr) for the bare and coated substrates according to biofilm formation	239
4.122	Comparison of the corrosion rate (mm/yr) for the bare and coated substrates according to electrochemical Tafel	239
4.123	Comparison of the corrosion rate (mm/yr) for the bare and coated substrates according to salt spray test	240
4.124	Comparison of the corrosion resistance for the bare and coated substrates	242

LIST OF ABBREVIATIONS

Al	-	Aluminum
AA	-	Aluminum alloy
ATRP	-	Atom transfer radical polymerisation
Cu	-	Copper
DNA	-	Deoxyribonucleic acid
EPS	-	Extracellular polymeric substances
E	-	Elastic modulus
E_{corr}	-	Corrosion potential
I_{corr}	-	Corrosion current density
IOB	-	Iron oxidizing bacteria
IRB	-	Iron reducing bacteria
MIC	-	Microbial-Induced Corrosion
MOB	-	Manganese oxidizing bacteria
MS	-	Mild steel
N^+	-	Positively charged nitrogroups
NPs	-	Nanoparticles
NPVP	-	Poly (4- vinylpyridine)-co-poly (4-vinyl-N-hexylpyridinium
PANI	-	Polyaniline
PDA	-	Poly (dopamine)
PMOX	-	Poly (2-methyl-2-oxazoline)
PEG	-	Poly (ethylene glycol)
PEO	-	Polyethylene oxide
PFPEs	-	Perfluoropolyethers
PTFE	-	Polytetrafluoroethylene

QASs	-	Quaternary ammonium salts
SI-ATRP	-	Surface initiated atom transfer radical polymerisation
SRB	-	Sulphate reducing bacteria
SEM	-	Scanning electron microscopy
FESEM		Field immersion scanning electron microscopy
TBT	-	Tributyltin
EDS		Energy dispersive spectroscopy
Ti	-	Titanium

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	XRD Analysis for Silicon Oxide Coating	263
B	FESEM Results for Nano-scratch Test	264
C	Publications	267

CHAPTER 1

INTRODUCTION

1.1 Research Background

In the majority of engineering structures operated in the marine environment, microbiological induced corrosion (MIC) is of great concern [1]. The issue of MIC could be particularly dangerous in marine structures such as ships and maritime platforms as well as offshore jetties and rigs [2]. Such constructions have to be protected against attack from the main components of the marine setting such as sea water, temperature, and biological attack, also referred to as “biofouling”. Indeed, biofouling is the colonization of submerged structure surfaces by organisms such as barnacles, bacteria, and algae. Maritime biofouling is a long-standing and pricey problem for the marine industry because the development of fouling assemblies on ship hulls, for instance, raises drag, decreases maneuverability, and increases fuel use and greenhouse gas release [3-6], leading to both high financial and ecological expenses [7]. Maritime fouling, or the settlement and growth of marine organisms on waterlogged structures, is predicted to have a worldwide expenditure of above \$3 billion yearly [8]. Shipping accounts for approximately 90% of global business, and seaborne trade has increased by four-fold during the previous 40 years [9, 10]. Generally, MIC is not a novel kind of corrosion. Most commonly it appears in the shape of localized

corrosion, whether pitting or crevice. MIC is instigated, extended, or proliferated because of the existence of microorganisms such as bacteria [11, 12].

Pseudomonas aeruginosa is one of the dominant bacterium found in the maritime surrounding, and is an aerobic slime-forming bacteria that creates a biofilm coat on the surface of the steel. The reaction of the biofilm layer with the steel surface and the generation of differential aeration cells provide conditions on the steel surface that instigate and hasten the corrosion process. The production of these concentration cells is harmful to the integrity of the oxide layer and increases the vulnerability of steels to corrosion [13-15].

Numerous conventional antifouling systems are in the form of paints, which is an inclusive word covering a diversity of substances: lacquers, enamels, varnishes, surfacers, undercoats, primers, fillers, sealers, plugs, and several others. The use of non-environmentally friendly and toxic antifoulants on ship hulls is one of the most widely used techniques of managing fouling even though biocides such as lead, mercury, arsenic, and their natural derivatives are banned owing to environmental concerns. Antifoulants comprise one of the numerous additives typically incorporated in the top-layer paint of a maritime defensive coating system [2].

In recent years, a new technique has shown a great promise for autonomic healing of micro-cracks and mechanical damage, this technique is the use of self-healing polymers [16]. Self-healing coatings are an extremely enhanced group of smart substances in which the aim is to repair the micro-cracks completely, in a passive way, with no necessity for detection or any kind of foreign interference [17-21].

A different method of mitigating against biofouling is the physical vapor deposition (PVD) coating approach, which features a set of diverse methods that can be employed to deposit silicon oxide coating onto steel substrates. PVD comprises

several vacuum deposition approaches and is a universal term employed to explain a process that deposits thin films through the concentration of a vaporized form onto diverse substrate surfaces. The basic process of PVD falls into two universal classes: sputtering and evaporation. The commercial applications of PVD methods vary over a broad range of uses from decorative, to extreme temperature superconducting layers [22].

1.2 Problem Statement

MIC of immersed structures in maritime environments is the effect of biological organisms colonization and adhesion on the surface. Given that the significant bio-interfacial processes which lead to fouling are nano-scale or micro-scale in size, the surface properties of the structures to manage biofouling are assumed to be on a similar size scale. An area of specific interest in recent years is the use of nanotechnology in combating MIC. There is a necessity to find ecologically harmless coatings to hinder MIC successfully. Certainly, current research has demonstrated the significant of coating protection with minimal environmental impact of self-healing coatings based on the release of healing agents when micro-cracks are instigated in the coated surface. Silicon oxide-based organic and inorganic coatings in addition to diamond-like carbon coatings have shown great potentials to combat antifouling with fewer negative impacts on the environment. The new methods are based on “fouling release” and “contact killing”. The former method, does not involve the discharge of biocides in maritime water and therefore should be ecologically responsible. The “contact killing” method may be considered a favorable approach, and polycationic coatings are utilized to hinder MIC using this method. Nevertheless, to attain such an objective, the coating should be modified so its surface properties have excellent smoothness and corrosion resistance, high hardness, good thermal stability, and low cost. Zeloite and polyaniline have good adhesion to the steel substrate and only destroy the microorganisms that come into contact with them without leaking out, while silicon oxide owing to its unique

characteristics of providing a smooth film which could minimize the adhesion of the microorganism on the steel substrates. Due to their biocide behavior and anticorrosive properties as well as environmental responsiveness, silicon oxide, polyaniline, and zeolite are excellent candidates to protect metal surfaces against MIC.

1.3 Objectives of the Research

The aim of this research work is to investigate on coatings that would be capable of inhibiting MIC. Foremost, the research induces an exploration on the mechanisms of MIC-on steel surfaces in bacteria-inoculated medium, which could be helpful to facilitate the use of efficient procedures to mitigate against MIC. Next, the research is also aimed at exploring the capabilities of the encapsulated zeolite, polyaniline, zeolite/polyaniline composite self-healing embedded in epoxy and silicon oxide hydrophobic coatings strategies in inhibiting MIC. The output of this research is anticipated to enhance the properties of MIC inhibition of coated steel that is exposed to bacteria-inoculated medium, and also to provide an environmentally friendly and suitable coating for the mitigation against MIC of steels in the marine environment.

The specific objectives of the research include:

- (i) To develop encapsulated zeolite, polyaniline, zeolite/polyaniline composite self-healing and silicon oxide coatings that can be utilized as coating materials to inhibit microbial-induced corrosion.
- (ii) To characterise the properties of newly developed self-healing and silicon oxide coatings on mild steel substrates.
- (iii) To evaluate the performance of self-healing and silicon oxide coatings as MIC inhibitive coatings.

1.4 Scope of the Research

The scope of research includes:

- (i) Synthesis of the self-healing core substances encompassing polyaniline, zeolite, and zeolite-polyaniline composites and their microcapsules by the in-situ chemical polymerization technique and applying them on steel substrates.
- (ii) Deposition of silicon-oxide based coatings on steel substrates with enhanced properties using the physical vapor deposition method.
- (iii) Characterization of the properties of synthesised and deposited coatings, including hardness and coating adhesion, using various characterization techniques such as Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), X-ray, Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Electrochemical Impedance Spectroscopy (EIS), and Electrochemical Tafel Analysis.
- (iv) Performance of biological assays to assess the antifouling capacities of the developed coatings versus *P. aeruginosa* microorganisms.
- (v) Determine the corrosion rate using immersion tests
- (vi) Microscopic examination of samples upon completion of immersion tests using standard characterization equipment.

1.5 Significance of Research

Many types of coatings used by the marine industries are toxic and affect the marine life. Therefore, many researchers are investigating on alternative coatings which are friendly to the environment but at the same time are effective on protecting the metal against MIC.

The fundamental goal of this research is to investigate the performance of encapsulated based self-healing and hydrophobic concept by physical vapor deposition coated steel substrates in inhibiting MIC when exposed to bacteria-inoculated medium. Therefore, the outcome of this study would benefit various sectors, particularly the marine, gas, and oil industries.

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