

EFFECTIVENESS OF ULTRAVIOLET TREATMENT IN MITIGATING
MICROBIOLOGICALLY INFLUENCED CORROSION

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requirements for the award of the degree of
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DEDICATION

This thesis is dedicated to

my mother; who taught me that never stop when you decide to start until you reach the finishing line.

my husband; you dried my tears and give me strength along the way.

my kids; all of you are parts of this war. This is the proved that I am once a fighter. In your future, don't ever quit in your war that you are facing. You were born by a fighter and you will be a great fighter too.

my beloved family and friends; who always supported me in every way they could.

“The path from dreams to success does exist. May you have the vision to find it, the courage to get on to it and perseverance to follow it “

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ABSTRACT

The destructive effect of microbiologically influenced corrosion (MIC) of carbon steel in pipelines has been widely found in soil and water environments. Chemical biocides are normally used for MIC mitigation in pipelines. However, many problems were encountered in its application, causing biocides usage to remain controversial. Ultraviolet (UV) radiation is seen as a possible alternative for chemical biocides. Nevertheless, information on the efficiency of UV treatment and the influences of UV parameters on corrosion process is limited, thus restricting any efforts to explore the potential application of UV as a chemical biocide replacement. This study aims to identify the effectiveness of UV disinfection against MIC caused by Sulfate Reducing Bacteria (SRB) strain. The investigation utilized two different samples of SRB sources: Baram-C and ATCC7757 strains. The Baram-C SRB consortium sample was cultivated from raw crude oil gathered from one of the main trunk lines at Baram Delta Operation, Sarawak, Malaysia, while the ATCC7757 SRB sample was sourced from the American Type Culture Collection (ATCC). The observation on bacteria growth revealed that the preferred pH and temperature for the active cultivation of Baram-C and ATCC7757 strains were pH 8.5 and 37°C, respectively inside the Modified Baar's media. The corrosion process was found more severe in biotic condition by approximately 50% based on metal loss results. The maximum corrosion rate in biotic environment was recorded at 0.3209 mm/year and 0.5042 mm/year for Baram-C and ATCC7757 strains, respectively, as compared to the 0.1791 mm/year corrosion rate in an abiotic sample. One-Factor-At-a-Time (OFAT) analysis was performed under the influence of UV time of exposure, types of UV lamps, numbers of UV lamps and treated volume. The optical density reading showed that UV treatment was able to suppress the number of bacteria up to almost 99% after 28 days of incubation. The effect on bacteria growth was similar for both strains. However, when a variety of UV treatment parameters were applied, different bacterial strains indicated different rates of metal loss. Furthermore, Response Surface Methodology (RSM) was used as a tool to determine the relationship between UV parameter and metal loss by using two different types of UV lamps (10 watts and 14 watts). The RSM models were successfully developed with R^2 of 0.8990 and 0.9020 for UV lamps with 10 watts and 14 watts, respectively. ANOVA results indicate that the effects of treated volume do not depend on the level of factors contact time and numbers of UV lamp for 10 watts lamps, whereas for 14 watts lamps, the contact time and number of UV lamp do affect each other. The result also suggests that the effectiveness of UV treatment does not only depend on UV lamp's intensity to provide optimum curing. The experimental test and numerical analysis performed in this research has provided a comprehensive understanding of the efficiency of UV treatment on the extermination of SRB strains and reduction of metal loss rates. The findings also produced a numerical measurement of metal loss rate due to SRB as a function of UV radiation. This can serve as an impetus for the transition of UV technology from its infancy level to the real-world practice of corrosion mitigation in the oil and gas industry.

ABSTRAK

Kesan pemusnahan mikrobiologi yang mempengaruhi kakisan (MIC) keluli karbon dalam saluran paip telah banyak ditemui didalam persekitaran tanah dan air. Biosid bertoksik biasanya digunakan untuk mengatasi masalah MIC dalam saluran paip. Walau bagaimanapun, penggunaan biosid mempunyai banyak masalah menyebabkan penggunaannya masih dipersoal. Radiasi Ultralembayung (UV) dilihat sebagai alternatif untuk menggantikan penggunaan biosid. Walau bagaimanapun, maklumat mengenai kecekapan rawatan UV dan pengaruh parameter UV pada proses kakisan adalah terhad, sekali gus menyekat sebarang usaha untuk meneroka penggunaannya sebagai pengganti biosid. Kajian ini bertujuan untuk mengenalpasti keberkesanan pembasmian kuman UV terhadap MIC yang disebabkan oleh Bakteria Pengurangan Sulfat (SRB). Siasatan menggunakan dua contoh sumber SRB yang berbeza: jenis Baram-C dan ATCC7757. Sampel konsortium SRB Baram-C diambil dari minyak mentah yang dikumpulkan dari salah satu garisan paip utama di Baram Delta Operation, Sarawak, Malaysia, manakala sampel ATCC7757 SRB diperoleh dari Koleksi Kultur Jenis Amerika (ATCC). Pemerhatian terhadap pertumbuhan bakteria menunjukkan bahawa pH dan suhu pilihan untuk Baram-C dan ATCC7757 untuk aktif membiak adalah pada pH 8.5 dan 37°C, masing-masing di dalam media Modified Baar. Proses karat didapati lebih teruk dalam keadaan biotik dengan kira-kira 50% berdasarkan hasil kehilangan logam. Kadar kakisan maksimum dalam persekitaran biotik dicatat pada 0.3209 mm/tahun dan 0.5042 mm/tahun bagi jenis Baram-C dan ATCC7757, berbanding dengan kadar kakisan 0.1791 mm/tahun dalam sampel abiotik. Analisis Satu-Faktor-Pada-Satu-Masa (OFAT) dilakukan di bawah pengaruh masa pendedahan, jenis lampu UV, bilangan lampu UV dan isipadu sampel yg dirawat. Hasil dari data kepadatan optik menunjukkan bahawa rawatan UV mampu mengurangkan jumlah bakteria pada hampir 99% setelah 28 hari diinkubasi. Kesan pertumbuhan bakteria adalah serupa untuk kedua-dua jenis. Walau bagaimanapun, apabila pelbagai parameter rawatan UV digunakan, jenis bakteria yang berbeza telah menunjukkan kadar kehilangan logam yang berlainan. Selain itu, Kaedah Tindakbalas Permukaan (RSM) digunakan sebagai alat untuk menentukan hubungan antara parameter UV dan kehilangan logam dengan menggunakan dua lampu UV berlainan kuasa (10 watts dan 14 watts). Model RSM berjaya dibangunkan dengan nilai R^2 0.8990 dan 0.9020 untuk lampu UV dengan kuasa 10 watts dan 14 watts. Dari analisis ANOVA, dapat diperhatikan bahawa kesan bagi isipadu sampel dirawat tidak bergantung pada faktor masa pendedahan dan keamatan UV untuk lampu berkuasa 10 watts, namun begitu pada lampu 14 watts, faktor masa pendedahan dan jumlah lampu adalah berkaitan antara satu sama lain. Hasilnya juga menunjukkan bahawa keberkesanan rawatan UV tidak banyak bergantung pada nilai keamatan lampu UV. Ujian eksperimen dan analisis berangka yang dilakukan dalam kajian ini telah memberikan pemahaman yang komprehensif tentang kecekapan rawatan UV pada pemusnahan jenis SRB dan pengurangan kadar kehilangan logam. Penemuan ini juga menghasilkan pengukuran berangka kadar kehilangan logam disebabkan oleh SRB sebagai fungsi sinaran UV. Ini boleh bertindak sebagai dorongan untuk mentransisi teknologi UV dari tahap awal kepada amalan di dunia nyata di dalam industri minyak dan gas.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
API	-	American Petroleum Institute
APB	-	Acid Producing Bacteria
ASTM	-	American Society of Testing of Materials American
ATCC	-	American Type Culture Collection
BBD	-	Box Behnken Design
BDO	-	Baram Delta Operation
CCD	-	Central Composite Design
CFD	-	Computational fluid dynamic
DOE	-	Design of Experiments
DNA	-	Deoxyribonucleic acid
EDS	-	Energy Dispersive X-ray Spectroscopy
EPS	-	Extracellular Polymer Substance
Fe	-	Iron
Fe(OH) ₂	-	Iron (II) Hydroxide
FESEM	-	Field Emission Scanning Electron Microscopy
GDS	-	Glow Discharge Spectrometry
H ₂ S	-	Hydrogen sulfide
HSD	-	Honest Significant Difference
IBM SPSS	-	International Business Machines Statistical Package for Social Science
IRB	-	Iron Reducing Bacteria
MCOT	-	Miri Crude Oil Terminal
MIC	-	Microbiologically Influenced Corrosion
MB	-	Magnetic Bacteria
MBM	-	Modified Baar's Medium
MMM	-	Molecular Microbiological Methods
NACE	-	National Agency of Corrosion Engineer
NGS	-	Next Generation Sequencing
NPI	-	Non-Physical Inhibitor
OFAT	-	One Factor at a Time Principle

OD	-	Optical Density
PMB	-	Postgate Medium B
PMC	-	Postgate Medium C
QAC	-	Quaternary Ammonium Compounds
rDNA	-	Recombinant Deoxyribonucleic Acid
RNA	-	Ribonucleic Acid
RSM	-	Response Surface Method
Si-C	-	Silicon Carbide
SEM	-	Scanning Electron Microscope
SRB	-	Sulfate Reducing Bacteria
TEM	-	Transmission Electron Microscopy
TTS	-	Total Suspended Solids
USD	-	United State Dollar
US	-	Ultrasonic
UV	-	Ultraviolet
X70	-	Pipe having a minimum yield strength of 70 ksi

LIST OF SYMBOLS

°C	- Degree Celcius
A	- Area
D	- Density
%	- Percentage
W_o	- Initial weight of coupon
W_a	- Final weight of coupon
R^2	- Coefficient of determination
K	- Constant
T	- Time of exposure

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CHAPTER 1

INTRODUCTION

1.1 Overview

Corrosion is one of the phenomena of natural deterioration that causes economic and environmental damage due to structural failure of oil and gas infrastructure. Its natural spontaneous process has a devastating impact upon the long-term integrity of oil and gas infrastructure (Norhazilan et al., 2011; Abdullah, 2017). Pipeline system is used to transport crude oils over long distances and hence, faces serious corrosion problem that can lead to system failure. For years, numerous failures of pipeline system that distribute crude oils and gas have been reported globally. Even though steel pipe materials with high strength grade such as X70 have been introduced, corrosion still persists and dominates the statistics as the major cause of pipeline failure. Of the many corrosion mechanisms, previous investigation results have concluded that the pipe is most likely to suffer severe corrosion damage due to Microbiology Influenced Corrosion (MIC) (Forte Giacobone et al., 2011; Abdullah et al., 2014; Nan et al., 2015; Afizza et al., 2016; Ching et al., 2016; Narenkumar et al., 2017).

In general, the oil field is an interesting place for microbes to multiply aggressively. The conditions encounter a range of features, from cold to hot, and from fully aerobic to anaerobic. These conditions breed different types of microorganisms that have adapted to the environments in which they live. Microbial activity in any environment occurs in the presence of water, a carbon source, an electron donor and an electron acceptor, all of which can be present in oil pipelines (Almahamedh et al., 2011). This implies that the increase in corrosion rate is due to the presence of bacterial activities such as Sulfate Reducing Bacteria (SRB) which accelerate the rate of anodic and/or cathodic reactions (Muthukumar, 2014). It is a huge challenge to mitigate this delicate phenomenon, albeit the fact that it cannot be

simply eliminated altogether from the deteriorating infrastructure. Nevertheless, with careful steps, it can be well-controlled. Until today, the recommended MIC mitigation method by most companies is via biocide consumption. However, several issues associated with biocide need to be addressed such as environmental pollution and high cost of operation (Ashraf et al., 2014). Therefore, alternative strategies to MIC mitigation method need to be readily available in the near future in order to accommodate the concern on biocide usages.

1.2 Background of Problem

Oil companies are constantly under significant pressure to cut production costs, including the maintenance program. The pipeline system network transports oil and gas products from oil wells to processing terminals, distribution sites and lastly to purchasers all across the country. During the oil and gas transportation process, a continuous interaction between the product and the pipeline steel surface could result in a variety of corrosion deterioration mechanisms (AlAbbas et al., 2013). A severely corroded pipeline is highly recommended to be replaced in order to maintain its integrity throughout its life span. However, this replacement requires enormous operational expenditure and substantial production loss. Nevertheless, the integrity of pipeline cannot be compromised as safety is the most crucial aspect that should be considered in this high-risk industry.

Microbiologically Influenced Corrosion has been identified as the major cause of corrosion failures (Javed et al., 2016). MIC is a common mechanism of corrosion and it is used to designate corrosion due to the presence of microorganisms and their activities (Li et al., 2016). It is also believed to be culpable for diminishing pipeline's integrity and increasing the costs of petroleum pipelines' operations and maintenance to over 40% (AlAbbas et al., 2013; Afizza et al., 2016). Muthukumar (2014) highlighted that the petroleum production environment is particularly suitable for the MIC activities because it handles large volumes of de-aerated water. Previous studies have investigated the impact of MIC and its mitigation efforts; however, its role in deteriorating engineered materials remains misunderstood (Abdullah et al.,

2014; Rasol et al., 2014; Mohd Ali, 2016). Electrochemical and microbial corrosion could exacerbate each other; thus, serious attention to control the phenomena should be raised to avoid greater risks of pipeline failure. The microbial contamination can result in the loss of production time and increased refining costs (Afizza et al., 2016); millions of dollars is an expected economic loss (Wang et al., 2005). Groysman (2017) stated that the oil, gas and refinery equipment are extremely vulnerable to a variety of corrosion phenomena that can lead to serious accidents and it is understood that SRB accounts for approximately 40% of internal corrosion in the oil and gas industry (Koch et al., 2001). Therefore, a minor yet critical element of microbial contamination control of petroleum production is a vital aspect that should be taken into consideration (Turkiewicz, Brzeszcz, & Kapusta, 2013).

Biocides injection such as glutaraldehyde is a typical technique to mitigate MIC. This toxic and abrasive chemical needs to be handled carefully because it is harmful to living creatures (Lavania et al., 2011; Gomes et al., 2016). It is also costly and contributes to serious environmental pollutions. Increasing the dose of biocide may or may not be successful in overcoming the protections since microorganisms tend to be resistant to different types of biocides over time (McKinney & Pruden, 2012; Otter et al., 2014). Driven by the environmental pollution concern, several engineers and researchers have investigated the potential use of several types of natural biocides, namely cow urine (Lavania et al., 2011); cumin (Morshedi et al., 2015) and eucalyptus oil (Ashraf et al., 2014) as alternatives to chemical biocides. However, these natural biocides are impractical from the operational cost perspective in mitigating MIC in the well-known oil and gas production due to its large network system. Furthermore, injection of biocides in the pipeline costs a handsome amount of money, namely due to raw material preparation and temporary termination of production operations.

Ultraviolet (UV) radiation is one of the potential substances which has been developed as a non-physical inhibitor (NPI) in the past decade (Mohd Ali, 2016). Bacterial disinfection using UV radiation has been successfully used in municipal wastewater treatment and thus, carries great potential for the implementation in drinking water applications (Ashraf et al., 2014). The usage of UV technology in

water treatment industry offers several inherent advantages over most traditional technologies. However, it is not a direct application when it comes to oil and gas industry because crude oil in a system could have an impact on the UV treatment effectiveness. Nevertheless, Allison, Clough & Park (2008) stated that many of the crude oil pipelines operation were reported with more than 40% water. Thus, at least the MIC living in the water produced along with the crude oil could be mitigated by using UV radiation. UV radiation is a non-reagent technology which imparts energy to water stream for disinfection process. It is a fast, effective and environmental-friendly bacterial disinfection method. Laboratory and field experiments have shown that injected UV radiation may be as effective as many biocides in acting as a treatment for microbial control (Abu Bakar et al., 2017). However, most previous studies focus on the level of effectiveness of the UV radiation to exterminate bacteria, rather than investigating its effect on mitigating corrosion, the after-effect of UV radiation on microbe reproduction and the impact to the carbon steel biocorrosion. If the performance of UV radiation treatment towards mitigating MIC in carbon steel pipelines can be further investigated and evaluated, perhaps it can be a great compliment or a substitute to the usage of costly chemical biocides.

1.3 Research Statement

The results from previous studies on the usage of UV to mitigate MIC in oil and gas pipeline is still fraught with many arguments, specifically on the role of MIC in the deterioration of engineering materials such as carbon steel pipeline. Most of the studies focused on the bacteria survival after the UV treatment or in other words, how much bacteria can be terminated by UV radiation (Clark, Luppens, Co, Tucker, & Petru, 1984; Lawal et al., 2010; Wang et al., 2005). Less attention was paid to the influence of the remaining bacteria on the continuity of the corrosion process in pipeline. This piece of information is extremely vital since the remaining small percentage of live bacteria, if not in dormant mode, can reproduce after the UV treatment is done and restart the corrosion process. If this happens, the whole process of UV treatment would be to no avail. Previous works on UV treatment also failed to interpret the efficiency of UV treatment under various operational and environmental

parameters. The question of how to optimize UV treatment for MIC mitigation according to different combination of operational and environmental parameters remains unrequited since previous experiments were done under fixed conditions. Various concerns emerge of its application in this regard: What is the suitable condition for UV operation? What about UV effectiveness on different type of microbe? Which one is more important, time of exposure to UV radiation or the intensity of UV lamp? All these questions must be answered with statistical evidences in order to uncover the capability of UV in MIC mitigation.

The statistical evidence and numerical modelling on the level of governance of UV parameters towards bacteria survivability and its impact on the pipeline material is greatly lacking. This effort is vital to ensure that UV treatment can reach its optimum capability during the mitigation process. Details on sensitivity analysis on the parameter of UV technology are also currently missing from the literature. Consequently, the waste from UV emission cannot be reduced and information on preliminary monitoring and MIC mitigation plan involving UV systems is barely available. The availability of data pertaining to UV parameters' influence on bacteria survival and corrosion impacts are crucial to ensure that the treatment system could reach its maximum efficiency during the treatment process. Furthermore, investigating the versatility of UV treatment on various bacteria in local environment conditions is essential to represent the data on UV treatment in the real site conditions. This is because different strains of MIC might have different responses towards different environments (Mohd Ali, 2016; Abdullah, 2017). In addition, there is no solid evidence proving that the commercially available Sulfate-Reducing Bacteria (SRB) can closely simulate the performance of the SRB strain which has been isolated from local site.

This research provides empirical evidence on what will happen to the remaining bacteria after UV treatment. If the bacteria are not in dormant mode, the research seeks to find out to what extend the level of impact towards corrosion severity can be practically measured? Moreover, statistical evidence can quantitatively display the performance of UV, not only on bacteria termination, but also on the mitigation of MIC. This information is highly required by the industry so

that UV technology can be well designed for full scale MIC mitigation exercise on the corroding pipeline, comparable to biocide injection.

1.4 Research Aims and Objectives

This research aims to investigate the performance of UV treatment in controlling Microbiology Influenced Corrosion (MIC) in steel pipeline caused by different strains of Sulfate Reducing Bacteria (SRB). The performance of UV treatment is measured using multi-regression numerical model, correlating metal loss volume, operational parameters and treated volume. The following objectives are identified as steps towards achieving the research aims:

1. To identify the microbial diversity in Baram-Consortium and most suitable enriched media for each SRB strain.
2. To investigate the optimum growth pattern of different strains of SRB under the influence of pH and temperature.
3. To identify the metal loss rate of grade X70 carbon steel coupon, subject to SRB optimum growth condition.
4. To determine the correlation between the effectiveness of UV radiation treatment on MIC mitigation process and the operational parameters, including time of exposure, types of UV lamps, numbers of UV lamps and treated volume.

1.5 Research Scope

This research consists of laboratory scale experimental work to reveal the effectiveness of UV radiation in controlling MIC activities and their impact on API 5L X70 carbon steel coupons. Two types of MIC samples that focus mainly on SRB strains were used as the experiment's substances under the simulation of anaerobic condition in laboratory. Samples of SRB consortium cultivated from raw crude oil gathered from the crude oil in one of the main trunk lines at Baram Delta Operation, Sarawak, Malaysia and American Type Culture Collection SRB (ATCC7757) growth were used for the comparative study. Investigation on bacteria growth and optimum environment was performed under various media, pH levels and temperatures for SRB to proliferate, respectively. The impact of UV exposure to bio-corrosion conditions on carbon steel coupon for 28 days in certain samples is discussed in this study for disinfection alternatives. One-Factor-At-a-Time (OFAT) analysis was performed under the influences of UV lamp consequent to the time of exposure, number of UV lamps, types of UV lamps and treated volume for both bacteria samples. Response Surface Methodology (RSM) was used as a tool to perform further analysis upon uncovering the aforementioned relationships between the UV parameter influences. However, only samples of Baram-C were used in the RSM analysis due to time and cost allocation constrains. Graphical and statistical approaches were also utilized to extend the understanding on the findings of this study.

1.6 Significant of Research

On this note, the outcome of this research will provide comparable data and profound understanding on the effect of several UV parameters on the extermination of several bacteria strains and metal loss. The optimum efficiency of the UV parameter usage can then be identified numerically. The proposed model from this study can also predict the response of metal loss after UV treatment. Therefore, future works on the development of the UV treatment related to financial and corrosion mitigation scheme can be properly designed. Solid evidence on the UV

performance needs to be established to ensure that UV radiation could be a viable option for mitigating MIC activity and simultaneously, minimizing the bio-corrosion impact triggered by MIC. This will shed light on the possibility of utilizing UV as the best complement or replacement for biocides application as an improved and more sustainable MIC mitigation technology. In addition, these findings may also be considered as a kick start towards serious efforts to harness UV technology as a practical technology in corrosion mitigation by oil and gas industry instead of applying it only as conceptual technology at a pilot scale.

1.7 Structure of the Thesis

This thesis is structured into six chapters. The general principle and background of the study are described in Chapter 1. This chapter also justified the research problem and significant of the conducted study. The relevant issues and literature of the research objective is described in Chapter 2. Comprehensive literature survey and overview from previous research are discussed among research subjects. Information on MIC mechanism and UV potential are also reviewed.

Chapter 3 is organized to describe the methodology of study in attaining research objectives. Particulars to conduct laboratory experimentation works, design of experiment and statistical approach are well elaborated. Overall research methodology is diverted into three components to give clear view and better understanding through all elements in the research study. Results and analysis focusing on the behaviour of research microorganism, their growth and preferable environment conditions are presented in Chapter 4. The detailed bacteria identification and information are also explained in this section. Impact to biocorrosion of the respected bacteria is explicated to verify their threat to the reliability and integrity to the pipelines system particularly to the carbon steel.

In Chapter 5, the data analysis for mitigation properties is reported. Influences of various UV parameters are shown and elucidated. The interaction between particular elements is analysed. Diagnostic on the Response Surface

Methodologies are described and predictive formula to estimate metal loss after the UV treatment is also presented. Argument in the optimization upon UV treatment and impact to the attached biofilm are also elaborated. Chapter 6 summarised the major conclusions drawn from the research objectives and the recommendations is also outlined for future research. Overall, this thesis provides visionary documents for future works and possible implementation of the UV treatment in oil and gas industry.

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