

Review Article

A Review on Microbial Mediated Corrosion on Mild Steel by Inactivating the Extracellular Polysaccharide Secreted by Aerobic/Anaerobic Microorganism

S. Chitra¹, B. Anand¹, R. Vaidyanathan¹, V. Balasubramanian²

¹Department of Chemistry, Mahendra Engineering College, Namakkal, Tamilnadu, India

²Department of Chemistry, AMET University, Chennai, Tamilnadu, India

Abstract

Microorganisms produce microbial biofilms, a structured community of cells enclosed in a self-produced polymeric matrix that is adherent to inert and living surfaces. In turn, this biofilm provides a protective shield for the microbes to thrive and resist damage from many extreme environmental conditions. In industry, biofilms lead to biofouling that inhibits heat transfer, increases energy consumption and shipping costs, and causes biocorrosion. In this study, the influence extra cellular polysaccharide produced by algae (or diatom has to be studied. Because the extracellular polysaccharide polymers can bind microbes to surfaces and can cause physical modification of the microbial

environment. Since uronic acids appear to be the components of these extracellular films that are most concentrated in a location outside the cell membrane, a quantitative assay for uronic acids was developed. To achieve this, an inhibitor which is used to inactivate the extracellular polysaccharide produce by algae cell wall was used to protect mild steel in an algal environment was reviewed.

Correspondence

S. Chitra,

Email chitrachem@gmail.com

B. Anand,

Email chemanand27@gmail.com

Keywords Microbial induced corrosion; Algae; EPS inhibitor; Extracellular polysaccharide; Biofilms

Introduction

Microbial-influenced corrosion (MIC) can be defined as the deterioration of metals by natural processes directly or indirectly related to the activity of microorganisms [1]. Microorganisms tend to attach themselves to the solid surfaces, colonize, proliferate, and form biofilm which may in turn produce an environment at the biofilm/metal interface radically different from the bulk medium in terms of pH, dissolved oxygen, organic and inorganic species. Since the biofilm tends to create non-uniform surface conditions, localized attack might start at some points on the surface leading to localized corrosion, usually in the form of pitting. Industrial systems are likely to contain various structures where microbiologically induced corrosion (MIC) and biofouling can cause problems open or closed cooling systems, water injection lines, storage tanks, and residual water treatment systems, and filtration systems, different types of pipes, reverse osmosis membranes, and potable water distribution systems[3].

Fig 1 represents the Current conceptual models concur that there are three stages in the pitting corrosion initiation, metastable pitting, and active pitting [2-4]. When microorganisms are involved in the corrosion of metals, the situation is more complicated than it is in an abiotic environment, because microorganisms not only modify the near-surface environmental chemistry via microbial metabolism but also may interfere with the electrochemical processes occurring at the metal-environment interface. The anaerobic corrosion of iron was noted in the 19th century and many theories were proposed about its mechanism. Decades of scientific research projects and investigations on the complex influence of microbes on increasing or decreasing corrosion rates have provided a much deeper insight in the role microorganisms play on the life of systems exposed to waters and grounds where they proliferate. The mechanisms potentially involved in MIC are summarized as (a) cathodic depolarization, (b) Formation of occluded surface cells (c), Fixing of anodic reaction sites (d) under deposit acid attack [6]. Certain microorganisms thrive under aerobic conditions, whereas others thrive in anaerobic conditions. The pH conditions and availability of nutrients also play a role in determining what type of microorganisms can thrive in a

particular soil environment [8-9]. Microorganisms associated with corrosion damage are Aerobic & Anaerobic bacteria.

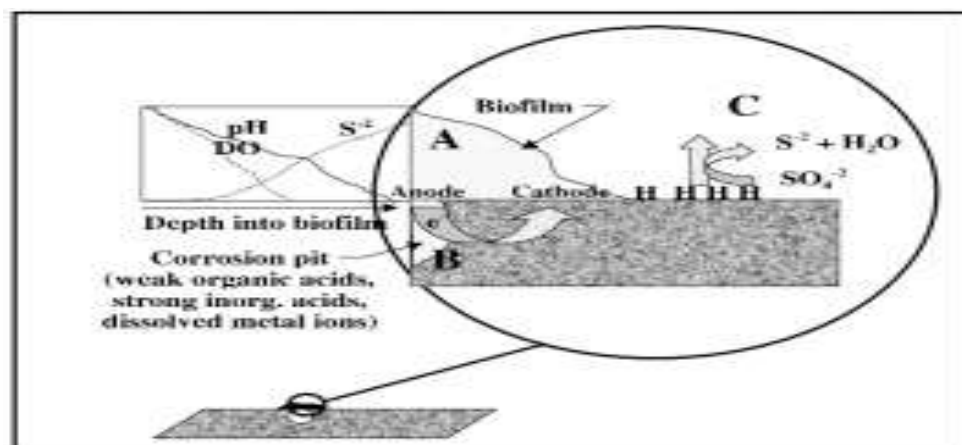


Fig. 1. Current conceptual models concur that there are three stages in the pitting corrosion initiation, metastable pitting, and active pitting.

Biofilm

A biofilm is any group of microorganisms in which cells stick to each other on a surface. These adherent cells are frequently embedded within a self-produced matrix of extracellular polymeric substance (EPS) [7]. This matrix protects the cells within it and facilitates communication among them through biochemical signals. Some biofilms have been found to contain water channels that help distribute nutrients and signaling molecules. Fig 2 represents the biofilm development by various stages. (1) Initial attachment (2) Irreversible attachment (3) Maturation I (4) Maturation II (5) Dispersion

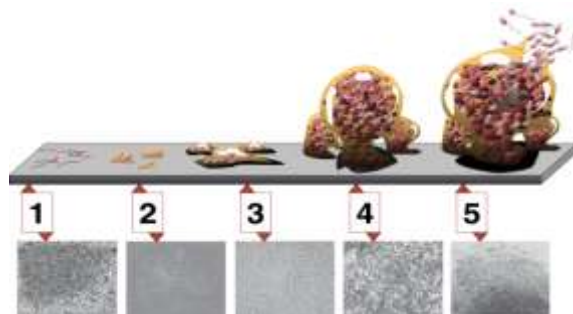


Fig. 2. Stages of biofilm development

Mechanism

Concentration Cells

Oxygen Concentration Cells

Respiring aerobic microbial cells on metal surfaces can result in local anodes and cathodes and formation of differential aeration cells. Under aerobic conditions, areas under respiring colonies become anodic and surrounding areas become cathodic.

Metal Concentration Cells

Microorganisms that colonize metal surfaces produce extracellular polymeric substances (EPS) and form a gel matrix on the metal. In general, EPS are acidic and contain functional groups that bind metals (21). Metal ions concentrated from the aqueous phase or from the substratum into the biofilm can increase corrosion rates by providing an additional cathodic reaction (22-24).

Inactivation of Corrosion Inhibitor

Biofilms reduce the effectiveness of corrosion inhibitors by creating a diffusion barrier between the metal surface and the inhibitor in the bulk medium (10-14). Aliphatic amines and nitrites used as corrosion inhibitors can be

degraded by microorganisms, decreasing the effectiveness of the compounds and increasing the microbial populations (20). Cooke and co-workers (22) reported that potassium chromate (K_2CrO_4) was ineffective as a corrosion inhibitor in an electricity generating station because of chromate reducing bacteria. The bacteria were causing blockage of pipes by precipitation of chromium (III) oxide.

Alteration of Anion Ratios

Microorganisms can alter the composition of an electrolyte and make it more corrosive. For example, molar ratios of aggressive ions to inhibiting ions (eg, Cl^- to $NO_3^- + SO_4^{2-}$) are used to predict whether an electrolyte can sustain a localized corrosion reaction [16-18]. Relationships between concentration of inhibitive and aggressive anions correspond to competitive uptake of the anions by adsorption or ion exchange at a fixed number of surface sites. Increasing chloride concentration shifts the critical pitting potential to more active (negative) values [15-16]. The potential is shifted to more noble (positive) values by the presence of other anions, particularly oxyanions (ClO^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , NO_2^- and OH^-). Salvarezza and co-workers demonstrated that during growth of the fungus *Cladosporium resinae*, nitrate, and phosphate were incorporated into the biomass increasing the chloride/inhibitor ratio [21]. In their experiments, fungal uptake of oxyanions was the principal cause of the pitting potential decrease during microbial growth. Predictions about pitting or crevice corrosion resistance in chloride-containing media cannot be based on anion ratios without consideration of potential microbial alterations [22].

Reactions within Biofilms

Reactions within biofilm are generally localized, affecting mechanisms and accelerating rates of electrochemical reactions leading to corrosion. While corrosion influencing reactions may be attributed to a single group of organisms, the most aggressive MIC occurs with natural populations containing many types of microorganisms. Furthermore, a single type of microorganism can simultaneously affect corrosion via several mechanisms (a) Methanogenesis (b) Sulfide Production (c) Acid Production (d) Ammonia Production (e) Metal Oxidation / Metal reduction.

The Role of Extracellular Polymeric Substances

Extracellular polymeric substances (EPS) are mainly high molecular weight secretions of microorganisms and consist of various organic substances such as polysaccharides, proteins, nucleic acids and lipids [19]. EPS bind the microbes together in a three-dimensional matrix and so affect the physico-chemical characteristics of the microbial aggregates such as mass transfer, surface characteristics, adsorption ability and stability [20]. The EPS are distributed in layers of varying depth through the biofilm [21]. They establish the structural and functional integrity of microbial biofilms, and significantly contribute to the organization of the biofilm community [22]. They also contribute to the mechanical stability of the biofilms, enabling them to withstand considerable shear forces [23]. EPS produced at the solid surface promote microbial adhesion by altering the physicochemical characteristics of the colonized surface such as charge, hydrophobic, and roughness [24]. They create scaffolds with suitable physical characteristics and interconnected pore structures that promote cell attachment [25]. Cell adhesion to solid surfaces is inhibited by electrostatic interaction at low EPS concentration but enhanced by polymeric interaction at high EPS concentration [29]. The forms of EPS that exist outside of cells can be subdivided into bound EPS (sheaths, capsular polymers, condensed gels, loosely bound polymer and attached organic materials) and soluble EPS (soluble macromolecules, colloids, and slimes) [25]. Bound EPS are closely bound to cells while soluble EPS are weakly bound to cells or dissolved in the surrounding solution. Soluble EPS are sometimes referred to as soluble microbial products (SMP) [25]. Soluble EPS have greater binding capacity for organic matter than bound EPS [26].

As the EPS accumulate, the deposited material forms a gel layer by cross-linking with the membrane surface. The gel layer then provides an environment that is rich in nutrients, ideal for further bacterial attachment. The attachment of EPS to form a gel matrix on membrane surfaces depends on a number of factors such as (a) cohesion characteristics of EPS; (b) flexibility and rearrangement characteristics of EPS; (c) adhesion characteristics between EPS and membrane; (d) morphology of membrane surface; (e) diffusion of EPS into the porous surface structure and (f) flow patterns near the membrane surface [30]. The biofouling potential of EPS is significantly greater than some types of natural organic matter and the permeate flux decline during biofouling is strongly related to the EPS content [31].

Measuring and Monitoring MIC

Electrochemical techniques used to study MIC include those in which no external signal is applied [eg, measurement of galvanic current with zero resistance ammeter (ZRA), measurement of redox potential

(ET/Q), corrosion potential (E_{corr}) and electrochemical noise analysis (ENA)[33], those in which only a small potential or current perturbation is applied [eg, polarization resistance (R_p), and electrochemical impedance spectroscopy (EIS)][34], and those in which the potential is scanned over a wide range (eg, anodic and cathodic polarization curves, pitting scans) [32]. Biofilm formation and corrosion can be monitored using metal coupons implanted either in-line or in a side stream. Several types of coupon holders have been developed. Typically, coupons are removed periodically and used for weight loss, microbiological analyses, or microscopic examination. Many techniques claim to monitor MIC; however, none have been accepted as an industry standard or as a recommended practice by ASTM or NACE International. The major limitation for MIC monitoring programs is the inability to relate microbiology to corrosion in real time. Some techniques can detect a specific modification in the system due to the presence and activities of microorganisms (eg, heat transfer resistance, fluid friction resistance, galvanic current) and assume something about the corrosion.

Others measure some electrochemical parameter (eg, R_p , ENA) and assume something about the microbiology. With experience and knowledge of a particular operating system either technique type can be an effective monitoring tool, especially for evaluating a treatment regime (biocides or corrosion inhibitors). All monitoring techniques used for MIC are based on assumptions that can only be validated by a thorough understanding of the system that one is attempting to monitor. Planktonic population does not properly reflect the type and number of organisms living in the biofilm. Polarization resistance is appropriate for indicating a change in the general corrosion rate, but the results are difficult to interpret for localized corrosion. Measurements of R_p will indicate that something is happening, but will not give an accurate measure of the localized corrosion rate. Impedance spectroscopy requires the area of attack to be determined in order to calculate the corrosion rate. When MIC is present, corrosion is usually highly non-uniform. Thus, knowing the electrode sample surface area used in the measurement is often not sufficient. The ENA techniques have failed to routinely predict MIC events accurately under field conditions and ZRA measurements of galvanic current cannot be directly converted to corrosion rate.

Strategies to Prevent or Mitigate MIC

Engineering designs that incorporate drains, eliminate traps for stagnant water, reduce the number of bends and elbows, and specify gasket materials that do not wick, reduce the potential for MIC. Components that typically remain stagnant for long periods of time should be designed to be cleaned or flushed. Where possible, the system design should provide control of the flow velocity that will limit bacterial growth [30]. Continuous flow is preferable to intermittent flow. Dead leg and bypass circuits should be avoided wherever possible. Side stream filtration and in-line filters should be included in the design when make-up water contains high levels of suspended solids. Provisions must be made to purge accumulations of suspended solids from the system when it is not possible to prevent their accumulation by insertion of pigs, air bumping, sand-jetting, or high pressure water spray. Strategies to mitigate-control the effects of MIC include the following reduce the numbers and types of organisms in the system or alter potential electron acceptors to inhibit specific groups of bacteria

Reduce Numbers and Types of Organism.

Numerous methods have been used for minimizing the accumulation of biofilms on engineering surfaces including the following addition of biocides (oxidizing and non oxidizing) to the bulk water to kill organisms entering the system or reduce the growth rate of microorganisms within the biofilm, mechanical removal of biofilms from the substratum (sponge balls, brushes), and water treatments to decrease the numbers and types of organisms (aeration, deaeration).

Alter Potential Electron Acceptors to Inhibit Specific Groups of Bacteria.

One practical application for controlling MIC by controlling the electrolyte composition has been used in seawater injection systems. In these systems, seawater is injected into oil reservoirs to maintain pressure. Oxygen is removed to minimize corrosion. However, in the anaerobic environment, growth of SRB is encouraged and corrosion of steel alloys results. Laboratory and field experiments have demonstrated that nitrate treatment can be an effective alternative to biocide treatment[21]. Nitrate addition causes a shift in the microbial population from SRB to nitrate-reducing bacteria (NRB)

Exopolysaccharide inhibitors

A whole spectrum of geo microbiological interactions between the microorganisms and the mild steel is mediated by extracellular polymeric substances (EPS) excreted by the growing sub-aerial biofilm (Gorbushina and Krumbein 2000). Attachment of microorganisms is the first step in biofilm formation on metal, and the adhesion

of cells to substrata is due to EPS. Also chemical dissolution of metal may be influenced by acidic polysaccharides present in EPS. Bacteria, fungi and algae produce different types of EPS. Chemicals are known which can inhibit the production of EPS, and therefore can be used to inhibit attachment of micro-organisms to stone surfaces. Koulali et al. (1996) demonstrated the inhibitory effect of monensine on the synthesis of EPS by the fungal genera *Botrytis* and *Sclerotium*, and Huang and Stewart (1999) demonstrated the inhibitory effect of bismuth dimercaprol in *Pseudomonas aeruginosa* biofilm.

Conclusion

Although corrosion inhibitors are widely used in industry, the problem of corrosion damages is still urgent. To certain extent this is due to the fact that microbially induced pitting corrosion is responsible for 30% of all cases of biodamages of industrial processing's. As a rule, these inhibitors do not work against this type of corrosion. There are different approaches allowing suppression of corrosive activity of microorganisms. Applications of different EPS inhibitor are currently highly popular. The efficiency of inhibitor depends on many factors like composition of micro flora, presence and structure of biofilm on the metal surface, chemical composition of the water phase, compatibility with corrosion inhibitors, application method and other factors .so the complex approach to application of EPS inhibitors is possible to reach effective application of them to combat corrosion in heat exchangers, desalination plants & marine equipment. The present work is a first step in realizing such complex approach to develop effective methods of application of EPS inhibitors for large application in industry.

Acknowledgement

The author wish to thank Dr. K. M. Govindharaju, Asst. Professor, Mahendra Engineering College for his help in preparing this review article.

References

- [1]. P. Angell, J.-S. Luo, D. C. While, "Studies of the reproducible pitting of 304 stainless steel by a consortium containing sulphate-reducing bacteria." International Conference on Microbially Influenced Corrosion (Houston, TX NACE International. 1995), p. 1/1-1/10.
- [2]. J. Boivin. I. J. Laishley. R. D. Bryant, J. W. Costerton, "The influence of enzyme systems on MIC." CORROSION 90. Paper no. 128 (Houston, TX NACE International, IW0).
- [3]. M. Brennenstuhl and T. S. Gendron, "The Use of Field Tests and Electrochemical Noise to Define Conditions for Accelerated Microbiologically Influenced Corrosion (MIC) Testing." in Microbiologically Influenced Corrosion resting, ASTM STP 1232. Eds. J. R. Kearns and B. J. Little, Philadelphia, 1994, pp. 15-27.
- [4]. C. S. Brossia. I. Yang. "Studies of microbiologically influenced corrosion using a coupled multielectrode array sensor." CORROSION 2003. Paper no. 03575 (Houston, TX NACE International. 2003).
- [5]. S. J. Bullard. B. S. Covino, Jr., J. H. Russell, G. R. Holcomb, S. D. Cramer, and M. Ziomek-Moroz (2002) Electrochemical Noise Sensors for Detection of Localized and General Corrosion of Natural Gas Transmission Pipelines Final report to US Department of Energy. 27 pp.
- [6]. A.H L. Chamberlain, P. Angell, H. S. Campbell, "Staining procedures for characterizing biofilms in corrosion investigations," British Corrosion Journal 23, 3 (1988) p. 197-198.
- [7]. V. Ferrante, D. Feron, "Microbially influenced corrosion of steels containing molybdenum and chromium a biological and electrochemical study," in Microbially Influenced Corrosion and Biodeterioration, eds. N. J. Dowling, M. W. Mittelman and J. C. Danko (Knoxville, TN University of Tennessee, 1991), p. 3-55-3-63.
- [8]. M. J. Franklin, D. C. White, "Biocorrosion," Curr Opin Biotech 2 (1991) p. 450-456.
- [9]. T. R. Jack. (i. van Boven, M. Wilmot, R. G. Worthingham, "Evaluating performance of coatings exposed to biologically active solis." Mater Performance 35, 3 (1996) p. 39-45.
- [10]. T. Kaeberlein, K. Lewis, S. S. Epstein, "Isolating "uncultivable" microorganisms in pure culture in a simulated natural environment," Science 249 (2002) p. 1127-1129.
- [11]. K. Kasahara. F. Kajiyama, "Electrochemical aspects of microbiologically influenced corrosion on buried pipes," in Microbially Influenced Corrosion and Biodeterioration, eds. N. J. Dowling, M. W. Mittleman and J. C. Danko (Knoxville, TN University of Tennessee, 1991), p. 2-33-2-39.

- [12]. R. A. King, B. S. Skerry, D. C. A. Moore, J. F. D. Stott, and J. L. Dawson. Corrosion behaviour of ductile and grey iron pipes in environments containing sulphate-reducing bacteria, in *Biologically Induced Corrosion*. Ed. by S. C. Dexter. NACE International, Houston. IX. 1986. pp. 83-91.
- [13]. G. J. Licina, G. Nekoksa. "On-line monitoring of biofilm formation for the control and prevention of microbially influenced corrosion," 1995 International Conference on Microbially Influenced Corrosion (Houston, TX NACE International. 1995), p. 42/1-42/10.
- [14]. R. Ray and B.J. Little (2003) Environmental electron microscopy applied to Biofilms. In *Biofilms in Medicine, industry and Environmental Biotechnology*. Edited by Piet Lens, A.P. Moran, T. Mahony, P. Stoodley and V. O'Flaherty. IWA Publishing, London, pp. 331-351.
- [15]. A.Reyes, M. V. Letelier, R. De la Iglesia, B. Gonzalez, G. Lagos, "Microbiologically induced corrosion of copper pipes in low-pH water" *Int Biodeter Biodegr* 61,2 (2008) p. 135-141.
- [16]. J. M. Romero, E. Velazquez, G.-V. J. L., M. Amaya, S. Le Borgne, "Genetic monitoring of bacterial populations in a sewerage injection system. Identification of biocide resistant bacteria and study of their corrosive effect." *CORROSION* 2005. Paper no. 05483 (NACE International, 2005).
- [17]. G. Schmitt. "Sophisticated electrochemical methods for MIC investigation and monitoring," *Materials and Corrosion* 48. 9 (1997) p. 586-601.
- [18]. P. S. N. Stokes, M. A. Winters, P. O. Zuniga, D. J. Schlottenmier, "Developments in on-line fouling and corrosion surveillance," in *Microbiologically Influenced Corrosion*
- [19]. Tsuneda, S.; Aikawa, H.; Hayashi, H.; Yuasa, A.; Hirata, A. Extracellular polymeric substances responsible for bacterial adhesion onto solid surface. *FEMS Microbiol. Lett.* **2003**, *223*, 287–292.
- [20]. Zhang, X.Q.; Bishop, P.L. Spatial distribution of extracellular polymeric substances in biofilms. *J. Environ. Eng.* **2001**, *127*, 850–856.
- [21]. Mayer, C.; Moritz, R.; Kirschner, C.; Borchard, W.; Maibaum, R.; Wingender, J.; Flemming, H.-C. The role of intermolecular interactions Studies on model systems for bacterial biofilms. *Int. J. Biol. Macromol.* **1999**, *26*, 3–16.
- [22]. Chen, V.J.; Ma, P.X. Nano-fibrous poly(L-Lactic acid) scaffolds with interconnected spherical macropores. *Biomaterials* **2004**, *25*, 2065–2073.
- [23]. Neilsen, P.H.; Jahn, A. *Microbial Extracellular Polymeric Substances Characterization, Structure and Function*; Wingender, J., Neu, T.R., Flemming, H.-C., Eds.; Springer-Verlag Heidelberg, Germany, 1999; 49–72.
- [24]. Rosenberger, S, Kraume M, Filterability of activated sludge in membrane reactors *Desal.***2002**, *146*, 373–379.
- [25]. Pan, X.L.; Liu, J.; Zhang, D.Y.; Chen, X.; Song, W.J.; Wu, F.C. Binding of dicamba to soluble and bound extracellular polymeric substances (EPS) from aerobic activated sludge A fluorescence quenching study. *J. Colloid Interface Sci.* **2010**, *345*, 442–447.
- [26]. Flemming, H.-C.; Leis, A. Sorption properties of biofilms. In *Encyclopedia of Environmental Micrology*; Flemming, H.-C., Bitton, G., Eds.; John Wiley & Sons, Inc. New York, NY, USA, 2002; Volume 5, 2958–2967.
- [27]. Spath R, Flemming H.-C, Wuertz, S. Sorption properties of biofilms. *Water Sci. Technol.* **1998**, *37*, 207–210.
- [28]. Liu, Y.; Fang, H.H.P. Influence of extracellular polymeric substance (EPS) on flocculation, settling and dewatering of activated sludge. *Crit. Rev. Environ. Sci. Technol.* **2003**, *33*, 237–273.
- [29]. Tansel, B.; Sager, J.; Garland, J.; Xu, S.; Levine, L.; Bisbee, P. Deposition of extracellular polymeric substances and micro-topographical changes on membrane surfaces during intermittent filtration conditions. *J. Membr. Sci.* **2006**, *285*, 225–231.
- [30]. Fonseca, A.C.; Summers, R.S.; Greenberg, A.R.; Hernandez, M.T. Extracellular polysaccharides, soluble microbial products and natural organic matter impact on nanofiltration membranes flux decline. *Environ. Sci. Technol.* **2007**, *41*, 2491–2497.
- [31]. R. E. Tatnall, K. M. Stanton, R. C. Ebersole. "Methods of testing for the presence of sulfale-reducing bacteria." *CORROSION* 88. Paper no. 88 (Houston. TX NACE International, 1988).
- [32]. M. Brennenstuhl and T. S. Gendron, "The Use of Field Tests and Electrochemical Noise to Define Conditions for Accelerated Microbiologically Influenced Corrosion (MIC) Testing." in *Microbiologically Influenced Corrosion testing*, ASTM STP 1232. Eds. J. R. Kearns and B. J. Little, Philadelphia, 1994, pp. 15-27.

- [33]. N. J. E. Dowling, J. Guezennec, M. L. Lemoine, A. Tunlid, D. C. White, "Corrosion analysis of carbon steels affected by aerobic and anaerobic bacteria in mono and co-cultures using AC impedance and DC techniques," *Corrosion* 44. 12 (1988) p. S69-S74.
- [34]. M. Enienand B. Yang (2001) Effective use of monitoring techniques for use in detecting and controlling MIC in coolingwater systems. *Biofouling The Journal of Bioadhesion and Biofilm Research*. 17(1) 47-57.

© 2014, by the Authors. The articles published from this journal are distributed to the public under "**Creative Commons Attribution License**" (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

Publication History

Received	19 th Sep 2013
Revised	18 th Nov 2013
Accepted	20 th Dec 2013
Online	05 th Jan 2014