ANAEROBIC BACTERIA TREATMENT BY BENZYL DIMETHYL (2-HIDROXYETHYL) AMMONIUM CHLORIDE FOR CARBON STEEL PIPELINE SYSTEM

Mohd Nazri Idris
School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, Engineering Campus,
14300 Nibong Tebal, Penang Malaysia
Email: srmnazri@usm.my

Nur Akma Mahat
School of Applied Physics, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Email: nurakmamahat@yahoo.com

Norinsan Kamil Othman
School of Applied Physics, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Email: insan@ukm.edu.my

Fathul Karim Shahrani
School of Environment and Natural Resources Science,
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Email: fatul@ukm.my

ABSTRACT

The performance of Benzyldimethyl (2-hidroxyethyl) ammonium chloride (BDC) as a microbiologically control on anaerobic consortium bacteria containing sulfate reducing bacteria (C-SRB) has been investigated. The efficiency of this organic compound toward carbon steel used as pipeline system had been analyzed by potentiodynamic polarization technique, weight loss test and scanning electron microscope. Tafel extrapolating plots indicated that BDC is capable of preventing microbiologically activities at concentration more than 4096 ppm, ascribed to retarding of active reaction between carbon steel and C-SRB metabolic product in the environment of VM medium I (VMNI). This performance was also supported by weight loss analysis. It is showed that all corrosion rates from weight loss measurement were tabulated in range of 0.10 to 0.13 mm/yr, which is acceptable to be applied in anaerobic condition. Morphology analysis proven that the biocorrosion product as well as the growth of C-SRB and their metabolic activities were successfully retarded. This study revealed that BDC is able to control the microbiologically activities and minimize the biocorrosion product at carbon steel pipeline surface.

Keywords: Sulfate reducing bacteria, biocorrosion, potentiodynamic polarization, weight loss

Introduction

Biocorrosion arise from microbiologically induced corrosion (MIC) was disrupted many equipments and facilities in various industries. This menace becomes more crucial in transportation pipelines system especially when involving crude oil product (Al-Jaroudi et al., 2011). Water and solids suspended are the most imperative factor in affecting likelihood of MIC and biocorrosion process. This is due to entrainment and settling of solids from crude oil transportation as well as precipitation of microbial and their metabolic by-product (Larsen, 2013). Therefore, preventive action for controlling MIC activities at the internal part of pipelines system is essential.

MIC contains several type of microorganism, which is inherently lived as a consortium. Thorough nutrient in their environment make these microorganism grow and precipitate with their biofilm by-product such as extra polymeric substance, organic acids, hydrogen sulfide (H_2S) and CO_2, which is arise from metabolic activities (Beech et al., 2005; Prabha et al., 2014). Among of these metabolic by-products, H_2S is the most reactive compound affecting in biocorrosion process. Sulfate reducing bacteria (SRB) play important role to reduce sulfate and others sulfur compound like sulfite and thiosulfate to sulfide ions. Existing of these sulfide ions and existing of hydrogen gas in medium lead to generating this H_2S, which is highly corrosive for any metallic compound (Sahrani et al., 2008). Several mechanisms have been proposed to elaborate this H_2S reaction on metallic surface and their biocorrosion products (Kakooei et al., 2012). Active mechanism definitely increase the corrosion rate and give rise to pitting process and stress corrosion damage.

Application of inhibitor and biocide materials are the most practical method for this biocorrosion menace (Aiad et al., 2014; Cetin & Aksu, 2009; Street & Gibbs, 2010). However, the application of both inhibitor and biocide are still involving separate compounds and the effort of developing single dwifunctional compound for both application as well as reducing corrosion management operation is still attracting the researcher worldwide (Liu et al., 2016; Raja et al., 2016). Meanwhile, chemical composition, transported fluid phase compositions, condition of pipeline surface, temperature and hydrodynamic modes of pipeline operation should also be considered (Sivokon & Andreev, 2012). Organic compounds containing heteroatom such as N, S and P were tremendously practiced by majority of industries especially in petroleum application. Among of these organic compounds, quaternary ammonium compound that containing nitrogen and benzyl functional group are claimed to form a thin film on the metal surface and can react as a barrier to suppress dissolution process of anodic materials as well as hydrogen evolution at cathodic reaction (Finšgar & Jackson, 2014). It is also proven that the presence of nitrogen together with several functional group are capable of inhibiting biocorrosion process by reducing the metabolic activity of SRB (Mahat et al., 2015). Due to these studies, we introduce benzyldimethyl (2-hidroxyethyl) ammonium chloride as a controlling agent for microbial activities. The objective of this study is to determine the performance of this organic compound as a microbiologically control for protecting carbon steel in pipeline system. Consortium bacteria containing sulfate-reducing bacteria from local crude oil of Peninsular Malaysia had been selected for this investigation. Study was carried out based on potentiodynamic polarization method, weight loss test and surface analysis.

MATERIALS AND METHODS

Chemical compositions (wt%) of carbon steel used in this study were 0.258 C, 0.466 Mn, 0.427 Si, 0.013 P, 0.015 Ni, 0.019 Cu, 0.132 Al and balance Fe. This steel was mechanically cut to a coupon size 12 x 10 x 5 mm and ground with emery paper from grit 240 to 1200. At each grinding steps, coupon was washed with distilled water and rinse with acetone. BDC was purchased from Sigma Aldrich Co. Ltd. The concentration of this organic compound was varied from 512 to 16384 ppm based on double dilution method.

C-SRB was obtained from Biological Laboratory, Faculty of Science and Technology, UKM, Malaysia. This C-SRB was isolated from local crude oil located in Peninsular of Malaysia. C-SRB was grown in VMNI medium as proposed by Zinkevich (1996), which is containing (g/L) 0.5 KH_2PO_4, 1.0 NH_4Cl, 4.5 Na_2SO_4, 0.3 $Na_3C_6H_5O_7$, 0.04 $CaCl_2.6H_2O$, 0.06 $MgSO_4.7H_2O$, 2.0 casamino acid, 2.0 tryptone, 6.0 sodium lactate, 0.1 ascorbic acid, 0.1 thioglycolic acid and 0.5 $FeSO_4.7H_2O$. VMNI medium was prepared using filtered sea water. The prepared medium was filtered with mixed cellulose ester membranes at size 0.45 µm and followed with 0.22 µm. Later, this VMNI medium was autoclaved at 121^oC for 15 minutes prior to pipetted with 0.1 mL trace elements and 0.2 mL vitamins at cold temperature.

5 mL C-SRB batches were pipetted into 28 mL VMNI medium and grew in incubator at 30^oC for three days. Then, these C-SRB batches were centrifuged at 3500 rpm for 5 minutes prior to added with test solution. Coupons for each potentiodynamic polarization and weight loss tests were immersed into these solutions and incubated again for 7 days at 30^oC.

Potentiodynamic polarization test was carried out by potentiostat model Gamry PC4/750. This test was performed in a conventional three electrodes. Platinum rod and saturated calomel electrode were used as auxiliary and reference electrodes, respectively. Working electrode was imbedded in resin epoxy, which is connected with a copper wire. All tests were begun after 20 minutes exposure time and the temperature was recorded as 25^oC. Potential scanned was set up in range of -250 to +250 mV of open circuit potential and the scan rate was standardized at 1.0 mV/s.

Weight loss test was performed in 100 mL test bottle. After 7 days incubation period, the coupons were withdrawn and cleaned according to ASTM G1-03. All tests were performed in triplicate. The weight of tested coupon, before and after incubation period was determined by analytical balance. Corrosion rate, C_R (mm/yr) from this analysis was measured based on equation 1:

$$C_R = \Delta WK/At \quad (1)$$

where ΔW (g) is the average weight loss, K = 87600 is the constant, A (cm^2) is the surface area and t (h) is the immersion period.

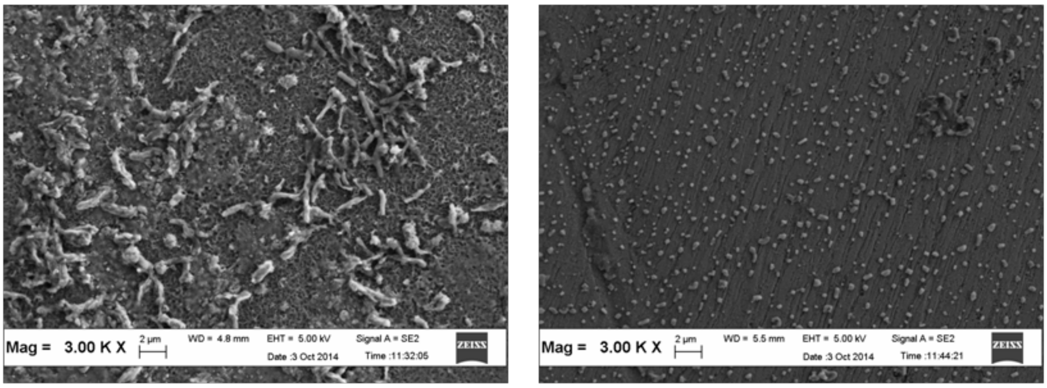
Biofilm analysis was performed by scanning electron microscope model Zeiss Supra 35VP. Samples were prepared as weight loss test and VMNI medium containing C-SRB batch without and with 4096 ppm BDC were applied. After 7 days incubation period at 30^oC, these samples were withdrawn, immersed in double distilled water, and dried with cold air. Samples were analyzed without any sputtering.

RESULTS AND DISCUSSION

The performance of BDC for controlling microbial activities toward carbon steel was analyzed by scanning electron microscope. Figure 1 represents the surface of carbon steel affected with C-SRB after 7 days incubation in absence and presence of 4096 ppm BDC. Micrograph in Figure 1(a) showed that carbon steel surface was fully covered with a variety of bacteria together with extracellular polymeric substance (EPS) and corrosion product. The figure also indicated that some features of bacteria are related to *Desulfovibrio* species. However, identifying of this *Desulfovibrio* genetic was not conducted yet and will be undertaken as future study. The micrograph revealed that SRB grew as a mix culture in VMNI medium. SRB and others bacteria survived on steel surface by developing EPS biofilm through their inherent metabolic process, which is containing polysaccharides, lipid and protein (Sheng et al., 2010). The presence of SRB in this micrograph was proven by a strong smell of rotten egg and a showing of black VMNI broth ascribed to reduction of sulfate compound and formation of H_2S and FeS. Similar observation was also presented by previous studied involving SRB (Abdullah et al., 2014; Fathul Karim Sahrani et al., 2008)

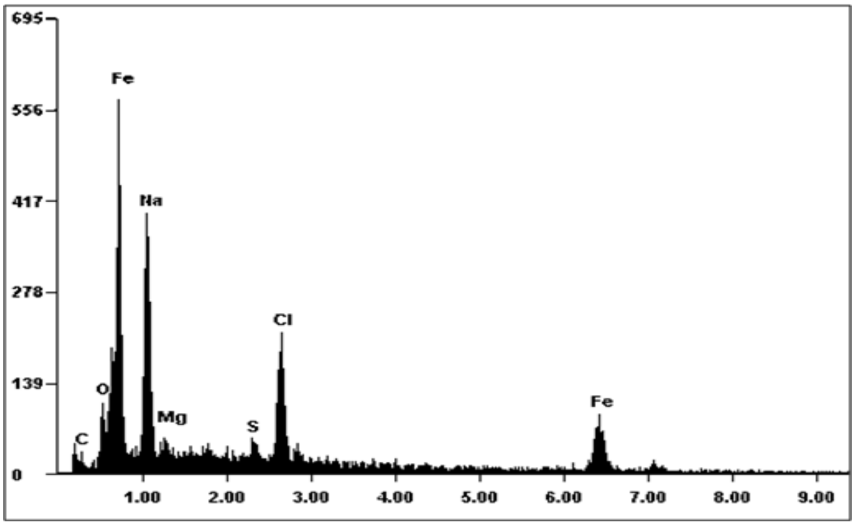
As depicted in Figure 1(b), there is neither bacteria nor EPS product were presented. In contrast to Figure 1(a), less damaging on carbon steel surface has been observed. EDX analysis confirmed that only corrosion product and precipitate compounds from VMNI medium were dominated on this surface as shown in Figure 2. It is confirmed that BDC was successfully retarded the growth of bacteria and their activities at present concentration and consequently provide better protection for carbon steel surface. It is believed that BDC react with presence bacteria through an electrostatic interaction. Attraction of opposite charges between BDC (definitely from ammonium) and the negative charges present on bacteria occurred at the center of cellular cell. This interaction will cause a strong damage on these functional permeability membrane and obviously disrupting the metabolic process within cytoplasm (Badawi et al., 2010).

Figure 1. SEM images of C-SRB growth on carbon steel surface after seven days incubation period (a) without BDC and (b) with 4096 ppm BDC



(a) (b)

Figure 2. EDX analysis of C-SRB growth on carbon steel surface after seven days incubation period with 4096 ppm BDC



It was also reported that BDC are capable of adsorbing onto carbon steel surface and react as a barrier for protecting the corrosion process (Idris et al., 2014). The existing of ammonium ion with adjoins of π-electron from benzyl group in this compound will synergistically increase the adsorption process and strengthening the formation of thin film on the carbon steel surface. Thus, dissolution process of anionic and charges transferring from electrolyte medium will be suppressed. Intuitively, it is reasonable for BDC to inhibit the corrosion process of steel surface as well as controlling the growth of microbial and their metabolic activities.

Figure 3 shows the potentiodynamic polarization curves of carbon steel in the presence of C-SRB at various BDC concentrations. This figure illustrated that all curves slightly shifted to lower current density as correspond to the control medium. Tafel extrapolating plot indicated the corrosion current density declined from 0.744 mA/cm^2, at the control medium to a range of 0.011 and 0.027 mA/cm^2, at presence BDC compound. At 4096 ppm and higher BDC concentration, the I_c values are remaining unchanged attributed to ability of BDC to adsorb and suppress the corrosion reaction of steel surface from actively react with corrosive species produced by C-SRB and water molecules. This analysis also marked that all corrosion rates are tabulated in range of 0.1 to 0.3 mm/yr, which is considering acceptable to protect carbon steel in anaerobic condition. Others electrochemical parameters from this analysis are presented in Table 1.

Relative to control medium, all curves in Figure 3 shifted on both positive and negative potential of anodic and cathodic regions, respectively. The result suggests that BDC actively affected on the process of anodic dissolution and inhibited the hydrogen evaluation process at cathodic regions. Similar inhibition mechanism was also reported when applying others organic compounds (Kumar & Mohana, 2014; Singh et al., 2012). Obtained corrosion potential, E_c of all BDC concentration were tabulated in range of -0.814 to -0.784 V. As Compared with the control E_c, these values were below than 0.085 V. Thus, it is confirmed that BDC acts as a mix-type inhibitor.

As observed in Table 1, both data of Tafel anodic, β_a and Tafel cathodic, β_c slopes are showing a little bit changes at all BDC concentrations applied. These results revealed that BDC molecules are affecting the corrosion rate of present carbon steel but certainly unchanging their metallic dissolution mechanism. This result is quite similar with other organic compound, when it is implied on carbon steel material (Migahed et al., 2010). In the other hand, increasing in the R_p values with the increasing of BDC concentration indicated that formation of protection layer occurred on this steel/solution interface. This layer can stand as a barrier for charges transferring and avoiding dissolution of anode into solution.

Figure 3. Potentiodynamic polarization plots of carbon steel after seven days incubation period at different BDC concentration.

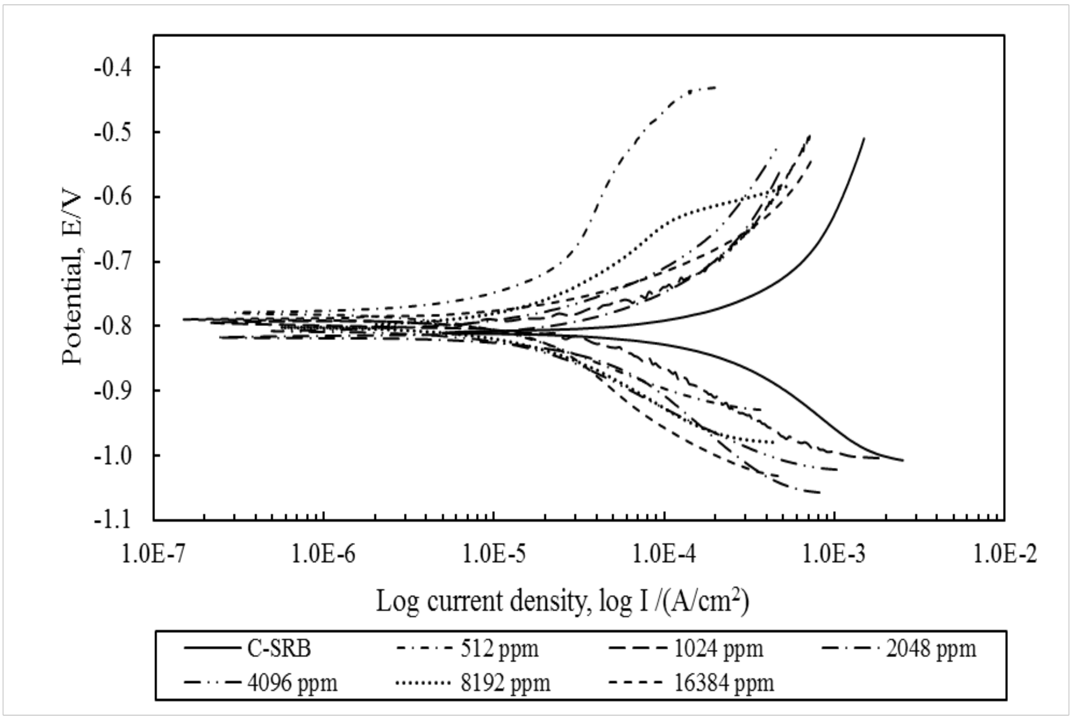
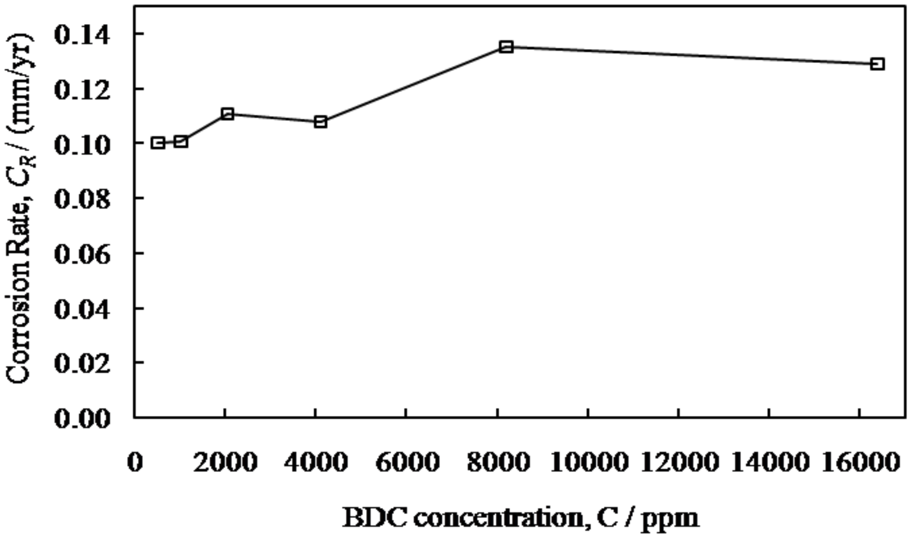


Table 1. Electrochemical data of carbon steel at different BDC concentration.

BDC conc. (ppm)	E_c (V)	I_c (mA/cm^2)	(-)β_c (V/dec)	β_a (V/dec)	R_p (Kohm.cm^2)	C_R (mm/yr)
0	-0.810	0.744	0.496	0.782	0.177	8.910
512	-0.814	0.014	0.090	0.426	2.361	0.165
1024	-0.784	0.027	0.147	0.086	0.877	0.323
2048	-0.801	0.024	0.186	0.092	1.093	0.295
4096	-0.808	0.011	0.120	0.097	2.209	0.127
8192	-0.804	0.012	0.130	0.166	2.710	0.141
16384	-0.802	0.013	0.166	0.101	2.142	0.153

Figure 4 represents the corrosion rate of carbon steel, which is calculated from weight loss analysis as Equation 1. The corrosion rates were slightly increased with the increasing of BDC concentration. As can be seen, all values were tabulated in range of 0.10 to 0.13 mm/yr, which is considering acceptable for carbon steel in anaerobic condition. The result expressed that BDC can be applied as an inhibitor as well as preventing agent for biocorrosion process. It is noticeable that the growth of C-SRB and their metabolic product especially hydrogen sulfide were successfully retarded. BDC molecules had tendency to adsorb onto steel surface and perform a barrier of thin layer. Strong interaction between N^+ ion in BDC molecules and contributing of π-electron in its functional group enhance the adsorption process on this carbon steel surface. Adsorption of N^+ with the presence of benzyl group strengthen the interfacial bonding and avoid the transferring charges from corrosive species produced by C-SRB and also the water molecules. This analysis is resembled with the surface morphology and was in good agreement with potentiodynamic polarization analysis.

Figure 4. Weight loss analysis after seven days incubation period at different BDC concentration.



CONCLUSION

Present study based on weight loss and potentiodynamic polarization methods revealed that BDC is capable of preventing carbon steel from actively corroded due to anaerobic C-SRB by-product. Based on present parameter and BDC concentration, the growth of C-SRB and their metabolic activities had been retarded. It is also proven that BDC which is containing nitrogen ion and benzyl functional group are able to form a thin film on the carbon steel surface and act as a barrier to protect the surface from actively react with H_2S solution arise from SRB metabolic process. This preliminary study suggested that BDC has shown a potential performance to be developed as dwifunctional compound in order to retard the dissolution of carbon steel and mitigate the microbiologically process especially SRB for protecting carbon steel in pipeline system. Further study on electrochemical method, biological approach and synergetic effect of BDC with other organic and inorganic compound can be considered.

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