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Allium sativum (garlic extract) as a green corrosion inhibitor with biocidal properties for the control of MIC in carbon steel and stainless steel in oilfield environments

Punniyakotti Parthipan[a,b,**], Punniyakotti Elumalai[c], Jayaraman Narenkumar[a], Laura L. Machuca[d], Kadarkarai Murugan[e,f], Obuli P. Karthikeyan[g,h,i], Aruliah Rajasekar[a,*]

[a] Environmental Molecular Microbiology Research Laboratory, Department of Biotechnology, Thiruvalluvar University, Serkkadu, Vellore, Tamilnadu, 632 115, India
[b] Electrochemical Energy Research Lab, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, 605 014, India
[c] Division of Biotechnology, Advanced Institute of Environment and Biosciences, College of Environmental and Bioresource Sciences, Chonbuk National University, Iksan, Jeonbuk, 54596, South Korea
[d] Curtin Corrosion Centre, WA School of Mines: Minerals, Energy and Chemical Engineering, Curtin University, Bentley, WA, 6102, Australia
[e] Division of Entomology, Department of Zoology, School of Life Sciences, Bharathiar University, Coimbatore, Tamil Nadu, 641 046, India
[f] Thiruvalluvar University, Serkkadu, Vellore, Tamilnadu, 632 115, India
[g] Institute of Subtropical Agriculture, Chinese Academy of Science, Changsha, China
[h] Queens University of Belfast, Belfast, United Kingdom
[i] ProLog Biologicals Pvt. Ltd., Hyderabad, India

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ABSTRACT

In the present study, the effectiveness of garlic extract to inhibit the bio-corrosion of carbon steel API 5LX (CS) and stainless steel 316 (SS) in the presence of *Bacillus subtilis* A1 and *Streptomyces parvus* B7 was estimated. The antibacterial activity of the garlic extract (GAE) was tested; 100 ppm of the GAE was identified as the minimal inhibitory concentration for bacterial growth. Weight loss and electrochemical studies including linear polarization and AC impedance along with surface analysis were used to examine the corrosion inhibition efficiency (IE) for both metals in the presence of GAE. The strains A1, B7 and their mixed consortium caused severe corrosion to both metals. In the presence of GAE the IE for abiotic system was about 81 ± 3% and 75 ± 3%, while in the presence of the mixed consortium the IE was 72 ± 3% and 69 ± 3% for CS and SS, respectively. Gas chromatography mass spectrum analysis of GAE indicated that GAE contains a sulphur rich compound which plays a key role in the inhibition of both bacterial development and corrosion. This is the first time garlic extract is proposed as a green corrosion inhibitor with biocidal activity to control biocorrosion in hypersaline corrosive environment containing microorganisms.

1. Introduction

Microbiologically induced corrosion (MIC) is an electrochemical process where microorganisms enhance metal deterioration (Rajasekar et al., 2007a; Dheilly et al., 2008; Machuca et al., 2016; Parthipan et al., 2018). Microbial metabolism in oil reservoir leads to fuel turbidity, contamination, and deterioration of storage tanks and pipelines (Hamilton, 1985; Rajasekar et al., 2010). The presence of microorganisms are key factors responsible for corrosion issues associated with the oil industries (Rajasekar et al., 2010; Stevenson et al., 2011; Lenhart et al., 2014; Lyles et al., 2014). Moreover, water can also stratify at the substructure of crude oil transporting pipeline, if the oil velocity is not enough to entrain water and sweep it through the transporting pipeline system (Rajasekar et al., 2007b).

Microbial corrosion can lead to pipeline failure and has been shown to increase the operation and maintenance costs of the crude oil industry (Lee et al., 2010; Suflita et al., 2012; Elumalai et al., 2017). Generally, 40% of the pipeline metal corrosion in the gas and oil industries is caused by numerous microorganisms (Rajasekar et al., 2007b). The microbial strains present near to metal surface might release metabolic products which are highly corrosive to the metals (Swaroop et al., 2016). Extracellular polymeric substances (EPS)

* Corresponding author.
** Corresponding author. Environmental Molecular Microbiology Research Laboratory, Department of Biotechnology, Thiruvalluvar University, Serkkadu, Vellore, Tamilnadu, 632 115, India.
E-mail addresses: pparthibiotech@gmail.com (P. Parthipan), rajasekargood@gmail.com, rajasekargood@tvu.edu.in (A. Rajasekar).

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participate as an important biological factors in the biofilm development on metallic surfaces (Javed et al., 2015). Biofilm formation initiates with the early attachment of microorganisms on the solid surface, and further secretion of EPS leads to the development of a thicker biofilm and further dispersal of cells which yet again begin with new biofilms on nearby metal surfaces.

Carbon steel is a commonly used engineering material for the transportation and storage of the oil products, due to their higher mechanical strength and known performance in diverse environments. It has been widely studied by many researchers in regards to biocorrosion (Rajasekar et al., 2007a, 2010; Bhola et al., 2014). Stainless steel has high mechanical strength and enhanced corrosion resistance potential compared to carbon steel. Corrosion of stainless steel represents a crucial research area due to their broad use and exceptional applications in chemical and mechanized industries under aggressive operating circumstances (Psyllaki et al., 2013; Vazdirvanidis et al., 2017; Xu et al., 2017). Several biocorrosion studies have also been conducted to study the corrosion performance of these materials in the presence of microorganisms (Machuca et al., 2013, 2014a, b; Machuca, 2017).

Prevention of biocorrosion may be achieved by minimizing biofilm development on metal surfaces. Chemical treatments applied to control biofilm formation include the use of biocides and other products such as inhibitors or dispersive agents (Guiamet and Gomez De Saravia, 2005). Several factors including spectrum of antimicrobial activity, compatibility with other chemicals, cost, and environmental impacts must be assessed when selecting corrosion inhibitors/biocides (Gaylarde and Videla, 1992).

Many chemical inhibitors like formaldehyde, ethylene glycol, glutaraldehyde, sodium molybdate and quaternary ammonium salts have been shown to restrict microbial activity effectively and also limit biofilm formation. However, environmental concerns regarding the application of these chemical inhibitors represent an ongoing challenge to the industry (Guiamet and Gomez De Saravia, 2005; Queiroz et al., 2005; Starosvetsky et al., 2007; Narenkumar et al., 2017,2018). Natural biocides/inhibitors such as plant materials have received increased attention lately. Plant derivatives are economical, easily available and environmentally friendly which make them ideal candidates for MIC control.

Different biocides include plant extracts and antimicrobial peptides which are eco-friendly and have been used to control bio-corrosion (Jayaraman et al., 1999). Recently neem extract was used as green corrosion inhibitor to control copper and carbon steel corrosion in the presence of *Arthrobacter sulfureus*, *Bacillus* sp., *Pseudomonas* sp., and *Acinetobacter* sp. (Swaroop et al., 2016; Parthipan et al., 2017a). Bhola et al. (2014) applied neem extracts to manage sulphate reducing bacteria (SRB) mediated bio-corrosion; neem extracts controlled microbial growth as well as biofilm development. Many plant derivatives have been used to control chemical corrosion, for instance *Ervatamia coronaria, Phyllanthus amarus*, garlic peel extract, *Aloe vera*, *Lemon verbena*, *Gossipium hirsutum*, bamboo leaves, *Artemisia pallens,* orange peel, *Musa Paradisica, Tagetes erecta*, among others (Abiola et al., 2009; Abiola and James, 2010; de Assuncao Araujo Pereira et al., 2012; Garai et al., 2012; Sethuraman et al., 2017; Li et al., 2014; Ji et al., 2015; Mourya et al., 2014; Mhiri et al., 2016; Anupama et al., 2016; Fattah-alhosseini and Noori, 2016). Garlic has many advantages over other plant extracts including availability and low cost. It contains a mixture of organo-sulphur compounds which have been shown to display inhibition properties against microorganisms (de Assuncao Araujo Pereira et al., 2012). Many researchers have used garlic extract as corrosion inhibitors for the control of acid corrosion. These studies have demonstrated the presence of sulphur-containing compounds, which play a key role in the corrosion inhibition activity (de Assuncao Araujo Pereira et al., 2012; Rajam et al., 2013; Al-Mhyawi, 2014; Rodriguez-Clemente et al., 2014, 2015). The corrosion inhibition of copper and carbon steel in acidic medium was over 70–96% in the presence of garlic extract at 400 ppm concentration. To our knowledge, there are no reports available on the inhibitory actions of garlic extract against microbial corrosion in hypersaline conditions.

The current investigation focused on the application of garlic extract (GAE) as a green inhibitor to control MIC of carbon steel API 5LX (CS) and stainless steel 316 (SS). Weight loss experiments, electrochemical studies including polarization and AC impedance, X-ray diffraction (XRD) and gas-chromatography mass spectroscopy (GCMS) were applied to assess the role of GAE in the different corrosion systems.

2. Material and methods

2.1. Microbial strains and culture conditions

Two bacterial strains were used in this study namely *Bacillus subtilis* A1 and *Streptomyces parvus* B7 which were isolated from an Indian crude oil reservoir. These strains were identified by 16S rRNA sequencing and deposited under NCBI Genbank accession numbers KP895564 and KP895570 respectively (Parthipan et al., 2017b). Both bacterial strains were retrieved from glycerol stocks and sub-cultured in Luria–Bertani (LB) agar plates (g/L 10.0 tryptone, 5.0 yeast extract, 10.0 sodium chloride with 15.0 agar (Himedia, Mumbai, India)) and incubated at 37 °C for 24 h. Bacterial inocula were prepared using single colony in LB broth (pH 7.0) and kept in an orbital shaker (150 rpm) for 24 h at 37 °C.

2.2. Biocide preparation

Aqueous garlic extracts were obtained by weighing 10 g of peeled garlic cloves and mashed with 100 mL of deionized water. This extract was filtered using Whatman filter paper to remove the residue and stored at 4 °C until further use (Arunachalam, 2011).

2.3. Chemical analysis of garlic extract

2.3.1. Gas chromatography analysis

GAE was analyzed using gas chromatograph mass spectrometry to identify the chemical nature of the inhibitor. 1 μL of sample was injected into a gas chromatography (Shimadzu QP2010 Ultra, Rtx-5Sil MS (30 m × 0.25 mm ID × 0.25 μm)). The carrier gas was He, the flow rate was set as 1.5 mL min^{-1} and the working temperature of the GC injector was 260 °C. The temperature was set between 60 and 260 °C, at a speed of 5 °C min^{-1}, through an isothermal phase of 10 min at the end of the analysis. The electron impact ion source was sustained at 200 °C. Mass spectra were recorded at 70 keV. The mass spectra were obtained with an m/z range: 40–600 ultra-high resolution modes with an acquisition speed of 6 spectra/second. The identification of components was done in scan mode by using NIST11 and Wiley8 library and the target mass spectra obtained from sample are compared with the mass spectra obtained from the library.

2.3.2. Fourier transform infra-red spectroscopy (FT-IR)

FT-IR analysis was carried to identify the chemical groups present in the garlic extract. For FT-IR analysis, a few drops of garlic extract were dried over glass plate and further dried sample was crushed with the addition of potassium bromide in 1:100 ratio and the pellet was fixed in the sample container, and analyzed using FT-IR (model Jasco) in the mid IR region 400-4000 cm^{-1}.

2.4. Antibacterial properties of garlic extract

2.4.1. Agar-well diffusion assay

To assess the antibacterial activity of the GAE, Mueller Hinton Agar (MH) (Himedia-India) plates were prepared as per the instructions of the manufacturer. Five different concentrations; 20 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm of the GAE were selected for evaluation of their bactericidal activity. Both bacterial strains A1 and B7 were