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Hybrid biocide application to control MIC in Hydrocarbon Pipelines

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ABSTRACT

Microbiologically induced corrosion (MIC) or bio-corrosion is a biological process which leads to the detoriation of metal surface caused by microorganism. This phenomenon can be reduced or controlled by using biocide which is a chemical formulation used to mitigate corrosion causing bacteria.Now-a-days most of the biocides available in the market are water based. Water acts as a nutrient to bacteria, which enhances the corrosion. So most of the hydrocarbon pipeline operators are not very keen to use such biocides, but as there is very limited alternatives available in the market, so they are compelled to use water bound biocides to control MIC in their hydrocarbon pipelines.In this paper, the author is applying a new concept to control SRB sulfide production that can be done by producing an oil based hybrids of biocide compounds and organic acids / chelating compounds/ nitrates etc. to mitigate bio-corrosion. Because of the various defence mechanisms adopted by biofilms, sessile cells in biofilms require 10 times the dosage of biocide for planktonic cells . The main aim is to limit the quantity of biocides and to increase its efficacy so that it can attack wide range of corrosion causing microbes .

INTRODUCTION

Microbiologically influenced corrosion (MIC) or bio-corrosion is blamed for causing serious failure of equipment, pipelines etc which leads to accidents in oil and gas industry, water treatment systems and sewer systems. Hydrocarbon pipelines are made up of carbon steel. Metal corrosion is an electrochemical reaction between the environment and a metal, in which microbes play a very

important role. The rates at which various types of metals corrode are dependent upon environmental conditions as well as on the type of metals [1].

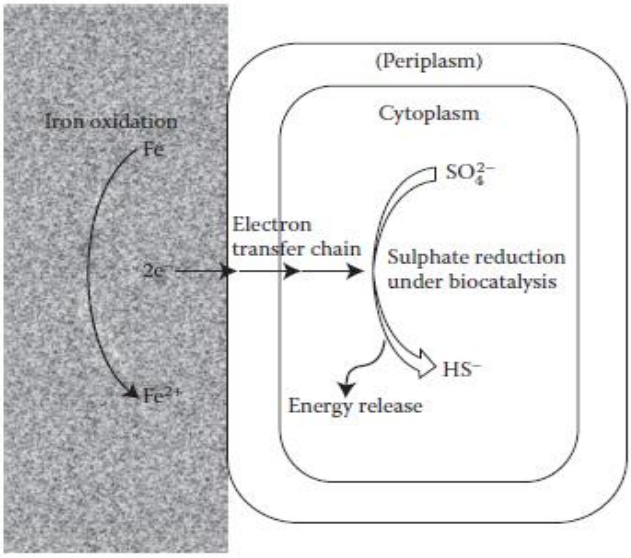


Figure 1: electron transport in MIC by SRB [1]

MIC has been classified into three categories to distinguish the various mechanisms [2]. Type I MIC is caused by electrogenic bacteria. Electrogenic bacteria, which can actively form pili for electron transfer and energy distribution, perform respiration metabolism [3]. They use carbon steel or other non-noble metals as electron donors intentionally because the reduction potentials of the ions in these metallic materials are sufficiently negative to form thermodynamically favourable redox reactions when coupled with the reduction of an oxidant such as sulphate and nitrate. Bacteria utilise electrons released from elemental metal oxidation and reduce the oxidant intracellularly [4].

Type II MIC is defined as the corrosion caused by the metabolites secreted by microbes. These metabolites are oxidants such as volatile fatty acids. The MIC caused by acid-producing bacteria (APB) belongs to this category [5]. Copper MIC caused by SRB is also Type II MIC. Type III MIC is caused by microbial species that secrete enzymes or other corrosive chemicals, which degrade non-metallic materials containing organic carbon as one of the components [6].

The most well studied bacteria involved in bio-corrosion are the anaerobic sulphate reducing bacteria (SRB) and other bacteria such as methanogens, acid producers as well as the aerobic iron respires and manganese oxidisers. They may be introduced in a system via multiple ways, including secondary oil recovery, hydro test etc [7]. SRB oxidise organic carbons to harvest electrons. The electrons are used for sulphate reduction that causes biogenic hydrogen sulphide release. Hydrogen sulphide gas is not only toxic to living organisms but also a corrosion threat to hydrocarbon pipelines [8].

The formation of tubercles is also often associated with MIC. Tubercles resemble blisters of corrosion product and are initiated from biofilm deposits and iron oxidizing bacteria, particularly at

low flow velocity areas in fluid piping systems.[9] The growth and decomposition cycle of the tubercle releases sulfates and provides a site for anaerobic sulfate-reducing bacteria on the interior of the blister. Tubercles also form an efficient oxygen concentration cell, dissolving iron under the blister. Unchecked tubercle growth in fluid transport systems will severely limit or even completely block fluid flow[10].

The biofilm produced by the microorganisms facilitates bio-corrosion by altering the chemistry such as pH, pressure, oxygen levels and nutrients at the interface between the metal and the bulk solution. Therefore biofilms can be used to alter the conditions at a metal surface, and to accelerate or inhibit corrosion.[11] Sessile cells in biofilms are notoriously far more difficult to treat than planktonic cells because biofilms can employ various defense mechanisms, including diffusional limitation, lowered metabolic rate to reduce intake, formation of persistent cells, up-regulation of resistance genes, efflux pumps, etc. Biofilms usually require 10X or higher antimicrobial concentrations to treat than planktonic cells[12].

Considerable efforts have been directed toward controlling SRB growth and inhibition of corrosion induced by its activity. Although biocide treatments are widely used to decrease bio-fouling and MIC in steel pipes and in closed systems, the results are far from satisfactory. This is because biocides are much less effective against sessile microorganisms with biofilms compared to their effectiveness against planktonic populations. In addition, biocide resistance may be developed and biocidal action reduced by dilution. [13]

EXPERIMENTAL PROCEDURE AND METHODOLOGY

Desulfovibrio vulgaris Hildenborough is a model organism for studying the energy metabolism of sulfate-reducing bacteria (SRB) and for understanding the economic impacts of SRB, including biocorrosion of metal infrastructure and bioremediation of toxic metal ions. The 3,570,858 base pair (bp) genome sequence reveals a network of novel c-type cytochromes, connecting multiple periplasmic hydrogenases and formate dehydrogenases, as a key feature of its energy metabolism.[ ]

Whole data for the study of target organism ,target protein and various drug molecules were taken from NCBI, Pubmed and Pubchem.

- Data is also retrieved from various publications and research results available on web databases. Different biofilm, intra cellular protein targets were studied and their fasta sequence were extracted from Uniprot .
- BLAST (Basic Local Alignment search tool) was used in order to study their alignment and retrieve atleast 4 or 5 template PDB id's.
- The Protein Data Bank (PDB) archive is the single worldwide repository of information about the 3D structures of large biological molecules, including proteins and nucleic acids. In addition, the RCSB PDB supports a website where visitors can perform simple and complex queries on the data, analyze, and visualize the results. Here we entered the PDB id of template protein and download the structure in PDB text .

Target proteins	PDB ID's	Ligand compounds
dcrA	1h2r, 1ubt, 1wuh, 1wuj	EDTA
Cytochrome c3	1a2i, 1c53, 2bpn, 2cth	THPS
Rex	1wuh, 1h2r, 1ubt, 1ubu	D-amino acids (D-tryptophan, D- leucine, D-tyrosine)
desulfoferrodoxin	1wuh, 1h2r, 1ubt, 1ubu	Glutaraldehyde
Trx B-2	1h2r, 1ubt, 1ubu, 1wuh	Ethylenediaminedisuccinate (EDDS)
Rubrerythrin	1dvb, 1ryt, 1lkm, 1lko	Methanol
		ADBAC
		Acrolein
		Citral

Figure 2: Table containing a list of Different target protein and ligand biocide compound.

- **Homology modeling using EASY MODELLER:**

EASY MODELLER is a program for automated protein homology modeling.It is one of the most widely used tool for homology and comparative modelling of protein 3D structures. The steps are given below:

(a) Open EASY MODELLER program.
(b) Enter the target protein sequence in a query sequence box.
(c) Enter The template sequence in load template structure.
(d) Align templates.
(e) Then aligned template with target protein sequence and build model.
(f) After that the modeled structure was visualized in PyMOL viewer.

- **Ligand identification (Pubchem):** PubChem, released in 2004, provides information on the biological activities of small molecules. Various potential drug molecules obtained are searched in pubchem in SDF format. Different biocides and ligand compound 2 D structures were downloaded from Pubchem .

Protein-Ligand Docking by using iGEMDOCK: iGEMDCOK is a suite of automated docking/screening tools. The interface of iGEMDOCK has two main tags, docking/screening tag and post-analyzing tag. The docking/screening tag is designed to predict how chemical molecules bind to a receptor of known 3D structure. The predicted protein-ligand poses can be further performed post-analysis in the post-analyzing tag .

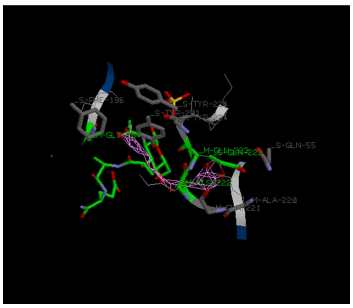
Firstly target template protein structures were loaded, then single or multiple ligand structures were loaded. After loading both the files, you can start your job by pressing "Start Docking". The status of you job will show on the screen. The number of docked compounds will present as complete percentage and the running prediction will show on the message window. During the docking/screening, you can view docked posed and make post-analysis for current job.

RESULTS

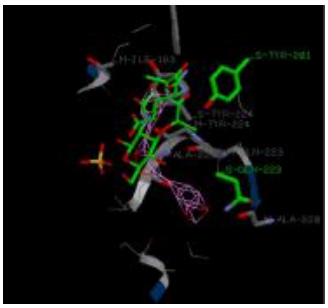
1. Protein- ligand docking using iGEMDOCK:

iGEMDOCK provides an analysis environment with visualized tool and post-analysis tools for users
.
(1).One can visualize the docked poses, and cluster the poses by the protein-ligand interactions.

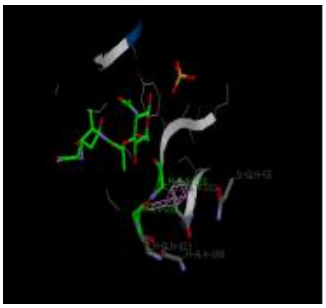
(2). the predicted poses and scores of ligands are saved in the user defined output path.
Multiple ligands were used to dock to different target proteins. Successful docking outputs are shown below:



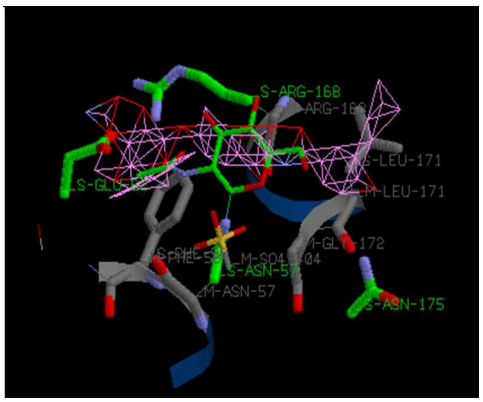
(1) Binding of THPS to dcrA protein.



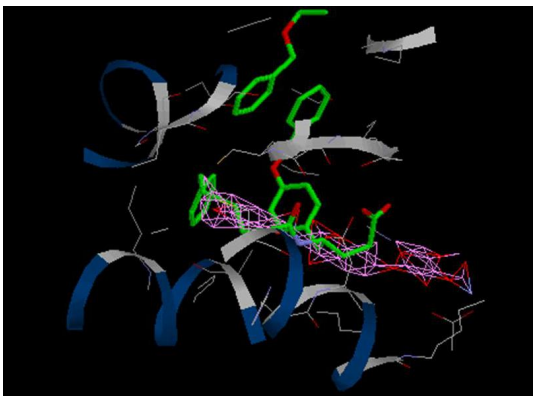
(2) Methanol and THPS binding to dcrA protein



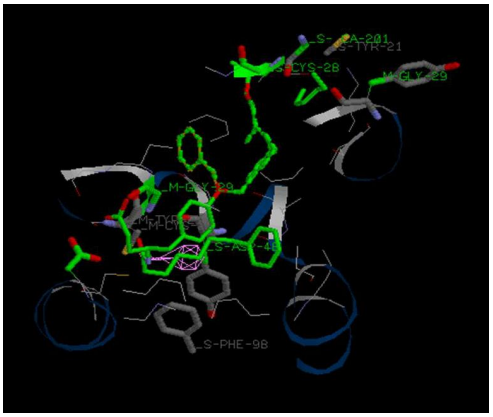
(3) methanol binding to dcrA protein



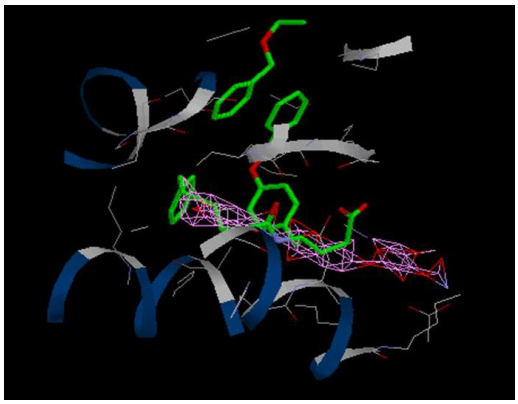
(4) THPS and EDTA binding to Rubrerythrin



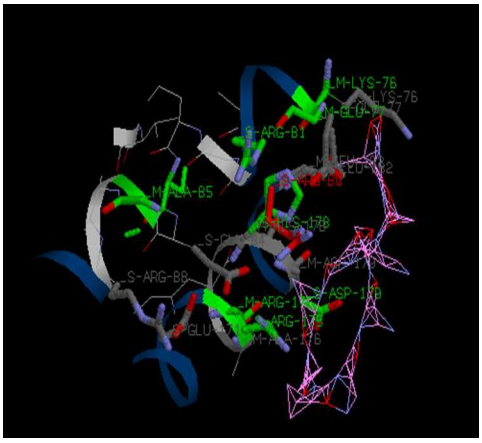
(5) THPS and D- tryptophan to rubrerythrin



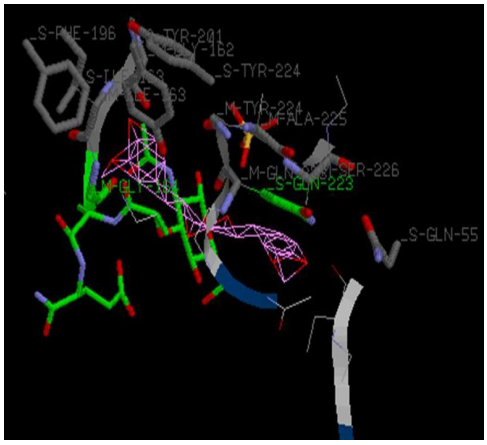
(6) citral binding to Rex protein



(7) D- leucine and EDDS binding desulfoferrodoxin



(8) EDTA + acrolein (No binding); dcrA



(9) Acrolein binding to dcrA

CONCLUSIONS

Chelators and D-amino acids can be used as antimicrobial/biocide enhancers. EDDS is more attractive than EDTA in industrial applications. This is because unlike EDTA, EDDS is readily biodegradable and will not accumulate in the environment. D-amino acids such as D-tyrosine, D-tryptophan, D-methionine and D-leucine are biocide enhancers that are effective at low concentrations. They are hypothesized as biofilm dispersal signalling molecules. By replacing the D-alanine terminus on the stem peptide of the peptidoglycan molecules in bacterial cell walls, they send a biofilm dispersal signal. Thus, D-amino acids can reduce biocide dosages considerably because planktonic cells are much easier to mitigate than sessile cells.

It is likely that a mixture of several D-amino acids will work more effectively in substituting the D-alanine termini in bacterial cell wall's peptidoglycan and thus sends a biofilm dispersal signal. More tests are needed to evaluate the efficacies of different D-amino acid(s) + biocide combinations, especially against field biofilm consortia. D-amino acids are naturally occurring.

They will likely find field applications in bio-fouling and bio-corrosion mitigation. They may prove to be particularly attractive biocide enhancers in environmentally sensitive applications such as hydraulic fracturing in shale gas production.

In addition, both Lemongrass essential oil (LEO) and citral showed an immediate killing effect against SRB in liquid medium, suggesting that citral is responsible for the antimicrobial activity of LEO against SRB. Transmission electron microscopy revealed that the MIC of LEO caused discernible cell membrane alterations and formed electron-dense inclusions. Neither biofilm formation nor corrosion was observed on carbon steel coupons after LEO treatment. LEO was effective for the control of the planktonic and sessile SRB growth and for the protection of carbon steel coupons against bio-corrosion Microbes develop resistance after prolonged use of the same biocide. The biocide selectively promotes resistant microbes by killing off susceptible microbes. As a consequence, biocide dosages escalate. Hybrid biocides can be used to increase its efficacy and usage in less concentration and thus eradicating broad range of microbes .

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