

Development and Characterization of the Epoxy-Based Chitosan Coated Zn/Ag Nanocomposite Coatings to Resolve Thermophilic Biofilms in Industrial Pipelines

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Abstract

This research focused on the development of epoxy resin-based Chitosan coated Silver and Zinc nanocomposites, respectively to solve the problem of the corrosion due to the biofilms formation on the industrial pipelines (oil and refinery pipe lines) developed by cost effective green (re-cycle) process. Specifically, we studied the electro-chemical behavior of thermophilic bacteria in pipelines. Biofilm formation in oil and petroleum pipelines is due to many factors including pH, temperature, salt, etc. Several studies have been carried out on oil and petroleum line distribution system for biofilms which show the presence of hygienically relevant microorganisms. The degradation problem of petroleum products arises since hydrocarbon acts as an excellent food source for a wide variety of microorganisms. Microbial activity leads to unacceptable level of turbidity, corrosion of pipeline and souring of stored product. In this study we will collect different biofilm samples and will be studied for the biofilm morphology, characterizing for the formation of biofilm on pipe lines will be analyzed by using the techniques, X-ray diffraction (XRD), Raman microscopy (RMS), X-ray fluorescence spectroscopy (XRF), Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscopy (SEM EDAX). We will report the design and evaluation of different bacterial species and genes from bacterial isolation, Phylogenetic analysis of sequenced genes to know the diversity of bacterial strains in the pipeline. In addition, localized biofilm of the pipeline in the presence of the consortia will be observed by scanning electron microscopy analysis and morphology by EPI fluorescence microscopy, and thus the advantages of nano-scale materials will be realized with their potential applications in diversified avenues. In this work we investigate Zinc and silver nanoparticles which will be integrated on Chitosan to obtain Chitosan coated silver and Chitosan coated zinc nanoparticles and it will be dispersed in coating matrix (Epoxy) to explore these Nanocomposites for coatings in pipelines by using with epoxy resins. Secondly these Nanocomposites analyzed for their optical and electric properties (Impedance and polarization) applications. This study involves microbiological aspects of biofilm formation and their role on electrochemical studies for biofilm degradation.

Keywords: *Thermophilic Biofilms, Pipelines, Zn/Ag Nanocomposite, Characterization, Coatings, Industrial And Innovation.*

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Introduction

Biocorrosion, also known as microbiologically influenced corrosion (MIC), causes billions of dollars in damage each year in the United States alone [1]. It affects numerous industries, including oil and gas, water utilities, and power generation. In the oil and gas sector, biogenic reservoir souring and biofouling are major operational challenges, and microbial biofilms are often responsible [2]. These problems have intensified with the widespread adoption of enhanced oil recovery, particularly through water injection. Because freshwater is scarce, it is generally not used in oil production. Instead, seawater is injected, often together with produced water recovered from the reservoir during extraction [3-7]. Seawater introduces nutrients (e.g., organic carbon), oxidants (e.g., sulfate), and microorganisms, including sulfate-reducing bacteria (SRB). Before injection, oxygen is typically removed from seawater using nitrogen gas stripping and oxygen scavengers. In some cases, biocides are added to control MIC and prevent reservoir souring [8-12]. Large volumes of biocides are required because the amount of treated seawater is substantial. For example, Saudi Aramco's Qurayyah Seawater Treatment Plant can supply up to 14 million barrels of treated seawater per day for oil production across the Kingdom. In the downhole environment, SRB metabolize organic carbon sources such as acetate, using sulfate as the terminal electron acceptor. This process produces hydrogen sulfide (H_2S), commonly known as sour gas, which provides energy for SRB growth. The accumulation of this corrosive and highly toxic gas leads to biogenic reservoir souring, which is typically controlled through periodic biocide dosing [3]. To manage biofilms, biocides are often applied alongside other treatment chemicals, including corrosion inhibitors for CO_2 and H_2S corrosion, oxygen scavengers, and scale removers during pigging operations [4]. Biocides are also incorporated into hydraulic fracturing fluids for shale oil and gas production to prevent biofouling that can block fractures [5]. Biofilm-associated cells (sessile cells) are significantly more resistant to biocides than planktonic cells due to multiple defense mechanisms [6]. Dense biofilms act as diffusion barriers, slowing the penetration of antimicrobial agents. Sessile cells can reduce their metabolic activity to limit the uptake of harmful chemicals. They may also upregulate genes that encode proteins capable of neutralizing or degrading biocides, and they possess efflux pumps to expel toxic substances. One of the most notable defense strategies is the formation of "persister cells." During biocide exposure, a biofilm can preserve a subpopulation of highly tolerant cells. Once the biocide stress is removed, these persister cells can rapidly repopulate the biofilm, leading to renewed contamination [7-11].

Problem Statement

Microbiologically influenced corrosion (MIC) remains one of the most persistent and economically damaging forms of pipeline deterioration, accounting for an estimated 20–30% of external corrosion in underground pipelines [13–18]. Unlike purely electrochemical corrosion, MIC is not caused by direct microbial consumption of metal. Instead, it arises from complex biochemical interactions at the metal–biofilm interface, where microbial metabolic by-products alter local electrochemical conditions and accelerate localized forms of attack such as pitting, crevice corrosion, and under-deposit corrosion [19–22]. This indirect yet highly aggressive mechanism makes MIC particularly difficult to predict, monitor, and mitigate. The challenge is further compounded by the cooperative behavior of mixed microbial communities. Aerobic bacteria (e.g., metal-oxidizing bacteria), facultative bacteria (e.g., acid-producing bacteria), and obligate anaerobes (e.g., sulfate-reducing bacteria) coexist within structured biofilms [23–28]. Within these consortia, oxygen gradients develop: aerobic microorganisms consume oxygen at the outer biofilm layers, creating anaerobic microenvironments beneath deposits that enable the proliferation of highly corrosive anaerobic species. This metabolic synergy intensifies localized corrosion and makes conventional corrosion inhibitors or biocides insufficient, as they often fail to penetrate or disrupt mature biofilms effectively [29, 30, 31]. Consequently, the most severe MIC cases are typically associated not with a single organism, but with structured, multispecies biofilm communities [32]. Despite extensive use of protective epoxy coatings and periodic biocide treatments, current mitigation strategies largely focus on chemical suppression rather than biofilm prevention at the material interface. These approaches are reactive, require continuous chemical dosing, and may promote microbial resistance or persister cell survival. Therefore, there is a critical need for a preventive, surface-engineered solution that simultaneously inhibits biofilm establishment and suppresses microbial metabolic activity directly at the coating–metal interface. This study addresses this gap by proposing a multifunctional nanocomposite coating system based on chitosan-integrated silver and zinc nanoparticles dispersed within an epoxy matrix. The novelty of this approach lies in combining (i) the inherent antimicrobial and film-forming properties of chitosan, (ii) the broad-spectrum biocidal activity of silver and zinc nanoparticles, and (iii) the mechanical and barrier performance of epoxy coatings. Rather than relying solely on bulk biocide dosing, this strategy targets early-stage biofilm formation and

microbial colonization at the surface level, aiming to interrupt the cooperative microbial processes that drive MIC. By integrating antimicrobial nanostructures directly into the coating matrix, the work seeks to develop a proactive, long-lasting defense against biofilm-mediated corrosion in underground pipeline systems. 1. How to isolate and characterize the Biofilms present in oil and gas pipelines (Industrial pipelines)?

1. How can industrial biofilms be identified and characterized using 16S rRNA gene sequencing?
2. How can chitosan-based silver and zinc nanoparticles be synthesized and systematically characterized?
3. How do the orientation and distribution of chitosan-based silver and zinc nanoparticles influence their physicochemical properties, and how can these novel properties be applied to control biofilms?
4. What mechanisms govern microbiologically influenced corrosion (MIC), and how do the developed nanomaterials contribute to biofilm degradation and corrosion mitigation?
5. How do epoxy coatings reinforced with chitosan-based silver and zinc nanoparticles enhance biofilm degradation in industrial pipeline systems through synergistic functional performance?
6. How can biofilm degradation and corrosion resistance of epoxy nanocomposite coatings be evaluated using electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and polarization studies?

Methodology

This study proposes the development of metal nanoparticle–reinforced epoxy coatings as an innovative strategy to mitigate biofilm formation and microbiologically influenced corrosion (MIC) in oil, refinery, and pipeline industries. The methodology integrates nanomaterial synthesis, microbial characterization, electrochemical evaluation, and application-oriented performance testing.

1. Development of Nanoparticle-Based Epoxy Coatings Metal-based nanoparticles (e.g., silver and zinc) were synthesized and incorporated into epoxy matrices to fabricate nanocomposite coatings. The dispersion quality, structural integrity, and physicochemical properties of the coatings was systematically characterized using standard material analysis techniques. This is aimed at producing cost-effective, durable, and scalable coating prototypes suitable for industrial deployment across diverse climatic conditions.

Biofilm Sampling and Microbial Identification

Biofilm samples was collected from heat exchanger tubes in oil and refinery industries, where biofouling commonly reduces heat transfer efficiency. Since most microorganisms in these systems are thermophilic and can tolerate temperatures of 50–60°C, special emphasis was placed on isolating and identifying thermophilic bacterial communities. Molecular techniques, including 16S rRNA gene sequencing, was employed to identify the dominant microbial species. Particular attention was given to sulfate-reducing bacteria (SRB), acid-producing bacteria, iron-oxidizing bacteria, and manganese-oxidizing bacteria, which are known contributors to MIC.

Electrochemical and Corrosion Studies

Electrochemical experiments were conducted at elevated temperatures (50–60°C) to simulate real operating conditions in heat exchangers. Techniques such as electrochemical impedance spectroscopy (EIS) and polarization studies were used to evaluate corrosion behavior and determine the mechanisms involved. The interaction between microbial activity and metal corrosion was systematically investigated under controlled laboratory conditions.

Material Performance Evaluation

Common industrial alloys, including SS316L stainless steel, Titanium Grade 2, Cu–Ni alloys, and copper alloys, was selected as substrate materials. Their electrochemical behavior in the presence and absence of biofilms and nanocomposite coatings was assessed to determine the corrosion resistance performance.

Temperature and Microbial Interaction Analysis

The impact of elevated temperatures (50–60°C) on microbial growth, biofilm development, and corrosion processes was examined. The synergistic relationship between bacterial metabolism and

corrosion mechanisms was analyzed to propose a comprehensive MIC mechanism model for heat exchanger environments.

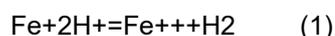
Biocide and Nanoparticle Dosage Optimization

Based on microbial identification and activity levels, suitable antimicrobial agents including nanoparticle-based biocides was selected. Optimal dosage levels were determined according to bacterial load and biofilm severity on heat exchanger tubes.

The developed metal nanoparticle-based epoxy coatings provided a simplified, versatile, and economically viable solution for industrial corrosion and biofouling challenges. Beyond oil and refinery sectors, the outcomes have broader applications in other industrial systems and potentially in medical or clinical antimicrobial surfaces. The findings will achieve the following:

1. Identify the bacterial component present in the biofilm on Heat exchanger tubes by molecular techniques.
2. Carry out the electro chemical behavior of various SRB (Sulphate Reducing Bacteria, Acid producers, Iron oxidizing bacteria and Manganese oxidizing bacteria at 50°C-60°C under flow corrosion.
3. Propose the mechanism of Thermophilic bacteria on Heat exchanger tubes.

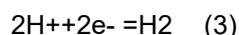
This research aims to design and synthesize chitosan-mediated nanoparticles and to investigate the relationship between biofilm-induced corrosion and epoxy-coated nanoparticles for industrial applications. The study focuses on understanding how these functionalized nanoparticles can mitigate corrosion, particularly in pipeline systems. Pipelines play a critical role worldwide in transporting gases and liquids over long distances from production sites to end users. Despite their vast network and importance, most pipelines operate unnoticed by the general public because buried pipelines are largely unobtrusive, becoming visible only at valves, pumping or compressor stations, and terminal facilities. Ensuring their structural integrity is therefore essential for safe and reliable operation. Iron and its alloys are widely used in pipeline construction; however, iron is thermodynamically unstable in aqueous environments and can spontaneously react with water, leading to corrosion. This reaction produces soluble iron ions and hydrogen gas. The practical usefulness of iron alloys depends on minimizing the rate of this corrosion. Steel corrosion is fundamentally an electrochemical process involving the transfer of electrons from iron atoms in the metal to hydrogen ions or dissolved oxygen in water. In acidic environments, the corrosion reaction of iron can be represented by Equation (1).



This reaction is made up of two individual processes, which are



The generation of soluble iron and electrons (this is the “anodic” process, the oxidation of the metal)] and



Oil field produced-water is formed during the processes of petroleum exploration and utilization, and is considered to be wastewaters. In order to decrease the consumption of clean water and protect the environment, it is necessary to find an effective way to reuse these waste waters, especially in water-deficient regions. The benefits of recycling and reusing produced-water include not only a saving of vast quantities of fresh water, but also an absolute recovery of the thermal energy. Thus, studies of effects of the produced-water on corrosion of the pipelines and the equipments in the petroleum industry have become more and more important. There are many studies of effects of the produced-water. In this work we investigate Zinc and silver nanoparticles which will be integrated on chitosan to obtain Chitosan coated silver and chitosan coated zinc nanoparticles and it will be dispersed in coating matrix (Epoxy). Secondly these nanocomposites analysed for their optical and electric properties (Impedance and polarization) applications. So, this research work presents a:

1. novel functional nanocomposite (Chitosan coated silver and Chitosan coated Zinc).
2. characterization of the biofilms (FT-IR, XRD, SEM, XRF and TEM) present in Industrial pipelines (Oil and petroleum).
3. characterization of the nanocomposites (UV, FT-IR, XRD, DLS, SEM and TEM).

4. the exploration of these nanocomposites for coatings in pipelines by using with epoxy resins.

In this study, we identified the microbes by molecular technique in heat exchanger tubes, the electro chemical study was done at 50°C-60°C temperature to find the mechanism on corrosion behaviors.

i. Sample collection: Thermophilic Biofilm samples were collected aseptically from heat exchanger tubes in a petroleum industry, India kept in an ice bucket and transported to laboratory for microbiological characterization. The physical and chemical characteristics of the cooling water were analyzed by standard procedures recommended.

ii. Selection of biocides for thermophilic bacteria:

Selection of biocides was done by using inhibition zone method and by using broth of specific cultures and using biofilm on metal surface at 50°C. The proposed methodology is presented in Fig. 1. Fig. 2 depicts the electrochemical study using the epoxy nanomaterials.

Results and Discussion

This section presents the results achieved.

Electrochemical Study

Open Circuit Potential (OCP) Measurements:

The OCP values were monitored for SS316L, Titanium Grade 2, Cu:Ni, and Copper alloy coupons immersed in simulated industrial water (pH 6.8–7.2, 50–60°C) both with and without biofilm-forming bacteria (SRB, IOB, AAB, MOB). A noticeable negative shift in OCP was observed in biofilm-exposed coupons, indicating increased thermophilic microbial activity and the onset of microbial-induced corrosion (MIC). However, upon application of epoxy resin-based chitosan-coated Ag and Zn nanocomposites, the OCP values shifted toward more positive potentials across all metal types. Silver-based coatings showed a more stable and noble potential, particularly on Cu:Ni and SS316L, suggesting effective inhibition of bacterial colonization.

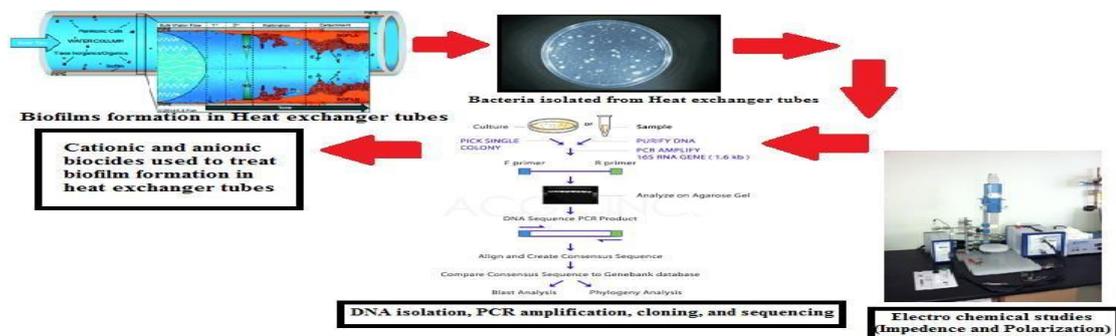


Fig. 1. Proposed Methodology

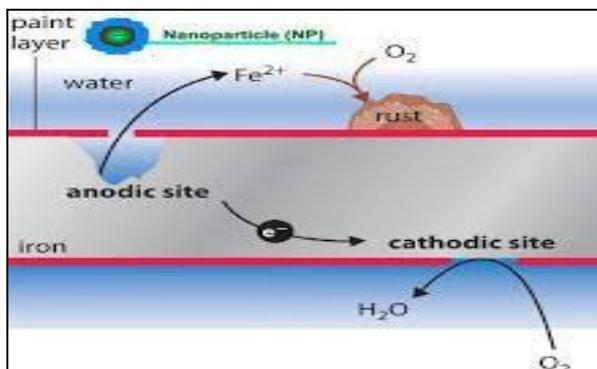


Fig. 2. Electrochemical study using epoxy nanomaterials.

Potentiodynamic Polarization

The potentiodynamic polarization study presented in Table 1 revealed significant reductions in corrosion current density (I_{corr}) for coated samples compared to uncoated controls.

Table 1: Results of potentiodynamic polarization study

Metal	Condition	$I_{corr}/$ ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate
SS316L	Uncoated + Biofilm	5.195	0.096
SS316L	Chitosan-Zn	2.110	0.037
SS316L	Chitosan-Ag	1.521	0.026
Cu:Ni	Uncoated + Biofilm	6.801	0.115
Cu:Ni	Chitosan-Zn	2.650	0.045
Cu:Ni	Chitosan-Ag	1.881	0.030
SS316L	Chitosan-Zn	2.110	0.037
SS316L	Chitosan-Ag	1.521	0.026
Cu:Ni	Uncoated + Biofilm	6.801	0.115
Cu:Ni	Chitosan-Zn	2.650	0.045
Cu:Ni	Chitosan-Ag	1.881	0.030

The results indicate that both Zn and Ag nanocomposite coatings significantly reduced corrosion kinetics. The Ag-based nanocomposites consistently outperformed Zn-based ones in reducing I_{corr} , particularly in high-temperature, biofilm-rich environments.

Electrochemical Impedance Spectroscopy (EIS)

EIS studies confirmed higher polarization resistance (R_p) values for nanocomposite-coated coupons as presented in Table 2.

The increased impedance suggests superior barrier and antimicrobial properties of the coatings. Chitosan facilitated uniform dispersion and surface adhesion of nanoparticles, while Zn and Ag provided antimicrobial activity via ion release and ROS (Reactive Oxygen Species) generation.

Table 2: Results of EIS

Metal	Coating Type	$R_p/R_{k\Omega \cdot \text{cm}^2}$
SS316L	Uncoated	1.22
SS316L	Chitosan- Zn	6.81
SS316L	Chitosan- Ag	9.52
Cu:Ni	Uncoated	0.92
Cu:Ni	Chitosan- Zn	5.41
Cu:Ni	Chitosan- Ag	8.10

SEM and EDS Surface Analysis

Surface morphology (SEM) of uncoated coupons after biofilm exposure showed pitting corrosion and dense bacterial mats. In contrast, coated surfaces were smooth with minimal microbial attachment. EDS spectra confirmed the presence of Ag and Zn ions on coated surfaces and significantly reduced Fe and S peaks—markers of SRB corrosion.

A summary of the findings suggested that Chitosan-Ag nanocomposites exhibited superior performance in reducing microbial-induced corrosion rates. The dual-action mechanism (barrier protection + antimicrobial activity) was effective across all materials. Biofilm adhesion was drastically

minimized in coated samples. These coatings are suitable for environments operating at 50–60°C under flowing industrial conditions, especially in heat exchanger systems.

Conclusions

This research provides a comprehensive investigation into the development and performance of chitosan-coated Zn/Ag nanocomposite coatings designed to mitigate thermophilic biofilm formation in industrial pipelines, particularly on heat exchanger tubes. Molecular identification of microbial communities, including sulfate-reducing bacteria (SRB), acid producers, iron-oxidizing, and manganese-oxidizing bacteria, revealed the complex and diverse nature of biofilm-forming consortia in high-temperature environments (50–60°C). The electrochemical evaluation of candidate industrial materials—SS316L, Titanium Grade 2, Cu:Ni, and Copper alloys—under these thermal and flow conditions confirmed differential susceptibility to biofilm-induced corrosion.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization studies demonstrated the effectiveness of the epoxy-based chitosan-Zn/Ag nanocomposite in inhibiting microbial colonization and subsequent corrosion. The temperature-dependent activity of thermophilic bacteria highlighted a distinct metabolic response that accelerates the deterioration of pipeline integrity, with proposed mechanisms including extracellular polymeric substance (EPS)-mediated adhesion, anaerobic respiration using metal ions, and biocatalyzed corrosion pathways. The use of chitosan as a natural biopolymer in nanoparticle synthesis was found to enhance both antimicrobial efficacy and coating adhesion.

The proposed nanobiocide coatings offer a dual function—preventing biofilm formation and providing corrosion resistance—at biocide dosages tailored to microbial presence, as informed by molecular diagnostics. The study recommends a targeted approach to biocide application, emphasizing environmentally responsible dosing strategies based on bacterial quantification and activity. Furthermore, the research establishes a scientific basis for selecting and optimizing nanocomposite coatings for specific industrial alloy surfaces, ensuring prolonged operational efficiency and reduced maintenance costs in thermophilic and corrosive environments.

Ultimately, the work advances an integrated strategy for industrial biofilm control by combining molecular microbiology, electrochemical assessment, and nanotechnology-driven surface engineering. The findings underscore the potential of epoxy-based chitosan-Zn/Ag nanocomposites as a promising material for extending the service life of critical infrastructure in heat-intensive industrial systems.

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