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Mitigation of Microbiologically Induced Corrosion (MIC) and Preventive Strategies

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Abstract

Microbiologically influenced corrosion, MIC, refers to the situations where the corrosion of metals is influenced by the presence of microorganisms and/or biofilms on their surfaces.

The MIC is a very problematic phenomenon which causes billions of dollars of economic losses in the monitoring and controlling every year. The MIC has been found to damage many metals and alloys in a range of situations, including marine environments, cooling water system, power generation and pipelines used by the oil and gas industry. Many parameters are believed to impact the rate of MIC.

The MIC is reported to account for about 50% of the total cost of corrosion. It is possible to save a net of 25% of that annual cost by applying currently available corrosion control technologies.

Therefore, it is of great significance to understand the mechanisms of MIC, and to find ways to mitigate MIC provided that these methods are both environmentally sustainable and economically viable.

Introduction

Microbiologically Induced Corrosion (MIC) refers to situations where the corrosion of metals is induced by the presence of microorganisms and/or biofilms on their surfaces [1]. MIC is a very problematic phenomenon which causes trillions of dollars of losses in monitoring and controlling every year**.** Microorganisms can initiate, accelerate, and/or inhibit corrosion processes through a number of different ways. This include modification of the localized environment at the metal/solution interface, destabilization of protective films or corrosion products on the metal surface, or by initiating pitting attack where microbial adhesion takes place on a metal.

MIC has been found to damage many metals and alloys in a range of situations, including marine environments, cooling water systems and power generation and pipelines used by the oil and gas industry. It is therefore of great significance to understand the mechanisms of MIC, and to find ways to inhibit MIC that are both environmentally sustainable and economically viable.

Many strategies have been used for controlling MIC by using inhibitors and/ or biocides [2]. Conversely, most of the traditionally used corrosion inhibitors are known to be toxic and harmful to the environment. There is a need to control corrosion and to minimize the use of these toxic and dangerous chemicals that

can contaminate the global environment. In view of that, attention was drawn to the development of novel corrosion controlling methods based on ecological approaches. In recent years, considerable efforts have been made to study the corrosion inhibition efficiency of some natural products, as green inhibitors [3]. Organic inhibitors are one of the most practical methods and economical choices for the protection of metals against corrosion [4]. Nanocomposites come to be a promising area of research and development which have an excellent antibacterial activity depending on the nanoparticle size. This leads to changes in the surface area for better interaction with bacterial cells [5].

In recent years, the synthesis and application of Montmorillonite (MMT-based) antibacterial drugs have attracted enormous interest due to global concerns regarding public health [6]**.** The montmorillonite clay is recently a current topic to study its utilization as additive and drug carrier material at the research level [7]. Also, Schiff bases heterocyclic organic compounds have gained importance in medicinal and pharmaceutical fields due to a broad spectrum of biological activities as antimicrobial and anticorrosion [8].

Definition of abiotic corrosion

Some typical corrosive environments are air and humidity, water (fresh, distilled, salt), atmospheres (natural, urban, marine, and industrial), steam and gases. Like metals, other materials (such as plastic, ceramics) also undergo degradation, but the term 'corrosion' refers (usually) only to metals. The iron corrosion is called rusting with the formation of corrosion products consisting of hydrous ferric oxides [9].

Metals have some technically important properties such as: tensile strength, ductility, electrical and thermal conductivity, which differ them from other materials. Normally all crucial components of machines, cars and instruments are made of metals. Therefore, the durability of all of them is dependent on their corrosion resistance.

A big problem with corrosion is that it is not realized until some damage is already done, mostly in industry (loss of efficiency, product, money due to repairs), storage (leaking, contamination), transport, construction (buildings, bridges - steel reinforcements in concrete [10].

Types of corrosion

There are two major corrosion forms: uniform and localized corrosion. Uniform corrosion represents evenly attacked metal over its entire surface. The cathodic and anodic sites are formed on the metal surface, but their position changes with time. The overall effect is that the metal is uniformly attacked, so the thickness of the metal is evenly decreasing. This type of corrosion is well recognizable, easier to monitor and could be solved by adequate protection of the metal surface. Localized corrosion takes place when the corrosion progression is not uniform. In this case the cathodic and anodic sites are fixed over the metal surface. The corrosion proceeds on established portions of the metal surface. There are more types of localized corrosion.

The most common forms are crevice corrosion, pitting corrosion and stress corrosion cracking (SCC). With pitting corrosion, the area where corrosion occurs is very small, the pits are much deeper than their diameter [11]**.** Crevice corrosion occurs at cracks, filled with corrosion medium, usually at junctions or threads. It occurs in crevices owing to the differences in param-

eters such as pH, oxygen availability, or corrosive substances concentration [9].

SCC corrosion occurs when the material is under mechanical stress and exposed to corrosive medium [12].

Microbiologically induced corrosion (MIC)

MIC is related to the adherence of the microorganisms on industrial pipes causing metal deterioration as a result of microbial activities modifying the local chemistry at metal / solution interface surfaces [13].

MIC refers to how the presence and activity of micro-organisms can induce corrosion [1]**.** Microorganisms induce several effects at the metal /solution interface under the microbial biofilm [2].

MIC is the outcome of interfaces between the metal surface, corrosion products, and the bacteria and their metabolites [14]. The corrosion rates that have been observed in the field in relation to MIC can be on the order of several mm/year, which is much greater than what would be normally expected for corrosion in the associated environment without microorganisms [15].

This rapid corrosion attack has the potential to cause significant structural damage before identification during routine maintenance. It is difficult to estimate the corrosion costs that are specifically due to MIC as it varies widely, and actual numbers cannot be given with certainty.

Still, MIC has been reported to account for a considerable fraction of the total corrosion costs [16].

Microorganisms and MIC

Once microorganisms form a biofilm, they can, multiply and degrade the material to which they are attached**.** The main groups are prokaryotes, which can be sub-divided into bacteria and archaea and eukaryotes [17]. As a result of their metabolic processes, microbes initiate corrosion, resulting in high corrosion rates, referred as pitting corrosion.

Biofilm formation

The MIC refers to the situations where the corrosion of metals is induced by the presence of microorganisms and/or the biofilm on their surfaces [18]. The biofilm is a group of microbial cells associated with specific surface and are enveloped by the Extracellular Polymeric Substance (EPS) [19].

The presence of the microorganisms helps in the formation of a biofilm which induces corrosion by different mechanisms such as formation of differential concentration of microbial cells, changing the anion ratios of the solution and production of corrosive materials [20].

Extracellular polymeric substrates (EPS)

EPS consists of polysaccharides, proteins, nucleic acids, and other metabolites [21]. It can be as high as 90% of the biofilm constituents [22] which is the highest component of the biofilm and plays an important role in determining both biological and physiochemical properties of biofilm.

The biofilm extracellular polysaccharide substance has sticky properties that aid the adherence to the metal surfaces and protect the bacterial elimination by the biocides, subsequently causing MIC [23]**.** Arafat, 2020, showed that The morphology of

the corrosion coupons indicated the formation of the corrosion products on the metal coupon exposed to iron oxidising bacteria suggesting the occurrence of MIC (Figure 1).

Figure 1: Corrosion of mild steel coupon after the exposure to iron oxidising bacteria.

Formation of biofilm on metallic surfaces

When a metallic surface is immersed in aqueous solution, a biofilm begins to be formed on the metal surface [24]. The formation of a biofilm generally starts with the adsorption of the macromolecules such as proteins, polysaccharides, fatty acids, and lipids at the metal surface [18].

This initial film developed on the surface is referred to as conditioning film. The conditioning film alters the surface chemistry of the material and helps microorganisms adhere to the surface [25]. Immediately after initial attachment, microorganisms start to excrete EPS which assists in the irreversible attachment and the formation of the microcolonies. The exopolymers produced are also responsible for: the easy and adherent attachment of bacteria to the surface, the cohesive forces within a biofilm, and the biofilm stability [26]. The microorganisms within these microcolonies interact with each other, multiply and grow, and finally establish a mature biofilm.

Stoodley *et al.* [27], reported five stages of biofilm development. First, the initial attachment of the bacteria on the surface of the material. Then, the excretion of EPS by the attached bacteria resulting in irreversible attachment. This is followed by the formation of micro-colonies and/or early development of biofilm structure. The bacterial colonization then grows to form mature biofilm. Lastly, bacteria detach from the biofilm and attach to other areas on the immersed surface.

Metabolic byproducts produced by the microorganisms

The microorganisms within the biofilm can excrete certain byproducts during their metabolism. These metabolic byproducts are often responsible for localized environmental changes within the biofilm, which can differ from the medium in pH, dissolved oxygen, as well as concentration of various inorganic and organic species resulting in high corrosion rates [28]. The ability of microorganisms to produce a wide variety of corrosive metabolites over a range of environmental conditions makes them a real threat for accelerating the corrosion of metallic surfaces.

Effect of biofilm formation on MIC

The formation of a biofilm on the metal substratum plays an important role in changing the local physical and chemical environment. The biofilms formed on a metal surface are capable of influencing corrosion processes by changing the electrochemical conditions at the metal/solution interface and either cause an increase or decrease in the metal degradation [18]. Characklis [29], reported the effects of biofilm formation on the metal surface and consequently on the corrosion rate as:

- Microbial activity on the substratum is higher if the biofilm is patchy.
- The effect of metabolic by-products of microorganisms on the substratum.
- Variation of movement of ions through the EPS of the biofilm.
- Modification of degree of conductivity of the solution by the EPS.
- The binding of metal ions by the EPS.
- A severe alteration of the resistance to biocides and deterioration of the corrosion inhibitors.

The formation of chemical gradients is one of the main ways in which biofilms influence the corrosion processes. The formation of a patchy biofilm on a metal surface can act as differential aeration or concentration cell, with different oxygen/ion levels inside and outside the biofilm [25].

Such concentration gradients and functional heterogeneities inside the biofilm often result in the localized corrosion of the metallic substrate [30]. On the other hand, the biofilm formation has also in some cases been reported to protect the metal surface, preventing diffusion of dissolved oxygen, aggressive anions and/or metabolic byproducts [31].

Microorganisms involved in MIC

Various mechanisms for MIC have been proposed, depending upon the different causative microorganisms involved in each mechanism. While MIC may be attributed to a single group of microorganisms, the most aggressive corrosion takes place in the presence of different species of bacteria (i.e. microbial consortia) within biofilms [18].

Most of the microorganisms associated with MIC come under the group chemotroph referring to those getting their energy from chemical source rather than a light source.

MIC can be classified into two kinds depending on the physical and chemical nature of the microorganisms, such as aerobic MIC and anaerobic MIC.

Mechanisms of MIC formation

According to Coetser and Cloete [32], MIC occurs in a number of different ways:

a) Utilization of oxygen by aerobic microorganisms resulting in the anodic areas. Localized differences in concentration shift the potential of the metal surfaces resulting in the formation of localized corrosion cells.

b) Consumption of hydrogen by microorganisms through a cathodic reaction depolarizes the cathode which boosts the rate of metal deterioration at the anode.

c) Microbial elimination of protective coatings on different metal surfaces.

d) Microbial consumption of corrosion inhibitors (e.g. carboxylic acid and ester-based components) which protects metals in oil field systems [33].

e) Microbial metabolites produced by microorganisms (organic and inorganic acids), which are corrosive in nature.

f) Development of anaerobic environments encouraging

the growth of Sulphate Reducing Bacteria (SRB).

The MIC is the corrosion of metal surface which is accelerated directly by the life activities of microorganisms or indirectly by their metabolites. A large part of MIC is often produced by a mixture of anaerobic Sulphate-Reducing Bacteria (SRB) and aerobic Iron Oxidizing Bacteria (IOB) [34].

Iron Oxidizing Bacteria (IOB). Under actual working conditions, these two microorganisms accelerate the corrosion of materials through synergistic actions. IOB consumes oxygen in the medium to create suitable growth environment for anaerobic SRB and then promote the corrosion of the matrix by SRB [34]. During this process, SRB and IOB cooperate together to form biofilms on metal surfaces which are usually composed of sessile cells, EPS and corrosion products.

The biofilm plays a very important role in MIC and the development of biofilm theory and analytical techniques have led up to a better understanding of the whole process of MIC [34].

MIC often occurs as results as of synergistic interactions between the metal surface, corrosion products, microbial cells and metabolic byproduct [35].

Iron bacteria

In the 1830s, iron bacteria were among the first group of microbes to be recognized for carrying out a fundamental geological process, namely the oxidation of iron. Due to permanent questions about their metabolism, coupled with difficulties in culturing important community members, studies of Iron Oxidizing Bacteria (IOB) have lagged behind other important microbial lithotrophic metabolisms.

Recently, research on lithotrophic, oxygen-dependent IOB that grow at circumneutral pH has been accelerated [36].

The iron bacteria was among the first prokaryotes to be observed and recorded by pioneer microbiologists, such as Ehrenberg and Winogradsky, in the 19th century.

This bacteria was originally considered to be the bacteria that catalyzed the oxidation of iron (II) (Fe2+, ferrous ion) to iron (III) (Fe3+, ferric ion), often causing the latter to precipitate ochre-like deposits.

Although the definition of what constitutes an iron bacterium has been extended to include prokaryotes like *Geobacter* spp., catalyze the dissimilatory reduction of ferric ion to ferrous ion [37].

Iron-oxidizing prokaryotes have continued to be the focus of a considerable articles of research due to not only the perceived importance of these microorganisms in the global iron cycle and industrial applications (chiefly biomining), but also discoveries over the past 20 or so years of novel genera and species that catalyze the dissimilatory oxidation of iron at neutral pH in micro-aerobic and anaerobic environments [36].

While classified species of iron-oxidizing bacteria occur in a number of phyla within the domain bacteria, including the Nitrospirae and the Firmicutes, the majority are included within the largest bacterial phylum, the Proteobacteria.

Within this phylum are found IOB that have different physiologies in terms of their response to oxygen (obligate aerobes, facultative and obligate anaerobes) and pH optima for growth (neutrophils, moderate and extreme acidophilic [37].

IOB have been implicated in biocorrosion since the 1960s [38]. These bacteria gain energy through the oxidation of ferrous ion (Fe2+) to ferric ion (Fe3+), which occurs at near neutral pH and may result in the formation of iron oxides. IOB are micro-aerophillic and therefore are found commonly associated with other microorganisms in aerobic environments in the presence of reduced iron [32].

The IOB species that have been studied most extensively in biocorrosion are *Gallionella*, *Leptothrix* and *Siderocapsa* [39]. The mechanism of IOB is due to the formation of a differential aeration cell in which the bacteria form iron oxide deposits. The area under the deposits is excluded from oxygen, thereafter serves as the anode and the areas uncovered by the deposits and exposed to high oxygen concentration serve as the cathode. The metal under the deposits dissolve and form cationic species that then undergo hydrolysis forming iron hydroxides and oxides.

The IOB corrosion in freshwater environments is much better understood than in the marine environments. In the presence of chloride ions, the IOB activity may result in the formation of ferric chloride, which is highly corrosive and may concentrate under ferric oxide deposits [39].

It was reported by Arafat [40], that corrosion products on the carbon steel was examined by SEM after immersion for 21days in the culture media of *Achromobacter xylosoxidans* SC1 (Figure 2) showing fine plates (flowery structures) and cotton balls shaped structure. The coverage of corrosion products almost expanded the entire surface of carbon steel.
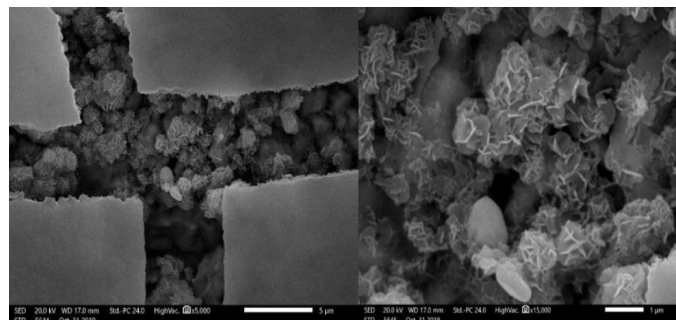

Figure 2: SEM analysis showing formation of corrosion products by Achromobacter xylosoxidans SC1 at magnification (5000X).

Factors affecting microbial induced corrosion

Many parameters are known to affect the rate of MIC. The parameters affecting MIC are physical, chemical and biological parameters. One of the parameters is the temperature. The temperature range for MIC is more complex to establish. DNV [41], reported an optimal range for MIC of 25-45 °C and a possible range for MIC of 0-80°C.

Another factor affecting MIC is the material nature. The MIC normally occurs in Carbon Steel (CS) (ISO, 2010). This may be due to that CS being the preferred metal alloy for construction. All metals and metal alloys can be subject to MIC [42].

The metallurgical features including non-equilibrium microstructure, grain boundaries, residual stresses, surface chemistry (texturing), and alloying elements have been shown to play an important role in MIC [43].

Features down to the level of microorganisms in size are very important for initial bacterial attachment and the subsequent colonization and proliferation in the biofilm formation. Microor-

ganisms most likely attach to the surface by chance in a random fashion, but their further proliferation and segregation at any specific location depends on different micro- and macro-scale metallurgical features. In addition, some types of inclusions in a metal may promote the production of high concentrations of metabolites and localized clusters of the biofilm i.e. tubercle formation [44].

Carbon Steel (CS) is an iron-based alloy, which usually contains carbon (max. 2%) and other minor alloying elements. It is one of the most widely used industrial materials and accounts for approximately 88% of the annual production of steel in the United States alone [45]. Despite having somewhat limited corrosion resistance, CS is still used as a construction material in large tonnages in many industries, including maritime, transportation, chemical and nuclear power plants, petroleum production and refining, mining, and metal-processing plants [45].

CS can have different grain sizes and microstructural phases (ferrite, pearlite and/or marten site) depending on the amount of carbon present, the rate of cooling applied during manufacturing and any subsequent heat treatment process. The metal working processes such as rolling, forging, and extrusion, can also affect the morphology of various microstructural features present in CS [46].

The MIC has been shown to be affected by several metallurgical parameters. Therefore, a fundamental understanding of these parameters is essential for better comprehension and interpretation of this complex corrosion process. This could also help us to develop efficient Lab-based tests for studying MIC of CS, which is an important industrial material [47].

The grain size is one of the most important characteristic features of metals and alloys. When a metal or alloy is processed, the atoms in each particular grain align themselves in a specific order which defines the spatial orientation of that grain. During grain growth, an interface is eventually formed when different grains having different spatial orientation impact on each other [48].

This interface is referred to as the grain boundary and it is a region of major atomic disarray [49]. It has been demonstrated that the corrosion properties of metals and alloys are affected by their grain size [50].

That has been also shown to influence bacterial attachment and the resulting MIC [47]. Small grained materials are more susceptible to bacterial attachment and later to MIC [51]. These areas are also susceptible to taking up hydrogen produced by the microorganisms, resulting in hydrogen embrittlement followed by SCC [52].

Another factor affecting MIC is pH. Energy Institute [53] reported that MIC often occurs at a neutral pH.

An important factor affecting MIC is the chemical composition of the culture medium used for growing the microorganisms and conducting MIC tests in the laboratory.

The composition of media has been shown to play an important role in MIC [54]. Alternative approaches use media which aim to replicate the actual environmental conditions e.g. Modified Baar's medium [55], artificial seawater [56] and Vaatanen Nine-Salt Solution (VNSS) **[57].**

The availability of nutrients in the test medium affects the growth and metabolic activity of the microorganisms. The bac-terial growth is limited when the essential nutrients in the culture/test medium have been used up by the bacterial cells during their metabolism and growth.

One way to avoid this is to refresh the bacterial growth medium during long term immersion studies (i.e. from weeks to months) to maintain the density of viable bacterial cells throughout the experiment. Many long-term MIC studies, however, have been carried out without any medium replenishment [58].

In one study that looked into this effect, Jayaraman *et al*. [57] observed that daily replenishment of the growth medium caused a significant difference in the corrosion inhibition of CS, with less corrosion observed in the replenished medium compared to the non-replenished medium.

Bio-Corrosion control and preventive strategies

The World Corrosion Organization (WCO) "Shenyang" Declaration 2019 reported that corrosion is a "cancer" of industry is difficult to solve. Therefore be, it resolved that there is a critical need to increase the corrosion awareness, develop and implement corrosion control technologies in order to protect human life and our environment [59].

According to a study by NACE [60], International Implementing corrosion prevention best practices could result in global savings of 15-35% of that cost, or $375-$875 billion [60].

The MIC is reported to account for about 50% of the total cost of corrosion [16]. According to corrosion experts, it is possible to save a net of 25% of that annual cost by applying currently available corrosion control technologies [61]. However, better corrosion management can be achieved using preventive strategies [62] that include:

- Increase awareness of large corrosion costs and potential savings,

- Change the misconception that nothing can be done about corrosion,

- Change policies, regulations, standards, and management practices to increase corrosion savings through sound corrosion management,

- Improve education and training of staff in recognition of corrosion control,

- Advance design practices for better corrosion management,

- Advance life prediction and performance assessment methods,

Advance corrosion technology through research, development, and implementation.

It is known that 40% of pipe corrosion for oil industry is attributed to the MIC and it causes havoc from the order of US$100 million in production, transportation and storage of oil every year in U.S. [63]. Nevertheless, notable MIC-related cases include the 2006 Prudhoe Bay oil spill and the corrosion of deep-sea tsunami early warning systems [64].

The methods used to prevent MIC by inhibiting the growth or metabolic activity of microorganisms thus changing the environment in which the corrosion process occurs [65].

The MIC can be controlled in several ways:

a) Physical methods, b) Chemical methods, and c) Biological treatments.

The physical method comprises mechanical cleaning which matches any method capable of promoting physical removal of the material deposited on the metal surface and includes the use of brushing, water jets, among others [66].

The mitigation of MIC, using physical treatments, involves the use of mechanical forces to scrap off the biofilm and is not only limited to pigging, but also involves the use of ultraviolet radiations and ultrasonic. The pigs work well in cleaning and inspection of the pipeline [67]. It is still not the ideal method to prevent MIC.

When using UV radiations for controlling biocorrosion, the DNA of the microorganisms is altered in a way that they cannot produce byproducts which are responsible to cause corrosion [68].

The ultrasonic has been recognized since several decades to destroy cell wall and cell membrane of the microorganisms. It can also cause damage to the metal surface and may enhance the crevice corrosion [69].

Physical and chemical methods (sanitization through the use of biocides and antifouling coatings such as inks or corrosion inhibitors) are used generally combined in order to improve corrosion control method [65].

The chemical methods intend to reduce or eliminate the metal exposure to the action of biocorrosion, either by direct elimination of microorganisms or reduce effect of their metabolites on the material. However, inefficient cleaning and monitoring strategies for systems and lack of skilled professionals in the area of MIC provide increased corrosion losses [66]. According to Videla [66], the biocides stands among the most commonly used effective control methods. However, some biocides may not have activity against certain types of microorganisms within the same group, due to the development of bacterial resistance.

Protective or antifouling coatings and corrosion inhibitors form a protective film adsorbed on the metal/solution interface [70]. They are widely used in industrial systems, however their use is associated with increased bacterial growth, since they are a nutrient source for some bacterial species [71], in addition of being highly toxic to humans and other non-target organisms [72]. The use of microbes (biological control of corrosion) to protect metals against corrosion has been shown to have great potential [2].

Zuo [73] described three possible mechanisms of the inhibition of biofilm-induced metal corrosion: First, removal of corrosive materials through microbial activity e.g, microbes utilize oxygen through aerobic respiration, second growth inhibition of MIC, e.g from antimicrobial production by non-corrosive microbes and finally the formation of a protective layer, which could be established by overproduction of EPS by non-damaging microbes [74].

In all cases the mechanisms of the corrosion inhibition are not fully understood, and different studies sometimes result in opposite conclusions, [74]. The above-mentioned studies are performed under controlled laboratory conditions with mostly single-species biofilms, which makes it difficult to extrapolate the results to realistic field conditions. In order to develop an application, there is a strong need for multispecies analysis under in situ conditions and samples from the field.

Green Chemistry which has emerged as a new branch of environmental chemistry provides eco-friendly corrosion inhibitors specifically termed as "Green inhibitor". The green inhibitors are non-toxic, biodegradable and eco-friendly, and have proven effective in corrosion control [75].

The traditional biocides themselves pose threat to environment due to forming harmful disinfection by products. Other disadvantages of traditional biocide treatment are low efficiency against biofilms and its high cost [76]. The green biocides such as nanomaterials having low toxicity, environmental acceptability, safety and ease of use can be replaced in place of traditional biocides to eliminate these disadvantages [77].

In the last two decades, the nanotechnology has been playing an increasing important role in supporting innovative technological advances to manage the corrosion of steel [78]. Nanomaterials are materials that have at least one of their morphological features such as grain size, particle size, structure size, etc., in the nanoscale (less than 100 nm) [79].

This is primarily due to their small sizes, which allow higher volume fractions at the surfaces and thus higher interaction areas [80]. The nanostructures materials are known for their outstanding mechanical and physical properties due to their extremely fine grain size and high grain boundary volume fraction.

The focus is now shifting from synthesis to manufacture of useful structures and coatings having greater wear and corrosion resistance [79].

The nanocomposites established excellent antibacterial activity depending on the nanoparticle size as this parameter changes the surface area that leads to better interaction with the bacterial cells [5].

Nanocomposites are "materials with a nanoscale structure that improve the macroscopic properties of products." Nanocomposites can then be defined as nanomaterials that combine one or more separate components in order to obtain the best properties of each component (composite). In nanocomposite, nanoparticles (clay, metal, carbon nanotubes) act as fillers in a matrix.

Okpala [81], reported the advantages of nanocomposites as: Highly dispersible in aqueous medium and uniform distribution of the active agent over an extended period of time.

The nanocomposite exhibits such advantages with addition of improvement of the environmental impact. It is very important to add corrosion inhibitors to prevent metal dissolution and minimize acid consumption in acid pickling. The good inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and the availability [82].

The application of nanotechnology in the corrosion protection of metals has recently increased [83]. The environmental impact can also be improved by utilizing nanostructure particulates in corrosion inhibition, coating, and eliminating the requirement of toxic solvents [84].

Nanocomposites are of two types: polymer nanocomposites and clay nanocomposites. The clay nanocomposites increase the additional properties and have dominated the polymer literature. But there are a large number of other significant areas of current and emerging interest [3].

The clay mineral that is generating the most interest in use in nanocomposites is montmorillonite (MMT). This clay is widely available and cost effective, thus becoming the most widely used clay in nanocomposite formulations [81].

The montmorillonite clay is recently a current topic to study its utilization as additive and inert carrier for the water insoluble organic compounds at the research level [7].

Recently, the synthesis and application of MMT-based antibacterial have attracted great interest due to global concerns regarding public health. Some resent researchers have reported modified MMT clay with antibacterial activity. For example, silver, copper, and zinc ions have been immobilized on MMT [85], cetyltrimethylammonium [86], tetradecyltrimethylammonium [87], have been intercalated into the MMT layers.

Arafat [40], showed that on using different concentration of two organic compounds thiophene schiff bases of the chemical structure compound I (2-((Furan-2-ylmethylene)-NH2)-4,5,6,7-tetrahydrobenzo- [b] thiophene-3-carbonitrile) and compound II (2-((2-Hydroxybenzylidene)-NH2)-4,5,6,7-tetrahydrobenzo-thiophene-3-carbonitrile loaded on Na-MMT clay nanocomposite, the corrosion rate decreased in comparison to the control indicating corrosion inhibition. Also, when using a concentration of 80 ppm NCI the IE% was about 100%. While in the case of NC II, the corrosion rate decreased in comparison to the control and IE % was about 100% at 60, 80 and 100 ppm (Table 1). The inhibition efficiency of NCI, NCII to MIC of CS coupons are related to the chemical structure of the two compounds.

Table 1: Corrosion rates of inhibited and uninhibited carbon steel coupon and inhibitive effeciency of concentrations of NCI and NCII by *Achromobacter xylosoxidans* SCI.

Conc. (ppm)	Initial weight (g)	Final weight(g)	Weight losses (g)	Weight loss without effect of the media (g)	CR without effect of the media (m p y)	IE%
(0 ppm) Bacterial cultural control	2.041 1.905	2.019 1.888	0.022 0.017	0.005 0	0.915 0	------- --------
NCI 40	1.868	1.845	0.023	0.006	1.099	ND
60	2.009	1.991	0.018	0.001	0.184	80%
80	1.730	1.721	0.009	0	0	100%
100	2.072	2.043	0.025	0.008	1.465	ND
NC H 40	1.965	1.947	0.018	0.001	0.199	80%
60	1.812	1.803	0.009	0	0	100%
80	1.942	1.930	0.012	0	0	100%
100	1.981	1.966	0.015	0	0	100%

In addition, pharmacology studies have revealed that MMT can adsorb to bacteria such as *Escherichia coli*, *Staphylococcus aureus* and immobilized cell toxins [6].

MMT is a natural clay and a safe carrier material with layered silicate structure, featuring with a large surface area, high adsorption capacity and ion exchanging properties [88]. In particular, Nano-sized MMT has been successfully used as drug carrier, catalyst [89]) food additives [90], issue engineering materials [91] and in drug delivery system [7], due to its excellent biocompatibility and extensive uses in a broad range of medical and pharmaceutical applications [92].

Kumari [3], mentioned that the future of nanocomposites in less than two years, will be the worldwide production of nano composite and is valued to go over 600,000 tones and is set to cover the following key areas in the next five to ten years: a) Anti-corrosion barrier coatings. b) Drug delivery systems. c) New fire-retardant materials. d) Lubricants and scratch free paints. e) UV protection gels. f) New scratch/abrasion resistant materials. g) Superior strength fibers and films, also, in biomedical sciences as anticancer drug targeting [93].

The chemical corrosion inhibitors play an important role in the protection and mitigation strategies for retarding corrosion of metals and alloys. Organic compounds especially those having heteroatoms, such as N, O, S, and P, have been frequently used as corrosion inhibitors to mitigate corrosion because of their effectiveness, ease of use, and economic aspect. In addition, the presence of heteroatoms acts as an active center to be adsorbed on the metallic surface and mitigate the metallic corrosion [8].

Organic corrosion inhibitors are a special group of substances or their mixtures that prevent or minimize the corrosion. Inhibitors are adsorbed on the surface of the metal and form a protective thin film [94].

The organic corrosion inhibitors are widely used in industry because of their effectiveness at wide range of temperatures, compatibility with protected metal materials, good surface solubility and relatively low toxicity [95]. These compounds act as cathodic and anodic type inhibitors.

Cathodic corrosion inhibitors shift the corrosion potential toward lower values and inhibit or delay the reactions occurring at the cathode (oxygen reduction and hydrogen evolution). In contrast, anodic-type corrosion inhibitors react with the metal cation to form an insoluble hydroxide and block the active sites on the metal surface.

It is very important to use the right amount of an anode inhibitor, because insufficient concentration to cover all the active sites can lead to localized corrosion which is difficult to detect. Mixed inhibitors provide the highest protection because they affect both cathodic and anodic reactions.

The mechanism of the action of the organic corrosion inhibitors is based on the adsorption on the surface to form protective film which displace water from the metal surface and protect it against corrosion [94].

The inclination towards eco-friendly corrosion inhibitors development intersects across several goals of pharmaceutical research, one of which is to discover or develop molecules with desired biological activity. Over the past two decades, extensive research and development have led to the discovery of new classes of corrosion inhibitors, and the importance of the use of several drugs as corrosion inhibitors has grown [96].

Because of their natural origin [97] as well as their non-toxic characteristics [98] and negligible negative impacts on the aquatic environment [99] drugs (chemical medicines) seem to be ideal candidates to replace traditional toxic corrosion inhibitors [96].

Organic compounds containing heteroatoms with electronic lone pair (N, O, S and P), or aromatic rings, can generally be used as anticorrosion. Recently, the attention of Schiff bases (organic compounds containing an azomethane group (-CH=N-) and their metal complexes have gained importance in medicinal and pharmaceutical fields due to a broad spectrum of biological activities such as antibacterial, antifungal, antimicrobial and anti-HIV1 activities [100] and anticorrosion [101].

The nitrogen atom of azomethine may be involved in the formation of a hydrogen bond with the active centers of cell constituents and interferes in normal cell processes [101]. Also, Schiff's bases are used as efficient inhibitors for steel corrosion due to the presence of C = N group [102].

The lone pair of electrons on N and S atoms, and the planarity of the molecule are useful for its adsorption to the metal surface. They are inexpensive, non-toxic, harmless to the environment, biodegradable and have a significant anticorrosive propety with low environmental impact [4].

The azomethine linkage and the donor atoms in the backbone of the schiff bases are responsible for their biological activity and industrial application, which can be altered depending upon the type of substituent present on the aromatic rings. Also, Schiff bases, since they contain an azomethine-N, are well-known organic inhibitors of metal corrosion [103]. Thiophene nucleus has very promising characteristic and therefore can be considered as a significant topic of study in the field of heterocyclic chemistry. The lone pairs of electrons present on an S atom are more effectively delocalized in the heterocyclic ring compared to other heteroatoms such as O and N in case of furan and pyrrole because of the larger size of S atom.

In recent years, 2-aminothiophene derivatives have attracted increasing importance in heterocycles with privileged structures. These compounds are known to have demonstrated broad spectrum of applications as antimicrobial, antibacterial, antioxidant and antifungal [104].

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