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Review

Influence of Organic Acids and Related Organic Compounds on Corrosion Behavior of Stainless Steel—A Critical Review

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Abstract: Stainless steel is one of the most commonly used structural materials in industry for the transportation of liquids such as water, acids, and organic compounds. Corrosion is a major concern in industry due to the use of strong mineral acids, feedstock contamination, flow, aqueous environments, and high temperatures. Stainless steel is the most commonly used material in the petrochemical industry because of its characteristics of self-protectiveness, offered by thin passive oxides, and its metallurgical composition. However, chlorides and mineral acids attack the stainless steel continuously, consequently breaking down the passivation film, causing a continuous challenge from corrosion. The corrosion in stainless steel is influenced by many factors including flow rate, temperature, pressure, ethanol concentration, and chloride ion content. This review describes the impact of organic compounds and organic acids on the degradation behavior of stainless steel. The review also summarizes the commonly used organic compounds and their applications. It has been demonstrated that organic acid concentration, temperature, and halide impurities have significant effects on susceptibility to pitting corrosion by damaging the passivation film. The phenomenon of corrosion in stainless steel is quite different in immersion tests and electrochemical potentiodynamic polarization. This review article discusses the importance of organic compounds and their corrosion behavior on steel. The article also puts emphasis on the roles of corrosion inhibitors, monitoring methods, corrosion management, and forms of corrosion.

Keywords: organic compounds; organic acids; stainless steel; corrosion behavior; pitting corrosion; corrosion mitigation

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1. Introduction

Organic compounds are a large class of hydrocarbons that may contain nitrogen, oxygen, halogens, and phosphorous atoms, in the form of solid chemical compounds, liquids, and gases. The most used foodstuffs in our daily life such as vinegar, starch, fats, sugar, etc., are organic compounds. They are known to humans since prehistoric times but practical studies began in the 18th century [1]. Organic compounds are insoluble in water but in organic solvents and are combustible in nature. The properties of organic solvents are determined by the active carbon atoms in the group. The presence of the covalent bond makes the organic compounds (a) have low boiling and melting points, (b) less strong acids and bases, (c) exhibit the phenomenon of isomerism, and (d) be volatile in nature [1,2]. The importance of organic compounds can be described by the fact that they are present in all organisms in the form of proteins, fats, and the basic structures of life. They are the basic components of the cycles that drive the earth such as the carbon exchange between animals and plants through cellular respiration and photosynthesis [3].

Organic compounds are the major source of energy in the form of fossil fuels. They are combined with metals to form organometallic compounds which are very beneficial for pharmaceuticals and the food industry in which they serve as stabilizers, analyzers, promotors, and catalysts [4]. Some of the organic compounds are tabulated below (Table 1).

Table 1. Organic compounds and their applications.

Organic Compound	Application	Organic Compound	Application
Gammexene	Insecticide/germicide	Urotropin	Urological disease treatment
Carbon-tetrachloride	Fire extinguishers	Ether	Coolant, solvent, anesthesia, and in alcohol production, etc.
Benzene Sulphonic acid	In the production of sulfa drugs, colored solutes, saccharin, etc.	Benzoic acid	In the food industry for preservation and drug production, etc.
Benzaldehyde	In perfume manufacturing and the color industry	Phenol	Used in the production of aspirin, predestine, insecticides, carbolic soap, etc.
Aniline	In drug manufacturing and colors etc.	Nitro benzene	In polishes and soap production, etc.
Chloro benzene	Used in phenol, aniline, etc., manufacturing.	Toluene	In the explosive industry, medicine production, dry cleaning, solvents, etc.
Benzene	Used as fuel in engines, solvents in dry cleaning, etc.	Glucose	In fruit/juices preservation, production of wines and medicines, etc.
Oxalic acid	Used in leather bleaching, printing, and colorization of clothes, making ink colors, cleaning ink spots with 10% solution, etc.	Urea	Used in the production of medicines, urea plastic, and formaldehyde. Used in the form of fertilizer, etc.
Ethyl acetate	Used in artificial perfumes and medicines, etc.	Acetamide	In misting paper and pulp, in softening cloth, and leather.
Acetic anhydride	Used in the making of medicine like aspirin, in the production of synthetic/artificial silk from cellulose, in the color industry, etc.	Glycerol	In wine and fruit preservation, cosmetics, and shoe polishes, medicines for pain relievers, watches for cleaning, in making nitro-glycerine, etc.
Acetic acid	In making jelly and sauces; in the laboratory, and food industry in the form of vinegar, etc.	Formic acid	In food preservation, used in insecticide production, in rubber, leather trade, etc.
Acetone	In making of chloroform, chloretone, sulfone, synthetic rubber, artificial silk, clodian cellulose, varnish, etc.	Acetaldehyde	Used in the production of plastic, metal acetaldehyde medicine, colors, etc.
Formaldehyde	Used in making waterproof clothes, gelatin film, insecticides, etc.	Acetyl chloride	In the production of acetic anhydride, acetamide, etc.
Ethyl alcohol	Used as insecticides for cleaning wounds, in stoves and spirit lamps, making artificial scents/colors in fruits and perfumes, solvents in methylated spirits, in varnishes and polish, in making wines and alcoholic drinking stuff, etc.	Methane	Used in the production of chloroform, formaldehyde, methyl alcohol, making tires, inks, and colors. Used as fuel for energy production, etc.

Table 1. *Cont.*

Organic Compound	Application	Organic Compound	Application
Methyl alcohol	In making polish, varnish, artificial color, methylated spirit, used as fuel in engines by mixing with petrol, etc.	Chloroform	Used as anesthesia in surgical operations, solvents for lac, fats, rubber, used as insecticides, etc.
Ethyl bromine	Used in surgical operations as local anesthesia.	Polystyrene	Used in making accumulator cells, caps of acid bottles, etc.
Polythene	Used in the production of uncrackable bottles, electrical resistance in cables and wires, etc.	Acetylene	Used for artificial ripening, Marcelin anesthesia, in producing artificial rubber, etc.
Ethylene	Used for anesthesia, fruit ripening, and preservation, in oxy-ethylene flame.	Butane	Used as fuel in liquid state in the form of LPG, etc.
Firmament	In the production of chewing tablets and medicines for the throat, etc.		

Organic acids are organic compounds with weaker acidic properties than mineral acids and their acidity is associated with one or more carboxylic groups (–COOH). The lower reactivity and weak acidity make organic acids usable at higher temperatures and for a longer time. The reactivity/strength of acids is characterized by the value of the acid-dissociation constant (K_a). It measures the acid-ionization strength. The logarithmic values of K_a are referred to as pK_a. A higher value of pK_a denotes a weak acid and a lower value indicates a strong acid. The pK_a value for formic acid is 3.75 and for HCl is less than unity. The most commonly used organic acids in the oil and gas industry are lactic acid, citric acid, acetic acid, and formic acid because of their ability to meet different application specifications. They are widely distributed in nature and release hydrogen ions when dissolved in water [5–7].

Organic acids have been produced from petrochemicals via fermentation or synthesized through chemical processes. They are commonly derived from agricultural waste, foods, and juices, and used in the process industry as catalysts or processing agents [8]. The commonly used production method for organic acids is one step acid-based fermentation process that induces corrosive contaminants such as sulfuric acid and chlorides [9]. The traditional fermentation process for crop-based organic acids focuses on the mechanical behavior, not the corrosion performance. The corrosion problems must be addressed in the production process of organic acids. Efficient and fast techniques have also been developed to extract organic acids from plant materials.

Organic acids exceptionally found applications in biochemical processes such as modulating transport across the cellular membrane, pH modification, signaling the messenger, and protein modification. They are promising chemicals for producing bio-plastic, polyester, and degradable polymers which have commercial applications in the processing of foods, pharmaceuticals, and chemical industries. Organic acids have been used in the oil and gas industry for well-stimulation treatments and to improve resistance against the corrosion of different metals such as phosphonates and act as corrosion inhibitors in stainless steel. The whole process of organic acid extraction and their application is summarized in Figure 1. The corrosion inhibition properties of organic acids are synergistically determined by surface energy, surface roughness, and wettability/hydrophobicity [10]. The wettability of the tail group commonly decreases in the order of $CH_2 > CH_3 > CF_2 > CF_2H > CF_3$. The stability of the hydrophobic surface on stainless steel is related to the chain length of the tail group.

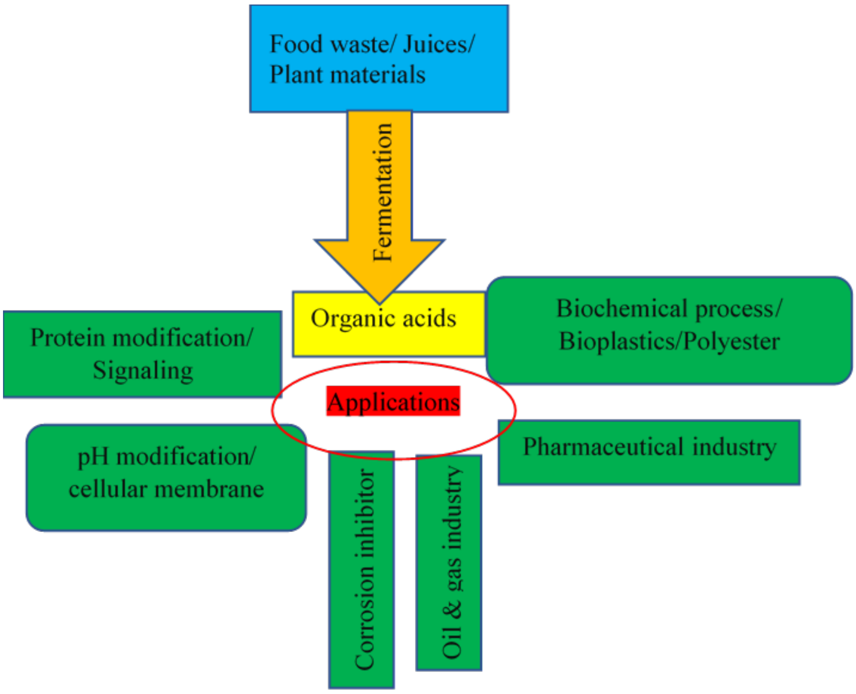

Figure 1. Organic acid extraction and their applications.

Stainless steel is used in the petrochemical, chemical, nuclear, and food industries for the transportation and storage of hydrocarbons [11–13]. The corrosion in pipelines in the petrochemical industry is caused by the presence of chlorides and water content in organic liquids [14–16]. Stainless steel is considered an excellent corrosion-resistant material in the industry due to the presence of high chromium content [17]. Therefore, many petrochemical industries experience greater uncertainty in selecting material for equipment to manufacture chemical products in organic/mixed solvents compared with the process that takes place in aqueous media [18]. The corrosion resistance of materials in organic solutions comprising acid contamination and low water concentration is of particular interest. Systematic studies of the corrosion performance of the different metals and alloys used in the chemical industry have been performed by many researchers.

Many industrial and research standards have been published over the last twenty years. The objective of the research was focused on critically reviewing the role of organic solvents and acids on the corrosion resistance of stainless steel. The impact of organic acid concentration, contact time, flow rate, oxygen level, and contaminants, including water content and inorganic additives has been carefully analyzed. The evaluation of the chemical and physiochemical mechanisms and mitigation for the occurrence and control of corrosion in organic acids and related solvents is discussed. The impact of organic acids and solvents on the corrosion behavior of ferrous and nonferrous materials is discussed. Types of corrosion under organic solvents, corrosion mitigation techniques, and process optimization are also briefly reviewed and discussed.

2. Corrosion Behavior of Stainless Steel in Organic Acids and Related Compounds

The advanced corrosion problems in metallic materials have been created due to the development of petrochemical industries and new products caused by advancements in chemical engineering and technology. Stainless steel is traditionally a widely used material in the pipelines of the petrochemical industry [19]. The corrosion behavior of stainless steel in an organic acid environment is influenced by many factors such as concentration, pH, temperature, length of tail group, chloride ions, etc., as summarized in Figure 2. A sufficient amount of nickel present in the steel improves the formability and ductility by retaining its austenite structure at ambient temperature. The presence of molybdenum with chloride ions also improves the corrosion resistance whereas aluminum enhances the scaling at higher temperatures. Other particular characteristics are improved by adding selenium, sulfur, nitrogen, niobium, silicon, titanium, and copper [20–22]. The corrosion phenomenon in steel is much less prevalent in the organic or mixed-solvent environment than in an aqueous medium. Organic solvent means all liquid organic compounds, irrespective of their practical use. Numerous research works have been carried out on the degradation performance of stainless steel in organic media. Some researchers found that the passivation film on stainless steel would be damaged in an anhydrous solution having a water content of less than 70 mole%. Additionally, the dissolution kinetics are activated in pits with the increase in water content in an organic acid/NaCl solution. The formation of the passivation film is dependent on the activity of water and pitting potential is considered as the function of water content in organic acid/HCl solution [23,24]. The higher viscosity and concentration of organic acids deteriorate the passivation film and the diffusion rate is dropped leading to localized corrosion in stainless steel [25]. The corrosion caused by organic solvents leads to deterioration in the mechanical properties and discoloration of the solvent [26]. The materials used in organic environments need immense corrosion resistance because of the inflammable, poisonous, and explosive nature of organic solutions [27–29]. Temperature, pH, chloride inclusions, and even traces of water have obvious effects on pitting and stress corrosion cracking (SCC) susceptibility [30]. Therefore, the pressure and temperature in corrosion are selected in such a way that aggressive agents are in the liquid state [31]. Researchers are focusing on the corrosion behavior of metals in organic solution with minor impurities such as chlorides and water to estimate the reliability of transportation pipelines [32].

The phenomenon of corrosion in organic solvents is the same as in aqueous corrosion—metal ions are transferred to the oxide by heterogeneous chemical reactions.

Organic solvents can be categorized into the following three systems (R refers to a saturated or unsaturated alkyl moiety):

(1) Protic-aprotic systems: carboxylic acids (RCOOH), alcohols (ROH), hydrocarbons (R-H), amines (R-NH_2), halogenated hydrocarbons (R-X), and esters (RCOOR).

(2) One-component/multi-component systems: examples are RCOOH, ROH, and R-X. Organic solvents are contaminated by O_2, H_2O, halogenides, and inorganic acids.

(3) One-phase/multiphase systems: the one-phase system can be a liquid (in most cases), vapor (i.e., RH, RX), or a solid (coatings, polymers). Multiphase systems may be dioxane + H_2O + HC1; RX + H_2O, heptane + C_2H_5OH + HCl.

Purified aprotic solvents may only react with electronegative metals (Al and Mg). Carboxylic acid and alcohols are the main representatives of the group. The number of carbon atoms is more influential in the homologous series of monocarboxylic acid [33–39]. The corrosion rates are decreased exponentially with the increased chain length of carboxylic acid which is due to the fact that the increase in chain length and steric hindrance enhances the viscosity while the diffusion coefficient is decreased. The number of carbon atoms has the same influence on corrosion in an alcohol series as in carboxylic acid [40]. Ethanol and methanol have higher corrosion reactivity than water. The concentration of Cl^- and water increases the corrosion in steel in the three-component system (water+formic acid + Cl^-). The pitting susceptibility of stainless steel is increased when the water content is $<$ 5 vol.%, while pitting is reduced for water content of more than 10 vol.% [41,42]. The long-term exposure of stainless steel to organic solvents makes it more susceptible to pitting corrosion [43,44].

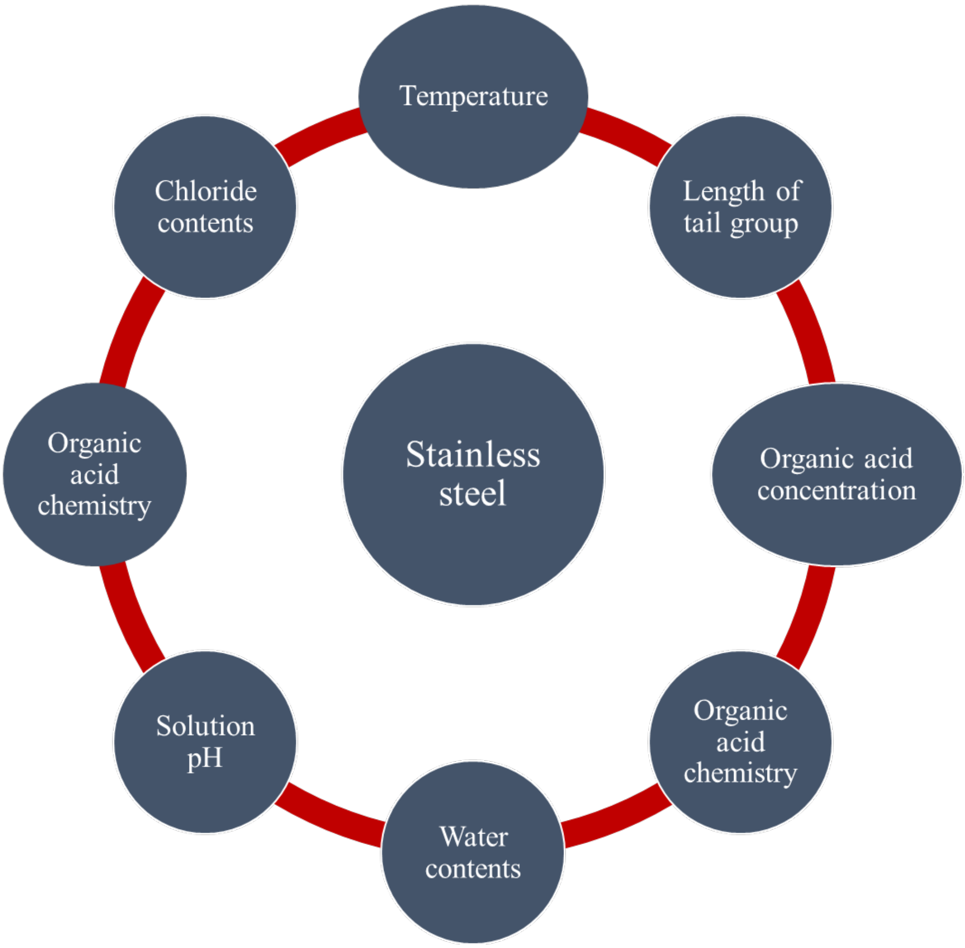

Figure 2. Symmetric diagram indicating the factors influencing the corrosion resistance of stainless steel in organic acids.

Recently, austenite steel (AISI 316L) has been operating in the petrochemical industry at higher temperatures for the last twenty years because of its improved mechanical and corrosion properties. Austenite steel is one of the most used steels (about 2/3) in the stainless-steel group [45]. The undesirable intermetallic phases are observed in stainless steel along with small quantities of carbides M23C6 (FCC, NaCl type, M = Mo, Fe, and Cr) and M6C (FCC, diamond-type, M = Mo, Fe, and Cr) during service or heat treatment at 550–900 °C. The most observed intermetallic phases in austenite steel are σ (sigma) (TCC, D8b, Fe-Cr-Mo), χ (chi) (Cubic, α-Mn type, A12, Fe-Cr-Mo), and η, (Leaves phase) (HCP, C14, Fe2M, M = Mo, Ti) [45]. The loss of corrosion resistance and ductility is caused by the occurrence of these intermetallic phases leading to improvement in matrix solid solution [46]. The investigative analysis of these phases is of great interest for the development of new compositions for excellent usage of this steel [47].

Uniform corrosion in stainless steel takes place in organic acids and alcohol. Stainless steel and aluminum experience the pitting type of corrosion in perchloroethylene, chloride-contaminated alcohols, and other protic solvents [48]. Uniform erosion–corrosion takes place in the stainless steel in the mixture of halogenated hydrocarbons. Crevice corrosion, erosion, and t-stress corrosion are caused by the mixture of trioxane, formic acid, water, and methanol in stainless steel and aluminum [49,50]. The corrosion failure of some organic compounds on some metals is given in Table 2.

Table 2. Corrosion failure in organic media.

Metal	Corrosion Medium	Type of Corrosion	Temperature	Prevention Method
Carbon steel	Dimethyl formamide	Uniform	100 °C	Anhydrous solvent ($<0.1\%$ H_2O)
AISI316	Acetic acid (30%) + propyl acetate (9%) + butyl acetate (42%) + propionic acid (18%)	Pitting	Boiling	Add titanium
Ti	Methyl acetate+acetals + HCl + H_2O	Intergranular stress corrosion	Boiling	Enamel coating
Al	Ethyl dibromide	High rate uniform	25 °C	Use galvanized steel

Wang and Zhu [51] studied corrosion inhibition in derivatives of lactones, quinoline, triazole, and diazole with different concentrations of HCl solution in different types of steel. Multilayer structure distribution was observed in the electrochemical behavior of the passivation film of stainless steel under ultrasonic and static state cavitation in an HCl solution. Organic acids are not aggressive against stainless steel at room temperature unless used at higher temperatures or contaminated with chlorides [52,53].

Constantinescu and Heitz [54] investigated the corrosion rates of AISI 304 stainless steel in oxygen-free butyric, propionic, formic, and acetic acids at different temperatures and chloride content. They observed that the influence of water in stimulating the corrosion reaction becomes more significant with less water, like organic solvents. The dependency of corrosion on temperature is analogous to that in the aqueous solution. The role of chlorides, acetic acid, water, and oxygen level in the pitting corrosion of carbon steel in simulated fuel-grade ethanol (SFGE) was observed by Lou and Sing [55]. They concluded that interface electrochemistry and surface film stability are strongly influenced by water content in SFGE. The pit instigation and growth are promoted by higher acidity and dissolved chlorides.

Ferreira et al. [56] recorded the EIS of 316L in (1 wt.%) H_2SO_4 and (3.5 wt.%) NaCl to prove that the passivation layer on the stainless-steel surface was decayed by acetic acid that could be affected by the higher concentration of Cl^- and H^+. The presence of chloride ions, methanol, H_2O, and dissolved oxygen in acetic acid are major factors influencing stress corrosion cracking.

Chloride is required for stress corrosion cracking (SCC) in ethanol but is not the controlling factor for crack growth. D.G Li et al. [57] investigated the effects of pH, H_2O, and chloride ions in the slow strain rate test and found that low pH and chloride ions promote the SCC. Gui et al. and Singh et al. [55,58] concluded that chloride, acetic acid, and water content promote localized corrosion by influencing the passivation film. The localized cells are created on the metal at the microenvironmental level by microcracks which are produced as a result of plastic deformation. The electrochemical properties of plastic deformation can be widely different from those of the undeformed.

Simulated fuel-grade ethanol with 5 vol.% water and 5.6 mg/L acetic acid has little effect on stainless steel. Later, the same researcher concluded that 560 ppm acetic acid inhibits the re-passivation of steel in the ethanolic environment. The existence of acetic acid in ethanol influences the crack growth rate and pitting corrosion by producing bacteria. The role of water, chloride ions, and oxygen has been suggested. However, the effects of other impurities have not been considered [55]. It was investigated by Schmitt [59] that an increase in chloride ion concentration inhibits CO_2 corrosion by decreasing the CO_2 solubility in a simulated solution. Moreover, chloride ions destroy the corrosion film and change the film morphology.

Pitting corrosion dynamics are more sensitive to chloride ion concentrations than pH and an increase in concentrations of chloride ions leads to an increase in pit propagation. But it has no significant effects on localized corrosion rate at 80 °C. The stainless steel experiences severe corrosion in the 100–110 °C temperature range and 0.5 MPa pressure.

The effects of Cl^- ions on the corrosion behavior of 316L steel at high temperatures were investigated by Zhang et al [60] in H_2S/CO_2 aqueous media. The corrosion was controlled by H_2S and an increase in chloride ions weakened the CO_2 corrosion. The corrosion behavior of mild steel in various concentrations of acetic acid has a resemblance in weight loss and electrochemical techniques at three different temperatures of 25, 35, and 45 °C. The maximum corrosion rate was observed in 20% acetic acid. The anodic polarization shifted to a higher current density with the increase in temperature at each concentration and the passive region became less distinguishable.

Otero et al. [61] prepared 316L stainless steel by powder metallurgy and investigated the corrosion behavior under an organic solution containing oxalic acid, lactic acid, formic acid, and acetic acid. AISI 316L steels had the highest corrosion rates. Subsequently, a kinetic study of the corrosion process observed the crevice corrosion mechanism. A localized crevice attack was observed in the pore areas, close to the powder particle contact zone. The corrosion rate in formic acid is time-dependent. The dissociation constant in formic acid is constant and consequently is more corrosive. The corrosion rates are high for a longer time, indicating that corrosion products also support the corrosion rate. The improvement in hardness competes against the decrease in corrosion resistance due to the formation of microcavities during the corrosion process which is balanced by the increase in hardness.

2.1. *Effects of Acetic Acid*

Acetic acid is a monoprotic acid (CH_3COOH) ($pK_a = 4.8$) and the second simplest carboxylic acid. It dissolves the carbonates by pairing them with another acid to be used as an iron agent. The corrosion behavior of stainless steel in acetic acid resembles weight loss and electrochemical processes. The maximum corrosion rate for stainless steel in 20% acetic acid at different temperatures was observed. The increase in temperature increases the corrosion current density, causing an enhancement in the corrosion rate. The passivation range is extended by the addition of sodium acetate [62]. The corrosion rate increases with the increase in temperature, flow speed, and concentrations but decreases with the increase in pH. The increase in the concentration of acetic acid leads to the formation of iron acetate which consequently reduces the reactivity of acetic acid. The primary corrosion product forming the passive film is ferrous carbonate ($FeCO_3$) at higher pH and temperature conditions. Stainless steel has high corrosion resistance in aqueous acetic acid and a passive film is formed on the surface which enhances the corrosion resistance. The addition of molybdenum has beneficial effects on the passivation film. The presence of aggressive ions influences the corrosion behavior of stainless steel. The chloride ions are more aggressive than the bromides. The addition of H_2S accelerates the corrosion rate in stainless steel by promoting the hydrogen evaluation reaction. Severe corrosion cavities are formed on the surface because cementite strips are formed on the grain boundaries. The loose corrosion products are formed on the surface and the passivation film is damaged. The addition of CO_2 in acetic acid activates the polarization curves and the cathodic current density is substantially increased to more active values. The dissociation of acetic acid takes place in one step as below:

$$4CH_3COOH \rightleftharpoons 4CH_3COO^- + 4H^+$$

The corrosion behavior of mild steel in citric acid, tartaric acid, lactic acid, malic acid, and glycolic acid has been investigated by many researchers [63–66]. It was observed that the corrosion rate increased in the order of glycolic acid < citric acid < lactic acid < tartaric acid. The corrosion rate was increased with the increase in the acid concentration of the citric, lactic, tartaric, and malic acid solutions while the glycolic acid concentration was kept constant. The glycolic molecules were observed on the steel surface. The corrosion rate of stainless steel (SS-304) remained constant under glycolic acid aqueous solution. The surface unevenness increased with the increase in immersion time and the corrosion behavior was not passive. The carboxylic anions were not observed on the surface.

The corrosion behavior of X70 steel was investigated in glacial acetic acid and NaOH solution under different pH conditions by Zhang et al. [67]. The corrosion rate was increased with the increase in hydrogen at pH = 3. The corrosion products inhibited hydrogen evaluation and the oxygen reduction process was promoted at pH $\geq$ 3. The corrosion rate was less for a pH $\leq$ 4 than that of the solution with pH ranging from 5 to 7. The different morphologies of the corrosion products were observed under different pH values. The corrosion mechanism changed from uniform to localized corrosion with the increasing corrosion rate, leading to an increase in pitting development.

2.2. *Effects of Formic Acid*

Formic acid (HCOOH) is considered as the most reactive organic acid after citric acid and assures strong reactivity with formation materials. The corrosion behavior of stainless steel in formic acid is a function of concentration and temperature. Formic acid can aid corrosion inhibition by forming carbon monoxide (CO) on the metal surface which intensifies the corrosion inhibition by different mechanisms. The 20% formic acid aqueous solution yielded the maximum corrosion rate. Cathodic polarization curves remained identical irrespective of formic acid concentration [68]. A high corrosion rate was observed at the boiling point of 100% formic acid. The conductivity of formic acid is increased with the temperature. The corrosion products on the surface are Fe_2O_3, FeO, and Cr_2O_3 [69]. The impact of acetic acid and formic acid on the corrosion performance of stainless steel was investigated by Invernizzi et al. [70] at different temperatures. The corrosion rate was higher in dissociated formic acid at the same concentration. The austenite phase was present in all solutions causing uniform corrosion. The contamination of sulfates was directly related to the corrosion rate. The corrosion rate increased linearly with the addition of sulfuric acid concentrations. But the addition of a few tens of ppm of oxidants (Cu^{2+} or Fe^{3+}) improved the corrosion resistance remarkably and the corrosion rate was negligible. The addition of H_2O_2 increases the corrosion potential up to the passivity of the steel. The corrosion rate of 316L stainless steel is greater in an aqueous solution of formic acid and acetic acid solution than in non-aqueous solution. The corrosion behavior is quite different in aqueous and non-aqueous solutions.

Peracetic acid is strong oxidizing acid, used for sterilization and disinfection due to its microbial activities. It is widely used in biocidal activities, particularly in viruses, fungi, yeasts, and bacteria. It is very corrosive to metals and elements used in hospitals and industries. The effects of temperature and the concentration of peracetic acid on the degradation behavior of cold-rolled steel were investigated by Qing et al. [71]. The maximum corrosion was observed at 20 °C. The concentration of peracetic acid significantly influenced the corrosion rate. The dominant corrosion product was Fe^{3+}. Pehkonen et al. [72] analyzed the corrosion behavior of stainless steel in peracetic acid and ozone. It was concluded that stainless steel experiences higher corrosion rates in peracetic acid solution than ozone.

2.3. *Effects of Citric Acid*

Citric acid ($C_6H_8O_7$) is a weak organic acid having three carboxylic groups (COOH) and is commonly present in citrus fruits. The anionic derivative $[C_6H_8O_7]^{3-}$ reacts with different ions to form salts. The degradation behavior of stainless steel is strongly influenced by the concentration and composition of organic matter. Citric acid is tricarboxylic acid and is very aggressive for corrosion in stainless steel. The increase in the amount of carboxylic groups leads to a high concentration of carboxylic ion concentration, thus, higher corrosion rates. The chain length in an organic acid is a determinant of the current density and produces mass transfer limitations. Higher current density is produced at lower concentrations of citric acid and forms the physical barrier at a higher concentration which reduces exposure to the corrosive environment. Citric acid is a nontoxic and renewable organic acid used as a corrosion inhibitor for lead surfaces exposed to sulfuric acids. It forms the passivation film on the anodic surface to inhibit corrosion effectively. The surface film is composed of an organic layer of Fe-citrate, FeOOH, $Fe(OH)_2$, and FeO at pH = 9. The overall composition of the passivation film is composed of $Fe_3O_4/FeOOH$. There is no clear presence of iron citrate in the passivation film, so poor passivation behavior is correlated with insufficient adsorption behavior of anions. The citric acid releases the hydrogen ions in the following three steps during the corrosion process:

$$C_6H_8O_7 \rightleftharpoons C_6H_7O^-{}_7 + H^+$$

$$C_6H_8O^-{}_7 \rightleftharpoons C_6H_7O^{2-}{}_7 + H^+$$

$$C_6H_6O^{2-}{}_7 \rightleftharpoons C_6H_5O^{3-}{}_7 + H^+$$

Citric acid is widely used in removing rust and scaling on equipment for chemical cleaning. It has been reported that sodium citrate acts as a corrosion inhibitor for carbon steel in water cooling systems. The current density decreases with the increase in pH. The corrosion analysis of 0.1 M citrate solution containing chlorides (pH = 8) exhibits four anodic peaks and two of them are related to ferrous species which release citrate ions causing pitting corrosion behavior. The citrate ions express poor corrosion inhibition behavior due to their complex-forming nature. The active corrosion behavior was observed in weak acidic solutions [73]. Severe damage occurs from locally initiated acid attacks when steel is in contact with spent acid.

2.4. Effects of Oxalic Acid

Oxalic acid is a dicarboxylic acid that is a purifying agent in the pharmaceutical industry and acts as a metabolic catalyst in the oxidation of phenol and coumaric acids. The corrosion rate is increased at higher temperatures and concentrations. The addition of anions such as $[SO_4]^{2-}$ and Cl^- reduces the oxide film thickness. The oxide film thickness is decreased with the increasing content of Cl^- ions [74]. The hydrogen ions are released in oxalic acid in the following step:

$$C_2O_4H_2 \rightleftharpoons C_2O_4H^- + H^+$$

Higher current density is produced at lower concentrations of oxalic acid and a physical barrier is formed at a higher concentration, which reduces exposure to the corrosive environment. The chain length in an organic acid is a determinant of the current density and produces mass transfer limitations. Oxalic acid has a higher current density than citric acid at the same concentration [74].

The corrosion in steel under organic solvents is influenced by many factors and its resistance can be improved by changing the composition of molybdenum, nickel, and selenium which leads to the formation of the passivation layer on the surface causing the reduction in degradability. The kinetics of degradability in stainless steel is a function of water content and is initiated by a single pit. The tail group of the organic solvents decides the type of corrosion in stainless steel. The concentration of chlorides, temperature, tail group length, steel composition, and chemistry of the solution are factors to describe the type and kinetics of the corrosion [75–77].

3. Influence of Alloying Elements on Corrosion Behavior of Steel in Organic Acids and Compounds

Erosion–corrosion is a prominent failure at the pipe outlet of the distillate column-free heater in the petrochemical industry [47]. The failure leads to leakage in the outlet and inlet of the radiant tube heater and piping systems due to the effects of temperature, pressure, flow, and corrosion. Erosion plays a key role in failure while pit corrosion formation is caused by electrochemical corrosion [48]. The root causes of leakage are the composition (chlorides and sulfur), fluid flow rate, temperature, and pressure of the corrosive environment [49]. The corrosion of nickel in organic solvent + H_2SO_4 exhibits unexpected behavior. The weight loss curves of nickel in acetic acid, ethanol, and acetone with a small amount of sulfuric acid were compared with weight loss curves in an aqueous solution [78,79]. It can be summarized that: (1) corrosion rates are very low in acetone solution; (2) corrosion rates are decreased in acetic acid by the addition of sulfuric acid; (3) ethanolic solution exhibits larger corrosion rates than aqueous solution; (4) the influence of temperature on corrosion is dependent on solvents [26,38]. Similar results were observed for Cu in the same environment. The nickel content is detrimental to the corrosion resistance of stainless steel in formic acid media which is a very aggressive corrosive agent. A similar phenomenon exists also for urea production. The difficulties lie in the solubility of nickel at high temperatures which can be addressed by ferric alloys [58]. An alloy with molybdenum can improve corrosion resistance against strong organic acids. Adding chromium enhances corrosion resistance at higher temperatures [80,81]. The corrosive attack is controlled by pH and chloride concentration in organic acids containing halides and can be changed, according to Jinyang Jiang and H. Sun [30,82].

It is believed that Mo and Cr contribute to the corrosion resistance of stainless steel in aqueous media and Ni contributes slightly. The corrosion resistance is mainly contributed by Cr and slightly by Fe and Mo in the nonaqueous solution of formic acid, changing the composition by adding corrosion-resistant elements such as nickel, and zinc [70,83]. Formic acid (HCOOH) is the most corrosive monocarboxylic acid at all concentrations and aeration increases the corrosion rates. The presence of chloride ions initiates corrosion and makes its general corrosion ability more severe [84].

The addition of chromium is effective for improvements in corrosion protection in Cl^- containing brines. The corrosion performance of the steel is strongly influenced by the grain size. The corrosion rate of steel is increased with the increase in grain size in an alkaline solution. Metal surfaces consist of boundaries, corners, edges, complex crystals, and disturbed layers which in turn dictate the properties of the surface [85]. The surface characteristics are determined by free energy because of the different arrangements of crystal faces. The physical properties of the surface are extensively changed when the grain size is reduced to 100 nm. The high grain density has a different corrosion behavior from that of polycrystalline materials [86].

The corrosion investigations of metallic biomaterials are of significance because of their critical applications. The increased corrosion rate leads to increased release of metallic ions. Lower corrosion rates are desired because of the corrosion interface with the cell metabolism. The corrosion behavior of titanium in uric acid was investigated by Liu et al. [87]. They observed the pitting holes on the surface at higher concentrations and the amount of TiO_2 was decreased. The titanium surface pretreated with uric acid becomes hydrophobic and the corrosion susceptibility of titanium is increased. The uric acid concentration influences the release of titanium ions and surface characteristics. The corrosion rate is increased by destroying the titanium oxide barrier and accelerating titanium ion release.

The corrosion behavior of stainless steel in tartaric acid, citric acid, and oxalic acid was investigated by Gouda et al. at different pH values. [88]. The corrosion potential decreased and the corrosion rate increased at higher concentrations of organic acids and up to pH = 4 of the medium. When the pH of the corrosive medium is increased to 5 and 6, the corrosion potential becomes nobler causing a decrease in corrosion rate. The steady-state corrosion potential (E) and concentration (C) of the organic acid is related below:

$$E = a - b \times \log C$$

where a and b are the constant. The corrosion mechanism is anodically controlled by the complexing of Sn^{2+} ions with organic acid anions. The aggressiveness of the organic acid increase in the order of tartaric acids < citric < oxalic. The corrosion is inhibited at a pH of 5 and 6 because of passive film formation on the surface.

Pitting is a key phenomenon in electrochemical corrosion and erosion is a key failure in nonferrous metals. Chloride and sulfur concentration, pH and pK_a value of organic acid flow rate, and pressure with some nickel content are the main reasons for the failure. Corrosion is controlled by halide ions.

4. Types of Corrosion

The corrosion type and mechanism are influenced by many factors such as metal structure, surface morphology, inhibitor type, and passivation characteristics of the organic acid and stainless steel. The parameters are summarized in the symmetric diagram in Figure 3. The common organic acid corrosion types and their effects are summarized here.

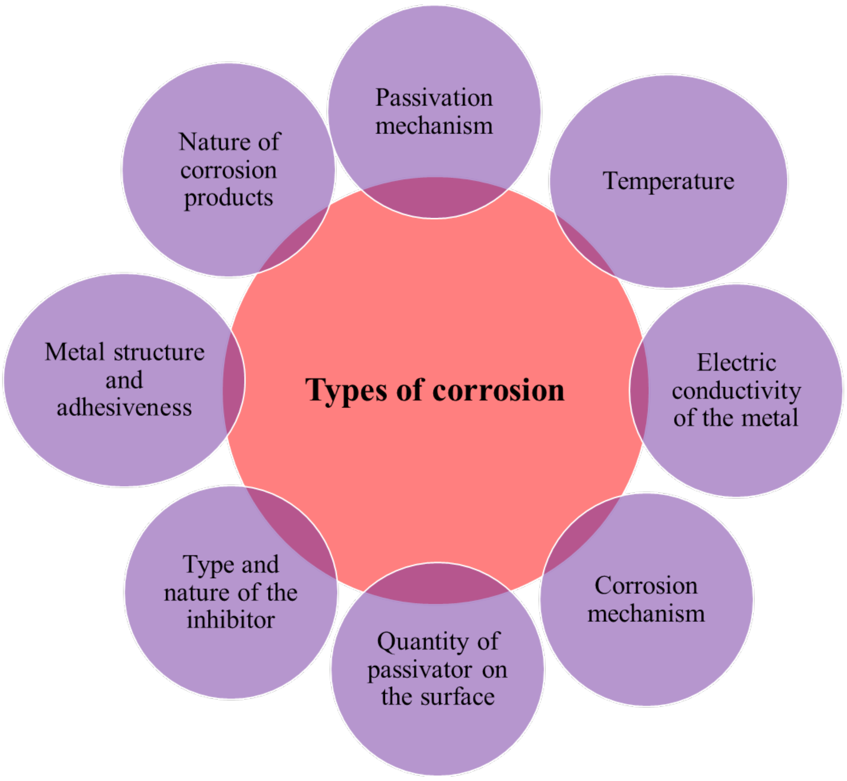

Figure 3. Parameters that determine the types of corrosion (a symmetric diagram).

4.1. Pitting Corrosion

Pitting corrosion is caused by the de-passivation of the passive layer. Some researchers claim that it is an intrinsic property of the acid used and the corrosive environment. Others claim that acid molecules penetrate into the metal surface and release the proton which in turn causes damage to the passivation layer. The oxygen pressure is decreased at localized sites which results in the formation of crevices and inhibits the regeneration of the passivation.

The corrosion of steel is directly related to organic acid concentrations. It has been observed that corrosion potential is decreased with the increased concentration of organic acids. The degradation of the metal matrix in pits is slowed down because of less diffusion of metal cations. Ethanolic solutions present a similar phenomenon. With the increase in the concentration of organic acids, breaking the potential is significantly decreased which indicates that pitting resistance deteriorates with no change in the thickness of the passivation film. The increase in organic acid concentration leads to the dispersion of breaking potential.

The pit density is increased exponentially with the increase in the concentration in the potentiodynamic polarization test but not in the immersion test. There are a finite number of precursor sites and sufficient time is required to incubate stable pits at the lower voltage. Thus, the reason for different pitting behaviors in immersion is because of the deprivation of precursor sites and inadequate activation time.

The pits on the surface of 316L steel were initiated in 1 M NaCl solution with 0 and 10 M ethanol at 1 mA·cm^{-2}. The dissolution charge was contributed by a single pit on the surface which rapidly developed and generated at higher current density. Several pits contribute to form a dissolution charge. The single pits fail to generate sufficient current density which causes the pits to grow pits in scale size. Multiple pits are generated at a current density of 1 mA·cm^{-2} and a single pit is generated at the breaking potential.

The pitting in the ethanolic solution is simplified and development is suppressed. The pits tend to be deeper. The growth of stable pits is an electrochemical process and is controlled by the viscosity of the ethanolic solution and metal cations. The inhibition of pitting development is ascribed to the drop-in ions diffusion rate. The deterioration of passivation films does not affect the pit initiation and the theory of alcohol electro-oxidation is not applicable to the ethanolic system [18,89,90]. The increase in concentration leads to an increase in metal cations at the pit's bottom and changes the solution's pH. The hydrolysis of metal cations is enhanced with an increase in organic acid concentration which consequently results in a decrease in the pH of the solution. The pitting is initiated when concentrations of cation M^{n+} are far from saturation. The pH of the solution is decreased with the increase in concentration. When the solution is saturated with metal cations M^{n+} and pits are developed; this results in the synergic effects of solubility reduction, and hydrolysis enhancement [55,91,92].

The metastable pits are initiated with the inclusion of chloride ions and the puncture behavior of chloride ions is not affected by the passivation film. The solution inflows during void expansion and the pits initiation is influenced by the difference in hydrolysis. The concentration of metal cations is lower with a higher content at the bottom of the pit than in a non-acidic solution, resulting in dissatisfaction with the pH on the surface. This results in more dissolution at the top and less dissolution at the bottom in alcoholic solutions, causing the formation of a lacy cover and steeper pits.

The current density of the pit in metal cation dissolution could be approximated by:

$$i_{diff,\ site} = \frac{3nFDC_{site}}{2\pi r}$$

where n is the average oxidation state of the metal cations, F is the Faraday constant, D is the effective diffusivity of the metal cations, C_{site} is the concentration of metal cations at the site, and r is the radius of the hemispherical pit.

4.2. General Corrosion

The commonly observed corrosion in stainless steel is uniform corrosion which is characterized by a thinning of the component wall. General corrosion occurs when the passivation film is damaged and a new passivation film is not attained either because of shear stress effects or higher pit density distribution. The randomly alternating anodic and cathodic spots cause uniform attacks and the entire metal surface would be damaged. The uniform or general corrosion is caused by hydrogen embrittlement which results in load redistribution causing local stress risers, and secondary bending stresses which accelerate the crack growth [23,38,93]. Reasonable corrosion resistance is offered by stainless steel in the presence of impurities such as HCl, sulfuric acid, and formic acid. An elevated operational temperate can result in rapid general attacks on steel. Elevated temperature and high acid concentration are of particular concern for corrosion protection. These conditions would cause the corrosion rate in steel to reach 500 mpy. Moderate operating conditions will prevent corrosion to a large extent because of the standard composition, especially molybdenum content.

4.3. Stress Corrosion Cracking

Stress corrosion cracking is a major corrosion problem in stainless steel in chloride-contaminated environments at higher temperatures. Stainless steel (316L) is more vulnerable to corrosion in 70–90% acetic acid-containing chlorides at 90 °C. The susceptibility of

316L stainless steel is higher in 400 ppm chlorides within a 30-day period. The vulnerability of stainless steel to stress corrosion cracking is influenced by many factors including local passivity breakdown, electrochemical potential, aqueous environment, halide salt contamination, elevated temperature, and the menace of sustained stress corrosion in petrochemical plants. These alloys have the intrinsic property of developing a thin protective film against corrosion [94]. Under typical conditions, EA plants operate at temperatures above 100 °C and concentrations higher than 70% EA. Thus, feedstock contamination and these parameters must be monitored during the processing to avoid SCC.

4.4. Other Types of Corrosion

Some other types of corrosion such as intergranular and crevice galvanic corrosion are also encountered in food process plants. Although they are less common, their impact cannot be eliminated in the production process. The crevice type of corrosion happens in sealed locations where differential concentration is present. The crevice type of corrosion in nuts, bolts, lap joints, and butt joints made up of 316L steel has been reported.

Galvanic corrosion is associated with welding active and noble metals. The massive difference in potential leads to preferential corrosion in less noble metals. The crevice and galvanic forms of corrosion can be controlled by proper material selection and design to ensure metal coupling and minimize the crevices.

Intergranular corrosion is affiliated with heat-affected zones of weldments in stainless steel. It happens due to the depletion of chromium and the formation of chromium carbide precipitates along grain boundaries at elevated temperatures. Intergranular corrosion occurs in aqueous media in which chromium carbides are activated at grain boundaries and the rest of the material is under passivation.

4.5. Interaction of Corrosion Types

The different types of corrosion occur and interact in EA plants due to complex processes. A typical example of corrosion interaction is pitting in the crevice. The feed streams are stocked in crevices and create a microenvironment that has a different composition than the bulk. The environment is suitable for pit initiation and proliferation through autocatalytic pitting. Thus, the occurrence of pitting corrosion coupled with rapid general corrosion has been reported [23,81,95].

Pitting acts as a stress raiser by localized loss in thickness. The continuous degeneration of pits leads to crack initiation and propagation which causes fatigue and SCC. The pit–crack transition phenomenon takes place and the crack grows subsequently. Pitting corrosion behaves as the denominator in localized corrosion such as SCC, fatigue, and hydrogen. Similarly, sensitized stainless steel is vulnerable to other types of corrosion such as crevices, SCC, and pitting. Stabilizing steel with titanium or niobium or using 316L stainless steel can prevent it from being sensitized and protect it from the intergranular corrosion property by developing a thin protective film [57,95–97]. Therefore, the supreme importance of this interaction between the different forms of corrosion in suitable and susceptible organic environments should be given due consideration.

5. Mechanism of Corrosion

Green chemistry represents the holistic approach to managing chemical risk. It eliminates chemical pollution and waste management. Ensuring the natural resources and minimizing the environmental effects and sustainability are the fundamental concepts in green chemistry. Green corrosion inhibitors and biodegradable inhibitors do not have toxic compounds. They potentially inhibit the corrosion of metals in alkaline and acidic environments.

In the corrosion inhibition process, a protective layer is formed on the metal surface by absorption of the molecules. The coordinate bonds are formed when these molecules donate the electron to the vacant d-orbital. The metal ions are transferred from the anode in the solution to the cathode during the corrosion process. The cathodic process requires hydrogen as an electron acceptor and oxygen as an oxidizing agent. Corrosion can be minimized by stopping the anodic or cathodic reactions. The inhibitors are absorbed on the surface, forming barriers to protect from corrosion. Then, they interact with cathodic, anodic, or both sites and decrease the reduction, oxidation, or both corrosive reactions.

Cathodic reactions are given by the following equations:

$$2H^+ + 2e^- \rightarrow H_2$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The reductions are given as:

$$2H^+ + 2e^- \rightarrow H_{ads} \rightarrow 2H_2$$

The hydrogen ions in combination with oxygen ions are absorbed into the surface of the metal and they act as catalysts in passive film formation. Then, hydrogen gas evolves at the cathode surface. The inhibitor molecules neutralize the metal surface by absorption onot the metal surface. The process is described by the following relation:

$$\text{Inhibitor} + nH_{ads} \rightarrow \text{Inhibitor}_{ads} + H_2$$

The most reliable and conventional ways to measure corrosion are electrochemical measurements, the kinetics of corrosion, and weight loss measurements.

It is well established that the metal reactions in protic media follow electrochemical reactions and the anodic reaction is the partial dissolution of the metal. Mixtures of aprotic and protic solvents are used in many industrial applications. The behavior of the system is determined by the nature of the protic component. The water content in the aprotic solvent with aggressive components causes inhibition, stimulation, or no effects on corrosion rates. The dissolution of the metal is an anodic partial reaction according to the following equation:

$$Me \rightarrow Me^{n+} + ne^-$$

The cathodic partial reaction (reduction process) is presented as:

$$HA + e^- \rightarrow 1/2H_2 + A^-$$

Most of the processes involve a direct reaction metal with a non-dissociated proton donor.

6. Mitigation Methods for Organic Acid Corrosion

Steel has versatile applications in construction, structure, and chemical industries owing to its excellent mechanical properties. However, it is susceptible to corrosion in an acidic environment and one-third of the steel is lost due to corrosion, causing a 3% loss in GDP. The corrosion is affected by temperature, pressure, surface impurities, and solution activities. Several protection techniques such as coatings, inhibitors, and different corrosion-resistant steels are used to mitigate the corrosion. Means of corrosion mitigation and their relations with control are summarized in Figure 4.

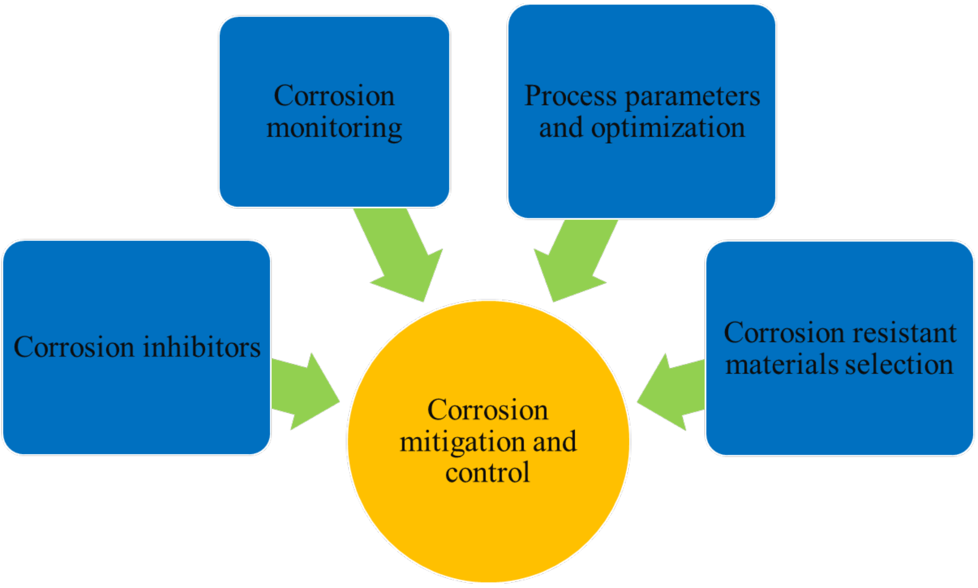

Figure 4. Parameters for corrosion mitigation and control.

6.1. Corrosion Monitoring Methods

Corrosion measurements and monitoring during the process minimize fatal accidents and reduce the chances of failure. They are useful in assessing the reliable life of equipment. Corrosion in organic media is controlled by many parameters such as flow, low pH, water content, and high temperature. It is difficult to predict the synergic effects of these parameters. Therefore, corrosion and elements that instigate the corrosion process should be monitored.

Monitoring techniques can be divided into indirect and direct techniques. The indirect techniques measure parameters that affect the corrosion rate such as ion count or pH. Direct measurement methods involve the monitoring of the parameters that directly influence corrosion. It can be categorized into intrusive and nonintrusive techniques with reference to monitoring from inside or outside the pipe, respectively, against corrosion [98,99].

Corrosion can be monitored continuously or periodically. Direct intrusive measurement techniques use electrochemical techniques (harmonic distortion, electrochemical impedance spectroscopy, electrochemical noise, potentiodynamic polarization), electrical resistance probes, and mass loss coupons. These are more sensitive and reliable techniques for measuring the corrosion rate.

Nonintrusive techniques use radiography, eddy current, magnetic flux leakage, ultrasonic acoustic emission, and electrical field mapping. The actual plant materials are tested for monitoring in this technique. These are used at critical locations such as tees, pipe bends, welds, and similar nonuniformities [100].

The indirect/continuous measurement techniques involve the monitoring of dissolved oxygen, corrosion potentials, process parameters, pH, pressure, temperature, and evaluation of corrosion products. The indirect/periodic techniques use the measurement of the total acid number, ion count and analysis, and water chemistry. The corrosion measurement and monitoring details are found in NACE standards.

The mass loss coupon technique is the most commonly used method in the petrochemical industry because of its cost implication and reliability. The coupons are periodically retracted for evaluation. It is compromised by localized corrosion at critical locations such as welds and tees. The above methods are employed in combination. The measures over a short period of time during operation permit the changing of the process parameters to obstruct the rate of corrosion. The corrosion monitoring techniques require improvement to obtain more sophisticated results. It has been a challenge to detect localized corrosion but technological advancements have made it possible to measure the hydrogenation penetration, pitting corrosion, and localized corrosion. Indirect monitoring is important to examine the daily operating parameters and corrosion condition trends.

6.2. Corrosion-Resistant Material Selection

Correct material selection is the primary approach for designing industrial equipment with protection against corrosion in particularly aggressive environments. Appropriate materials such as corrosion-resistant alloys are imperative in mitigating corrosion in petrochemical industries to enhance performance and life expectancy. The performance of the equipment's materials is affected by many factors such as operation, quality control, fabrication, materials' specification, and transportation. The unique environmental conditions for specific applications determine the extent and type of corrosion at all stages of component life including maintenance, operation, commissioning, installation, storage, transportation, fabrication, and procurement [101].

The corrosion can be controlled by modifying the microstructure, and surface structure of the equipment. The microstructure can be changed by changing the composition by adding corrosion-resistant elements such as nickel, zinc, and chromium. Stainless steel, titanium alloys, and nickel-based alloys are excellent corrosion-resistant alloys to mitigate the corrosion menace in petrochemical plants. These alloys have the intrinsic property of developing a thin protective film against corrosion [98].

Hastelloy, Inconel, and Monel alloys are employed as corrosion-resistant alloys in place of stainless steel. These materials offer excellent corrosion resistance properties under specific conditions and processes and experience severe corrosion attacks when the environment is slightly changed [80]. For instance, stainless steel 316L has outstanding corrosion resistance in an up to 90% concentrated acetic acid environment; however, a slight change in concentration enhances the corrosion rate by almost 400% [102]. Ferric alloys are preferred in the pulp and paper industry because of their corrosion resistance over stainless steel. In a similar way, Monel has excellent corrosion performance in unaerated acidic environments but is severely attacked in the aerated environment. Inconel has good corrosion resistance performance in strongly oxidizing conditions; however, it has less corrosion resistance in dilute acid at higher temperatures. Therefore, materials for equipment and components should be investigated for particular process conditions [103].

Stainless steel is considered to be an excellent corrosion-resistant material in ethyl acetate plants under process conditions. However, high flow velocity, contamination, strong catalysts, and elevated temperature cause various corrosion failures and problems. Nitrogen, molybdenum, and chromium content are optimized for excellent crevice and pitting corrosion resistance in steels [104,105]. The development of corrosion-resistant coatings is another good technique to control the corrosion process and rate degradation. The film thickness and elements in coating films are important parameters by which to estimate the performance of the coatings [99,106].

6.3. Process Parameters and Optimization

The parameters such as oxygen, suspended solids, dissolved metal chlorides, flow rate, corrosion potential, pH, pressure, temperature, and chemical residuals control corrosion. Any change in the above-mentioned parameters will influence the corrosion potential and the susceptibility of the plant can be assessed by using this information [107]. A significant impact on corrosion is induced by flow rate, pressure, and temperature. For example, the temperature in the reaction container is above 100 °C, and the pressure of 1 MPa under the flow rate of 2.5 m/s. If these parameters are adjusted according to the required yields in the plant, they will consequently affect the corrosion. A slight change in these parameters has significant effects on the breakdown of the passivation film, activity, increased dissolved ions, and increased chloride mobility [108–112].

The change in electrolyte activity can be indicated by the tendency in the concentration of dissolved metals such as Fe and Cr, which reveals the corrosion rate and corrosivity. The corrosion rate is significantly affected by pH, so controlling the pH monitors the corrosion rate [99,106]. The pH is influenced by chemical residuals, dissolved oxygen, and other impurities. The feedstocks in the plant are agitated for mixing and heat transfer and then transported through pipelines [113,114]. The shear stresses are induced by high feedstock velocity which causes additional erosion–corrosion problems in the equipment of the plant [115,116]. This becomes more severe when suspended particles are in the stream [39,96]. It has been reported that the corrosion rate approached 2.6 mm/y for 304 stainless steel at a flow rate of 2.4 m/s under 0.3% H_2SO_4 catalyst at 103 °C. This is how process parameters influence the corrosion process and corrosion can be managed in a better way by optimization.

6.4. Corrosion Inhibitors

Inhibitors are the best remedies to control corrosion in steel in various sectors owing to their economic efficiency, simple process, strong adaptability, and low cost. The characteristics of excellent corrosion inhibitors are summarized in Figure 5. Organic inhibitors reduce the dissolution of the steel in an acidic environment but are expensive, hazardous, and need expertise to manufacture. The inhibitors should be eco-friendly and must show more than 90% efficiency [117]. Most corrosion inhibitors are extracted from plants. The roots, leaves, seeds, flowers, and stems contain organic compounds such as tannins, heteroatoms, flavonoids, alkaloids, and nitrogen-based compounds. These organic inhibitors have excellent performance against corrosion and are safe and non-toxic. The green inhibitors include herbs, leaves, natural honey, yeast, flour, oil, roots, drugs, and chitosan. Natural and biodegradable biomaterials are effective inhibitors.

Corrosion is influenced by temperature, time, surface impurities, and other functions of the solution. Several techniques have been used to avoid thermal and mechanical degradation. Annealing, carburization, and design modifications have been used during the manufacturing process for optimum performance [96]. The application of a coating is one of the major techniques to reduce material degradation and consequently, the environment is one of the major factors influencing corrosion behavior.

The combination of propargyl and octyl in an HCl solution is an efficient corrosion inhibitor. Ethanol mixed with sulfuric acid is a better corrosion inhibitor than other organic inhibitors. The composition of corrosion deposits and the medium in which the corrosion of steel takes place are the factors that determine the corrosion inhibitors and their efficiency [118].

The corrosion inhibition of 304 stainless steel in 1M H_2SO_4 at 50 °C was studied using propargyl triphenyl phosphonium bromide (PgTPhPBr) [119]. The Tafel curves indicated that the cathodic region gave corrosion inhibition of 98% at 1×10^{-3} M. In the anodic region, PgTPhPBr acted as a good passivator. The impedance spectra of corrosion potential revealed that the charge transfer process controls the corrosion in inhibited and uninhibited states. The effects of chloride ions on the corrosion behavior of three stainless sheets of steel were investigated at 110 °C in an aqueous solution of H_2S/CO_2.

Stainless steel AISI 316L forms a high passivation film under higher temperature and pressure which consequently acts as a corrosion inhibitor [120]. A thicker passivation film could form on the surface at high temperatures and 316L steel would offer better resistance. The corrosion resistance of 316L steel can be improved by adding copper because copper can (1) stabilize the martensite restraints and austenite transformation, (2) replace the nickel and reduce the production cost, (3) enhance the corrosion resistance of the stainless steel [121]. It was investigated that Cu aggregates on the surface and forms oxides on the surface to protect against continuous corrosion [94]. The investigation of the electrochemical and passivation behavior of 304 steel in 0.1 M H_3PO_4 revealed that the current density and passivation current decreased with the increase in copper content because copper changed the stability of the passivation film [122]. The double-layer passivation structure could be formed on the surface of the steel containing copper in $0.1H_2SO_4$ solution [123].

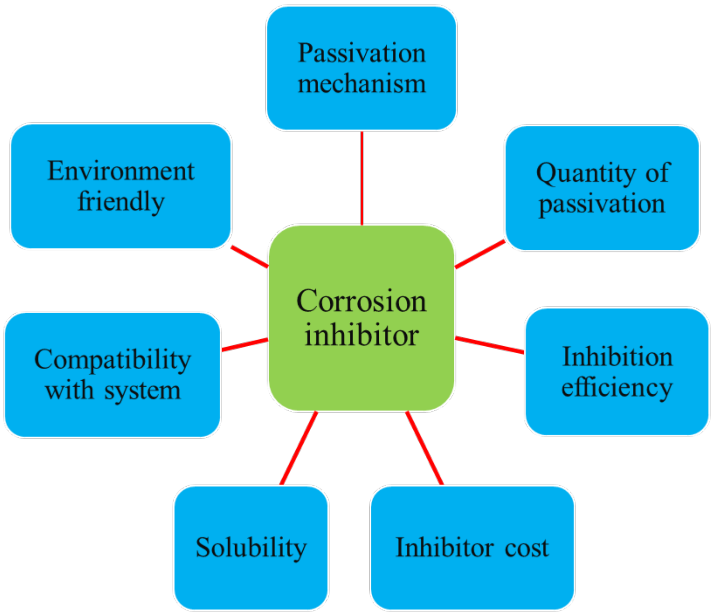

Figure 5. Factors that influence the characteristics of inhibitors.

A corrosion inhibitor was extracted from Ziziphora leaves and mixed with HCl acid to protect mild steel [97,117]. The corrosion rate was reduced to 93% after 2.5 h. The cysteine amino acid was used as a corrosion inhibitor for mild steel and excellent results were observed [118]. The pyrimidine derivatives were used with 15% hydrochloric acid and applied on N80 steel and a 96.4% reduction in corrosion rate was found [124].

Nonpolar compounds containing heterocyclic rings, functional moieties, aliphatic chains, aromatic rings, and polar compounds with nitrogen and oxygen are rich in plant extracts. These organic compounds are efficiently absorbed on the metal surface to protect from corrosion without spoiling the environment [125–127].

Corrosion can be prevented by cathodic protection, inhibitors, and coatings. There are two types of corrosion inhibitors: organic and inorganic [128]. Inorganic inhibitors include phosphate, dichromate, chromate, nitrate, and nitrite. On the other hand, organic inhibitors contain two or more polar groups, having S, P, N, and O atoms, and π electrons. Organic inhibitors are more effective than inorganic ones in preventing corrosion.

A cathodic corrosion protection system is used in the metallic substrate used in structural foundations, cables, oil and gas pipelines, and utility pipelines [75,129]. They are also used in aircraft, bridges, oil-drilling platforms, and condenser tubes in heat exchangers. However, the cathodic protection system is not suitable in the marine environment.

The inhibition effects of water are very common in organic solvents acidified with HCl for stainless steel. The presence of water causes the formation of a passivation layer which is lost at a higher content, consequently leading to higher corrosion rates [130]. Coatings are on the surface of the steel are advisable to avoid corrosion during production in an organic corrosive environment. The widely used coatings are of blunt materials such as graphite, alumina, epoxy, and polyaniline. However, there are still many difficulties in administering coatings in large tanks. Thus, it is necessary to investigate the corrosion behavior of stainless steel in organic solutions. Organic type, pH, water content, solution viscosity, and contaminants are the main factors that influence the passivation film and the corrosion behavior of the metals [131].

7. Future Aspects

The specific intention of this work was to analyze the existing experience of corrosion on stainless steel under organic solvents, the means of controlling the corrosion rate and how to improve the technical operation and metallurgical guidelines for the future.

There is consensus on the many possible factors contributing to corrosion in organic solvents that must be addressed to reduce the corrosion rate. The different natures of the sources of organic solvents have different compositions which influence corrosion and erosion in stainless steel.

The following factors must be addressed to mitigate and control corrosion in steel in an organic environment.

The selection of materials is one of the key parameters in the piping and process industries. The 316L stainless steel is an efficient alloy, having excellent corrosion resistance with a good metallurgical composition. The metallurgical composition plays a key role in improving the corrosion resistance.

The process parameters, for instance, flow rate, temperature, pH, concentration, and water content must be optimized. Corrosion inhibitors can play an important role in controlling the corrosion rate. Artificial intelligence and machine learning would be future tools for selecting the appropriate material composition, process parameters, and corrosion inhibitors.

8. Conclusions

Corrosion of stainless steel by organic compounds, specifically organic acids, is of great concern due to many factors such as flow, high temperature, chloride contamination, water content in feed, and the presence of strong acids. The increasing demands for food processing and preservation will lead to an increase in plant operation and consequently an increase in corrosion problems. The commonly used organic compounds and their impact on the corrosion behavior of stainless steel have been summarized. The influence of commonly used organic acids on the corrosion behavior of 316L steel has also been discussed.

A comprehensive understanding of the corrosion mechanisms, corrosion inhibitors, their efficiency, mitigating measures, corrosion challenges, and prevention techniques is necessary. Some conclusions can be drawn. (a) Stainless steel is the most widely used steel in the petrochemical, food and pharmaceutical industries because of its self-protective characteristics of forming a stable passive oxide layer on the surface. (b) Pitting corrosion is the most significant form of corrosion in stainless steel, causing damage to the material. Pitting corrosion is followed by uniform corrosion and SCC. (c) The presence of halides, especially chlorides, surface stress raisers, impurities, water, and oxides breaks down the passive film and acts as pit initiators. Pit initiation and growth are controlled by mechanical and chemical mechanisms.

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