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Short Review

Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes- A review.

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Acid solutions are widely used in process industries as inhibitors for the removal of deposited scales from metallic surfaces. Generally the applications of corrosion inhibitors have been an accepted practice for their aggressive nature towards acids. A variety of organic compounds were studied for investigating their corrosion inhibition potential. Literature reveals that the presence of N, S and O in these organic compounds reported excellent inhibition efficiency. But, unfortunately they have the undesired toxic effect on environment, aquatic and animal life and expensive as well. Therefore, plants and natural product extracts have been posed to achieve the target of employing as a cheap, environmentally acceptable, abundant source, readily available and effective molecules having very high inhibition efficiency and low or zero environmental impact. This article discusses properties, adsorption and inhibition mechanism and the efficiencies of natural products which are used as co-friendly corrosion inhibitors for various metals and alloys in different acid media.

Keywords: Metal and alloys; Acid pickling; Toxicity; Natural products; Green inhibitors

1. INTRODUCTION

Corrosion of metals and alloys particularly in acidic media is an important industrial problem. Hydrochloric acid which is widely used for pickling, cleaning, descaling and etching of metals, on the other hand also contributes to the corrosion of metal surface. A huge amount of money is wasted each year as a result of metallic corrosion, an estimated loss of 276 USD or equivalent to 3.1 percent of the United States GDP [1]. It is estimated that with proper corrosion prevention technologies, about 25 to 30 % of this loss could be avoided [1]. One of the best methods to reduce the rate of metallic corrosion is by the addition of inhibitors; even small concentrations can result in the decrease of the corrosion rate of the metal surface [2-8]. Several conditions must be fulfilled for the selection of a suitable inhibitor; (a) the cost and amount of the inhibitors, (b) long term toxicological effects on the environment and living species, (c) the inhibitor's availability and stability in the environment.

It has been found that different organic compounds could be used as effective corrosion inhibitors during acid pickling process [9-11]. Literature review reveals that organic compounds containing heteroatoms with high electron density such as phosphorus, nitrogen, sulfur, oxygen, with double or triple bonds in their structures are effective corrosion inhibitors due to their high tendency for adsorption [12-15]. It has been confirmed that the compounds having both nitrogen and sulfur in their molecular structure have excellent corrosion inhibition ability compared to those containing only nitrogen or sulphur, moreover sulfur containing compounds have generally stronger corrosion inhibition ability compared to nitrogen containing compounds [16–21]. Also the quantum chemical calculation analysis proves that enhancement of electron donor ability causes higher corrosion inhibition efficiency as a result of the presence of sulfur compounds [21]. It has been reported that the adsorption properties of organic inhibitors mainly depend on some physicochemical properties of the molecules; the functional groups, possible steric effects, electronic density of donor atoms and the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, establish a degree of adsorption of organic inhibitor molecules on the solid surface and results a barrier film for corrosion protection [22]. Literature study reveals a significant relationship between adsorption of organic compounds and corrosion inhibition process, as corrosion inhibition is a well-known surface phenomenon and adsorption is a function of degree of protection of the metal surface [23-26]. These organic compounds have been used as corrosion inhibitors in the petroleum industry since 1950s and in the concrete industry from the early 1990s [27].

Organic compounds acts as corrosion inhibitors by virtue of adsorption on the metal solution interface and the adsorption may takes place by the possible four types: (a) due to electrostatic attraction between the charged molecules of inhibitors and charged metal surface (b) interaction of unshared electron pairs of the molecules with the metal surface (c) interaction of the presence of conjugated bonds (π electron) in the compound with metal (d) adsorption may occur by the combination of (a) and (c) [28], as a result of adsorption and blocking the active surface sites, thus reducing the corrosion rate by: (1) slowing the anodic and/or cathodic reaction (2) slowing the diffusion of aggressive species to the metal surface and (3) decreasing the electrical resistance of the metal surface.

The adsorption mechanism of organic inhibitors at metal/solution interface may consist of one or more steps for the completion. In the first step, adsorption of an organic inhibitor on a metal surface usually involves replacement of one or more water molecules initially adsorbed at the metal surface [29]:

$$\mathrm{Inh}_{(sol)} + x\mathrm{H_2O}_{\,(ads)} \longrightarrow \mathrm{Inh}_{(ads)} + \mathrm{H_2O}_{\,(soln)}$$

Where $Inh_{(soln)}$ and $Inh_{(ads)}$ are the inhibitors in the solution which are adsorbed on the metal surface, where x is the number of water molecules displaced by the inhibitor. Subsequently the inhibitor may than combine with newly generated metal ions M^{+2} on surface as a result of metal oxidation or dissolution process, forming metal inhibitor complex [30]:

$$M \longrightarrow M^{+2} + 2e^-$$

$$M^{+2} + Inh_{(ads)} \longrightarrow [M\text{-}Inh]_{(ads)}^{+2}$$

Depending upon the relative solubility of the resulting complex, it can further may inhibit or catalyze further metal dissolution.

Depending on the surface observation and literature review [31-40], it is generally accepted that in the absence of the corrosion inhibitor, the acidic solution is always incontact with the metal and porous film surface causing corrosion as a result of metal dissolution, whereas in the presence of inhibited solution, the active or open sites in the porous film are almost blocked by the adsorption of the inhibitor resulting a barrier or a passive layer suppress the further corrosion.

Currently the use of toxic material as corrosion inhibitors has been limited by agencies such as the U.S. Environmental Protection Agency (EPA), U.S. Department of Transportation (DOT) and Occupational Safety and Health Administration (OSHA). Although several synthetic compounds have been proved as excellent corrosion inhibitors, but most of them are highly toxic in nature and having a serious threats to both human and environment and often expensive and non-biodegradable in nature as well [3]. Based on environmental and safety issues of using corrosion inhibitors in industries has always been a global concern. The consequences of these toxic inhibitors may cause temporary or permanent damage like kidney or liver or disturbing biochemical or enzyme system in body. The toxicity may arise during synthesis or its applications. Therefore, the uses of non-toxic and natural products as corrosion inhibitors have become important because of the advantages of their environmentally friendly and biodegradable in nature, readily availability, renewable sources, and ecological aspects and can be synthesized by simple procedure with low cost [41-46]. It must be mentioned that the selection of inhibitors are based on the choice of the solid substrate and the environment to which it should be exposed.

Regarding as the alternative of toxic-synthetic corrosion inhibitors with environmentally friendly types (eco-friendly, nature friendly or green), having a minimal or no harm on the environment, several researchers have proposed the use of eco-friendly materials in corrosive media. These compounds are natural products of plant origin (seeds [47], plants and leaves extracts [48]), non-toxic synthetic compounds e.g. dyes [49], rare earth elements [50-52], organic compounds [53-56], Schiff base compounds [57-62], rare earth elements [63-65], organic compounds [66-69], drugs compounds [70] etc. which have been classified as environmentally friendly materials. In order to investigate the inhibition efficiency of these eco-friendly inhibitors in various acid medium, there are several experimental methodologies have been employed including, gravimetric method [71], potentiodynamic polarization technique [72], electrochemical impedance spectroscopy (EIS) [73], hydrogen evaluation method [74], and energy disperse spectroscopy (EDS) [75].

Present review focuses on the application of various green corrosion inhibitors used for the corrosion protection of Iron and its alloys and some other metals and alloys (Copper, Aluminum, Zinc etc.) in hydrochloric and sulfuric acid pickling processes. Also, adsorption mechanisms of corrosion inhibition, inhibitor type, and their relative inhibition efficiency have been compared.

2. HYDROCHLORIC ACID (HCl)

HCl is one of the most commonly used acids, among the acid solutions for acid pickling process. It should be mentioned that the replacement of toxic inhibitors by eco-friendly inhibitors for the metal protection in acidic media has been suggested in the second half of the nineteenth century. In 1960, Baldvin et al. performed the first research in the field of corrosion inhibition by using molasses and vegetable oil as inhibitors for steel sheets in acid pickling process [19]. In a similar fashion, Hackerman et al. studied the effects of inorganic anions, organic compounds, and combinations of the two on corrosion of mild steel in various acids [76]. The corrosion inhibition effect of *N*-heterocyclic compounds on the dissolution of aluminium-copper alloy in HCl solution was studied by Talati and Ghandi, in 1983 [77]. In 1998, effect of some polyaza macrocyclic compounds has been studied to inhibit the corrosion of mild steel in both sulfuric acid and hydrochloric acid [78]. In this fashion, similar studies have been examined by Quraishi and Sardar by employing aromatic triazoles and dithiazolidines as a corrosion inhibitor for mild steel in sulfuric acid and hydrochloric acid [79].

Corrosion inhibition has also been conciliated for a variety of natural products as corrosion inhibitors like *Asteraceae* extract [80], *Osmanthus fragran* leaves extract (OFLE) [81], alkaloids extract [82] for mild steel dissolution in HCl solution were studied. Similar studies on Bamboo leaf extract [83], olive leaves extract (*Olea europaea*) [84], Murraya koenigii leaves extract [85] and *Ochrosia oppositifolia* [86] functions as green corrosion inhibitor due to the presence of phytochemical compounds which incorporates effective corrosion inhibition groups such as hydroxyl [OH], carbonyl [CO], NH, aromatic ring by blocking the active surface sites to reduce the corrosion of steel in HCl solution.

Corrosion inhibition activity of a variety of non-toxic synthetic Schiff base compounds have been investigated as green corrosion inhibitors for the protection of mild steel in HCl media due to its excellent anti-glycating agent, ease of synthesis from relatively cheap chemicals and the presence of electronegative nitrogen, oxygen and aromatic rings which functions as active centers for adsorption on the metal surface. [57-62].

In 1982, Saleh et al. [87] reported the inhibitive action of *Opuntia* extract, *Aleo eru* leaves, and some fruit peel extracts like orange, passion fruit, cashew and mango give subsequent protection to steel in different concentration of HCl at 25 and 40 °C. Srivatsava [88] examined that tobacco, black pepper, caster oil seeds, acacia gum and lignin were found to be excellent corrosion inhibitors for mild steel in HCl medium. As another research, Hammouti et al. reported the extracts of Ginger [89], and *Mentha pulegium* [90] for corrosion inhibition of steel in acid media. On the field of natural extracts, the anticorrosive activity of extract of olive leaves (Olea europaea L.) [91], carboxymenthylchitosan [92], leaf extracts of Sansevieria trifasciata [93], studiedjojoba oil [94], eugenol, acetyl-eugenol [95], artemisia oil [96] and methionine (MTI) [97], in HCl solution, have been reported as well. The existence of phytoconstituents such as piperine, starch, proteins and terpenoids (citral) may synergistically increase the strength of the barrier film on the metal surface and causes metal protection through adsorption.

Inhibition performances of some herbs such as (garden cress, coriander, anis, hibiscus and black cumin) were proved as new type of green inhibitors for the protection of steel in acidic medium [98]. In 2004, Parikh et al. reported the corrosion inhibition efficiency of garlic, onion and bitter gourd by using them as good corrosion inhibitors for mild steel in HCl media [99]. In a similar fashion, the inhibition activity of quinine and caffeine has been studied for their anticorrosive activity of carbon steel in HCl media [100, 101].

The non-toxic corrosion inhibitor for non-ferrous metals, the inhibitive property of Ananas Sativum leaves extract [102], Pactin from citrus peel [103], *Occium viridis* extract [104], *Sansevieria trifasciata* extract [105] *Opuntia* extract [106] these natural compounds have been successfully applied as corrosion inhibitors on the surface of aluminum and aluminum alloy in HCl medium. In this context, the corrosion inhibition of aluminum and zinc substrate in HCl medium using Aloe vera extract and *Hisbiscus subdariffa* extract were found adequate corrosion inhibitors [107, 108].

In this context, the inhibitive efficiency of methyl 3-((2-mercaptophenyl) imino) butanoate (MMPB), and triazole derivatives namely, 4-amino-4H-1,2,4-triazole-3thiol (ATT), 4-amino-5-methyl-4H-1,2,4-triazole-3thiol (AMTT), 4-amino-5-ethyl-4H-1,2,4-triazole-3thiol (AETT) have been investigated for copper in acidic media [109, 110]. The inhibition performance of these compounds are the presence of thiol, azole and carboxylate group responsible for dipole character exhibits intermolecular attraction between molecules adsorbed on metal surface. Similarly, the presence of heterocyclic compounds such as $-NH_2$, –SH, and alkyl groups responsible for the adsorption on the active site on metal surface in acidic medium.

Table 1. Properties of green corrosion inhibitor in HCl medium

Green corrosion inhibitor	Type of inhibitor	Type of corrosive medium	Type of metal	Maximum inhibition efficiency	Adsorption mechanism	References
Crude methanolic extract of	Mixed	HCl (1.0 M)	Mild Steel	96	Adsorption due to Fe-inhibitor complex at iron oxide layer	[76]
Artemisia pallens (Asteraceae)	-	-	-	-	-	
Bark of Ochrosia oppositifolia (OOB)	Mixed	HCl (1.0 M)	Mild Steel	96	Adsorption due to the formation of protective	
	-	-	-	-	layer of corrosion inhibitor	
2-((5-mercapto-1,3,4-thiadiazol-2-ylimino) methyl) phenol	Cathodic	HCl (0.5 M)	Mild Steel	97	Chemisorption	[59]
	-	-	-	-	-	
(NE)-N-(thiophen-3-ylmethylidene	Mixed	HCl (1.0 M)	Mil Steel	88.9	Chemisorption	[60]
	-	-	-	-	-	
Osmanthus fragran leaves extract (OFLE)	Mixed	HCl (1.0 M)	Carbon Steel	96.8	Physical Adsorption	[83]
Bis-Schiff bases of isatin	Mixed	HCl (1.0 M)	Mil Steel	-	Physical/Chemical Adsorption	[64]
(HZ-1)	-	-	-	92.3	-	
(HZ-2)	-	-	-	89	-	
(HZ-3)	-	-	-	84.7	-	

Pyridine derivate	Mixed	HCl (1.0 M)	Mil Steel	-	Physisorption/Chemisorption	[62]
Pyridine-2-thiol (P2T)	-	-	-	98.3	-	
2-Pyridyl disulfide (2PD)	-	-	-	98.1	-	
Alkaloid extracts	Mixed	HCl (1.0 M)	Mil Steel	95.3	Adsorption of extract and aniline onto the	[84]
Aniba roosa eodora plant	-	-	-	-	steel surface blocking its active sites	
Murraya koenigii leaves extract	Mixed	HCl (1.0 M)	Mil Steel	97.02	Adsorption of inhibitor molecules	[87]
					due to protonation of amino group	
Sulfa drugs compounds	Cathodic	-	-	-	Adsorption of sulfa compounds on solid substrate	[72]
(sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine)		HCl (1.0 M)	Mil Steel	66.3-94.9	-	
fast green dyes	Cathodic	HCl (0.5 M)	Mil Steel	98	Adsorption of large and flat inhibitor molecules by blocking	[152]
	-	-	-	-	the surface area of mild steel and adsorbed electrostatically	
Bamboo leaf extract	Mixed	HCl (1.0 M)	Cold Rolled Steel (CRS)	90.3	Adsorption id due to both physisorption and chemisorption	[85]
Olive leaves extract (Olea europaea)	Mixed	HCl (2.0 M)	Carbon Steel		Strong physical adsorption of olive leaf extracts	[86]
		-	-		components onto the steel surface	
(mango, orange, passion, cashew) peel	-	HCl (1.0 M)	Carbon Steel	80-95	Extracts in organic compounds adsorbed	[89]
		-	-		at the electrode active sites	
Black pepper extract	-	HCl (1.0 M)	C38 Steel	95.8	Chemisorption at solid surface	[90]
Ananas sativum leaves extract	-	HCl (1.0 M)	Aluminum	96.09	Chemisorption of phytochemical constituents of the extract	[104]
		-	-	-	on the metal surface by blocking active sites	
Pactin terrestrial plants	-	HCl (2.0 M)	Aluminum	91	Physisorption	[105]
Vernonia amygdalina (bitter leaf extract)	-	HCl (0.1 M)	2S Al Alloy	38.4- 49.5	chemisorption	[101]
Triazole derivatives	Cathodic	HCl (0.5 M)	Copper	-	Adsorption of Triazole derivatives on electrode surface	[112]
4-amino-4H-1,2,4-triazole-3thiol (ATT)		-	-	98.44	involve Physisorption and Chemisorption	
4-amino-5-methyl-4H-1,2,4-triazole-3thiol (AMTT)		-	-	99.1	-	
4-amino-5-methyl-4H-1,2,4-triazole-3thiol (AMTT)		-	-	99.06	-	
Aloe vera extract	-	HCl (2.0 M)	Zinc	67	The adsorption of organic compounds in the extract	[109]
					on zinc surface to the attack of aggressive ions	

Table 1 shows the summary of efficiency, inhibitor type and mechanism for the above mentioned inhibitors and the obtained results.

3. SULFURIC ACID (H_2SO_4)

Different concentration of sulfuric acid, have been widely used as anti-scaling agent for metal and alloy cleaning in different pickling processes [111]. Regarding to green corrosion inhibitors, usage of caffeic acid, Black cumin (Nigella sativa L.), Berberine an alkaloid isolated from *Captis* and kidney bean (Phaseolus vulgaris L.) have been proposed as eco-friendly corrosion inhibitor on mild steel in sulfuric acid by some researchers [112-114].

In the conspectus of using natural products as corrosion inhibitors, various organic plant extracts such as Murraya koenigii leaves extract [115], black peppers extracts [116], *Telforia* *occidentalis* extract [117] carboxymethyl cellulose (CMC) [118], Spirulina Platensis [119], Nauclea Latifolia [120], Alizarin violet 3B (AV3B) [121], as eco-friendly corrosion inhibitors on mild steel substrate, were studied in H_2SO_4 media. In another case, a non-toxic bamboo leaf extract was found to be an effective green corrosion inhibitor on cold-rolled steel (CRS) in H_2SO_4 medium [122].

To investigate non-toxic effects of imidazole derivatives Oxo-Triazole derivative (DTP) [123], synthesized glycine derivative (GlyD1) [124], Tryptophan [125], Cyproconazole [126] and phthalazin-1(2H)-one, were proposed as eco-friendly synthetic corrosion inhibitor for copper substrate in H_2SO_4 solutions [127, 128]. Also for copper and copper nickel alloy (Cu/Ni) alloy, non-toxic, propargyl alcohol has been evaluated to introduce it as green corrosion inhibitor in acidic solutions [129]. Phytochemical investigation reported that the presence of amino acids, fatty acids, proteins and some naturally synthesized biological compounds such as Monoterpene, Triterpene, Indole alkaloid from plant extracts causes the inhibitory action by adsorption on the active sites of the metal surface.

The application of organic dyes such as alizarin yellow GG (AYGG), safranine-O (SO) and thymol blue (TB) were proved as a non-toxic corrosion inhibitor on steel in H_2SO_4 media [73, 130]. The presence of benzene ring and heterocycles such as isoxazoles, thiophenes, pyridine and others in drugs, researchers have been investigating drug compounds as green corrosion inhibitors to replace the traditional toxic corrosion inhibitors. The above mentioned inhibitors, the efficiency, type of inhibitor and inhibition mechanisms are summarized in table 2.

Table 2. Properties of green corrosion inhibitors in H_2SO_4 medium

Green corrosion inhibitor	Type of inhibitor	Type of corrosive medium	Type of metal	Maximum inhibition efficiency	Adsorption mechanism	References
Caffeic Acid	Mixed	H_2SO_4 (0.1M)	Mild Steel	96	Adsorption of organic molecules by blocking	[114]
	-	-	-		the cathodic site of electrode surface	-
Murraya koenigii leaves extract	Mixed	H_2SO_4 (0.5M)	Mild Steel	94.66	Adsorption of inhibitor molecules on surface	[117]
	-	-	-		due to protonation of amino group	-
Black pepper extract	Mixed	H_2SO_4 (1.0 M)	Mild Steel	90	Adsorption of phytocon stituents of black peppers	[118]
	-	-	-		forming a protective layer on surface	-
Carboxymethyl cellulose (CMC)	-	H_2SO_4 (2.0 M)	Mild Steel	60.8	Physical adsorption mechanism by blocking the surface	[120]
Spirulina platensis	Mixed	H_2SO_4 (1.0 M)	Mild Steel	82	Physical Adsorption of inhibitor molecules on active site	[121]
Nauclea Latifolia (Ethanol Extract)	-	H_2SO_4 (5.0 M)	Mild Steel	94.26	Physical adsorption of the extracts on the surface by	[122]
	-		-		simply blocking the active corrosion site	-
Synthesized glycine derivative (GlyD1)	Mixed	H_2SO_4 (4.0 M)	Mild Steel	98	Physical adsorption	[126]
2-(4-(dimethylamino) benzylamino)	-	-	-	-	-	-
acetic acid hydrochloride	-	-	-	-	-	-
Memosa tennin	Mixed	H_2SO_4 (1.0 M)	Low Carbon Steel	66.1	Physisorption of tennin molecules on solid substrate	-
Bamboo leaf extract	Mixed	H_2SO_4 (0.5 M)	Cold Rolled Steel	79.2	Inhibition as a result of both physical and chemical adsorption on the	[124]
Dendrocalmus sinicus Chia et	-	-	-	-	surface by replacing water molecules and occupying	-
J.L. Sun leaves extract (DSCLE)	-	-	-	-	metal/liquid interface	-
Oxo-triazole derivative	Mixed	H_2SO_4 (0.5	Mild Steel	89.9	typical chemisorption at the interface by shearing of	[125]

(DTP)		M)			electron	
Tryptophan	Cathodic	Aerated H2SO4 (0.5 M)	Copper	80	chemisorption of hydrophobic protective film on solid substrate	[127]
Cyproconazole (CPA)	Mixed	H_2SO_4 (0.5 M)	Copper	85.6	Absorption on solid surface as a result of physical - chemical adsorption	[128]
Alyzarin yellow GG (AYGG)	Cathodic	H_2SO_4 (2.0 M)	Mild Steel	85	Physisorption of dye molecules forming a protective film	[75]
Safranine-o (SO)	Cathodic	H_2SO_4 (1.0 M)	Mild Steel	65	Physical adsorption of barrier layer at interface	[132]

4. RELATIONSHIP BETWEEN CORROSION INHIBITION CHARACTERISTICS AND TOXICITY

The application of organic compounds or chemicals which are less toxic, are the best alternative to inorganic compounds. The selection of organic or natural compounds as green corrosion inhibitors for acid pickling processes are related to the molecular structure of the compounds. The literature review reveals that the application of organic compounds and natural products as corrosion inhibitors are the best alternative to the more toxic inorganic compounds. To achieve the goal of using eco-friendly corrosion inhibitors for acid pickling process, the analysis of detailed data deals with the toxicity of the number of molecular structure resembles to corrosion inhibitor. The analysis of the chemical structure could provide information on its toxicity, electrostatic, hydrophobic, hydrogen bonding, polar, covalent bonding and/or steric factors [131]. Compounds with long aliphatic chains are the most common among the corrosion inhibitors. The increase of the side chains alters the hydrophobicity and also the toxicity of organic compounds. Similarly, the presence of double and triple bonds in the molecules make them strong corrosion inhibitors, but also increases its toxicity [131]. An isolated double and triple bond is more toxic than sterically crowded double bonds. A sterically hindered double and triple bond is less reactive than an isolated double or triple bond and this decreases the probability of reaction with enzymes, hence making them less toxic. Researchers have on the threshold concentration of materials as eco-friendly corrosion inhibitor during their synthesis and extraction to make to ensure low toxic effects on environment and human health with having satisfactory corrosive inhibition efficiency as well.

According to table 1 and 2, it is found that most eco-friendly inhibitors have high corrosion inhibition efficiency even at a low concentration. Inhibition efficiencies are mostly dependent on the concentration and surface coverage area. The non-toxic nature of plants extracts as eco-friendly and effective corrosion inhibitors are due to their low cost, high biodegradability, high availability and renewable source of material which can be also extracted by simple procedures [3].

From the above mentioned tables, the maximum efficiency is 99.3 % for Methyl 3-((2-mercaptophenyl)-imino) butanoate (MMPB), for the chemisorption of the MMPB complex as a protective film. The maximum efficiency for adsorption of a triazole derivative, 4-amino-5-methyl-4H-1, 2, 4-triazole-3thiol (AMTT) is 99.10 %, which means that both physisorption and chemisorption phenomena can provide good corrosion inhibition mechanism. However, a combined physisorption and chemisorption mechanism will result in a higher efficiency of inhibition compared to the individual physisorption or chemisorption mechanisms. Furthermore; some of the inhibitor molecules form a blocking barrier on the substrate surface by decreasing the surface area of corrosion and causing inactivation of the blocked part of the surface.

Black pepper extract gave a maximum corrosion inhibition efficiency up to (98%) for mild steel in hydrochloric acid medium and the inhibition is due to the attribution of an alkaloid " Piperine". During the electrochemical examination it was confirmed to be a mixed-type inhibitor and the corrosion process was controlled by the charge transfer. Similarly the presence of ally propyl disulphides in garlic, probably affects the potential cathodic process of steel. In a similar fashion, different electrochemical techniques reveals that the adsorbed caffeic acid on steel surface modify the activation energy for anodic reaction and reduces the available cathodic reaction sites.

Analysis of table 1 and 2 reveals the application of non-toxic materials for the corrosion protection of non-ferrous metals. The inhibitive properties of eco-friendly corrosion inhibitor is also employed for the protection of copper and copper-based alloy such as brass, bronze and cupronickels (used extensively in automobile radiators, heat exchangers, solar energy absorbing panels, home heating system etc.) [144] and for aluminium (due to its lower atomic mass and three electron transfer per atom) [145, 146].

5. ADSORPTION MECHANISM OF GREEN CORROSION INHIBITOR

As mentioned in table 1 and 2, adsorption is the main inhibition mechanism for most of the green corrosion inhibitors. This is generally agreed that the primary step of corrosion resistant in the presence of aggressive solution is mostly due to the adsorption on solid surfaces. This proves the assumption for the prevention of corrosion reaction over the active sites of the metals surface occupied by the adsorbed corrosion inhibitor species, where corrosion reaction normally occurred on the corrosion resistance-free area. [132]. Adsorption mechanism is usually explained through the help of different adsorption isotherms and metal inhibition by organic compounds as a result of the adsorption of (molecules and/or ions) at solid surface [133]. Several factors involves the adsorption of inhibitor on the solid surface including: adsorption mode, chemical and electronic characteristics of the inhibitor, Temperature, type of electrolyte employed, steric effects and the nature and surface charge of metals as well [134-136]. In order to obtain more important information about the interaction between the inhibitor and metal surface, several adsorption isotherms were tested including Langmuir, Temkin, Frumkin, Freundlich, Flory–Hugginsand and Bockris–Swinkels and are employed to fit the experimental data. Langmuir adsorption isotherm was found to be best fit generally as the inhibitors mostly obey this isotherm [137-139]. It is important to note that the adsorption on the corroded surfaces never approaches to real equilibrium rather it approaches to a steady state adsorption. In the presence of inhibitor, the corrosion rate is sufficiently diminished, then the steady state adsorption [140].

The adsorption of corrosion inhibitors on metal surface are mainly two types: physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption is due to the electrostatic interaction between charged centers of molecules and charged metal surface which results in a dipole interaction of the molecules and metal surface. Unlike physical adsorption, chemical adsorption is process which involves the transfer or shearing of electrons from inhibitor to the metallic surface results the formation of co-ordinate bond and the bonding strength is much larger than physical adsorption [141]. Furthermore, the value of ΔG^0_{ads} in aqueous solution until -20 kJ mol^{-1} indicates a physical adsorption phenomenon whiles the values around −40 kJ mol^{-1} or lower, indicates chemisorption [142, 143].

As mentioned in table 1 and 2, some of the eco-friendly corrosion inhibitors are of mixed type, they can both inhibit the partial reactions by decreasing the anodic metal dissolution and the cathodic hydrogen evolution reactions. This type of behavior results in the adsorption of the inhibitor molecules on the active sites of the solid substrate.

According to tables 1 and 2, the maximum efficiency is 98.95% for Oxo-triazole derivative (DTP) for chemisorption [123]. Also maximum inhibition efficiency for physisorption is 98% for Synthesized glycine derivative (GlyD1) [124] and for Triazole derivatives it is 99% for both physisorption and chemisorption [139] which reveals that physisorption, chemisorption and mixed adsorption are good in corrosion inhibition mechanisms. Moreover, inhibitor molecules reduces the corrosion by decreasing the active surface area of the substrate and inactivate only the available part of surface imposed into corrosive medium, which is termed as simple blocking the surface area.

6. DRUGS AND DYES

It has been considered to be more important and desirable for researchers to focus on the development of effective corrosion inhibitors of natural origin with non-toxic effects, in this context, drugs (chemical medicine) having its natural origin, with less harmful impacts on the human and aquatic environment, as well as their environmentally friendly characteristics, have been found to be one of the best contenders to replace the commonly used toxic corrosion inhibitors [147]. The presence of carbocyclic and heterocyclic systems, five and six-membered rings of aromatic compounds, commercially available drugs have also attracted much attention as green corrosion inhibitors.

Researchers investigated the applications of dyes such as *azo* compounds methyl yellow, methyl orange, methyl red and alizarin yellow GG dye [75, 148] as green inhibitors inhibition of mild steel in acidic media has been reported [149-152] mixed type inhibitor with predominant cathodic effect. Corrosion inhibition mechanism accomplished as the green dye molecules possess aromatic rings, electro-active nitrogen, and oxygen atoms, favoring the adsorption of dye molecules on the metal surface. In addition, dye molecules having large and flat structure occupying a larger area of the metal surface and thereby developing a protective coating.

Apart from the non-toxicity and biodegradable nature of various plants, dyes, drugs etc., the main problem lies with their cost and industrial scale production. They should be optimized on the basis of their availability and processing methods, so that they must be evaluated from an economical point of view before being used in industries.

7. CONCLUSIONS

It is important to minimize or control metal corrosion technically, economically and environmentally, which is a major industrial problem. Green corrosion inhibitors are found to be effective from an ecological and environmental perspective and can play a major role over toxic inhibitors. It is still amazing that the anticorrosion efficiency of green corrosion inhibitors are equal to or even more effective than synthetic inhibitors. It is certain that natural compounds and plants products emerge out as effective inhibitors of corrosion in the coming years due to their biodegradability, easy availability, inexpensive and non-toxic nature. Natural products as green corrosion inhibitors having the limitation of their production volume on larges industrial scales, therefore, their economic aspects must be evaluated for industrial usage.

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