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Advances in corrosion inhibition materials and technologies: A review

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Abstract

In view of the fact that corrosion costs large sums of money and touches countless facets of human activities, every possible effort needs to be made to find ways to stop it from starting. In this regard inhibition of corrosion has become a thriving commercial activity, worldwide. Much research has been devoted to discovering newer strategies to inhibit corrosion with concomitant improvements in corrosion inhibition materials. This review will focus on the advances in materials and technologies for corrosion inhibition, with particular attention to the evolution of technologies and materials prior to the advent of coatings, the exploitation of 'green methods' which use anti-corrosion materials, which protect materials without fouling the environment; and the present and projected role of nanotechnology in inhibition of corrosion. This review brings together the collected wisdom of several disciplines. The latter addressed and/or are continuing to address the need for cost-effective materials to protect strategic metals used in the domestic and industrial sectors of most countries. The scope for improving the quality of materials, required for shielding these metals from the ravages of degrading agents, present in the environments of most cities, is lucidly articulated. Copyright © 2019 VBRI Press.

Keywords: Corrosion inhibition, ionic liquid, nanocomposite, galvanization, organic coating.

Introduction

In considering the advances of materials used by human beings though various 'Ages', it is interesting to note that the Stone Age was followed by the Bronze Age which gave way to the Iron Age. The Iron Age marked the advent of new materials which, in retrospect, can be considered to be great advances on ones which were available in the previous epochs of man's existence. The technological advances in extracting iron from iron ore has resulted in the need for further advances to inhibit the tendency of elemental iron to return to its native state. The following brief introduction is given as a precursor to the review of the advances made to counter the tendency of iron and other strategic metals to corrode.

Historically, two of the early strategies to protect iron from attack by oxygen and water was to passivate the surface of the iron using a strong acid or coating the surface of iron with zinc metal. The processes, known as 'pickling' [**1, 2**] and 'galvanization' [**3**] respectively served very useful purposes and still have some users. However, these processes lost some importance and demand due to considerations such as environmental pollution (from pickling) and the cost of galvanization. Cast-iron and steel-making methods gained favour on account of the fact they required addition of very small amounts of low-cost carbon, to imbue iron with a fair measure of corrosion-resistance. The resulting products were stronger than iron, but their durability remained a problem. To address this drawback, steel was then 'plated' with metals such as chromium and nickel; by electro-deposition or alloyed with these and other metals such as vanadium to give 'plated' steels or 'stainless' steels respectively. However, the cost of these types of steels is so high that it is beyond the feasible costs of large-scale manufacture of these steels needed by the construction and other industries such as transport. Although metal-containing components have been replaced by various types of organic polymers, in motor vehicles and aero planes (for examples), there are still many heavy-construction applications where steel cannot be substituted by polymers. To meet the need for metal products with increased durability there will be an on-going demand for corrosion inhibitor materials and associated technologies. In the light of this, a wide range of technologies and materials have been and are still being developed. Some of the widely-researched and used methods for corrosion inhibition may be found under the following headings:

- plant extracts [**4**]
- under coatings and paints [**5**]
- organic coatings [**6**]
- nanomaterial coating [**7**]
- ionic liquids [**8**]
- nanocomposites [**9**]

Although the benefits of 'green chemistry' have been the motivation [**8**] for much of the research involving ionic liquids, it should pointed out that the first wave of 'green chemistry' was started by the need to use extracts of plants [**4**] as corrosion inhibitors. In retrospect, the main drivers for the use of plant extracts, as corrosion inhibitors, appear to be the hazards to the environment arising from the disposal of large volumes of spent acids from 'pickling' of steel. In spite of the research focus shifting to other corrosion inhibitors, some research still continues in this area [**1**].

The use of undercoats of primers [**5**] and topcoats of paints to protect iron products was, and still is, a widely-used method for protection of metal structures. Some well-performing undercoats contained chromate or phosphate. Ever since hexavalent chromium was alleged to be a cancer-causing agent, the frequency of use of chromate undercoats has decreased markedly, in spite of its good corrosion inhibition property. Other undercoats, including chromate-free [**10, 11**] ones have been developed to fill the need for primers. The advent of polymers gave impetus to much research on the development and use of organic coatings of various types [**12**] as cost effective, durable, moisture resistant materials for corrosion inhibition.

As alluded to earlier, ionic liquids have triggered the second wave of 'green chemistry' research. Among the many roles of ionic liquids, a germane one is its use as corrosion inhibitor [**13**]. However, it is noted that nanocomposites have also been developed with combinations of materials [**14**] which have the potential to contribute to the anti-corrosion property of the composite.

There are a very large number of books, research publications, patents and industrial manuals on corrosion inhibition covering a wide array of methods which are used for corrosion inhibition (as illustrated in **Fig. 1**). In the light of the enormous amount of research done on corrosion inhibition, this paper will not attempt to give an exhaustive review but will provide a limited number of snapshots of the successes and failures of the advances in materials and technologies aimed at inhibiting corrosion. Furthermore, it will be confined to methods and technologies which utilize the underlying principle of coating the surface to be protected.

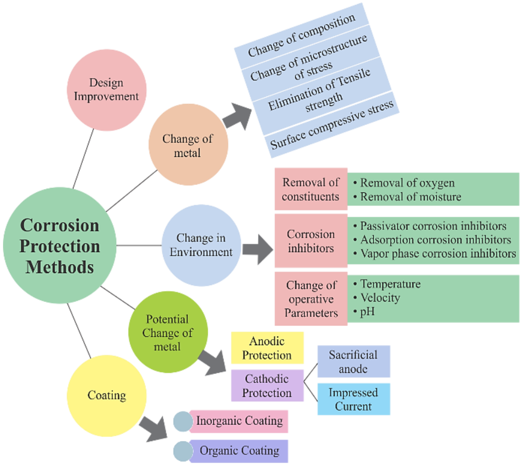


Fig. 1. Methods for corrosion inhibition.

Principle driving the design of corrosion inhibitors

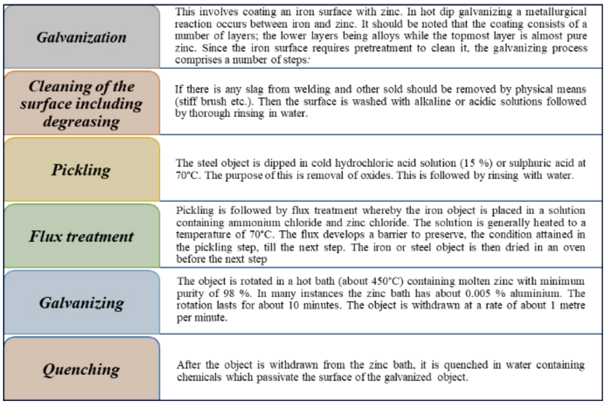
It is common knowledge that corrosion results from the interaction of a metal surface with 'corroding' species in the environment which cause the metal to be oxidized. The most implicated corrosion agent from the environment is oxygen which is aided by species such as chloride. The role of the latter is shown by the fact that automobiles or other metal objects tend to rust much faster at seaside locations than in high altitude locations in the hinterland. The decrease in the amount of oxygen in rarer atmospheres and the lack of salt spray account for the difference. This is obviously a very simplistic view of the cause of corrosion. However, it does indicate that corrosion needs an oxidizing agent as well as an electrolyte in an aqueous medium. While this concept is generally applicable, other corrosion initiating agents may perform the same function. It has been shown [**15**], for example, that even presence of bacteria on the surface of metals can initiate corrosion. One of the ways in which bacteria initiate corrosion is by producing acids in the course of creating conditions for their attachment to the metal surface. In addition to external agents as corrosion inhibitors, a point of greater concern is that 'defects', in the metal structure, can lead to the onset of corrosion. It is plausible that the structural defects give rise to areas on the metal, where there is an excess of electrons or a deficiency of electrons. If these sites are in close proximity, they may lead to the formation of cathodic and anodic areas. In the presence of an electrolyte they will couple to give electrochemical cells.

It is clear from the very brief account above, that corrosion inhibition requires that the inhibitor should prevent the corrosion agents from making contact with the metal surface but that this cannot overcome the effects of structural defects in the metal structure. The latter part of the preceding statement implies that research should also be expended on ways to eliminate defects in metal structures in the process of producing metals from metal ores. Over and above all else, it has to be conceded that metals are stable in their native state in ores where they are present in oxidation states higher than zero. Thus, the tendency of metal to revert is to original oxidation state should be accepted as a natural property of metals derived from ores.

Corrosion inhibition materials used prior to advent of conventional coatings

The early part of the 19^{th} century heralded the use of corrosion stoppers which consisted of dipping the steel into a solution of concentrated nitric acid or sulphuric acid, resulting in the formation of an oxide coating, which served to passivate the metal surface. This process later become known as 'pickling'. Since pickling had an adverse impact on the environment arising from disposal of large quantities of spent acids, much research was expended on the use of eco-friendly 'green corrosion inhibitors' as alternatives to pickling chemicals. In 1930 chelidonium majus (celadine) became the trailblazer for the use of parts of plants [**16**] as corrosion inhibitors. This should be regarded as the 'first green revolution' in corrosion inhibition methods. Several organic compounds such as urea, succinic acid and aldehydes and amino acids [**17**] were also used as green corrosion inhibitors. Compounds with pi bonds proved to be very efficient. However, this 'green strategy' soon gave way to other methods of corrosion inhibition; possibly due to the link to carcinogenic benzene compounds leading to the notion that all organic compounds were health risks.

From the middle of the 20th century, much was done to apply technology to produce corrosion- inhibiting materials. Galvanization of iron [**18**] was one of the most beneficial advances of this era. The summary of the steps in galvanization are given in **(Fig. 2)**.



Galvanization	This involves coating an iron surface with zinc. In hot dip galvanizing a metallurgical reaction occurs between iron and zinc. It should be noted that the coating consists of a number of layers; the lower layers being alloys while the topmost layer is almost pure zinc. Since the iron surface requires pretreatment to clean it, the galvanizing process comprises a number of steps:
Cleaning of the surface including degreasing	If there is any slag from welding and other sold should be removed by physical means (stiff brush etc.). Then the surface is washed with alkaline or acidic solutions followed by thorough rinsing in water.
Pickling	The steel object is dipped in cold hydrochloric acid solution (15 %) or sulphuric acid at 70°C. The purpose of this is removal of oxides. This is followed by rinsing with water.
Flux treatment	Pickling is followed by flux treatment whereby the iron object is placed in a solution containing ammonium chloride and zinc chloride. The solution is generally heated to a temperature of 70°C. The flux develops a barrier to preserve, the condition attained in the pickling step, till the next step. The iron or steel object is then dried in an oven before the next step
Galvanizing	The object is rotated in a hot bath (about 450°C) containing molten zinc with minimum purity of 98 %. In many instances the zinc bath has about 0.005 % aluminium. The rotation lasts for about 10 minutes. The object is withdrawn at a rate of about 1 metre per minute.
Quenching	After the object is withdrawn from the zinc bath, it is quenched in water containing chemicals which passivate the surface of the galvanized object.

Fig. 2. Steps in Galvanization process.

Although galvanizing was a great advance on passivation by 'pickling', it is not everlasting. In the process of protecting iron or steel against actions by aggressive components in the environment, the zinc, in the topmost layer formed by galvanizing, is sacrificed; by oxidation of Zn metal to ZnO_2. The life span of the surface zinc can however be extended by using a wash primer. One such wash primer containing polyvinyl butrayal resin pigmented with zinc tetroxy chromate and phosphoric acid was utilized [**19**] and resulted in the formation of a coating of chromate and resin. In spite of its high efficiency, its use has been curtailed on the grounds that the chromate may leach out and enter the environment. The alternative was to use wash primers [**20**] without chromate. In spite of the fact that a review by Kendig and Buchheit [**10**], of chromates as a corrosion inhibition coating, indicates that chromates may not be the species causing damage to DNA, as indicated in **Fig. 3**, chromate is still widely regarded as a toxic as well as a carcinogenic species [**21, 22**].

In the light of the above, the quest for an alternative inhibition material began in earnest. One outcome, of the above endeavor, was the discovery that a polyaniline-based wash primer is a good alternative to the chromate-based one [**23**]. Whereas the latter was found to form a double layer comprising an inner layer of ZnO and an outer layer made up of Cr_2O_3, $Cr(OH)_3$, $Cr(OH)CrO_4$ and $Zn(OH)_2CrO_4$, the polyaniline-based wash primer produces a double layer with passivated ZnO in the inner layer and phosphate in the outer layer [**24**]. Polyaniline not only has the property to be a component of the wash solution, it can also act as an organic coating in one of its many roles. In a very recent publication, Lyon *et al.*, [**25**] made the following statements: "Organic coatings are the single most widely applied method for corrosion protection of metallic materials and are of particular importance in transport and infrastructure. Nevertheless, despite over one hundred years of research and chromate-resin primer testing, the mechanisms of coatings failure are still somewhat obscure". A related claim (also in a recent paper [**26**]) states that most organic coatings can be penetrated by corrosion agents such as water, oxygen and chloride ions. In view of the foregoing, it would be informative to undertake a brief review of organic coatings followed by other coatings of relevance to this review.

Review of organic coatings

Some features polymer-based organic coatings

There are many types of commercially-available organic polymers. Among the well-used ones are: polyaniline, polyacetylene, polypyrrole and polythiophene. Such is the research activity in the area of polymers that a journal titled 'Polymer Reviews' is dedicated to it. Polyaniline, known by the acronym, 'PANI' is a versatile polymer; in that it is chosen for many applications [**27**]. Corrosion inhibition is just one of them. Polyaniline exists in three forms depending on the oxidation forms of the segments [**27**]. If the oxidized and reduced segments are in the ratio of 1:1 the polymer is known as emeraldine. The form with a preponderance of the reduced segment is known leucoemeraldine while that dominated by oxidized segments is known as pernigraniline. The forms can be generated by chemical or electrochemical methods [**28**]. The versatility of PANI will be shown by the applications described in the sections below.

Corrosion inhibitors containing polyaniline (PANI) for iron/steel

One of the earliest reports of the use of PANI appeared in 1985 [**29**]. This study by DeBerry showed that electro-deposited polyaniline, on ferrited steel, provided anodic protection for the steel. It is noted that the polyaniline was from a doped solution. A comparison of the efficacy of anodic protection, afforded by doped and undoped PANI electrodeposited on steel, was reported [**30**] in 1995. This work characterized the deposited layer as well as performing tests on the corrosion resistance of the PANI coating.

Investigations on comparisons of PANI as a primer with different dopants [**31**] and then top-coated with polyurethane and epoxy showed: firstly, that the primers generated from different doping solutions exhibited different corrosion inhibition properties. It was also found that the PANI primer, top-coated with polyurethane or epoxy, resisted corrosion for two years when tested in solutions containing 3.5 % of sodium chloride. Comparison of passivity [**32**] conferred by PANI on stainless steel was performed by oxidizing aniline monomer contained in two different acids to PANI, by an electro-deposition method. The acids used were sulphuric and phosphoric. The oxide films formed on the stainless-steel surface differed in composition: they contained different amounts of Fe, Cr and Ni; that is, the $PANISO_4$ layer was enriched with Cr, Fe and Ni while the $PANIPO_4$ layer had very little of these metals. In addition, it was found that sulphuric acid was superior in catalyzing the aniline monomer to PANI.

The direct deposition using PANI itself [**33**] on steels containing 1.3 and 4.4 % of Cr was done from two different solutions (one with sulphate ions and the other with phosphate ions). In contrast to PANI coating generated from aniline monomer compared to the coating generated from sulphate solution, very adherent and homogeneous PANI films [**34**] were generated in a one-step electrochemical process (cyclic voltammetry) using steel electrodes. It was found that PANI coating on iron and steel samples gave superior protection against corrosion than polypyrrole-coated steel, under the same conditions.

In a similar electrosynthesis method, a "compact hybrid" PANI-MoO_4^{2-} was prepared [**35**] in an electrochemical cell with molybdate ions in the cell, formed with steel electrodes. The corrosion inhibition increased, compared with use of PANI only. This was attributed to the formation of a MoO_4^{2-}- Fe complex in the film coating on steel.

Corrosion inhibitors for aluminium

As in the case of Fe and steel, polymer coatings are also used for protecting aluminium, which is regarded as a strategic or "commodity" metal by the aviation and construction industries.

A pigment represented as Al-Zn-vanadate hydrotalcite was synthesized; by first preparing hydrotalcite-vanadium by a co-precipitation method involving hydrotalcite and decavanadium anions [**36**]. Known amounts of pigment were then added to an alkyd paint which was applied to aluminium panels which were subjected to artificially aggressive corrosive conditions of humidity and salt spray. Corrosion inhibition performance was assessed using data from electrochemical impedance spectroscopy. It was found that corrosion inhibition increased with increasing amounts of vanadates released from Al-Zn-vanadate. The results were also compared with those achieved by chromate coatings [**10**].

Corrosion inhibitors for copper

Corrosion inhibition of copper plates by silane films, obtained by using various silanic groups such as 3-mercapto-propyl-trimethoxy-silane, PropS-SH and bis-silane) on oxygen free high conductivity copper (OFHC), was investigated [**37, 38**]. It was found to show poor interaction with OFHC. Silanes with long-chain aliphatics gave rise to films with better adherence to OFHC. Silanes with mercapto groups yielded films with strong adhesion to the copper substrate. The thickness of the coating was greater than that expected for a monolayer. Furthermore, the thickness of the coatings was pH-dependent.

The application of super-hydrophobic surfaces on copper plates, for corrosion inhibition purposes was reported by Liu *et al.,* [**48**]. These super-hydrophobic surfaces on copper plates were attained by one-step electro-deposition, using a cell comprising copper plates as electrodes. The electrolyte was prepared by mixing cerium chloride with myristic acid. By applying 20 V (DC) for 30 minutes, a cathodic surface was obtained. The super-hydrophobic layer was composed of "special hierarchical micro/nano" structure and cerium myristate. It was found that the extent of inhibition was dependent on the level of hydrophobicity of the applied layer.

Ionic liquids used for corrosion inhibition

As described and discussed in reviews on coatings in the preceding section, a major concern, regarding corrosion inhibitors, is their impact on the environment. The aim of much of the recent research in the area of corrosion inhibitors is to find 'green corrosion inhibitors' which can function on an industrial scale. To this end, concentrated research efforts have been expended, especially in the last decade, on the possibilities of exploiting the well-documented accounts of ILs as green solvents [**39-41**] in the design and manufacture of 'green corrosion inhibitors'.

One of the reasons for the intensified pace of research in using ILs for corrosion inhibition is that these 'green inhibitors' can reduce pollution of the environment caused by aggressive chemicals (released into the environment by anthropogenic activities) which attack metal surfaces [**29-59**] as shown in **Table 1** and ref [**60-64**]. Zhang and Hua [**65**] investigated the corrosion inhibition of mild steel by using 1-butyl-3-methylimidazolium chloride (BMIC) and 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]). They found that for both inhibitors, "the inhibition efficiency increased with increase in the concentration of the inhibitor and the effectiveness of the two inhibitors are in the order [BMIM][HSO_4] > BMIC". They also reported that the adsorption isotherm of the inhibitors on the surface of mild steel conformed to Langmuir's theory. In a similar study to the one above, Hanza *et al.,* [**42**] used 1, 4-di [1-methylene-3-methyl imidazolium bromide]-benzene as an IL on mild steel in 1 M H_2SO_4. They also confirmed that adsorption of the ILs on the steel surface obeyed Langmuir's isotherm. An additional finding was that the anti-corrosion efficiency was dependent on the concentration of the IL applied. A variation in research approach led to the testing of several ILs on the same metal surface in steel structures; but under different conditions [**66**]; for example, ILs with imidazolium and pyridinium cations have been shown to exhibit good corrosion inhibition capacity when coated on mild steel in 1.0M H_2SO_4 medium. It was also established that ILs with imidazolium cations proved to be superior in corrosion inhibition efficiency to ILs with pyridinium cations. This was attributed to the larger steric bulk of imidazolium cation compared to the same property of the pyridinium cation [**66**]. Another benefit to corrosion inhibition by imidazolium - based ILs such as dibencilimidazolio acetate and dibencilimidazolio dodecanoate is the observation that they deposit a dense layer of film on the surface of the metal. It is claimed that the density of the layer prevents the diffusion of ionic species from the film and saves the surfaces from the ionic attack by HCl and H_2SO_4 solutions [**67**].

As in the case of organic coatings, the protection against corrosion afforded by ILs can be cathodic or anodic in nature. For instance, Zheng *et al.*, using two imidazolium-based ILs such as 1-octyl-3-methylimidazolium bromide ([OMIM]Br) and 1-allyl-3-octylimdazolium bromide ([AOIM]Br) established [**68**] that the inhibition of corrosion of mild steel in H_2SO_4 media occurs via cathodic inhibition process. Regarding the identity of the atoms which are attached to the surface of the metal, it was shown [**68**] that the physical adsorption of OMIM and AOIM cations in ILs were occurring through the positively charged N atom of the heterocyclic imidazolium ring. It was also shown that this type of adsorption can be understood in terms the El-Awady thermodynamic-kinetic model.

Another aspect of corrosion inhibition, by ILs, which has been probed is the influence of the nature of substituents on the heterocyclic rings of cations of ILs. In this regard, the effect of corrosion inhibition on copper in 0.5M H_2SO_4 solution was investigated [**69**]. The following substituted imidazolium ILs were used: allyl-3-ethylimidazolium bromide ([AEIM]Br), 1-allyl-3-butylimidazolium bromide ([ABIM]Br),1-allyl-3-hexylimidazolium bromide ([AHIM]Br), 1-allyl-3-octylimidazolium bromide ([AOIM]Br), The mechanism of corrosion inhibition by these four ILs has been interpreted on the basis of data obtained from molecular dynamics and chemical quantum studies [**69**]. Scendo and Uznanska have investigated [**70**] the corrosion inhibition for copper, using 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium bromide ILs under conditions of 1.0M Cl- solutions and pH 1.0. They found that both inhibitors contain active sites comprising the imidazolium ring and its heteroatom. This was inferred from calculations using quantum chemistry. The order of the inhibition for these allyl imidazolium ILs were found to be [AEIM]Br < [ABIM]Br < [AHIM]Br < [AOIM]Br. This information clearly explains that the efficacy of corrosion inhibition depends on the length of the alkyl substituent. They found that the efficacy of corrosion inhibition performance increased with increase in the chain length of the substituent and this was attributable to an increase in hydrophobicity. However, it was observed [**70**] that longer alkyl chain length resulted in lower solubility of the IL in water and in the forming of foams. Thus, increase in alkyl chain length of the substituent on hetero atom appears to be counter-productive, as far as corrosion inhibition is concerned.

Like copper, aluminium is a strategic metal, for which corrosion inhibition is extremely important. It is therefore worth noting, that the mode of adsorption of ILs on surfaces of aluminium has been investigated by Zhang and Hua [**71**]. They attributed the excellent corrosion inhibition property shown by alkyl imidazolium ILs acting on aluminium, in mineral acid, to the mechanism of physi-sorption of the IL on the surface of aluminium. In a similar experiment, the of 1-butyl-3-methylimidazolium tetrafluoroborate IL on carbon steel, in alkaline chloride solution, resulted in a significant increase in inhibition of corrosion [**42**]. In another study [**72**] on adsorption on carbon steel, data from Langmuir adsorption isotherms were interpreted to indicate that the presence of a multicenter adsorption surface, resulted in effective suppression of both cathodic and anodic processes of corrosion. Surface analysis [**72**] was used to show that a layer comprising cations of an IL on a steel surface is an efficient barrier against the ingress of chloride ions from the environment surrounding the steel, on to the steel surface.

For reactive metals such as lithium and magnesium, novel ILs [**73**] were used to deposit a uniform protective surface on the metals. In spite of the research findings which revealed that ILs can be used as green corrosion inhibitors, it was only recently (10 to 15 years ago) that research on the corrosion inhibition by ILs became intensive. Furthermore, the investigations in this area predominantly involved the use of ILs with imidazolium and pyridine cations.

With regard to the effect of different cations on the thermal stability of ILs, it was found that ILs, which are classed as dicationic, have higher thermal stability than monocationic ILs [**74**]. This finding could be the reason for the increased use of dicationic ILs by researchers working on the use of ILs for corrosion inhibition. Furthermore, dicationic ILs have physicochemical properties which are amenable to greater manipulation. The effect of changing the anions of the ILs results in the variation in the toxicity of the ILs towards some organisms present in the media where ILs are used [**75**]. As an illustration, the toxicity of anions in ILs to aquatic organisms has been reported as follow: $[Br]<[DCA]<[Cl]<[BF_4]<[PF_6]<[NTF_2]$ [**75**].

In addition to the desired property of corrosion inhibition, the wear resistance of anti-corrosion agents is also an important consideration. Wear and related properties such as durability are covered by the use of an over-arching term, namely, ‘tribology’. Tribological properties of selected ILs have been attained by incorporating a functional group into an IL with the potential to confer tribological properties to the IL [**76**]. One such example involves the use of benzotriazole [**76**] IL, which was synthesized by neutralizing 1H-benzotriazole with tetrabutyl phophonium hydroxide. The benzotriazole IL was shown to exhibit good lubricating ability for steel, copper and combinations of these metals. The characterization of the ILs included the following aspects: thermal stability, viscosity, hydrolysis stability, corrosion and accelerated test resistance for copper and friction and wear tests.

Table 1. Ionic liquids and their combination with other agents as corrosion inhibitors.

S. No.	Corrosion inhibitors	ILs	Type of metal	Method	Ref.
1	1,4-di [1-methylene-3-methyl imidazolium bromide]- benzene	1,4-di [1-methylene-3-methyl imidazolium bromide	mild steel	electrochemical	[**29**]
2	3,4-diamino benzonitrile	-	steel	electro-chemical impedance	[**37**]
3	cationic gemini surfactants	N, N'-(cyclohexane-1,4-diylbis(oxy))bis(2-oxoethane-2,1-diyl)bis(N,N-dimethylalkan-1-aminium) methylsulfate[CHOGS-8, CHOGS-12 and CHOGS-16 compounds].	carbon steel	electro-chemical impedance	[**38**]
4	amino acid-derived ionic liquid	tetra-n-butylammonium l-methioninate [TBA][L-Met]	mild steel	-	[**39**]
5	Imidazolium ILs	1-butyl-3-methylimidazolium tetrafluoroborate [C_4C_1Im][BF_4], 1-butyl-3-methylimidazolium hexafluorophos- phate [C_4C_1Im][PF_6], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [C_4C_1Im][TFSI]	stainless steel	Electrochemical impedance spectroscopy (EIS).	[**40**]
6	Ionic liquids based gemini cationic surfactants	N1,N1,N1,N2,N2,N2-hexadodecylethane-1,2-diaminium bromide (G2IL), N1,N1, N1,N2, N2,N2-hexadodecylpropane-1,3-diaminium bromide (G3IL) and N1,N1,N1,N2,N2,N2-hexadodecylhexane-1,6-diaminium bromide (G6IL)	carbon steel	Potentiodynamic polarization, electrochemical impedance spectroscopy	[**41**]
7	novel methyl benzimidazolium ionic liquid	synthesized3-(4- chlorobenzoyl methyl)-1-methylbenzimidazoliumbromide ([BMMB]$^+$[Br]$^-$) ionic liquid	carbon steel	-	[**42**]
8	benzimidazoliumtetrafluroborate IL	3-(4-chlorophenylacylmethyl)-1-ethylbenzimidazolium tetrafluroborate ([BMEB]$^+$[BF_4]$^-$)	carbon steel	electrochemical noise analysis	[**43**]
9	benzimidazolium based IL	1.3-bis[2-(4-methoxyphenyl)-2-oxoethyl]-1H–benzimidazol-3-ium bromide (MOBB)	aluminium alloy composite	electrochemical impedance spectroscopy and Potentio dynamic polarization methods	[**44**]
10	Schiff Base-based cationic gemini surfactants	Synthesis of 3,3′-(pentane-2,4-diylidenebis(azanylylidene))bis(N-(2-(alkyloxy)-2-oxoethyl)-N,N-dimethylpropan-1-aminium) chloride [SBGS-10, SBGS-14 and SBGS-16 compounds]	mild steel	electrochemical	[**45**]
11	1-butyl-3-methylimidazolium tetrachloroferrate IL	1-butyl-3-methylimidazolium tetrachloroferrate([C_4C_1im][$FeCl_4$])	A36 mild steel	using immersion tests and other electrochemical techniques	[**46**]

12	trihexyl(tetradecyl)phosphonium diphenylphosphate ($[P_{6,6,6,14}]$[dpp]) IL	-	AA5083 aluminium alloy	Electrochemical	[**47**]
13	-	1-ethyl-3-methylimidazolium triflate, 1-ethyl-3-methylimidazolium bis (trifluoro methyl sulfonyl) imide, trihexyl tetradecyl phosphonium bis (trifluoro methyl sulfonyl) imide, butyl trimethyl ammonium bis (trifluoro methyl sulfonyl) imide, methyl trioctyl ammonium bis (trifluoro methyl sulfonyl) imide	stainless steels and nickel-based alloys	Electrochemical	[**48**]
14	-	1-ethyl-3-methylimidazolium ethylsulfate $[EMIM]^+$ $[EtSO_4]^-$, 1-ethyl-3-methylimidazolium acetate $[EMIM]^+$ $[Ac]^-$, 1-butyl-3-methylimidazolium thiocyanate $[BMIM]^+$ $[SCN]^-$, 1-butyl-3-methylimidazolium acetate $[BMIM]^+$ $[Ac]^-$and 1-butyl-3-methylimidazolium dicyanamide $[BMIM]^+$ $[DCA]^-$	mild steel	Electrochemical	[**49**]
15	-	1-allyl-3-butylimidazalium Bromine	X65 steel	Electrochemical	[**50**]
16	ODPEG-TS	Ethoxylated Octadecylamine IL	Steel specimens	Electrochemical	[**51**]
17		1,8-Bis(3-methylimidazolium-1-yl) octane di[bis(trifluoromethylsulfonyl) imide] (IL1), 1,10-bis(3-methylimidazolium-1-yl)decane di[bis(trifluoro methylsulfonyl) imide] (IL2), and 1,10-bis(3-methylimidazolium-1-yl) decane diphenylalanine (IL3)	Titanium and Cobalt Chromium Molybdenum Alloys Coated with	Electrochemical	[**52**]
18	Amine−IL Mixtures	$[bmim][BF_4]$	carbon steel	Electrochemical	[**53**]
19	benzotriazole IL (IL, $BTAP_{4444}$)	1-butyl-3-methyl imidazolium tetrafuoroborate ($bmimBF_4$)	steel/steel, steel/copper and steel/aluminum	Electrochemical	[**54**]
20	Imidazolinium Carboxylate Salt	2-MeHImn 4-OHC, 2-MeHImn Br	Mild steel	Electrochemical	[**55**]
21	Acidic-Functionalized Ionic Liquid	1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate ($[BsMIM]$-$[HSO_4]$) and 1-(4-sulfobutyl)-3-methylimidazolium tetrafluoroborate ($[BsMIM][BF_4]$),	304 Stainless Steel	Electrochemical impedance	[**56**]
22	-	$[BMIM][BF_4]$, [BMIM][Otf], $[P_{4441}]$[Acetate],and [Choline][Acetate]	carbon steel	Electrochemical impedance	[**57**]
23	Polymeric IL Nanoparticle Emulsions	1,4-Di(vinylimidazolium)butane bisbromide (DVIMBr)	Mild steel substrates (CA3SN-G	Electrochemical impedance	[**58**]
24	-	1-pentyl pyridazinium bromide (PPB)	copper	Electrochemical impedance	[**59**]

Nanomaterials used in corrosion inhibition

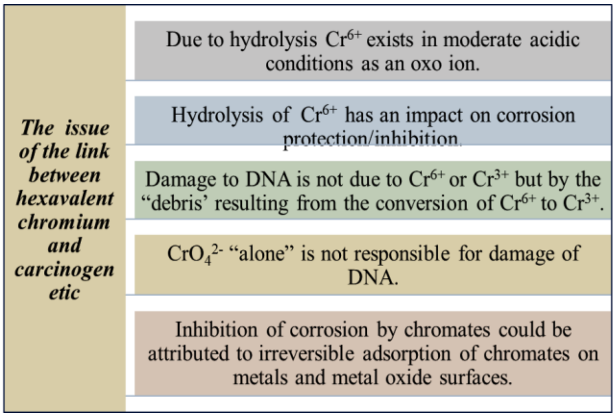
Nanoparticles

The rate of increase in research involving nanotechnology may, perhaps, be described as being exponential. The advent of nanoparticles has impacted on research trends in diverse fields such as pure science, many branches of engineering, health sciences including all branches of medical technology and manufacturing industries. Since corrosion of products generated by manufacturing industries costs consumers billions in the currencies of developing countries, there is a dire need to find ways to inhibit corrosion. However, it is not confined to the users of industrial products which are plagued by corrosion. Industrial infra-structure comprising materials of buildings, machinery and supply of services and waste disposal conduits, need to be protected against corrosion. The switch of focus in the search from, corrosion inhibition materials such as organic coatings, to the use nanomaterials is an advance based on the premise that the smaller size of components of nanomaterials will enhance adhesion to metal surfaces. In addition to the inherent interest in finding new applications for nanomaterials, the increase in research involving nanomaterials is also driven by factors such:

- The negative publicity of the link between hexavalent chromium and carcinogenicity arising from the use of chromate-based coatings **(Fig. 3)**.
- The dangers of the possible release of volatile organic compounds (VOCs), from organic coatings, into the environment.
- Only small quantities of nanomaterials are needed to give thin but adhesive films.

The following very brief review may serve to show that strategies to address the above have already received attention **(see Fig. 3)**:

Palanivel *et al.,* reported [**77**] that ultra-thin silane films, to which small amounts of nanoparticles were added, gave exceptional protection to metals. Very briefly this was achieved as follows: Silica nanoparticles were loaded into bisulphur silane to obtain colloidal solutions. The metal was then dipped into the latter solution for a fixed period. Upon drying, an ultra-thin film was formed on the metal. The addition of the nanoparticles not only conferred a corrosion inhibition property but also increased the mechanical strength of the coating, CeO_2 nanoparticles loaded into a silica-alumina hybrid coating exhibited corrosion inhibition for Cu. It proved to work well compared to normal cerium nitrate as an inhibitor [**78**]. Zand *et al.,* [**79**] reported that the electrochemical performance of cerium-silane hybrid coating was dependent on concentration of ceria nanoparticles. This information explains the significant impact of the concentration of the nanoparticle on the barrier properties of silane films, that is, the lower the content of the nanoparticles the better the performance of the silane films as a barrier to corrosion agents.



The issue of the link between hexavalent chromium and carcinogenetic

Due to hydrolysis Cr^{6+} exists in moderate acidic conditions as an oxo ion.

Hydrolysis of Cr^{6+} has an impact on corrosion protection/inhibition.

Damage to DNA is not due to Cr^{6+} or Cr^{3+} but by the "debris' resulting from the conversion of Cr^{6+} to Cr^{3+}.

CrO_4^{2-} "alone" is not responsible for damage of DNA.

Inhibition of corrosion by chromates could be attributed to irreversible adsorption of chromates on metals and metal oxide surfaces.

Fig. 3. Alleged link between hexavalent chromium and cancer.

An electroless technique has been used to deposit Ni-Phosphorus (P) and Ni-P-Re on copper discs [**80**]. The deposition of the Ni alloys was effected by using chemicals in such a way that both the electrochemical and the catalysis functions were exhibited by different chemicals in the same mixture. This method of depositing the Ni-containing film is said to be useful in various industries such as automobile and electronics manufacturers. In the latter sector, jointing methods using solder result in structures having crevices which are generally difficult to coat. It is claimed that this technique has overcome this problem. If this can substantiated for different types of solders, it could be a major advance in inhibiting corrosion for the electronics industry.

It is relevant to note that the improvement in the inhibition of corrosion was found to depend on the functionalization of the surface coating, during plating on aluminium. It was found that corrosion resistance was enhanced by the addition of nano-SiO_2 particles (NSPs) into electroless Ni-phosphorus coating. These silica nanoparticles were incorporated into the coating material to provide a multiple functional coating with improved physical properties. There was an increase in increase in hardness as well as a significant improvement in corrosion inhibition by the composite material [**81**]. Although brass is fairly self-sufficient in resisting corrosion, it cannot resist aggressive environmental conditions for prolonged periods. Hence it needs protection from coatings or films for protection. Monolayers of PropS-SH (3-mercapto-propyl-trimethyoxy) silane, self- assembled on brass, was doped with La_2O_3 nanoparticles [**82**]. The latter served to fill the holes in the silane film. In this way the density of the film was increased. This in turn led to an improved barrier against corrosion agents. The conversion of some of the oxide nanoparticles to hydroxides led to the blocking of the cathode sites by the generated hydroxides [**83**]. Thus, the ingress of corrosive agents onto the surface of the metal was effectively countered. Clay nanoparticles were combined with cerium salt to enhance anti-corrosion ability of the coating on mild steel due to the synergic effect between the nanoparticles and the clay [**83**]. In addition, both inhibitions of corrosion and antibacterial characteristics of Ag nanoparticles have been investigated for aluminium in HCl solution [**84**]. It was found that Ag nanoparticles were effective in inhibiting corrosion in both cases. It is worth emphasizing that corrosion inhibitors such nanoparticle of silver which have properties to perform the dual functions of inhibiting of corrosion and destroying bacteria are very valuable as bacteria have found on several steel surfaces [**84**]. These types of nanomaterials can save the cost of screening metal surfaces for the presence of bacteria prior to treating them with corrosion inhibitors.

Nano sheets

Nanomaterials comprising carbon only can be synthesized in several ways; thus, giving diverse products such as sheets, tubes and ribbons. The 2D nano form in sheets is known as graphene. For coatings needing carbon only, graphene is eminently suitable on the basis that it has very light mass and that its thinness will impact very little on metal properties such as heat conduction. In addition, graphene is an inert material which is impervious to oxygen, the main agent initiating corrosion. Coating using graphene is done using catalytic methods to deposit the film on the metal surface or by chemical reduction of graphene oxide [**85**].

Although graphene has commendable properties as a corrosion inhibitor on metal surfaces, it is not suitable for very large surface due to the possibility of defects or breaks in the coatings [**86**]. At the sites of the breaks the metal may act an anode and the graphene as the cathode. In the presence of an electrolyte, a galvanic cell will be formed. To counter the effects of the defects, an ultra-thin layer of a polymer was deposited [**5**] on a copper surface already covered with graphene. This is regarded as a hybrid coating. There are several reports of combinations of corrosion inhibitors which could be classed as hybrids or composites. A few of these will be considered in the next section.

Nanocomposites as corrosion inhibitors

Nanocomposites containing graphene

As mentioned in section 6.2, the deposition of graphene on very large areas may lead to breaks in the coating which could lead to the development of galvanic cells. To repair such type of breaks a filler with electroactive features to counter the effect of galvanic cells is required. One such material is polypyrrole. On the premise that incorporation of graphene into polymers may give enhanced corrosion protection, composites involving graphene and polyetherimide (PEI) were found [**87**] to afford protection to copper surfaces via two pathways: the PEI component acts as a barrier to ingress of corrosion agents such as water and oxygen while the graphene serves to depress the diffusion rate of these corrosion agents.

An increase in the hydrophobicity of the surface will work to decrease or stop the entry of water onto the surfaces of metals. In this regard, it was found [**88**] that composites of graphene with epoxy are imbued with the property of hydrophobicity. The epoxy in the composite acts as a physical barrier to corrosion agents as well as contributing to the hydrophobicity of the composite. The graphene nanosheets also function as a shield against corrosion agents.

Nanocomposites containing ionic liquids

Nanomaterials generally have excellent physical and chemical properties in terms of stability, surface area and activity. The inclusion of ILs in nanomaterials tends to enhance these properties. Ionic liquids contribute to an increase in electrical conductivity of the composites, comprising ILs and nanomaterials. Overall, an IL acts as a conductive binder in nanomaterials, so that the composition of the nanomaterials acts as a homogeneous material. The ionic liquid- nanomaterial composites have various applications including corrosion inhibition [**88a, 89**]. An illustration of this is shown in **(Fig. 4)**. The illustration shows that the uses of ILs-nanomaterial composites are not confined to corrosion inhibition applications. This new trend in the research [**88b, 90**] on the application of ILs-nanomaterial composites is motivated by the need to reduce cost in various processes.

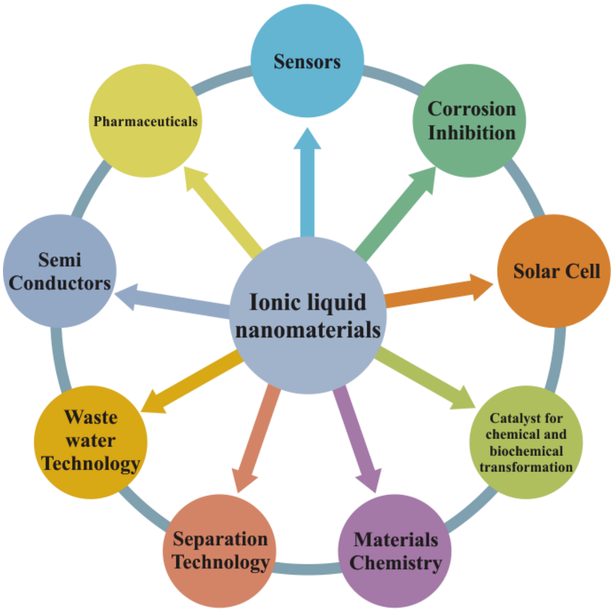


Fig. 4. Applications of ionic liquid nanomaterials in various fields.

Miscellaneous nanocomposites

The combination of two or more active nanomaterials to make effective nanocomposites has the potential to trigger tremendous growth in the synthesis and applications of nanocomposites. The following brief review will give an indication of the research efforts expended in finding cost-effective replacements for unsuitable coatings.

The corrosion inhibition of mild steel was developed using the product resulting from incorporation of ZnO nanoparticles into a chitosan matrix nanocomposite. This resulted in extraordinary chemical stability, controlled oxidation and anticorrosion properties of the composite in 0.1N HCl solution [**89, 91**]. A similar investigation of corrosion inhibition for carbon steel in HCl solution, at 25ºC, using the composite material generated by the infusion of Ag nanoparticles into chitosan grafted polyethylene glycol-based material were reported by Hefni *et al.,* [**90, 92**] to give extraordinary results.

Epoxy containers loaded with nanocontainers have found favour as corrosion inhibitors. The corrosion inhibition of an epoxy coating which comprises TiO_2 nanocontainers loaded with an inhibitor of 8-hydroxyquinoline was investigated for alloys of aluminium in 0.05M NaCl solution and it was observed an improvement of the performance of the coatings due to the loaded nanocontainers [**91, 93**].

Some natural ceramic oxides, for electrochemical coating with lower electronic conductance, like SiO_2, TiO_2, ZrO_2, Al_2O_3 or mixed oxides composites of coating have been documented for corrosion resistances [**92-108**]. Moreover, the important nanocontainers of clay nanoparticles such as montmorillonite, bentonite, hallosites, polymeric layer-by-layer (LbL), zeolite, assembled and cyclodextrins have been widely applied as a corrosion protector in recent years [**107, 109**]. In addition, various types of containers have been reported for corrosion inhibitions such as nanotubes, polymers, layered double hydroxides, polyelectrolytes and mesoporous oxide materials. The conventional coating could not usually provide sufficient corrosion resistance because of the instability of the coating material and inhibitor deactivation [**107, 109**].

In previous parts of the reviews, given above, it has been pointed out that Zn metal serves as an anti-corrosion agent in galvanized iron. Conducting polymers such as PANI have found use as anti-corrosion coatings whereas epoxy/resins have also been used in corrosion inhibition roles. It was therefore anticipated that combinations of anti-corrosion materials could be synthesized as composites with each component contributing to the overall efficiency of the composite. An illustration of the realization of this expectation was the preparation and uses of the composite comprising PANI/epoxy/Zn [**14, 108**]. The composite was synthesized in two stages. In the first step a coating consisting of PANI and Zn nanoparticles was prepared with varying percentages of Zn, with 4 % Zn giving the optimum results. In the second step, varying percentages (0-20 %) of epoxy resin was added to give the final formulation.

Sol-gel technology has been applied in many fields. Its exploitation for producing ultra-thin coatings for corrosion inhibition is a worthy addition to its other commendable contributions. Santana *et al.,* [**83, 109**] developed an anti-corrosion sol-gel coating incorporating clay nanoparticles and trivalent Ce. The latter functions as a self-healing agent; thus, reducing the chances of coating failure.

Qualitative descriptions of modes of action of corrosion inhibitors

Pickling and galvanization

Although pickling is the one the earliest strategies for providing a barrier against corrosion, it uses a mechanism which was later offered by other coatings, namely passivation of the metal surface so that reaction with environmental elements such oxygen is drastically reduced. Galvanization **(see Fig. 5)** was a substantial advance on pickling in that the Zn metal formed an alloy with Fe. However, under very harsh conditions the Zn was oxidized to ZnO powder which tended to drop off and expose iron to attack by corrosion agents.

Plant extracts

Generally, plant extracts provide corrosion inhibition by good adhesion to the metal surfaces **(Table 2)**. In some cases, the extracts also act as passivators of the metal surface.

Ionic liquids

It might appear to be far-fetched to read that rust can protect rust. But it is true that the products of corrosion such as Fe $[(H_2O)\ SO_4]$ might interact with ionic liquids, especially with the cation part, to create a protective functional multiple complex layer on the surface of the steel, which resists dissolution of iron to continue [**14, 110**]. Moreover, the active site of the substrate is blocked to provide protection by the formation of a multilayer and it also serves to drop the rate of the corrosion. In the cathodic process, the protonated imidazolium molecules, in competition with the H_3O^+ ions, could be electrostatically adsorbed by the activated metal surfaces. Thus, existing hydrogen evolution was reduced. Subsequently, the functional groups in cations of the ILs, such as alkyl chain and aromatic rings, being larger than the hydronium ions; can cover a large surface of the substrate, leading to displacement of water molecules from substrate surfaces. Furthermore, electro-neutrality was achieved during the electron transfer from substrate to cations of IL, and as a result a protective layer was deposited on the surface of metal to inhibit corrosion.

In cases where ionic liquids are applied to steel which has no rust, the mechanism is adsorption as described earlier under the section on ionic liquids. The adsorption is aided by the presence of hetero atoms on the cations. Furthermore, ionic liquids with hydrophobic properties serve to drive out any moisture on the metal surface; thus, eliminating one of the main agents of corrosion.

Table 2. Recently reported corrosion inhibitors which are based on polymers, bio-materials and nanocomposites.

S.No.	Corrosion Inhibitor	Metal	Ref.
1	Natural polymeric chondroitin-4-sulfate as anionic polyelectrolyte inhibitor	Aluminum	[**111**]
2	Multi-layer polymer coatings composed of the microfibers of a superabsorbent polymer (SAP)	Carbon steel	[**112**]
3	Magnetite nanoparticles/polyvinyl pyrrolidone stabilized system	Carbon steel	[**113**]
4	Bio-extract Polymer Coating Material	Mild Steel	[**114**]
5	Polyacrylamide	C-Steel	[**115**]
6	Hexa-anionic surfactant, and named; Sodium(2Z,16Z)-8,11-bis((Z)-3-carboxylatoacryloyl)-5,14-bis(2-((4dodecylphenyl)sulfonamido)ethyl)-4,15-dioxo-5,8,11,14-tetraazaoctadeca-2,16-dienedioate	Mild steel	[**116**]
7	2-amino-5-mercapto-1,3,4-thiadiazole and its TiO_2composit	Copper	[**117**]
8	Gum Arabic-silver nanoparticles composite	Steel	[**118**]
9	Two biomass monomers, syringaldehyde methacrylate (SMA) and eugenol methacrylate (EMA)	Metal	[**119**]
10	Extracts of date palm leaves and seeds	Carbon steel	[**120**]
11	Chitosan polymer	Copper	[**121**]
12	Dextran	Steel	[**122**]
13	Gelatin	Carbon steel	[**123**]
14	Pyrazines	Steel and Al and Mg alloys	[**124**]
15	Ferrochrome slag/polyaniline Nanocomposite	Carbon Steel	[**125**]
16	H_2Pc/Epoxy nanocomposites	Carbon steel	[**126**]
17	polycrystalline graphene	Mild carbon steel	[**127**]
18	Acid stimuli-responsive Ca-Na2MoO4-HNTs nanocomposite	Steel	[**128**]
19	Cu-BTA-Na2MoO4-HNTs	Carbon steel	[**129**]
20	Polymer and Ceramic-Based Nanocomposite Coatings	Cast Iron Pipeline	[**130**]

Organic coatings

To summarize what has been covered under the relevant section, polymeric coatings can be designed to afford protection not only through strongly adhering coatings which are impervious to entry of organic corrosion agents but also have a hydrophobic property which will keep out water and a conducting property to give anodic protection to the metal.

Nanomaterials and nanocomposites

If it is accepted that the effectiveness of coatings on metals is dependent mainly on the strength of the adhesion of the coating to the metal surface, nanomaterials should have better adhesion, weight for weight, than other coatings based on the fact that there are more 'particles' per unit area. Furthermore, if the nanoparticles are inert to corrosion agents, then the coating becomes a very efficient anti-corrosion barrier. Nanocomposites have an added appeal as anti-corrosion materials because they can incorporate components which could act synergistically to give better corrosion inhibitors **(Table 2)**.

Conclusions and direction of future research in corrosion inhibition

The aspects to be discussed are represented in **Fig. 5**; to show at a glance that advances have been made in respect of the development of materials and technologies for corrosion inhibition. However, all them are all are driven by the need to prevent access to the metal surface by developing coatings of various kinds.

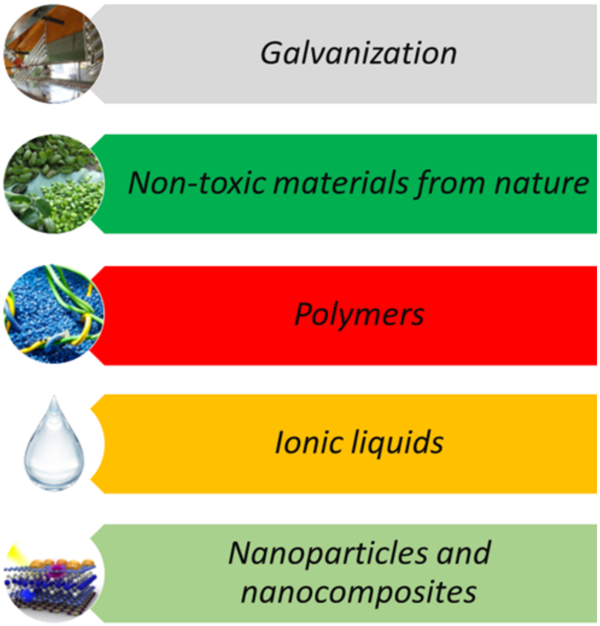
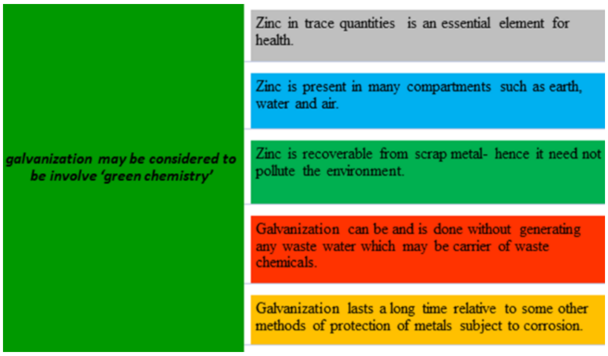


Fig. 5. Advances in technologies for corrosion inhibition.

Galvanization

In a broad sense galvanization may be considered to be involve 'green chemistry' in that it utilizes non-toxic chemicals in the main. Manufacturing companies which wish to meet the global requirements of industrial processes need to satisfy the standards set by the following code: DIN EN ISO 14001. At least one company [Kopp] in Germany which specializes in galvanization, claims to comply with the global code. Some of the points made by them in support of their claims are indicated in **(Fig. 6)**.



galvanization may be considered to be involve 'green chemistry'

Zinc in trace quantities is an essential element for health.

Zinc is present in many compartments such as earth, water and air.

Zinc is recoverable from scrap metal- hence it need not pollute the environment.

Galvanization can be and is done without generating any waste water which may be carrier of waste chemicals.

Galvanization lasts a long time relative to some other methods of protection of metals subject to corrosion.

Fig. 6. Green chemistry aspects of galvanization.

Non-toxic materials from nature

In terms of greenness of the method of inhibition of corrosion, nature's bounties may be at the head of the list (see **Table. 2**). The advantages in using parts of plants, such as fruits, leaves, stems and roots/rhizome for corrosion inhibition, arise from the following properties: predominantly non- toxic, readily available, relatively easy to extract, relatively inexpensive [**83, 110-139**]. In the light of these properties the protection can be renewed frequently and on a large scale because of the low cost of materials and methods. To illustrate some of these claims, a common-place material such as black pepper [**137, 140**] and lignum [**139, 141**] are used for corrosion protection of steel and the peel of a mango [**139, 142**] can provide the ingredients for inhibition of corrosion of zinc and aluminium while fruit shells of pomegranate contain the anti-corrosion agents for copper [**141, 143**].

As far as micro-organisms are concerned some of them can be used to combat the onset of corrosion while others actually induce corrosion when present on metal surfaces [**142-148**]. The former is achieved by the micro-organism being involved in the formation of a biofilm on the metal surface [**127, 129**].

On the other hand, sulphate-reducing bacteria, for example, are responsible for the initiation of corrosion in metals which are used in petroleum industries [**142**]. It is clear that more research is needed to identify the micro-organisms which can serve as precursors for formation of corrosion inhibitors.

Paints and polymers

Prior to the advent of polymer-based coatings, [**148-152**] paints [**153-155**] were widely used to protect metals from the elements of the environment. However, to serve as an anticorrosive agent, paints needed an undercoating with anti-corrosion properties [**153-155**]. Chromates and phosphates served this function admirably and at a relatively low cost until it became a health issue; in that hexavalent chromium in chromates was linked to cancer. Since paints serve an aesthetic role as well, to retain it use, research focused on finding suitable under-coatings for paints. This resulted in the synthesis of a variety of conducting polymers with anti-corrosion properties [**148-152**]. As the use of polymers resulted in a move away from green chemistry, research attention turned to ILs which have many properties which earned them the appellation of 'green solvents.'

Ionic liquids

The simplest mode in which ILs can act as corrosion inhibitors is through adsorption and passivation of metallic surfaces [**13, 72, 156-161**]. In selecting ILs for the passivation functionality, it has to be borne in mind that ILs may have, inter alia, acidic and basic properties in terms of the Bronsted theory of acids and bases. The use of ILs which behave as strong Bronsted acids should corrode materials such as carbon steel [**162**]. However, it was found that, for instance, [$(CH_2)_4SO_3$HMIm] [HSO_4], [**163, 164**] a Bronsted acid, can function as passivating agent on carbon steel under certain conditions; one of them being absence of water. The type of passivation occurring in this case is classed as "electrochemical passivation". It is thus interesting to note that the passivation study was effected in an electrochemical cell with 3 electrodes with steel being the working electrode, while graphite and platinum served as the other two electrodes with IL serving as an electrolyte. The formation of a passive a film on the steel electrode was attributed, on the basis of tests, to adsorption of the cations of the IL on the steel surface.

Much research has been expended on the effect of changing the cation of the IL. Different cations exhibit different amounts of protection for metal. Anions have also been shown to be involved in corrosion inhibition. Specifically, an IL with polyoxometalate anion has been shown to coat copper metal and afford good protection against acidic corrosion agents [**165**]. The coating also incorporates a self-repairing functionality. Using the polymerizability of ILs, polymeric IL nanoparticles were synthesized. Emulsions of these have been shown to have anti-corrosion properties [**165-169**].

Nanoparticles and nanocomposites

Nanoparticles play very important roles in corrosion inhibition [**170-175**]. Firstly, only small quantities of nanoparticles need to be added to coatings to provide the desired corrosion resistance property [**176, 177**]. Secondly nanoparticles play a role in functionalization of the surfaces of metals to improve physical properties of the surfaces of metals. Thirdly nanoparticles of rare earth group of elements are suitable for doping very thin layers of coatings.

Nanocomposites provide scope for expanded research in the area of corrosion protection on account of the fact that the number and variety of composites, which can be synthesized, is countless [**178-182**]. This also implies that the properties of these nanocomposites could be fine-tuned to serve specific function/s. The advances in the technology of corrosion resistance and other needs of both the industrial and domestic sectors can be met by utilizing nanocomposites containing ILs since they are highly amenable to changes in designs of structures to enhance desirable properties and / or decrease counter-productive ones. An overriding consideration should be to accentuate design factors which will tend to increase the adhesion between the surface and the coating as well as to find ways to increase the ability of the coating surface to be impervious to the passage of corrosion agents from the environment to the surface of the metal. Nanocomposites appear to hold most promise for achieving the required design changes.

Concluding remarks

This review, though not an exhaustive one on the subject, shows clearly that many commendable advances have been made with regard to the materials and technologies used. If a single concept has to be identified as the prime consideration in preparing newer materials and devising newer methods of applying them, then it has to be the idea of using a coating to act as a barrier to agents of corrosion. This review shows that the changes in the choices of materials and the techniques for applying them on the surfaces to be protected can be regarded as advances on the materials and techniques used previously. It would be both informative and useful to provide a hierarchy of materials and methods of application based on the effectiveness and durability of the coatings. However, this would require comparison studies involving a range of anti- corrosion materials and methods under identical weathering conditions. In the meantime, the idea that a combination of materials may perform better than a single material has resulted in the use of composites in general and nanocomposites in particular. This is very similar to the use of a cocktail of medicines to treat an ailment. For reasons given in the previous section, nanocomposites may prove to be the materials of choice for inhibition of corrosion.

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