International Journal of
Emerging Research in Management &Technology
ISSN: 2278-9359 (Volume-5, Issue-1)

Research Article | **January 2016**

A Review Article on Green Inhibitors of Reinforcement Concrete Corrosion

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Abstract:

Premature deterioration of reinforced concrete due to corrosion is a big problem worldwide as it leads to a significant loss of life and economy. Despite of several techniques, suitable methods to protect reinforced concrete from premature collapse is still a challenge. To combat this problem, use of corrosion inhibitors is one of the best methods considering its cost effectiveness as well as lower toxicity. A corrosion inhibitor is a chemical substance, when added in a suitable concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Considering the importance of corrosion inhibitors, researchers are dedicated to develop new inhibitors using several techniques like novel laboratory synthetic methods, mixing of different inhibitors in a particular ratio to enhance their anticorrosion property, and most importantly extracting them from natural resources i.e by incorporating green inhibitors. Green inhibitors are ecofriendly and cost effective. They create minimum natural hazards to the environment. In reinforcement corrosion green inhibitor extracts are either added to concrete admixture or applied on the surface of hardened concrete in the form of a protective layer to prevent ingress of destructive species like oxygen, carbon-di-oxide, sulfate, chloride, and moisture. Their effectiveness is solely dependent on the property of their chemical constituents. In this review article we have specifically highlighted green inhibitors which are increasingly being used against reinforcement corrosion including their effectiveness in concrete environment with special mention to their mechanism of actions.

Key Words: Rebar, Concrete, Corrosion, Inhibitors, Green inhibitors.

I. INTRODUCTION

Corrosion inhibitors are one of the best methods to combat premature falling of building materials, worldwide due to reinforcement corrosion under harsh environmental conditions. Environmental concerns require corrosion inhibitors to follow certain rules. Most of the conventional inhibitors that have been developed till today are non-biodegradable and highly toxic to human beings. Inhibitor biodegradation or biological oxygen demand (BOD) which is a measure of inhibitor persistence duration in the environment should at least be 60%. Recent studies have shown the ability of several inorganic and synthetic organic inhibitors to cause temporary or permanent damage to human organs, such as kidney or liver. Abdulrahman and Ismail measured inhibitor's toxicity LD_{50} and LC_{50}. The former was a chemical which was considered lethal for 50% of animals in 24 h exposure time and latter also had lethal properties in air or water and was known to kill 50% of test population. These studies have clearly indicated the hazardous effects of most of the inorganic or synthetic organic inhibitors and also their detrimental effects on the environment, which have compelled and motivated researchers to shift their focus to develop cheap, non-toxic and environment friendly corrosion inhibitors [1]. Over the years numerous studies have shown the effectiveness of green inhibitors against the corrosion of various steel types especially under acidic environment. But rebar embedded into concrete is under alkaline environment of pH nearly 12-13. So, this review is particularly focused on green inhibitors active in simulated alkaline environment of concrete to protect reinforced bar from its premature deterioration.

II. GREEN INHIBITORS

Most of these eco-friendly inhibitors are usually extracted from aromatic herbs, spices and from seeds, leaves or barks of medicinal plants, collectively termed as green inhibitors. These extracts are admixed to the concrete slabs in different concentrations. The steel reinforcements are embedded into these concrete blocks. The natural constituents of these extracts contain N, O, and S containing hetero cyclic macromolecules, which are reached to the steel surface by diffusion and adsorbed at the steel concrete interface by electronic interaction with the metal and metal oxide. There they form protective layers to repeal water molecules and inhibit ingression of destructive species like Cl^-, SO_4^{2-}, and CO2 which are responsible for the depassivation of steel.

A. Bambusa Arundinacea

One of the most important hydrophobic green plant inhibitor to repassivate the chloride induced corrosion of steel was extracted from Bambusa arundinacea. One of the earlier studies by Abdulrahman A. S. et al. first established Bambusa arundinacea as an effective mixed type corrosion inhibitor for steel reinforcement in concrete, when it is added to fresh concrete. In fact the polarization resistance, high concrete resistivity and chloride binding property by double layer capacitance data have shown its ability to inhibit the initiated corrosion of steel embedded into chloride contaminated concrete even better than calcium nitrite inhibitor. Further study by S.A. Asipita et al. to compare the inhibitor efficiency of Bambusa arundinacea leaf extract to that of two well established and effective corrosion inhibitors, calcium nitrite and ethanolamine showed that the pore blocking ability of Bambusa arundinacea extract in chloride contaminated concrete was far better than both of these two conventional inhibitors [1]. The surface analysis by FESEM (Figure 1-5) attributed to the strong hydrophobic effect of Bambusa arundinacea that facilitates the formation of a product layer of two high valent oxides (Fe_2O_3 and Fe_3O_4) adherent to the steel surface [1,2]. Moreover, the lower value of double layer capacitance (C_{dl}) in presence of Bambusa arundinacea was due to its strong adsorption parallel to the metal surface which led to reduce the number of surface active sites available for chloride ion ingression [1].

B. Vernonia Amygdalina
The inhibitor efficiency of Vernonia amygdalina (bitter leaf) extract on the corrosion behavior of embedded mild steel rebar in concrete was investigated by C.A. Loto by electrochemical potential measurement, pH and gravimetric (weight loss) methods. The test results revealed the inhibitor efficiency as well as pH changing property of the leaf extract.Corrosion potential measurement of the mild steel rebar embedded into concrete in presence of different concentrations (25%, 50%, 75% and 100%) of the inhibitor had shown maximum corrosion inhibition of the reinforcement by 25% inhibitor concentration with maximum positive potential value. On the other hand weight loss experiment also supported the potential measurement analysis. In this experiment weight loss was determined to be minimum, 0.1 with 25% inhibitor concentration. As the inhibitor concentration increased, weight loss of the rebar also increased. Both these experiments signified higher effectiveness of the inhibitor with lower concentration. Further characterization of the leaf extract by IR spectroscopic techniques and quantitative analyses had shown that the plant extract contained alkaloids, saponin and tannin. These chemical constituents of bitter leaf were expected to be strongly adsorbed to the surface of the embedded steel and thus enhancing its corrosion resistance in corrosive environments [2, 3]. Another study was conducted on carbon steel reinforcement in concrete exposed to chloride laden environment in presence of different inhibitors to compare their inhibitor efficiencies. Excellent positive corrosion potential (E_{corr}) of +95mV was obtained for Vernonia amygdalina extract which was even more than calcium nitrite within 70 days of immersion. From weight loss experiment inhibitor efficiency of 96% was derived for sodium nitrite followed by 91% for calcium nitrite with 2%v/v inhibitor concentration. However, vernonia amygdalina exhibited inhibition efficiency of 75% with 6%v/v inhibitor concentration [4]. All these experimental findings established vernonia amygdalina extract as a naturally obtained eco-friendly substituent for most of the commercially available inhibitors.

C. Chamaerops Humilis L. Leaves
The methanolic extract of Chamaerops humilis L. leaves was reported to effectively decrease the reinforcement steel corrosion enhancing the stability of the oxide film formed in alkaline solution and assured the formation of a more compact protective layer on the surface of the metal. The effect of the extract on the oxide film protective property on the reinforcement steel surface in alkaline medium (pH > 13) was investigated by electrochemical techniques. Using polarization resistance the inhibition efficiency was found to be 42% with 0.5g/L of inhibitor concentration at 25°C. Nyquist plots from EIS study for reinforced steel (R.S) electrode showed as the inhibitor concentration increased the diameters of the capacitive loops hanged, indicating an improvement of protective performance of surface film formed on electrode surface, and thus activity of reinforced steel was effectively reduced [5].

D. Morinda Lucida
Some recent studies have shown the inhibitory effect of leaf-extract of Morinda lucida on the corrosion-degradation of steel-reinforced concrete in 3.5% NaCl i.e. in simulating saline/marine environment using electrochemical analysis according to ASTM G16-95 R04. The optimal inhibition efficiency of Morinda lucida extract ($\eta = 95.64 + 1.50\%$) was found in presence of 0.1667% admixture concentration [6].

E. Tobacco
Tobacco plants produce 4,000 chemical compounds including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen containing compounds (nicotine), and alkaloids which may exhibit electrochemical activity, such as corrosion inhibition property. In an interesting study C.A. Loto and his coworkers had taken extracts of both tobacco leaves and different parts of kola tree (leaves, nuts and bark) and applied them in different concentrations to facilitate the formation of inhibitive film on the embedded rebar. Some previous work on extracts of tobacco had shown it to be effective in preventing the corrosion of steel and aluminium in saline environments; and in fact, exhibiting a greater corrosion inhibition effect than chromates. The investigation further added the combined effect of a mixture of both the extracts which was clearly better than the effect of kola leaves extracts alone, but not as good as the corrosion performance of the tobacco extract alone [7].

F. Rhizophora Mangle L Bark-Extract
Some recent studies reported that bark-extract of Rhizophora mangle L plant inhibited the corrosion of steel reinforcement embedded into concrete in acidic environment (0.5 M H_2SO_4). Tannin was found to be a constituent that provided inhibitor efficiency in acidic medium [8, 9]. Like most of the inhibitors it was also admixed to the acidified concrete pore solution. However the mechanism of action has yet not very clearly mentioned in any literature.

III. EFFECT ON CONCRETE PROPERTIES

Apart from showing inhibitor effectiveness against corrosion for steel in concrete, certain green inhibitors also change concrete properties which are equally important to be mentioned in this article. S.A. Asipita et al. reported that Bambusa arundinacea inhibitor increased the strength of chloride contaminated concrete specimen by 30%.when compared with conventional inhibitor like calcium nitrite and ethanolamine [1]. 0.1667% Morinda lucida leaf-extract showed optimal compressive-strength improvement when admixed to the concrete whereas 0.25% extracts exhibited compressive strength reduction relative to the blank samples [6]. In another study Rhizophora mangle L bark extract helped to increase the compressive strength of the concrete under certain inhibitor concentrations [9].

Table 1 Important Constituents of Some Green Inhibitors Used in Reinforcement Concrete Corrosion

Green Inhibitor	**Inhibitory Chemical Constituents**	**Effects on Concrete Properties**
Bambusa arundinacea	Not reported	Increase concrete strength
Vernonia amygdalina	alkaloids, saponin and tannin	No effect on concrete property
Methanolic extract of Chamaerops humilis L. leaves (MECHLL)	Lucenin 2 (42%), Dasycarpidan-1-methanol, acetate (ester) (11%), 1, 3-D-5-hexan-2-one-2, 4-dinitrophenylhydrazone (10%) and 9-Hexadecenoic acid (8%)	No effect on concrete property
Morinda lucida	Not reported	Both can increase or decrease concrete compressive strength
Tobacco	terpenes, nicotine, alkaloids	No effect on concrete property
Rhizophora mangle L bark- extract	tannin	Increase concrete compressive strength

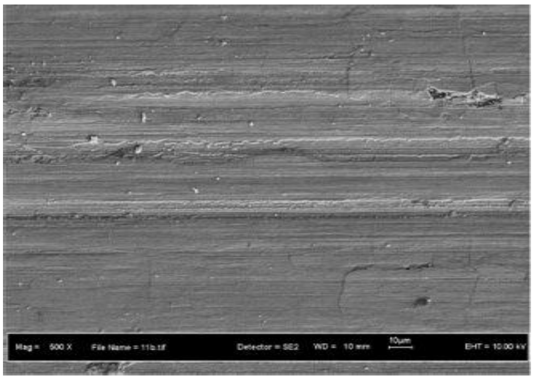

Fig. 1. FESEM of as-received steel specimens

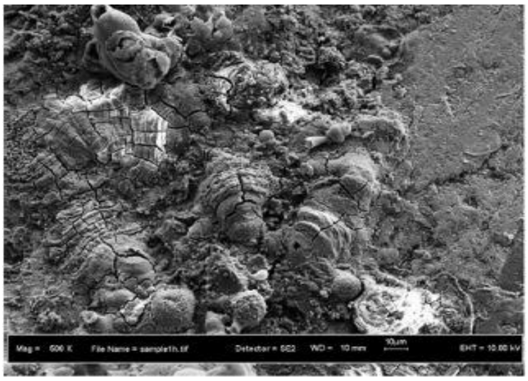

Fig. 2. FESEM of control steel specimen (no chloride)

Fig. 3. FESEM of contaminated steel specimen (1.5% $MgCl_2$)

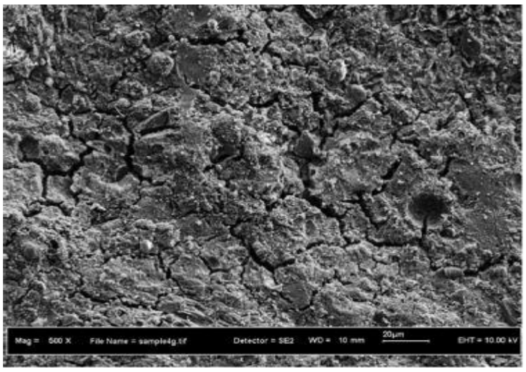

Fig. 4. FESEM of 2% $Ca(NO_2)_2$ additions to steel rebar incorporating 1.5% $MgCl_2$ in concrete

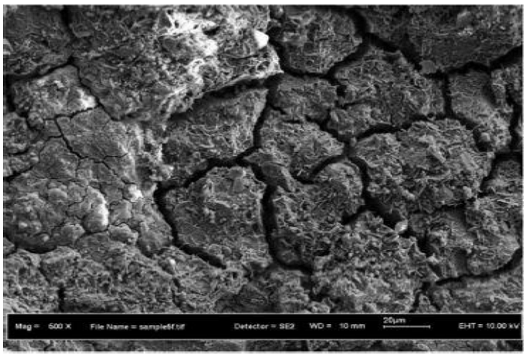

Fig. 5. FESEM of 2% C_2H_7NO additions to steel reinforcement incorporating 1.5% $MgCl_2$ in concrete

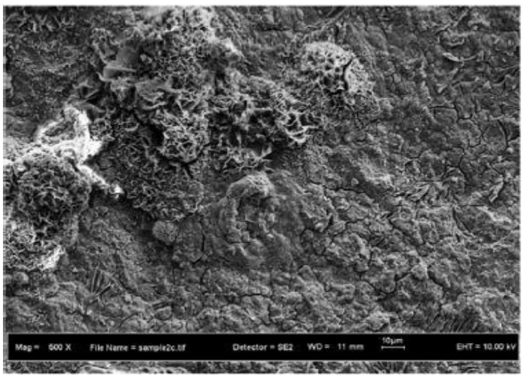

Fig.6. FESEM of 2% Bambusa arundinacea additions to steel reinforcement incorporating1.5% $MgCl_2$ in concrete

IV. CONCLUSIONS

This review is focused on various green inhibitors that reduce corrosion of steel reinforcement embedded into concrete. Green inhibitors create minimum natural hazards to the environment. The study shows that green inhibitors are found to be extremely effective against rebar corrosion especially in chloride contaminated concrete. It is also interesting to find out that some inhibitors changes concrete properties especially its compressive strength while admixed in a particular concentration. But the mechanism of action of these inhibitors contains lot of discrepancies. Hence more research; both theoretical as well as experimental are to be conducted to find out new green inhibitors to determine their inhibitory effects as well as compatibility in concrete environment.

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