INTERNATIONAL JOURNAL OF SUSTAINABLE CONSTRUCTION ENGINEERING AND TECHNOLOGY

VOL. 13 NO. 1 (2022) 1-8

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IJSCET

http://publisher.uthm.edu.my/ojs/index.php/ijscet

ISSN : 2180-3242 e-ISSN : 2600-7959

International Journal of Sustainable Construction Engineering and Technology

Use of Lawsonia Inermis and Sodium Nitrite as Surface Applied Corrosion Inhibitors

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DOI: https://doi.org/10.30880/ijscet.2022.13.01.001
Received 2 September 2022; Accepted 01 March 2022; Available online 16 May 2022

Abstract: This research provides an investigation to measure the rate of corrosion of steel bars coated with organic corrosion inhibitor Lawsonia inermis (Henna) and inorganic corrosion inhibitor Sodium Nitrite ($NaNO_2$) embedded in concrete. Presence of corrosion on the reinforcement bars reduces the bond strength between steel and concrete over a while and excessive corrosion on reinforcement bar can lead to loss of ductility, strength and in extreme cases collapse. Structures like marine structures, sewage pipes, which are prone to damage due to presence of excessive salts, acidic environment, the corrosion rate is accelerated when compared to normal structures, therefore there is need of protecting such type of structures. In previous researches, the corrosion inhibitors were added directly into the mix while preparing the concrete mix and inhibition efficiency was analysed. However, in this case, the corrosion inhibitors are applied to the reinforcing bars itself as the corrosion occurs on the bars and which has proven to be effective. In the present study, the reinforcement bars are coated with Henna paste and Sodium Nitrite paste as corrosion inhibitors. Inhibitors in the form of 2 layers, 4 layers and a combination were used. The beams specimens were cured for 58 days in saline environment. The difference in the corrosion potential is measured by half-cell potentiometer. Results suggested that the specimen with 4 layers of Henna coating had reduced the rate of corrosion by 46% when compared to original sample. Also, specimens with 2 coats of Henna and 4 coats of Henna and sodium nitrite showed better corrosion inhibition efficiency.

Keywords: Corrosion, inhibitors, Half-Cell Potentiometer, organic inhibitors, inorganic inhibitors

1. Introduction

In today's age, the primary construction material with most versatility is concrete. It is used for construction work in most countries all over the world. Concrete, a combination of sand, gravel, water and cement, wherein the cement is the main constituent of concrete as it the binding agent. But, the main drawback of concrete is that it is weak in tension. For the concrete to resist tensile stresses, reinforcement bars are introduced in the concrete. However, steel reinforcement bars are susceptible to corrosion which is its major shortcoming. Due to the chloride attack, acid or sulphate attack, degradation of reinforcement in concrete occur which leads to the breakdown of the passivation film surrounding the reinforcement and makes the steel vulnerable to corrosion. Corrosion due to chloride attack on steel reinforcement bars

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in concrete is more dangerous because chloride ion promotes and accelerates the corrosion reaction by forming an intermediate product but without the chloride ion being consumed through the reaction process (Okeniyi et al. 2018). Contaminated water, aggregate and admixtures containing chlorides are some of the ways the chlorides get into the fresh concrete. Similarly, in the hardened stage, chlorides get introduced through de-icing salts and structures exposed to the marine environment (Borade & Kondraivendhan 2018). Corrosion causes the concrete to swell which causes spalling, cracking which ultimately leads to the destruction of the structures affecting the serviceability and performance of structures. Various methods have been developed to prevent corrosion. Cathode protection, alternative reinforcement, applying inhibitor to the concrete surface, applying inhibitor to the reinforcement, corrosion inhibitors electrochemical methods are some of the methods to counter the corrosion. Some other systems to reduce or delay the corrosion initiation periods are the use of pozzolanic, supplementary cementitious materials, admixtures for concrete and epoxy coating for steel (Borade & Kondraivendhan 2018, Ann & Song 2007). Among all the methods, use of corrosion inhibitor is the most sought after because it is convenient, cost-effective and provides excellent corrosion resistance effect. The action of a corrosion inhibitor depends on the ability of the inhibitor to react and adsorb on the metal surface to form a protective layer against aggressive compounds.

The inhibitors resist the corrosion process by increasing the anodic or cathodic polarization behaviour, reducing the movement of ions of the metallic surface and increasing the electrical resistance of the metallic surface. The addition of corrosion inhibitors in concrete has gained immense popularity in recent years due to low cost and easy applications. The classification of inhibitors is based on the mechanism of protection, if it affects the anodic reaction, cathodic reaction or both and they are called as anodic, cathodic and mixed inhibitor respectively (Song & Saraswathy 2007). Presence of anodic inhibitors redirects the corrosion potential towards the cathode and in turn increases the polarization of the anode. On the other hand, cathodic inhibitors help to reduce the corrosion rate. Use of mixed inhibitors slows the flow of electrons at both anode and cathode, hence increases the protection (Zhou et al. 2012). Cr(VI) compounds are the most commonly used inhibitors because they are cheap and effective (Pourriahi et al. 2014, Finsgar et al. 2009) However, these compounds are highly toxic which can be carcinogenic and also pollute the environment (Mosher et al. 2006, Zhong et al. 2010). For the alternative, use of green, environmentally friendly extracts from natural plants is encouraged (Ismail et al. 2015). The inhibitive action of henna extract (Lawsonia inermis) and its main constituents (lawsone, gallic acid, a-D-Glucose and Tannic acid) on corrosion of mild steel in 1 M HCl solution through electrochemical techniques and surface analysis was also a point of research (Ostovari et al. 2009). Other plant extracts such as extracts of Chamomile, Halfabar, Black Cumin and kidney beans were studied for their inhibitive properties in acidic medium (Abdel et al. 2006). Similarly, marine alga (Spirulina platensis) was studied for its potential to control corrosion of mild steel in acid media (Kamal & Sethuraman 2010). Spirulina is used as an antioxidant for the production of nutraceuticals and also in food industries due to rich protein content (Wang & Zhao 2005, Diraman et al. 2009). Despite the good performance of plant extracts as inhibitors, there is limited research on the effectiveness of surface applied inhibitors directly on reinforcement itself. Hence, to address this gap, the study on the surface application of Lawsonia inermis and Sodium Nitrite onto the reinforcement bars embedded in concrete is conducted. However, more research works are necessary to ascertain the effectiveness of any kind of inhibitor. Corrosion inhibitor that had been effective on one material in the given corrosive environment may not necessarily be effective in the same environment or on the same material in a different environment (Soylev & Richardson 2008, Okeniyi et al. 2007).

2. Methodology

In this research, two corrosion inhibitors are used namely Lawsonia inermis (Henna) and Sodium Nitrite (NaNO2) which are coated on the reinforcement bars by layers of each inhibitor and mixture of both inhibitors followed by drying. The inhibitors are in powdered form and mixed with linseed oil to make it into a paste. Beams are cast using the coated reinforcement bars and half-cell potentiometer is used to measure the potential difference.
The materials used to prepare concrete are as follows:
Cement: The test on 43 grade OPC cement were performed as per IS 8112:1989, IS 4031 (Part 1): 1992, IS 4031 (Part 4):1988, IS 4031 (Part 5):1988. The normal consistency was found to be 28%. Initial and final setting time was 54 min and 386 min respectively. The fineness of cement was 4% and specific gravity was 3.10. Fine Aggregates: The test on Fine Aggregate were performed as per IS 383:2016. River sand conforming to grading zone II was considered as fine aggregates. The specific gravity was found to be 2.66. The water absorption was 1.41%. Fineness modulus was 2.73 and silt content was 3.26%. **Coarse Aggregates:** The nominal size of the aggregates was 20 mm. Testing on aggregates was in accordance with IS 2386:1963. Crushed type aggregates were used. The specific gravity was 2.69. The water absorption was 0.9%. Conplast SP 430 was used as superplasticizer. 10mm diameter reinforcement of 700mm length was used. Henna powder and sodium nitrite were used as a corrosion inhibitor.

Henna leaves are easily available in India and can be cheaply crushed and make into powder form. Likewise, sodium nitrite is a popular inorganic corrosion inhibitor that is widely used. The mix design was prepared as per IS 10262:2019. The mix ratio obtained was 1:1.8:2.44 with w/c 0.43 and superplasticizer 0.5%. The slump obtained was 30 mm. In this research work, 14 beams of size 700x150x150 mm were prepared for casting. Reinforcement bars of grade Fe 500 was used having length 700 m. Each bar was properly cleaned and coated with henna paste and sodium nitrite paste. Also, the mould was properly oiled such that it is easier to remove the beams after casting for 24 hrs. A beam specimen was casted having two reinforcement bars at top and two bars at bottom with 25mm cover. The beams were demoulded and placed in 3.5% NaCl curing solution after 24 hours.

Workability test for fresh concrete and compressive strength test for hardened concrete was performed. Also, the half-cell potentiometer test was used to measure corrosion. As per IS 1199:1959, the workability was determined by performing slump test of concrete. The compressive test was performed accordance to IS 516:1959. Cubes of size 150x150x150 mm were prepared. A total number of 12 cubes were cast- 6 cubes for 7 days and 6 cubes for 28 days. The moulds were properly cleaned and oiled. The cube specimens were prepared as per IS IS 516:1959. The cubes were then kept in steam curing tank (27°C) for 28 days for curing. After 7 days of curing, the compressive strength of 6 cubes were evaluated as per IS 516:1959. The 28 days compressive strength of the remaining cubes were obtained. The corrosion measurement was done using Half-cell potentiometer.

2.1 Corrosion Measurement

The half-cell potentiometer is used for corrosion measurement having $CuSO_4$ as the reference electrode. The readings are given in mili-Volts. The voltage and the corrosion potential are directly proportional to each other. After 28 days, the measure of potential difference was done at a gap of 15 days till 58 days, while the samples were cured in sodium chloride water. The results of half-cell potentiometer for casted samples cured in saline environment without coated bars are shown in table 1 and Fig. 1 respectively. Tests were done on materials, fresh concrete and hardened concrete.

Table 1 - Half-Cell Potential of control specimen (mV)

No. of Days	28	43	58
Bar 1	-419	-601	-811
Bar 2	-418	-598	-799
Bar 3	-405	-604	-805
Bar 4	-407	-609	-807
Bar 5	-413	-600	-798
Bar 6	-415	-597	-791
Bar 7	-412	-603	-810
Bar 8	-416	-608	-813

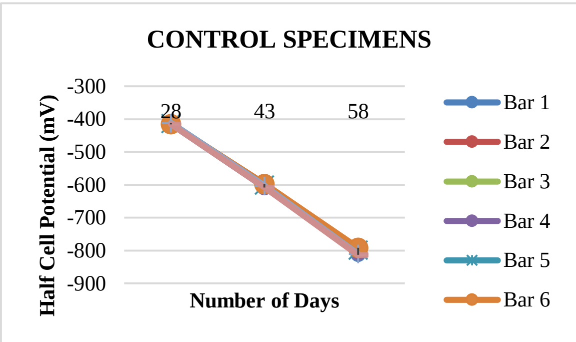

Fig. 1 - Half-Cell Potential of control specimens

Fig. 1 indicates that the corrosion in the control specimen without any coating is increasing linearly. Table 2 shows the comparison of average half-cell readings of 2 and 4 coated bars with Henna.

Table 2 - Average Half-Cell Readings of 2 and 4 coated bars with Henna

Number of Days	Henna 2 coats	Henna 4 coats
	Half Cell Potential(mV)	
28	-263	-239
43	-400	-339
58	-502	-430

Fig 2. shows the comparison between the average half-cell potential readings of 2 and 4 coated bars with Henna.

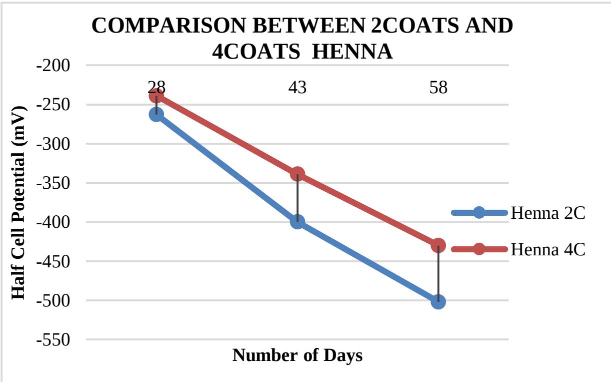

Fig. 2 - Comparison of Half-Cell Potential between 2 and 4 coated bars with Henna

As it can be concluded from Fig. 2 that 4 coats of henna coated specimen show better protection against the corrosion than 2 coats of the henna coated specimen. Table 3 shows the average half-cell readings of 2 and 4 coated bars with $NaNO_2$.

Table 3 - Average Half-Cell Readings of 2 and 4 coated bars with $NaNO_2$

Number of Days	$NANO_2$ 2 coats	$NANO_2$ 4 coats
	Half Cell Potential(mV)	
28	-445	-484
43	-585	-638
58	-643	-799

Fig 3. shows the comparison between the half-cell potential readings of 2 coats and 4 coats of $NaNO_2$.

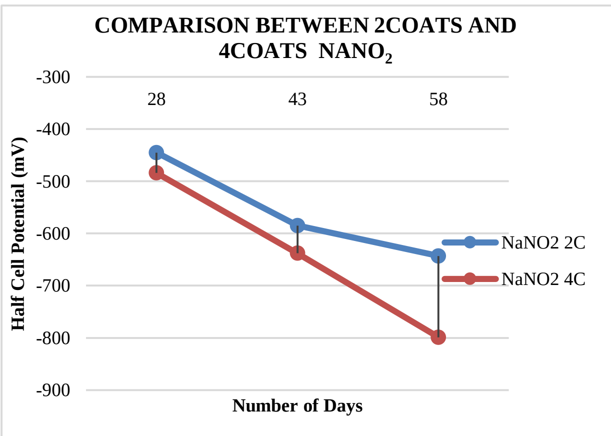

Fig. 3 - Comparison of Half-Cell Potential between 2 and 4 coated bars with $NaNO_2$

Fig. 3 illustrates those 2 coats of $NaNO_2$ coated specimen shows better protection against the corrosion than 4 coats of the $NaNO_2$ specimen. Table 4 gives the average half-cell readings of 2 coats and 4 coats of Henna and $NaNO_2$ and Fig. 4 shows the comparison between 2 coats and 4 coats of Henna and $NaNO_2$.

Table 4 - Average Half-Cell Readings of 2 coats and 4 coats of Henna and $NaNO_2$

Number of Days	Henna and $NaNO_2$ 2coats	Henna and $NaNO_2$ 4coats
	Half Cell Potential(mV)	
28	-384	-364
43	-548	-516
58	-722	-714

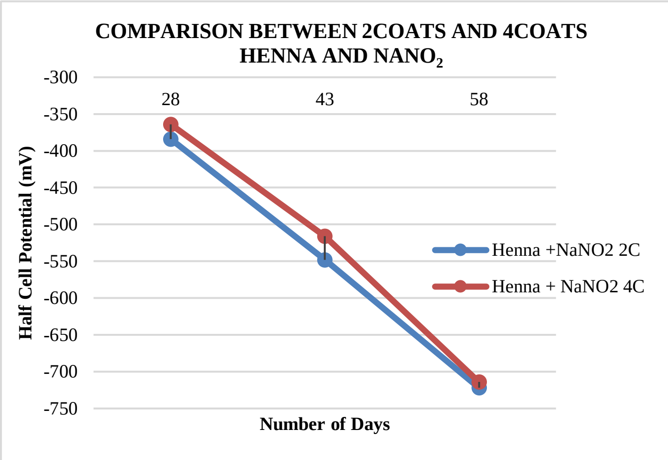

Fig. 4 - Comparison of Half-Cell Potential between 2 coats and 4 coats of Henna and $NaNO_2$

As evident from Fig. 4, henna plus $NaNO_2$, 4 coats provide slightly better protection against corrosion than 2 coats Henna plus $NaNO_2$. As evident from the research, the potential values are changing with respect to the various coating provided on the surface of the reinforcement bars which are embedded in concrete. It is evident that by the provision of coating, the rate of corrosion is delayed in the reinforcement bars. This is due to the fact that the water that ingresses through the cracks present in concrete does not reaches the reinforcement surface and thereby delaying the corrosion process. Table 5 shows the average potentials of all the specimens.

Table 5 - Average potential of specimens(mV)

Number Of Days	Control	Henna 2coats	Henna 4coats	$NaNO_2$ 2coats	$NaNO_2$ 4coats	Henna+ $NaNO_2$ 2coats	Henna+ $NaNO_2$ 4coats
	HALF CELL POTENTIAL (mV)						
28	-413	-263	-239	-445	-484	-384	-364
43	-602	-400	-339	-585	-638	-548	-516
58	-798	-502	-430	-643	-799	-722	-714

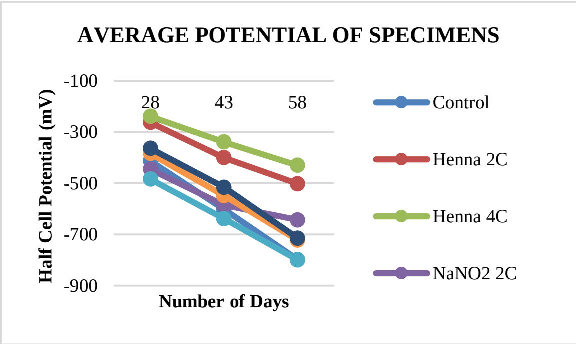

Fig. 5 - Average potential of specimens

In Fig. 5, the average potential difference of all the specimens is plotted. It is clear from the graph that the specimen with 4 coats of Henna paste shows less potential value i.e. the corrosion is less on bar coated with 4 coats of Henna as compared to other bars.

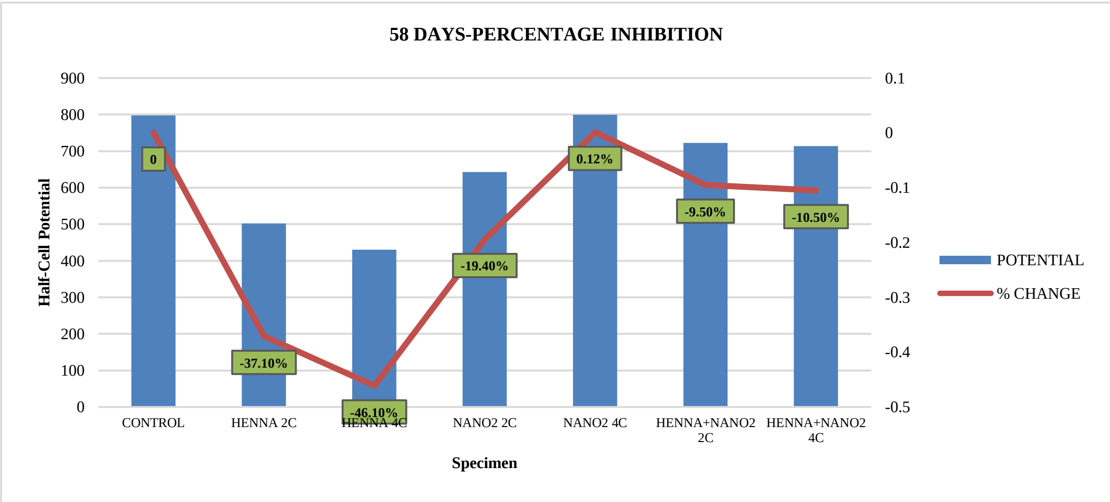

Fig. 6 - 58 days' percentage inhibition readings

Fig. 6 shows the 58-day percentage inhibition of bars specimens including the 58-day half-cell potential value and the percentage change. From the graph, it is clear that specimen coated with 4 layers of henna shows the maximum % change i.e., 46.1% efficiency. Also, the percentage of inhibition is described in Table 6.

Table 6 - Percentage inhibition

Specimen	Control	Henna 2c	Henna 4c	$NaNO_2$ 2c	$NaNO_2$ 4c	Henna+ $NaNO_2$ 2c	Henna+ $NaNO_2$ 4c
Half Cell Potential(mV)	-798	-502	-430	-643	-799	-722	-714
% Change	0	-37.1%	-46.1%	-19.4%	0.12%	-9.5%	-10.5%

Table 6 indicates the average half-cell potential value of 58-day corrosion inhibition and the percentage change between each coated specimens and control specimens which also indicates the corrosion efficiency.

3. Conclusion

In conclusion, the extensive use of corrosion inhibitors to prevent the formation of rust is undeniable. Protection of bars through corrosion inhibitors is quite efficient, convenient and cost-effective. Among the inhibitors used, the organic corrosion inhibitor surpasses the inorganic inhibitor on performance and efficiency. Based on the research, it can be concluded:

- Organic inhibitor showed a much better result as compared to inorganic inhibitor i.e. 2 coats of the henna coated specimen showed 37% inhibition efficiency as compared to 2 coats of NaNO2 (19.5%). Similarly, 4 coats of henna showed 46% inhibition efficiency whereas 4 coats of NaNO2 increased the corrosion activity by 0.12%.
- Bar specimens with 2 coats and 4 coats of Henna paste showed the best inhibition efficiency as compared to the control specimens i.e. 37% and 46%.
- The efficiency of 19.5 % inhibition was achieved with 2 coats of NaNO2 compared to control specimen.
- Also, Bar specimen with 2 coats and 4 coats of Henna and NaNO2 showed 9.5% and 10.5% inhibition efficiency respectively.
- Half-cell potentiometer is an effective method to determine the corrosion for a reinforced concrete structure.

To summarize, the organic inhibitor used in the research work i.e. Lawsonia inermis surpasses the inorganic inhibitor i.e. Sodium nitrite and proves to be a better corrosion inhibitor. Crack formation occurs frequently in concrete and results in decreased strength and hence durability of concrete. To attain and maintain the optimum durability of concrete, repair of these cracks is vital, but the costs involved for this repair are usually high. Providing a coating of Lawsonia Inermis will reduce the rate of corrosion and enhance the structure life, which in turn proves to be a reliable and cheaper solution to enhance the durability of the structure.

Acknowledgement

The authors wish to thank the Department of Civil Engineering, School of Engineering and Technology, Sharda University, to provide infrastructure and ample resources needed for the work done.

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