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Investigating Characteristics and Corrosion Treatment of Industrial Cooling Water by the Passivation Process using Lawsonia Inermis

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Abstract

A cooling water system plays a major role in the manufacturing activities and in controlling the internal environment of an industry. The cooling water must carry protective inhibitors to surfaces that require protection. In the present study, the performance and efficiency of the passivation process in a cooling water system using Lawsonia Inermis (Henna) was investigated. The wastewater samples were taken from two industries; Flexsys Chemicals (M) Pvt. Ltd and Cargill Palm Products Pvt. Ltd, Malaysia and their quality were analyzed in terms of total dissolved solids (TDS), chemical oxygen demand (COD), total organic carbon (TOC), turbidity, nitrite, iron, lead and pH. Results showed all the parameters measured contributed to the corrosion in the open circulating cooling systems. However, the water quality results complied with the parameter limits stated in the Standard B of the Environmental Quality Act (1974). In addition, the results showed there is a potential for Lawsonia Inermis to be applied as an efficient inhibitor for corrosion. The inhibition efficiency increased (17.19%) when Lawsonia Inermis concentration was increased gradually from 20 to 200 mL. Besides, the surface analysis on corroded nails showed color change from yellowish-brown to grey which was the original color of the nails.

Keywords: Antioxidant, corrosion, industrial cooling water, lawsonia inermis, passivation process.

Introduction

At present the Malaysian Government has focused its attention on improving and upgrading the existing water system and facilities, which are considered inadequate in terms of the treatment efficiency. In many cases, the quality of the effluent does not meet with the effluent standards required by the authorities. Untreated and inadequate treatment of wastewater has been the major factor in causing severe pollution in rivers and at shoreline areas due to the rapid industrialization and urbanization programmes since the 1980s. The polluted water in the rivers and surrounding seas has consequently increased health hazards for the Malaysian population who live in these areas and depend on these waters. The Government's latest policy is to change the numerous poorly equipped sewerage treatment plants to fewer, larger and more efficient centralized wastewater treatment plants to meet the effluent standard[1]. In the industrial plants, a cooling water system plays a major role in the manufacturing activities and in controlling the internal environment. Naturally occurring impurities in the water cooling system can leave the equipment vulnerable to fouling, scale formation, corrosion or rusting and growth of microorganisms. If left uncontrolled, any of these conditions can cause a loss of efficiency and shorten the life-span of the equipment. This problem will also involve, costs, time, reduce production and cause other aggravation[2].

Corrosion is an electrochemical process by which a metal returns to its natural state where it forms oxide when in contact with oxygen. The major factors that influence corrosion are chlorine, total dissolved solid (TDS), conductivity and temperature. Chlorine and conductivity can be related to TDS or total suspended solid (TSS) to form corrosion. This is due to the presence of chlorine in water which reacts with the moisture in the air to produce hydrochloric and hypochlorous acids that corrode steel. The higher the TDS or TSS values, the higher would be the conductivity of water and in turn the probability for corrosion to occur would also be higher[3].

Passivation is a process of making a material "passive" in relation to another material prior to using the materials together[4]. Passivators act as anodic inhibitors. They prevent the corrosion of the metal by shifting it in a "noble direction", where they themselves get reduced at the anodic sites on the metal surface producing the current density necessary for passivation[5].

The problems of scaling and corrosion are common phenomena in the industrial water cooling systems especially in the open cooling systems. This study was performed with the main aim of measuring water quality and metal content from wastewater samples from cooling tower. Moreover, performance of the passivation process using *Lawsonia Inermis* (Henna) (a natural antioxidant) on the corrosion of mild steel was also investigated.

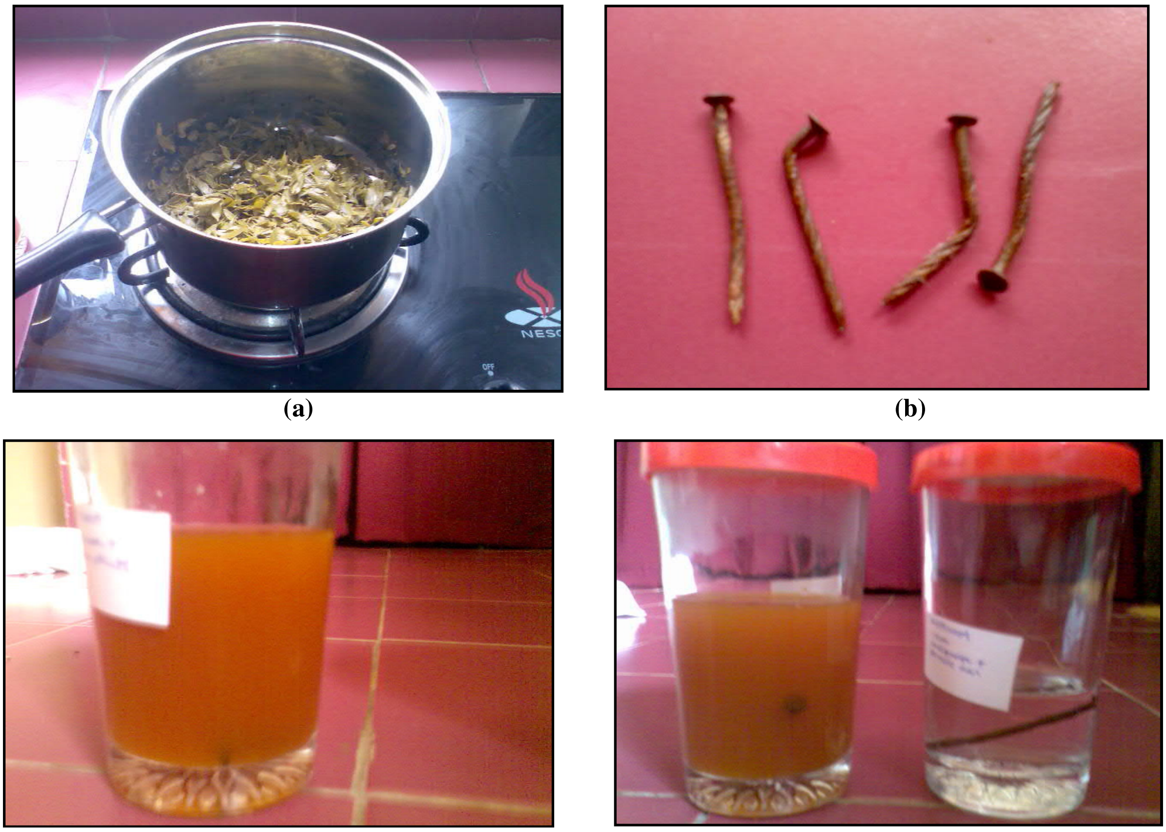
Material and Methods

Industrial cooling water: The present study was carried out at the Gebeng Industrial Park, Kuantan, Malaysia. The region was selected due to its rapid industrial growth and numerous factories that are equipped with cooling towers. In addition, there are large amount of wastewater being discharged daily into the nearest river and lake ecosystems that no longer support the full biological diversities. Other than that, Gebeng is the nearest petrochemical industrial area to Universiti Malaysia Pahang (UMP), where the chemical analysis was performed. Wastewater samples were taken from two industrial plants that use cooling tower; Flexsys Chemicals (M) Pvt. Ltd and Cargill Palm Products Pvt. Ltd., Malaysia.

Chemical analysis: The water samples were collected using plastic bottles at three locations; a) at the basin of the cooling system, b) at the surface area, and c) at an interval of one meter up to three meters of depth. These samples were taken to the laboratory in UMP, for chemical analysis. The laboratory analysis included chemical oxygen demand (COD), total organic carbon (TOC), Iron (Fe), Nitrite (NO_3), and Lead (Pb), all according to Standard Methods[6].

The wastewater quality analysis was based on the Standard B of the Environmental Quality Act (1974). The effluent quality of any discharge from a sewage treatment process into inland water (other than one having an ocean outlet) should meet the minimum requirements of the Environmental Quality Act (EQA) (1974) set by the Environmental Quality (Sewage Industrial Effluent Regulations, 1979).

Natural antioxidants: The second phase of the study was devoted to investigate the corrosion effects on the cooling tower pipes. Accordingly, an attempt was made to examine the treatment performance using a passivation process by natural antioxidants (corrosion inhibitor)[7]. There are several antioxidants that can be obtained in the form of phytonutrients, which are found in nature's whole foods, in fruits and vegetables.



(a) (b)

(b) (d)

Figure-1
Experimental preparation for passivation process; (a) boiled and crushed Lawsonia Inermis, (b) corroded nails used in study, (c) Lawsonia Inermis solution, 1(d) corrode nails immersed in Lawsonia Inermis solution

The deeper the color, the richer the anti-oxidant content would be. Some examples of antioxidants are; red apples, cherries, grapefruit, red grapes, raspberries, red plums, strawberries, tomatoes, watermelons, asparagus, green capsicums, broccoli, cucumbers, green grapes, spinach, cabbage, cauliflower and celery. Henna extract (*Lawsonia Inermis*) was selected in the present study due to its main constituent's (lawsone, gallic acid, α-d-Glucose and tannic acid) that act as an inhibitive on the corrosion of mild steel[8].

Experimental preparation: Initially*, Lawsonia Inermis* was crushed and extracted in hot water for 20 min (figure 1a) and then the required concentration was prepared[8]. The corroded nails (figure 1b) which had the nominal composition of 0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe were used as the mild steel specimens. A corroded nail, 50mm in length and 2.5g in weight was used for the weight loss[8]. The extracted solution of the henna was filtered and the water from the extract allowed evaporating. About 50ml of the wastewater (cooling water) solution was used to immerse the corroded nails (figure 1c and d). The *Lawsonia Inermis* extract had a concentration of 0.2 - 1.2 $g.L^{-1}$ [8].

The experimental study was performed at 27, 40, 50 and 60°C with different concentrations of henna extract. The immersion time for the weight loss was 6 h. The results of the weight loss experiment was from the mean of three runs; each with a fresh specimen and a 50 ml fresh waste water solution. The corroded nails were weighted before and after the immersion period and then the percentage of the Inhibition Efficiency (IE) was calculated using the following equation:

$$IE\% = \frac{W_2 - W_1}{W_2} \times 100 \qquad \text{…………(1)}$$

W_2 and W_1 are the weight loss of the corroded nails in the presence and absence of the inhibitor, respectively[8].

Results and Discussion

The results from this study were presented in two categories; water quality analysis of the industrial wastewater (cooling tower) and treatment using the passivation agent. The results were compared to the standard discharge limit stipulated in the Environmental Quality Act (1974). The comparison was made between the wastewater from the cooling tower and specifications of Standard B. For the passivation process, the performance was evaluated in terms of weight loss and surface analysis of the nails.

Water quality analysis: In this section, results of the wastewater (cooling water) quality analysis from Flexsys Chemicals and Cargill Palm Products industries were presented. The characteristics of the wastewater was evaluated in terms of total dissolved solid (TDS), chemical oxygen demand (COD), total organic carbon (TOC), turbidity, nitrite, iron, lead and pH. Details of the results are given below:

Figure 2a shows the maximum TDS (533 and 541 $mg.L^{-1}$) detected from the wastewater collected from Flexsys Chemicals and Cargill Palm Products, respectively. The TDS concentration for all the experimental period (4 d) complies with the Standard B requirement (1000 $mg.L^{-1}$). It should be pointed out here is that the TDS concentration should be below 1000 $mg.L^{-1}$ since it has the ability to increase the biological oxygen demand (BOD) of the receiving water. Moreover, it also facilitates microorganisms to escape disinfection and could clog soil absorption field in onsite systems. This is of particular concern because some industrial wastewater contains high amounts of salt, dissolved solids that may require expensive pretreatment to prevent harming the microorganisms that are the main agents for treating wastewater[9]. The pH results for Flexsys Chemicals were 7.85, 8.06, 7.96, and 7.97, whereas for Cargill Palm Products it was 3.05, 6.52, 6.77 and 6.97 (Figure 2b). The pH detected was relatively stable (6 - 9) for all the experimental period, except for 15 July. In general, for any wastewater effluent, the pH should be between 6.6 - 7.8 for satisfactory treatment process. Microbial groups involved in treatment process have a specific pH region for optimal growth and values outside this range can be quite detrimental to the process. Therefore, maintaining a suitable and stable pH of the wastewater influent should be a major priority for ensuring efficient treatment performance. The changes in the pH profile for both industries may be attributed by the different properties of the product. Acids and other substances from the industrial or commercial resources may affect the wastewater treatment process[10].

Similar trend was also observed for turbidity analysis for both Flexsys Chemicals and Cargill Palm Products (figure 2c) where it complies with Standard B (less than 35 NTU). The highest turbidity was measured at 31 and 33 NTU for Flexsys Chemicals and Cargill Palm Products, respectively. It was thought that the different measurements of turbidity from both industries were caused by the products they produced. For instance, Cargill Palm Products produces oily substances which may release impurities to the effluent wastewater. The turbidity of a wastewater is not merely associated with TSS, but also due to plankton and other organisms. The turbidity itself is not of a major health concern, however high turbidity can interfere with disinfection and provide a medium for microbial growth. It may also indicate the presence of microbes[9].

The concentration of COD was measured in the current experiment and the results were presented in Figure 2d. It can be seen that the COD concentration was in the range of 83 - 98 $mg.L^{-1}$ (Flexsys Chemicals) and 64 - 100 $mg.L^{-1}$ (Cargill Palm Products). The highest COD concentration measured was 99 $mg.L^{-1}$ and it complies with the standard requirement. In general, COD is the equivalent amount of oxygen required to chemically oxidize the organic matter contained in a known volume of wastewater using a standard test in which a strong oxidant (potassium dichromate) is used. Nearly all the organic material is typically oxidized in this test[9]. COD are non-biodegradable organics which are resistant to biological degradation. For example, constituents of woody plants, such as tannin and lignic acids, phenols, and cellulose, are found in natural water systems and are considered refractory (resistant to biodegradation)[10].

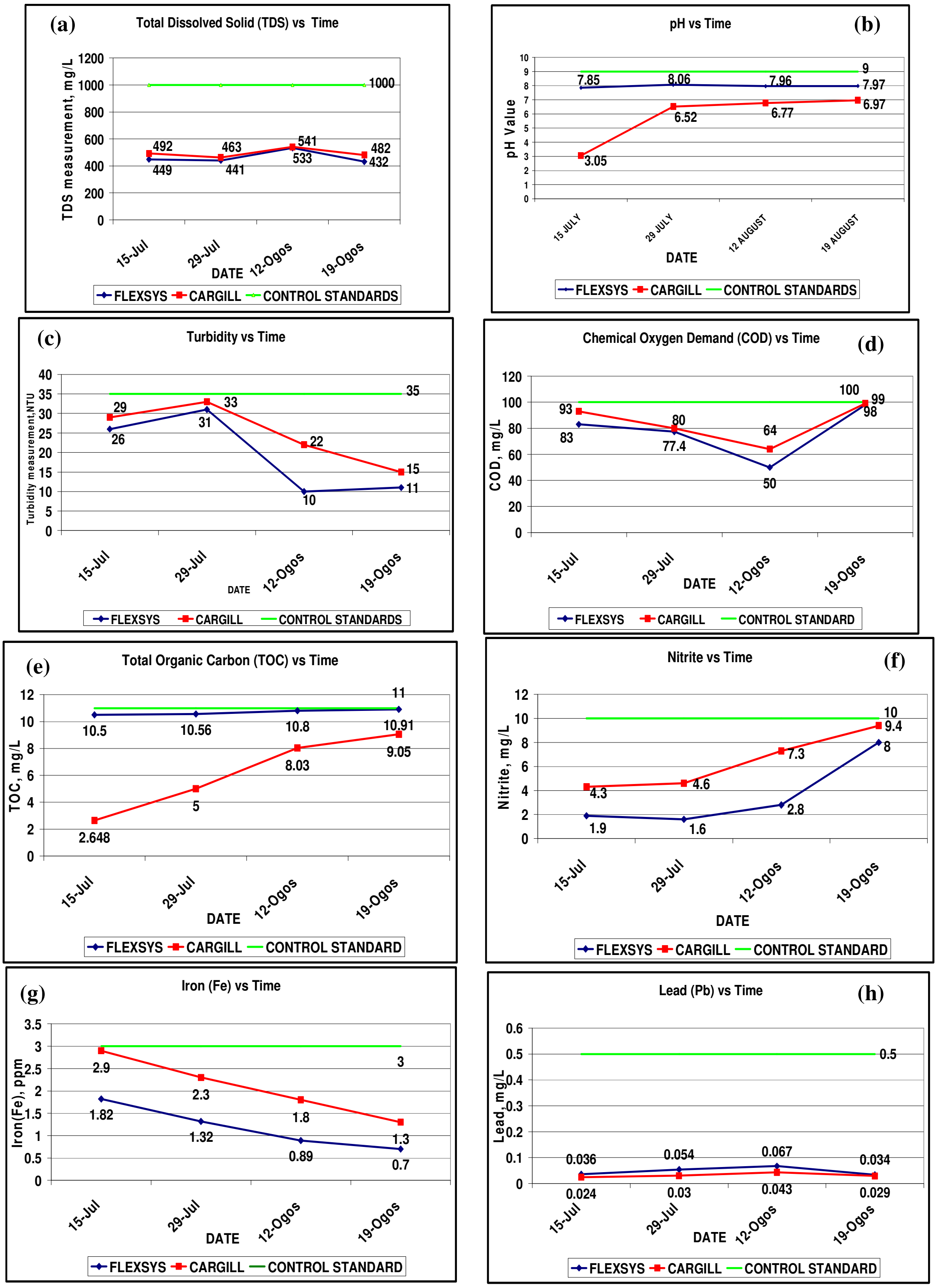


Figure-2
Results of the wastewater quality analysis

Total organic content (TOC) profile for both Flexsys Chemicals and Cargill Palm Products were illustrated in figure 2e. The TOC concentration was between 10.5 - 10.91 mg.L^{-1} (Flexsys Chemicals) and 2.65 - 9.05 mg.L^{-1} (Cargill Palm Products). According to the Standard B of the Environmental Quality Act (1974), it should be below 11 mg.L^{-1}. The presence of this organic matter in wastewater is troublesome for the following reasons: color formation, taste and odor problems, oxygen depletion in streams, interference with water treatment processes, and the formation of halogenated compounds when chlorine is added to disinfect water. When introduced into a treatment process, toxic inorganic compounds may have a serious effect on microorganisms and the treatment performance.

The highest nitrite concentration detected in Cargill Palm Products was at 9.4 mg.L^{-1} (figure 2f). The concentration of nitrites was lower at Flexsys Chemicals (8 mg.L^{-1}). According to the Environmental Quality Act (1974), the nitrite concentration should be below 10 mg.L^{-1}. The higher the nitrite concentration in wastewater, the higher is the potential for fungi growth in the cooling tower as nitrogen is essential for plant growth and easily dissolves in water.

Figure-2g illustrates the Iron (Fe) concentration profile during the experimental period. The Iron (Fe) concentration in Flexsys Chemicals was 0.7 - 1.82 ppm and 1.8 - 2.9 ppm for Cargill Palm Products. The maximum concentration of Iron (Fe) was found in Cargill Palm Products (2.9 ppm). The Iron (Fe) concentration in wastewater should remain under 3 ppm as stated in Standard B of the Environmental Quality Act (1974). In summary, a higher iron concentration may increase the rate of corrosion occurring in steel pipes.

Figure-2h shows that lead detected during the experimental period and it can seen that it was between 0.034 - 0.067 mg.L^{-1} (Flexsys Chemicals) and 0.024 - 0.043 mg.L^{-1} (Cargill Palm Products). The maximum and minimum concentration of lead was 0.067 mg.L^{-1} (Flexsys Chemicals) and 0.024 mg.L^{-1} (Cargill Palm Products), respectively. According to the standard requirement, lead should be below 0.5 mg.L^{-1}. Lead poisoning could cause irritability, aggressiveness, indisposition, migraine, convulsions, fatigue, abdominal pains and genetic mutation.

Performance of passivation process: The inhibitive action of *Lawsonia Inermis* extract and its main constituents on the corrosion of mild steel in wastewater (cooling water) was investigated through the weight loss and surface analysis. The weight was measured (before and after immersion) to determine the inhibition efficiency (IE) by using Equation (1). Table 1 shows the results of the IE for different concentrations of Henna and temperature. At 27°C, the IE was in the range of 0 - 17.19% (at 0, 20, 40, 50, 100, 150 and 200 mL of Henna). However, the IE decreased when the temperature was increased gradually to 40°C (1.17 - 7.42%), 50°C (4.37%) and 60°C (2.5%). These results demonstrated that an increase in temperature had affected the inhibition efficiency.

Table-1

	Inhibition efficiency, IE (%)			
Henna (mL)	27°C	40°C	50°C	60°C
0	0	1.17	1.14	0.39
20	4.28	1.95	1.93	0.93
40	5.86	2.34	1.95	0.97
50	6.75	3.52	2.73	1.42
100	13.95	3.91	3.14	1.67
150	16.22	5.08	3.16	2.34
200	17.19	7.42	4.37	2.54

In addition, the present study also showed that inhibition efficiency of the corrode nail increased at elevated concentration of henna (figure 3). The increase in the corrosion rate was more pronounced with the rise of temperature for the unhibited acid solution. In brief, the presence of inhibitor decreases the corrosion rate.

It was noted that at the beginning of the test the corroded nails were yellowish brown when they were immersed in the absence of an inhibitor (figure 4). At the end of the test, the corroded nails returned to grey (original color). This may be due to the presence of the corrosion inhibitor, deposited into the surrounding water.

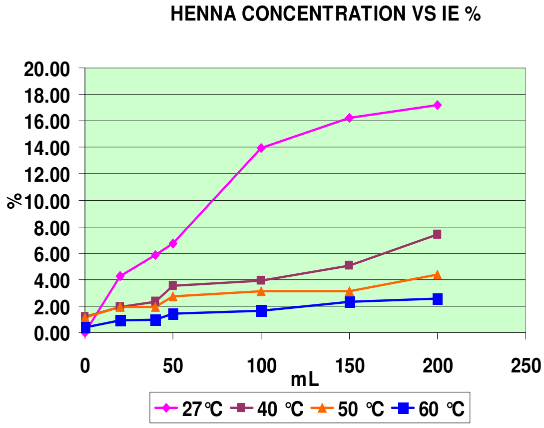


Figure 3
The effect of Henna concentration on inhibition efficiency

(a) **(b)**
Figure 4
Surface of nail; (a) before and (b) after the passivation process

Conclusion

This study has demonstrated that the characteristics investigated for the wastewater from the cooling tower complies with the standard requirement. All the parameters tested (e.g. TDS, Chlorine, Nitrite, COD, Iron, TOC, and Lead) comply with the parameter limit as stated in the Standard B of the Environmental Quality Act (1974).

The performance of the passivation process in the weight-loss measurement analysis showed excellent ability in reducing the corrosion on the surfaces of the nails with a certain inhibition efficiency percentage. The inhibition efficiency (IE) of corroded nails increased when the henna extract concentration was elevated. In addition, the corrosion rate is more pronounced with the rise of temperature. This study also proves that the henna extract can be successfully used to treat corrosion.

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