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COMPARING THE EFFICACY OF SELECT NATURAL AND SYNTHETIC CORROSION INHIBITORS ON COPPER AND IRON

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Abstract

Six corrosion inhibitors were evaluated for their effectiveness at preventing corrosion on copper and mild steel in a short-term experiment lasting two weeks. Half of the inhibitors tested were alcohol extracts of natural products (ginger, garlic, and black pepper), and the others were standard chemical reagents including benzotriazole (BTA), cysteine, and 5-amino-1,3,4-thiadiazole-2-thiol (AMT). Metal coupons of both mild steel and copper were immersed in a 0.007M dilute HCl solution with one of the six inhibitors or a combination of two inhibitors. The pH of each solution was monitored to track the corrosion rate and this method proved to be remarkably sensitive and nuanced, allowing for the subtleties of the decay mechanisms to be determined.

Keywords: Corrosion inhibitors; Benzotriazole; Cysteine; Ginger; Garlic; Black pepper; Copper; Iron

Introduction

After excavation, copper alloy and iron artifacts are at risk of deterioration due to corrosion. Copper alloys that contain chlorides are at risk of developing bronze disease, a cyclic reaction caused by nantokite reacting with oxygen and moisture to form cupric chloride, releasing protons, and recycling chloride ions. To protect metal artifacts from further corrosion, they are sometimes treated with a corrosion inhibitor. Benzotriazole (BTA) is the most commonly used corrosion inhibitor, despite the known risks associated with it being a possible carcinogen and its ineffectiveness at low pH. Research was conducted at the Japanese Institute of Anatolian Archaeology (JIAA) in Kaman-Kalehöyük, Turkiye, to compare potentially safer alternatives to BTA and evaluate their efficacy on both copper and iron. The corrosion inhibitors selected for testing were: BTA, a mixture of BTA and AMT, cysteine hydrochloride, and ginger, pepper, and garlic extracts that had been prepared by grinding the parent organic substrate and extracting the active ingredients with ethanol.

Benzotriazole has been used as a corrosion inhibitor by conservators since 1967 [1]. It is an organic heterocyclic aromatic inhibitor which has the ability to form insoluble complexes as well as being directly adsorbed onto the artifacts, i.e. it inhibits corrosion through both physical and mechanical mechanisms. The three nitrogen atoms in BTA form a complex with metal to create a passive film on the surface which serves as a barrier layer between the metal surface and the atmosphere [2, 3]). One of the drawbacks of BTA is its reduced efficacy in low pH environments [4]. This is an issue when treating objects with active bronze disease since they have a low pH.

5-amino-2 mercapto-1,3,4-thiadiazole (AMT) bonds to copper through the deprotonated nitrogen and sulphur atoms of the thioamide group [5]. Previous research has found that using a

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combination of BTA and AMT was significantly more efficient than using BTA on its own, due to the synergistic effect between the compounds [6]. AMT compliments BTA because it complexes with copper at low pH. Copper reacts with the BTA and AMT to form separate Cu-BTA and Cu-AMT complexes. The combination of BTA and AMT only appears to be used on copper alloy artifacts and has not been previously tested on iron, so an extension of the tests was made to allow for a comparison of the combination treatment between copper and iron.

Cysteine is a sulphur-containing amino acid found in proteins such as keratin. It has limited solubility in water which is why the hydrochloride salt was utilized. The amino (-NH₂) and thiol (-SH) groups in cysteine increase its affinity to copper and enable it to adsorb onto the metal surface, where it forms a stable film composed of copper-cysteine complexes. This film prevents oxygen from reacting with the metal and slows the corrosion process. Cysteine is a zwitterion between pH of 1.91-8.16, meaning it has an equal number of positively and negatively charged functional groups, and it is extremely effective in this range because it is attracted to the cathodic areas of metal [7, 8]. Objects with bronze disease are inherently acidic so it is important that a corrosion inhibitor is effective in environments with a pH as low as two. Research by *M. Gravgaard and J. van Lanschot* [9] found that cysteine was an effective corrosion inhibitor on copper but slightly less effective than BTA.

Ginger root (*Zingiber officinale*) has potential as a corrosion inhibitor due to the presence of phenylpropanoids such as 6-gingerol in its extract. These molecules adsorb onto the metal surface via heteroatoms such as oxygen and block the active sites on the metal [10]. Research thus far has focused on ginger's effectiveness as a corrosion inhibitor on steel rather than copper.

Black pepper (*Piper nigrum*) has been studied as a potential corrosion inhibitor on steel and copper. It was found to be an effective inhibitor for steel in acidic environments [11]. The alkaloid piperine is believed to be the main inhibitor molecule. In the case of copper, piperine functions as a mixed-type inhibitor which suppresses corrosion reactions at both anodic and cathodic sites [12]. For iron, piperine adsorbs onto the metal surface due to interactions between its nitrogen atom and the iron atoms. Pepper extract also increases the activation energy needed for corrosion to occur by a factor of 2.5 [13].

Garlic (*Allium sativum*) has been found to be an effective corrosion inhibitor on both steel and copper. Research by *K. Srivastava and P. Srivastava* [11] found that garlic was more effective in neutral environments than acidic environments for inhibiting corrosion on steel. Similar to ginger and pepper extracts, garlic functions as a mixed-type inhibitor that slows reactions at both anodic and cathodic areas. The compound diallyl trisulfide (DATS) is believed to be responsible for the inhibition mechanism on copper since the compounds adsorbed on the copper surface contain sulphur [14]. DATS molecules replace water molecules on the copper surface, thus forming a barrier film which prevents the corrosion reaction from taking place [14]. Allium is believed to be responsible for the inhibition mechanism on the surface [15, 16].

Experimental part

Materials

Copper coupons were made by cutting a 0.07cm thick copper sheet into 3cm squares. Pre-cut mild steel coupons (5.1cm squares, 0.31cm thick) were purchased from a metal supply store before traveling to Turkey. The mild steel coupons had a dark blue-black mill scale on their surface. Each coupon was weighed and degreased by immersion in acetone before starting the experiment. Twenty-eight coupons were used for each metal, with four coupons used for each of the six corrosion inhibitors as well as the control group.

A stock solution of .007M HCl was prepared by adding 1.0mL of 30-33% HCl to 5L of distilled water. This stock solution was used to prepare all of the experimental solutions, since

the HCl would induce corrosion in the metal coupons. The pH of this stock solution was 2.28, which reflected the pH values of pitting in archaeological metals. Standard solutions of BTA and cysteine were prepared by adding the dry chemicals to known volumes of the HCl stock solution. Research by *S. Golfomitsou and J.F. Merkel* [6] found that a combination of 0.1M BTA with 0.01M AMT was most effective.

Each of the ginger, pepper, and garlic powders were weighed and then immersed in 300mL of ethanol. The flasks were heated in warm water baths to increase the amount extracted into solution. The powders were immersed for three hours and then filtered through Whatman number 1 filter paper. After filtration, the powders were dried at 60 degrees Celsius and then weighed to determine the concentration of each solution in ppm. Each solution was then diluted using the HCl stock solution to obtain a 150ppm solution, which was found by Eid to be the most effective [17].

Methods

Each group of four coupons was placed in a glass beaker and immersed in an inhibitor solution. The control coupons were immersed in the HCl stock solution. After realizing that evaporation was affecting the pH readings, the beakers were covered with parafilm to slow the rate of evaporation. Due to the availability of beakers in the conservation lab, some of the mild steel coupons were separated into groups of two because there were not enough large beakers to fit all four of the coupons together. The cysteine and BTA coupons were placed in large beakers, while the other coupons (Control, BTA+AMT, ginger, pepper, garlic), were placed in smaller beakers in groups of two. The pH of the solutions was monitored periodically for 117-172 hours depending on the solution. The pH meter was temperature compensated using a thermocouple connected to the TPS Aqua pH meter (pH/ORP/oC) and the glass electrode was a VWR model no. W7567287. Since the amount of solution in each beaker varied from 179mL to 571mL, all pH readings were corrected to 500mL to standardize the results. The coupons were dried with acetone after the experiment and visually assessed.

Results and discussion

The main aim of the experiment was to find which corrosion inhibitor solution would result in the least injury to the metal coupons. Owing to the very short nature of the timeframe for the experiment and because of a Covid-19 outbreak, the experimental work was limited. Due to the lack of a 4-figure analytical balance, the traditional weight loss methods for determining which solutions were best for inhibiting decay of metal artefacts was not feasible. Instead, the solution pH was used to determine the rate of corrosion, based on the normal reaction of

 $Fe \rightarrow Fe^{2+} + 2e^{-}$ which is then combined with $2H^{+} + 2e^{-} \rightarrow H_2$ [1]

Since pH is defined by the value of the negative number associated with the log of the hydrogen ion concentration, the consumption of acid by the corrosion reaction outlined above will cause the pH to increase. The rate of corrosion was determined by first dividing the data for each inhibitor into phases based on what was chemically occurring in the solution. Then, the solution pH was plotted against the square root of experimental time in hours in order to linearize the relationship.

Copper

The results from the control experiment with copper in the standard weak hydrochloric acid solution showed a classic initial induction period. During this phase, which lasted for 41 hours, the pH increased at a steady rate of 0.087pH/hr1/2 which is likely to reflect removal of the cuprite patina, since the coupons were not abraded. The induction period was followed by an active corrosion phase that took place over the next 40 hours, during which the pH increased at the rate of 0.88pH/hr1/2 until the increasing pH values ceased due a turning point having

been reached due to evaporation of the solutions, which saw the pH fall at the rate of -0.15 pH/hr1/2 until covers were placed over the open beakers. An illustration of this corrosion phenomenon is shown in Figure 1.



Fig. 1. Plot of Induction, corrosion, evaporation, and passivation (steady pH) phases for cysteine, BTA and the control. The control values for copper are shown as yellow circles with a black border. The last data point (orange) indicates the end of the corrosion reaction for the copper control

The behaviour of the copper coupons in the BTA solution was similar to that of the control (Fig. 1), in that there was an 18-hour induction period in which the pH increased at the rate of 0.02 pH/hr1/2, or about one quarter the rate of the control, which indicated that there was a strong inhibition of the reactions involving dissolution of the cuprite patina. The pH oscillated around a mean pH of 2.38 ± 0.05 which corresponds to the starting position where the pH was 2.36. This means that the BTA solution at 0.1M was totally effective in preventing corrosion of the copper coupons.

The cysteine hydrochloride solution showed a similar induction period but the rate at which copper dissolved in the acid solution was roughly one quarter of the control solution, since the pH increased at only 0.07 pH/hr1/2 for the first four hours and then the pH increased, due to evaporation at a similar rate to the control (Fig. 1). This trend continued for a day until the problem was noted and Parafilm covers were made for the reaction vessels. Like the case of the BTA solution, the pH was steady at a mean value of 1.23 ± 0.03 which is very close to the starting point of 1.36. The reason for the pH of the cysteine solutions being more acidic than the BTA or the control is due to the amino acid being present as its hydrochloride salt. The results are summarized in Table 1, but in effect the cysteine can be seen as very effective in preventing corrosion of the copper coupons; the initial fall in acidity reflects the impact of the acidic solutions reacting with the small amount of cuprite on the coupon surfaces.

COMPARING THE EFFICACY OF SELECT NATURAL AND SYNTHETIC CORROSION INHIBITORS

In comparing the impact of having two corrosion inhibitors in the same solution for copper coupons, the combination of BTA and AMT was not a good outcome. Firstly, during the induction period the pH increased at the rate of 0.037pH/hr1/2 which was just under half the rate observed on the control solution (Fig. 2) for the first 24 hours before the evaporation of the solution caused the pH to fall at the rate of 0.06pH/hr1/2, which brought the pH back to the starting point, after which the pH continued to rise at the rate of 0.039pH/hr1/2, which is the same as the induction period (within experimental error).

Table 1. Summary of the kinetics of reaction of copper coupons with inhibitor solutions. Some of the inhibitors had a steady pH after the first phase and no further corrosion occurred, in which case n/a is written in the second phase

	First Phase			Second Phase		
Inhibitor	Induction slope	Induction intercept	R ²	Corrosion slope	Corrosion intercept	R ²
Control	0.087	1.89	0.94	0.88	-3.63	0.98
Cysteine	0.067	1.36	0.98	n/a	n/a	n/a
BTA	0.020	2.36	0.99	n/a	n/a	n/a
BTA & AMT	0.037	2.20	0.94	0.039	1.94	0.59
Garlic	0.042	2.22	0.95	0.042	1.99	0.73
Ginger	0.017	2.02	0.87	n/a	n/a	n/a
Pepper	0.023	2.22	0.92	n/a	n/a	n/a

Of the three natural product solutions tested, the ginger extract kept the pH of the solution to under 2.25. However, there was some steady corrosion, equivalent to the control induction period, but at a steady rate of 0.17pH/hr1/2 for the duration of the five-day experimental run (Fig. 2).



Fig. 2. Plot of the pH against the square root of time for the natural product extracts and the combination of BTA with AMT

The next most effective natural inhibitor was the pepper extract which had an initial corrosion rate of 0.23pH/hr1/2 and the fall in pH due to evaporation was half that of the mixed BTA+AMT solution, which is consistent with the surface-active materials from the ethanol extract increasing the surface tension of the solution. The least effective inhibitor was the garlic extract which had 50% of the reaction rate of the control on the copper coupons in the induction period which continued at the same rate for the duration of the experiment (see Table 1).

In addition to looking at the precise kinetics of the corrosion inhibition process, one can also look at the increased pH values, since they represent dissolution reactions associated with the cathodic evolution of hydrogen and the anodic dissolution of copper. When evaluating the inhibitors in terms of total pH change, cysteine performed the best with a 93% reduction in pH increase, while the garlic performed the worst with a 73% reduction in corrosion, which is still a significant amount of inhibition. This information is summarized below in Table 2 and Figure 3.

Inhibitor system	Total pH change	Inhibition (%)	Concentration	
Control	1.7	0	n/a	
Garlic	0.46	73	150 ppm	
Pepper	0.26	85	150 ppm	
Ginger	0.22	87	150 ppm	
BTA	0.18	89	0.1M	
BTA & AMT	0.14	92	0.1M + 0.01M	
Cysteine	0.12	93	0.1M	

Table 2. Total pH Change and Inhibition (%) for each inhibitor system on copper



Fig. 3. Plot of the total change in pH for copper coupons in six test environments. The red and yellow patterned columns are for the 0.1M standard chemical solutions and the blue columns are for the 150ppm plant extracts

All coupons were visually assessed at the end of the experiment. The copper control coupons had developed a cuprite patina on the surface, with small pits throughout. The copper coupons in cysteine as well as ginger and pepper extracts appeared unchanged from before the

experiment. The coupons in BTA and BTA + AMT had a duller surface. The coupons in garlic extract also had a thin cuprite film on the surface.

Mild Steel

After approximately one day ($t_{1/2} = 5.2$ or 27 hours) until $t_{1/2} = 8.1$ or 65 hours, the pH was falling due to evaporation of the solutions in the beakers. Covering the solutions with Parafilm reduced the evaporation and acidification of the test solutions. The mean pH of the control group at the plateau region was 4.23 ± 0.19 and the last readings showed an increase in pH indicating more reaction, due to the solutions having been stirred which dislodged the accumulation of red-brown rust on the surface and exposed bare metal to the acidic solution (Fig. 4).

Similar to the results of the copper test, cysteine lowered the pH of the solution due to it being supplied as a hydrochloride salt. There is a marked increase in the corrosion rate of the iron coupons after 78 hours when the $t_{1/2}$ was approximately 7.8. During the induction period when the pH was steadily increasing at the rate of $0.12 \text{pH/t}_{1/2}$ the blue-black color of the mill scale on the iron coupons was steadily being lost to the floor of the beaker. On coming into the laboratory after 81 hours ($t_{1/2} = 9$ in Figure 5) it was seen that there were white crystals on the coupons, which was cysteine coming out of the reacting solution. The initial concentration of the cysteine hydrochloride was 0.1M, so with less inhibitor present in solution the corrosion rate of the iron coupons increased from $0.12 \text{ pH/t}_{1/2}$ to $0.38 \text{ pH/t}_{1/2}$, or an increase of almost 2.2 times or 220%. Clearly the critical pH for the precipitation of cysteine had been exceeded and so there was a concomitant increase in the corrosion rate due to the lower surface and solution concentration of the corrosion inhibitor. Even after the loss of a significant proportion of the corrosion inhibitor the cysteine solution at a corrosion rate equivalent to $0.37 \text{pH/t}_{1/2}$ is still an effective inhibitor as the control corrosion rate was $0.51 \text{pH/t}_{1/2}$, with a 27% fall in iron dissolution rate. At the original concentration, the cysteine represented a 75% reduction in the rate of decay in what was a significantly acidic solution.



Fig. 4. Solution pH vs square root of time for the two sets of iron coupons set up as controls



Fig. 5. Reactivity of the iron coupons in cysteine showing variation in the mean pH with the $t_{1/2}$

The response of the iron coupons to being placed in the 0.1M BTA solutions is summarized in Figure 6. The overall behaviour of the BTA is similar to the control tests in that after a given amount of time, the increase in pH, due to dissolution of iron, stopped at a steady pH of around 4.00 ± 0.08 , compared to 4.23 ± 0.19 for the control group. This indicates that the BTA solution was acting as a corrosion inhibitor and that the kinetics were more favourable than for the control, which took 36 hours to reach a plateau while the BTA achieved it in a matter of 21 hours. However, the drop in the reaction rate was not all that large as the BTA solution had a mean pH increase of $0.46 \text{pH/t}_{1/2}$ compared with the control value of 0.51, which represents approximately a 10% corrosion inhibition, in terms of slowing down the cathodic reaction of hydrogen evolution.

During the immersion of the iron coupons in the BTA solution, some of the blue-black mill scale came away from the coupon surfaces and so they were clean looking and did not have any tell-tale red-brown corrosion products sitting on top of pitted areas. The pH at the first plateau points were at the same value as the first plateau level of 4.23 ± 0.19 as found in the control group. It is possible that the slight increase in acidity is due to oxidative hydrolysis of the iron corrosion products that had reported to the solution environment.

The behaviour of the combined inhibitors of BTA and AMT was very similar to the control group in that after a steady diffusion-controlled reaction in which the pH fell linearly with the square root of time, the pH reached a plateau value of approximately 4.13 ± 0.06 , which is experimentally the same as with the BTA alone. The time combined inhibitor solutions took slightly longer to reach the plateau level of 4.13 ± 0.06 , which indicates that there was roughly the same amount of corrosion as observed with the BTA test solutions in isolation. The rate at which the pH increased was 0.45pH/t^{1/2} which is experimentally the same, within the error margins, as the BTA alone. In short, the addition of AMT showed no appreciable impact on the corrosion inhibition efficiency of the system. The plot of the pH vs. the square root of experimental time is shown in Figure 7.



Fig. 6. Plot of the pH of iron test solutions in 0.1M BTA solution



Fig. 7. Plot of the rate at which the pH increased with the BTA+AMT combined inhibitor condition

Unlike the situation with the controls, the BTA and the BTA+AMT treatments, which all showed corrosion stopping around pH 4.2 ± 0.1 the ginger extracts had a turning point at around $t_{1/2}$ value of 7.0 or 49 hours (Figure 8). After two days the corrosion rate of the iron fell significantly to 0.092pH/t^{1/2} from a mean value of 0.36 which reflects a 30% reduction in the decay rate of iron compared with the control groups. This fall in corrosion rate is essentially the

same as the initial inhibition impact of the cysteine solutions. During the cleaning stage at the end of the corrosion experiments it was noted that the iron coupons had strongly adherent material on large areas of the surface. The direct adsorption of extracted species from the ginger onto the iron and their chemical transformation by the nascent hydrogen being generated by the continuing corrosion reaction was enough to slow down the rate of loss of iron metal. If the second stage of inhibition is compared with the values of the original control group, this represents an 82% fall in the iron corrosion rate. The higher pH intercept value of 2.05 for the ginger extracts can be compared with the value of 1.79 for the control group and it is possible that some of the extracted chemicals are acting as buffers.

Black pepper appeared to have an initially good inhibition at the level of 65% of the rate found in the control group which, after a period of six hours ($t_{1/2} = 2.45$) and 21 hours ($t_{1/2} = 4.58$) changed the surface to make it more inhibiting for acid attack of the iron. The second and more prolonged inhibition period was 75% efficient at inhibiting acidic attack on the mild steel coupons, as shown in Figure 9. With an intercept pH value of 2.23 for the first phase of the corrosion inhibition reaction, compared with the value of 1.79 for the control coupons, the black pepper, like the ginger extract, appears to have a collection of weak acid-weak bases in the extract since it has shifted the pH by 0.54 into the more alkaline region.



Fig. 8. Plot of solution pH showing iron corrosion in the presence of ethanolic ginger extracts

The corrosion behaviour of the iron coupons in the garlic extract was very similar to that observed with the black pepper in that there was an initial rate which was followed by a significantly slower rate for the balance of the duration of the experiment, as shown in Figure 10. As was observed for the black pepper reaction, a change took place overnight between total reaction times of 6-17 hours ($t_{1/2}$ between 2.45 and 5.48) which lowered the corrosion rate to the equivalent of 78% compared with the control group over the same time period. This makes the garlic extract possibly slightly more effective than the black pepper materials. The initial starting pH (intercept value on the Y-axis) was 2.27 compared with the 1.79 of the control group and this increased alkalinity at zero time means that there were extracted chemicals from

the garlic that functioned as buffers and this in turn will have lowered the iron corrosion rate by protecting the surface from the normally more acidic solutions.



Fig. 9. Plot of the pH of the iron coupon solutions in an ethanolic extract of black pepper



Fig. 10. Plot of the pH in the acidic solutions corroding iron coupons with garlic extracts

The effectiveness of the inhibitors is summarized below in Table 3. The garlic "b" solution was found to be the most effective, followed closely by pepper "b" and cysteine "a." The "a" and "b" slopes relate to the two different phases in the reactivity of the coupons. The slopes of the "a" values relate to the induction period and the "b" values relate to the inhibited solutions.

Test solution	pH slope	Intercept	R ²	Plateau pH	Plateau pH std dev	Time for Plateau/Turning pt., hours	Inhibition (%)
Control	0.51	1.79	0.979	4.23	0.19	36	0.0
BTA	0.46	2.48	0.988	4.00	0.08	21	9.8
BTA+AMT	0.45	2.08	0.955	4.13	0.06	30	11.8
Ginger	0.36	2.05	0.969	4.69	0.01	49	29.4
Cysteine "b"	0.37	-0.59	0.971	n/a	n/a	n/a	27.5
Garlic "a"	0.21	2.26	0.989	n/a	n/a	18	58.8
Pepper	0.17	2.23	0.999	4.58	0.09	18	66.7
Cysteine "a"	0.12	1.71	0.982	n/a	n/a	74	76.5
Pepper "b"	0.117	3.43	0.918	n/a	n/a	18	77.1
Garlic "b"	0.108	3.74	0.897	n/a	n/a	n/a	78.8

Table 3. Summary of the kinetic data on iron coupons in different inhibitor solutions

All of the tested inhibitors proved at least somewhat effective at preventing corrosion on the copper coupons, with both BTA and cysteine showing the most significant ability to stop the copper coupons from corroding. There appears to be no major benefit in using the combination of BTA with AMT in the same solution, but the addition of AMT to the BTA did result in a small improvement of the percentage corrosion inhibition. The ginger and pepper extracts were only slightly less effective than the chemical reagents, indicating they have potential use as alternatives to the more costly synthetic inhibitors.

When it comes to iron, the conclusion for the standard chemical inhibitors is that cysteine is much more effective for stopping iron corrosion in weak hydrochloric acid solution and that the impact of adding AMT to the BTA solution was minimal. Both BTA containing solutions exhibited classic behaviour shown by the control coupons in that once the acidity fell below a pH of between 4.0 and 4.2, the acid dissolution of iron ceased. The level of protection provided by black pepper was found to be equivalent to the corrosion inhibition produced by the acidic phase of cysteine. Black pepper extract shows remarkable promise as a natural product extract that could replace the costly cysteine hydrochloride salt.

Conclusions

The experimental research conducted at Kaman-Kalehöyük found that cysteine and BTA were the most effective corrosion inhibitors on copper, followed closely by ginger and pepper extracts. Cysteine, pepper, and garlic were found to be the most effective inhibitors on mild steel coupons. With iron, adding AMT to the BTA solution did not improve the effectiveness over using BTA by itself, but its addition to the BTA did improve the corrosion resistance for copper by a few percent. The natural inhibitors had promising results – particularly pepper since it was effective on both copper and iron. The success of the natural inhibitors is exciting since the conservation field is moving towards using more sustainable materials when possible, and the lower cost and easier accessibility of pepper versus BTA and cysteine means more conservators around the world and in more remote locations would still have access to an effective corrosion inhibitor. Hopefully these natural extracts will continue to be studied as potential corrosion inhibitors.

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