Voacanga Africana As A Green Corrosion Inhibitor On Concrete Sewers

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Abstract*: This study aims to investigate the inhibition of microbial concrete degradation mediated by acidithiobacillus thiooxidans in sewer wastewater using Voacanga Africana leaf extracts as an inhibitor. concrete samples were subjected to biogenic sulfuric acid corrosion in sewer wastewater for 26 months, the corroded concreted cubes were thereafter coated with plant extracts and subjected to sewer water for a further 5 weeks. Variations in weight loss, pH, and sulfate concentration were used to evaluate the effects of plant extracts on biogenic sulfuric acid corrosion of the coated concrete samples. The decline in SOB population, concentration, and formation of corrosion by-products were recorded. Corrosion rates of the raw concretes before coating were between 0.343364mpy - 1.323614 mpy. phytochemical analysis of the ethanolic extracts was positive for saponins, tannins, terpenoids flavonoids and alkaloids. GC-MS study of Voacanga Africana ethanolic extracts revealed the presence of 83 components. The major constituents were identified as; Thymol, Phenol, Pentanoic acid, and Eugenol. Biocorrosion control assessed the effects of plant extracts on concrete corrosion in sewer waters. A significant decline in corrosion rates with extract coating was observed for all extract coated concretes (0.001486mpy - 0.002622mpy). An increase in extract concentration was found to increase the inhibitory efficiency, which ranged from 68% to 72%. Scanning electron microscopy and X-ray diffractive analysis revealed differences in the morphology of the concrete before and after coating.*

Keywords— ***microbial corrosion, plant extracts, concrete, MIC, SOB. Voacanga Africana***

1. Introduction

Municipal wastewater management relies heavily on sewer systems, which handle effluent of more than 90% water along with pollutants from household, industrial, and urban origins. Household wastewater typically contains a blend of microbial and chemical substances, whereas industrial wastewater often includes more intricate and dangerous components such as heavy metals, including inorganic and organic compounds. Sewers are very expensive to maintain and damages in sewers are caused by microbial activities at the surface of sewer walls (majorly concrete) (Pramanik *et al,* 2024).

Concrete sewer systems are considered critical components of urban infrastructure, designed to transport wastewater away from residential, industrial, and commercial areas. However, over time, sewer pipes and concrete structures are subjected to various forms of degradation, microbial-induced corrosion (MIC) being the most significant. (Sun, 2015, Beech 2004, Videla and Herrera, 2005). Microbiologically induced corrosion (MIC) of concrete sewer infrastructures is mediated by the action of biogenic sulfuric acid (H_2SO_4) generated by the activities of sulfur-oxidizing bacteria in sewer systems. The biogenic sulfuric acid interacts with the cementitious materials in the concrete matrix, resulting in deterioration and degradation and in severe cases structural failures of the concrete structures. (Wu et al, 2018., Fytianos *et al*, 2021).

Microbial sulfide oxidation, which produces H_2SO_4, chemical reactions between acids and cementitious materials, and concrete deterioration as a result of chemical and biochemical reactions between H_2SO_4 and cementitious materials are all components of the intricate process of concrete sewer corrosion. (Jiang *et al*, 2016).

After a succession of events, corrosion begins in concrete sewer infrastructure with an initial step which involves the chemical dissociation and carbonation of hydrogen sulfide, this lowers the alkalinity of the wet concrete to a more neutral pH. (Vollersten *et al*, 2008).

This stage is followed by quick colonization of the concrete surface by various neutrophilic sulfide-oxidizing bacteria and fungi. As the pH of the concrete surface continues to drop below 2, the population of acidophilic organisms increases, with *Acidithiobacillus thiooxidans* (*A. thiooxidans*) becoming the dominant microbe (Okabe *et al*, 2007, Li *et al*, 2017).

The availability of moisture and low pH provide favorable conditions for the growth of organisms on concrete surfaces for the biodeterioration of concrete structures. High relative humidity (60–98%), long cycles of intermittent humidification and dehydrating, icing, and deicing, high volume of carbon dioxide, high concentrations of chloride ions or other salts, or high concentrations of Sulphate and high quantity of acids are all characteristics of biodeterioration-friendly environments. (Wei *et al*, 2013).

Researchers continually seek cost-effective and efficient methods to combat and mitigate corrosion and corrosion inhibitors are employed for this purpose. These inhibitors can be either inorganic or organic, depending on their chemical makeup. Despite their widespread use, there are challenges associated with it such as toxicity and short life span. Alternative approach to corrosion prevention involves the application of nanomaterials, and these nanomaterials serve as carriers for the corrosion inhibitors. Coating technology has also been used to inhibit or prevent corrosion, which act as a protective barrier, shielding against the infiltration of corrosive elements (Sheydaei *et al,* 2023 and Sheydaei 2024).

In light of the environmental concerns associated with corrosion inhibitors, industries are increasingly focused on utilizing eco-friendly, non-toxic, and cost-effective materials. Over the past few years, green corrosion inhibitors (GCIs), which include plant extracts and fruit waste, have garnered significant interest in this field (Sheydaei 2024).

A range of methods are commonly applied to protect concrete structures from biodeterioration and to reduce the effects of microbial-induced corrosion. Adjustments to the concrete mix design and the application of protective coatings to the concrete surfaces are among the strategies used. The rate of corrosion is inversely proportional to the alkalinity of the concrete, hence a modification of the concrete mix by increasing the alkalinity ultimately leads to the corrosion rate being reduced. (Cwalina, 2008). Biocidal chemicals are used to inhibit and minimize microbial corrosion. Biocides are single chemical compounds (or mixes of chemical compounds) that have bactericidal capabilities against bacteria and can be used to reduce or prevent microbial development. Organic biocidal chemicals include isothiazolones, quaternary ammonium compounds, and aldehydes like glutaraldehyde and acrolein. (Videla, 2002).

In 2011 to 2012, Australia had spent close to 70 Billion Australian dollars (AUD) in maintaining sewer infrastructure and in 2022, it estimated and expenditure of 125 Billion (AUD) to be spent in the next 20 years for sewer maintenance (Pramanik *et al,* 2024). Inexpensive and environmental friendly approach to combat concrete corrosion is the way to go in solving infrastructural degradation by microbial activities sewer environment.

The exploration of natural or green biocides as an alternative to biocidal chemicals for concrete bio-corrosion control is an extremely intriguing approach that research focused on solving bio-corrosion issues.

Voacanga Africana is a tiny tree or shrub with a low, widely spreading crown that can grow up to 6 meters tall. A mature *Voacanga Africana* crop is less than 10 meters tall, with a poorly branching stem and smooth grayish-white bark. The leaves are opposite and acuminate, with a dark green and glossy surface that contrasts with the greenish-green foliage and usually without stalks. (Koroch *et al,* 2012). *Voacanga Africana* is a deciduous shrub found in the Guinea Savannah woodland belt and the Tropical rainforest. Its milky latex is exuded by Slash. It has simple, petiolate, and decussately placed leaves. (Christopher, *et al* 2009). The use of *Voacanga Africana* plant-based extracts as environmentally friendly inhibitors to reduce microbial corrosion in concrete sewer systems is the aim of this research.

2. METHODOLOGY

Previous studies have published experimental methods for the preparation of concrete samples, identification and isolation of sewer microorganisms, concrete sampling, physico-chemical analysis of sewer wastewater, biocorrosion investigation, and weight loss measurement. (William-Porbeni and Gumus, 2021a, 2021b) Similarly, the comprehensive experimental procedures for the plant extraction, phytochemical analysis of *Voacanga Africana* plant extracts, and concrete coating using modified epoxy resins as well as corrosion inhibition studies are described in the publication William-Porbeni *et al* 2023a.

3. Results And Discussion

The initial findings of the chemical analysis of the sample sewer effluent, as well as the identification and isolation of the main sulfur-oxidizing bacteria present, have already been reported. (William-Porbeni and Gumus, 2021a, 2021b)

1. *Voacanga Africana* extracts composition

The presence of tannins, saponins, flavonoids, alkaloids, and terpenoids was confirmed by qualitative analysis of the ethanolic extracts. GC-MS study of *V. Africana* ethanolic extracts revealed the presence of 83 components. The major constituents were identified as; Thymol (peak area 23.88%, RT- 29.011), Phenol, 2,3,4,6-tetramethyl- (peak area 7.7498%, RT-26.5468), Pentanoic acid(peak area 7.04%, RT -36.0189), Eugenol (Peak area 4.4813, RT- 27.7998), Methyl(methyl 4-O-methyl-.alpha.-d-mannopyranoside) (peak area 2.3441%, RT-35.8499), Glycerin (Peak area 2.1395, RT-22.9351), Caryophyllene (1.8217 %, RT-29.1414), Naphthalene(1.7115%, RT- 30.454) and Cyclohexanol (1.7832%, RT- 19.8187).

Fig. 1. shows the GC-MS chromatogram of Thymol in *Voicanga Africana* extracts. With a percentage of 23.88%, the extracts' main ingredient was discovered to be thymol. Thymol ($C_{10}H_{14}O$) is a phenol derivative of P-cymene Isomeric with carvacol found in thyme oil and isolated from thymus vulgaris. It's a crystalline white material with antibacterial effects and a lovely scented odor. Thymol has antibacterial activity towards pseudomonas aeruginosa and gram-negative E.coli, as well as gram-positive bacillus cereus and staphylococcus aureus, according to studies. Its antibacterial effect is attributed to the inhibition of bacterial growth and lactate generation, as well as the reduction of cellular glucose uptake. According to a US EPA evaluation of thymol's toxicological and environmental implications, the substance has a low likelihood of toxicity and offers little concern. It rapidly decomposes in water and soil and is considered low risk because of its rapid dissipation and low-bound residues. (Hu and Coates, 2008).

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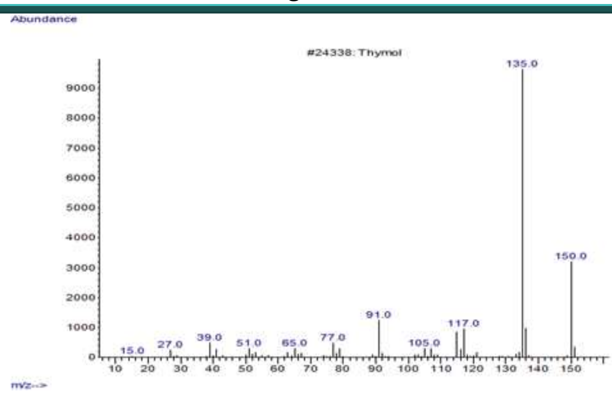

Fig. 1. GC-MS chromatogram of the peak fractions of the ethanolic extracts of Voacanga Africana. Showing Thymol.

Fig. 2. shows the GC-MS chromatogram of Pentanoic acid (7.04%) identified as one of the major constituents of the extracts. Pentanoic acid also known as valeric acid ($C_5H_{10}O$) hasg a strong antimicrobial activity against *E.coli* and *salmonella* strains. Also against other bacteria (gram negative and positive). Eugenol ($C_{10}H_{12}0_2$) with a percentage of 4.4813% was also identified. Eugenol has also been reported as having excellent antimicrobial and antiseptic properties. It has shown high potency in damage of bacterial membranes. (Mohammadi Nejad *et al*, 2017).

MICROBIAL INHIBITION OF EXTRACTS

The minimum inhibitory concentration (MIC) of plant extracts is the lowest concentration at which no discernible microbial growth was seen during the incubation period. The antimicrobial activities during this period confirms the inhibitory properties of the Voacanga africana extracts. The minimum concentration of V*oacanga africana* extracts with antimicrobial properties against fungi and bacterial isolates was between 15-25 mg/ml. The findings indicated that plant extracts have the ability to suppress isolates of fungus and SOB.

Plants extracts significantly inhibited SOB (-pseudomonas), Aspergillus and Rhizopus significantly. The results of the MIC showed a higher susceptibility of bacteria to the extracts than fungi.

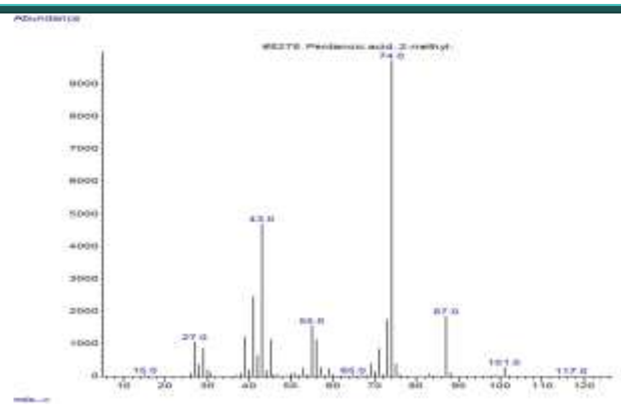

Fig. 2. GC-MS chromatogram of the peak fractions of the ethanolic extracts of Voacanga Africana. Showing Pentanoic acid.

CORROSION RATES AND INHIBITOR EFFICIENCY

The results of the corrosion rates calculation and inhibition efficiency of extracts relative to the commercial biocide glutaraldehyde is presented in Table 1.

Table 1: Concrete Corrosion Rates Before and After Coating.

Extracts	CR without extracts(mpy)	CR with extracts(mpy)	IE (%)
VA10% VA 25% VA 50%	1.323614 0.210449 0.343364	0.001486 0.00266 0.002622	68.55 71.85 72.12
BLANK	0.024195	0.000437	48.47
GLUTAR ALDEHY DE	1.290385	0.003266	86.43

The Voacanga Africana leaf extracts effectively inhibited concrete corrosion in sewer water. Table 1 shows that for extracts coated samples, an increase in extract/inhibitor concentration led to a corresponding increase in the inhibition efficiency of the extracts. With the percentage efficiency tending towards that of the commercial biocide at higher concentrations. 50% *V. Africana* extracts gave the highest inhibitor efficiency of 72.12%. It is theorized that at higher extract concentrations a gradual and corresponding increase in inhibitor efficiency performance of *Voacanga Africana* leaf extracts can be achieved. It is noteworthy that the observed efficiency increase with that of an increase in extract concentration compares well with the reported performance of green extracts on concrete in sewers in previous studies. (William-Porbeni *et al*, 2023a, b) These results suggest and support the effectiveness and suitability of medicinal herbs as an effective alternative to conventional biocides in inhibiting biocorrosion on concrete surfaces.

EFFECTS OF EXTRACTS ON SEWER PH

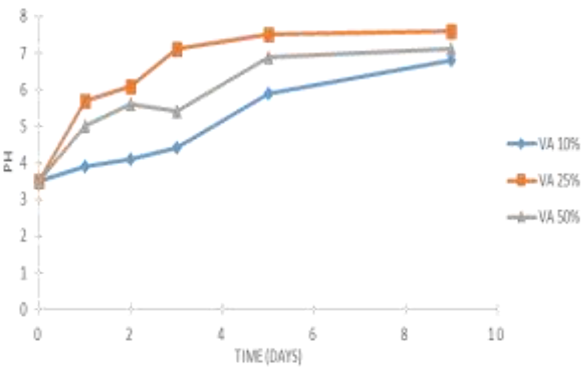

Fig. 3. pH Variation with *Voacanga Africana*

Figure 3 presents results of variation in pH of the *Voacanga Africana* extracts coated concrete sample. A gradual increase in pH towards the neutral/basic range was observed for all extracts coated concretes. This increase can be attributed to the be as a result of the presence of extracts phytochemicals and its various metabolites in the sewer water leading to a gradual neutralization of the sewer the pH and with a corresponding reduction in acidity. The reduction in acidity leads to a reduced biogenic sulfuric acid production with a subsequent decline in the growth and metabolism of the Sulfur oxidizing sewer micro-organisms. With this gradual sewer neutralization (to pH 7 and above), the activities of neutrophillic fungi and bacteria predominates while that of acidophillic bacteria is reduced. It has been established that substrate metabolism and growth of microbes is strongly correlated to the pH of the sewer corroding environment. (Mori *et al*, 1992, Li *et al*, 2023, Jiang *et al*, 2023)

EFFECTS OF PLANT EXTRACT ON SULFATE CONCENTRATION

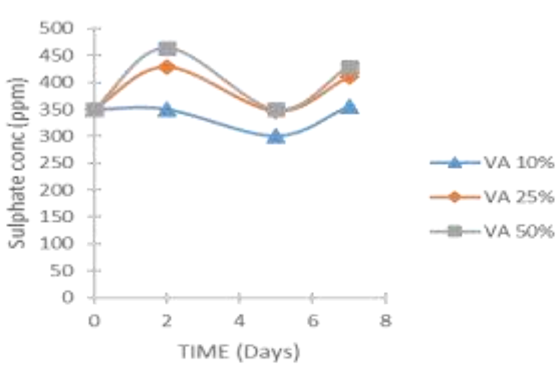

Fig. 4. Sulfate variation with *Voacanga Africana*

Figure 4 indicates the change in sulfate concentration with time for *Voacanga Africana* extract-coated concrete samples. For *Voacanga Africana* coated concrete samples, a slight increase at 10% extract coated sample within the first 24 hours followed by a drop and an increase by day 7. For 25% and 50% extract concentration, an increase in sulfate concentration followed by a decrease and an increase by day 7 to 41.0mg/l and 42.9mg/l respectively was observed.

ACIDOPHILIC SULFUR-OXIDIZING BACTERIA

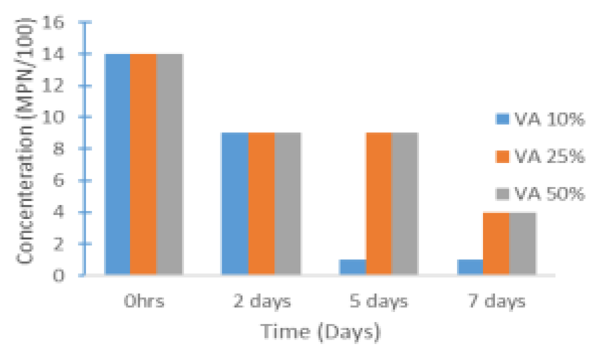

Fig. 5. SOB Variation in Sewer Water with *Voacanga Africana*

Figure 5 shows the variation in concentration with time for *Voacanga Africana* extract coated concretes. For all concentration of extracts coated concrete a gradual decline in SOB concentration was observed with time. From the results presented above it was observed that at low extracts concentration (10%) the concentration of SOB declined rapidly for all extracts coated samples studied. This is likely due to higher diffusion and dissolution rates of extracts into solution at these low concentrations. This increases the availability of extracts phytochemicals dissolved in solution, thus increasing the antimicrobial activity of the extracts at these concentrations. This decline was observed for a 9 days period until the MPN count become negligible.

MICROSTRUCTURAL ANALYSIS

Fig. 6. SEM for corroded concrete.

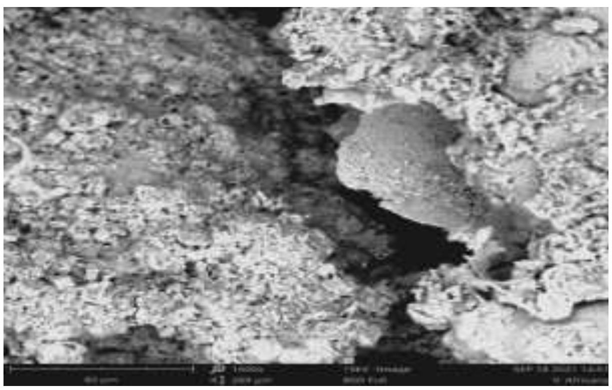

Fig. 7. SEM Voacanga Africana coated concrete

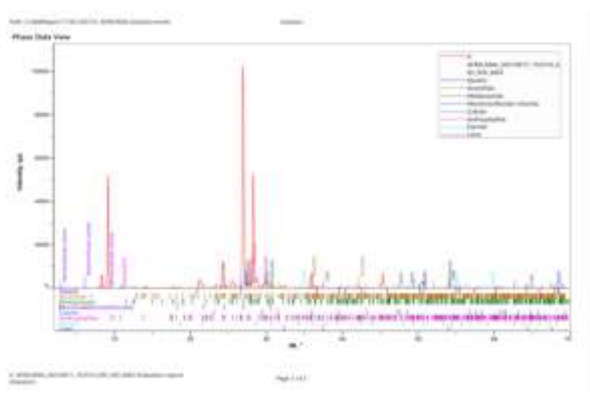

Fig. 8. XRD for Voacanga Africana *coated concrete*

Fig 6, Fig 7. and Fig 8 present the SEM and XRD results of *Voacanga Africana* uncoated (Fig 6) and coated concrete samples (Figs 7&8). SEM and XRD techniques were employed to analyze changes in surface morphology and mineral constituents of concrete before and after coating with plant extracts. SEM image of corroded concrete samples without extract coating reveals a severely corroded concrete morphology covered by corrosion byproduct highlighted above in SEM image figure 7. Results from the SEM analysis showed significant differences in the surface morphology and corrosion product formation between the concrete cube samples exposed to sewer wastewater before and after coating with *V. Africana* leaf extracts. Before inhibitor coating on concrete, characteristic corrosion byproducts gypsum which is seen as rough mass with a porous exterior were observed indicating a progressive corrosion process in the system due to an aggressive penetration of biogenic sulfuric acid into the concrete matrix. Conversely, the presence of *V.Africana* extracts coating on concrete to mitigate these corrosion effects saw a marked reduction in the intensity and formation of corrosion by-products. SEM results of the *Voacanga Africana* coated samples showed the formation of grainy, chalklike, and whitish compounds distributed within the concrete matrix. The SEM results confirmed the absence of any corrosion byproducts suggesting the inhibition properties of *Voacanga Africana* leaf extracts. The grainy whitish mass formed on the concrete acts as a shield to protect the concrete from corrosion of biogenic acid. (Guatam *et al,* 2024., Bahir *et al,* 2024)

The results of SEM analysis in the absence and presence of plant extracts provide valuable insights into the mechanisms of biogenic acid corrosion of concrete, byproducts formed and the efficacy of plant extracts as viable natural inhibitors. The observed differences in surface morphology and corrosion product formation highlight the potential of *V.Africana* leaf extracts as a corrosion inhibitor of concrete in sewer environments.(Didouh *et al,* 2024)

XRD results revealed the presence of crystals of quartz, anorthite, wollastonite, montmorillonite-chlorite, anthophyllite, and garnet. Similar crystalline structures were reported to have been formed with the other plant extracts coating on biogenic acid-corroded concrete. Similarly, no corrosion byproduct was present in extract-coated concretes. (William-Porbeni, et al, 2023a,b).

CONCLUSION

The leaf extract of Voacanga Africana was used to prevent concrete biocorrosion in wastewater from sewers. The effects of plant extract on concrete properties were studied. The study's conclusions were as follows:

1. *V.Africana* extract gave a marked alteration of sewer pH, sulfate concentrations, and variation in SOB populations.
2. The formation of grainy and chalk-like micro-crystalline compounds within the concrete matrix brought about a pore-blocking ability limiting the ingress of corrosive media into the concrete.

3. SEM and XRD images showed no observable corrosion by-products.

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