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Green corrosion inhibitors for steel and other metals in basic media: A mini-review

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Abstract

This work aims to investigate briefly, the effectiveness of plant extracts so far used for steel and other metals as inhibitors in combating the metallic corrosion in basic media. Corrosion inhibitors have been recommended by various researchers as one of the ways to slow down the rate of corrosion and to reduce the financial losses associated with it. Corrosion inhibitors can be organic or inorganic in nature. But due to their eco-friendly and regenerative nature, green corrosion inhibitors of natural origin are the preferred candidates as against synthetic inhibitors. Majority of corrosion studies today are focused on the application of plant extracts for corrosion protection in acidic media, whereas alkaline media has been used only in few studies, and yet with little or no recent work. Even the result of this review shows that plant-based inhibitors have been used mostly on steel products, aluminum products, and copper in that descending order for minimizing corrosion in alkaline media, while it has been rarely used on metals such as tin, iron, and zinc in the same alkaline media. As a result, it is beneficial to encourage more review and research on the use of plant extracts as corrosion inhibitors in basic media for steel and other metals. And the novelty of this review is based on this concept. Hence, this study is very vital for key players/readers in this field to improve their awareness regarding on how to design extract of plants origin according to their suitability and reproducibility for corrosion protection of metallic structures.

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1. Introduction

Metallic materials are critical to the advancement of technology and economy development of any nation. Numerous improvements in design development have been made possible as a result of material innovations, such as high-speed airplanes, bridges, contemporary dwellings, electronics, automobiles, and so on. Due to their exceptional qualities, metallic materials might be considered the most essential engineering materials [1], [2]. In spite of all, metals are still known to be the least corrosion resistant of all the engineering materials. This is because, while ceramics are an important class of material with desirable properties such as corrosion resistance, they are more difficult to design with than metals because they lack some vital properties which limits their uses when put side by side with metals [3]. Corrosion of metals can be thought of as extractive metallurgy in reversed manner as illustrated in Fig. 1, while extractive metallurgy itself is largely concerned with the extracting of metal from the ore and refining or alloying it for a better application. Verse majority of iron ores holds within them oxides of iron, and rusting of steel by water and oxygen results in a hydrated iron oxide. Therefore, rusting is a term designated for steel and iron corrosion, despite the fact that many other metals form their oxides when corrosion attack happens [4].

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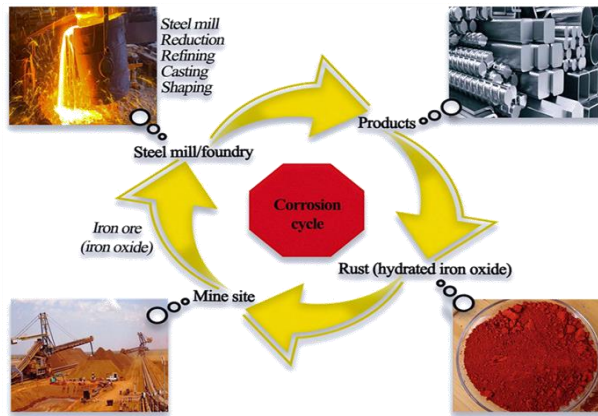


Fig. 1 Metallurgy in the reverse nature

Metallic corrosion has an impact on a variety of domains, including bridges, railways, buildings, industries, traffic lights, and household device [5]. According to a recent study [6] conducted by NACE, the economic impact of corrosion is estimated to be around 2.5 trillion dollars (USA). The financial costs of corrosion are depicted in detail in Fig. 2. However, if corrosion protection techniques are used, this loss can be minimized by up to 15–35 percent [6].

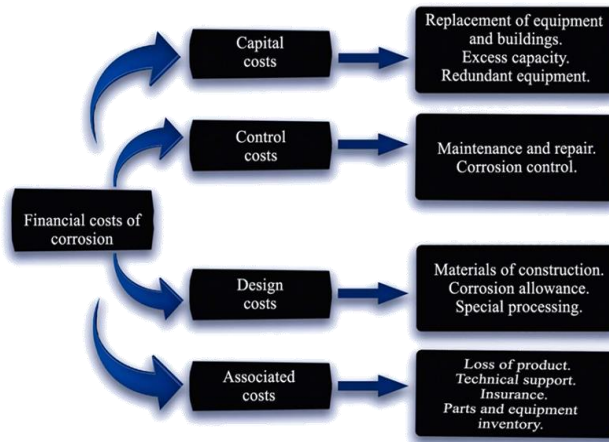


Fig. 2 The financial costs associated with corrosion

Thanks to the use of corrosion inhibitors, which have been recommended by various researchers as a way to slow down the rate of corrosion and so reduce the financial losses suffered by all major users of metallic materials. Corrosion inhibitors are organic or inorganic chemical substances that act as cathodic, anodic or mixed inhibitors by adsorbing on a corroding metal surface when added to a corrosive media, hence suppressing to a great extent the metal's corrosion rate [7], [8]. The presence of organic substances comprising O, S, and N atoms in their compounds with numerous bonds through which they can adsorb on the metal surface makes most inorganic inhibitors harmful to the environment. This has fueled the search for green corrosion inhibitors that are biodegradable, eco-friendly, low-cost, incredibly easy to find, and regenerative, and yet having no heavy metals [9] – [12].

Most corrosion studies today are concentrated on the use plant inhibitors for corrosion protection in strong acidic media like sulfuric acid, hydrochloric acid and other weak acidic media like H_3PO_4 , CH_3COOH , and $HCOOH$, etc. While only little investigations were done using alkaline media. Therefore, it has become imperative to encourage a review on the use of plant extracts on steel and other metals as corrosion inhibitor in basic media. Under this premise lies the novelty of this review, hence, been unique, it is believed that it will contribute immensely to knowledge and learning in the area of corrosion of metals, and on how to create plant extracts in accordance with their suitability and reproducibility for protecting metallic structures from corrosion.

2. Corrosion Inhibitors and Their Functions

Corrosion inhibitor might function in two different ways. Firstly, through contact with the corrosive species, the added inhibitors can sometimes transform the corrosive medium into a noncorrosive or less corrosive medium. In other circumstances, the corrosion inhibitor can react only with the metal surface, and through which, prevents the metal from corroding. As a result, there are two broad types of inhibitors based on how they interact [5]:

- Environment modifiers.
- Adsorption.

The action and method of inhibition in the case of environment modifiers is just by a simple interaction with the aggressive species in the environment, which leads to reduction in the aggressive species' attack on the metal. Oxygen scavengers like Na_2SO_3 or N_2H_4 , as well as cobaltous nitrate and biocides used to prevent microbiological corrosion, are examples of this. The cathodic reaction in corrosion in neutral and alkaline environments involves oxygen reduction, which can be resisted by oxygen scavengers and so impede corrosion [5].

There are two processes in the case of inhibitors that adsorb on metal surfaces and control corrosion: (a) transport of the inhibitor to the metal surface; and (b) metal – inhibitor reactions. The procedure is similar to drug molecule transport in the human's body to the needed location and its engagement with the location to provide relief from the symptoms. The interaction of the metal surface with the inhibitor molecule is perhaps the most crucial step. But however, depending on whether the added inhibitor decreases the cathodic or anodic interaction, inhibitors could be further categorized as follows [5];

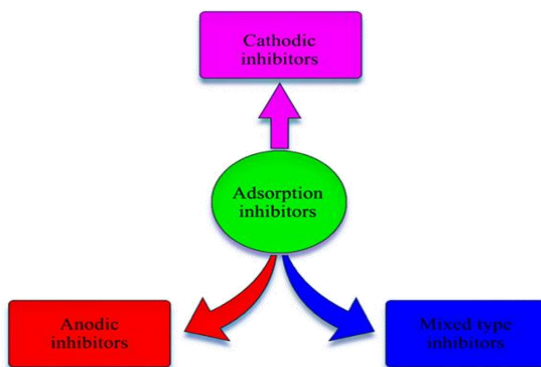


Fig. 3 Different types of adsorption inhibitors

2.1 Cathodic Inhibitors

Cathodic inhibitors inhibit hydrogen from forming in acidic media and/or reduce oxygen formation in neutral or alkaline media. Cathodic inhibitors are substances that have a high hydrogen overpotential in acidic solutions and those that produce insoluble compounds in alkaline solutions. Inorganic phosphates, silicates, and borates in alkaline solutions are examples of inhibitors that prevent oxygen reduction at the cathodic sites. Cathodic sites are blocked by substances like calcium and magnesium carbonates, which have a low solubility [5], [13].

2.2 Anodic Inhibitors

In the pH range of 6.5–10.5 (which is near neutral to basic), anodic inhibitors are often effective. Oxyanions such as molybdates, chromates, sodium nitrite and tungstites, among others, are particularly potent anodic inhibitors. These oxyanions are believed to have a role in mending deficiencies in the iron surface's passive iron oxide layer. The concentration of the inhibitor applied in the case of chromate or dichromate is crucial. When a significant amount of inhibitor is employed, corrosion is slowed, but when the inhibitor is insufficient, corrosion is increased. As an inhibitor, dichromate exhibits this common behavior [13].

2.3 Mixed Type Inhibitors (both Cathodic and Anodic)

Organic substances are commonly used to represent mixed type inhibitors. Regardless of the type of inhibitor, the inhibition process entails transporting the inhibitor to the metal location, and through the subsequent interaction of the inhibitor with the metal's surface, corrosion protection will result. Organic inhibitors when deposited on the metal surface act as a barrier to anode dissolution and cathodic oxygen reduction. The organic mixed-type inhibitors' protective functional groups can be carboxyl, amino, or phosphonate [5], [13].

3. Use of Plant Extracts as Corrosion Inhibitors

Plant extracts are versatile and cost-effective group of corrosion inhibitors. The application of plant extracts as a corrosion inhibitor is done in accordance with green chemistry principles, making the procedure more environmentally benign [14]. Plants produce phytochemicals as a result of their primary or secondary fermentation. Phytochemicals are divided into two classes based on their role in plant metabolism: primary and secondary metabolites. Carbohydrates, proteins, amino acids, and chlorophylls are examples of primary metabolites, while saponins, alkaloids, steroids, tannins, flavonoids, and other secondary metabolites are examples of secondary metabolites [15] - [16]. The phytochemical ingredients in plant extracts have the capacity to inhibit steel and other metals from corroding. These chemicals establish a protective coating on the metal surface by adsorbing to it. The plant population is extremely diverse, containing a vast spectrum of phytochemicals with different redox potential. If we understand the mechanism of action of phytochemicals, we can take advantage of their varied properties to harness them on a commercial scale for corrosion inhibition of metals, since phytochemicals offer a cost-effective, environmentally acceptable, non-toxic, and non-hazardous alternative to conventional corrosion inhibitors [14].

The type of metal, the test medium, the chemical structure of the inhibitor, the kind of substituents present in the inhibitor, the presence of additives, the solution temperature, and the solution concentration all influence the adsorption of green corrosion inhibitors on metal surfaces [17]. Table 1 below shows some latest studies by host of numerous researchers where plant extracts have been employed successfully as excellent steel and other metals corrosion inhibitors in various alkaline media.

Table 1. List of plant extracts evaluated as green corrosion inhibitors in various alkaline media for steel and other metals.

S. no.	Inhibitor	Electrolyte/metal	Method	Nature of adsorption/isotherm	Max. IE (%)	Ref.
1	Moringa Oleifera, Psidium Quajava	NaOH/mild steel	WL	-	> 80	[18]
2	Jatropha curcas, Hibiscus Sabdariffa calyx	NaCl/mild steel	3D SI, ATR, FTIR, LC-MS, EIS, WL, PDP, EDS, SEM	Formation of inhibitor film on mild steel surface	90.26	[19]
3	Hibiscus sabdariffa	NaOH/aluminum	HE, WL, PDP, EIS	Physical adsorption, Langmuir, Dubinin- Radushkevich	84.68	[20]
4	Gum arabic	NaOH/aluminium	HE, TM	Chemical adsorption, Langmuir, Freundlich	> 75	[21]
5	Vigna unguiculata	NaOH/aluminium	WL	Chemical adsorption, Freunlich, Temkin	79.63	[22]
6	Ipomoea involcrata	NaOH/aluminium	HE	Physical adsorption, Langmuir	60	[23]
7	Gossipium hirsutum	NaOH/aluminium	WL	Adsorption of the phytochemicals in the plant	97	[24]
8	Phyllanthus amarus	NaOH/aluminium	WL	Langmuir	76	[25]
9	Gongronem a latifolium	KOH/aluminium	HE	Physically adsorbed	97.54	[26]
10	Garlic	Rain water/aluminium	WL, FTIR	Protective film formed	98	[27]
11	Lupine, Fenugreek, Pomegrana e, Doum, Mango, Aloe eru, Opuntia, Orange	NaOH/aluminium	WL		84,80, 85, 56, 65, 54, 85, 64	[28]
12	Peony	NaCl/carbon steel	WL, FTIR, EIS, GIXD, FESEM, XPS, LC- MS, PDP, XRD, SEM	Frumkin	65.8	[29]
13	Kudingcha	NaCl/steel	FTIR, EIS, SEM,PDP	Langmuir	96.53	[30]
14	Tomato pomace	NaCl/mild steel	SEM, PDP, GC-MS, AFM	Protective layer formed on the metal surface	93.01	[31]

15	Myrmecodia pendans	NaCl/carbon steel	PDP, EIS, FTIR	Langmuir	91.41	[32]
16	Rosmarinus officinalis	NaCl/Al-Mg alloy	PDP, EIS	Freundlich	-	[33]
17	Equisetum arvense	Seawater/copper	PDP, EIS, LPR, SEM, FTIR, GC-MS	Mixed-type inhibitor adsorbed onto the metal surface	87.5	[34]
18	Ziziphus lotus	Natural seawater/copper	WL, SEM, PDP, FTIR	Formation of chemisorbed films	93	[35]
19	Olive	NaCl/copper	WL, PDP, EIS	Cathodic-type corrosion inhibitor	90	[36]
20	Saffron	Seawater/copper	WL, PDP	Cathodic-type inhibitor	84	[37]
21	Beta vulgaris	Well water/mild steel	WL, PDP, FTIR, SEM, ACI, AFM	Mixed-type inhibitor	94	[38]
22	Cleome droserifolia	NaOH/aluminium	WL, SEM	Temkin	78.6	[39]
23	Psidium guajava	NaOH/mild steel	WL, PDP, SEM, FTIR	Langmuir	89.0	[40]
24	Pterocarpus	Na ₂ CO ₃ /mild steel	WL, HE	Langmuir	64.29	[41]
25	Amaranthus cordatus	NaCl/mild steel	WL	Physical adsorption	99.51	[42]
26	Allium sativum	NaCl/mild steel	FTIR, XRD, SEM, PDP, EIS	Mixed-type inhibitor	95	[43]
27	Ricinus communis	NaCl/steel	EIS, PDP, AFM	Temkin	87	[44]
28	Thyme	NaCl/mild steel	WL, PDP	Temkin	80.49	[45]
29	Neem	Ca(OH) ₂ /mild steel	WL, PDP	Chemisorption	86	[46]
30	Morinda lucida	NaCl/steel	WL, CST	Optimal corrosion inhibition	95.64	[47]
31	Rice straw	NaCl/steel	WL, EDX, XRD, FTIR, PDP, SEM	Interphase inhibition	92	[48]
32	Rhizophora mangle	NaCl/steel	AAS, FTIR	-	-	[49]
33	Arecanut husk	NaOH/copper, mild steel	WL, PDP, SEM, ATR-FTIR, XRD	Langmuir	94.34, 93.75	[50]
34	Origanum majorana	NaCl/mild steel	PDP	Physical adsorption	90	[51]
35	Euphorbia hirta, Dialium guineense	NaOH/aluminium	WL	Langmuir, Temkin	87.5, 87.5	[52]
36	Henna	NaOH/tin	WL, FTIR	Physical adsorption	95.45	[53]

37	Water hyacinth	NaOH/iron, aluminium	WL, OM, PDP	Adsorption of the phytochemical constituents of the extract on the surface of the metals	98.93	[54]
38	Citrullus colocynthis	NaCl, NaOH/copper	WL, PDP	Langmuir	77.08, 84.61	[55]
39	Gnetum africana	NH ₄ OH/copper	WL, PDP	Langmuir	87.83	[56]
40	Piper longum	NaOH/aluminium	PDP, EIS, WL	Mixed-type character	89	[57]
41	Mansoa alliacea	NaCl/zinc	PDP, EIS, FTIR, HPLC	Mixed-type inhibitor	92	[58]
42	Cascabela thevetia	NaCl/carbon steel	WL, PDP, EIS, AFM, EFM	Freundlich	95	[59]
43	Bitter leaf	NaOH/Al-Si alloy	WL	Physical adsorption	91	[60]
44	Calotropis	NaOH/mild steel	WL, SEM	Formation of layer on the mild steel	80.89	[61]
45	Robinia pseudoacacia	NaCl/copper	PDP, WL, SEM, EDX	Mixed inhibitory effect	93.5	[62]
46	Gelatin	NaOH/Al-Si alloy	PDP, EIS, CV	Freundlich	65.71	[63]
47	Garcinia indica	NaOH/aluminium	PDP, WL	Chemisorption	70.25	[64]
48	Derris Indica	NaOH/aluminium	WL, PDP, EIS, OP	Langmuir	60.2	[65]
49	Skytanthus acutus meyen	NaCl/carbon steel	WL, EIS, LC-MS	Formation of protective film	90	[66]
50	Litchi chinensis	NaCl/aluminium	PDP, EIS, FTIR, SEM	Langmuir	90	[67]
51	Cardamom, Nutmeg	Sea water/mild steel	WL, PDP, EIS, SEM, FTIR	Protective coating formed	99	[68]
52	Cymbopogon citratus	Seawater/mild steel	UV-Vis, FTIR, WL, EIS, SEM	Formation of a protective film due to the adsorption of inhibitor on the mild steel	34	[69]
53	Vicia faba peel	Marine water/mild steel	GC-MS, PDP, EIS, SEM	Langmuir	97.84	[70]

3.1 Inhibitors are Used in Four Types of Environments

1. Supply waters, natural waters, industrial cooling waters in the 5–9 pH range.
2. Liquid acid media utilized in pickling of metallic materials, and post-service cleaning of metal surfaces.

3. In primary and secondary oil production and refining.
4. Environments of many other types, [13].

3.2 pH Impact on Inhibitor Performance

When choosing a corrosion inhibitor with high inhibition and cost effectiveness, the electrolyte solution's pH is crucial. It is frequently important to evaluate the pH value to guarantee the constant inhibitory performance of the inhibitor during treatment. All inhibitors have a pH range in which they are most efficient. The formation of stable surface layers needs a certain minimum pH. Temperature, chemical species, and flow rate are only a few of the additional factors that affect this minimum pH value. Several inhibitors lose their effectiveness at pH levels that are either too low or too high. Inhibitors of polyphosphates, for instance, must be utilized between pH 6.5 and 7.5. Nitrites are ineffective at pH levels below 5.5-6. Despite the fact that chromates are less prone to pH changes, it is typically used at pH 8.5. Because no insoluble protective iron benzoate film can form at lower pH values, sodium benzoate is ineffective in electrolytes with pH less than 5.5 [71-74].

3.3 Inhibitors and Some Influencing Factors

The performance of inhibitors depends on various factors. The Figure 4 below provides the discussion concerning them [75-76].

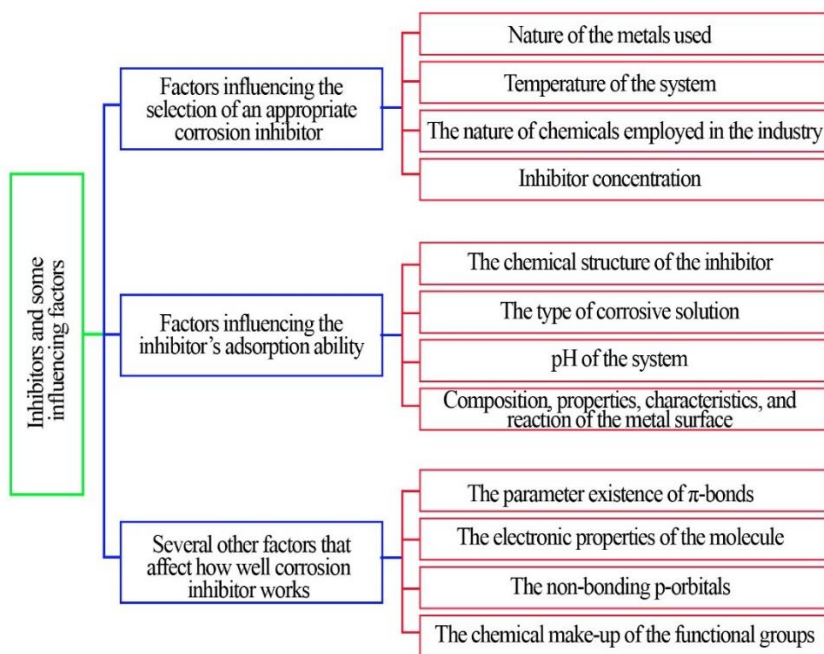


Fig. 4 Inhibitors and some influencing factors

4. Conclusion and Future Outlook

This paper has successfully examined the most recent developments in corrosion protection of metallic materials by different plant extracts in alkaline environments. From the literatures looked into, it can be summarized that,

- Plant extracts are excellent candidates to be harnessed on a commercial quantity as better replacement to inorganic corrosion inhibitors against metal corrosion, which are both costly and very harmful to the environment.
- Researchers suggested using corrosion inhibitors of plant origin as a strategy to slow down corrosion in metallic materials.
- The pH of the system has a significant impact on the corrosion inhibition process and must be considered when selecting the appropriate corrosion inhibitor.
- The phytochemical ingredients in plant extracts are said to have the capacity to inhibit steel and other metals from corroding by adsorbing to it.
- This study has also identified and briefly reviewed the wide varieties of corrosion inhibitors and their functions, plant extracts, and corrosion characterization methods employed by different researchers in their search of ideal inhibitors of natural origin for corrosion protection of metallic materials.
- This work is highly important for key participants and readers in this field to increase their understanding of how to create plant extracts based on their appropriateness and reproducibility for protecting metallic structures from corrosion.
- It has also looked into the economic costs of corrosion as it impacts the economy of a nation, the use of steel and other metals in alkaline environments.
- Majority of the existing studies concentrated more on alkaline media like NaCl and NaOH, while there were less researches on alkaline media like Na₂CO₃, NH₄OH, and Ca(OH)₂.
- According to the findings of this review, plant-based inhibitors have been employed most notably in steel products, followed by aluminum products, and copper, in that order. But only one piece of literature supports the use of plant extracts in alkaline medium for other metals like tin, iron, and zinc.

Therefore, it is advantageous to promote/recommend more reviews and studies on the application of plant extracts as corrosion inhibitors in basic media for steel and other metals in the near future using other basic media like Mg(OH)₂, NaHCO₃ and / or KOH.

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Conflicts of Interest

The authors of this research work have no conflicts of interest to disclose.

Abbreviations

OM:	Optical Microscope
EFM:	Electrochemical frequency modulation
WL:	Weight loss
AFM:	Atomic force microscope
GIXD:	Grazing incidence X-ray diffraction
FTIR:	Fourier transform infrared spectroscopy
DFT:	Density functional theory
HE:	Hydrogen evolution
N ₂ H ₄ :	Hydrazine
MDS:	Molecular dynamics simulation

ATR:	Attenuated total reflection spectroscopy
XRD:	X-ray diffraction
KOH:	Potassium hydroxide
NaCl:	Sodium chloride
Mg(OH) ₂ :	Magnesium hydroxide
Na ₂ SO ₄ :	Sodium sulfate
3D SI:	3D Surface inspection
LPR:	linear polarization resistance
EDS:	Energy-dispersive X-ray spectroscopy
Na ₂ SO ₃ :	Sodium sulfite
FESEM:	Field emission scanning microscopy
CV:	Cyclic voltammetry
HPLC:	High-performance liquid chromatography
EIS:	Electrochemical impedance spectroscopy
PDP:	Potentiodynamic polarization
Ca(OH) ₂ :	Calcium hydroxide
OPM:	Optical microscope
Max. IE (%):	Maximum inhibition efficiency
ACI:	AC impedance
LC-MS:	Liquid chromatography-mass spectrometry
XPS:	X-ray photoelectron spectroscopy
NaOH:	Sodium hydroxide
NH ₄ OH:	Ammonium hydroxide
GC-MS:	Gas chromatography-mass spectrometry
NaHCO ₃ :	Sodium bicarbonate
CST:	Compressive-strength testing
ATR-FTIR:	Attenuated total reflection-Fourier transform infrared
AAS:	Atomic absorption spectroscopy
TM:	Thermometric method
UV-Vis:	Ultraviolet-visible spectroscopy

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