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Review Paper

Green corrosion inhibitors for copper in NaOH, NaCl and Sea Water-A Review

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Abstract

Corrosion like environmental pollution is inevitable and is a serious problem for most of the industries in rapidly developing tropical countries like India. It is a constant and continuous problem. Plant extract has been used as green inhibitors to prevent the metals and alloys against corrosion as they are non-toxic, biodegradable and readily available and eco-friendly. Adsorptions of ingredients of plant extract on metal surface obey various adsorption isotherms. Corrosion inhibition study of copper was carried out by weight loss method with various time and temperatures. Electrochemical methods such as Potentiodynamic polarization (PP) and Electrochemical Impedance Spectra (EIS) were also employed. To study the nature of surface films was done by using various techniques such as, FT-IR and Ultra Violet Visible Spectroscopy, Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscope (SEM) and Electrochemical Frequency Modulation (EFM). Other methods like High Performance Liquid Chromatography (HPLC), Electric Noise (EN) analysis, EMP, quantum chemical computations techniques were also used. The results obtained from weight loss data and by electrochemical techniques were in good agreement with each other. The present review paper covers the research works done by various researchers on corrosion inhibition of copper in NaOH, NaCl and Sea water media using a plant extract as green inhibitors.

Keywords: Copper corrosion, green inhibitors, polarization, EDX, UV, FT-IR.

Introduction

Corrosion is defined as the deterioration of metal or its properties due to interaction between metal and its environment. Copper is noble metal. Copper and it's alloy are widely used in chemical and microelectronic industry. It is also used in the manufacture of integrated circuits[1].

Most convenient method for the protection against corrosion of copper metal in aggressive environments is the use of corrosion inhibitors. Inhibitors are usually used in small concentrations which were added to aggressive medium to reduce corrosion. However, synthetic compounds used as inhibitors are expensive and for the most part, they are very dangerous for environment.

The plant extracts such as seeds, leaves, flowers, fruits and barks etc are eco-friendly, non- toxic, biodegradable, readily available and potentially low cost, and can be used nowadays as 'Green Inhibitors'. Generally, extracts of plant materials contain heteroatoms such as Oxygen, Phosphorous, Nitrogen and Sulphur. Adsorption of these atoms depends mainly on functional groups, steric factors, electron density at the donor atoms and also on the electronic structure of the inhibitor. The objective of the present review to summarize the results regarding corrosion inhibition of copper by using various green inhibitors in NaOH, NaCl and Sea water medium published earlier than this review. Various plant materials used for Copper in NaOH, NaCl and Sea water were presented in Table-1 to Table-3.

Table-1: List of Corrosion inhibition studies of Copper in NaOH solution.

Inhibitor	Medium	Methods	Findings	I.E. (%)	Ref. No.
Capparis, spinosa L. extract.	1M NaOH	Weight loss with temperature. polarization and potentiodynamic measurements cyclic voltammetry.	Mixed-type inhibitor. Langmuir adsorption isotherm.	79.30 Wl 74.00 PP 87.60 EIS	2
Cassia, siamea Lam root extract	.5MNaOH	Weight loss method.	Langmuir adsorption isotherm.	78.30 Wl	3
Citrullus colocynthis Fruits	1M NaOH	Weight loss with time and temperature. Electrochemical polarization methods.	Mixed-type inhibitor. Langmuir adsorption isotherm.	84.61 Wl 86.33 pp	4

Inula viscosa	1M NaOH	Weight loss with temperature.	Langmuir adsorption isotherm.	86.49 Wl	5
Lawsonia inermis, Date palm, Phoenix dactylifera, and Corn	NaOH	Weight loss and Potentiodynamic polarization methods.	Temkin adsorption isotherm.	--	6

Note: Wl= Weight loss, PP= Potentiodynamic Polarization, EIS=Electrochemical Impedance Spectroscopy.

Table-2: List of Corrosion inhibition studies of Copper in NaCl solution.

Inhibitor	Medium + Additive	Methods	Findings	I.E. (%)	Ref. No.
Chitosan	3% NaCl	Weight loss, Polarization and EIS techniques. Quantum chemical computations, SEM	Cathodic inhibitor. Langmuir isotherm	87.00 Wl 79.00 PP 83.00 EIS	7
Citrullus colocynthis Fruits	1M NaCl	Weight loss with time and temperature. Electrochemical polarization methods	Mixed-type inhibitor. Langmuir adsorption isotherm	77.08 Wl 97.00 PP	4
Extract from coffee bagasse oil	3.5% NaCl	Temperature effect, PP, EIS, SEM, EMP, EDX, FT-IR and Gas Chromatography (GC) studies.	Inhibitor behave as Mixed-type. Langmuir Adsorption isotherm	95.00 PP	8
Natural honey	0.5M NaCl	Weight loss method. Polarization techniques.	Langmuir Adsorption isotherm	89.00 Wl 97.60 PP	9
Some plant leaves	NaCl +S^{-2} ions	Potentiodynamic polarization, EIS and EDX methods	Complex formation by inhibitor molecules on copper surface.	--	10
Olive leaf extract	0.5M NaCl	Potentiodynamic polarization and EIS. Voltammetry and High Performance Liquid Chromatography (HPLC).	Cathodic-type inhibitor.	90.00 PP	11
Olive mill waste water *(OMW)*	3wt.% NaCl	Polarization and EIS methods, Voltammetry and HPLC	Inhibitor behave as Mixed-type. Langmuir Adsorption isotherm	84.16 PP	12
Phosphory-lated chitin	200ppm NaCl	Weight loss with temperature. Potentiodynamic polarization and EIS	----	88.20 Wl 89.10 PP 92.04 EIS	13
Propolis	0.5M NaCl	Potentiodynamic polarization and EIS techniques.	Cathodic type inhibitor.	71.35 PP 79.64 EIS	14
Rhizophora mucronata tannin	3% Wt. NaCl	Weight loss with temperature. FT-IR.	---	80.00 Wl	15
Vegetal Tanin water	0.1M NaCl	Potentiodynamic polarization. EIS, SEM, Cyclic voltammetry. EDX spectra.	Anodic inhibitor.	93.20 PP 97.00 EIS	16
Vitex donian leaves	3.5% NaCl	Weight loss with temperature. polarization and EIS techniques. Quantum chemical calculations	Mixed-type inhibitor	73.00 Wl	17
Pimpinella Anisum, Carum Carvi, Cuminum Cyminum and Hibiscus Sabdarriffa	0.5M NaCl	Electrochemical noise analysis (EN) and EIS	Cathodic inhibitors	----	18

Table-3: List of Corrosion inhibition studies of Copper in Sea water.

Inhibitor	Medium+Additive	Methods	Findings	I.E. (%)	Ref. No.
Chitosan	Synthetic Sea Water +	Weight loss, polarization, EIS	Mixed-type inhibitor.	89.00 Wl	19

biopolymer	20 ppm S^{-2}	and EFM methods. SEM and FT-IR. Quantum chemical calculations, EDX studies.	Langmuir adsorption isotherm	85.49 PP 90.53 EIS	
Crocus sativus L. (Saffron extract)	Natural Sea water	Weight loss with temperature. potentiodynamic polarisation measurements.	Cathodic–type inhibitor	84.00 Wl 82.00 PP	20
Emblica officinalis (Amla) Leaves	Natural Sea water	Weight loss with time and temperature. UV and IR spectrum	Langmuir and Temkin adsorption isotherms	79.99 Wl	21
Equisetum arvense	Synthetic Sea water	Potentiodynamic polarization, EIS and linear polarization resistance. SEM, FT-IR, GC-MS	Mixed-type inhibitor	53.78 PP 87.50 EIS	22
Mimusops elengi leaves (MEL)	Natural Sea water	Weight loss with time. Temperature effect study. SEM, EDX, UV, FT-IR.	Langmuir adsorption isotherm	86.84 Wl	23
Vitis vinifera Seed and skin	Natural Sea water	Weight loss method temperature effect and time	Langmuir and Temkin adsorption isotherm	76.08 Wl	24
Xanthosoma Spp leaf (XLE)	Sea water	Weight loss with temperature	Langmuir's adsorption isotherm	85.00 Wl	25
Ziziphus lotus	Natural Sea water	Weight loss with temperature, potentiometry polarization technique and SEM	Cathodic process	89.00 Wl 93.00 PP	26

Type of Plant materials used as green inhibitors: Different parts of plant materials were used as corrosion inhibitors such as, Leaves[10,17,21,23,25], Seeds[24], Skins[24], Fruits[4], Roots[3] and Plant extract[2,5-9,11-16,18-20,22].

Extracts used: Various solvents like double distilled water[18,25] and alcohol[2,4,10,14,17,21,23,24] were used to prepare extract of plant materials.

Medium: In this Review, for corrosion study media like NaOH[2-6], NaCl[7-18] and Sea water[19-26] has been investigated.

Additives: Additive such as S^{-2}[10,19] used with green inhibitors to enhanced I. E. Their synergistic effect was also studied.

Methods: Weight loss method[2-9,13-17,19-21,23-26], Weight loss with temperature[2,4,5,13-15,17,20,21,23-26], Weight loss with time[4,21,23,24], Potentiometric polarization[2,4,6,9-13,16,17,19,20,22,26], Electrochemical Impedance Spectroscopy (EIS)[7,8,10-13,16-19,22] and Synergistic effect[10,19] were used to calculate the percentage I. E. of green inhibitors.

Metal surface analysis: Surface of film form on metal were examined using techniques, such as SEM[7,8,16,19,22,23,26], FT-IR spectroscopy[8,15,19,21-23], UV spectroscopy[21,23], EDX technique[8,10,16,19,23], EFM[19], GC[8], GC-MS[22] and Cyclic Voltammetry[2,11,12,16]. Other methods like HPLC[11,12], Electric Noise analysis (EN)[18], EMP[8] and Quantum Chemical Computations and Molecular Dynamics Simulations[7,17,19] techniques were presented.

Adsorption isotherms: Various types of adsorption isotherms, such as Langmuir adsorption isotherm[2-5,7-9,12,19,21,23-25] and Temkin adsorption isotherm[6,21,24] were suggested.

Active phytoconstituents present in green inhibitors: i. In NaOH media: *Capparis spinosa L.*[2,27] contains glycosides, tannins, phenolic compound, flavonoids, steroids and alkaloids. *Citrullus colocynthis* fruits[4,28] contain Alkaloids, flavonoids and saponins compounds. *Inula viscosa*[5,29] contain 3-Omethylquercetin, viscic acid, ilicic acid, resveratrol, cynaric acid, isocostic acid, carabrone, tomentosin and hispidulin. Date palm[6] leaves contain carbohydrates, dietary fibre, enzymes, protein, fat, minerals, vitamins, phenolic acids and carotenoids. *Lawsonia inermis (Henna)*[6] contain mainly laws one. ii. In NaCl media: *Citrullus colocynthis*[4,28] fruits contain Alkaloids, flavonoids and saponins compounds. Natural honey[9] contain saccharides, organic acids such as acetic, formic, amino acids and gluconic acid, Glucose and fructose, polyphenols, trace amounts of enzymes, vitamin B and C.*Olive* leaf[11] extract contain Oleuropein. *Olive mill* waste water *(OMW)*[12] contain oleuropein and its derivatives hydroxytyrosol and tyrosol, cafeic acid, p-coumaric acid, oleuropein aglycone, lut´eolin, apigenin, fulvic acid, gallic acid, dihydrox yphenyl glycol, dihydroxy phenyl acetic acid and p-hydroxy phenyl acetic acid. Propolis[14] contain Luteolin, p-methoxycinnamic acid and prenylated coumarin. *Rhizophora mucronata tannin*[15] contain Catechin. Cumin (*Cuminum Cyminum*)[18,30] contain mainly cuminaldehyde, p-cymene and terpenoid. Hibiscus (*Hibiscus Sabdarriffa)*[18] consists of proteins, glucosides, organic acids (citric, malic, and traces of tartaric acid). iii. In Sea water media: *Crocus sativus L.* (Saffron extract)[20] contain Picrocrocine, Safranal and Crocine. *Emblica officinalis* (AMLA)[21] leaves contain Emblica A and B,

phyllanththin, Punigluconin and Pedunculagin. *Equisetum arvense*[22,31] contain chlorogenic acid, ferulic acid, caffeic acid, kaempferol, quercetin, isoquercetin, apigenin and luteolin. *Mimusops elengi* (MEL)[23] leaves contain flavonoids, alkaloids, saponins, triterpenes. *Vitis vinifera*[24] Seed and skin extract contain Proanthocyanidin and Resveratrol. *Xanthosoma Spp* leaf[25,32]. Leaves contain glycosides, saponins, alkaloids, terpenes, tannins, phenolic substances and flavonoids. *Ziziphus lotus*[26,33] is a fruit pulp which contains linoleic acid, vitamins like A, C and E.

Conclusion

This review paper presents the research works carried out by various researchers on copper corrosion and it's inhibition in NaOH, NaCl and Sea water using a plant extract as green inhibitors. Weight loss (gravimetric) with time and temperature effect are common methods to investigate the corrosion rate and I. E. for green inhibitors. Several studies indicates that with increase in temperature corrosion rate increases while percentage of I.E. decreases.

Electrochemical methods like Potentiodynamic polarization and EIS was also done by many researchers for comparison of data obtained by weight loss method. Other methods like SEM, FT-IR, EFM, UV-Spectroscopy, EDX, EN, HPL, GC, GC-MS and Cyclic voltammetry were also used to study surface of metal. Results obtained from weight loss data are in good agreement with Polarization and EIS methods.

References

1. Oteino-Alergo, V., Huynh, N., Notoya, T., Bottle, S.E. & Schwcinsberg, D. P. (1999). Inhibitive effect of 4- and 5-carboxybenzotriazole on copper corrosion in acidic sulphate and hydrogen sulphide solutions. *Corros. Sci*., 41(4), 685-697.

2. Wedian, F., Al-Qudaha, M. A. & Abu-Baker, A. N. (2016). The Effect of Capparis spinosa L. Extract as a Green Inhibitor on the Corrosion Rate of Copper in a Strong Alkaline Solution. *Port. Electrochim Acta*, 34(1), 39-51 DOI: 10.4152/pea.201601039.

3. Mihajlovic´ M.B.P. and Antonijevic M.M. (2015). Copper corrosion inhibitors. Period 2008–2014. A Review. *Int. J. Electrochem. Sci*., 10, 1027–1053.

4. Al-Dokheily, M. E., Kredy, H. M. & Al-Jabery, R. N. (2014). Inhibition of Copper Corrosion in H_2SO_4, NaCl and NaOH Solutions by Citrullus colocynthis Fruits Extract. *J. Nat. Sci. Res.*, 4(17), 60-73.

5. Nawafleh, E., Irshedat, M.,Bataineh, T., Muhaidat, R., AlQudah, M.& Alomary, A. (2012). The Effects of Inula viscosa Extract on Corrosion of Copper in NaOH Solution. *Res. J. of Chem. Sci.*., 2(9), 37- 41.

6. Rehan, H. H. (2003). Corrosion control by water-soluble extracts from leaves of economic plants. *Material wissenschaft und Werkstofftechnik*, 34(2), 232-237.

7. Oukhrib, R., El Ibrahimi, B, Bourzi, H., El Mouaden, K., Jmiai, A., El Issami, S. Bammou, L.& Bazzi L. (2017). Quantum chemical calculations and corrosion inhibition efficiency of biopolymer "chitosan" for copper surface in 3% NaCl. *J. Mater. Environ. Sci*., 8(1), 195–208.

8. Velazquez-Torres, N., Martinez, H., Porcayo-Calderon, J., Vazquez-Velez, E., Gonzalez-Rodriguez, J.G., & Martinez-Gomez, L. (2018). Use of an amide-type corrosion inhibitor synthesized from the coffee bagasse oil on the corrosion of Cu in NaCl. *Green Chem. Lett. Rev*., 11(1), 1–11. https://doi.org/10.1080/17518253.2017.1404645.

9. El-Etre, A. Y. (1998). Natural honey as corrosion inhibitor for metals and alloys. I. Copper in neutral aqueous solution. *Corros. Sci*., 40(11), 1845–1850.

10. El-Dahan, H. A. (2006). Natural products as corrosion inhibitors for copperin saline water in presence of sulphide. *Egyptian J. of Chem*., 49(5), 589-600.

11. Rahal, C., Masmoudi, M., Abdelhedi, R., Sabot, R., Jeannin, M., Bouaziz, M. & Refait, P. (2016). Olive leaf extract as natural corrosion inhibitor for pure Copper in 0.5 M NaCl solution: a study by voltammetry around OCP. *J. of Electroanal. Chem*., 769, 53-61. https://doi. org/10.1016/j.jelechem.2016.03.010.

12. Masmoudi, M. Rahal, C. Abdelhedi, R. Khitouni, M.& Bouaziz, M. (2015). Inhibitive action of stored olive mill wastewater (OMW) on the corrosion of copper in a NaCl solution. *RSC Adv*., 5, 101768– 101775.

13. Kumar, K.V., Appa Rao, B.V. & Hebalkar N.Y. (2017). Phosphorylated chitin as a chemically modified polymer for eco-friendly corrosion inhibition of copper in aqueous chloride environment. *Res. Chem. Intermed*., 43, 5811–5828. https://doi.org/10.1007/s1116 4-017-2964-x.

14. Vrsalovic, L., Gudic, S., Gracic, D.,Smoljko, I., Ivanic, I. Kliskic, M. & Oguzie, E. E. (2018). Corrosion protection of copper in sodium chloride solution using propolis. *Int. J. Electrochem. Sci*., 13, 2102–2117. https://doi.org/10. 20964/2018.02.71 .

15. Agi, A., Junin, R., Rasol, M., Gbadamosi, A. & Gunaji, R. (2018). Treated Rhizophora mucronata tannin as a corrosion inhibitor in chloride solution. *PLoS One*, 13(8), e0200595. https://doi.org/ 10.1371/journal.pone.0200595.

16. Mabrour, J., Aksirra, M. & Azzi, M. (2004). Effect of Vegetal Tannin on Anodic Copper Dissolution in Chloride Solution. *Corros. Sci*., 46(8), 1833–1846.

17. Oguike, R.S., Ayuk, A.A., Eze, F.C. & Oguzie, E.E. (2016). Experimental and Theoretical Investigation of Vitex Doniana Leaves Extract as Corrosion Inhibitor for Copper

in 3.5% NaCl Solution. *J. of Basic and Appl. Res. Int.*, 17, 184-197.

18. Nagiub, A. M. (2017). Electrochemical Noise Analysis for Different Green Corrosion Inhibitors for Copper Exposed to Chloride Media. *Port Electrochim Acta*, 35(4), 201-210. DOI: 10.4152/pea.201704201.

19. El Mouaden, K., El Ibrahimi, B., Oukhrib, R., Bazzi, L., Hammouti, B., Jbara, O., Tara, A., Chauhan, D.S.& Quraishi, M. A. (2018). Chitosan polymer as a green corrosion inhibitor for copper in sulfide containing seawater. *Int. J. Biol. Macromol*., 119, 1311–1323. https ://doi.org/10.1016/j.ijbiomac.2018.07.182.

20. Oukhrib, R., El Issami, S., Chaouay, A., El Mouaden, K., Jmiai, A., El Ibrahimi, B., Bazzi, L., Bammou, L. & Hilali, M. (2015). The inhibitory effect of saffron extract (Crocus sativus L) on copper corrosion in seawater. *Chem. Sci. Review and Lett.*, 4(13), 241-251.

21. Rani, P. D. and Selvaraj, S. (2010). Emblica officinalis (AMLA) leaves extract as corrosion inhibitor for copper and its alloy (Cu-27Zn) in natural sea water. *Arch. Appl. Sci. Res*., 2(6), 140–150.

22. Esquivel-Rojas, A., Cuevas-Arteaga, C. & Valladares-Cisneros, M. G. (2020). Study of corrosion inhibition of copper in synthetic seawater by Equisetum arvense as green corrosion inhibitor. *Rev. Mex. Ing. Quím* , 19(2), 603-616. DOI: https://doi.org/10.24275/rmiq/Mat629 .

23. Deivanayagam, P., Malarvizhi, I., Selvaraj, S. & Rani,P. D. (2015). Corrosion inhibition efficacy of ethanolic extract of Mimusops elengi leaves (MEL) on copper in Natural Sea Water. *Int. J. of multidisciplinary Res. and Develop*., 2(4), 100-107. DOI: 10.13140/RG.2.1.1205.7129 .

24. Rani, P.D. and Selvaraj, S. (2010b). Inhibitive action of Vitis vinifera (grape) on copper and brass in natural sea water environment. *Rasayan J. Chem*., 3(3), 473–482.

25. Hart, K.G, Orubite-Okorosaye, K. & James, A.O. (2016). Corrosion Inhibition of Copper in Seawater by Xanthosoma Spp Leaf Extract (XLE). *Int. J. of Adv. Res. in Chem. Sci*., 3(12), 34-40. http://dx.doi.org/10.20431/ 2349-0403.0312005.

26. Oukhrib, R., El Issami, S., El Ibrahimi, B., El Mouaden, K., Bazzi, L., Bammou, L., Chaouay, A., Salghi, R., Jodeh, S., Hammouti, B. &Amin-Alami, A. (2017b). Ziziphus lotus as green inhibitor of copper corrosion in natural sea water. *Port Electrochim. Acta*, 35, 187–200. https://doi.org/10. 4152/pea.201704187.

27. Khanfer, M. A., Sabri, S. S., Abu Zargaa, M. H. & Zeller, K. P. (2003). The Chemical Constituents of Capparis spinosa of Jordanian Origin. *Natural Prod. Res*., 17(1), 9-14.

28. Djilani, A., Legseir, B., Soulimani, R., Dickob, A. & Younos, C. (2006). New Extraction Technique for Alkaloids. *J. Braz. Chem. Soc*., 17(3), 518-520.

29. Ortal, D., Hugo, E.G., Shlomo, G. & Margalit, B. (2009). Antioxidant activity of 1,3-dicaffeoylquinic acid isolated from Inula viscose. *Food Res. Int*., 42, 1273.

30. Ladha, D. G., Naik, U. J. & Shah, N. K. (2013). Investigation of Cumin (Cuminum Cyminum) extract as an eco-friendly green corrosion inhibitor for pure Aluminium in Acid medium. *J. Mater. Env. Sci.*, 4(5), 701-708.

31. Al-Snafi, A. E. (2017). The pharmacology of Equisetum arvense - A Review. *IOSR J. of Pharm.*, 7, 31-42.

32. Khaled, K. F. (2008). Molecular simulation, quantum chemical calculations and electrochemical studies for the inhibition of mild steel by triazoles. *Electrochim. Acta*, 53, 3484-3492.

33. Borgi, W. and Chouchane, N. (2009). Anti-spasmodic effects of *Ziziphus lotus* (L.) desf. extracts on isolated rat duodenum. *J. Ethnopharmac*., 126(3), 571-573.