FTIR Analysis of Halloysite Nanotubes Loaded with Corrosion Inhibitors

Subhalakshmi Suresh Kumar, Saeid Kakooei*, Mokhtar Che Ismail, Muhammad Haris

Centre for Corrosion Research, Department of Mechanical engineering, Universiti Teknologi Petronas, Seri Iskandar, Perak.

Abstract

Halloysite nanotubes loaded with various corrosion inhibitors have been widely used to control corrosion in different fields and sectors, in specific, the oil and gas pipeline industries. One of the main factors to be considered is the loading capacity of the halloysite nanotubes. In this study, Halloysite nanotubes are loaded with various inhibitors like sodium diethyldithiocarbamate, green inhibitors like vanillin, thyme oil and a combination of both vanillin and thyme oil. The end products were characterized by Fourier Transform Infrared Spectroscopy. The formation of end stoppers in the halloysite nanotubes using Copper sulfate was also studied. It is evident from the FTIR analysis that the halloysite nanotubes were efficiently loaded with the corrosion inhibitors and the end stoppers have formed.

Keywords: halloysite nanotubes, green corrosion inhibitor, loading capacity.

Article Info

Received 14th October 2019
Accepted 10th March 2020
Published 1st April 2020
*Corresponding author: Saeid Kakooei; e-mail: saeid.kakooei@utp.edu.my

ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Self-healing coatings with containers were first introduced in 2001 by White, S.R., et al., [1]. The containers impart a major effect on the smart coatings and are based on their structure and properties [2-6]. The containers used in smart coatings can generally be classified into organic and inorganic containers. Inorganic containers can be clay nanotubes, mesoporous silica, polyelectrolyte multilayer, mesoporous zirconia, hybrid materials and so on [7]. Inorganic containers can be PUF, PMF, etc. [8]. The current trend is to encapsulate the nanocontainers to achieve easy leaching of corrosion inhibitor, triggering mechanism is enabled, prolonged storing period and so on. In this paper, Halloysite nanotubes are chosen as nanocontainers, loaded with green corrosion inhibitors like vanillin and thyme oil, and end stoppers are formed by using copper sulfate pentahydrate.

Halloysite nanotubes, shown in Figure 1, are inorganic aluminosilicate clay mineral found commonly in countries like China, Brazil, Mexico, United States, New Zealand, and Australia. Halloysite nanotubes consist of two basal surfaces. The outer Si-O-Si layer is tetrahedral, hydrophilic and can be etched with an alkaline, while the inner Al-OH layer is octahedral, hydrophobic and can be etched with acid. These significant features enable HNTs to load and release compounds with different natures. The inner lumen of HNTs can be loaded up to 30 vol% with proper pre-treatment. Moreover, HNTs are cheap, biocompatible and easy to work with. The release of inhibitors can be controlled by layer by layer deposition of alternatively charged polymer layers on the outer surface of the HNT or by the formation of end stoppers at the ends of the nanotubes by metal ion-inhibitors compound [9-11].

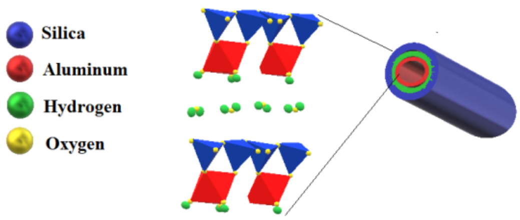

Figure 1: Schematic representation of halloysite nanotubes

Vanillin, as shown in Figure 2, is a non-toxic, environment-friendly corrosion inhibitor obtained from vanilla beans. They have proven to exhibit 93-98% corrosion inhibition for carbon steel in acid media [12].

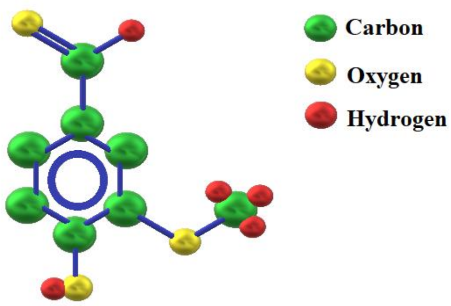

Figure 2: Schematic representation of Vanillin

Thyme oil, as shown in Figure 3, is an essential oil obtained from Thymus vulgaris. It is non-toxic and environmental-friendly which has a proven corrosion inhibition efficiency.

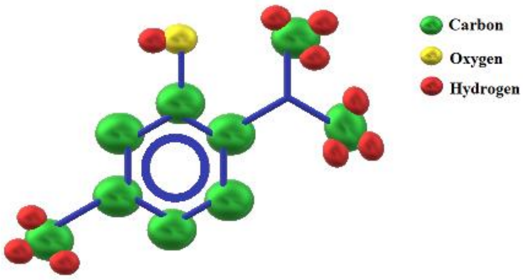

Figure 3: Schematic representation of thyme oil

The end stoppers were formed using copper sulfate pentahydrate seen in Figure 4, as they have shown better results in comparison to other chemicals for end stopper formation [13].

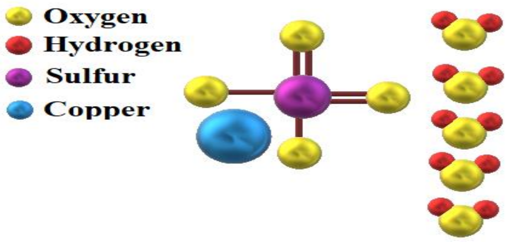

Figure 4: Schematic representation of copper sulfate pentahydrate

This study focuses on the FTIR study of halloysite nanotubes loaded with vanillin and thyme oil. End stoppers were also formed. The FTIR spectra show that the nanocontainers were successfully loaded with the corrosion inhibitors and the formation of end stoppers has been done. To the best of our knowledge, this is the first time halloysite nanotubes have been loaded with two green corrosion inhibitors, the only other instance was the loading of halloysite nanotubes with non-eco-friendly corrosion inhibitors by Xing et al [13].

Materials and methods

Materials

Materials used for the research were halloysite nanoclay, vanillin, thyme oil (white), and copper sulfate pentahydrate from Sigma Aldrich, and Ethanol from HmbG chemicals.

All reagents were of analytical grade and used without further purification.

A. Experiment

a) Loading of corrosion inhibitor into nano-containers

Loading of vanillin into halloysite nanotubes

Vanillin and ethanol were taken in 1:2 ratios. The saturated solution was then taken and 5 g of halloysite nanotubes were added to it. One batch was stirred manually as per previous literature and the other was stirred using a magnetic stirrer at 350 rpm for 1 hour. The solutions were then placed in a vaporizer at 200 rpm, 175 mbar pressure and room temperature for 4 minutes. The obtained vanillin loaded HNT batches were dried in an oven for 8 hours at 40^{o} C. Batch I was labeled VHNT A and batch II was labeled VHNT B.

Loading of thyme oil into halloysite nanotubes

30 ml ethanol was used to dissolve 5 ml thyme oil and 4 g halloysite nanotubes. Two batches were made. The batch I was mixed using a magnetic stirrer at 350 rpm, room temperature for 24 hours. Batch II was mixed using a magnetic stirrer for 15 minutes at 350 rpm, room temperature. The solutions were then placed in a vaporizer at 200 rpm, 175 mbar pressure and room temperature for 3 minutes. The obtained thyme oil loaded HNT batches were dried in an oven for 12 hours at 40^{o} C. Batch I was labeled THNT A and batch II was labeled THNT B.

Loading of vanillin and thyme oil into halloysite nanotubes

Vanillin, thyme oil, halloysite nanotubes, and ethanol were taken in 1:2:2:5 ratios. They were stirred together using a magnetic stirrer at 350 rpm, room temperature for one hour. The solution was then placed in a vaporizer at 200 rpm, 175 mbar pressure and room temperature for one hour. The obtained vanillin and thyme oil loaded HNT were dried in an oven for 12 hours at 40^{o} C. The Batch was labeled VTHNT.

Formation of end stoppers

Among the batches, the best were chosen based on FTIR results. The green corrosion inhibitor loaded halloysite nanotubes VHNT B, THNT B, and VTHNT were then mixed with 0.8 mol copper sulfate pentahydrate solution and dried. The end stopper formed loaded halloysite nanotubes were labeled as VHNT ES, THNT ES, and VTHNT ES respectively.

Results and discussion

Fourier Transform Infrared Spectroscopy (FTIR)

The end products were all characterized by Fourier Transform Infrared Spectroscopy (FTIR). Vanillin and Thyme oil were also characterized and the spectra showed the required curves with significant peaks a seen in Figure 5.

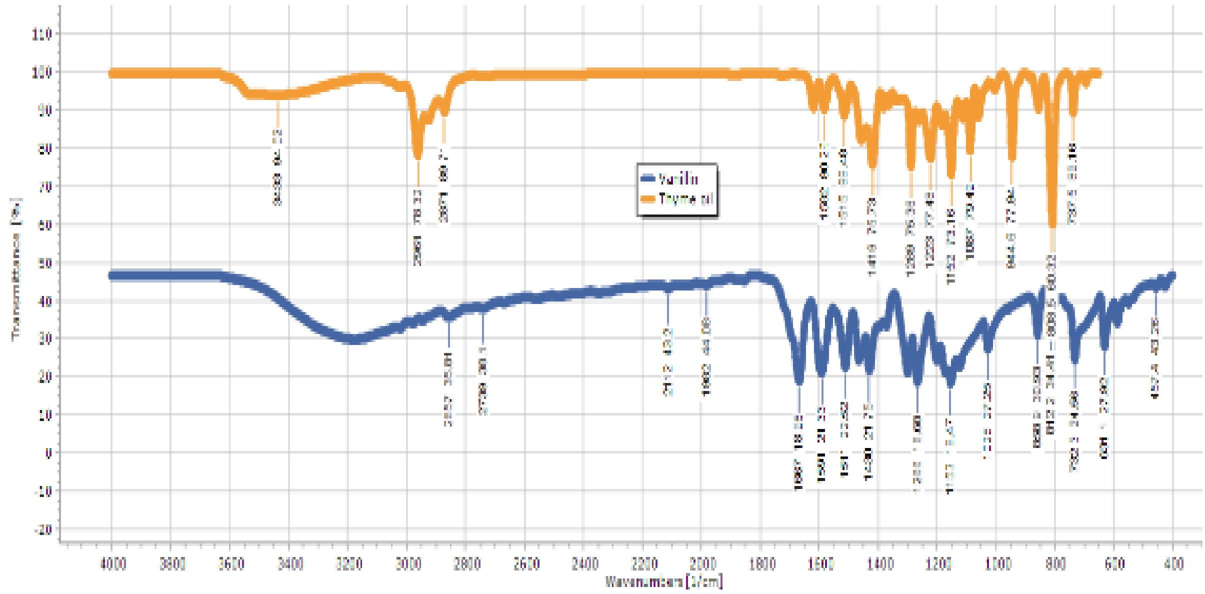

Figure 5: FTIR spectra of vanillin and thyme oil

Vanillin loaded halloysite nanotubes

VHNT A and VHNT B both showed similar curves and peaks as shown in Figure 6. But the transmittance of VHNT A > VHNT B making VHNT B, a better option with increased loading.

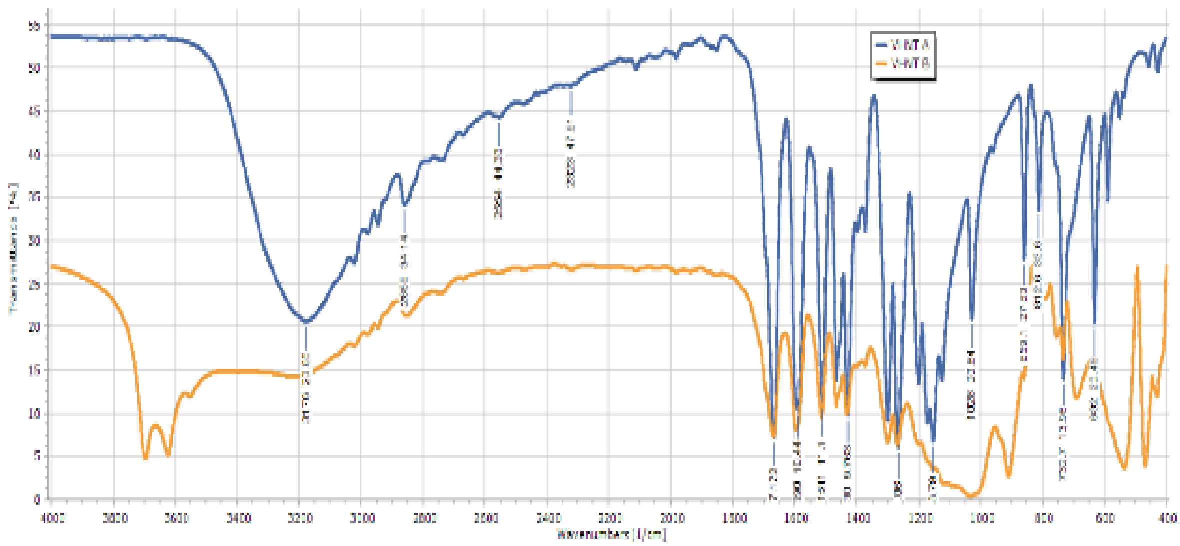

Figure 6: FTIR spectra of vanillin loaded HNT: VHNT A and VHNT B

Thyme oil loaded halloysite nanotubes

THNT A and THNT B both showed similar curves and peaks as shown in Figure 7. But the transmittance of THNT A > THNT B making THNT B, a better option with increased loading.

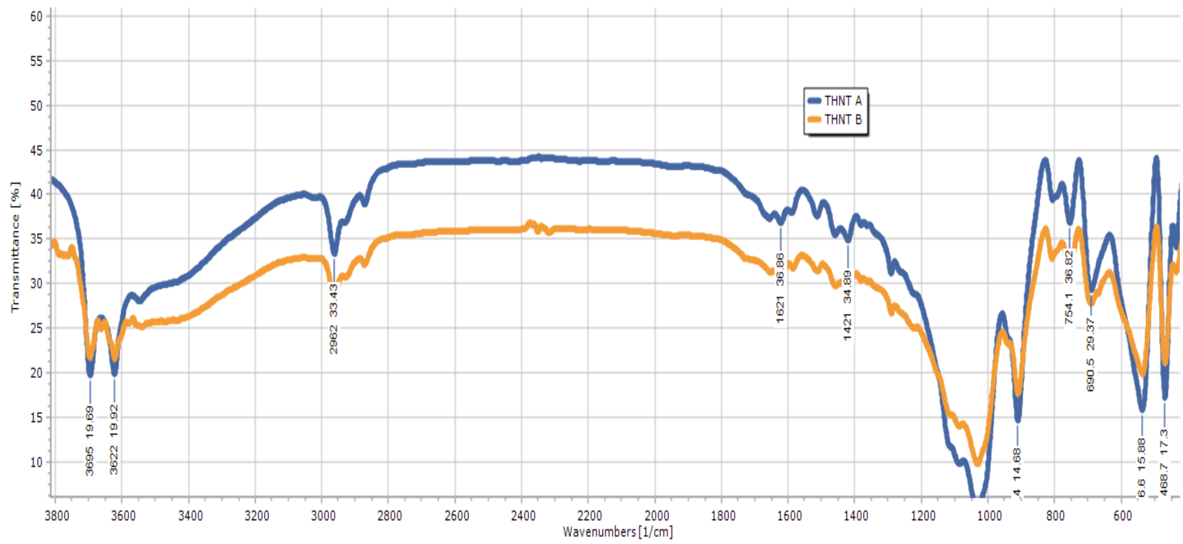

Figure 7: FTIR spectra of thyme oil loaded HNT: THNT A and THNT B

Loaded halloysite nanotubes with end stoppers

VHNT ES, THNT ES, and VTHNT ES all showed characteristic peaks (shown in Figure 8) with a transmittance % of 48, 47 and 44 respectively. The multi green inhibitor loaded HNT showed better loading efficiency.

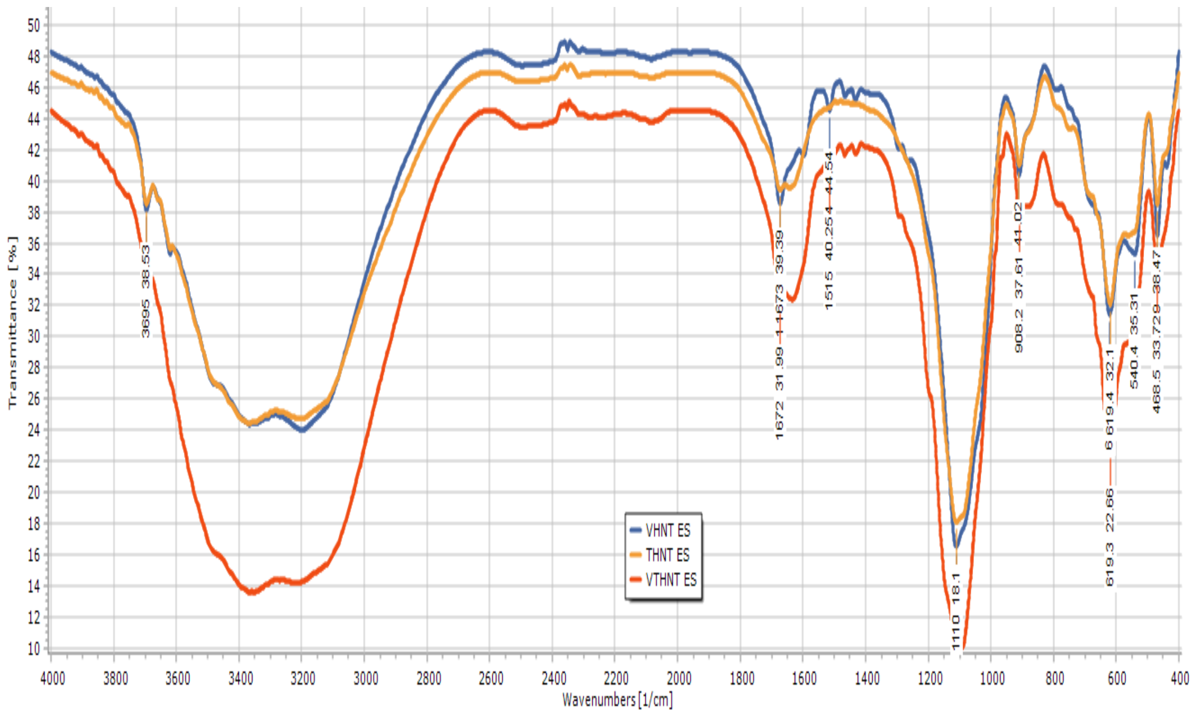

Figure 8: FTIR spectra of loaded HNT with end stoppers: VHNT ES, THNT ES, and VTHNT ES

Conclusion

Experiments were done to load vanillin, thyme oil and both together into halloysite nanotubes. The loading efficiency was characterized using FTIR results. UV- Vis analysis, thermogravimetric analysis (TGA) and field emission scanning electron microscope (FESEM) characterization will be done to get more accurate results on the loading ability of Halloysite nanotubes.

Acknowledgment

This research is financially supported by Yayasan Universiti Teknologi Petronas (YUTP) -FUNDAMENTAL RESEARCH GRANT (YUTP-FRG) (15LC0-165) and Universiti Teknologi Petronas.

Author Contributions

S.K. and S.S.K conceived the idea of the present work. S.S.K performed the experiments and wrote the manuscript. S.K supervised the project. The results were discussed by S.S.K and M.H. The resources were provided by M.C.I.

Disclosure of Conflict of Interest

The authors declare that they do not have any conflict of interest.

Compliance with Ethical Standards

This article does not contain any studies involving animals / humans performed by any of the authors.

References

[1] S. R. White, N.R. Sottos, P.H.Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, S.Viswanathan, "Autonomic healing of polymer composites," *Nature*, vol. 409, no. 6822, p. 794, 2001.

[2] D. Y. Zhu, M. Z. Rong, and M. Q. Zhang, "Self-healing polymeric materials based on microencapsulated healing agents: From design to preparation," (in English), *Progress in Polymer Science*, Review vol. 49-50, pp. 175-220, 2015.

[3] A. Yabuki, A. Kawashima, and I. W. Fathona, "Self-healing polymer coatings with cellulose nanofibers served as pathways for the release of a corrosion inhibitor," *Corrosion Science*, vol. 85, pp. 141-146, 2014.

[4] A. Yabuki, T. Shiraiwa, and I. W. Fathona, "pH-controlled self-healing polymer coatings with cellulose nanofibers providing an effective release of corrosion inhibitor," *Corrosion Science,* vol. 103, pp. 117-123, 2016.

[5] S. J. García, H.R. Fischer, P.A. White, J. Mardel, Y. Gonzalez-Garcia, J.M.C. Mol, A.E. Hughes, "Self-healing anticorrosive organic coating based on an encapsulated water reactive silyl ester: Synthesis and proof of concept," *Progress in Organic Coatings,* vol. 70, no. 2-3, pp. 142-149, 2011.

[6] M. Kouhi, A. Mohebbi, and M. Mirzaei, "Evaluation of the corrosion inhibition effect of micro/nanocapsulated polymeric coatings: a comparative study by use of EIS and

Tafel experiments and the area under the Bode plot," *Research on Chemical Intermediates*, vol. 39, no. 5, pp. 2049-2062, 2013.

[7] Huige Wei, Yiran Wang, Jiang Guo, Nancy Z.Shen, Dawei Jiang, Xi Zhang, Xingru Yan, Jiahua Zhu, Qiang Wang, Lu Shao, Hongfei Lin, Suying Wei, Zhanhu Guo, "Advanced micro/nanocapsules for self-healing smart anticorrosion coatings," (in English), *Journal of Materials Chemistry A*, Review vol. 3, no. 2, pp. 469-480, 2015.

[8] H. Pulikkalparambil, S. Siengchin, and J. Parameswaranpillai, "Corrosion protective self-healing epoxy resin coatings based on inhibitor and polymeric healing agents encapsulated in organic and inorganic micro and nanocontainers," (in English), *Nano-Structures and Nano-Objects*, Review vol. 16, pp. 381-395, 2018.

[9] S. J. Antill, *Halloysite: A Low-Cost Alternative*. 2003.

[10] E. Joussein, S. Petit, J. Churchman, B. Theng, D. Righi, and B. Delvaux, "Halloysite clay minerals–a review," ed: De Gruyter, 2005.

[11] E. Abdullayev and Y. Lvov, "Halloysite for controllable loading and release," in *Developments in Clay Science*, vol. 7: Elsevier, 2016, pp. 554-605.

[12] O. S. Shehata, L. A. Korshed, and A. Attia, "Green Corrosion Inhibitors, Past, Present, and Future," 2018.

[13] X. Xing, X. Xu, J. Wang, and W. Hu, *Chemical Physics Letters*, vol. 718, pp. 69-73, 2019.