Effect of bath temperature on sodium diethyldithiocarbamate trihydrate loading of halloysite nanotube

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Abstract. Smart coatings have become one of the most sought after solutions for corrosion control in industries. A need to encapsulate the corrosion inhibitor by means of a nano/micro container has come into the picture as the conventional methods are not favourable and has demerits. Halloysite nanotube based smart coatings are effective given that it is environment-friendly unlike most of its competitors. The current work focuses on the effect of bath temperature in a vaporizer on the loading ability of Halloysite nanotube is studied with Sodium diethyldithiocarbamate trihydrate as a corrosion inhibitor. The loading was carried out at three different bath temperatures which are 40, 60 and 80 °C and the resultant samples were investigated by characterization using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and UV-Vis Spectroscopy. It was found that an increase in bath temperature to 80 °C, it will increase the loading capacity of halloysite nanotubes.

1. Introduction
The presence of serious metal corrosion problems has increased the need for using inhibitors in coatings. Direct addition of inhibitor to the coatings is not favourable as it has demerits like pore formation in coating due to removal of inhibitors. Hence, a need to encapsulate the corrosion inhibitors by means of a container in micro/nano scale came into picture. Different types of materials like carbon nanotubes, polymer, and silica capsules can be chosen to be used as carriers. However, halloysite nanotubes had an edge over these due to its exceptional properties. Halloysite nanotubes 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. 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 [1-3]. A number of ways are employed to load halloysite nanotubes (HNT) with corrosion inhibitors. Soaking of the container in a saturated solution of corrosion inhibitors, stirring the mixture of container and inhibitor solution, vacuum negative pressure method, impregnation method, hydrothermal method, layer by layer assembly method are some of the methods used for loading. The factors affecting the loading of HNTs include molar mass or molar weight of inhibitor, the morphology of HNT, pH of inhibitor, its solvent and the solution and nature of inhibitor. If the inhibitor is hydrophilic in nature, the vacuum negative pressure method is employed using a vaporizer as shown in figure 1.
For inhibitors with high solubility, HNT is loaded by blending the inhibitor with appropriate polymer, whereas low melting inhibitors are loaded in liquid form [3-5]. Sodium diethyldithiocarbamate trihydrate (C₂H₅₂NCSSNa·3H₂O) with IUPAC name sodium diethylaminomethanedithioate trihydrate is a corrosion inhibitor with a molar mass of 225.31 g/mol, readily soluble in water and has a melting point of 93 °C. It is a catenulate organosulfur compound containing nitrogen and sulfur function group and a potent metal-chelating agent. Moreover, it is non-toxic in nature [6, 7].

The loading of the corrosion inhibitor into the halloysite nanotubes is a crucial stage and the many applications of halloysite nanotubes depends on the loading capacity. The loading capacity can be increased by pre-treatment like inner lumen or outer surface etching. The inner lumen etching has been effective and has shown 4 times more loading capacity than the conventional method [8]. However, to the best of our knowledge, much concern has not been given to other factors affecting the loading capacity like the bath temperature, solvents used, pressure, and so on.

This current work focuses on the effect of bath temperature on the loading capacity of halloysite nanotubes using sodium diethyldithiocarbamate as corrosion inhibitor, by loading at different bath temperatures. Characterization using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis Spectroscopy were carried out to investigate which of the three samples synthesized at different temperatures had undergone maximum loading.

2. Methodology

2.1. Materials and instrumentation

Halloysite nanoclay, Sodium diethyldithiocarbamate trihydrate were obtained from Sigma Aldrich. Ethanol was obtained from HmbG chemicals. All reagents were of analytical grade and used without further purification. Scanning Electron Microscopy (SEM, Phenom Pro X), Fourier Transform Infrared Spectroscopy (FTIR, Spectrum One/BX, Perkin Elmer Inc.) and UV-Vis Spectroscopy (Cary 100 instrument) were used to characterize the samples.

2.2. Experiment

The method used was based on the literature [9-11]. HNT and sodium diethyldithiocarbamate trihydrate were taken in 5:6 ratios. First, 2 gram sodium diethyldithiocarbamate trihydrate was dissolved in 250 ml ethanol in a magnetic stirrer at 350 rpm for an hour (room temperature). A weight of 2.4 grams HNT was added to the solution and the mixture was stirred at 350 rpm for 24 hours (room temperature). The precipitate formed was transferred to a conical flask and partially submerged in a water bath maintained at 80 °C. Pressure of 175 mbar was applied and the conical flask was set to rotate at 60 rpm. Slight buzzing indicated the evacuation of air from the lumen of HNT. Ethanol evaporated from the solution.
leaving behind HNT and corrosion inhibitor. The mixture was brought back to atmospheric conditions. The process was repeated twice to ensure an increase in the loading capacity of HNT. The entire experiment was repeated for different bath temperatures of 40, 60 and 80 °C. The obtained loaded HNTs were labelled as HNT40, HNT60, and HNT80 based on the bath temperature.

3. Results and discussion
The bath temperature had a significant effect on the evaporation rate of ethanol. As the bath temperature increased, ethanol evaporated in a short period of time. When the bath temperature was set to be 60 °C and 80 °C, 250 ml of ethanol evaporated from the solution in approximately 8 minutes and 23 minutes respectively. Whereas, it took approximately 530 minutes to evaporate 10 ml ethanol from the solution when the bath temperature was set to 40 °C. The experiment was not continued as it was not practical.

The morphology of the inhibitor loaded halloysite nanotubes can be studied from the scanning electron microscope image shown in figure 2. Clusters of thin, long structured halloysite nanotubes loaded with inhibitor are visible along with some impurities. The impurities are assumed to be sodium diethyldithiocarbamate particles which have failed to load into the lumen of the halloysite nanotubes. The presence of impurities outside the lumen can be due to various intrinsic and extrinsic factors like ratio of carrier to the inhibitor, solvent, time and method of loading, time gap between loading and characterization [11].

![Figure 2. SEM image of halloysite nanotubes loaded with sodium diethyldithiocarbamate taken at 10000X magnification.](image)

The UV-Vis characterization was done using a Cary 100 instrument. Pure ethanol was used as a baseline. The suspensions were made by stirring 2 mg of HNT40, HNT60, and HNT80 in 1-liter ethanol each. The wavelength range was from 200 nm to 400 nm. The scan rate was set at 600 nm/min. The absorbance (%) versus wavelength (nm) plot as shown in figure 3 illustrates that the absorbancy of HNT80 at 208 nm is 0.5, absorbancy of HNT60 at 208 nm is 0.316 and that of HNT40 at 276 nm is 0.083. This clearly shows that the loading was better when the bath temperature was set higher. The loading efficiency of inhibitor can be ranked as HNT40 < HNT60 < HNT80. The results of UV-Vis spectroscopy lies in agreement with the points concluded from the observation of SEM images.
Figure 3. UV-Vis spectra for halloysite nanotubes loaded with the corrosion inhibitor at HNT40, HNT60, and HNT80.

Figure 4 shows the FTIR spectra of HNT40, HNT60, and HNT80. The spectrum of the three are similar and exhibits peaks at the same wavenumber as listed in Table 1. Prominent peaks can be seen in the range of 400 to 3000 1/cm for all three samples of loaded halloysite nanotubes. The peaks at 3696 and 3623 1/cm shows the presence of inner OH stretching vibrations seen in the alumina layers of the halloysite nanotube. The peak at 2978 1/cm maybe due to the interaction of the inhibitor to the inner lumen. The Si-O-Si vibration and interlayer water molecules vibration are indicated by the 1032 and 1655 1/cm peaks respectively. The inner surface hydroxyl groups are the reason for the peaks at 911 1/cm, followed by typical O-H translation, Al-O-Si and Si-O-Si vibration peaks at 754, 536, and 468 1/cm respectively. The transmittance (%) plays a vital role in determining the loading capacity of the halloysite nanotubes. Based on the fact that transmittance decreases with increase in the density of the sample, it can be understood that the samples muc tightly packed or loaded with corrosion inhibitor will allow less infrared light to transmit through it. Thus, it is clear from the reasoning and the spectra in the figure 4 that the loading capacity is higher in halloysite nanotubes loaded with the inhibitor at 80 °C as the transmittance (%) of HNT40 > HNT60 > HNT80. The FTIR results is in agreement to the results of UV-Vis and images of SEM.

Table 1. Significant peaks in FTIR spectra of halloysite nanotubes with corrosion inhibitor of HNT40, HNT60, and HNT80.

| Peaks (1/cm) | Assignment                  |
|-------------|------------------------------|
| 3696, 3623  | O-H stretching               |
| 1655        | Interlayer water             |
| 1032        | Si-O-Si vibration            |
| 911         | Inner surface hydroxyl group |
| 754         | O-H translation              |
| 536         | Al-O-Si vibration            |
| 468         | Si-O-Si vibration            |
4. Conclusion
This study set out to determine the effect of bath temperature on the inhibitor loading of Halloysite nanotubes is done successfully. The investigations on the loaded halloysite nanotubes synthesized at various temperatures like 40, 60 and 80 °C by characterization conclude that the bath temperature has a major role in determining the loading capacity of the halloysite nanotubes. It also confirmed that the loading capacity is enhanced as the bath temperature increases. Overall, this study lays the groundwork for future research by strengthening the idea that loading of Halloysite nanotube at high temperature such as 80 °C will yield better results. However, it is crucial to take notice of the flash point of the solvent and care must be taken to ensure that bath temperature does not exceed the same.

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