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Title: Insights into grafting of (3-Mercaptopropyl) trimethoxy silane on halloysite nanotubes surface

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Keywords: Halloysite, nanoclay, Organosilanes, grafting, thermogravimetric analysis, FT-IR, SEM.

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Abstract: Functionalization of halloysite nanotubes surface by using organosilanes is sensitive to the reaction conditions. Halloysite nanotubes (HNTs) were modified using (3-Mercaptopropyl) trimethoxy silane (MPTMS). The experiments were performed under different reaction conditions including, various solvents [Toluene, Tetrahydrofuran (THF), Ethanol, n-Hexane, 1,4 Dioxane and Acetonitrile], water content in the reaction media, volume of solvent, number of moles of silane and catalysts (triethyl amine, ammonia solution and tetra-ethoxy titanium). The elemental analysis, FT-IR analysis were used to identify the samples, which attained the highest percent of functionalization. SEM image and thermogravimetric analysis were provided for the pristine halloysite nanotubes and the modified halloysite nanotubes samples. This work provides a systematic investigation of the reaction conditions highlighting the best protocol to perform such a modification that represents a relevant strategy to control the surface properties of halloysite nanotubes as well as the optimization of the first step toward further modifications of this nano clay.

Highlights:

- Halloysite has been modified by (3-Mercaptopropyl) trimethoxy silane.
- Nature of solvent has a great effect on the grafting process.
- Changing the number of moles on the grafting process has been tested.
- The influence of catalyst on the grafting process has been tested.

Replies to Reviewer's comment

We thank the reviewer for his careful job in revising the MS and for giving us the opportunity to improve it before publication. All suggestions have been taken into account as detailed below.

- Equations should be numbered within the MS.
- Text was revised

- Figure 2 b. The unit for derivative mass should be indicated in the y-axis.
- Figure was revised

- Figure 3. The scale bar within SEM images is not clearly visible. Please check and revise.
- Figure was revised

- Figure 4. The spectra look arbitrarily shifted along the y-axis. Accordingly, the unit for transmittance should be indicated as "a.u." (arbitrary unit) and the values should not be reported.
- We have revised the figure to make it more clear and correct.

- Table 2 could be removed and errors for the sorption capacity data (Table 3) should be estimated and reported.
- Table 2 was removed and errors estimation for table 3 was added in the footnote

- Details for the temperature calibration of TGA should be added in the experimental section.
- Experimental details were added

Insights into grafting of (3-Mercaptopropyl) trimethoxy silane on halloysite nanotubes surface

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Abstract

Functionalization of halloysite nanotubes surface by using organosilanes is sensitive to the reaction conditions. Halloysite nanotubes (HNTs) were modified using (3-Mercaptopropyl) trimethoxy silane (MPTMS). The experiments were performed under different reaction conditions including, various solvents [Toluene, Tetrahydrofuran (THF), Ethanol, n-Hexane, 1,4 Dioxane and Acetonitrile], water content in the reaction media, volume of solvent, number of moles of silane and catalysts (triethyl amine, ammonia solution and tetra-ethoxy titanium). The elemental analysis, FT-IR analysis were used to identify the samples, which attained the highest percent of functionalization. SEM image and thermogravimetric analysis were provided for the pristine halloysite nanotubes and the modified halloysite nanotubes samples. This work provides a systematic investigation of the reaction conditions highlighting the best protocol to perform such a modification that represents a relevant strategy to control the surface properties of halloysite nanotubes as well as the optimization of the first step toward further modifications of this nano clay.

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1. Introduction

Kaolin is a type of the clay materials that have been used in a wide range for a variety of applications, such as in ceramics, paper coating, paper filling, paint extender, rubber or plastic filler and cracking catalysts because they are naturally available, in-expensive and environment-friendly silicate resources. Halloysite is one of the minerals in kaolin clays, and it represents a small percentage of the content [1-3]. It is found in nature as aluminosilicate mineral with the formula $(Al_2Si_2O_5(OH)_4 \cdot 2H_2O)$ [4-6]. It has interesting mechanical and thermal properties, which are the result of its formation by hydrothermal alteration of aluminosilicate minerals [7]. It has been described as a dioctahedral 1:1 clay mineral of the kaolin group which includes octahedral gibbsite $Al(OH)_3$ and tetrahedral SiO_4 sheets and comprises of hollow cylinders formed by multiple rolled layers (i.e., halloysite nanotubes, HNTs) [8-11]. The characteristic sizes are strongly dependent on the geological deposit [12,13]. The outer surface of Halloysite nanotubes has chemical properties which are like that of silica (SiO_2), and bears a negative charge in a wide pH range (4 to 10) while the inner core constitutes of alumina (Al_2O_3) and provides a positive charge under acidic conditions[14,15]. The oppositely charged outer surface and lumen of the halloysite nanotube enables it to be further modified in order to change its properties and to increase its loading capacity[16–18]. The great importance of halloysite nanotubes is due to their ability to be used in numerous applications as nanocontainers with controlled release properties that make them attractive for smart formulations with encapsulated active molecules[19–22]. It can also be used as a filler for polymer or hydrogel matrices, drug carrier and delivery, biomedical implants, corrosion protection of metals, biosensors, organic synthesis, flame retardant coatings, specific ion adsorbents, materials for sustained release of herbicides and anti-microbials, and energy storage devices [23–29].

The surface modification involves the modification of nanotube's inner lumen and the outer surface with different functional agents. Several chemical agents have been used for modification process because of being HNTs as silicate-based material containing aluminium and silica groups on the inner and outer surface of HNTs. The modification of the inner lumen and the outer surface of HNTs can be performed using alkalis, organosilanes, polymers, surfactants and nanomaterials[30–32]. Taking this into consideration, organosilanes were proved to

be effective agents for surface modification of HNTs, rendering the surface less hydrophilic by decreasing the number of Si–OH groups at halloysite nanotubes surface[33]. Organosilanes can be grafted on the outer surface of halloysite nanotubes by the condensation reaction between hydrolysed silanes and the hydroxyl groups of halloysite nanotubes external surface defects or that located on the edges [34-36]. The halloysite lumen contains the Al-OH groups that are very reactive towards organosilanes. On the other hand, the external halloysite surface possess siloxane (Si-O-Si) groups and few silanols (Si-OH). The hydroxyl groups that result from the presence of some defects on halloysite surface, are confirmed to be the potential reactive sites for the external surface modification of halloysite nanotubes [37-39].

Covalent modification of the outer surface improves the halloysite dispersibility into the polymer matrix, reinforcing the performances of the hybrid materials in terms of thermal stability and tensile properties [40]. This work aims to optimize the conditions of grafting (3-Mercaptopropyl) trimethoxy silane (MPTMS) on the surface of halloysite nanotubes. The modified nanotubes not only can be further functionalized via the reactivity of the newly introduced functionalities but also, they are attractive because of promising properties as adsorbent for metal ions.

2. Experimental

2.1. Materials

The Halloysite nanotubes (HNT) were provided by Sigma-Aldrich. The organo-silane used for the modification of the HNTs is (3-Mercaptopropyl) trimethoxy silane (MPTMS) and was supplied by Alfa Aesar. Triethyl amine (Et_3N), Tetraethoxy titanium ($\text{Ti}(\text{OEt})_4$) were Sigma-Aldrich products. All the solvents that were used in this work were of reagent grade and were used as received.

2.2. Silane functionalization of HNTs

The method followed for grafting (3-Mercaptopropyl) trimethoxy silane (MPTMS) on the surface of halloysite nanotubes is illustrated in Fig. 1.

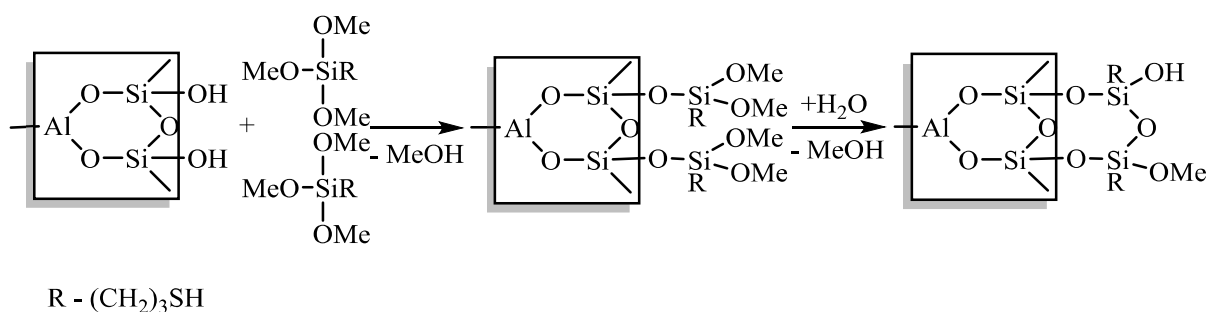


Fig. 1. Synthetic route that was used during the modification process. Details are provided below.

2.2.1 Grafting of (3-Mercaptopropyl) trimethoxy silane:

HNTs powder (1.3 g) was mixed in 20 ml of different solvents for 10 min. then different amounts of (3-Mercaptopropyl) trimethoxy silane was added as shown in Table 1. The mixture was dispersed ultrasonically for 60 min. then refluxed at time reaction mentioned at Table 1 under constant stirring and using temperature that corresponds to the boiling point of each solvent used in the experiment. The modified halloysite nanotubes were separated by centrifugation and extensively washed three times with 30 ml of the used solvent to remove the unreacted organosilanes. The separated product (HNTs-MPTMS) was finally dried at 60 °C for 12 hours. Some experiments were done in the presence of water and others were done in the presence of triethyl amine, tetraethoxy titanium and ammonia solution as mentioned at Table 1.

Table 1. Reaction conditions of grafting (3-Mercaptopropyl) trimethoxy silane on HNTs surface, the data of elemental analysis and the calculated value of the degree of functionalization for the samples treated with MPTMS.

Sample	HNTs/MPTMS/water/catalyst (molar ratio)	Solvent	Temperature (°C)	Refluxing Time (hour)	Content, %		Degree of functionalization %
					C	H	
HNT -A1	1/1.33/0/0	40 ml Toluene	110	4	5.58	1.97	51.63
HNT -B2	1/1.33/0/0	40 ml THF	66	4	0.95	1.80	8.79
HNT-C3	1/1.33/3/0	40 ml Toluene	110	4	4.30	0.20	39.78

HNT -D4	1/ 2.64/0/0	40 ml Ethanol	79	4	1.31	1.87	8.07
HNT -E5	1/1.33/0/0	40 ml Acetonitrile	82	4	0.93	1.80	8.6
HNT -F6	1/1.33/0/0	10 ml Acetonitrile	82	4	1.96	0.42	18.13
HNT-G7	1/1.33/0/0	40 ml Toluene	110	48	3.04	2.16	28.12
HNT-H8	1/2/0/0	40 ml Toluene	110	48	3.51	1.98	25.13
HNT-I9	1/1.33 /0/0	10 ml Toluene	110	4	3.29	2.02	30.44
HNT-J10	1/1.33/0/0	75 ml Toluene	110	4	3.77	2.12	34.88
HNT-K11	4.64/6.034/0/0	40 ml n- Hexane	69	4	3.44	2.255	32.19
HNT-L12	1/1.3/0/0	40 ml 1,4- Dioxane	100	4	3.46	1.923	32.37
HNT-M13	1/1/8.26 /0	20 ml Toluene	110	4	2.98	2.26	33.49
HNT-N14	1/1/0/3.09 (C ₂ H ₅) ₃ N	20 ml Toluene	110	4	4.76	2.39	53.53
HNT-O15	1/ 1/0/1.027 Ti (OC ₂ H ₅) ₄	20 ml Toluene	110	4	2.70	2.03	30.39
HNT-P16	1/1/0/5.59 NH ₄ OH	20 ml Toluene	110	4	8.9	3.155	99.8

2.3. Characterization of HNTs-MPTMS:

Elemental analysis of carbon, hydrogen and nitrogen (EA) of the modified HNT samples which were grafted using (3-Mercaptopropyl) trimethoxy silane was carried out using an elemental analyzer Perkin Elmer PE 2400. The degree of functionalization (DF) of (HNTs-MPTMS) samples was computed using Eq.1 and 2:

$$DF = \frac{\% \text{ of carbon obtained from EA}}{\text{theoretical \% of carbon content}} \quad (1)$$

Where theoretical % of carbon content calculated using the following equation:

$$\text{Theoretical \% of carbon content} = \frac{\text{No. of carbon atoms in silane} \times \text{No. of moles of silane} \times 12}{\text{No. of g of HNTs} + \text{No. of g of silane} - \text{No. of g of alcohol eliminated}} \quad (2)$$

Fourier transform infrared (FTIR) spectra were used to confirm the presence of bands for (CH₂) group that indicate the condensation reaction between silane and hydroxyl groups on the surface of halloysite nanotubes. FT-IR diffuse reflectance spectra obtained with a Spectrum-One spectrometer, Perkin Elmer. The measurements were performed in the wave number range (4500-500) cm⁻¹.

Thermogravimetric analysis (TGA) was performed using a Metler Toledo instrument for the pristine halloysite nanotubes and the best sample of grafted (HNTs-MPTMS). The mass of the sample was measured over time as the temperature changes from 30°C to 1000°C under a nitrogen flow of 60 ml/min. Calibration was performed following literature procedure[41,42].

Scanning electron microscope (SEM) images obtained by using a Carl instrument Zeiss EVO LS 10. It was used to study the morphology of the pristine halloysite nanotubes and the sample with largest grafted efficacy (HNTs-MPTMS).

3. Results and discussion

3.1. Effect of polarity of solvent

Owing to the role played by solvent in wetting the surface of halloysite nanotubes, the solvent has a great influence on the silanization process which occurs by the reaction between silicate-based material and the alkoxy silanes[43]. In the present work, Toluene, Tetrahydrofuran, Ethanol, n-Hexane, 1,4 Dioxane and Acetonitrile have been used as solvent for the grafting process. These solvents have different polarity and dielectric constant. The FT-IR spectra for HNTs modified with MPTMS, in the presence of these solvents, have been shown in Fig. S1 (ESI)*. The bands that appear at 1258 cm⁻¹ for HNT-A1 indicate the presence of Si-CH₂-R deformation vibration and the intensity tends to decrease as the length of the aliphatic chain increases[44]. Table 1. summarizes the data for the elemental analysis and the degree of functionalization of HNTs samples which grafted by MPTMS in the presence of variety of solvents. The highest degree of functionalization was given by HNT-A1. The sample HNT-A1 was the best functionalized by MPTMS and this indicates that toluene is the best solvent for

grafting MPTMS on HNTs surface. The lowest degree of functionalization obtained by the polar solvents like tetrahydrofuran and ethanol, indicating that these solvents are not favourable for grafting process because of the competition reaction between alkyl siloxane and hydroxyl groups of the solvents through H-bonding rather than hydroxyl groups of the surface [45, 46]. Increasing the number of moles of water in the reaction mixture from 13.92 mmol to 38.33 mmol, generated a decrease in the degree of functionalization from 39.78% to 33.49% as mentioned at Table 1. This confirms the hypothesis raised in case of solvents with increased polarities.

3.2. Effect of number of moles of MPTMS

Though that increasing the number of moles of silanes in the reaction media allowed more active silanol groups to interact with hydroxyl groups attached to halloysite nanotubes surface, the data obtained by elemental analysis showed that as the number of moles of silane increases, the functionalization degree decreases. Although the influence of the amount of silane on the grafting process has been discussed by many articles. There is no complete clarification why the functionalization degree reduces when the silane amount increases [47-51]. Fig. S3 (ESI)* shows new bands for HNT-N14 at 2927 cm^{-1} , 2857 cm^{-1} which represent symmetric stretching of CH_2 group[44]. This indicates the condensation reaction between alkoxy silane and hydroxyl groups on HNTs surface. According to the data obtained from elemental analysis and FT-IR spectra (Table 1. and Fig. S3 (ESI)*), the amount which is equal 4.633 mmol of MPTMS has been chosen to be the best amount of silane for the grafting process.

3.3. Influence of the volume of solvent

Fig. S4 (ESI)* shows the FT-IR spectra for the samples which is treated by using different volumes of toluene. The calculated values of the functionalization degree for these samples have been shown in Table 1. The volume which is equal to 40 ml of toluene has been chosen as the best volume of solvent for grafting of MPTMS on HNTs surface. Fig. S4 (ESI)* shows bands at 1252 cm^{-1} , 1303 cm^{-1} for HNT-M13, HNT-A1 which represents the deformation vibration of $\text{Si-CH}_2\text{-R}$ which occurs at $1250\text{-}1175\text{ cm}^{-1}$ and CH_2 wagging vibration which occurs near 1305 cm^{-1} respectively and the other band that appears at 2884 cm^{-1} for HNT-F6 represents the

C-H stretching vibrations which occurs in the region $2975\text{-}2840\text{cm}^{-1}$ [44]. This indicates the condensation reaction formation between hydroxyl groups on HNTs surface and methoxy groups of silanes.

3.4. Effect of catalyst on the grafting process

In the investigated chemical reaction, the catalyst provides an alternate pathway by the reduction of the activation energy between reactants and products. Namely, triethyl amine (Et_3N), ammonia solution (NH_4OH) and tetra ethoxy titanium ($\text{Ti}(\text{OEt})_4$) have been used as a catalyst for the grafting of MPTMS on halloysite nanotubes surface because they act as proton acceptor and this will facilitate condensation reaction between hydroxyl groups on HNTs surface and methoxy groups of silanes. The FT-IR spectra and elemental analysis data for the samples which were treated by using these catalysts for grafting MPTMS on HNTs surface have been shown in Fig. S5 (ESI)* and Table 1. Fig. S5 (ESI)* shows bands at 1239 cm^{-1} , 2849 cm^{-1} and 2916 cm^{-1} for HNT-P16 and at 2925 cm^{-1} , 2832 cm^{-1} and 1233 cm^{-1} for HNT-N14. The peaks with medium intensity that appear at 2849 cm^{-1} , 2832 cm^{-1} , 2916 cm^{-1} and 2925 cm^{-1} represent the C-H stretching vibrations which occurs in the region $2975\text{-}2840\text{ cm}^{-1}$. The peaks that appear at 1239 cm^{-1} and 1233 cm^{-1} are very weak and represents the CH_2 wagging, rocking and twisting vibrations which occur in the region $1430\text{-}715\text{ cm}^{-1}$ and these bands are usually of weak intensity in infrared spectra and of medium intensity in Raman[44]. These peaks indicate that the condensation reaction formation between hydroxyl groups on HNTs surface and methoxy groups of silanes. These data give an indication about the positive effect of the catalyst on the progressing of the reaction.

3.5. Characterization of the modified sample with higher efficiency

The best modified sample has been characterized by using thermogravimetric analysis (TGA), scanning electron microscope (SEM), FT-IR analysis and elemental analysis as shown in Figs. 2, 3 and 4 and mentioned at Table 1. respectively. Fig. 2 shows that the main mass loss for pristine HNT occurred in the temperature range of $(400\text{-}550\text{ }^\circ\text{C})$ and this may be attributed to the dehydroxylation

of structural hydroxyl groups of HNT[52] while the main mass loss for HNT-P16 occurred in the temperature range of (250-500 °C). This may be attributed to the condensation reaction between hydroxyl groups on HNTs surface and methoxy groups of silane and formation of covalent bond. Fig.4 shows bands at 1241 cm^{-1} , 2849 cm^{-1} and 2921 cm^{-1} for HNT-P16 which are not present in pristine HNTs. The peaks with medium intensity that appear at 2849 cm^{-1} and 2921 cm^{-1} represent the C-H stretching vibrations which occurs in the region $2975\text{-}2840\text{ cm}^{-1}$. The peak that appears at 1241 cm^{-1} is very weak and represents the CH_2 wagging, rocking and twisting vibrations which occur in the region $1430\text{-}715\text{ cm}^{-1}$.

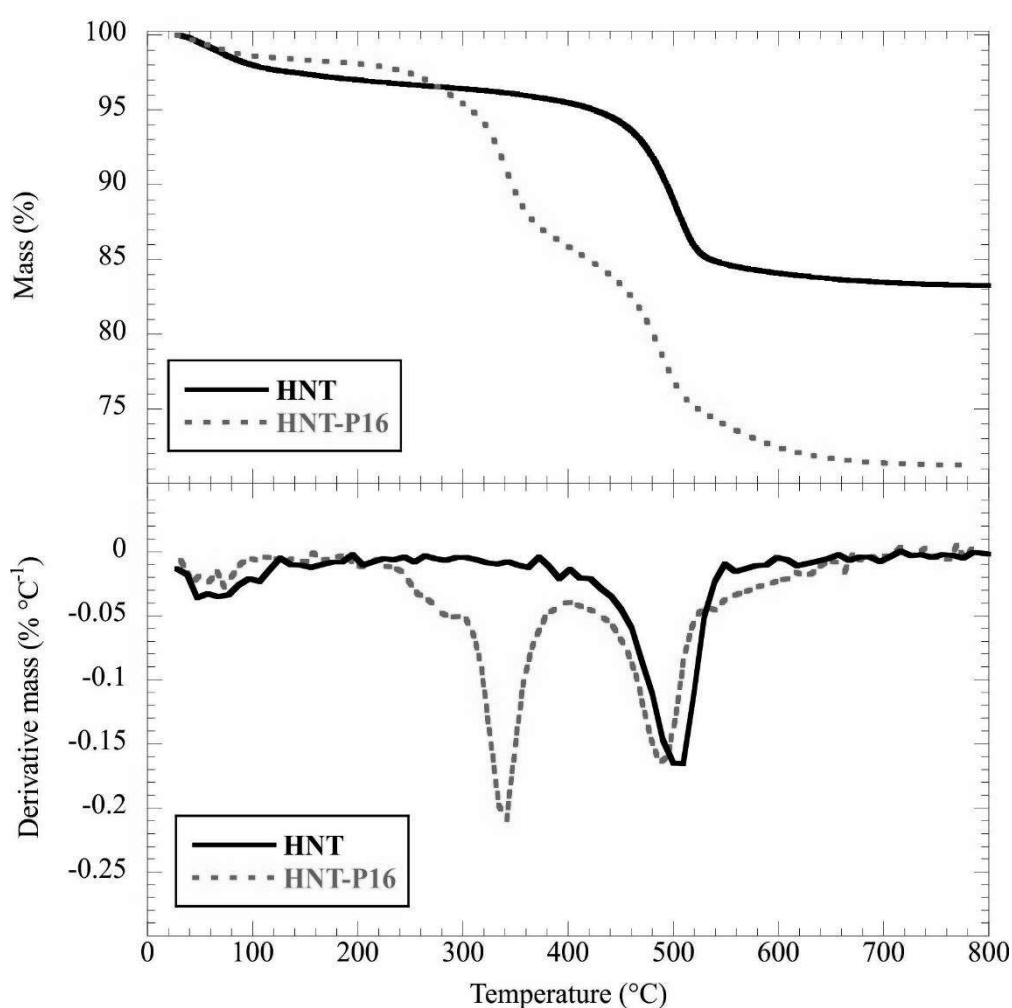


Fig. 2. TGA and DTG curves of pristine HNTs and the HNT-P16 sample.

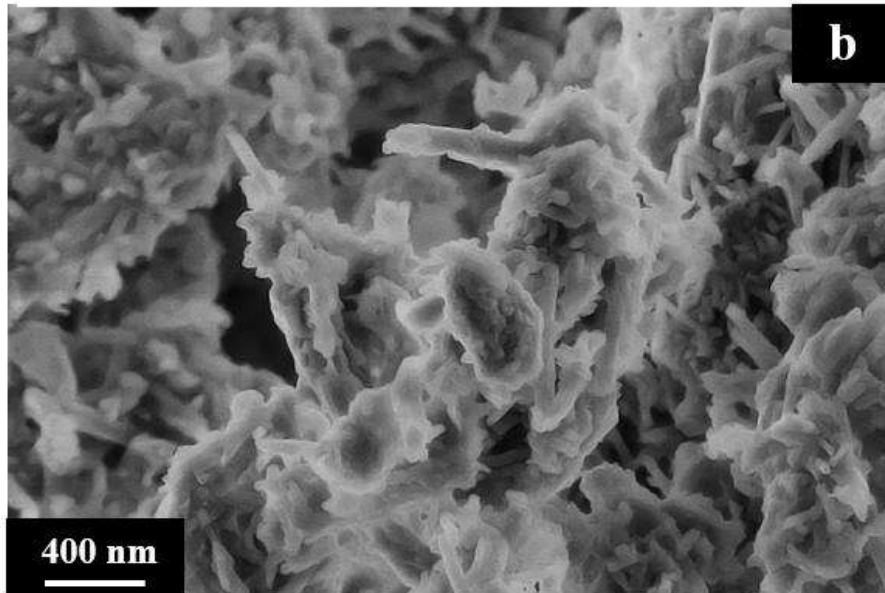
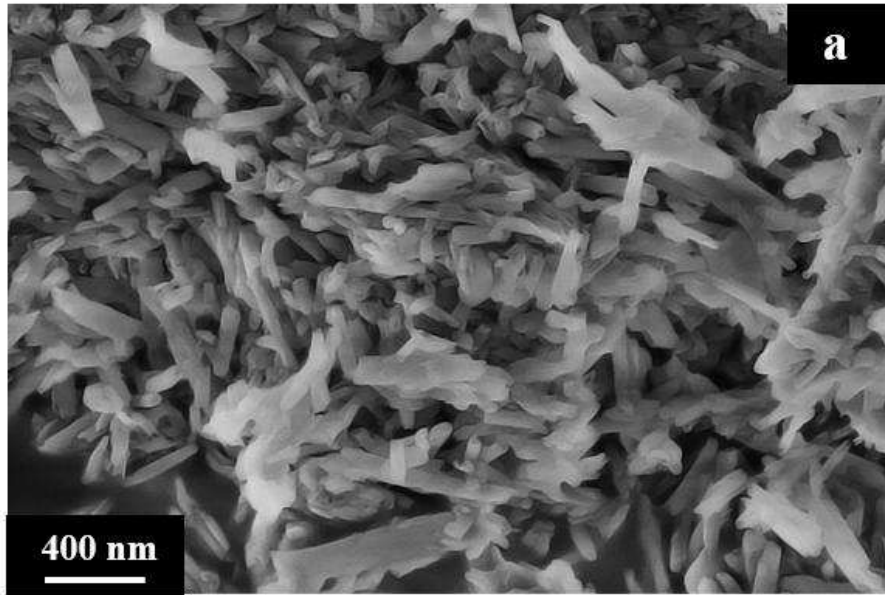


Fig. 3. SEM image of pristine HNTs (a) and the HNT-P16 sample (b).

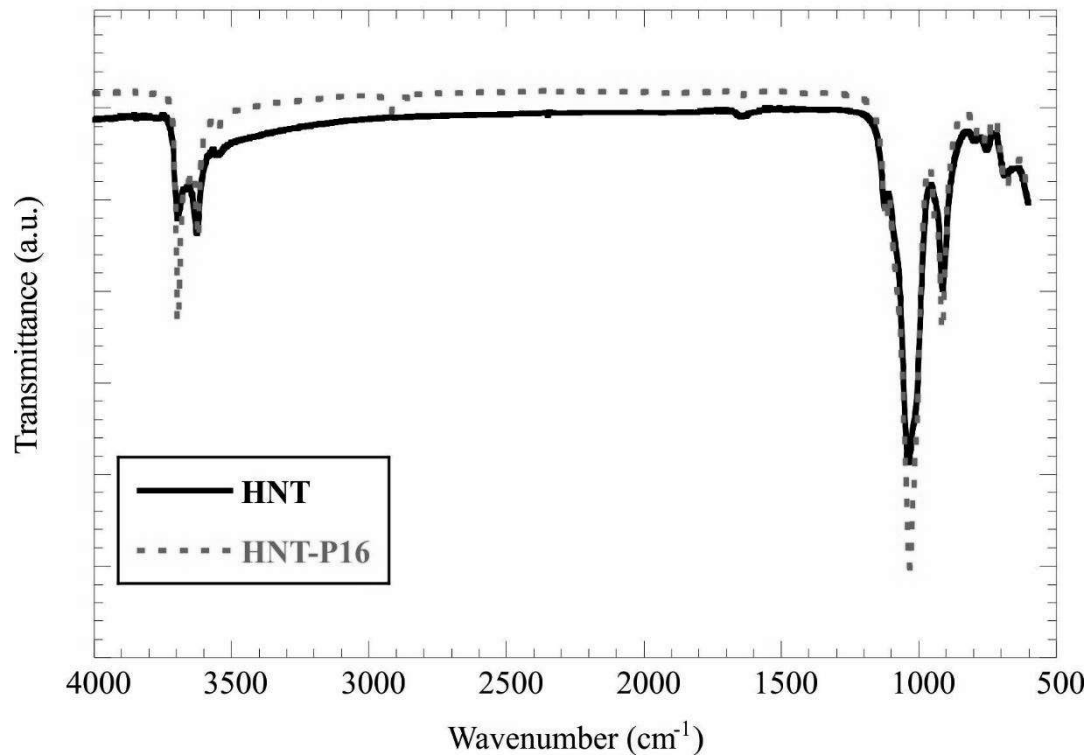


Fig. 4. FT-IR spectra of pristine HNTs and the best modified HNTs sample.

3.6. Sorption experiments:

The sorption capacity of both HNTs and the best modified HNTs sample were tested by contacting of a small mass (0.1 g) of (HNTs) and (HNT-P16) with a fixed volume (8 ml) of aqueous solution which containing a mixture of metal ions with concentrations ca. 1500 mg/l and pH = 6.5 in a conical flask. The flasks were agitated for 24 hours. (rotation speed, $v = 700$ rpm) at 25 °C. After equilibration and phase separation, the residual metal ions concentration in the aqueous phase (C_{eq} , mg/l) was measured by using Inductively coupled plasma Optical Emission Spectrometer (relative error 0.08 %). The capacity of the sorbent was determined by using the mass balance equation ($Q_{eq} = ((C_o - C_{eq}) V/m)$, while C_o , C_{eq} are the initial and equilibrium concentration of metal ions in the solution (mg/l), (V) is the volume of the solution (L) and (m) is the mass of pristine HNT or HNT-P16 (g).The obtained results showed that the maximum sorption capacity for Cu ions was changed from 1

mg/g to 28 mg/g by using pristine HNTs and HNT-P16 respectively (Table 2). These data provide an indication on the effect of modification of HNTs on the sorption capacity of Copper ions and its selectivity for Copper ions.

Table 2. Data of the sorption capacity of both pristine HNTs and HNT-P16 using a solution of metal acetate, at 25°C, pH= 6.5 and agitation time 24 hours.

Sample	Sorption capacity, mg/g			
	Co	Cu	Ni	Zn
HNTs	0	1	0	0
HNT-P16	0	28	0	2

Error is 5% on sorption capacity.

4. Conclusions

Halloysite nanotubes has been functionalized by using (3-Mercaptopropyl) trimethoxy silane (MPTMS). The work has been done by using different reaction conditions. The obtained data showed that the best solvent for the grafting process is toluene, decreasing the amount of water in the reaction media gave a significant increase in the degree of functionalization. As the volume of solvent in the reaction media decreased, the degree of functionalization increased. Increasing the number of moles of silane has a negative influence on the degree of functionalization. The use of catalyst has a positive effect on the proceeding of the reaction. The modification of HNTs causes a selective increase of its sorption capacity for Copper ions.

List of abbreviations

HNTS	Halloysite nanotubes
MPTMS	(3-Mercaptopropyl) trimethoxy silane
(Et ₃ N)	Triethyl amine

(Ti (OEt)₄) Tetraethoxy titanium

(ESI)* Electronic supplementary information

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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***Declaration of Interest Statement**

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

List of Tables:

Table 1. Reaction conditions of grafting (3-Mercaptopropyl) trimethoxy silane on HNTs surface, the data of elemental analysis and the calculated value of the degree of functionalization for the samples treated with MPTMS.

Sample	HNTs/MPTMS/water/catalyst (molar ratio)	Solvent	Temperature (°C)	Refluxing Time (hour)	Content, %		Degree of functionalization %
					C	H	
HNT -A1	1/1.33/0/0	40 ml Toluene	110	4	5.58	1.97	51.63
HNT -B2	1/1.33/0/0	40 ml THF	66	4	0.95	1.80	8.79
HNT-C3	1/1.33/3/0	40 ml Toluene	110	4	4.30	0.20	39.78
HNT -D4	1/ 2.64/0/0	40 ml Ethanol	79	4	1.31	1.87	8.07
HNT -E5	1/1.33/0/0	40 ml Acetonitrile	82	4	0.93	1.80	8.6
HNT -F6	1/1.33/0/0	10 ml Acetonitrile	82	4	1.96	0.42	18.13
HNT-G7	1/1.33/0/0	40 ml Toluene	110	48	3.04	2.16	28.12
HNT-H8	1/2/0/0	40 ml Toluene	110	48	3.51	1.98	25.13
HNT-I9	1/1.33 /0/0	10 ml Toluene	110	4	3.29	2.02	30.44
HNT-J10	1/1.33/0/0	75 ml Toluene	110	4	3.77	2.12	34.88
HNT-K11	4.64/6.034/0/0	40 ml n- Hexane	69	4	3.44	2.255	32.19
HNT-L12	1/1.3/0/0	40 ml 1,4- Dioxane	100	4	3.46	1.923	32.37
HNT-M13	1/1/8.26 /0	20 ml Toluene	110	4	2.98	2.26	33.49
HNT-N14	1/1/0/3.09 (C ₂ H ₅) ₃ N	20 ml Toluene	110	4	4.76	2.39	53.53
HNT-O15	1/ 1/0/1.027 Ti (OC ₂ H ₅) ₄	20 ml Toluene	110	4	2.70	2.03	30.39
HNT-P16	1/1/0/5.59 NH ₄ OH	20 ml Toluene	110	4	8.9	3.155	99.8

Table 2. Data of the sorption capacity of both HNTs and HNT-P16 using a solution of metal acetate, at 25°C, pH= 6.5 and agitation time 24 hours.

Sample	Sorption capacity, mg/g			
	Co	Cu	Ni	Zn
HNTs	0	1	0	0
HNT-P16	0	28	0	2

Cover letter

Dear Editor,

I am writing to express my interest in journal of organometallic chemistry.

It'll be a great pleasure to submit my article which entitled:

“Insights into grafting of (3-Mercaptopropyl) trimethoxy silane on halloysite nanotubes surface”

for peer review in your journal.

I will be very happy if you accept my paper.

With my best wishes

Asmaa

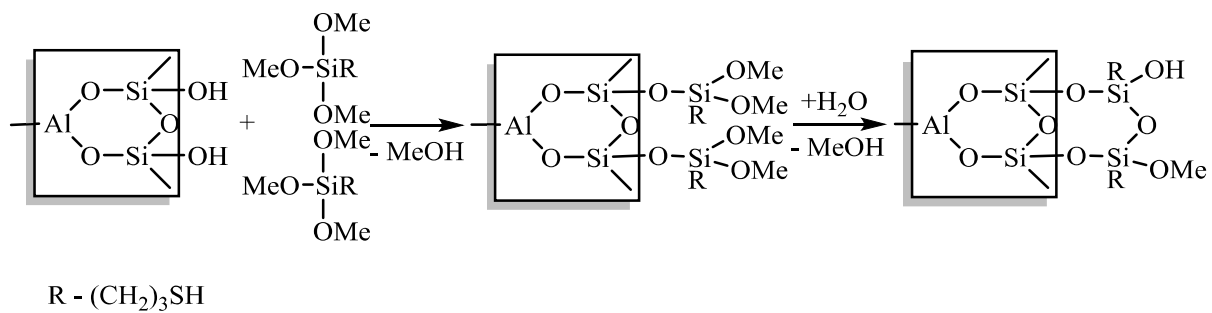


Fig. 1. Synthetic route that was used during the modification process.

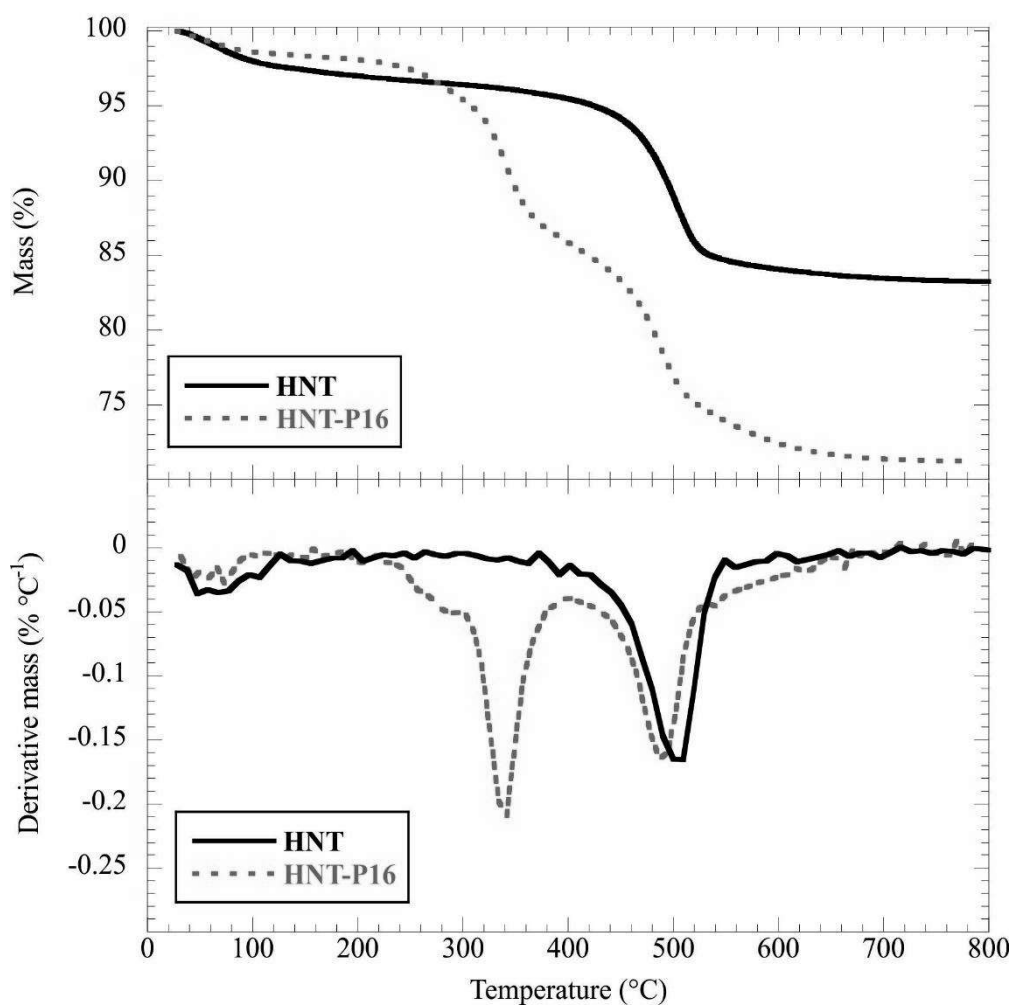


Fig. 2. TGA and DTG curves of pristine HNTs and the best grafted HNTs sample.

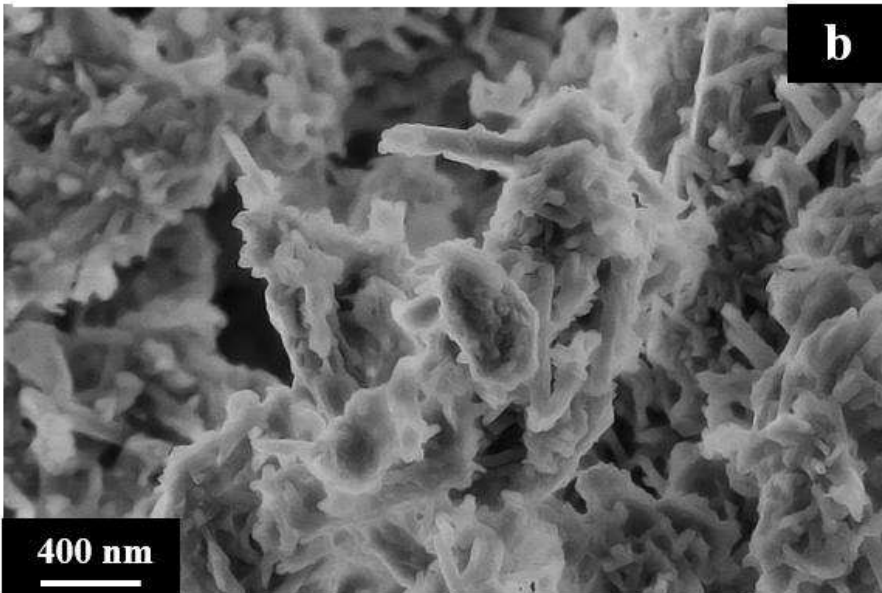
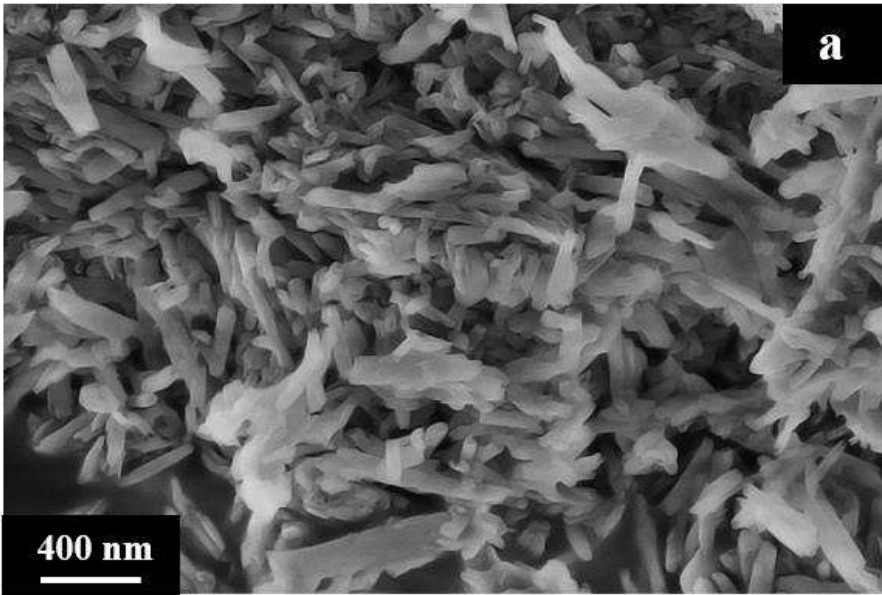


Fig. 3. SEM image of pristine HNTs (a) and the best grafted HNTs sample (b).

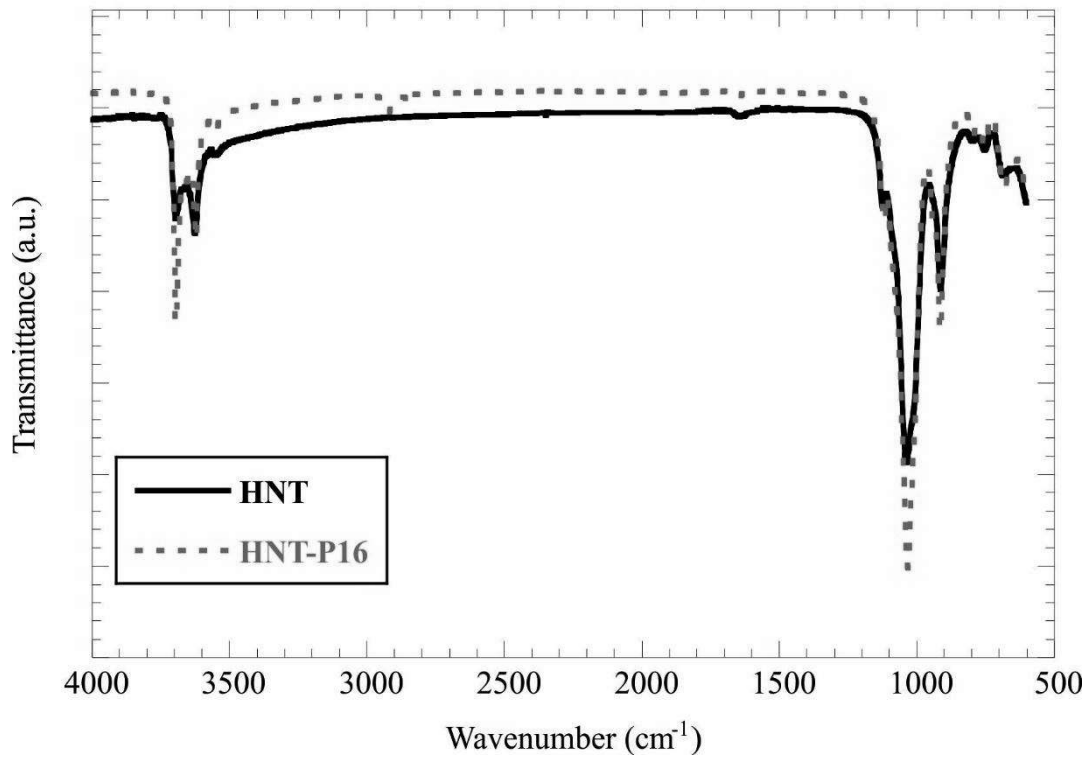


Fig. 4. FT-IR spectra of pristine HNTs and the modified HNTs sample.

Figure captions:

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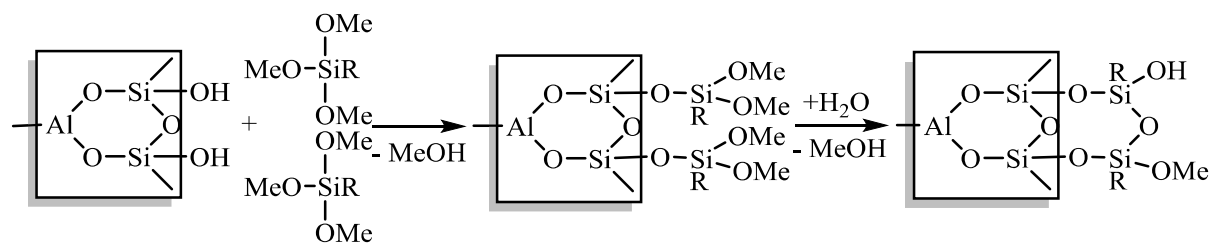
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Graphical abstract



R - (CH₂)₃SH