Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Review Article

Halloysite Nanotubes and Applications: A Review

Ravindra Kamble*[1], Manasi Ghag[2], Sheetal Gaikawad[1], Bijoy Kumar Panda[3]

*[1] *Department of Pharmaceutics, Poona College of Pharmacy, Bharati Vidyapeeth Deemed University, Pune, Maharashtra, India*
[2] *Poona College of Pharmacy, Bharati Vidyapeeth Deemed University, Pune, Maharashtra, India*
[3] *Department of Clinical Pharmacy, Poona College of Pharmacy, Bharati Vidyapeeth Deemed University, Pune, Maharashtra, India*
**Corresponding author: kravi_73@rediffmail.com*

ABSTRACT

Various successful results of nanotechnology like carbon nanotubes, nanofluids, nanoparticles, nano emulsions, nano capsules, etc are not considered to be safe for humans as well as for environment because of their toxicology potencies**.** Halloysite nanotubes are naturally occurring eco-friendly nanotubes with low cost that are harmless to human. Halloysite Nanotubes (HNTs) are unique and versatile nanomaterials composed of double layered aluminosilicate minerals with a predominantly hollow tubular structure in submicron range. They are nontoxic in nature, have tuneable release rates and fast adsorption rates. These nanotubes have got wide range of applications in anticancer therapy, sustained delivery for certain agents, act as template or nanoreactor for biocatalyst, have found use in personal care and cosmetics and even used as environment protective.

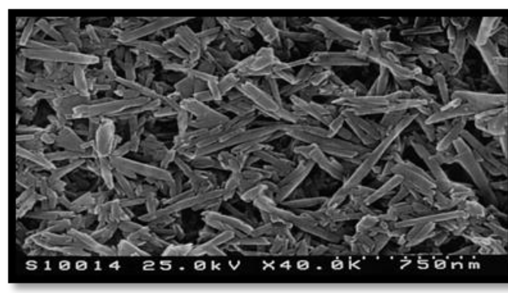
Keywords: Halloysite nanotubes, Applications of HNTs, Halloysite Cytotoxicity, Nanoreactor, biocatalyst.

1. INTRODUCTION

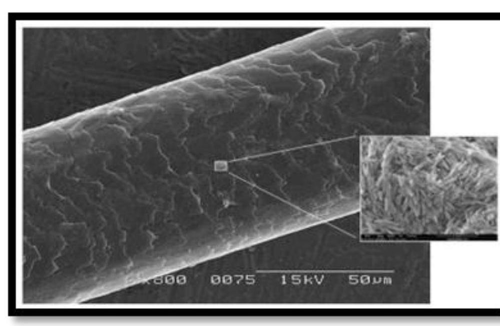
In the field of pharmacy and health care, effectiveness of medicine and therapy is very important, failure or drawback in the drug therapy may lead to either ineffectiveness or side effects which hamper human health. Green nanotechnology aims at developing environment safe and less harmful nano products. Halloysite clay nanotubes, nanocomposites, nano powders, etc are now emerging as trend setters in green nanotechnology. Halloysite nanotubes are eco friendly nanotubes with low cost than carbon nanotubes. In recent years there has been growing concern about the effect of carbon nanotubes on human health and on environment because of their potential toxic nature. Halloysite nanotubes find numerous commercial applications such as, additives in polymers and plastic, electronic components, drug delivery vehicles, cosmetics and in home and personal care products.

2. HALLOYSITE CLAY NANOTUBE [1, 2]

Naturally formed in the Earth over millions of years, halloysite nanotubes are unique and versatile nanomaterials that composed of double layer of aluminium, silicon, hydrogen and oxygen. Halloysite nanotubes are ultra-tiny hollow tubes with diameters typically smaller than 100 nanometres (100 billionths of a meter), with lengths typically ranging from about 500 nanometres to over 1.2 microns (millionths of a meter). Halloysite nanotubes are formed as a result of strain caused by lattice mismatch between adjacent silicon dioxide and aluminium oxide layers.



(a)



(b)

Fig. 1: (a) SEM image of HNT, (b) a bundle of HNTs compared to the width of human hair

2.1. Advantages of Halloysite Nanotubes

- Natural, non toxic, biocompatible and EPA 4A listed material
- Fine particle size, high surface area and superb dispersion
- High cation exchange capacity

- Maintains uniform, sustained release rates and no initial overdosage
- Capable of prohibiting release unless triggered and tuneable release rates
- Protects active agent within its lumen during harsh material processing
- Capable of loading multiple active agents simultaneously
- Reduces the volume of costly active agents
- Implementable in many forms such as powders, creams, gels, lotions and sprays
- Superior loading rates to other carriers, Fast adsorption rate and high adsorption capacity
- High aspect ratio, high porosity and non swelling
- Regeneration ability and increased efficacy

2.2. Physical Properties [3]

- ➢ Halloysite specifications (used in research studies)
- ➢ Typical specific surface area - 65 m2/g
- ➢ Pore volume ~ 1.25 mL/g
- ➢ Refractive index - 1.54
- ➢ Specific gravity - 2.53 g/cm3
- ➢ Average tube diameter - 50 nm
- ➢ Inner lumen diameter - 15 nm

2.3. Electro-Chemical Properties [4]

1. The outer surface of the halloysite nanotubes has properties similar to SiO_2 with negative charge at pH 6 – 7 (zeta potential) while the inner cylinder core is related to Al_2O_3 which is slightly positively charged.

2. The positive (below pH 8.5) charge of the inner lumen promotes loading of halloysite nanotubes with negative macromolecules within void spaces, which are at the same time repelled from the negatively charged outer surfaces.

2.4. Halloysite Cytotoxicity and Cytocompability [5-7]

The current research suggests that HNTs are not toxic for cells and those with 50 to 70 nm in external diameter, 15 nm diameter lumen and 1to 0.5 µm in length are chemically stable.

2.5. Chemistry [8]

Halloysite ($Al_2Si_2O_5$ $(OH)_4$ $.2H_20$) is chemically related to kaolin**.** HNTs contain two types of hydroxyl groups, inner and outer hydroxyl groups, which are situated between layers and on the surface of the nanotubes, respectively. The surface of HNTs is mainly composed of O Si O groups, and the siloxane surface.

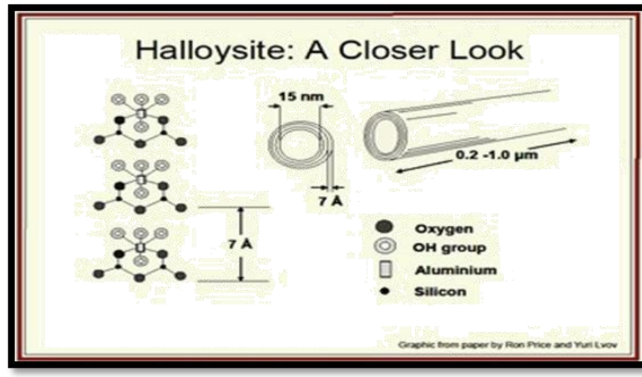


Fig. 2: Chemical representation of HNT

3. TYPES OF HALLOYSITE NANOTUBE [8,9]

Two types of halloysite nanotubes models are developed for effective studies in field of nanotechnology.

- Single Walled Halloylsite Nanotube Model
- Multi Walled Halloylsite Nanotube Model

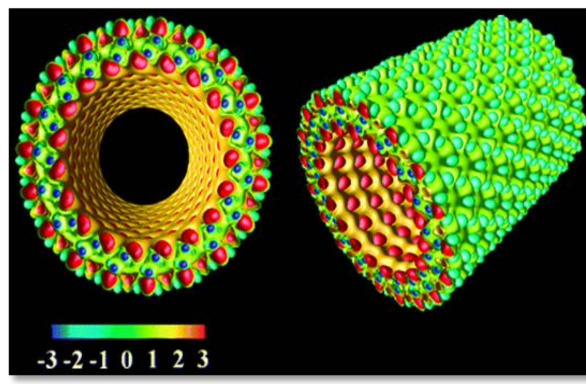


Fig. 3: HNT model

4. LOADING OF HALLOYSITE NANOTUBES [10]

A vial containing the mixture of halloysite and saturated solution of targeted molecules was transferred to a vacuum jar and then repeatedly evacuated using a vacuum pump.

- Slight fizzing of the suspension indicates the air being removed from the halloysite interior. After the fizzing stopped, the vial was sealed for 30 minutes to reach equilibrium in molecule distribution.
- The halloysite suspension was centrifuged to remove excess dissolved molecules and washed.
- The process may be repeated twice to ensure that the halloysite is filled with the maximum amount of the targeted molecules.
- With this simple loading technique, nanotubule lumen can be filled with any material.

5. FUNCTIONALIZATION OF HALLOYSITE NANOTUBES

It can be carried out-

- By Grafting with γ-Aminopropyltriethoxysilane (APTES) [11]
- With 2-hydroxybenzoic acid as a solid-phase extraction [12]
- By grafting hyperbranched (co) polymers via surface-initiated self-condensing vinyl (co)polymerization [13]

6. STABILITY AND SOLUBILITY OF HALLOYSITE NANOTUBES [14,15]

A study on solubilisation and dispersion of halloysite nanotubes (HNTs) to obtain a supramolecular adduct of HNT and DNA was carried out which is environmentally safe and no organic solvents are used.

The long term stability of natural halloysite nanotubes was studied at room temperature (22 ± 2°C) in pure water, acidic and basic aqueous suspensions. It has been revealed that, in 1 mol dm−3 H_2SO_4 solution, the dissolution of halloysite is initiated on the inner surface of nanotubes, leading to the formation of amorphous spheroidal nanoparticles of SiO_2 whereas, in 1 mol dm−3 NaOH solution, dissolution of the inner surface of nanotubes is accompanied by the formation of $Al(OH)_3$ nanosheets.

7. CHARACTERIZATION OF HNTs [16]

Scanning electron microscopy (SEM), Scanning force microscopy (SFM) and Transmission electron microscopy (TEM) reveal that majority of sample consists of cylindrical tubes of 40 – 50nm diameter and length of 0.5 - 2μm. HTNs are rather polydispersed in length. TEM images clearly indicate the empty lumen of halloysite with 15 – 20nnm diameter. HNTs elasticity is considerably smaller than CNTs which has Young's modulus of around 1 TPa.

The typical morphologies of HNTs are shown [16]

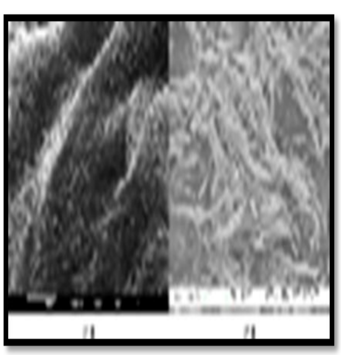


Fig. 4: SEM images of HNTs

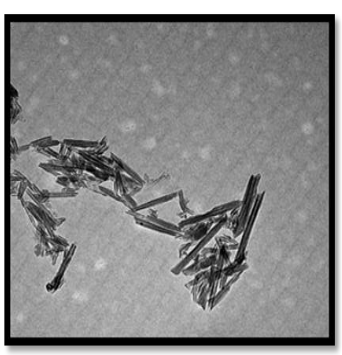


Fig. 5: TEM of 50nm HNTs

8. APPLICATIONS

8.1. Use of Naturally Occurring Halloysite Nanotubes for Enhanced Capture of Flowing Cells [17]

Capturing of circulating tumour cells (CTCs) in blood can be targeted more effectively by incorporation of Halloysite Natural Tubes (HNT) onto the surface of devices used to capture circulating tumour cells (CTCs) in blood. It was found that halloysite nanotube coatings promote increased capture of leukemic cells and have determined the key parameters for controlling cell capture under flow: halloysite content and selectin density.

8.2. HNTs as Nanoreactors or nanotemplates [18]

Recently HNTs have been used as alternative nanoreactors to fabricate nanowires, nanoparticles and for similar purposes. For instance,

a) Intercalation and polymerization of aniline within a tubular aluminosilicate, which suggests that the polyaniline, which can act as a molecular wire, could be prepared in the lumens of HNTs.
b) HNTs could be used as biomineralization nanoreactors for carrying out enzyme-catalyzed inorganic synthesis, where HNT lumen acts as biomimetic nanoreactors.[19]
c) Porous carbons rich in mesopores and with large pore volumes have been prepared by polymerization and carbonization of a carbon precursor, sucrose, within HNTs. The process gave mesoporous carbons with total pore volume and large specific surface areas.
d) Polymeric nanotubes and nanowires have been fabricated using HNTs as templates by atom transfer radical polymerization and a non-woven porous fabric was prepared with good wetting characteristics by direct casting of a composite dispersion followed by sequent thermal crosslinking.
e) Encapsulation of anionic and cationic metalloporphyrins into the lumens of HNTs showed these novel immobilized catalysts are a promising system for selective oxidation reactions.

8.3. Halloysite Tubes as Nanocontainers

8.3.1. Anticorrosion Coating with Benzotriazol [20]

Halloysite clay nanotubes were investigated as a tubular container for the corrosion inhibitor benzotriazole. Halloysite may be used as an additive in paints to produce a functional composite coating material.

8.3.2. Releasing entrapped corrosion inhibitors [21]

Active corrosion protection coatings composed of hybrid sol−gel films doped with halloysite nanotubes are able to release entrapped corrosion inhibitors in a controllable way. The sol−gel film with the nano-containers reveals enhanced long-term corrosion protection in comparison with the undoped sol−gel film because of the self-controlled release of the corrosion inhibitor triggered by the corrosion processes.

8.4. Halloysite Clay Nanotubes for Controlled Release

8.4.1. Protective Agents [22]

By variation of internal fluidic properties, the formation of nano shells over the nanotubes and by creation of smart caps at the tube ends it is possible to develop various means of controlling the rate of release. Thus, halloysite nanotubes can be used as protective coating for the loading of agents for metal and plastic anticorrosion and biocide protection.

8.4.2. Entrappment of active agents (Tetracycline HCl, khellin and nicotinamide adenine dineculeotide) [23]

Halloysite nanotubes are capable of entrapping active agents within the core lumen and in any void spaces contained in the multilayered walls of the cylinder. Halloysite is capable of retaining and releasing both hydrophilic and hydrophobic agents may be entrapped following appropriate pre-treatment of the clay to render it lipophilic. For hydrophilic molecules (like kellin, NAD, tetracycline) a typical release time was 2-5 hours and for molecules with low solubility in water (like dexamethasone, furosemide, nifedipine) release time 5-20 hours was observed.

8.5. Special Delivery System

8.5.1. Clay nanotubes in sustain drug delivery systems [3]

Halloysite nanotubes are combined with existing pharmaceuticals for sustained drug delivery. Compared to carbon nanotubes, halloysite nanotubes are less expensive and have large surface area which allows for greater control of drug loading and elution profiles.

8.5.2. Transdermal Patches

Loading pharmaceuticals into halloysite nanotubes can enable a more controlled elution profile. Benefits are: - Low initial concentrations, eliminating the high initial delivery rate and improving the safety profile; particularly with drugs such as stimulants or hormones, uniform drug delivery, cost efficiency, less drug loading is required per patch, much of which is currently discarded when the patch is removed.

8.5.3. Wound Care

Wound care products promote healing and reduce the chances of infection and scarring. Using halloysite, as a drug delivery system in cases of burn care can be very beneficial. Drugs loaded into halloysite tubes and embedded into the base layer of a bandage can be released over an extended time period. This increases the duration of drug effectiveness and reduces the frequency with which a bandage needs to be changed.

8.5.4. Nanotubes in Personal Care [20]

Safety or efficacy tests on halloysite nanotubes used in personal care formulas are to be conducted. Natural nanocontainer for the controlled delivery of glycerol as a moisturizing agent for the loading and extended release of glycerol for cosmetic applications.

8.5.5. Skin cleanser agent [24]

When applied without an active agent, the adsorptive nature of the HNT serves as a hypoallergenic skin cleanser capable of removing unwanted toxins and aesthetically unpleasing oils. The clay performs as a gentle exfoliator, drawing dead skin cells away from the surface to leave it fresh, young, and healthy.

8.5.6. Use of HNTs in synthesis of

8.5.6.1. Silver Nanorods for Antibacterial Composite Coating [20]

Silver nanorods were synthesized inside the lumen of the halloysite by thermal decomposition of the silver acetate, which was loaded into halloysite from an aqueous solution by vacuum cycling. The composite of silver nanorods encased in clay tubes with the polymer paint was prepared, and the coating antimicrobial activity combined with tensile strength increase was demonstrated.

8.5.6.2. Gold nanoparticles [25]

Gold nanoparticles were synthesized by reduction of $HAuCl_4$ using halloysites. The results show that the gold nanoparticles have strip-like, subcircle, and irregular shape, which are single crystals or polycrystals.

8.5.7. Use of HNTs in protecting environment

Sorbents for contaminants and pollutant:
HNTs can be used as nano-adsorbents for the removal of the cationic dye methylene blue from aqueous solutions. Also it can be used in removal of Zn (II) from aqueous solution [26].

9. FUTURE STEPS IN DEVELOPING ECO - FRIENDLY NANAOTECHNOLOGY [26]

- US-based Applied Minerals (formerly Atlas Mining) is commercialising halloysite nanotubes as a polymer additive under the Dragonite trade name.
- Further testing now in progress is aimed at achieving additional savings through reducing wall thicknesses by taking advantage of the improvement in physical properties.
- To increase the compatibility between PP and HNTs, grafting PP chains onto the surface of HNTs is being carried out to increase the mechanical performance of nanocomposites.
- Recently, research has focused on HNT-incorporated polymer nanocomposites. It exhibit markedly improved properties, such as superior mechanical performance, much higher flame retardancy and thermal stability, reduced CTE, etc.

10. CONCLUSION

Halloysite nanotubes are unique nanomaterials composed of double layer of aluminium, silicon, hydrogen and oxygen. Thus being small in size, HNTs does not show any toxicity even at high concentrations and cytotoxicity will not be an issue in future applications. Due to characteristics such as nano sized lumens, high L/D ratio, low hydroxyl group density on the surface, etc., more and more exciting applications have been discovered for these unique, cheap and abundantly deposited clays. So it can be concluded that HNTs possess promising prospects in the preparation of new structural and functional materials.

11. REFERENCES

1. Katie Schaefer. Cosmetics and Toiletries Special Delivery: Clay Nanotubes for skin. 2008; Feb-Mar. from the March 2008 issue of C & T – Special Delivery: Clay Nanotubes for skin.
2. Mingliang Du, Baochun Guo, Demin Jia. *Polym Int*, 2010; **59 (5):**574-582.
3. Nanoclay, www.nanoclay.com
4. Nano by Nature, (Bernhardt Fudmya Design Group), www.bfdg.com (2011).
5. Viviana Vergaro et al. *Biomacromolecules*, 2010; 11 (3): 820-826.
6. Dmitry R, Shchukin Dr et al. *Small,* 2005; **1(5):**510-513.
7. QiR, Caox, Shen M, Guo R, Yu I, Shix. *J Biomater Sci Polym,* 2012; **23(1-4):** 299 – 313.
8. Sun YJ, Kill DS, Chung KS. *J Nanosci Nanotechnol*, (2009); **11(1):** 661-665.
9. Elshad Abdullayev et al. *Journal of Physical Chem C*, 2010; **114 (26):** 11358-11363.
10. Nano by Nature, (Bernhardt Fudmya Design Group), www.bfdg.com (2010).
11. Peng Yuan, Peter DS, Zongwen Liu, Malcolm ER Green, James MHook, Sarah J et al. *Phys. Chem. C*, 2008; **112(40):** 15742-15751.
12. Ruijun Li, Zheng Hu, et al. *Int J Environ Anal Chem*, 2011, 1-3.
13. Bin Mu, Mingfei Zhao, Peng Liu. *J Nanopart Res*, 2008; **13(12):** 831-838.
14. Rachel D White et al. *Nanotechnology,* 2010; **23(6):** 065705.
15. Mohtashim H Shamsi, Kurt E Geckeler. *Nanotechnology*, 2008; **19:** 075604.
16. Mingliang Du, Baochun Guo, Demin Jia. *Polym Int*, 2010; **59 (5):** 574-582.
17. Andrew D. Hughes, Michael R. King. *Langmuir,* 2010; **26(14):** 12155-12164.
18. Sun YJ, Kill DS, Chung KS. *J Nanosci Nanotechnol*, 2005; **11(1):** 661-665.
19. Elshad A, Ronald P, Dmitry S, Yuri Lvov. *ACS Appl. Mater. Interfaces*, 2009; **1(7):** 1437-1443.
20. Dmitry GS, Lamaka SV et al. *J Phys Chem C,* 2008; **112(4):** 958-964.
21. Yuri ML, Dmitry GS, Helmuth M, Ronald R. *ASC Nano,* 2008; **2(5):** 814-820.
22. Price RR, Gaber BP, Lvov Y. *J Microencapsul*, 2001; **18(6):** 713-722.
23. Sundararajan G, Mahajan YR, Joshi SV, Nisha CK. *Nanotech insights*, 2011; **2(2):** 19.
24. Jianjin Cao, Xianyong Hu, Dan Jiang. *EJSSNT*, 2009; **7:** 813-815.
25. Xing B, Yin X-B. *PLoS ONE,* 2009; **4(7):** 6451.
26. Mingxian Liu, Baochun Guo, Ming Ciang Du. *Polymer*, 2009; 3022-3030.