

Double-walled carbon nanotubes suspending by natural active substances (saponins and humic acids)

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Abstract. Carbon nanotubes (CNTs) discovered over the past fifteen years are very interesting materials because of their structural, mechanical, chemical and electronic properties. However, their poor dispersion after synthesis constitutes a real obstacle to their use in varied fields. To respond to a topical issue, we proposed a new concept based on the use of natural active substances such as saponins; biosurfactant extracted from the tree *Sapindus Mukorossi* and humic acids.

The results showed that for a concentration of 1.5 mg/l of saponin and 5 mg/l of humic acids, the stable suspensions were obtained; the zeta potential measurements have justified these results.

1. INTRODUCTION

Carbon nanotubes are materials with exceptional properties, mechanical, electrical, catalytic, electrochemical, and electromechanical. Since their discovery by Iijima, the research has focused on the characterization of these properties. Therefore, current research focuses more on the modification of carbon nanotubes to obtain macroscopic materials taking the best advantage of their intrinsic properties. To achieve this, it is essential to have previously perfectly homogeneous dispersions. This is why many laboratories provide great efforts to optimize and develop new processes forming carbon nanotubes.

Currently, different dispersion techniques are often associated. It combines type processes “chemical” (functionalization, surfactants) to those phenomena involving “physical” (breaking of aggregates by ultrasound, centrifugation). The carbon nanotubes are insoluble, to disperse, it is generally necessary to modify their surface properties. A promising avenue is the dispersion of carbon nanotubes by the use of biodegradable surfactant. Moreover, the study of CNTs requires a good and stable dispersion, it is essential to evaluate their toxicity of amphibins.

2. MATERIALS AND METHODS

Carbon nanotubes: were synthesized at interuniversity Center for Materials research and engineering in Toulouse by the process Catalytic Chemical Vapor Deposition, after extraction, they are stored in wet form. Saponins were extracted by soxhlet with appropriate solvents, characterization of the extracts revealed the high content of active compound in these vegetable materials. One of the chemical structures of the saponins is

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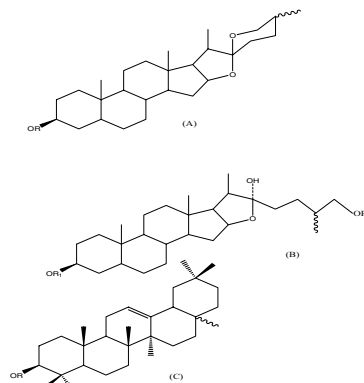


Figure 1. Structures of saponins.

2.1. Dispersions of CNTs by Natural Surfactants

Studies of suspending CNTs have been taken in particular to describe exposure to CNTs in terms of concentration in ecotoxicity testing, and we suppose that we could gain access to specific biological effects due to the nanometric dimension of the object evaluated. The raw CNTs are hydrophobic they sediment very quickly in water. Tests suspending (stability) were performed on 24 hours since the exposure media were change daily during testing in vivo.

2.1.1. Dispersion with saponins

Saponins in different concentrations were tested for the dispersion of CNTs. At first we studied the influence of the ratio dispersant / CNTs samples on their dispersal ability. Samples of dispersant/CNTs are then introduced in an ultrasonic tank for 30 min. An ultrasound probe is used to type (Vibra Cell 75042, 20 kHz, 500 W). The instrument is used at 25% amplitude, for 45 min (30 min to 10 seconds ON and 5 seconds OFF).

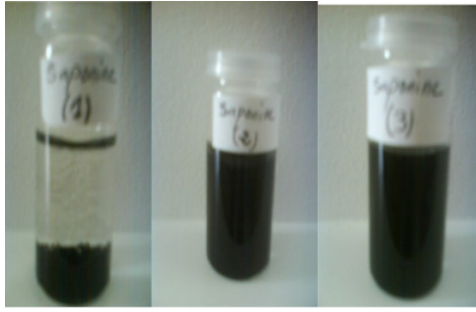


Figure 2. Images of dispersions of CNTs / saponin (1): 50 mg/l of saponin / 50 mg/l of CNTs, (2): 0.5 g/l of saponin / 0.5 g/l of CNTs, (3): 1.5 g/l of saponin / 1.5 g/l of CNTs.

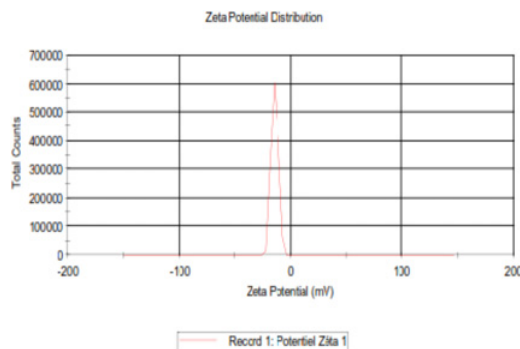


Figure 3. Distribution of system of zeta potential NTC / saponin (1.5 g/l).

2.1.2. Dispersions of carbon nanotubes by humic acid

Humic acid color the solutions in brown. Therefore it is more difficult to observe the sedimentation that in the use of other surfactants which are color less in aqueous solution. Initially, the suspension of 10 mg / L humic acid presents aggregates.

The structure of humic acids is very complex. The brown suspension appears (Figure 4).

2.1.3. Characterization of dispersions

The zeta potential measurements were performed on volumes of about 6 ml of suspension, Using an instrument (Zetasizer 4, Malvern, model ZET5000) as a function of pH. The suspensions should not be too concentrated (not focusing laser beam) or too weak (no signal) and the measurement time is about 5 minutes.

3. RESULTS AND DISCUSSION

3.1. Report NTC / saponin (5ml/5ml)

We tested the saponin at different concentrations (50mg/l, 0.5 g/l and 1.5 g/l). The figure below illustrates the dispersions obtained after 8 days storage.

The image clearly shows that in the case of the aqueous suspension prepared from 50 mg/l of CNTs / saponin, CNTs sediment quickly. The supernatant solution is transparent and clear. Increasing the concentration

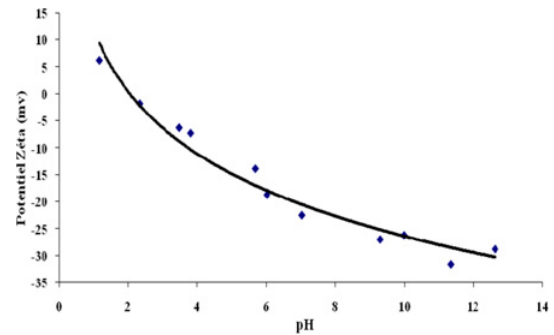


Figure 4. Variation of zeta potential versus pH of system Saponin 1.5 g/l with CNTs 1.5 g/l.

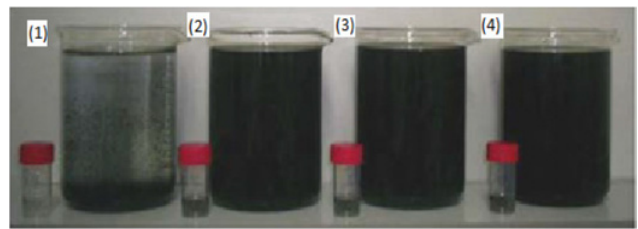


Figure 5. Images of dispersions of CNTs / humic acids (1): 0.1 mg/l of humic acids, (2): 1 mg/l of humic acids, (3): 5 mg/l of humic acids, (4) 10 mg/l of humic acids.

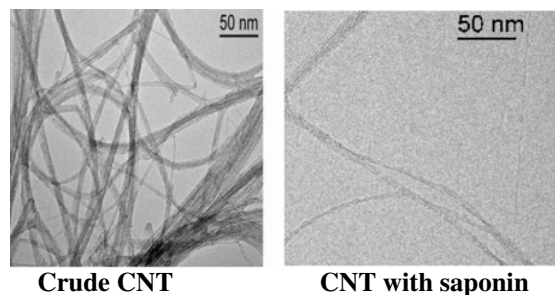


Figure 6. Images MET of carbon nanotubes.

of saponin / CNTs, suspensions become visually homogeneous and stable. The distribution of the zeta potential of the system 1.5 g/l of saponin / 1.5 g/l of CNTs is shown in figure below, the negative value of potential (-14.1 mV) gives us information on the anionic character of the system.

The figure below shows the variation of zeta potential versus pH of the system (saponin 1.5 g/l CNTs + 1.5 g/l), we see clearly the displacement values of the zeta potential toward more positive values with the addition of acids until the appearance in the vicinity of the isoelectric point $\text{pH} = 2.08$. There is also that there is a stable dispersion in the acid range because of the variation in absolute value of the zeta potential is greater than 30 mV.

3.2. Report CNTs / humic acids

Figure below shows the dispersions obtained with different concentrations of humic acid.

The concentration that seems most effective to keep the CNTs in suspension is 5 mg/l. However within 24 hours, sedimentation is visible whatever the concentration of HA. For the three lower concentrations of HA, the concentration of CNTs kept in suspension is about 2, 2.5 and 3.5 mg/l respectively for 0.1, 1 and 5 mg/l of HA. The solution of 10 mg/l of HA does not maintain CNTs in suspension and at 10 mg/l the formation of aggregates is immediate. For this surfactant and it was shown that a too high concentration can have a destabilizing effect.

The dispersions were characterized by microscopic to electronic transmission.

Images are shown in the figures below meadows, we see the state's dispersed, CNTs are individualized

4. CONCLUSION

Saponins, bioactive substances extracted from plants allow a suspending of carbon nanotubes to a concentration of 1.5 g/l for an long terms period, the relatively high proportion does not constitute an obstacle to the availability of natural raw material and the ease extraction of the surfactant.

Dispersions of Carbon nanotubes obtained with humic acids were sediment after 24 hours, results which not encourage us to classify them as dispersing agents for carbon nanotubes especially for high levels.

It remains to verify the inherent toxicity of saponins extracted in order to consider their application in ecotoxicity studies for the preparation of aquatic amphibians.

References

- [1] Iijima S. "Helical microtubules of graphitic carbon. Nature", 1991, 354, 56–58.
- [2] Ebbesen T.W., Ajayan P.M. Large-scale synthesis of carbon nanotubes. Nature 1992, 358, 220–222.
- [3] Kroto H.W., Heath J.P., O'Brien S.C., Curl R.F., Smalley R.E. C60: Buckminsterfullerene. Nature, 1985, 318, 162.
- [4] Flahaut, E., Laurent C, and Peigney A, "Catalytic CVD synthesis of double and triple-walled carbon nanotubes by the control of the catalyst preparation". Carbon, 2005, 43(2) 375–383.
- [5] Tagmatarchis. D, Bianco, M. Prato, "Chemistry of Carbon Nanotubes", Chemical Reviews, 2006, 106 (3), 1105.
- [6] Wagner. L H.D., Marom G, "The role of surfactants in dispersion of carbon nanotubes", Advances in Colloid and Interface Science, 2006, 37, 128–130.
- [7] Mitchell. K, Krishnamootri R., "Small-angle neutron scattering from surfactant-assisted aqueous dispersions of carbon nanotubes", Journal of the American Chemical Society, 2004, 126 (32), 9902.
- [8] Van der. A, Schoot P., Meuldijk J., Koning C.E., "Determination of the Surface Coverage of Exfoliated Carbon Nanotube by Surfactant Molecules in Aqueous Solution", Langmuir, 2007, 23 (7), 3646.
- [9] Zhu. J, Kim. J, Peng, H Margrave, V. Nano Lett. 2003, 3, 1107–1113.
- [10] J. Che, W. Yuan, G. Jiang, J. Dai, S.Y. Lim, M.B. Chan-Park, Chem. Mater, 2009, 21, 1471–1479.
- [11] Hamano H.T., Hayashi K., Kikuchi J.I., "Water-Solubilization of Nucleotides-Coated Single-Walled Carbon Nanotubes Using a High-Speed Vibration Milling Technique", Organic Letters, 2006, 8 (6), 1153.
- [12] Poulin. S.P., Maugey M., Zakri C., "In-situ measurements of nanotube dimensions in suspensions by depolarized dynamic light scattering", Langmuir, 2004, 10, 10367
- [13] Lorimer. T.J., "Applied Sonochemistry", Wiley-VCH, Verlag GmbH, Weinheim; 2002.
- [14] Price. K., "Applications of ultrasound to materials chemistry", Annual Review Materials Science, 1999, 29, 295.
- [15] Vaisman, L., H.D. Wagner, and G. Marom, *The role of surfactants in dispersion of carbon nanotubes*. Advances in Colloid and Interface Science, 2006, 128–130, 37–46.
- [16] Sato, H. and M. Sano, *Characteristics of ultrasonic dispersion of carbon nanotubes aided by antifoam*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008, 322(1–3) 103–107.
- [17] Liu, Y., et al., *Dispersion of multiwalled carbon nanotubes by ionic liquid-type Gemini imidazolium surfactants in aqueous solution*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2010, 359 (1–3) 66–70.
- [18] Wang, H., *Dispersing carbon nanotubes using surfactants*. Current Opinion in Colloid & Interface Science, 2009, 14(5) 364–371.