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Preparation, Characterization and Purity Dependant Heat Transfer Properties of MWCNTs Nanofluids.

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ABSTRACT

This paper deals with preparation of water based MWCNT nanofluids and investigates the thermal conductivity of the nanofluids prepared with varying the purity level of water. Distilled water, mineral water and spring water with different TDS content were taken as base fluids. By dispersing 0.02% and 0.04% volume fraction of MWCNTs, six different nanofluids were prepared by the two-step preparation process. Thermal conductivity of the prepared specimen was measured and the result proves that as the TDS content of water increases the enhancement in the thermal conductivity of the nanofluid gradually decreases. Also the nanofluid prepared with spring water as the basefluid exhibited a lower thermal conductivity compared to the plain spring water. The reduction in the thermal conductivity in the case of spring water based nanofluids is due to the poor stability of the suspension which is apparent from the results of the zeta potential analysis. This anomalous behaviour extends the application of MWCNTs for primary water treatment process.
Keywords: Multiwalled Carbon nanotubes (MWCNTs), Nanofluids, Thermal conductivity, Totaldissolved solids (TDS), Zeta potential

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INTRODUCTION

The fluids that were traditionally used as coolants had a problem of exhibiting low thermal conductivity. Nanofluids is a colloidal suspension obtained by dispersing ultrafine particles of size 10^{-9} into a base fluid that exhibit better heat transfer properties. The term nanofluid is proposed by Choi [1] of Argonne National Laboratory, U.S.A. for such type of fluids. Commonly used base fluids are water, oil and ethyl alcohol. These are experimentally found to possess enhanced thermophysical properties compared to its parent base fluid. Nanofluids are of more need in upcoming future due to their ultra-heat transfer ability, less friction co-efficient, less corroding and clogging properties in micro channels. In such cases the conventional fluids are not found to be effective and safe. Previous results show that of all the nanofluids, the one prepared using MWCNTs and distilled water as the base fluid produced a maximum enhancement in the thermal conductivity up to 105% as reported by Xinwei et al. [2]., for a very small volume fraction of MWCNTs. This widens the potential scope of MWCNTs nanofluids as coolants in different applications. In spite of the exceptional properties of MWCNTs, dispersion of MWCNTs in organic solvents is very difficult. Though various functionalization techniques have been introduced to improve their dispersibility, further study needs to be done to reduce the cost and the time taken for these techniques to widen the applications of MWCNTs nanofluids.

Challenges ToNanofluids

Though the nanofluids are emancipated to a wide range of applications, the preparation of a long term stable nanofluid has always been a tedious process due to thermal aging and coagulation Thermal aging is the degradation in the thermal conductivity of a nanofluid due to prolonged exposure to elevated temperature. Coagulation is the process of agglomeration of particles of the suspension. Coagulation is started by aggregation of the particles and then followed by sedimentation. Both thermal aging and coagulation have an adverse effect on stability and thermal conductivity of the nanofluid during its long term usage. Though various techniques have been instigated to maintain the long term stability of the nanofluids, these techniques are time consuming and are not usually cost effective as stated by Xiang Qi et al [3]. Also one of the main disadvantage of these classes of fluids is that the preparation and characterization of these fluids must be done in a highly isolated and dust free environment.

Raman Spectra of Multi Walled Carbon Nanotubes

Raman spectroscopy is one of the most familiar techniques for determining diameter distribution, purity and structure of carbon nanotubes. The generally found characteristic of Raman spectra in multi-walled carbon nanotubes is the appearance of Raman peaks. Due to the confinement of wave-vectors along the circumference, there are two nodes which are named as G^+ and G^- respectively. In this G^+ does not vary with respect to the diameter of carbon nanotubes, whereas G^- varies with the diameter of carbon nanotubes [4] [5]. In other words, the Raman spectra help in characterizing the multi-walled carbon nanotubes for determining their properties such as diameter distribution, chirality and purity. Based on the results obtained from the Raman spectrum (Figure 1), the outer diameter of MWCNTs was calculated to be in the range of 50-60 nm, the length of the tubes was found to be in the range of 30-35 micrometer and the purity was found to be in the range of 90-94%.

Experimentation

Functionalization of Carbon Nanotubes

As discussed earlier, CNTs do not have a chemical affinity towards organic solvents which in turn hinders the dispersion of MWCNTs in organic solvents. The main problem with the majority of popular synthetic methods is that they produce samples yielding a mixture of various diameters and chiralities of nanotubes that are normally contaminated with metallic and amorphous impurities. Thus, post-synthesis chemical processing protocols (Strano et al. [6] & Li et al. [7]) that purify the tubes that can also separate individual tubes according to diameter and chirality by taking advantage of their differential reactivities are often the only viable routes to rational and predictable manipulation of the favourable electronic and mechanical properties of these materials (Niyogi et al. [8] &Tasis et al. [9]). Since CNTs are hydrophobic in nature, they tend to agglomerate hindering their dispersion in solvents. Functionalization is a surface modification process through which hydrophilic functional groups are introduced to the nanotubes, thereby improving their dispersibility into organic solvents. Post synthesis chemical treatment using strong acids was employed to functionalize MWCNTs. Functionalization was started by weighing a small amount of carbon nanotubes and was followed by adding a specific quantity of concentrated sulphuric acid and concentrated nitric acid which was taken in the ratio of 3:1 by volume. The mixture was stirred continuously for 3 hours with the help of a magnetic stirrer in a constant temperature water bath of about 65 ^{o}C. The well stirred mixture was poured into a 1 litre beaker and distilled water was filled up to the mouth of the beaker to neutralize the pH level. The mixture was then left undisturbed for 24 hours, allowing the carbon nanotubes to settle down. After the CNTs settled down completely, the same was filtered by filter papers. The filtered CNTs was then dried in a hot air oven at 60-70^{o}C to obtain functionalized carbon nanotubes. It gave a lustrous appearance (Figure 2). These CNT powders are to be maintained in a highly dust free environment to avoid the CNTs from undergoing agglomeration. Though the above process improves the dispersibility of MWCNTs in organic solvents, they induce some intrinsic defects in the nanotubes which was found to alter the size distribution of MWCNTs as predicted by In-Yup et al.[10]

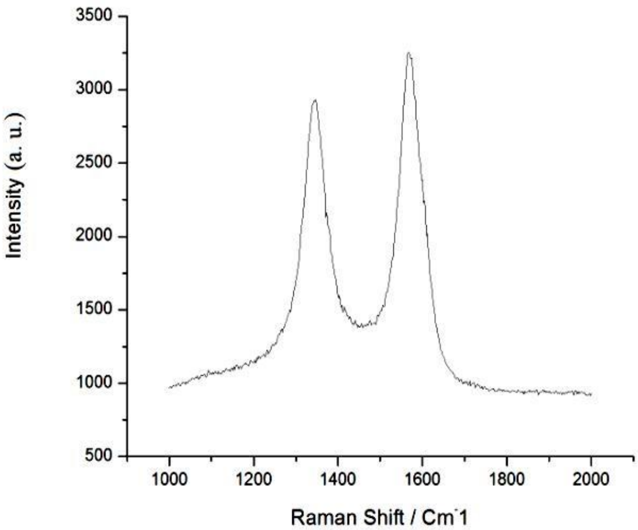

Figure 1: Raman Spectra of Multi-Walled Carbon Nanotubes

Figure 2: Functionalized MWCNTs powders exhibiting lustrous appearance

Preparation of Water Based MWCNT Nanofluid

There are mainly two techniques used to produce nanofluids: the single-step and the two-step method. The single-step direct evaporation approach was developed by Akoh et al. [11] and was called the VEROS (Vacuum Evaporation onto a Running Oil Substrate) technique. A modified VEROS process was proposed by Wagener et al. [12] They employed high pressure magnetron sputtering for the preparation of suspensions with metal nanoparticles such as Ag and Fe. Eastman et al. [13] developed a modified VEROS technique, in which Cu vapour is directly condensed into nanoparticles by contact with a flowing low-vapour-pressure liquid (EG).Six samples of nanofluids were prepared with water as the base fluid. The nanofluids were categorized based on the total dissolved solids content of the water and the two different volume fraction of MWCNTs. The TDS content of ultrapure distilled, mineral water, spring water were measured to be 1 ppm, 32 ppm, 1150 ppm respectively using a TDS meter. 10 ml of each of the water samples were taken in a beaker and 0.02%, 0.04% volume fraction of CNTs was added to the same. The beaker was then placed in an ultrasonic agitator. Sonication was carried out for a period of 1 hour to obtain water based MWCNTs nanofluids. Though the base fluid containing functionalized carbon nanotubes was agitated for a less period of time, the CNTs were found to be thoroughly dispersed and a clear suspension with any powder sediments was obtained (Figure 3) as the result of post synthesis chemical method of functionalization of MWCNTs.

Figure 3: Nanofluid prepared with 0.02% volume fraction of MWCNTs and distilled water as the base fluid

Zeta potential measurement

Zeta potential is the potential difference between the nanoparticle surface and the dispersant medium. Spring water and distilled water based nanofluids with 0.005% and 0.01% volume fraction of MWCNTs were subjected to zeta potential analysis. The zeta potential of the prepared nanofluid samples were measured using an instrument named Zeta sizernano at the Indian Institute of Technology, Madras.

Measurement of Thermal conductivity

Addition of nanoparticles to a base fluid usually improves its thermal conductivity. Thermal conductivity of different water and nanofluid samples were measured by a device named KD 2 PRO which works on the principle of transient line heat source method. The thermal conductivity values of different water samples before the dispersion of MWCNTs are shown in Table 1.

Table 1: Comparison of Thermal Conductivities of Various Water Samples

Water Sample	TDS (ppm)	Average Thermal Conductivity (W/mK)
A - Distilled water	1	0.58
B - Mineral water	32	0.62
C - Spring water	1150	0.717

RESULTS AND DISCUSSION

Zeta Potential Analysis

Measurement of Zeta potential provides an aid in determining the long term stability of a colloidal suspension. Lesser the value of zeta potential of a suspension higher is its tendency to get aggregated. The measured values are expressed in terms of millivolts.

Table 2: Comparison of Zeta Potential Values of Various Samples of Nanofluids

Nanofluids	0.005% DW	0.01% DW	0.005% SW	0.01% SW
Trial 1	-5.2	-10.9	-20.3	-23.1
Trial 2	-3.6	-14.6	-20.7	-21.3
Trial 3	-4.6	-11.9	-19.6	-22

Thus from the results of the zeta potential analysis detailed in Table 2, it is proved that spring water based nanofluid with a highest TDS content exhibits the highest tendency to get agglomerated with an average zeta potential value of 22.13 mV. In other words, spring water based nanofluid possesses least stability.

Purity Dependant Heat Transfer Properties of Nanofluids

From the Table 3, as the TDS content of water increases, the enhancement in thermal conductivity of the nanofluid prepared with the corresponding water sample was found to be reduced. Nanofluid prepared with distilled water as the base fluid produced an enhancement in its thermal conductivity by 11.72%, whereas the nanofluid prepared with mineral water as the base fluid produced an enhancement in its thermal conductivity only by 1.9% both for a volume fraction of 0.02% of MWCNTs. Surprisingly in the case of spring water based nanofluid where a maximum enhancement was expected, a reduction in its thermal conductivity was resulted. This anomalous behavior is due to the fact that with the increase in particle content there are greater chances of the MWCNTs to agglomerate together with the particles of water. Agglomeration is followed by sedimentation. This disturbs the dispersibility of nanoparticles and thus the stability of the nanofluid which is proved from the results of the zeta potential analysis. Due to this, the thermal conductivity substantially reduces. Also, as the volume fraction of MWCNTs is increased, the enhancement in the thermal conductivity is increased. The same is agreed in the case of distilled water and spring water based nanofluid. However, in the case of spring water based nanofluid as the volume fraction of MWCNTs increases, its thermal conductivity is further reduced as depicted in Figure 4 because of increased rate of agglomeration with the increasing volume fraction of MWCNTs.

Table 3: Comparison of Thermal conductivities of Various Water Samples and Nano Fluids

Nanofluids	Thermal Conductivity of corresponding water samples (W/mK)	Thermal Conductivity of Nanofluids (W/mK)	Enhancement in Thermal Conductivity (%)
Distilled water based with 0.02% vol fraction of MWCNTs	0.58	0.648	11.72
Distilled water based with 0.04% vol fraction of MWCNTs	0.58	0.792	36.55
Mineral water based with 0.02% vol fraction	0.62	0.632	1.93

of MWCNTs			
Mineral water based with 0.04% vol fraction of MWCNTs	0.62	0.657	5.96
Spring water based with 0.02% vol fraction of MWCNTs	0.717	0.604	-15.76
Spring water based with 0.04% vol fraction of MWCNTs	0.717	0.516	-28.04

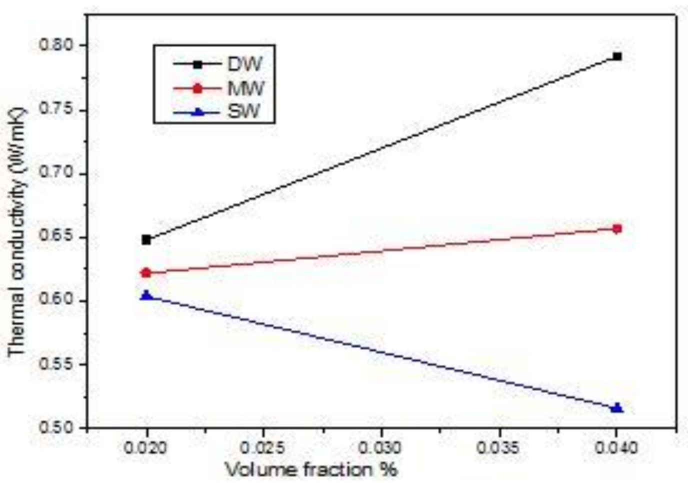

Figure 4: Variation of Thermal conductivity of Different Water Samples with Varying Volume Fraction of MWCNTs

Anomalous Behaviour Aiding in Water Filtration

Nanofluid with spring water as the base fluid underwent coagulation and settled down within 30-45 minutes of its preparation. As the coagulated particles were filtered from the spring water, the TDS content of the spring water was found to be lesser than the original TDS content of the same. The sedimented particulates of the spring water based nanofluid were filtered after allowing the suspension to settle down completely. The resulting spring water after filtration possessed a TDS value much lesser (247ppm) than the original TDS value (1150ppm) possessed by the same. Thus this anomalous behaviour can be associated with primary water treatment processes. However, since CNTs pose threat to the human beings and animals when consumed, the treated water should strictly be subjected to applications without direct human and animal interact.

CONCLUSION

(i) Nanofluids possess a better heat transfer properties than the parent base fluid.
(ii) As the nanoparticle volume fraction increases, the thermal conductivity of the base fluid increases, but as the particle content of the parent base fluid becomes very high, a low volume fraction nanofluid will have a better conductivity than a high volume fraction nanofluid both prepared using the same base fluid.
(iii) Nanoparticles can be used for primary water treatment process – for applications without direct human interaction.

Thus, we conclude that, in the preparation process of nanofluids, it is important that the base fluids chosen should be of high purity, which is a key in maintaining the long term stability of the nanofluids.

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