Study of environmentally friendly and facile functionalization of graphene nanoplatelet and its application in convective heat transfer

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The chemical functionalization of carbon-based nanomaterial typically involves toxic and corrosive inorganic acids that are harmful to environment and human health. In this study, an environmentally friendly, facile and cost effective procedure for synthesizing a novel and highly dispersed functionalized graphene nanoplatelets (GNPs) nanofluids for use as a heat transfer fluids was developed. In the new approach, GNPs were functionalized covalently with Gallic Acid (GA) in a one-pot free radical grafting method. The Gallic acid-treated graphene nanoplatelets (GAGNPs) were dispersed in distilled water (DI water) with different weight concentrations to prepare GAGNPs-water nanofluids (nano-coolants). The effectiveness of the functionalization process was verified by the Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The UV–visible absorption spectroscopy was used to show a sustained stability of nanoparticles. Thermo-physical and rheological properties of GAGNPs aqueous suspensions with different weight concentrations were experimentally investigated. This was followed by measurement of the convective heat transfer coefficient, Nusselt number and friction factor for fully developed turbulent flow of GAGNPs nanofluids at a constant heat flux. The experimental results were compared with those of the base fluid. The GAGNPs nanofluids showed a significant increase in the convective heat transfer coefficient and Nusselt number, while the increases in the friction factor and pumping power were small. Furthermore, the comparison showed that the overall performance index was higher than 1. The novel and eco-friendly GAGNPs nanofluids have the potential to be used as highly effective working fluids for various heat transfer applications.

1. Introduction

Energy optimization has been identified as the most important issue in sustainable development including the infrastructure, transportation, defense and many industries. To realize energy optimization, different kinds of cooling systems with various designs have been employed over the past century. Convective heat transfer plays an important role in most of thermal equipment including cooling devices, solar collectors and heat exchangers which usually use water, propylene glycol, ethylene glycol and oil as working fluids. These fluids, however, show low thermal conductivity that leads to low heat transfer efficiency [1]. In the last decade the potential usage of suspension of nanoparticles with high effective thermal conductivity has gained considerable attention [2–10]. Such suspension, referred to as nanofluids have attracted researcher’s interest since the materials in the nanometer size has unique physical and chemical properties. In particular, nanofluids exhibit high thermal conductivity and good heat transfer coefficient which makes them suitable candidate as high performance heat transfer fluids [3,11,12]. Various nanoparticles, such as carbon nanotubes (CNT), Graphene nanoplatelets (GNPs), Graphene oxide (GO), fullerene, copper oxide (CuO), aluminum oxide (Al2O3), and silicon dioxide (SiO2) have been used to produce nanofluids with enhanced thermal conductivity. More recently, remarkable enhancement in thermo-physical, rheological and heat transfer properties of carbon based nanofluids was reported in the literature [13–19].

Lee et al. [20] experimentally studied the thermal conductivity of alumina (Al2O3)–water, alumina–ethylene glycol (Al2O3–EG) and CuO–EG. They reported about 23% enhancement in the thermal
conductivity of EG in presence of CuO. Murshed et al. [21] investigated the thermal conductivity of TiO$_2$–water nanofluids. Their results suggested that there was a nonlinear trend between thermal conductivity and volume concentration of nanoparticles. Pak and Cho [22] investigated the turbulent convective heat transfer characteristics of water–Al$_2$O$_3$ and water–TiO$_2$ nanofluids flowing through a horizontal tube. The results showed that the Nusselt number of nanofluids increased with increasing Reynolds number and the volume concentration. Xuan and Li [23] explored experimentally the flow and convective heat transfer of copper based-water nanofluids, and reported that the friction factor of the nanofluids for dilute concentration was approximately the same as that of water. The thermal conductivity and heat transfer of multiwalled carbon nanotubes (MWCNTs)-based water nanofluids were investigated in previous investigations [24,25] where a noticeable enhancement of heat transfer was reported that was attributed to the thinning of the thermal boundary layer by MWCNTs and the associated reduction of the thermal resistance.

Among various carbon-based nanostructures, the graphene-family nano-materials have received more attention due to their attractive thermal, electrical and mechanical properties [26–29]. Graphene, an atomically thin, two dimensional lattice of Sp$^2$-hybridized carbon has exhibited exceptional thermo-physical properties [30]. These unique properties make it a promising additive for many applications such as inkjet printing, conductive thin films, solar cells, polymer composites, aerogels and heat exchangers [26,31]. In addition to high specific surface area, graphene presents tendency to agglomerate by strong π–π stacking interaction, while the dispersibility of graphene in aqueous media is considered as one of the most important factor in heat transfer equipment, films and composites [32]. Hence several methods were employed to improve stability of graphene in aqueous and organic media by chemical and physical methods containing covalent and non-covalent functionalization of graphene.

Recently, chemical functionalization with the hydrophilic organic group like carboxyl, esters, alkalis and amine group on the surface of GNP has promised the stability of the graphene sheet in aqueous media. Oxidizing GNP by the usage of strong acids, the mixture of sulphuric acid and nitric acid, is reported as an effective method of synthesizing water soluble GNP [32,33], although there are many covalent reactions on carbon based nanomaterials such as, radical addition, alkali metal reduction, Bingel cyclopropanation, Nitrene cycloaddition, 1,3-dipolar cycloaddition, electrophilic addition, nucleophilic addition, carbene addition and Diels-Alder cycloaddition [34,35]. The free radical coupling is a promising method of covalent functionalization of carbon nanostructure. In this method, proxides and aryldiazonium salts have substituted anilines and benzophenone were utilized as starting materials [36]. In comparison with other functionalizations methods, the covalent functionalization technique may produce defects on the GNP sheets and also generates hazardous and toxic wastes.

The non-covalent functionalization of GNP's based on the π–π stacking interaction and polymer wrapping of surfactants such as sodium dodecyl benzene sulphonate (SDBS), sodium dodecyl sulphate (SDS), gum arabic (GA) and cetyltrimethylammonium bromide (CTAB) improves GNP's solubility in polar solvents. However, there are some undesirable effects of the above mentioned surfactants on the thermophysical properties of carbon based nanofluids such as increasing viscosity and foam formation in the colloidal suspensions which have limited surfactant applications [37]. In addition, both strong acids and some organic solvents often cause environmental pollution, equipment corrosion and health hazard. Therefore, it is imperative to develop an environmentally friendly method to functionalize carbon base nano-structures [38].

Recently, green chemistry and green chemical processes has attracted considerable attentions due to their benign effects on the environment and their ability to function well or even better than other more toxic traditional options [39,40]. Green chemistry was proposed by chemists which contains some important principles such as 1 – the elimination of chemical waste, 2 – design of safer chemicals 3 – reduction of hazardous chemical synthesis, 4 – real time analysis for pollution prevention, 5 – improved energy efficiency, 6 – use of renewable source, 7 – inherently safer chemistry for accident prevention [40,41].

Among the green materials, Gallic acid (GA) is a natural polyphenol antioxidant extracts from green tea, berries, grapes, wine and also found in some hard wood plant species [42]. It can act as a non-toxic corrosion inhibitor by adsorbing on the metal surfaces [43]. Moreover, Gallic Acid has been shown to be an effective stabilizing agent for the protection of biodiesel oxidation [44].

Due to the Gallic acid structure (phenol) and green properties, it can be a suitable candidate for improving the functionalization of GNP's in aqueous media. The main objective of the present study is developing an environmentally friendly, cost-effective, and industrially scalable method for synthesizing covalent Gallic acid-treated graphene nanoplatelets (GAGNPs). The other objective is to develop a stable nanofluid of suspension of GAGNPs in aqueous media, and demonstrate its effectiveness in improving the convective heat transfer in a closed conduit. To validate the successful implementation of the functionalization, the treated nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and UV–visible absorption spectroscopy. In addition, the thermo-physical and rheological properties of the synthesized nanofluids were measured at different weight concentrations and temperatures. Furthermore, the convective heat transfer and friction factor were experimentally evaluated for the nanofluids at different concentration and the data were validated against the empirical correlations. Afterwards, the heat transfer coefficient, Nusselt number, friction factor, pumping power and performance index were evaluated for the synthesized water-based GAGNPs nanofluids under turbulent flow conditions in a horizontal stainless tube.

2. Materials and methods

Pristine Graphene nanoplatelets (GNPs) of maximum particle diameter of 2 μm, specific surface area 750 m$^2$/g and purity 99.5% were obtained from, XG Sciences, Lansing, MI, USA. Rest of the chemical materials were of analytical grade such as Gallic acid (3,4,5-trihydroxybenzoic acid) and hydrogen peroxide (H$_2$O$_2$, 30%) were procured from Sigma–Aldrich.

2.1. Preparation of the GA-treated GNP's aqueous suspensions

Free radical grafting of Gallic acid onto GNP's was achieved using hydrogen peroxide (H$_2$O$_2$) and heat, respectively, as redox and thermal initiator. As a first step hydrogen peroxide as a free-radical oxidizer that generates non-toxic by-products and leaves no chemical residue at high temperatures becomes unstable and decomposes spontaneously into hydroxyl radicals. These producing hydroxyl radicals will then attack Gallic acid to produce free radicals on the Gallic acid structure, which leads to linkage of the activated molecules onto the surface and edges of GNP's. In addition, the hydroxyl radicals can attack the GNP's directly, leading to formation of hydroxyl groups on the surface of GNP's. For synthesizing GA-treated GNP's, 5 g pristine GNP's and 15 g Gallic acid was poured into a vessel filled with 1000 ml of distilled water (DI water) and then stirred for 15 min at 80 °C to reach a uniform black suspension. Concentrated hydrogen peroxide (35 ml) was slowly poured into the vessel during the sonication time. The
resulting mixture was ultra-sonicated with a probe-sonicator for 30 min at 80% amplitude. Then, the mixture was allowed to reach 80 °C under reflux for 12 h. The functionalized GNPs were centrifuged and washed several times with large amounts of DI water until the pH was neutral. The functionalized sample was dried overnight at 60 °C in a vacuum oven. To synthesize the GAs-treated GNPs, the mixture was allowed to reach 80 °C under reflux for 12 h. The functionalized GNPs were centrifuged and washed several times with large amounts of DI water until the pH was neutral. The functionalized sample was dried overnight at 60 °C in a vacuum oven. To synthesize the GA-treated GNP based water coolant (GAGNP-water nano-coolant), the GA-treated GNP was sonicated with water as a base-fluid for 15 min. The GAGNP-water nano-coolant was much more soluble in water than the pristine GNP. The GAGNPs nanofluids were synthesized at the weight concentrations of 0.025%, 0.075% and 0.1%.

The mechanism of the functionalization reaction is shown in Fig. 1.

2.2. Experimental methods

Experiments were performed in several steps. First the nanofluids were synthesized, and their thermo-physical properties, as well as, those of the base fluid were evaluated. Nanofluids were characterized using different analytical equipment and finally the heat transfer and frictional properties of nanofluids flowing in a closed conduit were evaluated.

To investigate the morphological characteristics of the samples, transmission electron microscope (TEM) analyses were performed by HT 7700 (Hitachi, Japan). For the TEM analysis, the sample was prepared by ultrasonically dispersing the material in ethanol prior to collection on Lacey carbon grids. Characterization of the GAGNPs and GNPs was carried out using Fourier transform infrared (FTIR) spectroscopy (Bruker, IFS-66/S, Germany) and thermogravimetric analysis (TGA-50, Shimadzu, Japan). We used Shimadzu UV-1800 spectrophotometer to determine the dispersibility of GAGNPs-DI water nanofluids. For the UV–vis analysis, we diluted the nanofluids with DI water at a dilution ratio of 1:20 in order to ensure that the detectable wavelengths of the UV–vis spectrometer are able to pass through the samples. Following this, the samples were poured into quartz cuvettes specialized for transmission of UV wavelengths and the absorbance of the samples at pre-defined time intervals over the course of 63 days at the wavelength of 255 nm was measured. The thermal conductivity of the samples was measured using KD-2 PRO portable field and laboratory thermal property analyser (Decagon Devices, USA). The KS–1 probe has a length and diameter of 60 and 1.3 mm, respectively. The accuracy of the thermal conductivity measurements is around 5%. In order to ensure equilibrium of the nanofluids, an average of 20 measurements were recorded over a 5-h period for each nanoparticle concentration and temperature. Calibration of instrument with DI water was performed before the measurements of nanofluids. The thermal conductivity of DI water at 30 °C was measured and a value of 0.611 W/mK was found, which is in agreement with the previous investigations [45,46]. We measured the viscosity of the GAGNP-water nanofluids using Anton Paar Physica MCR rotational rheometer. This rheometer includes a moving cylindrical plate placed in parallel to a stationary cylindrical surface with a small gap in between them. The density of the samples was measured using DE-40 density meter (Mettler Toledo, Switzerland), with an accuracy of 10^-4 g/cm^3. The measurements were recorded three times for each sample and temperature. The experimental set-up for convective heat transfer measurements comprised of a horizontal stainless steel tube as a test section, a reservoir tank, a pump, a cooling unit, a data acquisition system, and measuring instruments containing a differential pressure transmitter (DPT) and a flow meter. The schematic layout of the experimental set-up is shown in Fig. 2. The Araki EX-70 R magnet pump was used to pump the GAGNP-water nano-coolants from a 10 L stainless steel jacketed tank at a flow rate of 0–14 L/min. The pressure loss and flow rate measured by Foxboro® differential pressure transmitter and Bürkert Contromatic SE 32 inline paddle wheel transmitter with display, respectively. The Hoffman Muller inverter used to regulate the pump flow. The test section of our experimental set-up consists of a straight, seamless, stainless steel tube having the length, outer and inner diameter of 1400, 12 ± 0.1 and 10 mm, respectively. The test section carefully was wrapped with ultra-high-temperature flexible tape heater (length × width: 3600 mm × 12.5 mm, maximum power: 940 W) in order to prepare the final heated section of 1.2 m. The heater was connected to a QPS VT2-1 variable voltage transformer and we adjusted the voltage and current in order to set the heating power. The five K-type thermocouples were inserted into stainless steel thermocouple sleeves and then attached onto the upper surface of the test...
section using high-temperature epoxy adhesive. The axial distances of the thermocouples from test tube inlet are 20, 40, 60, 80, and 100 cm as it can be seen in Fig. 2. Moreover, the bulk temperature of the flow was measured by 2 RTD (PT-100) sensors, which were inserted into the flow stream at the outlet and inlet of the test section. All RTDs and the thermocouples were calibrated before installation. The errors of all the thermocouples are up to ±0.1 °C. The thermocouples were connected to the Data Logger (Graphitec MIDI logger g1220), in order to monitor and record the temperature data by a personal computer. The thick fiberglass wool was wrapped around the test section, in order to decrease the heat loss to the surroundings, which was covered by rubber insulation dressing. In addition, all the fittings and piping were covered by rubber insulation to reduce heat loss to the surroundings and achieve a steady-state temperature at the outlet and inlet of the experimental test section.

2.3. Data processing

The experimental data for evaluating the hydrodynamic and heat transfer performance of GAGNP-water nano-coolants flowing through a closed conduit was compiled and processed in the following sections. The thermocouples were located at the outer surface of the tube in order to prevent disturbance in the boundary layer caused by protruding of thermocouple probes into the tube internal surface. Considering the conduction in the tube wall and convection heat transfer with the fluid at the test section, a calibration was required to determine the temperatures at the internal tube surface. Hence, an analysis based on the Wilson plot technique [47] was done by equating the resistance between various sections in the direction of heat transfer and measuring the inner surface temperatures of the horizontal pipe via mathematical manipulation. To study the effect of the GA-treated GNPs on thermal properties of distilled water the heat transfer coefficient (h), the Nusselt number (Nu) and pressure drop (DP) are the important parameters. The experimental heat transfer coefficient was evaluated from the measured surface, bulk, outlet and inlet temperatures via the Newton’s cooling law. That is,

\[ h = \frac{q''}{(T_w - T_o)} \]  

where \( T_o, T_w \) and \( q'' \) are the bulk temperature, wall temperature and heat flux, respectively. \( T_b \) is defined as \( \frac{T_i + T_o}{2} \), where \( T_i \) and \( T_o \) is the inlet and outlet flow temperature, respectively. The heat flux can be calculated using,

\[ q'' = \frac{Q}{A} \]

where Q is the input power (VI) provided by the power supply, \( A \) is the heated inner surface area of the tube. Here, \( A = \pi DL \). The input power (VI) of 600 W was used in this experiment.

The Nusselt number is the non-dimensional heat transfer coefficient defined as:

\[ Nu = \frac{h \times D}{K} \]

where K, h and D are, respectively, the thermal conductivity, convective heat transfer coefficient and the tube inner diameter.

For single-phase fluids, the empirical correlations for Nusselt number were suggested by Gnielinsky [48], Petukhov [49] and Dit-tuse Boelter [50], respectively, as

\[ Nu = \left( \frac{1}{3} \right) \left( \frac{Re}{1000} \right) Pr \left[ \frac{1}{1 + 12.7 \left( \frac{Pr}{3} \right)^{0.5} (Pr^2 - 1)} \right] \]
Here $Re$ is the Reynolds number, $Pr$ is the Prandlt number and $f$ is the friction factor. Eq. (4) is used in the range of $3 \times 10^4 < Re < 5 \times 10^6$ and $0.5 \leq Pr \leq 2000$.

$$Nu = \frac{\left(Re^{0.6}Pr^{0.3}\right)}{1.07 + 12.7\left(f^{0.5}\right)}$$

Eq. (5) is applicable for the range of $10^4 < Re < 5 \times 10^6$ and $0.5 \leq Pr < 2000$.

$$Nu = 0.023Re^{0.8}Pr^{0.4}$$

Eq. (6) is used in the range of $Re > 10^4$ and $0.7 < Pr < 160$. The friction factor, $f$, in Eqs. (4) and (5) is given as Petukhov [49].

$$f = (0.79\ln Re - 1.64)^{-2}$$

Eq. (7) is used in the range of $10^4 < Re < 10^6$. The friction factor of distilled water and nanofluids was measured from the experimentally recorded pressure drop data across the test section, using

$$f = \frac{\Delta P}{\frac{1}{2} \rho U_0^2 L}$$

The empirical correlation used to determine the friction factor of the base fluid proposed by Petukhov [49] and Balsius [51] is given by Eqs. (7) and (9), respectively.

$$f = 0.3164Re^{0.25}$$

For the range of Reynolds numbers, $3000 < Re < 10^5$. The uncertainty values of the measured data containing Nusselt number, heat transfer coefficient, friction factor and Reynolds number are calculated according to the procedure of Kline and Mcclintock [52] as well as Taylor and Thompson [53]. To evaluate the uncertainty of parameter $R$, the following correlation is employed:

$$U_R = \left[\sum_{i=1}^{n} \left(\frac{\partial R}{\partial V_i} U_{V_i}\right)^2\right]^{0.5}$$

where $U_{V_i}$ and $U_R$ are the uncertainties associated with the independent variable $V_i$ and the parameter $R$, respectively. Moreover, $n$ is the number of independent variables. The uncertainty values measured using Eq. (10) and the results are presented in Table 1.

### 3. Result and discussion

#### 3.1. Characterizations of the GA-functionalized GNPs nanoparticles

To analyze the GAGNPs, the FTIR spectroscopy was employed to investigate chemical groups that are attached to the GNPs. The FTIR spectra of the pristine GNPs and GAGNPs are shown in Fig. 3(A). In contrast to the pristine GNPs, it is seen that the GAGNPs sample provides some cues of the GA molecules. The spectrum of GAGNPs indicates a board peak at 3448 cm$^{-1}$, which could be ascribed to the O–H stretching vibration. This peak could be because of the reaction of one of the hydroxyl groups of the GA with GNPs and/or the attached hydroxyl groups on the GNPs. The symmetric and antisymmetric fundamental vibrations of CH bonds are observed at 2920–2980 cm$^{-1}$ for the GAGNPs. The peaks in the range of 1579–1639 cm$^{-1}$ are attributed to C=C graphitic stretching mode of GNP, which is infrared-activated by functionalization. Moreover, GNPs functionalization via GA was confirmed by the appearance of the peaks at 1451 cm$^{-1}$, 1388 cm$^{-1}$ and 1056–1189 cm$^{-1}$, respectively, for the CH$_2$ bending vibration, out of plane CH vibration and C–O stretching vibrations. The peaks at 1014 and 877 are in agreement with the stretching vibration of C–C and COH out of plane deformation. TGA provides information about the quantitative amount of functional groups on GNPs surface by thermal analysis of samples. Fig. 3(B) shows evidence of the functionalization of GNPs with GA. According to the figure, there is no significant weight loss in the pristine GNPs; however, a steady weight loss between 150 and 400 °C is seen in the GAGNPs, which confirms the decomposition of the functional groups. Also, the second mass loss after 500 °C is associated with the degradation temperature of the main graphitic structures in the air. Furthermore, the results show that the functionalization of GNPs with GA is successful, since a steady weight loss of GAGNPs with increase of temperature is observed. GA as a functional group can provide suitable dispersibility, and also does not have any corrosive effects for different metals.

The TEM images of the GAGNPs and pristine sample are shown in Fig. 4. Fig. 4(a) is the pristine GNPs, which show flakes with smooth surface and layer edge. The TEM image for the GAGNPs shown in Fig. 4(b) shows surface deterioration and wrinkles of the GNPs that formed as a result of functionalization with GA. As it is clear from TEM images, the GAGNPs flakes preserved their size and shape compared with GNPs. The presence of wrinkles within the GAGNPs flakes can be ascribed to the inherent instability of the 2D structures and the improved flexibility of GNPs flakes after functionalization.

UV–vis spectroscopy, which is a common procedure used for investigating stability of nanoparticles aqueous suspensions as a function of sedimentation time, is used in the present study. Fig. 5 illustrates the variation of relative solid concentration of GAGNPs nanofluids with the number of days after preparation. It is seen that the relative concentrations of GAGNPs suspensions decreases with the number of days after sample preparation and all samples maintained a roughly constant concentration after the day 50. The maximum sedimentation magnitudes of 8, 9.47 and 10.7% are found, respectively, for the weight concentration of 0.025, 0.075 and 0.1%. This verifies the stability of the GAGNPs–water nano-coolants. Digital image of gallic acid-functionalized GNPs (GAGNPs) dispersed in DI water after 90 days, is represented in Fig. 5(B).

#### 3.2. Thermo-physical properties of GAGNPs nanofluids

The thermal conductivity of gallic acid-treated graphene nanoplatelets (GAGNPs) nanofluids was measured experimentally and the results are presented in Fig. 6. Three different concentrations of 0.025, 0.075 and 0.1 wt%, and a range of temperatures from 20 to 45 °C are considered and variations of thermal conductivity with temperature and concentration are studied. To prevent a drastic increase in viscosity, nanofluids with low concentrations of GAGNPs are selected. The thermal conductivity of the base fluid is also shown in the Fig. 6 for comparison. It is seen that the experimental values of thermal conductivity for DI water shows good agreement with the NIST database [54] with an error less than 1%. Moreover, the thermal conductivity of the GAGNPs–water nanofluids is markedly higher than that of the DI water. In addition, Fig. 6 clearly shows that the thermal conductivity of GAGNPs nanofluids as well as DI water increases with the fluid temperature. However, the rate

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Uncertainty range</th>
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<tbody>
<tr>
<td>Reynolds number, $Re$</td>
<td>±2.23%</td>
</tr>
<tr>
<td>Convective heat transfer coefficient, $h$</td>
<td>±1.11137%</td>
</tr>
<tr>
<td>Nusselt number, $Nu$</td>
<td>±3.55%</td>
</tr>
<tr>
<td>Friction factor, $f$</td>
<td>±1.39168%</td>
</tr>
</tbody>
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Table 1: Uncertainty analysis data for heat transfer experiment.
of increase is noticeably higher for the GAGNPs nanofluids at higher solid concentrations. The main mechanism for the enhancement of thermal conductivity with increase of temperature is attributed to the Brownian motion of the nanoparticles suspended in the base-fluid [24]. In addition, the formation of nanolayers in nanofluids is a significant mechanism for enhancing the thermal conductivity of GAGNPs nanofluids. These layers are generated around the GAGNPs by liquid molecules and the local ordering of the liquid layers increases at the interface region. These liquid layers have greater thermal conductivity than the base fluid [24]. The higher slope in thermal conductivity of GAGNPs nanofluids with concentrations of 0.1 and 0.075 wt% reveals the greater rate of generation of the nanolayers.

The percentage of thermal conductivity enhancement was computed using 

$$\frac{k_{nf}}{k_{bf}} \times 100$$

where ‘$k_{nf}$’ corresponds to thermal conductivity of nanofluids and ‘$k_{bf}$’ that of the base fluid. Over the range of temperatures tested, the maximum enhancement in thermal conductivity for concentrations of 0.025, 0.075 and 0.1 wt% are, respectively, about 6.28, 16.64, and 24.18% at 45°C.

The effective viscosity of gallic acid-functionalized graphene nanoplatelets (GAGNPs) aqueous suspensions and DI water was experimentally measured at a shear rate of 150 s$^{-1}$ and the results

![Fig. 3. (A) FTIR spectra, (B) thermogravimetric analysis of the pristine and GA-treated GNPs nanoparticles.](image)

![Fig. 4. TEM images of (A) pristine and, (B) GA-treated GNPs nanoparticles.](image)

![Fig. 5. (A) The colloidal stability of GA-functionalized GNPs dispersed in water, (B) photograph of GA-treated GNPs dispersed in water after 3 months.](image)
are shown in Fig. 7 for temperature range of 20–50 °C. This figure shows rather small increment in the measured viscosity of nano-fluid with an increase in concentration of GAGNPs compared to that of the DI water. This is indeed expected since we only used a low concentration of GAGNPs in our samples. This also shows the benefit of covalent functionalization using gallic acid in contrast to non-covalent approach via the use of surfactants such as SDBS, triton X-100 and gum Arabic (GA), which lead to higher viscosity of the resultant nanofluids. In agreement with the earlier studies of Sadri et al. [55] and Aravind et al. [24], Fig. 7 shows that the viscosity of nanofluids and DI water decreases with an increase in temperature, which is due to the weakening of the intermolecular forces. The rather mild increase in the effective viscosity with nanoparticle concentration is an important advantage, since a high increase in viscosity could undermine the overall positive impact of enhanced heat transfer due to the pumping fluid penalty [56,57].

The density of the GA-treated GNPs aqueous suspensions and the DI water as the base fluid is also measured as function of temperature and weight concentration and the results are listed in Table 2. It can be seen that the density of GAGNPs nanofluids as well as the base fluid decreases with an increase in temperature, which is related to the thermal expansion of liquid. There is also a slight increment in the density of GAGNPs aqueous suspensions when the weight concentration of GAGNPs increases. The higher density of nanofluids can be attributed to the density of GAGNPs which is higher than that of the base fluid.

### 3.3. Average Nusselt number and heat transfer coefficient

A series of systematic experiments were conducted using DI water at constant heat flux boundary conditions prior to running the experiments using GAGNPs-water nano-coolants to validate the reliability and accuracy of the experimental approach. The average Nusselt numbers were measured using Eq. (3) according to our experimental data and the values compared with those determined from empirical correlations proposed by Gnielinski [48], Petukhov [49] and Dittus-Boelter [50], then the results were plotted in Fig. 8. These empirical correlations are given by Eqs. (4)–(6) and are applicable for turbulent flow. As expected, the Nusselt number increases with an increase in Reynolds number. It is also clear that the Nusselt number values calculated from experimental data are in good agreement with those determined from empirical correlations for the base fluid flowing through the horizontal stainless steel tube over the range of Reynolds number investigated in this study. The average error between the experimental values and the values measured from Gnielinski’s [48], Petukhov’s [49] and Dittus-Boelter’s [50] empirical correlation is about 7.11, 2.01 and 7.96%, respectively. Therefore, our experimental set-up can be used to evaluate the heat transfer characteristics of the GAGNP-water nano-coolant.

To study the convective heat transfer and Nusselt number of the nano-coolants under turbulent flow regime, a series of experiments for three GAGNPs weight concentrations of 0.025, 0.075 and 0.1%, several Reynolds numbers in the range of 6371–15,927, an input power of 600 W and an inlet temperature of 30 °C were performed. The convective heat transfer coefficient of the GAGNPs nanofluid and DI water was calculated using Eq. (1) and the results are shown in Fig. 9 as a function of Reynolds number for various weight concentrations. It is seen that the convective heat transfer coefficient of the nanofluids as well as base fluid, increases with the Reynolds number. Also it is clear that an increase of nanoparticles concentration has a direct effect on heat transfer coefficient of aqueous suspensions. The significant improvement in convective heat transfer coefficient of working fluids was largely attributed to the reduced thermal boundary layer thickness as well as the increased thermal conductivity in the presence of water-based GAGNPs nanofluids. Based on [14,24], carbon nanomaterials such as GNP and CNTs have a tendency to decrease the thermal boundary layer thickness. In addition, improvement of convective heat transfer coefficient strongly depends on the specific surface area, Brownian motion of the nanoparticles. The presented data shows that the convective heat transfer coefficient increases by 9.89%, 28.39% and 38.58%, respectively, for nanoparticle weight concentrations of 0.025, 0.075 and 0.1 wt.%. The average of experimental Nusselt numbers for GAGNP nano-coolants were evaluated from Eq. (4) and the results are presented in Fig. 10. It can be seen that the Nusselt number increases markedly with an increase in Reynolds number and nanoparticle concentration. The higher Nusselt number for the GA-treated GNPs aqueous suspensions is attributed to the enhanced thermal conductivity as well as the Brownian motion of GAGNPs dispersed in the base fluid [58]. The maximum enhancement of Nusselt number for nanoparticle concentration of 0.025, 0.075 and 0.1 wt.% are, respectively, 4.91, 13.85 and 18.75% for Reynolds number Re = 15,927.

### 3.4. Friction factor and pressure drop

Variation of the measured friction factor for the DI water is shown in Fig. 11. The semi-empirical correlations of Blasius [51] and Petukhov [49] for friction factor are also reproduced in this figure for comparison. It is seen that the experimental data for friction factor are in good agreement with the empirical model predictions.
The average error of measured friction coefficient with the empirical correlations of Blasius [51] and Petukhov [49] are, respectively, 2.66% and 2.54%. This figure shows that these deviations reduce with an increase in Reynolds number. Therefore, the current experimental set-up can be used to assess the hydrodynamic properties of the GAGNP nano-coolants over the range of studied Reynolds number.

The experimental pressure drop data for the GA-treated GNPs nanofluids and DI water were collected at different weight concentrations. Then the corresponding friction factors were calculated using Eq. (8) and the results are shown in Fig. 12. It is seen that the friction factor for GAGNP nanofluids show slight increase compared to that of DI water. The maximum increase in the friction factor of nanofluids for weight concentration of 0.025, 0.075 and 0.1% is, respectively, about 1.46, 3.35 and 3.9%. The enhancement in friction factor is largely attributed to the increase in the viscosity of nano-coolants. Note that for a constant Reynolds number, an increase in viscosity requires a small increase in fluid velocity. Therefore, the increase in the velocity of working fluid can be considered as the reason for increase of the friction factor of the nano-coolants in convective heat transfer systems.

### 3.5. Pumping power and performance index

The power consumption of a heat transfer set-up is a significant parameter in terms of economy and energy saving in various thermal applications. The pumping power for turbulent flow regime can be measured using following equation [59]:

$$ W = 0.158 \left( \frac{4}{\pi} \right)^{1.74} \left( \frac{\ln^{0.75} \mu^{0.25}}{\rho^{2} D^{3/4}} \right) $$

### Table 2

<table>
<thead>
<tr>
<th>Density (kg/m³)</th>
<th>Concentration/temperature (°C)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td></td>
<td>998.00</td>
<td>996.85</td>
<td>995.50</td>
<td>993.90</td>
<td>992.00</td>
</tr>
<tr>
<td>0.025 wt%</td>
<td></td>
<td>998.10</td>
<td>997.00</td>
<td>995.90</td>
<td>994.35</td>
<td>992.35</td>
</tr>
<tr>
<td>0.075 wt%</td>
<td></td>
<td>998.40</td>
<td>997.25</td>
<td>995.65</td>
<td>994.05</td>
<td>992.10</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td></td>
<td>998.55</td>
<td>997.30</td>
<td>996.00</td>
<td>994.45</td>
<td>992.50</td>
</tr>
</tbody>
</table>

The average error of measured friction coefficient with the empirical correlations of Blasius [51] and Petukhov [49] are, respectively, 2.66% and 2.54%. This figure shows that these deviations reduce with an increase in Reynolds number. Therefore, the current experimental set-up can be used to assess the hydrodynamic properties of the GAGNP nano-coolants over the range of studied Reynolds number.
where \( m \) is mass flow rate. Using \( \rho = \frac{\mu}{V} \) and \( \nu = \frac{\mu}{\rho} \) for a fixed \( Re = \frac{\rho D V}{\mu} \), and substituting \( m \) into the Eq. (11), the relative pumping power \( \left( \frac{W_{nf}}{W_{bf}} \right) \) for constant Reynolds number is given as,

\[
\frac{W_{nf}}{W_{bf}} = \left( \frac{\rho_{bf}}{\rho_{nf}} \right)^{2} \left( \frac{D_{nf}}{D_{bf}} \right)^{3} \frac{\mu_{df}}{\mu_{bf}}
\]

where \( W_{bf} \) and \( W_{nf} \) is the pumping power of the base fluid and GAGNP nano-coolants, respectively. The relative pumping power of the GAGNP nano-coolants is calculated employing Eq. (12) and the results are presented in Fig. 13 for various weight concentrations. This figure shows that the pumping power required for the nano-coolants with various GAGNPs nanoparticles loading is quite close to that of DI water.

To assess the economic performance of a new working fluid (GAGNPs) as a suitable alternative candidate for use in heat transfer equipment such as car radiators, heat exchangers and solar collectors, the performance index parameter \( (E) \) is evaluated. The performance index is defined as the ratio of the enhancement in convective heat transfer coefficient (desired efficiency) to the enhancement in pressure drop (unpleasant efficiency) of nanofluid relative to the base fluid. The performance index is given as:

\[
E = \frac{h_{df}/h_{bf}}{\Delta P_{df}/\Delta P_{bf}} = \frac{R_{df}}{R_{bf}}
\]

where \( E \) is the performance index, \( h_{df} \) and \( h_{bf} \) are the convective heat transfer coefficients of the nanofluid and base fluid, \( \Delta P_{df} \) and \( \Delta P_{bf} \) are the pressure drops of the nanofluid and base fluid, and \( R_{df} \) and \( R_{bf} \) are the ratios of the convective heat transfer enhancement and pressure drop. The performance index of the GA-treated GNPs versus Reynolds number at different concentrations.

Here \( Re \) is the ratio of the convective heat transfer enhancement, and \( R_{df} \) is the ratio of pressure drop. The performance index of GAGNPs aqueous suspensions is determined for a range of Reynolds number and concentration and the results are presented in Fig. 14. It is seen that the performance index for all concentrations is higher than 1. This shows the advantage of the newly synthesized nanofluids for use in the heat transfer equipment. Fig. 14 also indicates that as the weight concentration of the GAGNPs in base fluid increases, the performance index also increases, which is the proof of higher effectiveness of this new coolant at higher concentration. In addition, the Fig. 14 shows a rising trend of performance index with Reynolds number for all concentrations. Thus, the results indicate that the GAGNPs nano-coolants could be an appropriate alternative coolant for use in heat transfer applications for a range of \( Re \).

4. Conclusions

An environmentally friendly and facile functionalization approach for synthesizing highly dispersed Gallic acid-treated Graphene nanoplatelets was developed. This cost-effective method could be used for industrial mass production. The nanofluids made by the suspension of GA-treated GNPs in water was tested as a high performance heat transfer fluids for improved convective heat transfer in closed conduit flows in turbulent flow regime. The successfully implemented functionalization process was validated by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and UV-visible absorption spectroscopy. It was shown that the nanofluid shows remarkable stability even 63 days after preparation. The measured thermo-physical and rheological properties showed that the new GAGNPs nano-coolants are suitable for usage in heat exchangers. The presented heat transfer data showed significant enhancement in the convective heat transfer coefficient and Nusselt number, respectively, up to 38.58% and 18.75% for the weight concentration of 0.1%, at the constant heat flux of 12,752 W/m² and Reynolds number of 15,927. The corresponding increase in the friction factor of the GAGNPs nanofluids was about 1.46%, 3.35% and 3.9%, respectively, for concentrations of 0.025, 0.075 and 0.1 wt% compared to that of the base fluid, which is remarkably low. It was also shown that the pumping power need is close to that of DI water for all GAGNP-water nanofluids prepared in this study. In addition, the performance index for these nano-coolants is greater than one indicating that these green synthesized working fluids can be a suitable alternative for use in heat transfer equipment in terms of energy saving and overall thermal performances.
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References


