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Heat transfer intensification using polyaniline based nanofluids: Preparation and application

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ABSTRACT

The present work reports on the use of ultrasound assisted emulsion polymerization for the synthesis of polyaniline (PANI) nanoparticles. The study of heat transfer characteristics of PANI based nanofluids at different loading (0–1.2 wt%) of PANI nanoparticles in water (reference fluid) was performed at fixed Reynolds number. The heat transfer coefficient enhancement was also studied at two different Reynolds numbers by keeping loading of PANI in the range of 0.2–1.2 wt%. The heat transfer performance of PANI nanofluid was studied in a copper tube under constant heat flux conditions. The results showed that the heat transfer coefficient increases with an increase in the colloidal PANI concentration and Reynolds number. For 0.2 wt% PANI nanofluids, 33% increment in heat transfer coefficient was observed while it was 63% for 1.2 wt% addition of PANI nanoparticles.

1. Introduction

Nanofluids are nanoscale colloidal suspensions containing nanoparticles in the reference fluids [1–3]. In comparison to micron sized particles, nanoparticles exhibit enhanced thermal properties. Several methods are available for the preparation of nanofluids using metal and metal oxide nanoparticles in the literature [4–12]. There are important challenges in the preparation of nanofluids which includes, long term stability of suspension against sedimentation of particles, agglomeration of particles, Oswald ripening during in situ preparation of nanofluids, etc. specifically related to inorganic particles [13–15].

Polyaniline (PANI) is the most investigated conducting polymer owing to its better conducting properties, ease of doping process, environmental stability and potential applications in electrochemical devices [16–23]. The agglomeration and stability issues can be eliminated, if a conducting polymer colloidal suspension is used in place of the metal/metal oxide. It is well known fact that the fibrous structure gives high surface area. The PANI may be synthesized in fiber structure form by using conducting oxidative polymerization of aniline in the presence of acidic aqueous environment. Srinivas et al. [17] synthesized PANI in emeraldine salt form by chemical oxidation method with controlled pH. It has been reported that PANI possesses structures resemble as rods. Abdolahi et al. [24] reported the interfacial polymerization process for the uniform formation of PANI nanofibers. Recently, PANI is incorporated in the reference fluids in order to enhance the thermal conductivity of reference fluid [25]. However, it is found that the use of conventional oxidative polymerization method produces non uniform structures of PANI and hence, it may affect the properties of nanofluid. Further, number of authors reported the enhancement in the heat transfer characteristics of spherical nanoparticles, carbon nanotubes and carbon nanofiber based nanofluids [2–10]. However, no work is reported on the study of heat transfer characteristics of conducting polymer fibers based nanofluids. PANI nanofibers are preferred due to their one dimensional nanostructure which is easy to disperse in reference fluid. PANI-Au nano composite was reported by Sivakumar and Gedanken [26] using H_2O_2 where they found that H_2O_2 enhances the rate of polymerization. Lee et al. [27] have studied the metallic transport in polyaniline. Wan et al. [28] have prepared PANI nanofibers and their nanofluids in water. The thermal conductivity of PANI nanofluids in water has been observed to be enhanced. This enhancement in the thermal conduction performance in nanofluids is attributed to higher crystallinity and morphological

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uniformity of reinforced nanofibers. Some of the colloidal hybrid materials like polyvinyl pyrrolidone or polypyrrole encapsulated with metal particles have been used as nanofluids. But, considering the heat transfer applications, PANI nanofluids not yet reported in detail.

So in this work, ultrasound assisted miniemulsion polymerization has been carried out for the preparation of nanosized PANI latex [24,28] and it was used in the preparation of nanofluid. In cavitation based polymerization, collapse of cavitation bubbles near the interface of immiscible liquids will cause disruption of the phases resulting in the formation of very fine uniformly sized emulsion droplets in nanometer range [29–33]. The prepared colloidal PANI nanoparticles were stable and were used for the preparation of PANI nanofluids. Further, the enhancement in convective heat transfer properties of colloidal polyaniline nanofluid were studied and compared with reference fluid i.e. water.

2. Experimental

2.1. Materials

Aniline ($C_6H_5NH_2$), ammonium persulphate (APS) and sodium dodecyl sulphate were procured from S.D. fine chemicals Pvt. Ltd., Mumbai and used as received. Purity of the all chemicals used was above 98%. De-ionized water ($<1\ \mu$S conductivity) from Millipore was used for the preparation of aqueous solutions of precursors. All the experiments were performed thrice and the deviations in results were ±3%.

2.2. Preparation of colloidal PANI nanofluids

Initially, the surfactant and initiator solutions were prepared separately by adding 0.3 g sodium dodecyl sulphate (SDS) in 100 mL deionized water and 7.3 g of ammonium persulphate (APS) in 50 mL of deionized water, respectively [21]. Both solutions were transferred to the sonochemical reactor. Further, 1 g of aniline was added to a 250 mL sonochemical reactor in which an ultrasound probe (20 mm diameter) was inserted (Dakshin Pvt. Ltd., Mumbai 20 kHz and 120 W). The mixture of surfactant and initiator solution and remaining 8 g aniline were added continuously over a 20 min period. Reaction temperature was maintained around 5 °C throughout the experiment. 1 M aqueous solution of hydrochloric acid (dopant) was added into the reactor for protonation purpose. Experiments were carried out in sonochemical reactor in order to accelerate the polymerization rate and to generate nanometer sized monomer droplets. After 20 min sonication, a dark green suspension was observed, confirming the formation of PANI. The reaction was allowed to continue for next 10 min and then resulting polymerized colloidal suspension was taken (Total reaction time = 30 min).

2.3. Experimental setup for heat transfer studies of nanofluid

The heat transfer studies were carried out using copper tube of 1.5 m length and 9.5 mm diameter. The schematic of experimental setup for heat transfer studies was reported in an earlier article [29]. Experiments were carried out at different weight fractions of PANI nanoparticles in nanofluid and at different volumetric flow rates of nanofluid. In order to study the effect of weight fraction of PANI nanoparticles on heat transfer characteristics, experiments were carried out for 0 wt% (pure water) to 1.2 wt% of PANI nanoparticles in a reference fluid at $12.5\times10^{-6}\ m^3/s$ volumetric flow rate. Aqueous dispersion of PANI nanoparticles (i.e., nanofluid) was prepared in 3 L pure water (reference fluid). The test section was heated by using a heating coil placed around the copper tube and connected to dimmerstat which set to 120 V. The experiments were carried out under constant heat flux conditions. PANI Nanofluid from sink was pumped through a copper pipe using 0.5HP pump. Nanofluid temperatures were measured using four thermocouples placed at equal distance on the copper tube. In order to get desired inlet temperature of nanofluid, cooling arrangement was provided to sink. Once the steady state of temperature was achieved, the inner copper tube wall temperature, fluid temperature at different locations in the copper tube and sink temperature were measured. Experiments were carried out to study the effect of weight fraction of PANI nanoparticles in nanofluid and varying flow rates of nanofluid. Further experiments were performed by keeping weight fraction of PANI nanoparticles (0.2 and 1.2 wt%) constant and varying the volumetric flow rate (Reynolds numbers 1600 and 2000).

2.4. Characterization

In order to study the morphology of prepared PANI nanoparticles, transmission electron microscopic (TEM) images were taken on a Philips Tecnai 20 model, which has resolution of 2 Å unit and Acceleration Voltage 200 kV with magnification of 100,000×. The change in absorbance value was monitored using UV spectrophotometer (SHIMADU 160 A). FTIR analysis of the sample was performed by PerkinElmer spectrometer using the KBr pellet method in the region of 4000–400 cm^{-1}.

2.5. Evaluation of physical properties

The properties such as density (ρ), thermal conductivity (k), viscosity (μ), and specific heat (Cp) of nanofluids were used for determination of heat transfer coefficient of nanofluid which was determined using theoretical correlations reported in literature [8,34–37]. The effective viscosity of nanofluid was predicted using well known Einstein correlation [8,34–36]. The effective thermal conductivity calculation was carried out by using correlation reported in literature [34–37]. Convective heat transfer coefficient characteristics were calculated by measuring the heat energy supplied, when the fluid flows with mass velocity ‘m’, the differential heat energy ‘dq’ can be calculated as using following equation [8,28,34–36].

$$dq = 2\pi rh \times (T_W - T) \times dx \tag{1}$$

$$\ln\frac{T_W - T_2}{T_W - T_1} = -\frac{2\pi r\Delta L}{C_P m}h \tag{2}$$

$$h = -\frac{C_P m}{2\pi r\Delta L}\ln\frac{T_W - T_2}{T_W - T_1} \tag{3}$$

where T_1 = Inlet temperature, T_2 = Outlet temperature, T_W = wall temperature

Reynolds number, Re, was derived from $Re = (\rho uD/\mu)$, where ρ, u, D and μ are the density of the fluids, the velocity of the fluids, the diameter of the tube, and the viscosity of the fluids, respectively.

3. Results and discussion

PANI is a conducting polymer having enhanced thermal conductivity due to the availability of free electrons at molecular level [13]. There are several proposed theories that describe the enhancement in thermal properties of nanofluids. Keblinski et al. [11] have proposed following possible mechanisms: (1) Brownian motion of nanoparticles, (2) liquid layer at liquid/particle interface and (3) ballistic nature of heat transport in nanoparticles. It is believed that micro-convection generated by the Brownian motion of nanoparticles may be one of the main reasons responsible for the increase in nanofluid thermal convection [23]. When a particle is immersed in a fluid, it moves randomly due to the interaction between particles and its surrounding fluid molecules and this random motion is called "Brownian motion". The Brownian motion of large particles is negligibly small and it is not considered in the conventional particulate flow [23]. However, when the size of particle is as small as nanoparticles, the Brownian motion becomes significant. So as concentration of PANI nanoparticles increases particle–particle interaction increases leading to an enhancement in heat transfer performance.

In this work, for the preparation of the polyaniline, ultrasound assisted cavitation process was used for the polymerization. During ultrasound assisted emulsion polymerization, the particle size of polyaniline remains the same as the emulsion droplet size. It is also reported that the radicals generated due to cavitational effect of ultrasound helps in polymerization of aniline. The reaction is carried out at low temperature (0–10 °C). As the intense cavity collapse leads to generation of extreme conditions of higher temperature and pressure, it helps in the dissociation of the APS subsequently improves the rate of polymerization. The possible reactions in the presence of ultrasound during polymerization to form polyaniline are given as follows which are reported by Bhanvase et al. [38] and Tao et al. [29].

The cavitational effects aroused because of ultrasonic irradiations are accountable for the cleavage of an O—H bond in water molecule that leads to the formation of an extremely reactive hydroxyl radical

$$H_2O \xrightarrow{\text{Ultrasound}} H^{\bullet} + OH^{\bullet} \quad (4)$$

Further cleavage of surfactant molecules takes place in the presence of ultrasound due to cavitational effects according to following reaction:

$$S \xrightarrow{\text{Ultrasound}} 2R^{\bullet} \quad (5)$$

where S is surfactant molecules.

These generated radical reacts with aniline monomer that initiate the polymerization reaction [38].

$$OH^{\bullet} + C_6H_5NH_2 \xrightarrow{\text{Ultrasound}} OH^{-} + C_6H_5NH_2^{\bullet+} \quad (6)$$

$$C_6H_5NH_2^{\bullet+} \xrightarrow{\text{Polymerization}} ([C_6H_4NH]_2[C_6H_4N]_2)_n \Rightarrow \text{Polyaniline} \quad (7)$$

3.1. Characterization colloidal PANI nanoparticles used in preparation of nanofluids

Fig. 1 shows an absorbance band at 280 nm which is consistent with the literature reported data [39–42]. This band corresponds to the π–π^* transition of the conjugated polymer. The polymerisation process is attributed to the use of ultrasound, which generates the free radicals due to cleavage of water molecule and these free radicals helps in accelerating the emulsion polymerization rate [42].

Structural characterization of PANI was carried out using FTIR analysis. FTIR spectrum of a polyaniline is shown in Fig. 2. The spectrum shows vibration bands at 3445, 2981.9, 1529.3, 1492.3,

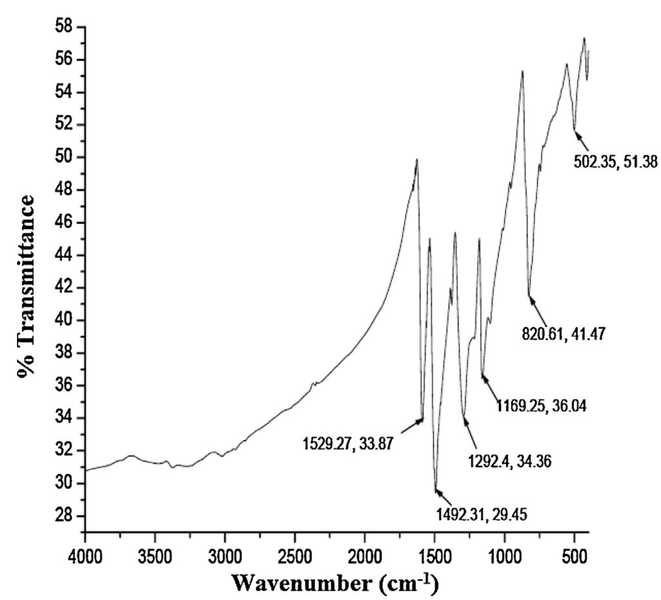

Fig. 2. FTIR spectrum of prepared colloidal PANI nanoparticles by ultrasound assisted emulsion polymerization.

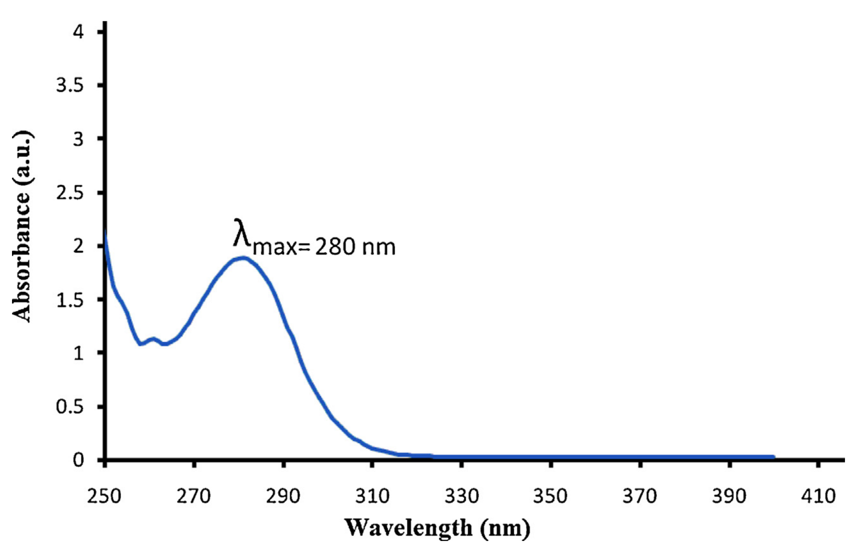

Fig. 1. UV spectrum of prepared colloidal PANI nanoparticles by ultrasound assisted emulsion polymerization.

1292.4, 1169.25, 820.61 and 502.35 cm^{-1}. These values are characteristics of polyaniline chain and are in agreement with theoretical predictions [22,23]. The 3445 cm^{-1} vibration band is attributed to the stretching vibration of secondary amine. The vibration band seen around 2981.9 cm^{-1} is attributed to the aromatic C—H vibration. The vibration band around 1529.3 cm^{-1} is due to the C=N double bond of quinonoid rings whereas 1492.3 cm^{-1} vibration band arises due to vibration of C=C double bond associated with the benzenoid ring. The characteristics at 1292.4 cm^{-1} is due to C—N stretching mode of the benzenoid ring while 1169.25 cm^{-1} is attributed to the quinonoid unit of doped PANI [36]. The characteristics peak at 820.61 cm^{-1} is assigned to an out of plane C—H bending of 1,4 disubstituted benzenoid rings. This is a confirmation of the formation of PANI [41].

The morphology of the prepared PANI nanostructures was characterized by transmission electron microscopy (TEM) and is depicted in Fig. 3. As reported in TEM images, it is found that PANI nanofibers are in the range of 50–60 nm. The nanofibers tend to agglomerate into interconnected nanofiber networks, rather than forming bundles of nanofibres.

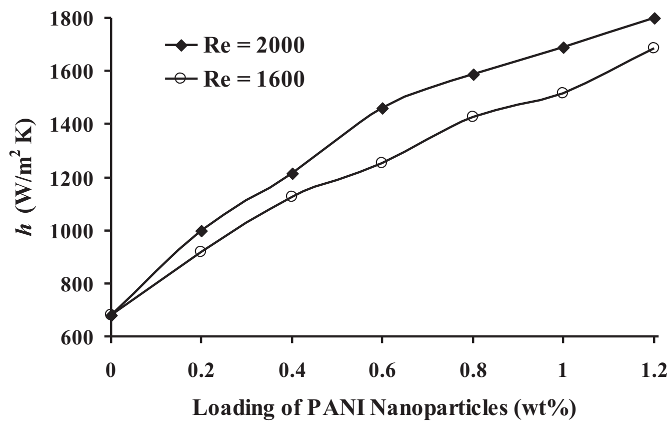

Fig. 4. Heat transfer coefficient as a function of weight% of colloidal PANI nanoparticles at Re = 1600 and 2000.

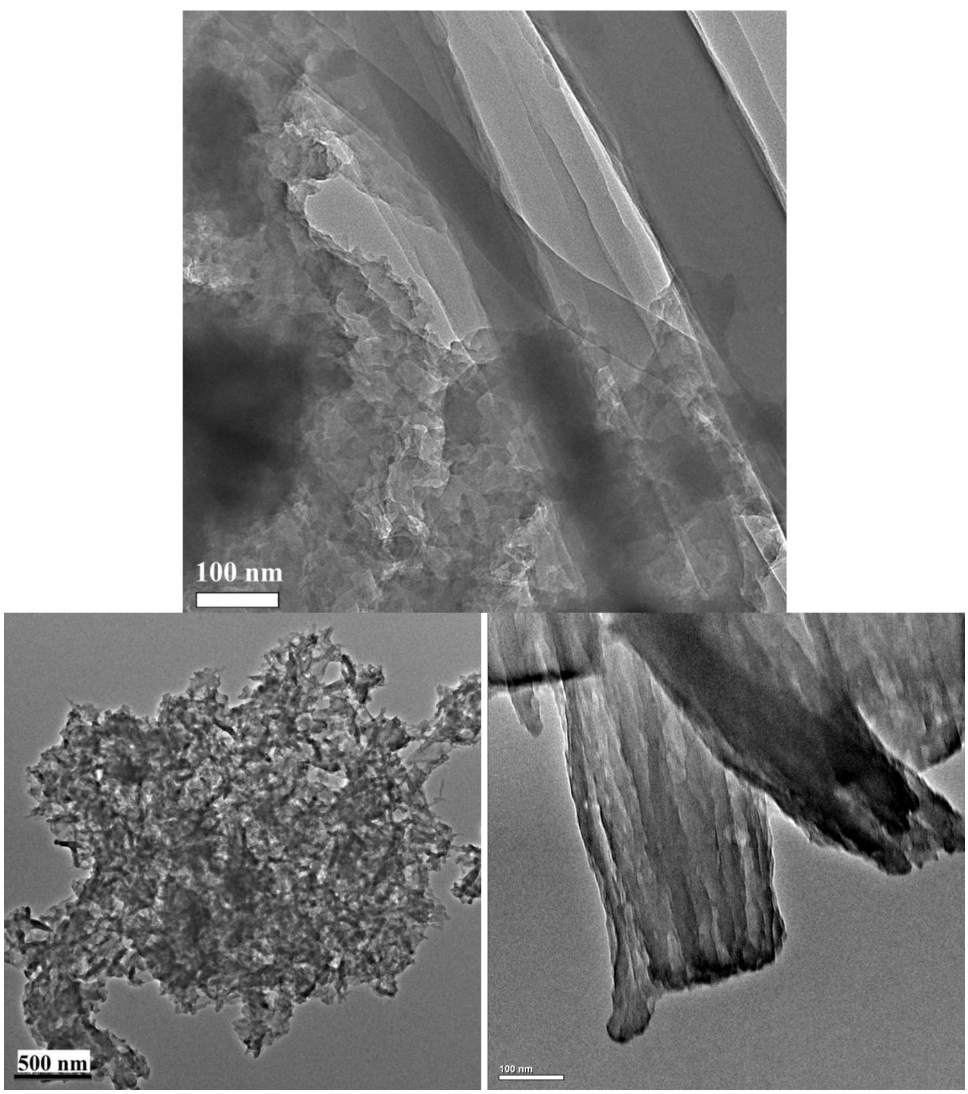

Fig. 3. TEM images of prepared colloidal PANI nanoparticles by ultrasound assisted emulsion polymerization.

3.2. Effect of loading of PANI nanoparticles on heat transfer coefficient with respect to Reynolds number

It has been reported in literature that the thermal properties such as, heat transfer coefficient, thermal conductivity etc., are significantly affected by concentration of nanoparticles in nanofluids. In the present work, the effect of PANI nanoparticles concentration (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 wt% of PANI nanoparticles) on heat transfer coefficient was investigated. The variation in the heat transfer coefficient with concentration of PANI nanoparticles at Reynolds number of 2000 and 1600 is depicted in Fig. 4. The significant enhancement in heat transfer coefficient is observed with an increase in PANI concentration at Reynolds number of 1600. This significant increase in heat transfer coefficient from 920 W/m^2K at 0.2 wt% to 1685 W/m^2K was observed at 1.2 wt% of PANI nanoparticles. It has been observed that improvement in heat transfer coefficient for 0.2 wt% was 27%. Addition of 1.2 wt% PANI nanoparticles concentration in reference fluid shows improvement near to 60% in heat transfer coefficient when it is compared the performance to reference fluid. Water (reference fluid) has a heat transfer coefficient of 670 W/m^2K. The effect of concentration of PANI nanoparticles on heat transfer coefficient was studied at 2000 Reynolds number value and the results are shown in Fig. 4. At Reynolds number 2000, the value of heat transfer coefficient for 0.2 wt% PANI nanoparticles was 997 W/m^2K and 1800 W/m^2 at PANI nanoparticles concentration of 1.2 wt %. It is observed that 33% increment in heat transfer coefficient is observed for concentration of 0.2 wt% of PANI nanoparticles and 63% for 1.2 wt% of PANI nanoparticles concentration.

Also the heat transfer coefficient is a function of velocity of the fluid, orientation to the flow, geometric shape, surface condition and viscosity. However, the velocity has great effect on the heat transfer coefficient. In the present study, the increase in the Reynolds number indicates the increase in the velocity. This increase in the velocity of nanofluid at different particle concentration increases the heat transfer coefficient, which is observed in Fig. 4.

3.3. Effect of loading of PANI nanoparticles on Nusselt number

Nusselt number is the ratio of convective heat transfer to the conductive heat transfer. Generally it can be expressed as Nusselt number $(Nu) = f\,(Re, Pr)$ where, Re is Reynolds Number and Pr is Prandtl number. Fig. 5 shows change in Nusselt number with respect to concentration of PANI nanoparticles in nanofluids. The Nusselt number values are estimated for the condition of fully developed flow. For a pure Newtonian fluid flowing through a tube with a circular cross section was considered fully developed hydrodynamic and heat transfer flows at $x/D_i \geq 0.05\ Re$ and $x/D_i \geq 0.05.\ Re\ Pr$, respectively. The effect of concentration (wt%) of PANI nanoparticles in reference fluid (water) on Nusselt number was investigated by keeping Reynolds number constant (Re = 1200, 1600). At constant Reynolds number, Nusselt number shows increasing trend with an increase in the concentration of PANI nanoparticles in nanofluid. At constant Reynolds number of 1200, Nusselt number is found to be increased from 15.33 at 0.2 wt% to 25.68 at 1.2 wt% PANI nanoparticle concentration. Similarly for Reynolds number 1600, the Nusselt number value showed an increment from 16 to 27% over the range of concentration of 0.2–1.2 wt% of PANI nanoparticles in nanofluid. Experimentally estimated Nusselt numbers (Eq. (8)) were almost identical with the values of Nusselt number calculated theoretically (Eq. (9)). Fig. 5 also show a comparison of experimental and theoretical values of Nusselt number for variable concentrations of PANI nanoparticles.

$$Nu(x) = \frac{h(x)D_i}{k} \quad (8)$$

$$Nu = 1.86Re^{1/3}Pr^{1/3}(\mathrm{D/L})^{1/3} \quad (9)$$

Further, the Nusselt number was found to increase with an increase in Reynolds number from 12.67 to 13.88 when pure water was used as a working fluid. This is attributed to an increase in the velocity which increases the heat transfer coefficient. The increase in the heat transfer coefficient in turn increases the Nusselt number. Fig. 5 illustrates variation tendency of the Nusselt numbers of the nanofluid with the weight fraction of PANI nanoparticles and the Reynolds number (Re). The experimental results indicate that the suspended PANI nanoparticles in nanofluid remarkably improve the heat transfer performance of the reference fluid. Compared with water, the Nusselt number of the nanofluid is increased by more than 45% for the nanofluid with the 1.2 wt% concentration of PANI nanoparticles. The particle weight fraction is one of the main factors affecting the Nusselt numbers of the nanofluid. The enhanced heat transfer by the nanofluid may result due to either the suspended particles increasing the thermal conductivity of the two-phase mixture or the chaotic movement of ultrafine particles accelerating the energy exchange process in the fluid [7,8,11,13,23]. The predicted results are obtained in such a way that all the transport properties involved in the correlation are respectively replaced by the effective conductivity, viscosity and diffusivity of the nanofluid.

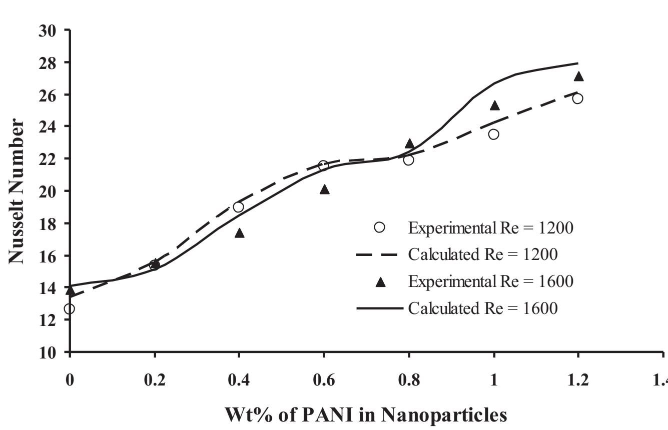

Fig. 5. Nusselt Number as a function of weight% of colloidal PANI nanoparticles at Re = 1200 and 1600.

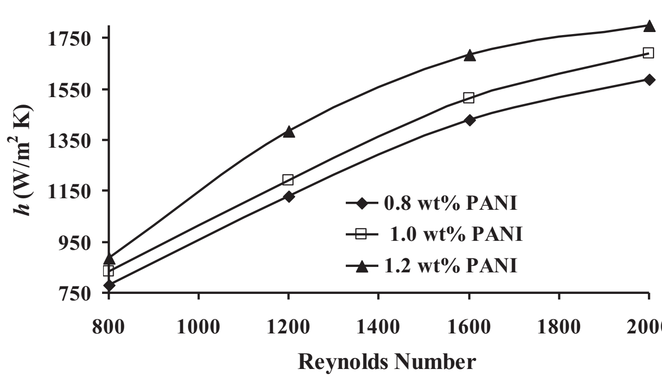

Fig. 6. Heat transfer coefficient as a function of Reynolds number at 0.8, 1.0 and 1.2 wt% of colloidal PANI nanoparticle in reference fluid.

3.4. Effect of flow rate of PANI nanofluid on heat transfer coefficient

It is well known that flow regimes have considerable influence on heat transfer in the fluid [28–30]. Therefore the effect of flow rate (with respect to various Reynolds number) on heat transfer coefficient was studied in PANI nanofluids keeping concentration of PANI nanoparticles constant. The effect of Reynolds number (Re = 800, 1200, 1600, 2000) on heat transfer coefficient was studied separately at different selected concentrations of 0.8, 1.0, 1.2 wt% of PANI nanoparticles. Fig. 6 depicts the variation of heat transfer coefficient with respect to Reynolds number at 0.8 wt% PANI nanoparticle concentration in nanofluids. As found from Fig. 6, for 0.8 wt% PANI nanoparticles concentration, the heat transfer coefficient at Reynolds number 800 is 780 W/m^{2}k and for Reynolds number 2000, the value of heat transfer coefficient observed is 1590 W/m^{2}k. Similarly for 1.0 wt% PANI nanoparticles concentration, the values of heat transfer coefficients were 835, 1190, 1515 and 1690 W/m^{2}K for Reynolds number values 800, 1200, 1600 and 2000, respectively. Further the observed heat transfer coefficient values for 1.2 wt% PANI nanoparticles concentration at Reynolds number values 800, 1200, 1600 and 2000 were 887, 1385, 1685 and 1800 W/m^{2}K, respectively. The reason for this enhancement in convective heat transfer is attributed to the effect of increasing Reynolds number on particle movements. Increase in Re number causes the velocity to increase substantially. Higher velocity causes rapid movement and collision between particles and this would increase the heat transfer rate [32,33]. Further for 0.8 wt% of PANI nanoparticles heat transfer coefficient is showing 50% enhancement for Reynolds number from 800 to 2000. Similarly for 1.2 wt% its showing 51% enhancement in heat transfer coefficient for Reynolds numbers from 800 to 2000. It is clearly seen from the data shown in figures that as Reynolds number approaches 2000, increment in heat transfer coefficient becomes less. So, as flow regime approaches the transition state from laminar to turbulent, mixing is maximum and flow regimes are fully developed.

Also the enhancement in the heat transfer coefficient values with an increase in the Reynolds number which is attributed to the reduction of agglomeration and intensification of mixing due to dispersion of the nanoparticles. The effect of Reynolds number on the heat transfer was found to be sufficient in laminar regime, which can be further extended in the turbulent regime to get more enhancements in heat transfer performance. Thus, improving the heat transfer characteristics and their use in the wide range of temperature can be a great option in heat transfer equipments.

4. Conclusion

In the present work, the convective heat transfer performance of PANI nanoparticle based nanofluids in copper tube has been studied. The formation of PANI is confirmed through UV–vis spectroscopy and FTIR analysis. 32% enhancement in the heat transfer coefficient was observed for 0.2 wt% PANI concentration in reference fluid, i.e., water at Reynolds number of 1600 while for concentration of 1.2 wt% of PANI nanoparticles, 62% improvement was observed. Thus, it can be concluded that the addition of PANI nanoparticles to reference fluid enhances the heat transfer performance of the fluid. The heat transfer coefficient was found to be increased with an increase in the Reynolds number and is attributed to the reduction of agglomeration effect considerably and intensification of mixing due to fine dispersion of the PANI nanoparticles in reference fluid. The effect of Reynolds number on the heat transfer performance is found to be adequate in laminar regime, which can be further extended in the turbulent regime to get more enhancements in heat transfer performance. Thus improving the heat transfer characteristics and their use in a wide range of temperatures can be a great benefit in heat transfer equipments.

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