Photo-thermal characteristics of water-based Fe$_3$O$_4$@SiO$_2$ nanofluid for solar-thermal applications

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Abstract

This work proposes and demonstrates the novel idea of using Fe$_3$O$_4$@SiO$_2$ core/shell structure nanoparticles (NPs) to improve the solar thermal conversion efficiency. Magnetite (Fe$_3$O$_4$) NPs are synthesized by controlled co-precipitation method. Fe$_3$O$_4$@SiO$_2$ NPs are prepared based on sol–gel approach, then characterized. Water-based Fe$_3$O$_4$@SiO$_2$ nanofluid is prepared and used to illustrate the photo-thermal conversion characteristics of a solar collector under solar simulator. The temperature rise characteristics of the nanofluids are investigated at different heights of the solar collector, for duration of 300 min, under a solar intensity of 1000 W m$^{-2}$. The experimental results show that Fe$_3$O$_4$@SiO$_2$ NPs have a core/shell structure with spherical morphology and size of about 400 nm. Fe$_3$O$_4$@SiO$_2$/H$_2$O nanofluid enhances the photo-thermal conversion efficiency compared with base fluid and Fe$_3$O$_4$/H$_2$O nanofluid, since the silica coating improves both the thermodynamic stability of the nanofluid and the light absorption effectiveness of the NPs. At a concentration of 1 mg/1 ml of Fe$_3$O$_4$@SiO$_2$/H$_2$O, and with the utilization of kerosene into the solar collector, and exposure for radiation for 5 min, the photo-thermal conversion efficiency has shown an enhancement at the bottom of the collector of about 32.9% compared to the base fluid.

1. Introduction

In the last decade, magnetite (Fe$_3$O$_4$) nanoparticles (NPs) have attracted the interest of many researchers because of their broad range of applications in the fields of biology and energy, such as biocatalysis, bio-labeling, immunoassay, biosensors, separation and purification of biomolecules, magnetic resonance imaging (MRI), and molecular interactions in live cells [1, 2], drug delivery [3], CO$_2$ capture [4] and thermal absorption systems [5]. In photo-thermal applications, Fe$_3$O$_4$ NPs have attracted researchers’ attention because they have an extensive photon absorption cross-section, and strong intermolecular bonds, economical, and environmental friendly [5]. Fe$_3$O$_4$ NPs are used in photo-thermal therapy, where Fe$_3$O$_4$ NPs possess the ability to absorb near infrared to kill cancer cells under light irradiation, as the photon energy converts effectively into heat, subsequently the local temperature of tumor raises and scorchs the cancer cells [6–8]. Furthermore, in solar energy field, the Fe$_3$O$_4$ NPs are used in thermal energy conversion systems, where NPs are mixed in transparent base fluids to form nanofluids. The nanofluids are utilized in varieties of collectors for direct absorption of the solar radiation [5].

In spite of the above benefits, there are some challenges in using Fe$_3$O$_4$ for photo-thermal energy conversion, as concerns stabilizing the Fe$_3$O$_4$ nanofluids and suppressing the reflection of light. Fe$_3$O$_4$ NPs show poor dispersion and high tendency to agglomerate in water and organic solvents. That is due to the large surface to volume ratio and existence of strong dipole–dipole interaction between the NPs. Furthermore, the thermal effect of light can also induce the oxidation of magnetite (Fe$_3$O$_4$) to be transformed to hematite (Fe$_2$O$_3$) which has different properties [10].

To protect magnetite NPs from agglomeration and oxidation, they are typically coated with a more inert material, such as silica (SiO$_2$) [11]. Silica coating shields the magnetic dipole interaction, and enhances the coulomb repulsion due to being negatively charged. Usually, SiO$_2$ coating on the surface of Fe$_3$O$_4$ NPs prevents their aggregation in solution, improves their chemical stability, provides better protection against toxicity [12], and
provides a good surface for subsequent functionalization for bioimaging, diagnosis, therapeutic [13–17] and bioelectronic [18] applications. Fe₃O₄@SiO₂ NPs have strong affinity with water which helps realize an efficient and stable nanofluid. Light absorption is enhanced in Fe₃O₄@SiO₂ NPs because silica coating minimizes the light reflection allowing its use in solar thermal applications. To the best of our knowledge, so far, no study has been reported on solar photo-thermal conversion of water-based Fe₃O₄@SiO₂ nanofluids.

Several researchers have investigated the photo-thermal effect of iron oxide and other NPs (e.g. TiO₂, Al₂O₃, Ag, Cu, SiO₂, graphite NPs, and carbon nanotubes) dispersed in fluids for heat transfer enhancement [5, 19–23]. Their studies reported remarkable outlet temperature and efficiency improvement by using nanofluids as compared to conventional fluids in energy conversion. Fe₃O₄ nanofluid is used in solar thermal systems to enhance efficiency through radiative properties (i.e. absorption and scattering) and thermo-physical properties such as thermal conductivity and heat capacity enhancement [22]. Hybrid Graphene/Fe₃O₄ has been synthesized and prepared as a kerosene-based nanofluid aiming for the heat transfer enhancement [24].

A novel approach in order to combine the advantages of both SiO₂ and Fe₃O₄ nanomaterials is to utilize Fe₃O₄ NPs coated with silica for solar photo-thermal conversion application. According to the literature, the photo-thermal effect induced by solar radiation has never been investigated for Fe₃O₄@SiO₂ nanofluid. In the present work, the synthesis procedure and characterization of Fe₃O₄@SiO₂ NPs will be elaborated in section 2, where nanofluid preparation and experiment setup will be further discussed. Finally photo-thermal characteristics of the water-based Fe₃O₄@SiO₂ nanofluid and the solar collector performance are investigated in section 3. Section 4 summarizes our main experimental findings.

2. Experimental procedure

2.1. Materials

The materials used in the synthesis of Fe₃O₄@SiO₂ NPs are; ferric chloride hexa-hydrate (FeCl₃ · 6H₂O), ferrous chloride tetra-hydrate (FeCl₂ · 4H₂O), and polyethylene glycol 4000 (PEG) were purchased from Pareac (Spain). Ammonium solution (26% of ammonia) from Analar (England). Ethanol from Molar Chemicals Ltd (Hungary); and nitrogen gas (N₂) with 99.9% purity. Tetraethyl orthosilicate (TEOS) from Sigma Aldrich (US). All chemicals were of analytical grade and were used without further purification. Deionized water was used for all experiments.

2.2. Fe₃O₄@SiO₂ NPs synthesis

The Fe₃O₄ NPs were prepared by a chemical co-precipitation method [25]. The procedure is described as follows: 2.36 g of FeCl₃ · 6H₂O and 0.86 g of FeCl₂ · 4H₂O (2:1 M ratio) were dissolved in 40 ml deionized water under atmospheric nitrogen. This aqueous solution containing both Fe²⁺ and Fe³⁺ ions, it was then heated and kept exposed to nitrogen while maintaining a rigorous magnetic stirring. Once the temperature of the solution reached 80 °C, 5 ml of ammonium hydroxide was added quickly after which the magnetic NPs were formed and started to agglomerate as indicated by a black precipitate. Then 5 ml of PEG aqueous solution was added drop wise, while the suspension was kept at 80 °C for 1 h. PEG which is a hydrophilic and biocompatible polymer, used as an additive coating polymer during the co-precipitation process, in order to increase the content of surface hydroxyl in the composite, and to get very stable and highly water soluble magnetic NPs. The Fe₃O₄ NPs were precipitated due to both the large surface to volume ratio of the NPs and the magnetic dipole–dipole attraction between them. The resulting black products were washed several times with distilled water and ethanol, and dried in vacuum at 60 °C for 6 h. Fe₃O₄ NP formation can be described according to the following reaction [26]:

\[ \text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \]

The core/shell structured Fe₃O₄@SiO₂ NPs were synthesized using a modified Stöber method [27, 28]. The typical process was as follows: 200 mg of Fe₃O₄ NPs were ultrasonically dispersed in 150 ml ethanol and kept immersed in an ice bath over 15 min under sonication. Then a mixture of 12 ml ammonia solution and 400 µL TEOS as the volume ratio of ammonia to TEOS is 30–1 was added dropwise to the Fe₃O₄ suspension, the reaction proceeded for 2 h under sonication in an ice bath. Finally, the NPs were collected by using NdFeB magnet, and rinsed with distilled water and ethanol several times by centrifugation; and then dried under vacuum at 60 °C for 6 h prior to further use. The silica coating on the surface of Fe₃O₄ NPs can be described according to the following reaction [29]:

\[ \text{Si(OH)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_4\text{OH} \text{(hydrolysis)} \]

\[ \text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O} \text{(condensation)} \]

2.3. Photo-thermal conversion experiment

The Fe₃O₄@SiO₂ NPs were ultrasonically dispersed in water with concentrations of 1 mg/1 ml and 2 mg/1 ml. The collector is a glass cylinder with diameter of 3.6 cm and height of 5 cm. The cylinder walls were insulated by a thick layer of polystyrene except from the top, where it was covered with a glass plate to minimize the heat loss.
and allow the light passage through the fluid. The fluid was exposed to illumination using a sunlight simulator. The distance between the light source and the collector was adjusted to measure average heat flux of 1000 W m$^{-2}$ incident on the collector’s surface. Several K-type thermocouples were fixed on the wall of the cylinder through the insulation material. The thermocouples were installed at different heights of the outer side of the cylinder to measure temperatures. The other ends of the thermocouples were connected to a data acquisition unit. Finally, the measurement data was transferred to a computer for analysis. The experimental setup is shown in figure 1. The photo-thermal conversion experiments were conducted by preparing mainly two collectors. The first collector was filled completely with 30 ml of the nanofluid. The second collector was the same except for its bottom was black color, filled with 10 ml of the nanofluid and 20 ml kerosene, in order to trap the heat into the bottom of the collector and reduce the heat dissipation from the top surface.

2.4. Characterization methods

The morphology and the size of the prepared NPs were visualized by a transmission electron microscope (TEM, FEI, TecnaiG2 Spirit Bio Twin, Netherland). The x-ray powder diffraction (XRD) patterns of the samples were obtained by x-ray diffractometer (Shimadzu, XRD—6100, Jaban) using Cu Kα radiation ($\lambda = 1.5405$ Å). The chemical structure was determined by a Nicolet Fourier transform infrared spectroscopy (FT-IR, Nexus TM 670) spectrophotometer for which the samples were prepared by mixing the product with KBr and pressing into a compact pellet. The size distribution measurements were done by dynamic light scattering (DLS) technique using Zeta Sizer Nano ZS (Malvern, Model ZEN360, England) at 25 °C. Photo-thermal conversion performance was investigated using solar simulator (Newport, Model 71445, US) under illumination of air mass 1.5 global (AM 1.5G) (Arc Lamp Source, Model 66906) that corresponds to 1 kW m$^{-2}$. Temperature versus time graphs were recorded in a computer using the Lab VIEW software, with K-type thermocouples (Omega 5TC-TT-K-36-36), which were connected to a data acquisition unit (thermocouple input devices, NI, USB-9211, 4-Channel, 24-bit).

3. Results and discussion

3.1. Characteristics of Fe$_3$O$_4$@SiO$_2$ NPs

The first step of this work involved the synthesis of the magnetite cores and their coating with silica shells through the hydrolysis and condensation of TEOS in the presence of the magnetic NPs. Figure 2 shows the TEM images of the magnetic NPs before and after the SiO$_2$ coating. The results indicated that Fe$_3$O$_4$ NPs were successfully coated with a thin layer of silica and both Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ NPs were approximately spherical in nature. Figure 2(a) shows TEM image of Fe$_3$O$_4$ NPs with sizes ranging from 2 to 10 nm in diameter. Figures 2(b)–(d) shows that Fe$_3$O$_4$ NPs have been aggregated into clusters, and coated by SiO$_2$ thin layer (Fe$_3$O$_4$@SiO$_2$ core/shell structure). The particles are discrete and spherical in shape. The sizes of particles are in the range of 400–500 nm. Moreover, the Magnified TEM images (figure 2(d)) show that the thickness of silica coating to be around 50 nm.

Figure 3(a) shows the size distribution of Fe$_3$O$_4$ NPs dispersed in H$_2$O to have a narrow size distribution in the range of 5–10 nm with an average size of 7.8 nm. Figure 3(b) shows the size distribution of Fe$_3$O$_4$@SiO$_2$ NPs
dispersed in H₂O to have a narrow size distribution in the range of 350–600 nm. Most of the particles sizes were less than 500 nm with an average of 475 nm, which is consistent with the size determined using TEM.

Figure 4 shows the XRD patterns of Fe₃O₄ and Fe₃O₄@SiO₂ NPs, as 2θ in the range of 10–80°. The diffraction peaks at around 2θ of 30.1°, 35.5°, 43.2°, 53.4°, 57.2°, 62.8° and 75° are assigned to the reflection of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) planes of Fe₃O₄, respectively (JCPDS card No. 19-629) [30, 31]. These peaks are sharp and intense, demonstrating the well crystallized structure of Fe₃O₄ with typical cubic inverse spinel structure. The XRD pattern of Fe₃O₄@SiO₂ core/shell NPs shows a broad peak between 10° and 30° ascribed to the amorphous SiO₂ (JCPDS No. 29-0085) [30, 31], in addition to peaks from Fe₃O₄ cores which exist with less intensity, compared to the resulted XRD patterns of uncoated Fe₃O₄. The decrease of diffraction peaks intensity of Fe₃O₄ indicates that Fe₃O₄ NPs are coated with a thin layer of SiO₂. Due to the absorption of x-ray through the SiO₂ shell.

Figure 5 shows the FTIR spectra of Fe₃O₄ and Fe₃O₄@SiO₂ NPs in the range of 400–4000 cm⁻¹. Fe₃O₄ spectrum shows a broad band at 3400 cm⁻¹, which is attributed to the asymmetric and symmetric stretching vibrational modes of O–H bond. The peak at 1600 cm⁻¹ is due to the hydroxyl groups of molecular water; the H–O–H bending of the coordinated water [32]. The peak at 590 cm⁻¹ corresponds to the stretching vibration of the Fe–O bond functional group of Fe₃O₄ [33]. Fe₃O₄@SiO₂ spectrum shows a sharp peak at around 1080 cm⁻¹ that corresponding to the strong asymmetric stretching vibration of Si–O–Si. A peak at 797 cm⁻¹ should be related to symmetric vibrational modes of Si–O–Si cm⁻¹, a peak at 960 cm⁻¹ is assigned to the symmetric stretching vibration
of Si–OH bond, and a peak at 464 cm\(^{-1}\) due to Si–O–Si bending [34]. The broad band at 3400 cm\(^{-1}\) is attributed to the surface hydroxyl group that was adsorbed on the surface of Fe\(_3\)O\(_4\)@SiO\(_2\) NPs. The band around 570 cm\(^{-1}\) corresponds to Si–O–Fe stretching vibration [35] proving the attachment of SiO\(_2\) on the surface of the Fe\(_3\)O\(_4\) as well as demonstrates the successful synthesis of Fe\(_3\)O\(_4\)@SiO\(_2\).

### 3.2. Photo-thermal conversion properties of Fe\(_3\)O\(_4\)@SiO\(_2\) nanofluid

In order to investigate the photo-thermal conversion characteristic of the nanofluids compared to the base fluid, the fluids were irradiated by a simulated solar light under a solar intensity of 1000 W m\(^{-2}\). Figures 6(a)–(c) shows the temperature distributions with time for 280 min at three different heights of the solar collector. At the beginning the nanofluid temperature was 17 °C. Figure 6(a) shows the temperature distribution with time of Fe\(_3\)O\(_4\)/H\(_2\)O (1 mg/1 ml) nanofluid. After 10 min of irradiation the temperature difference between bottom and top surface of the collector was 2.7 °C. The temperatures at locations; T1, T2, T3 were 20.3 °C, 21.2 °C and 23 °C with temperature increments from the initial value of 3.3 °C, 4.2 °C and 6 °C, respectively. Figure 6(b) shows the temperature rise characteristics corresponding to the case of Fe\(_3\)O\(_4\)@SiO\(_2\)/H\(_2\)O (1 mg/1 ml) nanofluid. After 10 min of irradiation the temperature difference between bottom and top surface of the collector became 3.2 °C. The temperatures at locations; T1, T2, T3 were 20.8 °C, 22 °C and 24 °C with temperature increments of 3.8 °C, 5 °C and 7 °C, respectively. The graphs demonstrate the effect of SiO\(_2\) coating on temperature rise enhancement since the silica layer suppresses the light reflection and improves the light absorption by Fe\(_3\)O\(_4\) NPs. Figure 6(c) shows the temperature rise characteristics of pure deionized water. After 10 min of irradiation the temperature difference between bottom and top surface of the collector was 1.4 °C. The temperatures at locations; T1, T2, T3 were 18.5 °C, 19 °C and 19.9 °C with temperature increments of 1.5 °C, 2 °C and 2.9 °C. Figure 6(d) shows the transient temperature curve of temperatures measured at the top surface after an irradiation time of 65 min which clearly indicates that even such low concentrations of Fe\(_3\)O\(_4\)@SiO\(_2\) NPs can significantly increase the bulk

![Figure 4. X-ray diffraction patterns of Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@SiO\(_2\).](image)

![Figure 5. FTIR spectra of Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)@SiO\(_2\).](image)
nanofluid temperature. The surface temperature of the nanofluid was higher than that of the base fluid (H₂O) due to the enhanced solar light absorption of Fe₃O₄@SiO₂ NPs dispersed in the base fluid. At concentrations as low as 1 mg/ml (0.001 weight), the temperature of H₂O increases from 21 °C to 30.2 °C within 65 min, with a temperature increase of 8.2 °C. The temperature of the nanofluid increases from 21 °C to 33.7 °C within 65 min, with a temperature increase of 12.7 °C, indicating a significant photo-thermal effect compared to H₂O. It is concluded that the temperature rise of Fe₃O₄@SiO₂ nanofluid is higher than the water base fluid. This should be attributed to the strong absorption and the capturing of solar radiation as well as the scattering effect of the NPs dispersed in the water. Hence, under the same radiation conditions, the temperature of nanofluids is higher than that of pure water.

It is observed from the graphs that the temperature increases steeply with the radiation time at the initial heating stage. Afterward, for the irradiation time above 25 min the heating rate is decreased noticeably until it reaches almost a steady state at the late stage, due to the heat dissipation to the surrounding. Additionally, at the initial heating stage (i.e. about 20 min) the temperature distribution shows decrease with depth, where the temperature at location T₁ (the bottom of the container) is the least while the temperature at location T₃ (top of container) is the highest. Due to the optical absorption of liquids, the intensity of irradiated solar light weakens with the increase of liquid depth. Hence, the bottom temperature increased slightly and was clearly different from the surface temperature during the first 60 min of the test time. After this initial time period it is noticed that the surface temperature (T₃) decreases at a faster rate than the other two locations. This is attributed to the heat dissipation or exchange to the surroundings which is more pronounced in the surface region.

To evaluate the distribution homogeneity of different fluids based on temperature, a coefficient $D$ can be calculated by taking the difference between the maximum temperature of the nanofluid at all temperature measurement positions and the minimum temperature of the nanofluid at all temperature measurement positions after the exposed time $\Delta t$ [36]. $D$ for the nanofluids are calculated based on the final temperature to evaluate the distribution homogeneity of the temperatures. After 280 min the values for $D$ are 3.94 °C and 2.97 °C for Fe₃O₄ and Fe₃O₄@SiO₂ nanofluids, respectively. The temperature distribution homogeneity coefficient reduced with SiO₂ coating of Fe₃O₄ NPs. It can be concluded that Fe₃O₄@SiO₂ nanofluid has a higher thermal conductivity than Fe₃O₄ nanofluid. As the thermal conductivity improves the heat transfer become better and result in a more homogenous temperature distribution [36].

The collector thermal efficiency is defined as the ratio of the usable thermal energy to the incident radiation energy on the collector surface [37–39]. In the current experimental setup, the solar radiation is uniform and the fluid depth is small so it can be assumed that the temperature of the NP is the same as the surrounding fluid, measured by the thermocouple. The photo-thermal conversion efficiency ($\eta$) can then be calculated by the following equation [40, 41]:

![Figure 6. Temperature rise distributions with time under 1000 W m⁻² simulated solar illumination ((a)–(c)) at different heights for (a) Fe₃O₄/H₂O nanofluid, (b) Fe₃O₄@SiO₂/H₂O nanofluid, (c) deionized H₂O, (d) at T3 location of Fe₃O₄@SiO₂/H₂O nanofluid and pure H₂O.](image-url)
\[ \eta = \frac{(c_w m_w + c_m m_n) \Delta T}{A G \Delta t} \times 100\% \]

(1)

Where, \( c_w \) and, \( m_w \) are the specific heat and the mass of the water, respectively; \( c_m \) and \( m_n \) are the specific heat and the mass of the NPs, respectively; \( \Delta T \) is the temperature difference of the nanofluid after an exposed time \( \Delta t \); \( A \) is the irradiation area; \( G \) (W m\(^{-2}\)) is the irradiation intensity. The photo-thermal conversion efficiency is proportional to the temperature gradient of the nanofluid. As the particle concentration is very small, i.e. \( m_n c_m / m_w c_w \to 0 \) the collector efficiency can be simplified to become [42]:

\[ \eta \approx \frac{\Delta T c_w m_w}{\Delta t AG} \times 100\% \]

(2)

Figures 7(a)–(c) shows the photo-thermal conversion efficiency variation with time for the water and the nanofluids, at positions T1 (bottom), T2 and T3 (surface), respectively. Figure 7(d) shows the overall photo-thermal conversion efficiency, which is calculated by taking the average temperature for the three temperature measurements at different heights of the collector (T1, T2 and T3). The calculated efficiencies after 10 min of irradiation are represented in Table 1. It is obvious that, the efficiency increase in the first 10 min due to the high initial temperature rise and the negligible heat losses to the surrounding at the beginning. The calculated efficiency at the surface of the collector (i.e. T3) after 10 min of irradiation for Fe\(_3\)O\(_4\)@SiO\(_2\) nanofluid is higher than that for Fe\(_3\)O\(_4\) nanofluid (figure 7(c)) by 6%. This is attributed to the light absorption improvement, consequently the temperature enhancement in the case of Fe\(_3\)O\(_4\)@SiO\(_2\) nanofluid.

The solar collectors exhibit exponential decay of efficiency after 15 min of irradiation due to the decrease of the heat rate of the nanofluid with time as shown in figure 6, which resulted in lowering the collector efficiency. Possible reasons can be analyzed from several aspects. When the temperature rises, the Brownian motion of the dispersed NPs is intensified. This motion will enhance the heat transfer and move the peak temperature away from the surfaces to reduce heat loss to ambient. As a contradictory effect; as the temperature gradient within the nanofluid decreases the heat transfer to the environment will be enhanced. On the other hand, the stability of NPs decline with the increase of temperature as agglomeration is increased due to Brownian motion, consequently the concentration of the NPs decreases with time, leads to an obvious reduction in photo-thermal conversion efficiency. These aspects interact in the photo-thermal conversion process, which has been shown to decrease the photo-thermal conversion with time beyond 15 min (figure 7).

Table 1. Photo-thermal conversion efficiency after 10 min of irradiation at different heights of the collectors.

|                     | Fe\(_3\)O\(_4\)@SiO\(_2\) nanofluid | Fe\(_3\)O\(_4\) nanofluid | H\(_2\)O |
|---------------------|-----------------------------------|---------------------------|----------|
| T1                  | 30%                               | 27%                       | 10%      |
| T2                  | 38%                               | 35%                       | 11%      |
| T3                  | 89%                               | 83%                       | 17%      |
3.3. Photo-thermal conversion properties of the solar collector

In order to enhance the temperature of the interior fluid mainly at the bottom of the collector, the bottom of the collector was covered with a black colored paper and a test was conducted with 10 ml of Fe$_3$O$_4$@SiO$_2$/H$_2$O (1 mg/1 ml) nanofluid and 20 ml of kerosene in the collector. The nanofluid settled beneath the kerosene as the density of water (0.997 g cm$^{-3}$) [43] is more than the density of kerosene (0.783 g cm$^{-3}$) [44]. Water-based nanofluid and kerosene have different optical and thermal properties utilizing both fluids in one collector improves the photo-thermal conversion performance of the collector.

Figure 8 displays the temperature rise characteristics of the solar collector, which is shown in the inserted sketch in the figure. After 300 min of irradiation the temperature difference between bottom and top surface of the collector reached 9.45 °C. The temperatures in the nanofluid part at locations; T1 and T2 were 57.3 °C and 55.5 °C with temperature increments of 34.3 °C and 32.5 °C, respectively. The temperatures in the kerosene part at locations; T3 and T4 were 50.7 °C and 47.8 °C with temperature increments of 27.7 °C and 24.8 °C, respectively. The temperature distribution homogeneity enlarged with kerosene. The solar energy absorption of Fe$_3$O$_4$@SiO$_2$ nanofluid (i.e. T1 and T2 locations) is stronger than in the case of only pure kerosene (i.e. T3 and T4 locations) which increases the nanofluid temperature and leads to a more uneven temperature distribution. In order to evaluate the temperature distribution homogeneity for the 10 ml of Fe$_3$O$_4$@SiO$_2$ nanofluid of the collector in the presence of kerosene, the coefficient $D$ is calculated after 300 min of irradiation to be 1.8 °C. It is clear that the temperature were trapped at the nanofluid part of the collector which has higher temperature than the upper layer of kerosene.
The advantages of using kerosene are: (i) kerosene has a higher refractive index (1.4) [45] than water (1.33) [46], so the optical path of photons entering the system increases, which is beneficial to the capturing and absorption of light; (ii) specific heat capacity of kerosene (2.01 J/g °C) is less than water (4.186 J/g °C) [43] so the temperature of kerosene can be raised faster than water; (iii) the thermal conductivity of kerosene (0.145 W mK⁻¹) is less than water (0.613 W mK⁻¹) which reduces the heat loss and transfer of the nanofluid through the collector top surface.

Figure 9 displays the temperature rise characteristics at the bottom of the collector at T1 location, the collector is composed of 10 ml of the water-based nanofluid and 20 ml kerosene. The temperatures were recorded for duration of irradiation time of 250 min of pure water and Fe₃O₄@SiO₂/H₂O nanofluids at different concentrations. It is clear that the temperature rise of the nanofluid is much higher than pure water, and the temperature rise of the Fe₃O₄@SiO₂/H₂O nanofluid with concentration of 1 mg/1 ml is more than that with concentration of 2 mg/1 ml. This might be attributed to the tendency of the NPs to agglomerate by attractive forces (Van der Waal forces) as their concentration in the nanofluid increases. Another reason might be the decrease of the transparency of the nanofluid which reduce the light intensity and so the optical absorption of the liquid when the particle’s concentration in the nanofluids becomes large. The photo-thermal conversion efficiencies of the collectors were calculated for the temperature rise in the first 5 min of the irradiation. It is found that the collectors which contain kerosene and the nanofluid with concentration of 1 mg/1 ml and 2 mg ml⁻¹ Fe₃O₄@SiO₂/H₂O exhibit efficiencies of 98.5% and 85.4%, respectively. This is a high photo-thermal conversion efficiency compared to the collector which contains kerosene and pure H₂O (65.6%).

Further research is proposed to investigate the photo-thermal characteristics of kerosene-based Fe₃O₄@SiO₂ nanofluid. However, one of the key parameters in nanofluids is the stability of NPs. In order to form a stable kerosene-based Fe₃O₄@SiO₂ nanofluid a suitable hydrophobic modification procedure is needed [47, 48].

4. Conclusion

This work experimentally investigates the photo-thermal conversion characteristics of Fe₃O₄@SiO₂ NPs dispersed in H₂O under a solar simulator with intensity of 1000 W m⁻². The synthesized Fe₃O₄ NPs have average size of about 7.8 nm and the Fe₃O₄@SiO₂ NPs have core/shell structure with average size of about 475 nm. Fe₃O₄ and Fe₃O₄@SiO₂ NPs have been applied in water-based nanofluids. They have remarkable performance in improving the photothermal conversion efficiency of the water–base fluid. The silica coating enhances the raise of the fluid’s temperature. The temperature distribution homogeneity coefficient reduces with the coating of Fe₃O₄ NPs with SiO₂. It can be concluded that Fe₃O₄@SiO₂ nanofluid has a higher thermal conductivity than Fe₃O₄ nanofluid. The improvement of thermal conductivity results in the enhancement of the heat transfer and homogeneity of temperature distribution. Regarding the solar collector with 10 ml of the nanofluid and 20 ml kerosene, we deduced the following. At the bottom of the collector, after 5 min of radiation the efficiency of Fe₃O₄@SiO₂/ H₂O (1 mg/1 ml) nanofluid is about 98.5%, whereas, the efficiency of Fe₃O₄@SiO₂/H₂O (2 mg/1 ml) nanofluid is about 85.4%; both are greater than that of H₂O (65.6%). The usage of kerosene in the solar collector enhances the temperature rise, when used with the optimum concentration as 1 mg/1 ml corresponding to the NPs/H₂O. Further research is proposed to prepare a stable kerosene-based Fe₃O₄@SiO₂ nanofluid, and to investigate its photo-thermal characteristics.

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