Investigation of the Stability of Cerium Oxide in Diesel Fuel for Nano-Enhanced Fuel Formulation

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Abstract. Enhancing fuels through nano-addition has become a prospect in keeping both renewable and non-renewable fuels as energy sources for the transportation sector. One of the challenges when using nanofluids in a specific system is the fluid's ability to be stable for a longer period. Undesired settlement of nanoparticles can cause damage to the system operating within its limits due to contamination, therefore stability study has paramount importance in the nano-enhanced fuel introduction in internal combustion engines. checking nanofluid stabilization consider a challenge since it takes time and it has tendency to aggregate in certain time, therefore UV vis device was a perfect tool to investigate the stability of the nano fuel. Three-step method using UV-Vis spectral absorbency device was selected to measure the nanofluid and ensure the stability of the solution daily. Cerium oxides consider one of the challenging nano additives to blend with fuel. To measure its stability, it was observed that when the nanofluid fuel was mixed with nanoparticles in quantities estimated at 25, 50, and 75 ppm, the nano fuel solution showed a high stability capacity in the first days, which indicate revealed that blending at high speeds followed by ultrasonication in an ultrasonic homogenizer for 40 minutes increases the stability of the mixes. The nano fluid fuel was gradually decreasing during the next following 8 days, but all of the blended fuel remains stable for percentage above 80 percent that UV-Vis 3 step method is trustable for investigating the stability of the nano enhanced fuel.

INTRODUCTION

Diesel engines are known for their excellent thermal efficiency, which has led to their widespread usage in automobiles. However, diesel engines are a significant source of hazardous pollutants such as hydrocarbons and particulates and nitrogen oxides and Sulphur oxides. Such emissions are very harmful and responsible for phenomena such as acid rain and photochemical pollution, and therefore it is subject to strict environmental legislation. Therefore, the use of diesel engines increases the rate of harmful threats in the form of nitrogen oxides and hydrocarbon emissions. NPS (nanoparticles) are a new type of additive that has a small range in size approximated between 1 to 100 nm. Therefore, it can be categorized into different classes depending on the size, shape, and properties. NPS groups include metallic, fullerenes, polymeric and ceramic [1]. Adding such metal and metal oxide nano powder to the base fuel may improve the fuel's characteristics, which contribute to the reduction of the negative aspect of commercial diesel and biodiesel [2][3]. Besides the ability of nano additive to dissolve in the substance that is added to it, it possesses high-level physical and chemical properties as a result of nanoscale size and the high surface area. The nano additive has a main purpose: to improve, develop, improve, develop, and provide useful properties for the fuel without affecting the combustion parameters and performance [4]. Nano additives are organic-based or metal-based substances that are easily dissolved in a medium such as oil and water. Nanofluids are one of the newest liquids classes that have been engineered by dispersing nanomaterials in the base fluids, another meaning, it is nanoscale colloidal suspensions that contain nanomaterials with high condensation

[5]. Nanoparticles have improved physical properties such as conductivity, thermal diffusion, viscosity, and convective heat transfer coefficients compared to primary fluids such as water and oil [6, 9].

There are two methods to produce nanofluid, which can present as one-step method and two-step method. In the first-step method producing nanofluid is implemented using physical vapor deposition technology, through which nanoparticles are updated and developed or through chemical liquids in order to synthesize nanofluids. The two-step method is the most common and widely used method for producing nanofluids at a lower cost and more productive. Nanomaterials utilized in this method has been produced trough chemical or physical method as dry powder. After that, the dispersion of nano powder and mixed with the fluid in order to be synthesis is processed with the aid of specific devices such as in this step as homogenizer, sonication, magnetic stir, and high shear mixing.

The important technique to enhance the stability of nanoparticles in fluids is the use of surfactants. However, the functionality of the surfactants under high temperature is also a big concern, especially for high-temperature applications. The preparation of homogeneous suspensions remains a technical challenge since the nanoparticles always form aggregates due to powerful van der Waals interactions. The stability of nanoparticles as a fuel additive is an essential consideration because nanoparticles, in turn, tend to aggregate due to their large surface area and surface activity [10]. With the development of technology, techniques for examining the stability of nanofluids have evolved, and this is manifested in new methods such as UV-visible absorption spectroscopy, Field emission scanning electron microscopy (FESEM), and Transmission Electron Microscopy (TEM), visual sedimentation photograph and pH evaluation [11]. UV-Vis spectrophotometer analyses are an efficient method for quantitatively measuring the colloidal stability nanofluid dispersion [11-13]. This method consists of a three-step method considering that energy absorption depends on the intensity of UV light passes through a liquid, by considering the fact that the absorption of energy depends on the intensity of the UV light passes through a fluid. In this presented work, the diesel nanofluid fuel blends are prepared using Ce_2O_3 as additive and stability investigated using three step method using magnetic stir and emulsifier with a Hight frequency to sanitize the cerium oxide nanoparticles in neat diesel solution without adding surfactant, then applying Uv-vis spectrometer for fuel stability comparison. The novelty of this study is that This study is useful in increasing the understanding about the study of the stability of the developed fuel by adding nanoparticles, due to the lack of research in it, especially when using nanomaterials such as cerium.

MATERIALS AND METHODS

Ce_2O_3 NPS (Nanoparticles)

Ceric oxide, ceria, cerium oxide, cerium dioxide is commonly known as cerium oxide. It is an oxide of the rare metal cerium and appears physically as a pale-yellow white powder with the chemical formula Ce_2O_3. Cerium oxide is also a valuable industrial product and an intermediary in the extraction of elements from their ores. This material's distinguishing feature is its reversible conversion to a non-stoichiometric oxide, in addition, many studies has reported the importance of cerium in combustion, where it has a major rule in enhancing the combustion efficiency and emission reduction beside that it assists in increase the pressure of the cylinder and decrease the ignition delay. The detailed properties of cerium oxide that include the symbol, purity, and an average size are described in Table 1. According to the literature, the particle size for the nanoparticles used for enhancing diesel fuels is in the range of 20 to 75 nm. For the current work, a nanoparticle with a size ranging from 30-50 nm is chosen.

TABLE 1: Ce_2O_3 nanoparticle average size range

Nanoparticle	Symbol	Purity	Average diameter of most probable particles	Range of particle size
Cerium oxide	Ce_2O_3	99.95 %	30-50 nm	30-50 nm

Nanoparticles characterization for the experiment was performed using a scan electron microscope in this work (SEM). The elemental compositions of the sample were determined using energy dispersive X-ray (EDX) analysis to determine the purity of the nanoparticles. Table 2 shows the elemental composition extracted from the spectrum in Figure 1. Figure 2 shows the same micrograph of the nanoparticle at a magnification of a hundred thousand time.

TABLE 2: EDX spectrum data analysis

Element	Weight %	Weight % σ	Atomic %	Element
Oxygen	20.509	1.044	69.322	20.509
Cerium	79.491	1.044	30.678	79.491

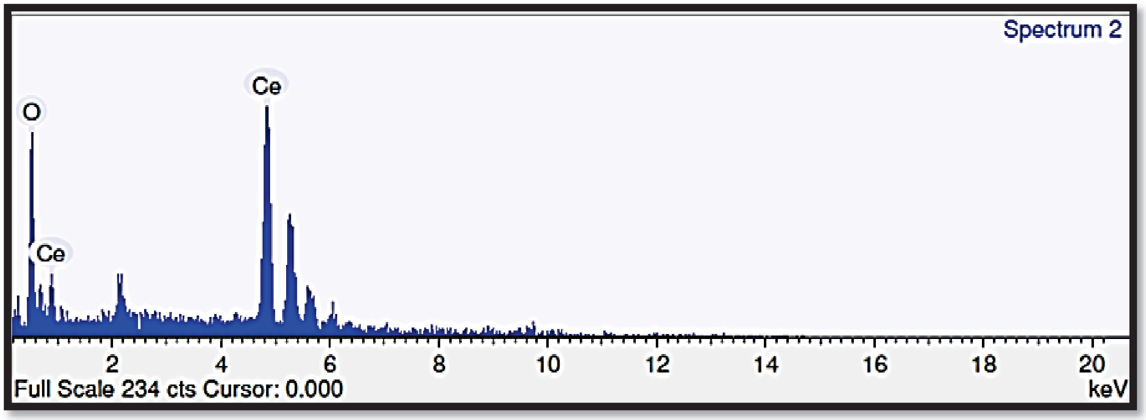

FIGURE 1. EDX spectrum of (Ce_2O_3) nanoparticle

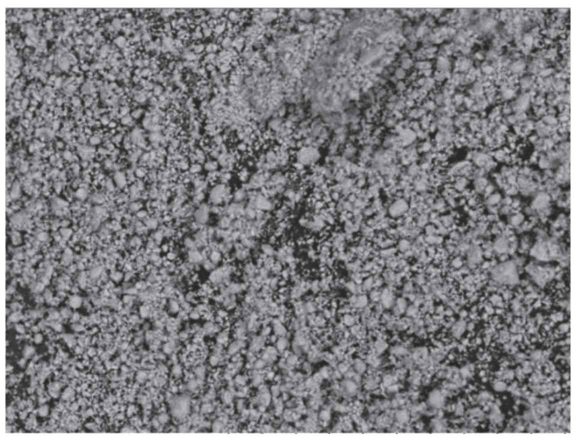

FIGURE 2. SEM micrograph of (Ce_2O_3) nanoparticles

Nano-Enhanced Fuel

Nanoparticles have a greater surface area than their size, resulting in increased surface tension that keeps particles from separating, causing smaller particles to cluster together, resulting in sediment formation. (Ce_2O_3) nanoparticles (diameter 30-50 nm) were employed in this experiment. The process for preparing nanofluids is one of the most important factors to consider in order to achieve the maximum levels of stability, which leads to the development of the solution's physical and chemical characteristics. In order to mix the nanoparticles additives with the pure diesel, it needs to pass certain process starting from determining the proper amount that needs to dopped and dissolve in the enhanced diesel. Nanoparticles are commonly measured by (ppm) unit, which refers to parts per million. at the concentrations included in the current study are 25, 50, and 75 ppm. The selection of these concentrations is based on the overview of the literature in the area of nano-enhanced fuel additives. In order to determine the proper amount of nano additive volume needed to be added in the pure diesel, an equation was proposed by [14, 15] as shown in Equation (1) as where the ppm formula is calculated depending on the amount of the nano mass into the solution:

$$\%\ volume\ concentration, \emptyset = \left[\frac{\left(\frac{m_{nano}}{\rho_{nano}}\right)}{\left(\frac{m_{nano}}{\rho_{nano}} + \frac{m_{bf}}{\rho_{bf}}\right)} \right] \times 100 \tag{1}$$

where $\emptyset$ %= Solid volume concentration of nanoparticles, m_{nano} = mass of nanoparticle in gram, m_{bf} = mass of fuel in ml, ρ_{nano} = density of nanoparticles and ρ_{bf}= density of the fuel.

After getting the mass of the nanoparticle powder in grams, the powder was weighted by digital balance GR-300. In addition, the weighted nano powder particle requires mixing and synthesis for a long time, which needs to go through two stages. The first stage is by mixing the nanoparticles with the diesel in a magnetic stir for 40 minutes. Subsequently, UP400S ultrasonic homogenizer was used to synthesize the nanoparticle and the diesel to get a higher stability. The mixed solutionize the nanoparticle and the diesel to get higher stability.

Physical and Chemical Properties of Cerium Oxide Enhanced Fuel

In this experiment the type of diesel fuel was used is neat diesel which has been provided by Petronas company which later have mixed with the cerium oxide nano particles. The improved physical and chemical properties of the improved fuel were measured more than once, and the average was taken. It is noticed from the results that there is an improvement in the properties in all respects, and this indicates that the added nanoparticles have an effective effect in improving the properties of the fuel. Table (1) lists some of the physical and chemical characteristics of cerium oxide nanofluid after mixing with the neat diesel. In contrast, Table 3 illustrate the characteristics of the nano additive. For each of the testing, readings have been collected three times, and an average is taken. The average error for the experiment is for density

TABLE 3: Cerium oxide enhanced diesel fuel

Fuel	Neat Diesel Fuel (DF)	DF+Ce25	DF+Ce50	DF+Ce75
Fuel Density (Kg/m^3)	845	867	868	870
Cetane number	56	56.8	56.8	56.9
Thermal viscosity	3.1145	4.4136	4.4250	4.4642
Calorific value (MJ/kg)	48.58	50.36	50.66	50.68

Experimental Setup

All the prepared samples were mixed at 600 ml for each blend, and the nanoparticle was doped based on this quantity. After that, the enhanced fuels were ready for use, and it was subjected for observation to detect and observation for the fuel sedimentation process. According to [16], the nanofluid as stable when the particle size and concentration of the enhanced fuel remained suspended. The sedimentation observation for nanoparticle diesel fuel blend is shown in figure (3). It can be observed that the cerium blended fuel at higher concentrations became darker compared to those with lower concentration and that can be noticeable by checking the concentration of the enhanced fuel at dosage level 75 ppm. However, when the enhanced fuel concentration decreased, it became lighter, and that can be noticeable at DF+Ce25 and DF+Ce50. After eight days, blends show a bit of significant color change due to the sedimentation process.

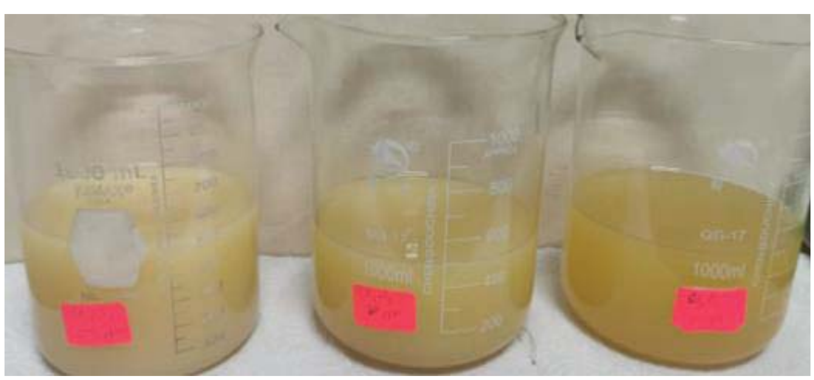

FIGURE 3. Df+(Ce_2O_3) nanoparticles in concentrations 25, 50, and 75 ppm from right to left accordingly.

Device (GENESYS 50 UV-Vis) was used to test the samples, represented by the DF+Ce25and DF+Ce50 and DF+Ce75. UV-Vis spectral absorbency analysis is generally used to check liquids' stability with nanomaterial added into the enhanced fuel and evaluate it. Thus, it gives a better understanding of the stability and when the enhanced fuel starts to sediment and aggregate. Firstly, the samples of the enhanced fuel need to fill in small objects called cuvette, this tool allows the light to pass through it and let the UV-Vis detect the absorbance and the wavelength .as the light pass troughs the cuvette inside the UV-Vis, it is noticeable that the beginning of the light becomes more intense, meanwhile, the intensity of the light decrease while it passes to the end of it. The first place of obtaining the stability values for the enhanced nano fuel is by obtaining the absorbance values. The peak absorbance was found to be between 300 to 316 nm via scanning, exactly at 310 nm. The highest absorbance will be presented at absorbance at the highest peak wavelength at 310 nm, which will serve as a reference for the following step. The absorbance of the of various enhanced fuel was taken at the second step, which demonstrates that enhanced fuel with nanoparticle suspension forms a linear relation (Figure 4) among the absorbance and the concentration and this has been approved by Beer-Lambert [16, 17] law, which presents through Equation 2:

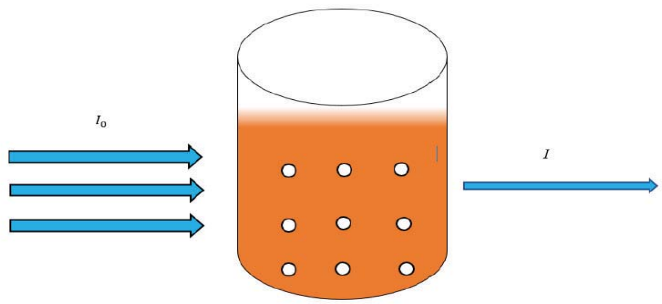

FIGURE 4. Working principle of the UV-Vis spectrophotometer.

$$A = \frac{I_0}{I} \varepsilon C L \tag{2}$$

Where A is the absorbance, I_0 is referring to the light initial intensity, I is referring to the final light intensity, ε is the molar absorptivity, C is referred to the concentration, and L is the path length through the sample. The last step of this method, which is the third step, is to prepare nanofluid with different concentrations and then measure the absorbance through a period.

Nanoparticle-Diesel Fuel Blends Stabilization

Samples of 600 ml for each blend have been prepared to observe fuel sedimentation. According to [16], the nanofluid was stable when the particle size and concentration remained suspended. The sedimentation observation for nanoparticle diesel fuel blend is shown in Figure 5. It can be observed that the cerium blended fuel DF+Ce75 became darker as the concentration increased compared to the DF+Ce25 and DF+Ce50 nano additive, and that is related to the increment of the concentration. After eight days, (Ce_2O_3) blends show a bit of significant color change.

DF+Ce25and DF+Ce50 and DF+Ce75 stability have been tested by (GENESYS 50 UV-Vis) device. The UV-Vis spectral absorbency analysis is commonly utilized to evaluate nanofluid stabilization. The UV light passing through the nanofluid dispersion, as shown in Figure 4 illustrates that the intensity of the light passing through the nanofluid decreases exponentially with the increase of nanofluid concentration. Measuring the stability starts by figuring out the peak absorbance of the dispersed nanoparticle where it is set at a range between 300 to 316 nm via scanning using the UV-Vis Spectral Absorbency Analysis. The highest peak wavelength presents the highest numbers of absorbance. In addition, it act as a reference point for the next step. In the second step of this method, the absorbance for different concentrations of nanofluid was measured. The measurement for different concentration of nanofluid was taken at the same wavelength, this is to illustrate that the nanofluid suspensions will have a linear relationship between the absorbance and the concentration which follow the Beer–Lambert Law [16, 17] which is presented on Equation (2).

RESULTS AND DISCUSSION

Spectrophotometer was used to determine the spectral absorption of the nanoscale fluid and further to measure the colloidal stability. In the first stage of the experiment, the light ray scattering and absorbability were measured by making the main base of the material for experimentation with pure diesel, as the concentration in the intensity of light is essential in the comparison between the base sample that is used as a base and the rest of the nanoscale liquids added later. The nanofluid that will be studied in this paper will be compared to the original sample, which is used as a reference. The light intensity of the nanoparticle-diesel fuel blends with the base fluid, as shown in Figure 5. The graphs below illustrate the absorbance scanning of the nano diesel fluid where it was based between 300 and 313 wavelengths, and it indicates that the peak absorbance of cerium with the concentrations of 25, 50, and 75 ppm stands at 310 nm. Thus, at the same peak wavelength, it is noticeable that nanofluid possesses various absorbance values that meet their concentration equivalently.

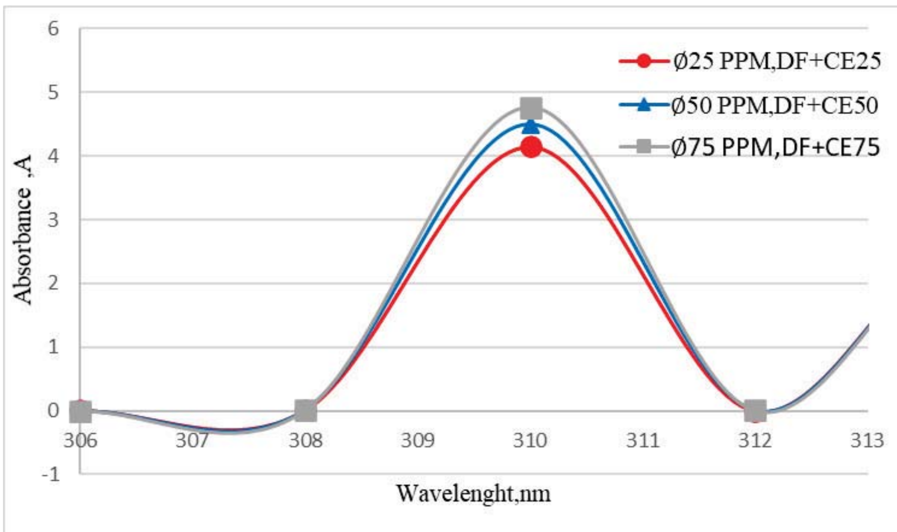

FIGURE 5. Absorbance scanning from 300 to 313 nm wavelength for DF+CE25, DF+CE50 and DF+CE75

The concentration versus absorbance for the three different concentrations of the nano-enhanced fuel has been illustrated in Figure 6, where the enhanced nano fuel at the concentration 25,50 and 75 ppm It is located along a consistent line where the amount of the nano additive mass has a role in this matter. In addition, figure 7 illustrate the linear relationship between the concentration of the nanofluids and the absorbance at the same wavelength. This indicates that any increase of concentration leads to an increment in absorbance, as the higher the concentration, the higher the absorbance at the same wavelength. The initial and current concentration comparison for the nanofluids at a given time, provides a specific idea about how much well nanofluid is stable and precipitate by measuring the absorbance and nanofluid concentration. Hence, for predicting the stability of the nanofluid this relation is considered to be useful.

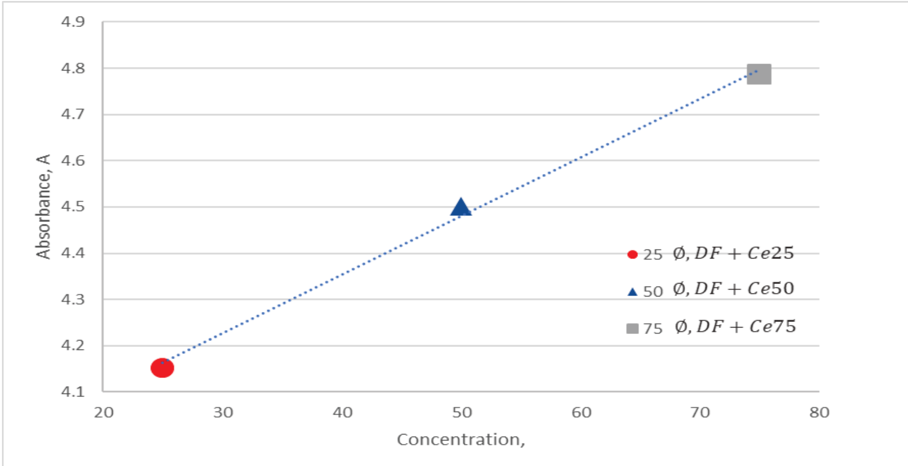

FIGURE 6. Absorbance and concentration linear relationship for Ce_2O_3 nanofluid at 25,50 and 75 ppm

The nanofluid, which is pure diesel, was prepared with cerium oxide nanoparticles added to it at different concentrations of 25, 50, and 75 ppm. It was mixed for 40 minutes and then mixed in an emulsifier device at 70 Hz and 0.7 cycles. The samples were left for 8 days, estimated at 200 hours, where the absorbance of the nano-solution was measured every day. The graph in Figure 7 has shown particle uptake versus sedimentation time. The absorption of the nanofluid increases with the increment of the concentration of the nanofluid. Because a higher concentration of nanofluids results in a higher nanofluidic mass, the possibilities of lowering absorption are also increased [18], [19]. Furthermore, because of the settling of nanoclusters over time, increasing nanocluster size results in faster decreases in absorbency. However, after 8 days, all nanofluids remain stable. Even after 8 days, the absorption of all three concentrations decreased compared to their respective initial absorbances but remained over 80% higher than the original absorbance.

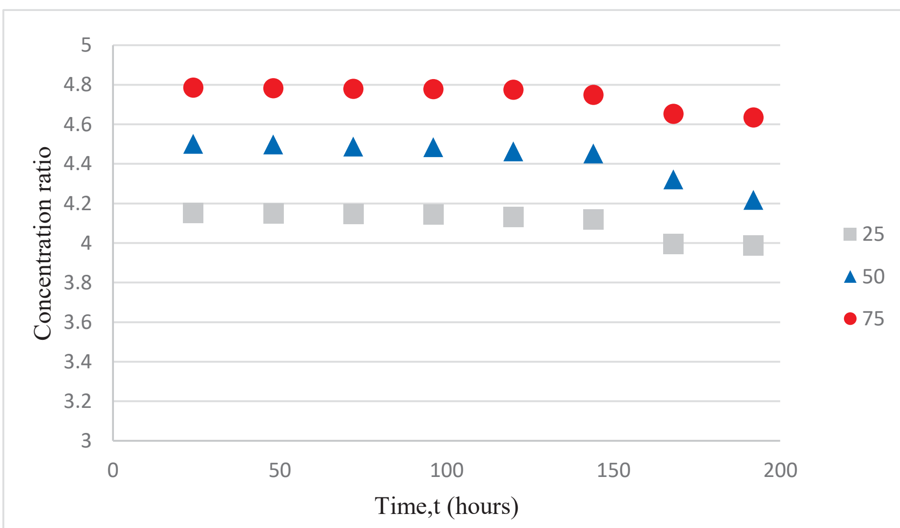

FIGURE 7. Nanofluid concentration alongside absorbency for 200 hours.

CONCLUSION

The enhanced fuel's stability was assessed using a UV-vis instrument. The findings show how long it takes for cerium oxide nanoparticles to stabilize diesel. With a rotational speed of 0.7 cycles and a high amplitude of up to 70% The stability of nano-enhanced diesel fuel, made up of pure diesel and cerium oxide particles, was tested. The different concentration nano-enhanced fuels (DF+CE25, DF+CE50, and DF+CE75) were investigated using a three-step method using a UV-vis spectral absorbency device. The different concentration nano-enhanced fuels (DF+CE25, DF+CE50 and DF+CE75) has been investigated through three-step method using a UV-vis spectral absorbency device, the enhanced fuel showed a high stabilization after it subjected to the high amplitude-frequency and after it starred in the magnetic stir which made stay stable for 200 hours without adding a surfactant. The three-stage method of using the UV-vis spectral absorbency analysis was adopted to make sure of enhancing and developing the stability was accomplished through finding the peak absorbance , the obtain the linear relationship between the absorbance and the concentration of the enhanced fuel than by determining the sedimentation with the independent time, all of this steps approved that the results are from this experiment is trustable and provide us with the information required to study the stability and enhanced it. After testing the time-dependent versus the absorbance, we can conclude that most of the enhanced fluid remains stable in percentage over 80%.

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