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EFFECT OF VARIOUS SURFACTANTS ON THE STABILITY OF HYBRID NANOFLUIDS: AN EXPERIMENTAL STUDY

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ABSTRACT

The most common approach to evaluating the stability of nanofluids is sedimentation analysis; however, further research is needed to confirm stability and determine optimal operating conditions for various nanofluid compositions. This study aims to systematically investigate the stability of nanofluids containing different volume fractions (0.1 wt%, 0.2 wt%, and 0.3 wt%) of Al_2O_3, CuO, and TiO_2 nanoparticles dispersed in distilled water (DW). Several homogenization techniques were employed, including the use of specific surfactants sodium hydrogen carbonate ($NaHCO_3$), carboxymethyl cellulose (CMC), and ultrasonic treatment, to enhance nanoparticle dispersion and prevent aggregation. A two-step preparation method was used to ensure proper integration of nanoparticles into the base fluid. Experimental results revealed that CuO/DW nanofluids exhibited sedimentation stability for up to 58 days without surfactant and up to 77 days with CMC at 0.3 wt%, followed by TiO_2/DW nanofluids, which showed an increase in stability from 7 days without surfactant to 32 days with CMC at 0.1 wt%. Al_2O_3/DW nanofluids demonstrated sedimentation stability ranging from 23 to 52 days depending on concentration and surfactant presence. Notably, the sedimentation stability of TiO_2 nanofluids was significantly improved due to electrostatic repulsion induced by CMC. Additionally, adjusting the pH and incorporating $NaHCO_3$ further enhanced the stability of hybrid nanofluids by minimizing nanoparticle agglomeration and ensuring uniform dispersion throughout the suspension. This study contributes to the development of more stable and efficient nanofluid systems by demonstrating the critical roles of surfactant type, concentration, and ultrasonic treatment in improving the stability of metal oxide-based nanofluids.

1. Introduction

Enhancing heat transfer and minimizing the size of heat exchange systems are critical challenges in modern thermal engineering. Traditional heat transfer fluids such as water, ethylene glycol, and oils are constrained by their inherently low thermal conductivity. An ideal heat transfer fluid should possess low viscosity, high specific heat capacity, good thermal conductivity, minimal corrosiveness, and be cost-effective. The emergence of nanotechnology has introduced a promising solution, nanofluids which are engineered by dispersing nanoparticles (NPs) into base fluids to improve their thermal properties.

Since Choi and Eastman first introduced the concept in 1995, nanofluids have demonstrated superior thermal performance compared to conventional fluids. The inclusion of metallic or metal oxide nanoparticles such as Al_2O_3, CuO, and TiO_2 significantly alters the thermo-physical properties of the base fluid, including density, viscosity, specific heat, and especially thermal conductivity. These improvements have positioned nanofluids as promising candidates for a wide range of applications, including solar thermal systems, electronic cooling, and automotive heat exchangers. Despite these advantages, a major challenge remains ensuring the long-term stability of nanofluids. Aggregation and sedimentation of nanoparticles can lead to inconsistent properties and diminished heat transfer efficiency. Sedimentation is the most widely used method for assessing nanofluid stability as shown in Figure 1, relying on the observation of particles settling at the bottom of a liquid column under forces such as gravity, centrifugal acceleration, or electromagnetic fields These sediments move through the fluid in response to forces acting upon them (Muruganandam and Mukesh Kumar, 2021). Stability is primarily governed by the interplay between particle aggregation and sedimentation, with longer dispersion times indicating greater resistance to flocculation (Ilyas, Pendyala and Marneni, 2014; Chakraborty *et al.*, 2018),(Rostam, 2025). Surfactants play a crucial role in controlling nanoparticle interactions and preventing the precipitation of clusters (Cacua *et al.*, 2019; Xian, Sidik and Saidur, 2020; Bahari, Che Mohamed Hussein and Othman, 2021; Tiwari *et al.*, 2021),(Hamad and Talabany, 2025),(Saeed, 2025). Therefore, achieving a stable, homogeneous dispersion of nanoparticles is crucial. Stabilization methods such as pH control, surfactant addition, and ultrasonication are widely used to prevent agglomeration and maintain performance over time. Studies have shown that nanofluid stability is significantly influenced by antiparticle forces, surfactant concentration, and the use of ultrasonic agitation. Agglomeration results from a balance between van der Waals attractions and electrostatic repulsion. Surfactants reduce surface tension and prevent clustering of particles, although excessive concentrations can increase viscosity and pressure drop, adversely affecting system performance. Researchers such as Fedele et al. (2011), Sajid and Ali (2019), and Sezer et al. (2019) have underscored the importance of stability in maintaining nanofluid efficiency.

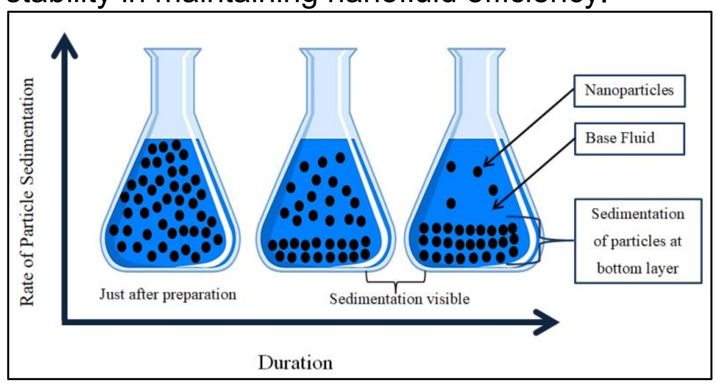

Figure 1: Illustrative diagram of sedimentation.

Ghadimi and Metselaar (2013) reported optimal dispersion of Al_2O_3 nanoparticles using 0.1 wt% surfactant with one hour of ultrasonication, where SDS and PVP produced the most stable formulations. However, they also noted that higher SDS concentrations led to thermal conductivity decline and visible sedimentation within 48 hours.

Other researchers have explored the influence of surfactant type and concentration on nanofluid behavior. Saleh et al. (2014) found that surfactants like Span 80, SDS, and CTAB improved the thermal conductivity of TiO_2-based nanofluids by up to 4.7% compared to surfactant-free formulations. Shanbedi et al. (2015)

demonstrated that increasing surfactant concentration in CNT-based nanofluids significantly impacted viscosity and shear stress. Topuz et al. (2017) showed that ZnO nanofluids exhibited the highest stability over 21 days when dispersed with SDS and ultrasonication. Adil et al. (2016) further noted that the presence of salts decreased the critical micelle concentration (CMC), enhancing surfactant efficiency. The importance of surfactant type and ultrasonication duration is evident in many studies. Asadi et al. (2017) found that cetrimonium bromide yielded the most stable $Mg(OH)_2$ nanofluid after 30 minutes of sonication. Zhou et al. (2018) optimized silica nanofluid stability at pH 10 with 0.1 wt% nanoparticle concentration. Similarly, Ouikhalfan et al. (2020) reported that TiO_2 nanofluids stabilized with CTAB provided slightly better thermal conductivity enhancement (15%) than SDS (10%) and remained stable for over two weeks. Muruganandam and Mukesh Kumar (2021) found sodium dodecyl butane sulfonate to be effective in prolonging shelf life beyond two months. Additionally, (Khalife *et al.*, 2024) have demonstrated that carbon nano additives (CNTs, GO) improve diesel combustion and fuel properties and have potential in nanofluid applications, despite challenges with NOx emissions. (Asokan *et al.*, 2024) shows that tamarind biodiesel blends with BHT and DEE additives improve diesel engine performance and emissions, making them viable biofuel alternatives.

Recent advancements include hybrid nanofluids, such as those synthesized by Xian et al. (2020), who combined TiO_2 and graphene nanoplatelets in distilled water and ethylene glycol. Hexadecyltrimethylammonium bromide was the most effective surfactant, maintaining colloidal stability for over 40 days. Zainith and Mishra (2021) compared Al_2O_3, CuO, and TiO_2 nanofluids, finding that carboxymethyl cellulose (CMC) significantly improved dispersion, with TiO_2 formulations remaining stable for up to 30 days, as verified by UV-vis spectroscopy. Mukherjee et al. (2020) observed that although surfactants initially decreased thermal conductivity in Al_2O_3 nanofluids, they helped sustain uniform dispersion and prevent sedimentation. Altun et al. (2022) confirmed that SDS-stabilized nanofluids were most stable at 0.4–0.8 wt%, while instability occurred at 0.2 wt%. Despite progress, most previous research focused on single nanoparticle types or specific surfactants, and there remains a lack of comprehensive comparison between different oxide nanoparticles dispersed with varied stabilization techniques.

In particular, the combined effects of surfactant type, pH control, and ultrasonication on long-term nanofluid stability require further investigation. Additionally, the potential of low-cost, unconventional stabilizers such as Baking Powder is largely unexplored in scientific literature. This study aims to systematically investigate the sedimentation stability of nanofluids containing Al_2O_3, CuO, and TiO_2 nanoparticles dispersed in distilled water at different weight concentrations (0.1%, 0.2%, and 0.3%). A two-step preparation method is employed, using surfactants including CMC and Baking Powder and ultrasonic treatment. The goal is to identify the most stable formulation and evaluate the feasibility of Baking Powder as a novel, environmentally friendly, and economical stabilizer for metal oxide-based nanofluids. The objective of identifying the most stable formulation for thermal management applications. These nanofluids are particularly relevant for use in solar thermal systems, where long-term stability is essential for sustained heat transfer performance.

2. Experimental Procedures

2.1 Materials

The three types of nanoparticles used in this study as nanoadditives were aluminum oxide (Al_2O_3) (supplied by Skyspring Nanomaterials, USA), copper oxide (CuO), and titanium dioxide (TiO_2) (both provided by Hongwu International Group Ltd., China). All nanoparticles had an average diameter ranging from 30 to 50 nm and a purity of 99.9%. They were dispersed in 200 milliliters of distilled water at three different weight concentrations: 0.1 wt%, 0.2 wt%, and 0.3 wt%. Figure 2 shows the SEM images of the nanoparticles (a, b, and c), revealing their morphological characteristics. Al_2O_3 nanoparticles display relatively uniform, spherical shapes, whereas TiO_2 nanoparticles exhibit a relatively smaller particle size distribution with some degree of agglomeration visible, which could contribute to their sedimentation behavior. CuO nanoparticles appear slightly aggregated with irregular shapes, which may influence their dispersion stability. The thermo physical properties of the nanoparticles, as reported by the suppliers, are summarized in Table 1(Hassan, Yaqob and Abdullah, 2023, Sarkar, 2011) .

In addition, 0.4 wt% carboxymethyl cellulose (CMC) obtained from SINOCMC Company Ltd., China, was used as a surfactant in this study. CMC is a non-toxic, granular compound with the chemical formula $C_8H_{16}O_8$, and its structure is shown in Figure 3(a). Sodium hydrogen carbonates ($NaHCO_3$), illustrated in Figure 3(b), and was also used at the same weight concentrations as the nanoparticles in distilled water.

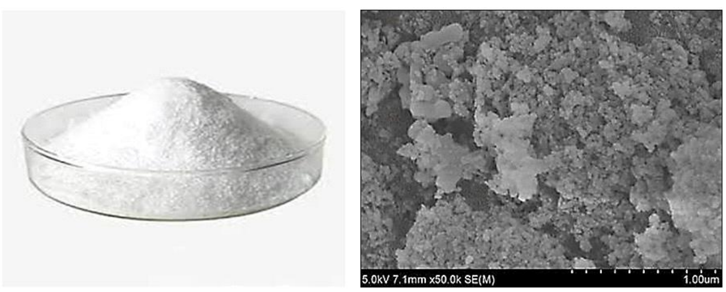

Figure 2 (a): SEM images of Al_2O_3 nanoparticle (adopted from Skyspring Nanomaterials) (www.ssnano.com)

Figure 2 (b): SEM images of TiO_2 nanoparticle (adopted from Hongwu International Group Ltd.)

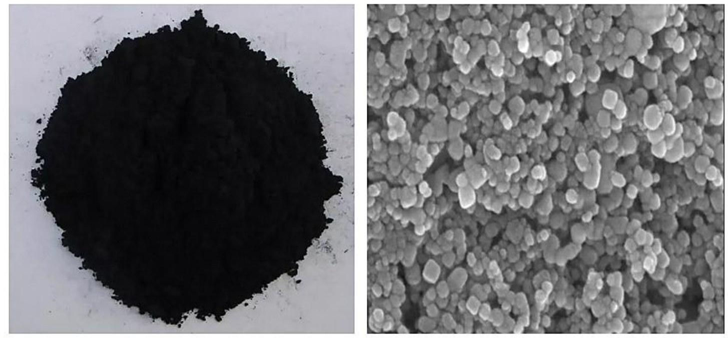

Figure 2 (c): SEM images of CuO nanoparticle (adopted from Hongwu International Group Ltd.)

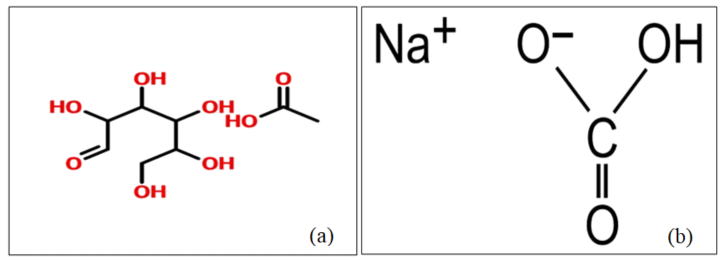

Figure 3: Detailed Structure of (a) CMC ($C_8H_{16}O_8$), (b) Sodium Hydrogen Carbonateas ($NaHCO_3$)

2.2 Preparation of Nanofluid

One of the most significant factors affecting the enhancement of nanofluid properties is their stability. The preparation method plays a crucial role in determining the stability of nanofluids (Ali, Teixeira and Addali, 2019; Asadi, Alarifi and Foong, 2020). Nanofluids can be synthesized using either one-step or two-step methods. In the one-step method, nanoparticles are synthesized and dispersed into the base fluid simultaneously. In contrast, the two-step method involves synthesizing nanoparticles first, followed by their dispersion into the base fluid in a separate stage. The two-step method is the most widely adopted approach for preparing nanofluids due to its practicality and scalability. In this study, the two-step method was employed, where powder-form nanoparticles were dispersed in distilled water, serving as the base fluid. To minimize nanoparticle agglomeration and enhance dispersion stability, ultrasonication was used as a physical treatment technique.

Table 1: Thermo physical properties of the working fluids.

Particle & base fluid	Particle size (nm)	k (W/m.K)	C_p (J/kg.K)	ρ (kg/m^3)	μ (mPa.s)
Water	-	0.605	4179	997.1	0.89
CuO	30-50	33	551	6000	-
Al_2O_3	30-50	40	773	3960	-
TiO_2	30-50	8.4	692	4230	-

This approach ensures the breakdown of nanoparticle clusters and promotes a uniform distribution, thereby improving the long-term stability of the nanofluids. In the first step of preparation, the volume fraction of each type of nanoparticle was calculated using the following equation (Zainith and Mishra, 2021):

$$\varphi(\%) = \frac{(\frac{w}{\rho})}{(\frac{w}{\rho})_{np}+(\frac{w}{\rho})_{bf}} \times 10 \qquad (1)$$

Where, φ , w and ρ are represents volume fraction (%), mass (g) and density (g·cm^{-3}) respectively, The volume concentration ($\boldsymbol{\varphi}$) is first calculated and then converted to weight concentration (ω, wt.%).

Afterward, the nanoparticles were added to distilled water and mixed using a magnetic stirrer for 10 minutes. Subsequently, an ultrasonic homogenizer operating at a frequency of 40 kHz was applied for approximately 30 minutes to disperse the nanoparticle mixture and reduce agglomeration, thereby achieving a more homogeneous and stable suspension. In the second step, 0.4 wt% of carboxymethyl cellulose (CMC) was added to the distilled water, and the same stirring and ultrasonication procedures were repeated as described above. In the third step, after completing the experiments with mono nanofluids, the same preparation procedure was repeated for hybrid nanofluids specifically CuO+Al_2O_3, CuO+TiO_2, and Al_2O_3+TiO_2 at concentrations of 0.1 wt%, 0.2 wt%, and 0.3 wt%. Figure 3 illustrates the overall procedure for nanofluid preparation. Finally, the same preparation steps were performed for hybrid nanofluids using baking powder as a surfactant instead of CMC. Figure 4 shows the magnetic stirrer and ultrasonic homogenizer used during the preparation process. All experimental procedures were conducted in the Heat Transfer Laboratory at Erbil Polytechnic University.

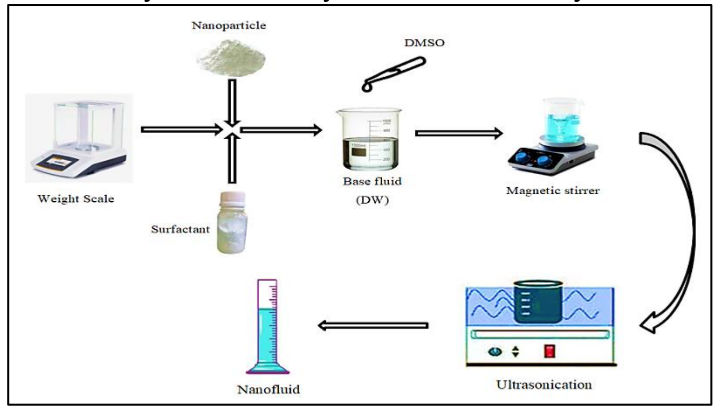

Figure 4: Nanofluid preparation diagram

3. Results and Discussion

To obtain a stable nanofluid, preliminary experiments were conducted to evaluate the effects of different homogenization methods on the stability of various nanoparticles (Al_2O_3, CuO, and TiO_2) dispersed in distilled water (DW). These methods included the addition of surfactants, ultrasonic bath treatment, and, ultimately, the incorporation of sodium hydrogen carbonate. The stabilization of nanoparticles by carboxymethyl cellulose (CMC) and sodium hydrogen carbonate is primarily attributed to electrostatic repulsion and steric hindrance, likely arising from physical adsorption onto the nanoparticle surface.

Figure 5: Magnetic stirrer and ultrasonic homogenizer (Hassan, Yaqob and Abdullah, 2023)

3.1 Stability of Mono-Nanofluid

This study employed the two-step method for nanofluid preparation, in which commercially available Al_2O_3, CuO, and TiO_2 nanoparticles were individually dispersed into distilled water at three different concentrations (0.1 wt.%, 0.2 wt.%, and 0.3 wt.%). This method involved the mechanical mixing of nanoparticles into the base fluid to achieve initial dispersion. Following this, to improve the stability of the nanofluids and mitigate nanoparticle agglomeration, two enhancement techniques were applied, ultrasonic treatment, which was used to disrupt agglomerates and promote uniform dispersion, and the addition of carboxymethyl cellulose (CMC) as a surfactant to further stabilize the suspension. These procedures aimed to prolong sedimentation time and maintain dispersion quality, as illustrated in Figure 6 (a and b). The sedimentation behavior of the prepared nanofluids was evaluated over time. Results indicated that sedimentation stability depended on the nanoparticle type, concentration, and the presence of CMC. Among the tested samples, CuO/DW nanofluids at 0.3 wt.% showed the highest stability, remaining well-dispersed for up to 58 days without significant sedimentation. When CMC was added, this duration extended to 77 days. Al_2O_3 nanofluids exhibited moderate stability, also benefiting from the use of CMC. Conversely, TiO_2 nanofluids demonstrated the least stability, with visible sedimentation occurring after 30 days at 0.3 wt.%; the presence of CMC increased this duration to 50 days. A summary of sedimentation durations for all nanofluid types, both with and without CMC, is provided in Table 2.

Figure 6 (a): Nanofluids Preparation Process without Adding CMC

Figure 6 (b): Nanofluids Preparation Process with Adding CMC

Addition of CMC, at various concentrations. This figure provides a clear visual comparison of the influence of CMC on the sedimentation stability of each nanofluid. The results highlight the significant effects of both nanoparticle type and concentration on nanofluid stability. In general, increasing the nanoparticle concentration enhances stability. Furthermore, the data demonstrate the stabilizing effect of CMC. Among the nanofluids without surfactant, CuO exhibited the highest stability, followed by Al_2O_3 and TiO_2. However, with the addition of CMC, TiO_2 nanofluids displayed the greatest stability, followed by Al_2O_3 and CuO. This suggests that CMC interacts particularly well with TiO_2 nanoparticles, likely due to favorable molecular interactions that reduce sedimentation.

Overall, the addition of CMC surfactant significantly enhances the stability of nanofluids, with the degree of improvement varying notably depending on the type of nanoparticles used. Surfactants, or surface-active agents, reduce the interfacial tension between nanoparticles and the base fluid, thereby minimizing particle agglomeration and promoting a more uniform and stable suspension. This enhanced stability is crucial for preserving the superior thermal properties and heat transfer performance of nanofluids over extended periods, making them more effective for applications such as cooling systems and heat exchangers. In some cases, elongated or larger nanoparticles may require higher surfactant concentrations to prevent coagulation and sedimentation, which can otherwise compromise long-term thermal efficiency. However, appropriate dosing of CMC has been shown to effectively stabilize a wide range of nanoparticles, maintaining dispersion even under elevated temperatures.

Table 2: Days of Sedimentation for Mono-Nanofluid (with and without CMC)

Concentration	CuO		Al_2O_3		TiO_2	
	Without surfactant	**CMC**	**Without surfactant**	**CMC**	**Without surfactant**	**CMC**
0.1wt.%	32	37	23	30	7	32
0.2wt.%	48	54	25	36	13	37
0.3wt.%	58	77	49	52	30	54

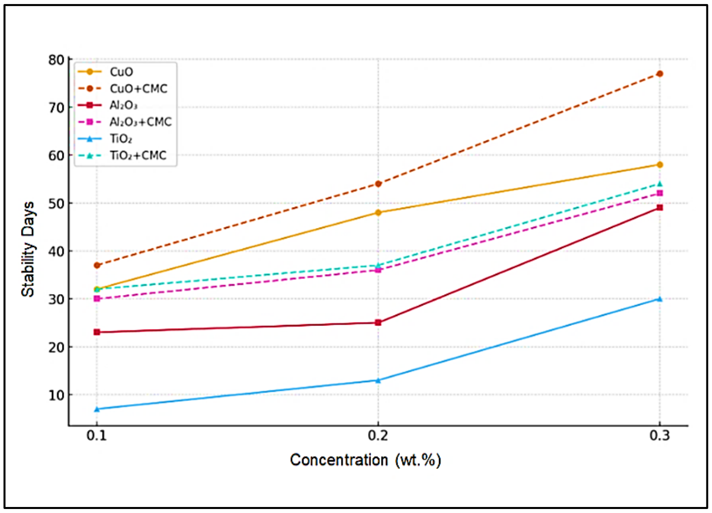

Figure 7: The effect of improving the concentration of nanoparticle on the nanofluid stability (with and without CMC)

3.2 Influence of NaHCO3 on the Stability of Hybrid-Nanofluid

Hybrid nanofluids prepared without surfactants are prone to agglomeration, resulting in nanoparticle sedimentation and a decline in both thermal conductivity and long-term stability. However, the inclusion of sodium hydrogen carbonate has proven effective as a stabilizing agent by promoting uniform particle dispersion within the base fluid and mitigating destabilizing interparticle interactions. To assess the influence of sodium hydrogen carbonate on the stability of hybrid nanofluids at varying nanoparticle loadings, suspensions were prepared with and without the surfactant at concentrations of 0.1 wt.%, 0.2 wt.%, and 0.3 wt.% for the following combinations: $CuO–Al_2O_3$/DW, $Al_2O_3–TiO_2$/DW, and $CuO–TiO_2$/DW. Figure 8 (a&b) illustrates the visual appearance of $CuO–Al_2O_3$/DW nanofluids with and without the addition of sodium hydrogen carbonate ($NaHCO_3$), respectively. It is evident that the nanofluid without $NaHCO_3$ exhibited poor stability agglomeration began within 2 hours, and complete sedimentation of the nanoparticles occurred after 12 hours. In contrast, the inclusion of $NaHCO_3$ significantly enhanced the stability of the nanofluid. This improvement is primarily attributed to the increase in pH, which plays a crucial role in stabilizing the suspension. The elevated pH alters the surface charge density of the nanoparticles, increasing electrostatic repulsion and reducing the tendency for aggregation. Moreover, changes in pH during preparation can influence the size and morphology of nanoparticles, further contributing to the overall stability of the nanofluid (Li *et al.*, 2010; Ilyas, Pendyala and Marneni, 2014). The effects of counting sodium hydrogen carbonates to the hybrid-nanofluid in various concentrations have been demonstrated in Figure 9.

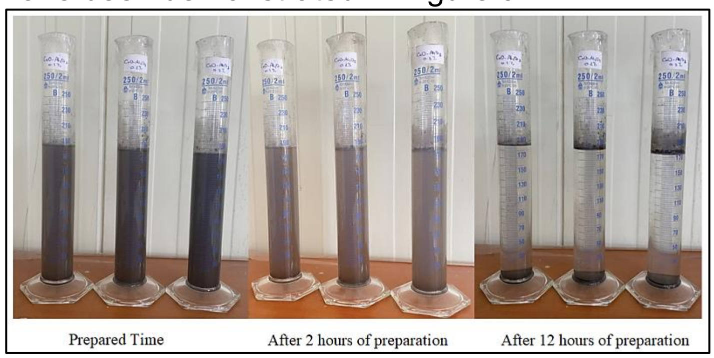

Figure 8 (a): Sedimentation behavior of $CuO-Al_2O_3$/DW without $NaHCO_3$

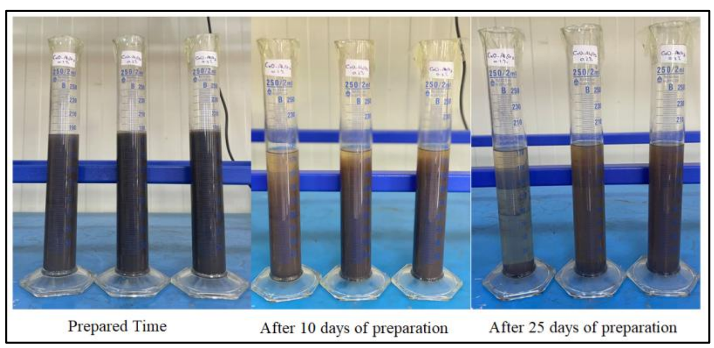

Figure 8 (b): Sedimentation behavior of $CuO-Al_2O_3$/DW with incorporating $NaHCO_3$

Importantly, the combination of different nanoparticles in hybrid nanofluids introduces potential synergistic effects. For example, nanoparticles with varying sizes, shapes, and surface charges can interact to form more stable suspensions by filling voids and reducing sedimentation rates. The electrostatic and steric interactions between CuO, Al_2O_3, and TiO_2 nanoparticles can lead to enhanced dispersion and reduced agglomeration compared to mono-nanofluids. These interactions also influence thermal conductivity; hybrid nanofluids often exhibit improved heat transfer properties by combining the high thermal conductivity of CuO and Al_2O_3 with the excellent dispersion stability of TiO_2. The presence of sodium hydrogen carbonate further amplifies these benefits by maintaining nanoparticle dispersion over time, making these hybrid nanofluids highly promising for advanced cooling and heat transfer systems. Overall, this investigation found that the addition of sodium bicarbonate as a stabilizing agent in hybrid nanofluids produced promising results in enhancing both stability and thermal performance. Sodium bicarbonate acts as an effective buffering and dispersing agent, enabling various types of nanoparticles to be uniformly distributed throughout the base fluid. This uniform dispersion is essential for minimizing the aggregation and sedimentation commonly observed in hybrid nanofluids. As a result, sodium bicarbonate-stabilized hybrid nanofluids exhibit improved thermal properties. Its ability to increase pH and suppress aggregation through electrostatic stabilization suggests a viable mechanism for maintaining long-term dispersion. This finding advances the application of hybrid nanofluids in systems that demand sustained thermal performance, such as renewable energy collectors and high-performance electronics cooling devices, where stability under continuous operation is essential.

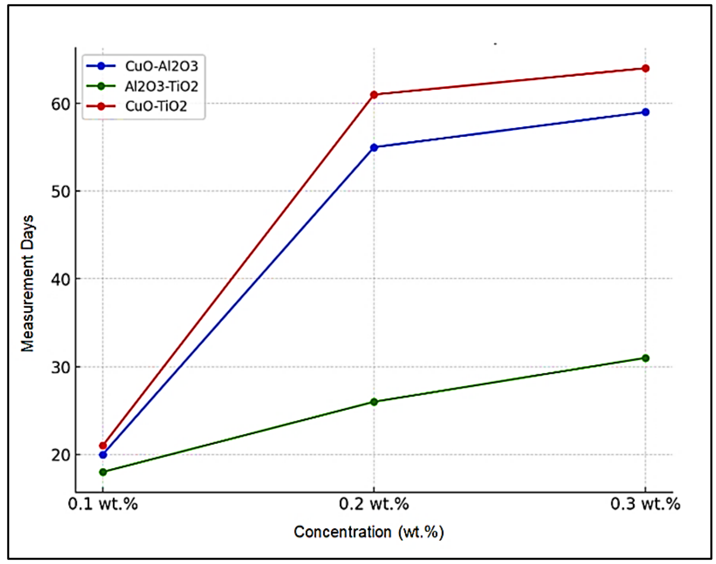

Figure 9: Effect of Effect of adding NaHCO3 on enhancing the stability of hybrid-nanofluid

Conclusion

This study investigates the stability of Al_2O_3, CuO, and TiO_2 nanoparticles suspended in distilled water (DW) at three concentrations: 0.1 wt.%, 0.2 wt.%, and 0.3 wt.%. Surfactants and ultrasonic treatment were applied to enhance dispersion. The primary objective was to evaluate sedimentation stability using carboxymethyl cellulose (CMC) and sodium bicarbonate ($NaHCO_3$), which is important for maintaining thermal properties and efficiency in nanofluids under the tested conditions. The conclusions are specific to nanofluids prepared with distilled water as the base fluid. Based on the experimental data, the following findings are presented:

- CMC and $NaHCO_3$ surfactants significantly reduced sedimentation rates in the tested nanofluids.
- CuO/DW nanofluids at 0.3 wt.% showed excellent stability, with minimal sedimentation after 58 days; stability extended to 77 days with CMC addition.
- Al_2O_3 nanofluids showed moderate stability improvements with CMC.
- TiO_2 nanofluids exhibited improved sedimentation duration from 30 to 50 days with CMC, despite relatively lower baseline stability.

- Hybrid nanofluids ($CuO-Al_2O_3$/DW, $Al_2O_3-TiO_2$/DW, $CuO-TiO_2$/DW) showed rapid sedimentation without surfactants.
- $NaHCO_3$ increased stability by raising pH, affecting electrical potential, enhancing diffusion, and reducing aggregation, leading to long-term stability in hybrid nanofluids.
- Both surfactants contributed to more uniform nanoparticle dispersion within the distilled water base fluid.
- $NaHCO_3$ demonstrated potential for applications requiring long-term stability and optimal heat transfer in distilled water-based nanofluids.

In summary, this study utilized carboxymethyl cellulose (CMC), an anionic surfactant, along with sodium hydrogen carbonate ($NaHCO_3$) as stabilizing agents. While these additives provided effective dispersion and stability for the nanofluids, the exclusion of non-ionic surfactants limits the generalizability of the results. Although the findings demonstrate the effectiveness of CMC and $NaHCO_3$ in enhancing nanofluid stability under ambient conditions, several limitations should be acknowledged. The scalability of surfactant-assisted nanofluid preparation for industrial applications remains uncertain, and associated cost implications could affect feasibility. Furthermore, the stability of surfactants under elevated temperatures typical of many thermal systems is a critical concern, as degradation may reduce long-term effectiveness.

Future work

Further research could focus on:

- Future studies should consider evaluating a broader range of surfactant types, including non-ionic variants, to assess their comparative effectiveness in nanofluid stabilization.
- Optimizing surfactant concentrations and pH adjustments for each nanofluid type.
- Exploring the thermal conductivity, viscosity, and other thermophysical properties at various concentrations to assess the best-performing nanofluid composition under specific conditions.
- Assessing the long-term stability of the nanofluids with various environmental conditions or cyclic loading, this is essential for practical applications. Although, evaluate the effectiveness of surfactants at different temperature ranges to ensure nanofluid stability in practical thermal systems.
- Future studies should investigate the specific interactions between surfactants and nanoparticles such as physical adsorption or covalent bonding as these may significantly influence nanofluid stability.

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