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SYNTHESIS OF ZnO NANOPARTICLES AND THEIR NANOFLUID STABILITY IN THE PRESENCE OF A PALM OIL-BASED PRIMARY ALKYL SULPHATE SURFACTANT FOR DETERGENT APPLICATION

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ABSTRACT

ZnO nanoparticles were successfully synthesized by a solochemical method using zinc chloride as the precursor in a sodium hydroxide solution with $ZnCl_2$:NaOH ratios of 1:2 and 1:3. The effects of the thermal treatment on the functionalities of the nanoparticles were investigated by comparing calcined ZnO with uncalcined ZnO. Calcined ZnO underwent a drying process at 120°C, followed by calcination at 500°C, while uncalcined ZnO underwent the drying process only. The synthesized nanoparticles were characterized by XRD and FESEM-EDX analysis. The photoactivity of synthesized ZnO was evaluated through methylene blue degradation. In addition, ZnO nanofluids were synthesized by dispersing nanoparticles into the base fluid. The nanofluidic stability in the presence of a Palm Oil-Based Primary Alkyl Sulphate (palmPAS) surfactant were investigated using a spectrophotometer UV-vis with varied PalmPAS concentrations. XRD and FESEM analysis showed that the nanoparticles exhibited a hexagonal wurtzite structure, and confirmed that the particle size increased on calcination. All the synthesized ZnO nanoparticles exhibited good photoactivity under UV light irradiation due, to some extent, to their good crystallinity. The calcined ZnO from the $ZnCl_2$:NaOH ratio of 1:3 offered the best photocatalytic performance compared to its ZnO counterparts. It was also found that the nanofluids of uncalcined ZnO from the $ZnCl_2$:NaOH ratio of 1:3, at a ZnO:palmPAS ratio of 1:9, offered the best stability.

Keywords: Detergent; Nanofluid stability; PalmPAS surfactant; Solochemical method; ZnO

1. INTRODUCTION

Conventional detergents are generally derived from fossil-based petroleum and are difficult to decompose, causing major problems to the environment. Bio-based surfactants are expected to be able to serve as substitutes for petroleum-based ones. Many advantages can be claimed for the use of bio-based surfactants, including biodegradability, low toxicity, and compatibility with people and the environment (Sekhon, 2013). In terms of detergency, the ability of surfactants/detergents can be improved by introducing additives, such as semiconducting photocatalysts. A series of metal oxides such as TiO_2, MgO, and ZnO have been developed for the degradation of organic pollutants in the presence of light illumination (Guo et al., 2011). Another study has used a doped metal oxide such as C-N-titania (Slamet et al., 2017). In fact, its composites, such as CNTs-titania have also been utilized for such applications (Wibowo et al., 2015).

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Along with TiO_2, ZnO is recognized as one of the most studied photocatalysts and has been often used in a wide range of applications. The advantages of ZnO include its cost effectiveness, large specific surface area, low toxicity, and high volume of pores (Franklin et al., 2007). Besides its excellent photoactivity in degrading organic pollutants, the antibacterial properties of ZnO against bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* are also renowned (Dobrucka & Długaszewska, 2016), and may be beneficial in improving the performance of detergents in the form of nanofluids.

For commercial nanofluidic detergent applications, synthesis of ZnO nanoparticles through a simple and cost-effective method is preferred. Different morphologies of ZnO nanoparticles can be produced by both chemical and physical methods. Physical methods usually involve complicated processes, severe operating conditions, and sophisticated equipment. The solochemical method is one of the chemical processes; it is cost effective and simple, and can be implemented to produce ZnO nanoparticles. In this process, chemical reactions of the zinc precursor in a heated alkaline solution are conducted at a controlled temperature (Vaezi & Sadrnezhaad, 2007; Gusatti et al., 2010). Owing to its simplicity and versatility, the solochemical method is a promising approach to commercial production of ZnO.

Another issue in the context of nanofluidic systems is the stability of the nanoparticles dispersed in the medium. Addressing such a topic is of great importance, because ZnO nanofluids have a tendency to agglomerate, interrupting their effectiveness as photocatalysts. Several factors affect nanoparticle stability, including pH, ionic strength, particle surface chemistry, and interactions of nanoparticles with other pollutants and natural organic molecules (Baalousha et al., 2008; Jiang et al., 2009; Molina et al., 2011; Omar et al., 2014). Aggregates or agglomerates of nanoparticles and microparticles are formed because of Van der Waals force or other attractive forces (Chabni et al., 2011). Agglomeration is a reversible process and in most cases can be broken down with sonication or homogenization, or the addition of ions (changing H^+) into the system (Berg et al., 2009).

A study has been conducted by Tso et al. (2010) on the stability of ZnO nanoparticles in waste water, showing that they can retain their nanoparticle size even after hours of suspension, due to the existence of organic colloids, such as humic substances or surfactants in the water. The results of Tso et al. are in line with those of Keller et al. (2010), who reported that the sedimentation rate is quite high when ZnO is dispersed on natural aqueous matrices, where the total organic content is low and ionic strength is high. Several surfactants have been employed in ZnO nanofluidic systems, such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and sodium carboxymethyl cellulose (NaCMC). Marsalek (2014) suggests that adding CTAB improves ZnO stability around neutral pH, while adding that NaCMC does not significantly affect the stability. In the same report, it was also suggested that adding SDS improves stability around alkaline pH. Brine was used in another study with the addition of sodium dodecyl sulfate, sodium dodecylbenzenesulfonate and oleic acid at pH 2, and it was revealed that all the surfactants were able to improve the stability of the nanoparticles (Adil et al., 2016).

In this paper, we report the effects of natural-based surfactants, specifically palm-oil based primary alkyl sulphates (palmPAS) on the stability of ZnO nanofluids, which, to our knowledge, has not been studied before. The study investigates the stability of ZnO nanofluids in the presence of palmPAS. ZnO nanoparticles were synthesized via a solochemical method and the photoactivity of ZnO was evaluated via degradation of methylene blue. This report specifically addresses a simple way of synthesizing ZnO nanoparticles and evaluates the stability of their nanofluid in the presence of palmPAS. Further research on detergent formulation and performance will be made in a subsequent study.

2. METHODOLOGY

$ZnCl_2$ and NaOH were acquired from Merck Chemicals, aquadest was acquired from Wiloso Chemicals, palmPAS was acquired from Kao Chemicals, and TiO_2 P25 was acquired from Evonik. All the chemicals were of analytical grade and used as received.

2.1. Synthesis of ZnO Nanoparticles

An amount of $ZnCl_2$ was prepared in 200 ml aquadest to produce a 0.5 M solution, while 1 M NaOH was prepared separately in 200 ml aquadest with constant stirring. The NaOH solution was heated to 90°C and the $ZnCl_2$ solution was slowly added into the hot NaOH solution while the temperature was maintained at 90°C for 2 hours. The nanoparticles formed were then centrifuged and washed using aquadest several times, followed by drying at 120°C for 1 hour. Subsequently, they were ground using a pestle and mortar. Half of the nanopowders then were calcined at 500°C for 2 hours.

2.2. Characterization of ZnO Nanoparticles

The nanoparticles were characterized for their crystallite structure using a PANalytical Empyrian X-Ray Diffractometer with Cu k-α radiation (λ = 0.15406 nm). Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) were performed using a Focused Ion Beam JEOL JIB-4610F.

2.3. Photocatalytic Evaluation

Methylene blue (MB) photodegradation was examined as a model reaction to evaluate the photocatalytic activities of ZnO. The photocatalytic experiments were performed using a mercury lamp as a light source. 0.1 g of synthesized ZnO and 5 ml of 10 ppm methylene blue were added into a vessel. Commercial TiO_2 nanoparticles were used as a benchmark for the photocatalytic performance. Subsequently, the vessels were put inside a photoreactor prototype. Every hour, each vessel was moderately shaken to redistribute the nanoparticles. A photographic method and spectrophotometer were used to investigate the photocatalytic activities. The photographic method was performed by visually comparing the color of each vessel and a spectrophotometer UV-vis was used to evaluate their absorbance before and after 6-hour photoreaction.

2.4. Preparation of ZnO Nanofluids

Palm oil-based primary alkyl sulphate (PalmPAS) surfactants were added into 100 ml aquadest with constant stirring. 0.1 g of uncalcined ZnO nanoparticles were directly poured into the palmPAS solution, stirred for 30 minutes and dispersed by ultrasonication for 30 minutes. The PalmPAS:ZnO ratios varied between 1:1, 1:5, and 1:9. This procedure was followed for ZnO from the $ZnCl_2$:NaOH ratio of 1:2 and ZnO from the $ZnCl_2$:NaOH ratio of 1:3 for both uncalcined and calcined ZnO nanoparticles. ZnO from the $ZnCl_2$:NaOH ratio 1:2 and ZnO from the $ZnCl_2$:NaOH ratio of 1:3 are subsequently reffered to as ZnO 1:2 and ZnO 1:3 respectively.

2.5. Nanofluidic Stability Evaluation

Nanofluidic stability was measured using an Agilent Cary 60 UV-Vis Spectrophotometer by evaluating the absorbance of the nanofluids periodically for three hours.

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnO Nanoparticles

3.1.1. XRD analysis result

According to the x-ray diffraction patterns in Figure 1, the ZnO samples reveal sharp and narrow peaks, indicating good crystallinity. The observed peaks conform to 100, 002, 101, 102, 110, 103, 200, 112, and 201 Miller indices, which correspond to a hexagonal wurtzite structure (ICSD card no. 57 450), similar to those reported by Gusatti et al. (2010). The average crystallite size of the samples was determined using the Debye-Scherrer formula (Cullity & Weymouth, 1957):

$$D = \frac{k.\lambda}{\beta.\cos\theta} \tag{1}$$

where D is the average crystallite size in nm, k is a shape factor constant equal to 0.9, λ is the wavelength of the x-ray used (Cu k-α radiation = 1.5406Å), β is the full width at half maximum (FWHM) of the (101) peak in radians, and θ is the Bragg angle in radians.

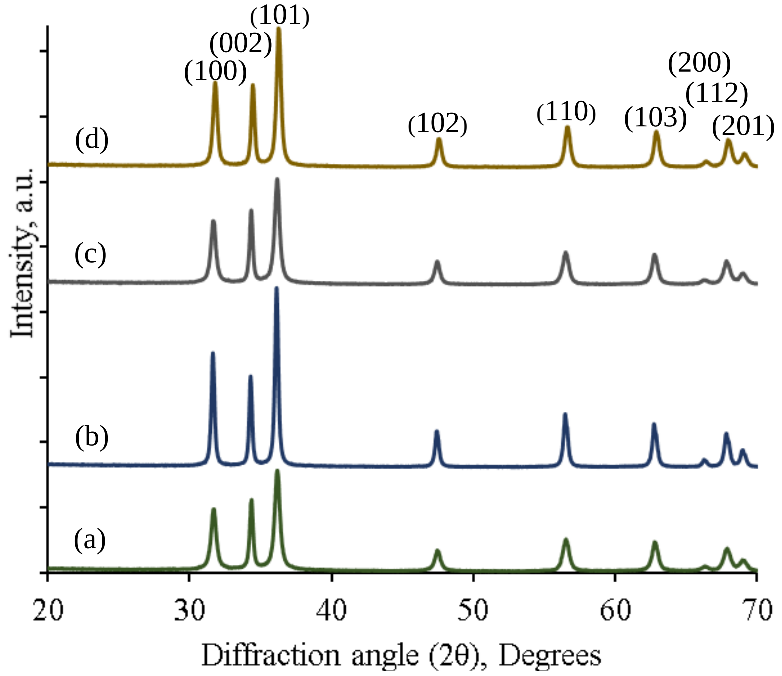

Figure 1 XRD pattern of the ZnO samples prepared at 90°C: (a) ZnO 1:2 uncalcined; (b) ZnO1:2 calcined; (c) ZnO 1:3 uncalcined; and (d) ZnO 1:3 calcined

Table 1 Crystallite size of synthesized samples

Sample	Crystallite size (nm)
ZnO 1:2 uncalcined	30
ZnO 1:2 calcined	36
ZnO 1:3 uncalcined	27
ZnO 1:3 calcined	27

*Estimated from Scherrer equation

It is shown in Table 1 that uncalcined ZnO has a slightly smaller crystallite size than the calcined ZnO. This can be attributed to the fact that the synthesized ZnO nanoparticles already have good crystallinity, even without calcination. This result is in line with previous studies in which a solochemical process produced nanoparticles with good crystallinity (Vaezi & Sadrnezhaad, 2007). Moreover, it is well known that calcination can further improve crystallinity and crystallite size. Heat that is supplied during calcination increases the kinetic energy of the particles. Higher kinetic energy leads to an increase in the probability of inter-crystal collisions, as well as the initiation of particle growth. It is also observable in the FESEM results (Table 2) that particle size increases after calcination. A previous study has also confirmed that the degree of crystallinity and particle size increased with an increasing calcination temperature (Al-Hada et al., 2014).

3.1.2. FESEM-EDX analysis result

The FESEM images in Figure 2 show that both uncalcined and calcined ZnO are of irregular spherical shapes. Agglomeration is observed due to the interaction of nanoparticles during both synthesis and storage. Aggregation of commercial nanoparticles during prolonged storage was also reported in a previous study (Tso et al., 2010). EDX analysis was performed to investigate the chemical composition of the ZnO nanoparticles. It can be seen in Table 3 that Na are incorporated in the nanoparticles, which most likely originated from the use of a high concentration of NaOH during synthesis. Similar results were also found with other synthesis methods using a lower NaOH concentration by Aneesh et al. (2007), who reported that the amount of residual Na are proportional to the amount of NaOH used.

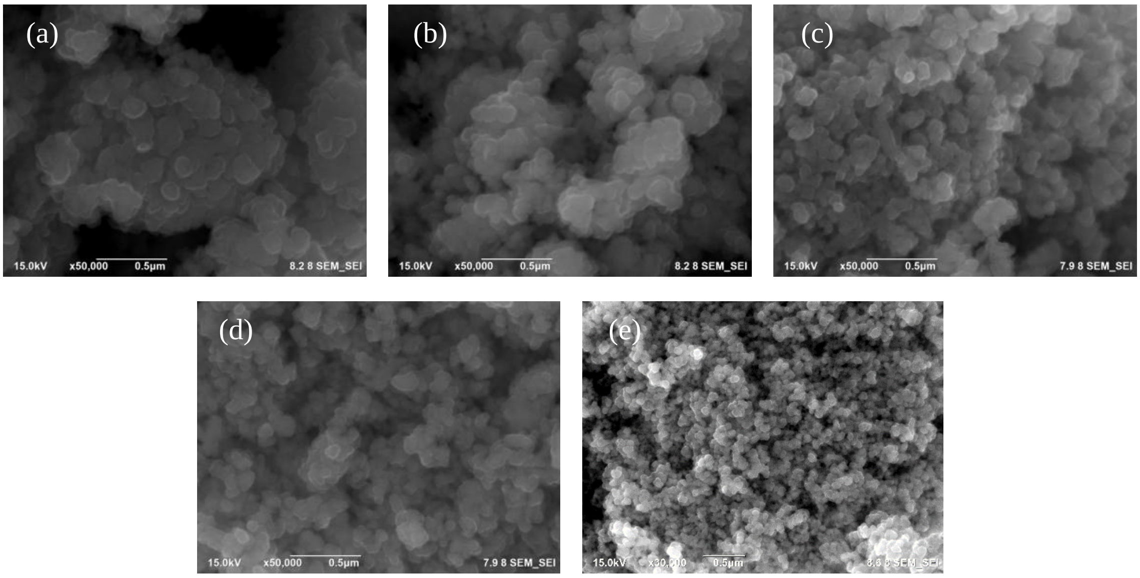

Figure 2 FESEM images of the ZnO samples prepared at 90°C: (a) $ZnCl_2$:NaOH 1:2 uncalcined; (b) $ZnCl_2$:NaOH 1:2 calcined; (c) $ZnCl_2$:NaOH 1:3 uncalcined; (d) $ZnCl_2$:NaOH 1:3 calcined; and (e) Commercial TiO_2

Table 2 Average nanoparticles size

Sample	Average particle size (nm)
ZnO 1:2 Uncalcined	87
ZnO 1:2 Calcined	96
ZnO 1:3 Uncalcined	77
ZnO 1:3 Calcined	83
TiO_2 P25	66

*Estimated from FESEM data

Table 3 Elemental composition of ZnO nanoparticles

Sample	Elemental composition, % Weight			
	Zn	O	Na	Cl
ZnO 1:2 Uncalcined	72.54	17.90	8.88	0.72
ZnO 1:2 Calcined	70.53	19.20	9.90	0.40
ZnO 1:3 Uncalcined	75.74	16.71	7.27	0.32
ZnO 1:3 Calcined	72.58	18.12	9.07	0.22

* Obtained from EDX analysis

3.2. Photocatalytic Evaluation

Figure 3 shows a visual observation of methylene blue photo-degradation by ZnO. It was revealed that even without calcination, ZnO nanoparticles exhibited decent photocatalytic activity due to their good crystallinity, corroborating what is confirmed by XRD analysis. Upon calcination, the photocatalytic activity is improved, as shown in Figure 3. However, the synthesized ZnO nanoparticles exhibit inferior photoactivity when compared to the commercial TiO_2 nanoparticles used in this study. It can be seen in Table 2 that the particle size of the commercial TiO_2 is smaller than that of the synthesized ZnO. Average particle size is related to surface area; i.e., a smaller size of nanoparticles constitutes a higher surface area (Gonçalves et al., 2017). Corroborative data were found using BET analysis, estimating the surface area of the calcined ZnO 1:3 sample. It was found that its surface area was *ca.* 42.728 m^2/g, considerably lower than that of the TiO_2 nanoparticles, which was 53.6 m^2/g (Slamet et al., 2005). Besides the effect of surface area, impurities incorporated in the ZnO nanoparticles could also contribute to the limited photocatalytic activity. Giraldi et al. (2012) suggest that impurities adsorbed on the surface of nanoparticles might occupy the adsorption sites which are otherwise designated for photocatalytic reactive sites. It is therefore expected that ZnO 1:3 would offer better photoactivity than ZnO 1:2, because the former has fewer impurities on its surface, as shown in Table 4. In the case of the ZnO 1:3 sample, the calcination process slightly enhanced its photoactivity, while the ZnO 1:2 sample offered inferior photoactivity compared to its uncalcined counterpart. The calcination process improves particle crystallinity, leading to higher photoactivity, but also increases the crystallite size and may cause agglomeration, which leads to lower photoactivity. It is then stipulated that in terms of photocatalyst calcination, adjustment is always performed as a trade-off between enhancement of crystallinity and inhibition of excessive crystallite growth and agglomeration.

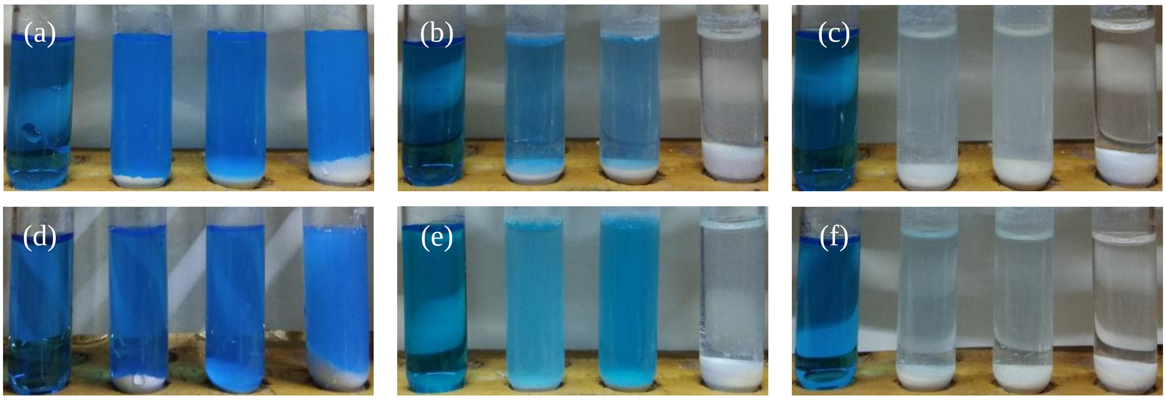

Figure 3 Photodegradation test of methylene blue: (a) ZnO 1:2 at 0 minutes; (b) ZnO 1:2 at 180 minutes; (c) ZnO 1:2 at 360 minutes; (d) ZnO 1:3 at 0 minutes; (e) ZnO 1:3 at 180 minutes; and (f) ZnO 1:3 360 minutes. Left to right: no catalyst, uncalcined ZnO, calcined ZnO and TiO_2 P25

Table 4 Photodegradation test of the synthesized ZnO nanoparticles

Sample	Absorbance 0 minutes	Absorbance 360 minutes	Degradation (%)
No catalyst	1.8180	1.8115	0.36%
ZnO 1:2 Uncalcined	1.8914	0.3014	84.06%
ZnO 1:2 Calcined	1.8896	0.3462	81.68%
ZnO 1:3 Uncalcined	1.8176	0.2309	87.30%
ZnO 1:3 Calcined	1.7958	0.1023	94.30%
TiO_2 P25	1.7396	0.0559	96.79%

3.3. Nanofluid Stability Evaluation

The addition of surfactants into a nanofluid is expected to increase its stability due to the adsorption of anionic surfactant. The hydrophobic tail of palmPAS attached to the surface and the negative charged head interacting with water result in more negatively charged ZnO nanoparticles, as well as the formation of an electrically charged double layer. Particles of similar charge are prone to induce a repulsive force between each other, hence hindering agglomeration, which in turn improves the stability of nanofluids. At some point, adding an excessive amount of surfactant will result in the formation of micelles. These micelles tend to settle due to gravity, hence disrupting the system or even dragging the nanoparticles while on their way to the bottom. The study of the effect of palmPAS concentration on the stability of nanofluids is focused on ZnO 1:3, since it has the highest photoactivity amongst the ZnO samples. Figure 4 illustrates the effect of the palmPAS surfactant on the stability of the ZnO nanoparticles over time. It can be seen that the nanofluid with a ZnO:palmPAS ratio of 1:9 has good stability, because the surfactant added into the nanofluid has not yet reached its saturation point. A previous study documented that the addition of excessive free-surfactant led to lower nanofluidic stability (Adil et al., 2016).

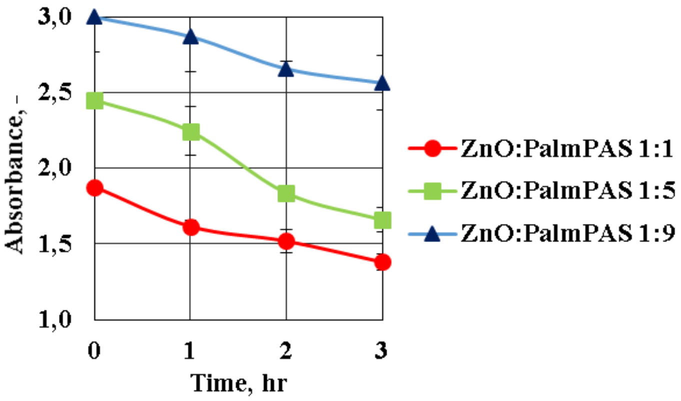

Figure 4 Effect of PalmPAS concentration on the stability of uncalcined ZnO 1:3 nanofluid over time

The effect of the calcination of the nanoparticles on nanofluidic stability is illustrated in Figure 5. It shows that calcination could reduce the stability of nanofluids due to the relatively large size of crystals, hence leading to a decent degree of agglomeration.

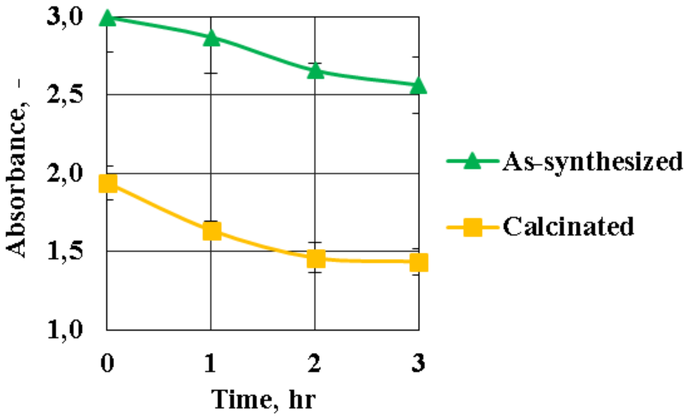

Figure 5 Effect of the calcination process on the stability of ZnO 1:3 nanofluid with a ZnO:palmPAS ratio of 1:9 over time

Figure 6 depicts the effect of the $ZnCl_2$:NaOH ratio during ZnO nanoparticle synthesis on nanofluidic stability. It was found that ZnO 1:3 is more stable than ZnO 1:2, attributable to the smaller particle size. Particle size plays an important role in the stability of nanofluids. According to Stokes's law, sedimentation velocity is positively correlated to particle size, so reducing this size can improve nanofluid stability. Iyahraja and Rajadurai (2016) also obtained similar results, with smaller particle size leading to more stable nanofluids. It must be taken into account that smaller particles have a higher surface area and increase the probability of aggregation (Wu et al., 2009).

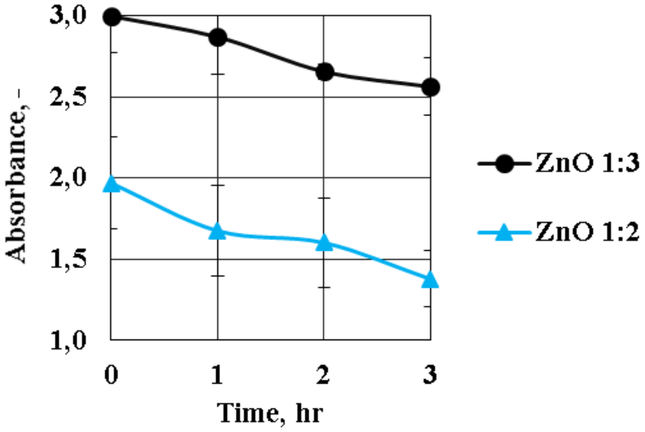

Figure 6 Effect of the $ZnCl_2$:NaOH ratio during ZnO synthesis on nanofluid stability over time

4. CONCLUSION

ZnO nanoparticles were successfully synthesized using a simple solochemical process. XRD analysis shows that the nanoparticles have a hexagonal wurtzite structure with good crystallinity. Estimated particle size from the FESEM data is shown to increase after the calcination process. Calcined ZnO with a $ZnCl_2$:NaOH ratio of 1:3 has optimum photocatalytic activity compared to the other synthesized ZnO samples. A bio-based surfactant (palmPAS) can be used to improve the stability of ZnO nanofluids, with uncalcined ZnO having the $ZnCl_2$:NaOH ratio of 1:3 and ZnO:palmPAS ratio of 1:9 offering the best stability.

5. ACKNOWLEDGEMENT

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