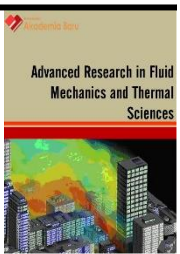
Penerbit
Akademia Baru

Journal of Advanced Research in Fluid
Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Characterization and Nanofluid Stability of $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA Nanoparticles

Anis Arisa Roslan[1,*], Hasnah Mohd Zaid[1], Siti Nur Azella Zaine[1], Mursyidah Umar[2], Beh Hoe Guan[1]

[1] Department of Fundamental and Applied Science, Centre of Innovative Nanostructure and Nanodevices (COINN), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
[2] Department of Petroleum Engineering, Universitas Islam Riau, Pekanbaru, Riau, Indonesia

ARTICLE INFO

Article history:
Received 2 May 2020
Received in revised form 10 August 2020
Accepted 15 August 2020
Available online 23 November 2020

ABSTRACT

Nanofluid contains nanoparticles that enhanced the property of the base fluid. However, the separating layer between the nanoparticles and base fluids may interfere the nanofluids performance. Studies have been made that surface modification of nanoparticles may improve the dispersion of nanoparticles in base fluids. This paper reports the study of the colloidal stability of surface modified nanoparticles using a polymer and an amino-silane. The nanoparticles were prepared by one-step and two-step methods using cobalt iron oxide nanoparticles with brine solution and deionized water as the base fluids. Functionalization by surface modification of the nanoparticles to enhance the nanofluids stability was carried out using (3-aminopropyl) triethoxysilane (APTES) and polyvinyl alcohol (PVA). Characterization using Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscope (FESEM) and X-ray Powder Diffraction (XRD) were performed to study the functionality and morphology of the synthesized nanoparticles. The extra IR peaks such as Si-O-Si at 1063 cm^{-1} for $CoFe_2O_4$-APTES and C=O at 1742 cm^{-1} for $CoFe_2O_4$-PVA showed that there are additional elements in the cobalt ferrite due to functionalization. The size of synthesized $CoFe_2O_4$-APTES ranged between 15.99 nm to 26.89 nm while $CoFe_2O_4$-PVA is from 25.70 nm to 54.16 nm. The stability of the nanofluid were determined via zeta potential measurements. $CoFe_2O_4$-APTES nanofluid has zeta potential of -35.7 mV compared to $CoFe_2O_4$-PVA at -15.5 mV.

Keywords:
Nanofluid; nanoparticles; stability; polymer; silane

1. Introduction

The preparation of highly stabilized nanoparticles in base fluid, especially brine solution, is always a real challenge. Many characteristics which include the size of nanoparticles, suitable acidity or basicity, thermal stability and adequate concentration have to be met. The elemental features are affected by the synthesis methods and by the properties of the system physically and chemically. For

---

[*] *Corresponding author.*
E-mail address: roslan_18003534@utp.edu.my

https://doi.org/10.37934/arfmts.78.1.7987

example, the size of nanoparticle depends on the temperature and duration of heating during the synthesis, which influences the nanofluid stability. The bigger the size of nanoparticles, the tendency for the nanoparticles to agglomerate at a faster rate is higher.

The methods used to synthesize nanoparticles also affect the rate of dispersion of nanoparticles in base fluids [4]. One-step method and two-step method give different results in term of the stability of nanofluids [12]. Two-step method is the synthesis of nanoparticles in powder form and preparation of the nanofluids afterwards by dispersing the nanoparticles in base fluids with the aid of magnetic force agitation, ultrasonic agitation or other ways of mixing tools. One-step method is when the nanoparticles are synthesized and dispersed simultaneously in the base fluid. Most studies show that one-step method give better results for the stability of nanofluids compared to two-step method. One-step method requires less storage and less heat which result in smaller size nanoparticles. Nanofluid might not perform at its optimum level due to the separating layer between the base fluid and nanoparticles. The base fluid can be any form of liquid, such as oil, water or gas [1].

The formulation of nanofluids from metal oxide nanoparticles is quite popular due to their impressive features [10]. The electronic structure of metal oxide nanoparticles can exhibit as insulator, semiconductor or metallic which may be applied in the fabrication of fuel cells, sensors, microelectronic circuits and catalysts [5]. $CoFe_2O_4$ is one of magnetic nanoparticles that has attracts great interest due to its dynamic thermal parameter and magnetic properties, suitable for applications in catalysis, magnetic fluids, high-density magnetic recording, solar cells, spintronics and data storage [13]. $CoFe_2O_4$ nanoparticles are widely utilized due to their mechanical hardness, chemical stability, electromagnetic performance and excellent cubic magneto crystalline anisotropy [9]. However, due to its high surface area, nanoparticles tend to agglomerate especially in high salinity solvent because of the high ionic strength.

In this study, the stability of nanofluids of different base fluids, namely brine and deionized water, with one-step and two-steps synthesis methods and concentrations were compared. Besides that, the dispersion of surface modified nanoparticles with silane and polymer in base fluid were studied. In this work, surface modification was conducted using water soluble polymer, polyvinyl alcohol (PVA) and amino-silane, (3-aminopropyl) triethoxysilane (APTES).

2. Methodology

The experimental methods consist of the preparation of brine, synthesis of cobalt iron oxide nanoparticles, surface modification, preparation of nanofluids and characterizations. A&D Weighing GR-202 analytical balance was used for all the weight measurements done in this study with precision of up to 0.0001 g.

2.1 Preparation of Brine

Table 1 shows the compounds needed to formulate 1 L of brine to mimic the salinity of sea water. The compounds were purchased from Merck and distilled water as the solvent for brine solution was prepared from Water Still-WS 4L.

Each compound stated in the Table 1 is weighed using analytical balance. The weighed compounds were mixed in enough deionized water such that the resultant volume was 1L and stirred with magnetic stirrer to ensure that the chemicals were dissolved completely. The solution was then filtered with 0.45 mm pore size filter paper.

Table 1
List of compounds for 1L of brine

Compounds	Weight (*mg*)
$CaCl_{22}H_2O$	1330.479
$MgCl_{22}.6H_2O$	10283.569
KCl	720.728
NaCl	24927.525
$NaHCO_3$	216.168
Na_2SO_4	3196.751

2.2 Synthesis of $CoFe_2O_4$ Nanoparticles and Surface Modification

Cobalt nitrate, iron nitrate and sodium hydroxide were purchased from Merck. For the surface coating purposes, polyvinyl alcohol and (3-aminopropyl) triethoxy silane were also obtained from Merck.

2 mol of cobalt nitrate and 4 mol of iron nitrate were dissolved in 15 ml of deionized water. The mixture was stirred for 15 minutes at room temperature with magnetic stirrer. Then, 1M of sodium hydroxide was slowly dropped into the mixture until it reached a pH of 12. After stirring for another 15 minutes, hydrothermal growth by autoclaving was conducted for 5 hours at 200°C. The product was washed by centrifugation.

For surface modification, 3 g of polyvinyl alcohol and (3-aminopropyl) triethoxy silane were mixed in deionized water before adding in the precursors for all of the nanoparticles. After the polymer solution and the precursors of the nanoparticles was stirred, it was sonicated using ultrasonic horn at 200W for 1 minute.

2.3 Preparation of Nanofluids

The nanofluids were prepared by one-step and two-step methods with 0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.% and 0.5 wt.% of nanoparticles dispersed in 10 ml of either brine or deionized water as the base fluids. For the one-step method, the nanoparticles were synthesized and dispersed simultaneous into the base fluid. During washing, it was centrifuged with ethanol 3 times and with brine solution during the fourth time. In the two-step method, the powder form of the synthesized nanoparticles was dispersed in the based fluid. During washing, the nanoparticles were centrifuged with ethanol 3 times followed by drying in the oven at 70°C for 10 hours and then dispersed in base fluid by ultrasonic bath.

2.4 Characterizations

The physicochemical properties of the synthesized $CoFe_2O_4$ were characterized by advanced analytical equipment such as Fourier Transform Infrared (Thermo Scientific Nicolet iS50), X-ray Powder Diffraction (Bruker AXS D8), Field Emission Scanning Electron Microscope (Ziess Supra 55 VP) and Zeta Potential (ZP). The synthesized $CoFe_2O_4$ nanoparticles were characterized by X-ray Powder Diffraction (XRD) for its phase peaks. The presence of the polymer and amino-silane in the $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA nanoparticles were analysed by Fourier Transform Infrared (FTIR) peaks. The stability of the prepared nanofluids were observed physically based on the rate of dispersion of nanoparticles in base fluids. The stability of nanoparticles in base fluids were verified by zeta potential analysis. The stability of nanofluids with different chemicals used for surface modification were compared.

3. Results and Discussion

3.1 XRD Results

The XRD pattern of the prepared functionalized $CoFe_2O_4$ were compared with pure $CoFe_2O_4$ as shown in Figure 1. The characteristic peaks at angles 30.40°, 35.71°, 43.40°, 53.75°, 57.27° and 62.81° are indexed as the reflection planes of (220), (311), (400), (422), (511) and (440) respectively confirmed the single-phase inverse spinel structure of $CoFe_2O_4$-PVA nanocrystals when the mentioned synthesis procedure was performed [8]. The additional peaks for $CoFe_2O_4$-PVA showed the additional elements due to functionalization process. However, $CoFe_2O_4$-APTES showed low intensity for every peak which might be due to its amorphous structure. The XRD pattern illustrates that silane group affects the crystal structure of $CoFe_2O_4$.

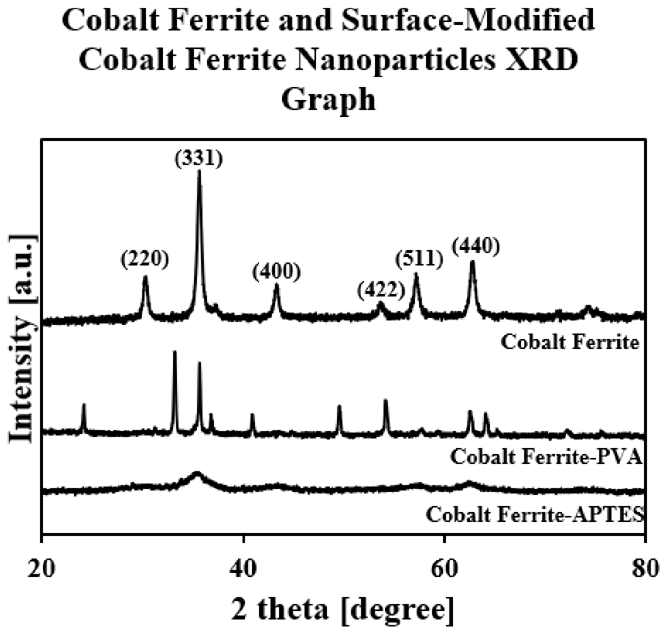


Fig. 1. $CoFe_2O_4$ and Functionalized $CoFe_2O_4$ XRD pattern

3.2 FESEM Imaging

Imaging of the surface-modified nanoparticles was conducted using Field Emission Scanning Electron Microscope (FESEM) at 100k times magnification. The image of $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA are shown in Figure 2.

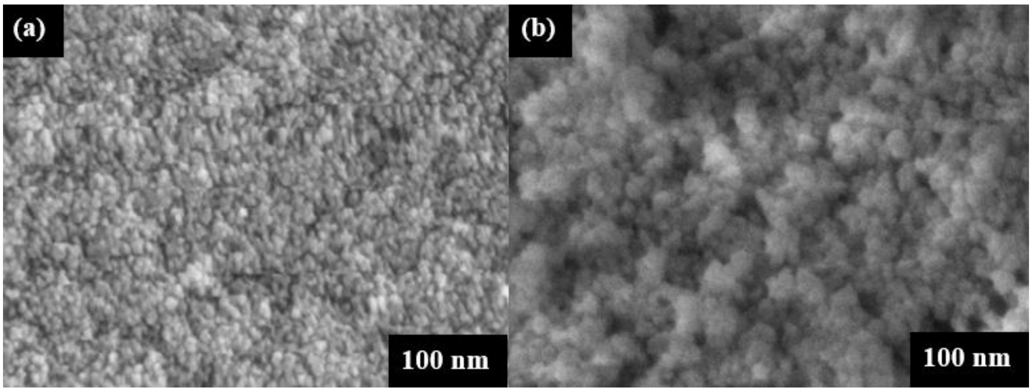


Fig. 2. Size and morphology of (a) $CoFe_2O_4$-APTES and (b) $CoFe_2O_4$-PVA from FESEM

Figure 2(a) shows that the size of the $CoFe_2O_4$-APTES particles ranged from 15.99 nm to 26.89 nm, whereas from Figure 2(b), $CoFe_2O_4$-PVA ranged from 25.70 nm to 54.16 nm. Comparing both images, the morphology of $CoFe_2O_4$-APTES shows less agglomeration. The images show that $CoFe_2O_4$ with APTES functionalization gives better separation among the nanoparticles making the size of $CoFe_2O_4$-APTES nanoparticles smaller than $CoFe_2O_4$-PVA. The size for $CoFe_2O_4$-APTES varies at 10.90 nm while the size variation for $CoFe_2O_4$-PVA is high which is around 28.46 nm.

3.3 FTIR Results

FTIR bands of $CoFe_2O_4$ and polymer-functionalized $CoFe_2O_4$ were observed to be in the range 4000-400cm^{-1} as shown in Figure 3. Pure $CoFe_2O_4$ shows IR peaks at 3400cm^{-1}, 1624 cm^{-1}, 1383 cm^{-1} and 578 cm^{-1}. The Co-O stretching vibration in $CoFe_2O_4$ and octahedral group Fe-O correspond at the 600-500 cm^{-1} range. The bands at 3500-3200 cm^{-1} and 1620 cm^{-1} are assigned due to the stretching and bending modes of H_2O on the surface of the synthesized $CoFe_2O_4$ samples due to drying procedure [6]. $CoFe_2O_4$-APTES shows characteristics for Si-O-Si at 1063 cm^{-1}, -NH at 1630 cm^{-1} and C=N at 1615 cm^{-1} [2]. The main FTIR peaks for $CoFe_2O_4$-PVA are seen at 2927cm^{-1} for -CH_2 asymmetric stretching vibration, 1742cm^{-1} for C=O carbonyl stretch, 1090cm^{-1} for C-O stretching and 833cm^{-1} for C-C stretching vibration [7].

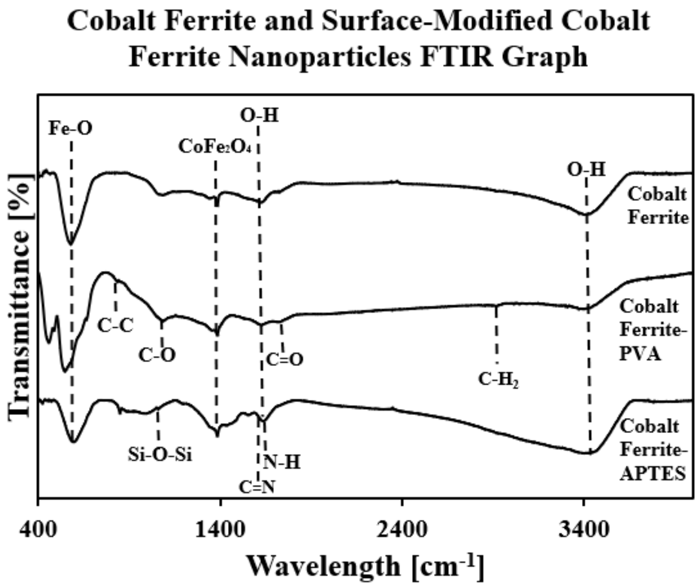


Fig. 3. FTIR spectra for $CoFe_2O_4$ and functionalized $CoFe_2O_4$

3.4 Nanofluids Stability

The prepared nanofluids were observed to compare the stability between those prepared by the one-step and two-step methods. Comparison between the stabilities of the nanofluids in the two different base fluids was also conducted. Nanofluids synthesis methods were studied first before proceeding to the surface modified nanofluids. The colloidal stability of nanofluids from one-step and two-steps synthesis methods from Figure 4 and Figure 5 were compared.

Figure 4 shows the visual observation of $CoFe_2O_4$ nanofluids, synthesized by one-step method with concentrations ranging from 0.1 to 0.5 wt.%. While Figure 5 is the physical observation of $CoFe_2O_4$ nanofluids that have been formulated by two-steps method.

Based on Figure 4(a) and Figure 5(a) the stability of the nanofluids in brine solution shows agglomeration after 6 hours for both one-step and two-step method of nanofluids preparation. On the other hand, the $CoFe_2O_4$ nanofluid in deionized water shows good dispersion even after 4 days.

Hence, from Figure 4 and Figure 5, it is reckoned that the dispersion of nanoparticles was affected by the base fluid since the nanofluids from both synthesis methods showed good stability in deionized water but vice versa in brine solution. However, based on Figure 4(a), the nanofluids at below 0.3 wt.%, the dispersion of nanoparticles still can be seen in the brine solution. Meanwhile, in Figure 5(a), all of the nanofluids from 0.1 to 0.5 wt.% concentration showed two separation with clear liquid at the top and the nanoparticles were already agglomerated at the bottom. Therefore, the formulation nanofluids of the surface modified nanoparticles were done with the one-step synthesis method.

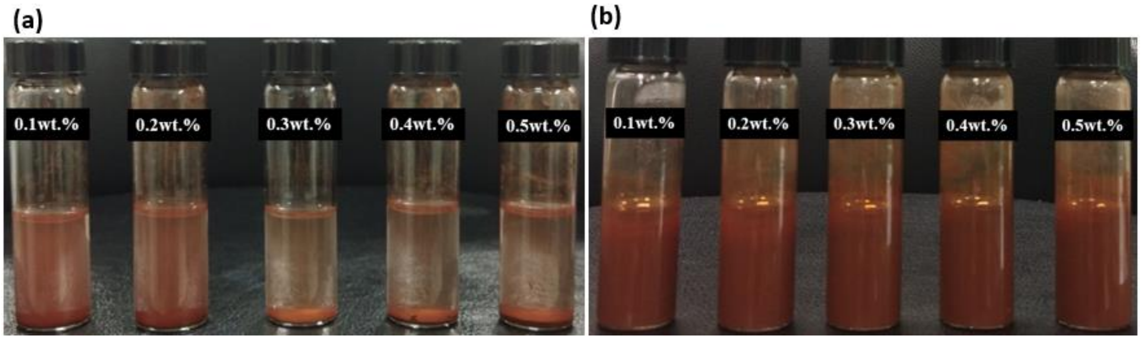


Fig. 4. Visual observation of $CoFe_2O_4$ synthesized by one-step method with 0.1 to 0.5 wt.% concentration in (a) brine solution and (b) deionized water

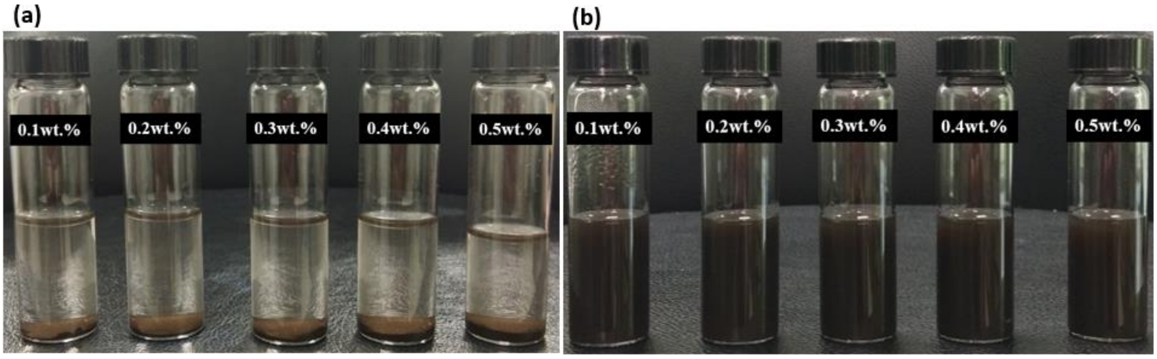


Fig. 5. Visual observation of $CoFe_2O_4$ synthesized by two-steps method with 0.1 to 0.5 wt.% concentration in (a) brine solution and (b) deionized water

Visual observation of $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA synthesized by two-steps method with 0.1 to 0.5 wt.% concentration in brine solution and deionized water is shown in Figure 6 and Figure 7 respectively. The nanofluids prepared in Figure 6(a) and Figure 7(a) were using brine solution as the base fluid while Figure 6(b) and Figure 7(b) used deionized water as base fluid.

$CoFe_2O_4$-APTES nanofluids in Figure 6(a) and $CoFe_2O_4$-PVA nanofluids in Figure 7(a) were prepared with brine solution as base fluid. Both types of nanofluids show two separation layers with clear liquid at the top and brown settlement at the bottom due to agglomeration of the nanoparticles after 13 hours. From Figure 7(b), $CoFe_2O_4$-PVA nanofluids with brine solution as base fluid and $CoFe_2O_4$-APTES nanofluids with deionized water as base fluid from Figure 6(a) show two separation layers with cloudy liquid at the top and brown settlement at the bottom. at 0.1 to 0.3 wt.%. From physical observation of the stability of nanofluids, the optimum concentration is below 0.3wt%. Hence, the zeta potential analysis for the nanofluids stability were done at 0.25 wt.% concentration.

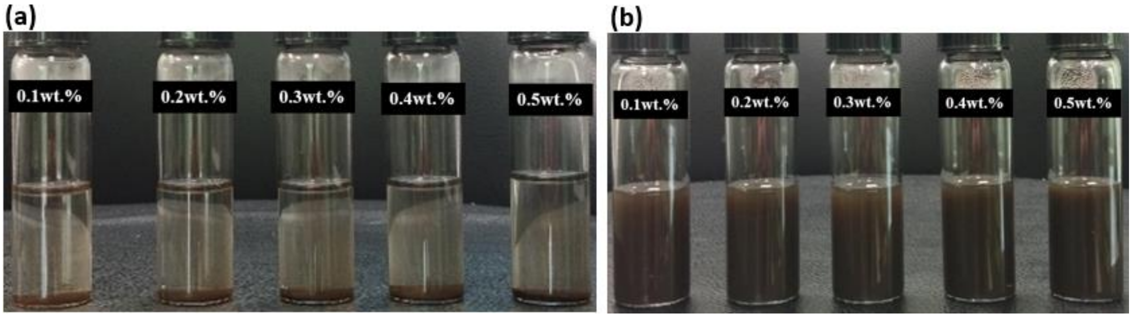


Fig. 6. Visual observation of $CoFe_2O_4$-APTES nanofluids in (a) brine solution and (b) deionized water

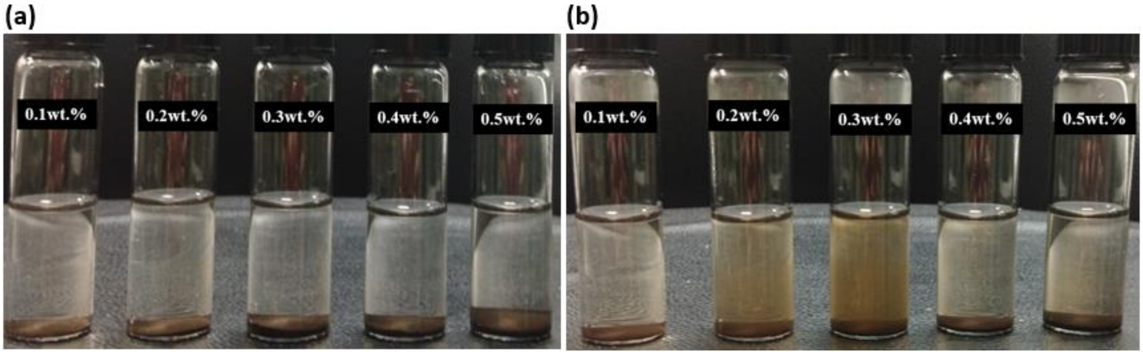


Fig. 7. Visual observation of $CoFe_2O_4$-PVA nanofluids in (a) brine solution and (b) deionized water

Zeta potential analysis was conducted on nanofluids at 0.25wt% concentration in 10ml of brine solution and deionized water respectively. From the results as shown in Table 2, the dispersion of nanoparticle in deionized water is better compared to brine solution due to the charge of ions presence in the saline water, which is reflected by the higher value of zeta potential.

The charges of the ions in brine solution might interrupt the charges of the nanoparticles in the fluid, resulting in lower zeta potential value as shown in Table 2. The electrophoretic mobility measurements made by zeta potential analysis obtained might be distorted due to high salt concentrations of the base fluid. High salinity solvent gives high current which might cause the Joule heating. The electrical double layer collapses because of the high ionic strength which leads to low zeta potential value [11]. From Table 2, it can be deduced that $CoFe_2O_4$-APTES may give better dispersion of nanofluid compared to $CoFe_2O_4$-PVA since the zeta potential value is above +30mV [3].

Table 2
Zeta potential value of 0.25wt% $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA in brine solution and deionized water

Sample	Zeta Potential Value for Brine Solution as Base Fluid (mV)	Zeta Potential Value for Deionized Water as Base Fluid (mV)
$CoFe_2O_4$-APTES	-10.7	-35.7
$CoFe_2O_4$-PVA	-7.19	-15.5

Figure 8(a) shows the distribution peaks for three runs of zeta potential analysis for 0.25wt% $CoFe_2O_4$-APTES in deionized water. From the peaks, the values obtained are -30.9mV, -36.8mV and -39.3mV. Hence, it can be deduced that the average zeta potential value for CoFe2O4-APTES is -35.7mV. The zeta potential value for $CoFe_2O_4$-APTES shows good stability since it is above 30mV.

Meanwhile, Figure 8(b) shows the distribution peaks for three runs of zeta potential analysis for 0.25wt% CoFe2O4-PVA in deionized water. From the peaks, the values obtained are -14.6mV, -

16.3mV and -15.7mV. Hence, it can be deduced that the average zeta potential value for CoFe2O4-PVA is -15.5mV. Comparing obtained average values from both colloidal stability of surface modified nanoparticles, it can be concluded that APTES functionalization for $CoFe_2O_4$ nanoparticles gives better stability for nanofluids as compared to PVA. The polymer coating suppressed the charges, as polymer itself carries no charge. The adhesion of PVA on the surface of the synthesized $CoFe_2O_4$ might cause the charge to facilitate the adsorption of polymer, and hence, gives lesser value of zeta potential.

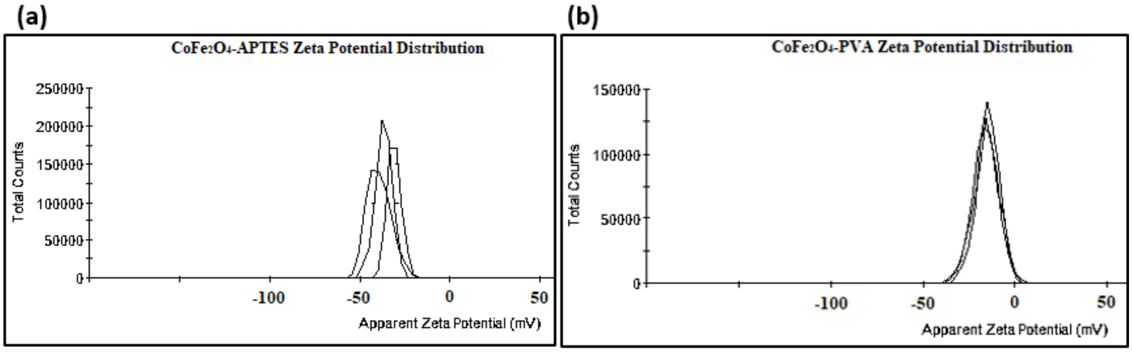


Fig. 8. Zeta Potential Distribution for (a) $CoFe_2O_4$-APTES and (b) $CoFe_2O_4$-PVA

4. Conclusion

The surface modifications of $CoFe_2O_4$ nanoparticles using APTES and PVA were confirmed by FESEM and FTIR analyses. The IR peaks for $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA showed additional functional groups due to the functionalization process. From FESEM images, the size of $CoFe_2O_4$-APTES and $CoFe_2O_4$-PVA nanoparticles are 15.99 nm and 25.70 nm, respectively. $CoFe_2O_4$ nanoparticles which are surface-modified with APTES and PVA, and the nanofluids prepared one-step method showed better dispersion as observed physically and the values of zeta potential. $CoFe_2O_4$-APTES nanofluid has zeta potential value of -35.7 mV while $CoFe_2O_4$-PVA has zeta potential of -15.5mV. The colloidal stability for $CoFe_2O_4$-APTES is above 30mV which deduce that APTES functionalization optimize the dispersion of $CoFe_2O_4$ nanoparticles in base fluid.

Acknowledgements

The authors would like to acknowledge UTP Graduate Assistantship (GA) scheme, International Grant UIR-UTP 015ME0-042 and Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS for their support in the research work.

References

[1] Afolabi, Richard O. "Enhanced oil recovery for emergent energy demand: challenges and prospects for a nanotechnology paradigm shift." *International Nano Letters* 9, no. 1 (2019): 1-15. https://doi.org/10.1007/s40089-018-0248-0

[2] Aneja, Karanveer S., Sivasambu Bohm, A. S. Khanna, and HL Mallika Bohm. "Graphene based anticorrosive coatings for Cr (VI) replacement." *Nanoscale* 7, no. 42 (2015): 17879-17888. https://doi.org/10.1039/C5NR04702A

[3] Bahru, Raihana, Abdul Rahman Mohamed, Wei-Ming Yeoh, and Khatijah Aisha Yaacob. "Electrophoretic Deposition of Carbon Nanotubes on Heat Spreader for Fabrication of Thermal Interface Materials (TIM)." *Sains Malaysiana* 46, no. 7 (2017): 1075-1082.https://doi.org/10.17576/jsm-2017-4607-09

[4] Choudhary, Rajesh, Deepak Khurana, Aditya Kumar, and Sudhakar Subudhi. "Stability analysis of Al2O3/water nanofluids." *Journal of Experimental Nanoscience* 12, no. 1 (2017): 140-151. https://doi.org/10.1080/17458080.2017.1285445

[5] Garcia, M. F., and J. A. Rodriguez. *Metal Oxide Nanoparticles, Brookhaven National Laboratory*. BNL-79479-2007-BC, 2007.

[6] Guerrini, Luca, Ramon A. Alvarez-Puebla, and Nicolas Pazos-Perez. "Surface modifications of nanoparticles for stability in biological fluids." *Materials* 11, no. 7 (2018): 1154. https://doi.org/10.3390/ma11071154

[7] Kharazmi, Alireza, Nastaran Faraji, Roslina Mat Hussin, Elias Saion, W. Mahmood Mat Yunus, and Kasra Behzad. "Structural, optical, opto-thermal and thermal properties of ZnS-PVA nanofluids synthesized through a radiolytic approach." *Beilstein Journal of Nanotechnology* 6, no. 1 (2015): 529-536. https://doi.org/10.3762/bjnano.6.55

[8] Mushtaq, M., M. Imran, S. Bashir, F. Kanwal, and L. Mitu. "Synthesis, structural and biological studies of cobalt ferrite nanoparticles." *Bulgarian Chemical Communications* 48, no. 3 (2016): 565-570.

[9] Shenker, Henry. "Magnetic anisotropy of cobalt ferrite (Co 1.01 Fe 2.00 O 3.62) and nickel cobalt ferrite (Ni 0.72 Fe 0.20 Co 0.08 Fe2O4)." *Physical Review* 107, no. 5 (1957): 1246. https://doi.org/10.1103/PhysRev.107.1246

[10] Suganthi, K. S., and K. S. Rajan. "Metal oxide nanofluids: Review of formulation, thermo-physical properties, mechanisms, and heat transfer performance." *Renewable and Sustainable Energy Reviews* 76 (2017): 226-255. https://doi.org/10.1016/j.rser.2017.03.043

[11] Weiner, Bruce B. "A Review of High Salt Zeta Potential Measurements with the Brookhaven ZetaPALS: Red Blood Cells." *Brookhaven Instruments Corporation Technical Information: USA*, 2010.

[12] Yu, Wei, and Huaqing Xie. "A review on nanofluids: preparation, stability mechanisms, and applications." *Journal of Nanomaterials* 2012 (2012). https://doi.org/10.1080/00304948.2012.657565

[13] Zi, Zhenfa, Yuping Sun, Xuebin Zhu, Zhaorong Yang, Jianming Dai, and Wenhai Song. "Synthesis and magnetic properties of CoFe2O4 ferrite nanoparticles." *Journal of Magnetism and Magnetic Materials* 321, no. 9 (2009): 1251-1255.https://doi.org/10.1016/j.jmmm.2008.11.004