Surface-Functionalized Superparamagnetic Nanoparticles (SPNs) for Enhanced Oil Recovery: Effects of Surface Modifiers and Their Architectures

Munawar Khalil,§† Ghufran Aulia,‡ Emil Budianto,‡ Badrul Mohamed Jan,‡ Saiful Hafiz Habib,§ Zulhelmi Amir,‖ and Muhamad Fazly Abdul Patah‡

†Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Indonesia, 16424 Depok, West Java, Indonesia
‡Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
§Institute of Advanced Technology, University of Putra Malaysia, 43400 Seri Kembangan, Selangor, Malaysia

ABSTRACT: Superparamagnetic nanoparticles (SPNs) have been considered as one of the most studied nanomaterials for subsurface applications, including in enhanced oil recovery (EOR), due to their unique physicochemical properties. However, a comprehensive understanding of the effect of surface functionalization on the ability of the nanoparticles to improve secondary and tertiary oil recoveries remains unclear. Therefore, investigations on the application of bare and surface-functionalized SPNs in EOR using a sand pack were carried out in this study. Here, the as-prepared SPNs were functionalized using oleic acid (OA) and polyacrylamide (PAM) to obtain several types of nanostructure architectures such as OA-SPN, core−shell SPN@PAM, and SPN-PAM. Based on the result, it is found that both the viscosity and mobility of the nanofluids were significantly affected by not only the concentration of the nanoparticles but also the type and architecture of the surface modifier, which dictated particle hydrophilicity. According to the sand pack tests, the nanofluid containing SPN-PAM was able to recover as much as 19.28% of additional oil in a relatively low concentration (0.9% w/v). The high oil recovery enhancement was presumably due to the ability of suspended SPN-PAM to act as a mobility control and wettability alteration agent and facilitate the formation of a Pickering emulsion and disjoining pressure.

INTRODUCTION

The rapid increment in global population has led to a growing need for petroleum products, not only as fuels but also as an essential raw material for many industrial processes. Although recent drops in oil price due to the high supply of crude oil have hampered the exploration of new oil reserves, the application of enhanced oil recovery (EOR) methods is still desired to improve the production of oil from matured fields.1−3 In a typical matured oil field, more than 50% of original oil in place (OOIP) is still unrecovered, and EOR via chemical injections is among the most applied methods to harvest the remaining oil.4−6 Traditionally, various types of chemical injections can be used to recover oil from matured fields, i.e., polymers, surfactants, alkalis, or their binary/ternary mixtures.7−9 In general, the objective of these chemical injections is primarily to reduce the interfacial tension (IFT) between oil and water. By having an ultralow IFT, the residual oil trapped in the porous media can easily be mobilized due to the generation of moving displacement fronts.9 Furthermore, chemical injection is also carried out to alter the wettability of the reservoir rock surface from oil-wet to water-wet. Mohammed and Babadagli reported that this alteration of rock properties could significantly reduce or even eliminate the capillary forces that retain oil in porous media and enables them to be recovered during the EOR process easily.10 However, the utilization of certain types of surfactants and polymers was sometimes unable to effectively attain the required ultralow IFT and sufficient wettability alteration due to extreme reservoir conditions. Besides, most of the currently used surfactants and polymers are made of environmentally unfriendly substances, which require additional cost for postproduction treatment.

Injection of nanoparticle suspension, as opposed to surfactants and polymers, has attracted vast attention as it offers many benefits, such as the ability to significantly improve secondary and tertiary oil recoveries, low cost, excellent stability at extreme reservoir conditions, and environmental friendliness.11 Many works have reported that various types of inorganic nanoparticles such as SiO2, TiO2, Al2O3, ZrO2, and NiO have successfully been applied in EOR.12−16 Besides,
nanoparticle injection is also preferred due to its intrinsic physicochemical properties, depending on the type of the nanoparticles, such as large specific surface area, excellent thermal and electrical conductivities, and the ability to penetrate into remote regions inside the porous media. It is reported that the superiority of these nanoparticles in EOR could be associated with its ability to significantly reduce the IFT and to efficiently alter the wettability of porous media. Recently, a new additional mechanism for the improvement of oil recovery using a nanoparticle-based EOR process has also been reported elsewhere. Using experimental and theoretical approaches, it is reported that the injection of nanoparticles causes the formation of a two-dimensional layered structure in the space between the oily soil and rock surface, creating a disjoining pressure between them. This pressure becomes more significant as more nanoparticles are injected during EOR and move forward to occupy the rock surface and ultimately detach the oily sands from it. Zhong and co-workers reported that the magnitude of this pressure is significantly affected by the type, size, charge, polydispersity, and volume fraction of the nanoparticles.

Very recently, the potential of superparamagnetic nanoparticles (SPNs) for subsurface applications has substantially increased due to their unique physicochemical properties. Among various types of SPNs, magnetite (Fe₃O₄) has been considered as one of the most studied due to its high chemical stability, low cost, nontoxicity, and ease of fabrication in a controlled fashion. Similar to their applications in MRI, SPNs could potentially be employed for oil field magnetic-field-based reservoir imaging via magnetomotive acoustic imaging and cross-well electromagnetic tomography. Furthermore, the high magnetic susceptibility also enables them to be quickly recovered and reused for further EOR injections. Nevertheless, the harsh conditions in the oil reservoirs can sometimes hinder the mobility and distribution of the nanoparticles inside porous media. It is reported that high reservoir salinity (up to >1 M of monovalent and divalent salts) and high temperatures (up to more than 150 °C) could induce the agglomeration and aggregation of the nanoparticles. Besides, the mobility of certain types of nanoparticles with high surface energy such as metal oxides in porous media could also be disturbed by their strong attachment to the surface of minerals.

Tremendous efforts have been carried out to avoid the potential aggregation of nanoparticles and their attachment to the surface of minerals during the subsurface injection. One of the simplest potential ways is via surface functionalization. Recently, Khalil and co-workers highlighted that several types of organic acids and polymers could be used as surface modifiers for different types of nanoparticles in oil and gas applications. In general, depending on the nature of the nanoparticles, these surface modifiers can be attached via the formation of coordination interaction due to the presence of functional groups such as thiols, carboxylic acids, phosphonic acid, amines, silanes, and alcohols. Nevertheless, the investigation of the surface functionalization of SPNs and the ability of surface modifiers to improve their colloidal stability at extreme subsurface conditions have received little attention. Therefore, the study on the influence of the surface functionalization of SPNs on their ability to improve secondary and tertiary oil recoveries in EOR was carried out. Here, oleic acid (OA) and polyacrylamide (PAM) were used as surface modifiers to fabricate three different types of surface-functionalized SPN composites with various architectures, i.e., OA-SPN, core–shell SPN@PAM, and SPN-PAM, characterized using various methods. In addition, the ability of these surface modification techniques to improve the colloidal stability of SPNs was also evaluated by measuring the ζ-potential of each sample at various concentration of NaCl. Furthermore, the performance of the as-prepared surface-functionalized SPN composites in enhancing oil recovery during EOR was also assessed using a home-made sand pack.

**Figure 1.** (a) Schematic illustration of the surface modification of SPN, (b) XRD patterns, (c) Fourier-transform infrared (FTIR) spectra, (d) thermogravimetric analysis (TGA) thermograms, and (e) magnetization curves of the as-prepared nanostructures.
RESULTS AND DISCUSSION

Preparation and Characterization of Bare and Surface-Functionalized SPNs. In nanofluid flooding, surface properties of the injected nanoparticles play a vital role in improving the recovery of oil.11 Here, oleic acid (OA) and polyacrylamide (PAM) were utilized as modifiers to fabricate surface-modified SPNs with different architectures. Figure 1a shows the schematic illustration of the surface-modified SPN used for EOR in this study. Furthermore, several investigations were also carried out to study the physicochemical properties of the as-prepared nanostructures. Figure 1b presents the X-ray diffraction (XRD) patterns of the samples. Based on the result, it is apparent that all of the samples could be unambiguously ascribed as magnetite (Fe₃O₄). This is true since the obtained Bragg’s peaks were in a good agreement with characteristic peaks of the inverse cubic spinel phase of Fe₃O₄ in database (JCPDS card no. 85-1436) and other reports.2,22,29,31 Results also suggest that the surface modification using OA and PAM has no effect on the crystal structure of the SPN.

FTIR spectroscopy was used further to confirm the surface functionalization of SPN using OA and PAM. The obtained FTIR spectra could be used not only to confirm the presence of surface modifiers but also to study the interaction between the modifiers and the surface of SPN. Figure 1c shows the FTIR spectra of SPN before and after surface modification. According to the result, it was evident that all of the as-prepared nanostructures show sharp absorption peaks in the range of 520−610 cm⁻¹ known for the iron oxide Fe−O stretching backbone vibrations at tetrahedral sites.32 Nevertheless, it is also noticed that the peak was shifted to shorter wavenumbers as the SPN was surface functionalized. FTIR spectra revealed that the Fe−O peak for bare SPN was observed at 543.88 cm⁻¹. Meanwhile, the Fe−O peaks for OA-SPN, SPN@PAM, and SPN-PAM were found at 534.16, 524.45, and 514.73 cm⁻¹, respectively. This suggests that the interaction between OA or PAM and SPN could result in the weakening of the Fe−O bond, which is possibly due to chemical bonding. For OA-SPN, this bonding formation was also proven by the absence of the C=O stretch peak of OA for the carboxyl group at 1710 cm⁻¹, which was replaced by the appearance of two new peaks for the symmetric (νₛ) and asymmetric (νₐₛ) peaks of COO⁻ at 1545.26 and 1688.76 cm⁻¹, respectively.33 In addition, the presence of OA was also confirmed by the presence of two CH₃ stretching peaks at 2913 and 2837 cm⁻¹. For the case core−shell SPN@PAM and SPN-PAM, the presence of PAM was proven by the appearance of strong peaks at 1640.65 and 1612.99 cm⁻¹, which can be attributed to amidic C−O stretching vibration and N−H bending vibration, respectively.34 Additionally, the broad peak at 3000−3500 cm⁻¹ due to the stretching vibration of N−H groups also indicated the presence of PAM. Surface functionalization of SPN using OA and PAM was also proven by TGA analysis. In Figure 1d, TGA thermograms revealed that a weight loss was observed in the surface-functionalized SPN samples due to the decomposition of modifiers at high temperature. However, no significant weight loss was found in the corresponding pristine SPN. According to the result, the organic coating (OA) was decomposed at a reasonably low temperature (below 300 °C), whereas the polymeric modifiers (PAMs) started to decompose at a higher temperature.
Based on the magnetization curves.35 magnetization with the lack of a hysteresis loop in the behavior. This is proven by the shape of symmetrical sigmoidal analyses also suggested that surface functionalization with PAM had the average particle sizes of 10.74 ± 3.59 nm. Meanwhile, the corresponding OA-SPN, core–shell SPN@PAM, and SPN-PAM had the average particle sizes of 10.74 ± 2.98, 15.38 ± 6.56, and 15.34 ± 7.57 nm, respectively.

**Colloidal Stability of Bare and Surface-Functionalized SPNs.** To further investigate the influence of surface modification on the colloidal stability of the nanoparticles, both bare and surface-functionalized SPN nanoparticle samples were dispersed in water, resulting in dark-black suspensions. Based on the result in Figure 3a, it is apparent that all of the as-prepared nanostructures could be efficiently dispersed in water and exhibited no sign of severe particle agglomeration. It is also found that no particle sedimentation was observed even after seven days (Figure 3b). This high colloidal stability is desirable in many applications since it is essential to preserve the high surface area of the nanoparticles. Unlike ferromagnetic nanoparticles, which tend to lose their colloidal stability caused by magnetic dipole–dipole interaction, superparamagnetism in SPNs allows the particles to avoid rapid agglomeration due to their zero coercivity ($H_c$) in the absence of an external magnetic field. This superparamagnetic state is mainly obtained when the size of particles is smaller than the zero-coercivity diameter ($D_h$). At this stage, the presence of single domain magnetism causes all of the magnetic spin in the same direction. Nevertheless, the nanoparticles can show an excellent magnetic response when subjected to an external magnetic field (Figure 3e). As shown in Figure 3c, both bare and surface-functionalized SPNs could easily be separated from the suspension using a permanent external magnet.

In addition, further investigations were also carried out to study the influence of surface modification on the colloidal stability of the nanostructures in artificial brine. Here, the colloidal stability of the samples was studied by measuring the ζ-potential of the nanostructures at various concentrations of NaCl. In general, a stable colloidal system can be indicated by its high absolute value of ζ. Typically, nanoparticles with ζ value higher than +25 mV or lower than −25 mV have a high degree of colloidal stability.37,38 Meanwhile, nanoparticles with low value of ζ are more likely to aggregate due to van der Waals interaction. Figure 3d shows the result from the measurement of ζ for both bare and surface-modified SPNs.

Based on the result, even though no specific correlation between ζ and concentration was observed, it is apparent that surface-functionalized SPNs had substantially larger ζ value than bare SPNs. Results showed that the unmodified SPNs tend to aggregate in artificial brine since the absolute ζ values were found to be less than 20 mV (Figure 3d). This colloidal instability is believed primarily due to the strong Van der Waals interaction as a result of free hydroxyl groups in the crystal edge of the bare SPN surface. Nevertheless, a significant

**Figure 3.** Photograph of aqueous suspensions of the as-prepared nanostructures after (a) 10 min and (b) 7 days; (c) separation of the nanostructures using a permanent magnet; and (d) ζ-potential (ζ) of the nanostructures at different concentrations of NaCl.
increase in electrostatic stabilization was obtained when SPN was functionalized with OA and PAM. According to the result, the increment in colloidal stability can be indicated by the large value of the negative \( \zeta \) obtained for the surface-functionalized SPN, i.e., 30.6, −28.3, and −31.9 mV for OA-SPN, core−shell SPN@PAM, and SPN-PAM, respectively. Although no adequate models to accurately estimate such effect and its magnitude exist, it is believed that the presence of surface modifiers is responsible for increasing the electrical double layer repulsion and ultimately avoiding aggregation and sedimentation. The presence of a long-chain hydrocarbon tail of OA and amine residues in the PAM backbone is presumed to be one of the main factors responsible for the increment of the colloidal stability of surface-functionalized SPNs. A similar phenomenon was also reported elsewhere when SPN was coated with SiO\(_2\).\(^{39}\) It is also argued that polymeric steric stabilization could also contribute to the stabilization of core−shell SPN@PAM and SPN-PAM colloidal systems.\(^{40}\)

**Mobility Ratio of Nanofluids.** Typically, an excellent displacing fluid for EOR should have a higher viscosity value than oil. Figure 4a shows the viscosity of the colloidal suspension of the as-prepared nanostructures at various loading concentrations.

![Figure 4](image)

Figure 4. (a) Viscosity and (b) mobility ratio of the colloidal suspensions of the as-prepared nanostructures at various loading concentrations.

In general, most of the currently used viscosity models are inadequate models to accurately estimate such effect and its magnitude exist, it is believed that the presence of surface modifiers is responsible for increasing the electrical double layer repulsion and ultimately avoiding aggregation and sedimentation. The presence of a long-chain hydrocarbon tail of OA and amine residues in the PAM backbone is presumed to be one of the main factors responsible for the increment of the colloidal stability of surface-functionalized SPNs. A similar phenomenon was also reported elsewhere when SPN was coated with SiO\(_2\).\(^{39}\) It is also argued that polymeric steric stabilization could also contribute to the stabilization of core−shell SPN@PAM and SPN-PAM colloidal systems.\(^{40}\)

**Mobility Ratio of Nanofluids.** Typically, an excellent displacing fluid for EOR should have a higher viscosity value than oil. Figure 4a shows the viscosity of the colloidal suspension of the as-prepared nanostructures at various concentrations. Based on the result, it is apparent that the viscosity of the nanofluid increases with its loading concentration. This is true for both bare and surface-functionalized SPNs. In most cases, a nanofluid behaves as a Newtonian fluid and increasing the concentration of disperse particles gives rise to the increment in viscosity. However, many classical analytical models, such as Einstein (1906), Brinkman (1952), or Batchelor (1977) models, failed to accurately estimate the effect of concentration on the viscosity when the size of the solute particles is in the range of nanoscale.\(^{41−45}\) Recently, tremendous efforts have been made to understand the relationship between the loading concentration of nanoparticles and the viscosity.

In general, most of the currently used viscosity models are based on the Brownian motion of the nanoparticles.\(^{46−47}\) Udawattha and co-workers suggested that the Brownian motion occurs when nanoparticles are suspended in the base fluid as the result of the relative viscosity of the base fluid and the nanoparticles.\(^{48}\) It is also reported that the magnitude of this motion is highly affected not only by temperature but also by the loading concentration of the nanoparticles. At low concentration, particle aggregation due to van der Waals attraction forces is minimum, making the suspended nanoparticles experience less resistance to flow. This will lead to a lower viscosity value. However, when the mass fraction of the nanoparticles is increased, the particles are inclined to aggregate due to the reduction of the average distance between them. As a result, the van der Waals interaction becomes more prominent, causing an increase in shear stress within the nanofluid and making it harder to flow (Figure 4a).

Interestingly, it is also noticed that the type and architecture of the surface modifiers have a different effect on the viscosity of the resulting nanofluids. At low loading concentration (0.1 wt%), surface modification caused the viscosity of nanofluids to increase, regardless of the type and architecture of the modifiers. However, the viscosity seemed to behave differently when more nanoparticles were suspended in the base fluid (loading concentrations of 0.5 and 0.9%). As shown in Figure 4a, the viscosity values of OA-SPN and core−shell SPN@PAM were found to be lower than that of the colloidal solution of bare SPN. On the other hand, SPN-PAM was found to render a more viscous nanofluid. It is assumed that such a phenomenon occurred mainly due to different hydrophilicities of the nanoparticles. According to Zhang and Han, hydrophilic nanoparticles tend to exhibit higher viscosity than hydrophilic−lipophilic nanoparticles.\(^{49}\) It is believed that water molecules can easily be absorbed and form a water layer around the nanoparticles, causing an increase in their average equivalent radius. This can cause the formation of high interfacial resistance, which can hamper the mobility of nanoparticles in the base fluid and ultimately increase the overall viscosity value. Meanwhile, less hydrophilic nanoparticles (OA-SPN and SPN-PAM) tend to exhibit better colloidal stability in aqueous and brine suspensions (Figure 3d). Therefore, the nanoparticles experience lesser van der Waals interaction between them and smaller restriction to flow.

Recently, it has been reported that the mobility of the nanofluid in porous media (\( \lambda d \)) has also known to be one of the major factors in enhancing oil recovery.\(^{1,2}\) This value is highly dependent on the viscosity of the nanofluids. Furthermore, it is also believed that the ratio between the mobility of the nanofluid and oil, commonly referred to as mobility ratio (M), should also be made as low as possible to ensure the optimum sweep efficiency of the displaced oil. In general, \( M < 1 \) is required to obtain optimum secondary and tertiary oil recoveries during EOR.\(^{50}\) Figure 4b presents the value of M for the nanofluids at various concentrations. Based on the result, it is apparent that the value of M decreases with nanoparticle loading concentration. This is true since, at high concentration, the nanoparticles tend to have more prominent van der Waals interaction, causing the fluid to have a higher viscosity value. Additionally, results also demonstrated that the mobility of the nanofluid was significantly affected by the hydrophilicity of the nanoparticles due to the presence of a surface modifier and its architecture. As shown in Figure 4b, at high loading concentration, hydrophilic SPN and SPN-PAM nanofluids exhibited a significantly lower M value than the hydrophilic−lipophilic OA-SPN and SPN@PAM due to their high viscosity values. In addition, the presence of a large PAM polymeric chain in SPN-PAM might also contribute to the further increment of its viscosity and thus reduce the mobility of the nanofluid in porous media.

**Nanofluid Flooding.** To further investigate the application of both bare and surface-functionalized SPNs in EOR,
nanofluids with three different nanoparticle loading concentrations were prepared for sand pack tests. Figure 5 presents the oil recovery performance of nanofluids made from the as-prepared nanostructures at various concentrations. As shown, it is clear that the majority of the oil production was obtained during the initial primary water flooding. During this initial water flooding injection, water is believed to be moving rather uniformly throughout porous media and tends to be imbibed in small- and medium-sized pores and displaces oil to larger pores.\(^{51,52}\) As a result, the remaining oil is trapped and immobile. However, when the nanofluid was injected, the suspended nanoparticles could interact with the trapped oil droplets and mobilize them for secondary recovery. Finally, almost no further significant oil production was observed when additional chasing brine was injected since all of the remaining oil was already mobilized by the nanofluid. Table 1 shows the summarization of sand pack test results.

Over the past several years, tremendous efforts have been made to understand the mechanism of the efficient enhancement of the oil recovery during EOR by nanofluids.\(^{11}\) One of the reasons was their excellent ability in changing the rock wettability from oil-wet to water-wet. This wettability alteration ability is believed primarily due to high surface energy of nanoparticles, which enables them to be strongly adsorbed on the rock surface and change its wettability.\(^{53}\) In other reports, the enhancement in oil recovery due to nanofluid flooding is often associated with the ability of nanoparticles to significantly reduce the interfacial tension (IFT) between the oil and water.\(^{21}\) Furthermore, nanoparticles can also facilitate the generation of a Pickering emulsion, which unlike classical emulsions formed in the presence of surfactants tends to have greater stability against coalescence at reservoir conditions.\(^{44−50}\) Additionally, the formation of structural disjoining pressure between crude oil—brine—rock during the injection of nanofluids has been considered as one of the most dominant mechanisms in oil displacement.\(^{57}\) According to the literature, this disjoining pressure can be formed at the space between oil droplets and the rock surface as the result of formation of a wedgelike nanoparticle film at the wetting wedge.\(^{58}\) Zhang and co-workers reported that this disjoining pressure is greater at the wedge tip and its magnitude is significantly affected by the nanoparticle size, charge, volume fraction, and surface properties.\(^{21}\)

Further investigation of the result from sand pack tests also reveals that the ability of the nanofluid to recover oil was found to increase with nanoparticle loading concentration. A similar observation was also reported elsewhere.\(^{59,60}\) Such an increment was anticipated since the mobility of the nanofluid with larger content of nanoparticles was relatively smaller than the mobility of the oil. Hence, this would result in better oil displacement efficiency. In addition, the greater amount of loading concentration also contributed to the increment of disjoining pressure in the wetting wedge between oil droplets and the rock surface. Moreover, results also demonstrated that the largest oil recovery was obtained when the nanofluid containing SPN-PAM was injected into the sand pack. Based on the result, an additional 19.28% of oil could be extracted during secondary recovery (Table 1). This is consistent with the results obtained from both viscosity and mobility ratio measurements, where SPN-PAM had the highest viscosity value and the lowest mobility ratio (Figure 4).

Nevertheless, it is noteworthy that such a phenomenon is absent when the SPN was modified with OA. It is observed that the secondary oil recovery was rather constant even though the amount of OA-SPN was increased to 0.9% w/v. This might be due to the lipophilicity of the surface of the nanoparticles, which originated from the presence of the long hydrocarbon tail of OA. It is suspected that, when in contact with oil, some part of the suspended OA-SPN particles might be transferred from the aqueous phase to the oil phase. As a result, the ability of the nanoparticles to form the disjoining pressure and mobility control would be lower than expected. In general, the schematic illustration of the mechanism for the oil displacement by the nanofluid is depicted in Figure 6.

### Table 1. Summarization of Sand Pack Test Results

| nanofluid  | concentration (% w/v) | initial water flooding | secondary nanofluid flooding | chase brine injection | total |
|------------|------------------------|------------------------|-----------------------------|----------------------|-------|
| SPN        | 0.1                    | 48.72                  | 3.85                        | 1.28                 | 53.85 |
|            | 0.5                    | 47.44                  | 6.41                        | 1.28                 | 55.13 |
|            | 0.9                    | 46.14                  | 11.54                       | 1.28                 | 58.96 |
| OA-SPN     | 0.1                    | 44.87                  | 5.13                        | 1.28                 | 51.28 |
|            | 0.5                    | 46.15                  | 5.13                        | 1.28                 | 52.56 |
|            | 0.9                    | 47.44                  | 5.13                        | 1.28                 | 53.85 |
| SPN@PAM    | 0.1                    | 46.15                  | 11.54                       | 1.28                 | 58.97 |
|            | 0.5                    | 44.87                  | 12.82                       | 1.28                 | 58.97 |
|            | 0.9                    | 48.72                  | 12.82                       | 1.28                 | 62.82 |
| SPN−PAM    | 0.1                    | 46.15                  | 17.95                       | 1.28                 | 65.38 |
|            | 0.5                    | 43.60                  | 19.23                       | 1.28                 | 64.11 |
|            | 0.9                    | 48.72                  | 19.28                       | 1.28                 | 69.28 |

Figure 5. Oil recovery performance of nanofluid flooding at different concentrations of (a) SPN, (b) OA-SPN, (c) SPN@PAM, and (d) SPN-PAM.
CONCLUSIONS

Three types of surface-functionalized superparamagnetic nanoparticles (SPNs), i.e., OA-SPN, core−shell SPN@PAM, and SPN-PAM, were successfully prepared, and their abilities to improve oil recovery were compared with that of bare SPN using a sand pack. According to the result, it is revealed that the viscosity value of all nano fluid types increased with the loading concentration of suspended nanoparticles due to the strong van der Waals interaction between each particle. Based on the estimation of the mobility ratio between the nano fluid and oil, it is also found that higher nanoparticle loading concentration was desired to obtain smaller fluid mobility, which is essential for EOR applications. However, it is also observed that both the viscosity and mobility of the nano fluid could also significantly be affected by nanoparticle hydrophilicity, especially at high concentration (0.5−0.9% w/v). Among the as-prepared nanostructures, results demonstrated that SPN-PAM exhibited the highest viscosity value (1.1 cP) and the smallest mobility ratio (0.74). This is consistent with the result obtained from the sand pack tests. The investigation of the application of nano fluid injections revealed that the highest secondary oil recovery (19.28% of OOIP) could be achieved when SPN-PAM was used as the nano fluid. It is believed that the nanoparticle was able to not only control the mobility of the injected nano fluid and alter the wettability of the rock surface but also facilitate the formation of a Pickering emulsion and disjoining pressure.

MATERIALS AND METHODS

Materials. Iron(II) chloride tetrahydrate (FeCl2·4H2O) (purity: 98%), iron(III) chloride hexahydrate (FeCl3·6H2O) (purity: 97%), NH4OH solution (28–30% NH3 in H2O), and oleic acid (purity: ≥93%) were purchased from Sigma-Aldrich and used in the synthesis of SPN and OA-SPN. Besides, acrylamide (purity: 98%), potassium persulfate (K2S2O8) (purity: 98%), ethanol, and acetone were also obtained from Sigma-Aldrich and used for the synthesis of SPN@PAM. In addition, polyacrylamide (PAM) with an average molecular weight of 20 000−30 000 g/mol was used in the fabrication of SPN-PAM. Finally, n-decane was purchased from Sigma-Aldrich and used as the oil model in EOR injection.

Synthesis of SPN. In this study, SPN was synthesized via co-precipitation of Fe(II) and Fe(III) ions in basic condition. Here, 1.7 g (0.008 mol) of FeCl2·4H2O and 3.6 g (0.01 mol) of FeCl3·6H2O were dissolved in 100 mL of deionized water in a three-necked flask. The mixture was then mixed using a
magnetic stirrer under a nitrogen atmosphere while being heated to 80 °C for 30 min. Subsequently, 20 mL of NH4OH was slowly added into the mixture, and the reaction was continued for another hour. After the reaction, the black precipitate was then collected using an external magnet and washed using deionized water and ethanol. Finally, the precipitate was dried in an oven at 60 °C for 24 h, and the resulting black powder was collected and used for further investigations.

Synthesis of OA-SPN. To prepare the OA-SPN, we employed similar co-precipitation protocols with slight modifications. Typically, 1.8 g (0.009 mol) of FeCl2·4H2O and 4 g (0.015 mol) of FeCl3·6H2O were mixed with 100 mL of deionized water in a three-necked flask. The mixture was then heated to 80 °C for 30 min under a nitrogen atmosphere while being vigorously mixed using a magnetic stirrer. Afterward, 20 mL of NH4OH was slowly added into the mixture and let to further react for 1 h until the color of the mixture was turned into black. Into the mixture, 0.6 mL of OA was then added while being vigorously mixed for another 1.5 h. After the reaction, the mixture was then cooled to room temperature and the precipitates could be collected using an external magnet. The obtained black precipitate was then washed with deionized water and ethanol to remove the remaining unreacted precursors. Furthermore, the precipitate was then dried in an oven overnight at 60 °C, and the resulting product was used for further characterizations.

Synthesis of Core−Shell SPN@PAM. Core−shell SPN@PAM was fabricated according to a method reported by Song and co-workers with a slight modification.31 In this method, 1 g of the as-prepared SPN and 0.5 g of acrylamide were mixed with 50 mL of deionized water under ultrasonic irradiation for 40 min. Then, 0.1 g of K2S2O8 was added dropwise into the mixture while vigorously stirring using a magnetic stirrer. The mixture was then further mixed for another 24 h at 50 °C to let the polymerization reaction occur. After the reaction, the resulting products were separated using an external magnet and washed with deionized water and acetone. Finally, the obtained final product was dried in an oven overnight at 60 °C and used for further analyses.

Synthesis of SPN-PAM. In this study, SPN-PAM was made by incorporating SPN into the PAM polymer matrix. Here, 0.1 g of PAM was diluted in 30 mL of deionized water while vigorously mixing at 800 rpm using a magnetic stirrer for 1 h. In a separate flask, 0.5 g of the as-prepared SPN was dispersed in 20 mL of deionized water using ultrasonic irradiation. The SPN colloidal solution was then slowly added to the PAM mixture, which was then stirred at 1000 rpm at 45 °C for 8 h. Afterward, the precipitate was then collected using an external magnet and washed with deionized water and ethanol. Subsequently, the resulting black powder was dried in an oven at 60 °C for 24 h and collected for further investigations.

Characterization. Various types of characterization methods were employed to study the physicochemical properties of the samples. Here, X-ray diffraction (XRD) analysis was carried out to determine the crystal structures of the as-prepared SPN using PANalytical X’Pert Pro MPD (PANalytical B.V., Amelo, the Netherlands) and Cu Kα as the X-ray source. Fourier transform infrared spectroscopy (FTIR) using a Thermo Scientific Nicolet iS50 FTIR Spectrometer and thermogravimetric analysis (TGA) using TA Q500 (TA Instrument) were also carried out to study the attachment of surface modifiers on the surface of SPN. Besides, the magnetic properties of the samples were also studied using a vibrating sample magnetometer (VSM) (OXFORD VSM 1.2H).

Measurement of Colloidal Stability. To evaluate the effect of surface functionalization on the colloidal stability of SPN, we measured the ζ-potential of each sample using an SZ-100 Nanoparticle Size and Zeta Potential Analyzer (Horiba Scientific). In this study, the measurement of ζ was carried out by dispersing 0.05 g of the as-prepared samples into 10 mL of artificial brine at different concentrations of NaCl ranging from 5000 to 30 000 ppm.

Estimation of Mobility Ratio. The potential application of the as-prepared nanoparticles in EOR was first evaluated by estimating the mobility of the nanofluid in porous media. According to the literature, the mobility of the fluid in porous media (λ) can be estimated as the ratio between the effective phase permeability (k, Darcy) and the viscosity of the fluid (μ, cp), according to the following equation.50

$$\lambda = \frac{k}{\mu}$$

(1)

Furthermore, to study the sweep efficiency of the nanofluid to displace hydrocarbons, mobility ratio (M) was estimated by comparing the mobility of the nanofluid (λd) and the mobility of the oil (λD), according to eq 2. In this study, the viscosity of both the nanofluid and the oil (n-decane) at different concentrations was measured using a Brookfield Thermosel viscometer.

Sand Pack Design and Nanofluid Flooding. A homemade sand pack was fabricated to investigate the performance of the as-prepared nanofluid samples in improving the oil recovery. In this study, the flooding was done at atmospheric pressure and room temperature. Here, sand with an average particle size of 100 mesh (0.150 mm) and primarily composed of SiO2 and CaO was utilized. The sand was packed in a glass holder (32 cm in length and 3 cm in diameter), equipped with stainless steel sieves to avoid any sand invasion out of the glass holder. Figure 7 presents the experimental setup of the sand pack design.

In this work, the efficiency of the nanofluid in improving oil recovery was initiated by injection of 2 pore volume (PV) of artificial brine (5000 ppm of NaCl), followed by the injection of 2 PV of n-decane as the oil model to reach water and oil saturation. For the primary oil recovery, 1 PV of artificial brine was injected, and the recovered oil was collected in the sample collector. Subsequently, 2 PV of the nanofluid was injected for the secondary recovery, which was prepared by dispersing the as-prepared nanoparticle samples in artificial brines at various concentrations, i.e., 0.1, 0.5, and 0.9% w/v. Finally, the sand pack was further flooded with additional 3 PV of brine for the tertiary oil recovery. Here, the injection flow rate was fixed at 0.83 mL/min (2 ft/day) to mimic the real field injection rate.61–63 The summary of the sand pack properties and flooding experiment is listed in Table 2.

I AUTHOR INFORMATION

Corresponding Author

*E-mail: mkhalil@sci.ui.ac.id.

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