Advanced Ceramics Progress

Research Article

Crude Oil Interfacial Tension Reduction and Reservoir Wettability Alteration with Graphite or Activated Carbon/Silica Nanohybrid Pickering Emulsions

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P A P E R   I N F O

A B S T R A C T

In this research, two carbon structures silica nanohybrids Pickering emulsions were prepared. Graphite and activated carbon were carbon allotropes with different morphologies of laminar and spherical, respectively. The effect of carbon morphology investigated on the related silica nanohybrids Pickering emulsions for C-EOR. Therefore, nanohybrids were prepared with graphite and activated carbon through the sol-gel method based on different weight percents and two different methods. X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and Thermal Gravimetric Analysis (TGA) used characterize the synthesized samples. Pickering emulsions of these nanohybrids were prepared by utilizing octane as oil model, suitable anionic surfactants and an alcoholic co-surfactant with pH=7 at room temperature using distilled water. The apparent stability of Pickering emulsion studied over a period of one month. The results of analyses indicated that graphite/silica nanohybrids Pickering emulsions had superior properties for C-EOR in comparison to activated carbon/silica nanohybrids Pickering emulsions. It concluded that laminar morphology is more significant than the spherical morphology of carbon structure for the mentioned purpose. According to emulsion phase morphology, the optical microscopic images showed that the best samples were 70% graphite/silica (method 2) and 50% activated carbon/silica (method 2). The results of contact angle measurement represented that the 70% graphite/silica nanohybrid (method 2) is more effective on the stone reservoir improvement, which can change the wettability from oil-wet to water-wet. Nanofluid of 70% graphite/silica nanohybrid (method 2) could reduce interfacial tension.

1. INTRODUCTION

S. Pickering discovered Pickering emulsion, which referred to as emulsion, stabilized by solid particles in 1907 [1]. Solid particles adsorbed onto the interface between the two phases [2]. The particles tend to stabilize O/W or W/O emulsions depending on whether they are more hydrophilic or hydrophobic, respectively. Effective parameters such as the particle size and the surface wettability are key factors in controlling emulsion properties [3]. Pristine carbon structures have amphiphobic nature. Therefore, they are accumulated at the water/oil interface rather than dispersing in any of the bulk phases. Silica particles have also extensively investigated regarding oil-in-water Pickering emulsions as hydrophilic emulsifiers [4].
The oxidation process causes the dispersion of graphite oxide sheets in water and other polar solvents because of functional groups such as carboxyl, epoxy and

hydroxyl in the edges [5-8]. The activated carbon is a form of carbon with low pore volumes, which increases the available surface area for adsorption or chemical reactions [9-15]. In this research, two carbon structures silica nanohybrids are prepared. Graphite silica nanohybrid shows better Pickering emulsion properties for C-EOR in comparison with similar silica nanohybrids prepared with activated carbon. According to the results of contact angle and interfacial tension measurement, 70% graphite/silica nanohybrid (method 2) is more effective to improve the stone reservoir wettability alteration from oil-wet to water-wet and reduce the interfacial tension.

2. MATERIALS AND METHODS

Graphite and activated carbon (commercial grade) obtained from the Nanotechnology Research Center of

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Research Institute of Petroleum Industry (RIPI). Commercial sodium silicate solution ($SiO_2/Na_2O=3.35$) was used as the precursor for silica structure. Sodium dodecylbenzene sulfonic acid (SDBS), 2-propanol and n-octane purchased from Merck Chemical Company, which used without further purification.

Morphology evaluation of the as-prepared nanohybrids performed with Field Emission Scanning Electron Microscopy (FE-SEM) by a Holland Phillips XL30 microscope. A Holland Philips X-ray powder diffraction (Cu K_α, $\lambda=1.5406$Å) was used to record XRD patterns of the samples at a scanning speed of 2˚min^{-1} from 20˚ to 80˚. A Philips EM 208 FEG instrument operating at 90kV used to perform transmission Electron Microscopy (TEM). A Quantimet-570 microscope used to prepare optical microscopic images.

2.1. Functionalization of carbon structures

Carbon structures were acid-treated using concentrated HNO_3. Thus, carbon structures (2g) first added to a mixture of distilled water (160ml) and nitric acid (140ml) and they allowed refluxing for 10h. The sample dried at 60ºC after the filtration and neutralization with distilled water.

2.2. Synthesis of carbon structures/silica nanohybrid

2.2.1. Method 1: Addition of carbon structure in media before starting the synthesis of silica nanoparticles

Suitable amount of the functionalized carbon structure for 70wt%, 50wt%, and 10wt% nanohybrids were dispersed individually in 2.5% HCl solution (30ml) in ambient temperature. After this step, sodium silicate (2-3ml) added to the mixture. The solution washed with distilled water and then, dried at 60ºC after mixing for about 5h.

2.2.2. Method 2: Addition of carbon structure during silica nanoparticles synthesis steps

Sodium silicate (2-3ml) first dissolved in 2.5% HCl (30ml) at ambient temperature. The suitable amount of the functionalized carbon structure for 70wt%, 50wt%, and 10wt % nanohybrids was then dispersed in 2.5% HCl solution (30ml) in ambient temperature. The solution washed with distilled water and then dried at 60ºC after mixing about 5h.

2.3. Preparation of Pickering emulsions

Nanohybrid (0.05g) dissolved in distilled water (50ml) and then sonicated for 10 minutes in an ultrasonic bath.

Afterward, SDBS (0.15g), 2-propanol (3ml) and n-decane (3ml) added to the solution as the model oil and the mixture sonicated for 10 minutes again. The stability of Pickering emulsions of these nanohybrids studied over a period of one month.

3. RESULTS AND DISCUSSION

### 3.1. Modification of carbon structure

The hydrophilicity of carbon structure was enhanced by modification with nitric acid to produce O/W emulsion. The amount of oxygenated groups on the surface of the carbon structure related to the treatment time with HNO_3. Oxygen containing groups (e.g., alcohols) are located on the surface and edges of graphite sheets as well as the surface of activated carbon.

3.2. Synthesis of carbon structures/silica nanohybrids

Nanohybrids determined by XRD, SEM, and TGA analyses with the most emulsion stability. Figures 1a, 1b, and 1c, show XRD patterns of silica nanoparticles, 70% graphite/silica nanohybrid (method 2) and 50% activated carbon/silica nanohybrid (method 2), respectively. As shown in Figure 1a, silica nanoparticles have amorphous structures with a broad peak at 24° [16]. Figure 1b shows that 70% graphite/silica nanohybrid (method 2) has a crystalline structure with two main peaks at 31° and 64°, indicating that the carbon phase dominates the silica phase. In addition, 50% activated carbon/silica nanohybrid (method 2) has an amorphous structure (Figure 1c).

Figures 2a, 2b, and 2c show the SEM images of silica nanoparticles, 70% graphite/silica nanohybrid (method 2) and 50% activated carbon/silica nanohybrids (method 2) , respectively. As observed in Figure 2a, spherical silica nanoparticles have been formed with diameters as much as 50 nm. Figure 2b shows that spherical silica nanoparticles attached to graphite sheets with an average diameter of 40nm (calculated with the special software program. According to Figure 2c, silica nanoparticles are perched on activated carbon.

Figures 3a and 3b show thermal Gravimetric Analysis (TGA) results of 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid in a nitrogen atmosphere with 0.1ºC.min^{-1} temperature rate increase, respectively. The diagram drop at 100°C related to the moisture outflow from the sample. Carbon structures were degraded at about 260-270°C. The Silica nanoparticles remain stable even at 800ºC due to their high thermal stability.
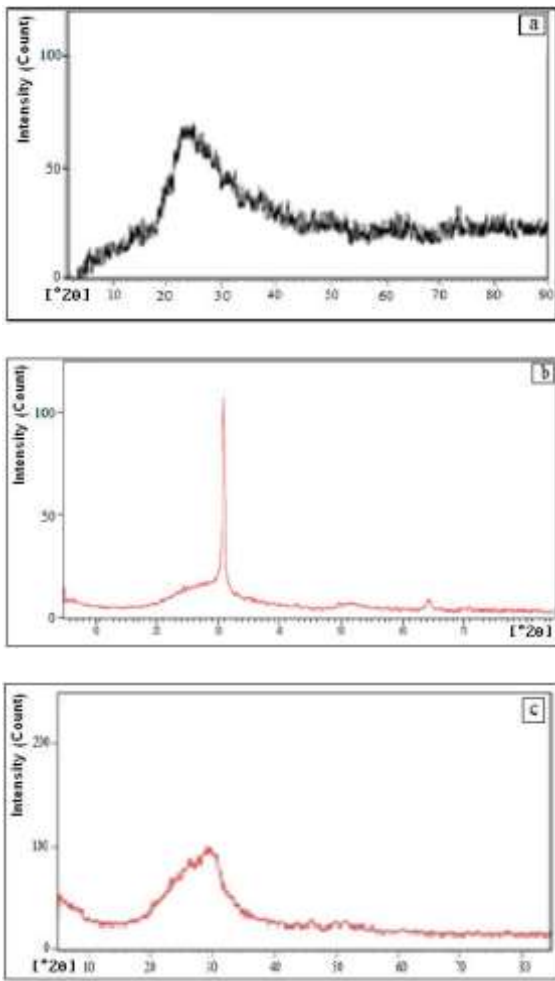
Figure 1. XRD patterns of (a) silica nanoparticles (b) 70% graphite/silica (method 2) (c) 50% activated carbon/silica (method 2)

This result suggests that the assemblies of silica nanoparticles have good stability on MWCNT which is attributed to the unique structure. Two kinds of binding forces may exist between the silica and MWCNT. Silica precursors would adsorb onto the walls of MWCNT during the sol-gel process due to the porous nature of MWCNT, and eventually the silica nanoparticles would physically anchor onto the MWCNT. On the other hand, as there are defects on the walls of MWCNT (e.g., hydroxyl group existing on the defects), some silica precursors would covalently

Nanohybrids prepared by the addition of a carbon compound during the silica nanoparticle preparation through the sol-gel method via two different mixing methods:
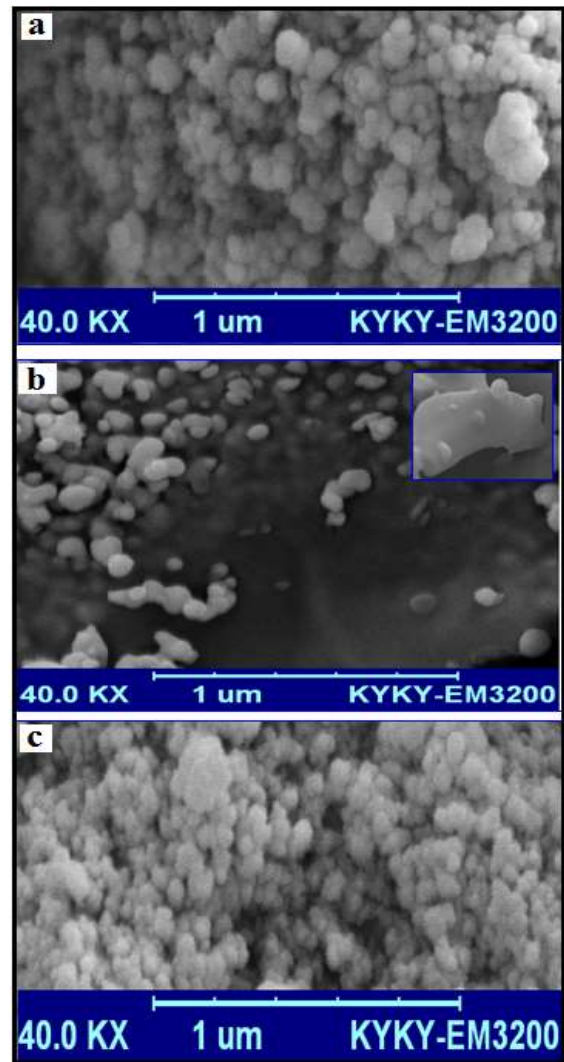

Figure 2. SEM images of (a) silica nanoparticles (b) 70% graphite/silica (method 2) (c) 50% activated carbon/silica (method 2)

bond to MWCNT. The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbents capable of forming a hydrogen bonding with the OH groups or undergoing donoracceptor interaction. On the SiO_2 surface, there also exist surface siloxane groups or -Si-O-Si- bridges with oxygen atoms on the surface [11].

Method 1: Addition of carbon compound before the beginning of silica nanoparticle synthesis.

Method 2: Addition of carbon compound during the step of synthesizing silica nanoparticle.
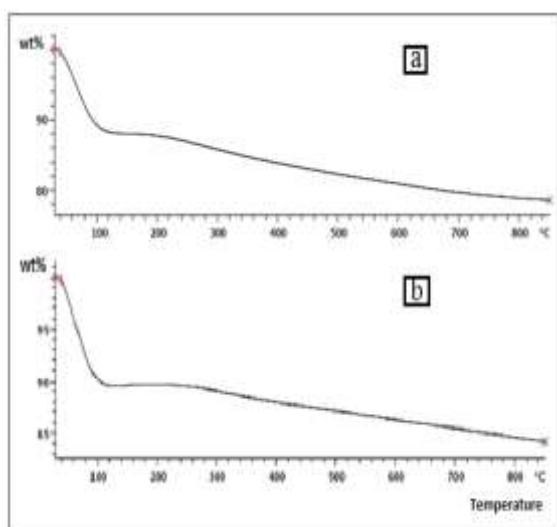
Figure 3. Thermal Gravimeteric analysis (TGA) of (a) 70% graphite/silica (method 2) (b) 50% activated carbon/silica (method 2)

Figure 4 shows the schematic formation of Pickering emulsions of the as-prepared nanohybrids. Nanohybrids act as surfactants in oil recovery processes and they can reduce the interfacial tension (IFT) between oil and water. The emulsion stability of nanohybrids Pickering emulsions for one month, and the corresponding images have shown in Figure 5. The stability of graphite/silica and activated carbon/silica nanohybrids Pickering emulsions prepared after a month by two different methods are shown in Figures 5a and 5b, respectively.
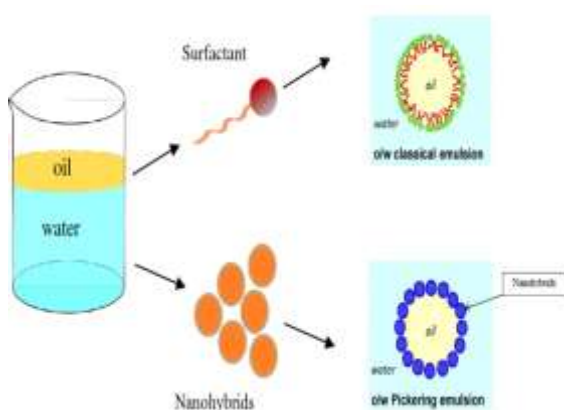
Figure 4. Schematic formation of the Pickering emulsion

Therefore, 70% graphite/silica Pickering emulsion were prepared by method 2 possesses the least precipitation

and the best stability (Figure 4a). Figure 4b shows the comparison between the emulsion stability of activated carbon/silica nanohybrids. As represented in the Figure, 70% and 50% activated carbon nanohybrid emulsions prepared by method 2 showed good stability. However, 50% activated carbon/silica had the lowest precipitation. Thus, the best stability achieved by Pickering emulsions including 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid prepared through method 2.
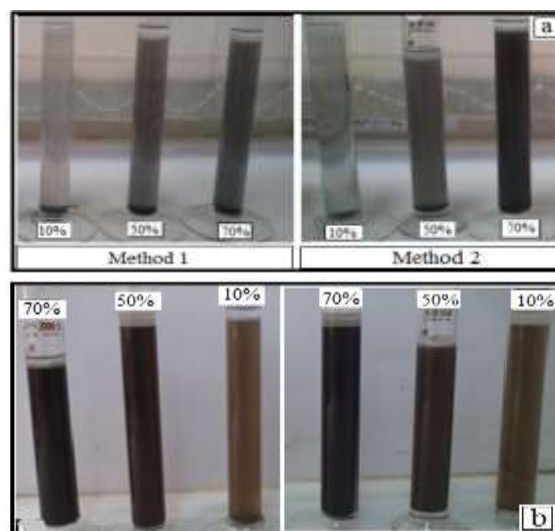

Figure 5. Nanohybrids Pickering emulsions of (a) graphite/silica (b) activated carbon/silica

Optical microscopic images of the nanohybrid Pickering emulsions have shown in Figure 6. As observed in Figure 6, 70% graphite/silica nanohybrid and 50% activated carbon/silica nanohybrid prepared by method 2 have small droplet size with spherical shape and solid particles have surrounded the droplets very well [17-19]. This can explain Pickering emulsion stability results derived for 70% graphite/silica nanohybrid. Moreover, 50% activated carbon/silica nanohybrid prepared by method 2 shows homogenously dispersed emulsion droplets with the smallest precipitation.

Figure 7 indicates that the contact angles for (a) water droplet and stone reservoir, (b) water droplet and stone reservoir with a layer of 50% activated carbon/silica nanohybrid (method 2) and (c) water droplet and stone reservoir with a layer of 70% graphite/silica nanohybrid (method 2) are 143.47, 75.03, and 65.67, respectively. As observed, the 70% graphite/silica nanohybrid (method 2) with the smallest contact angle is more hydrophilic and can better alter the carbonate reservoir rock wettability from oil-wet to water-wet.
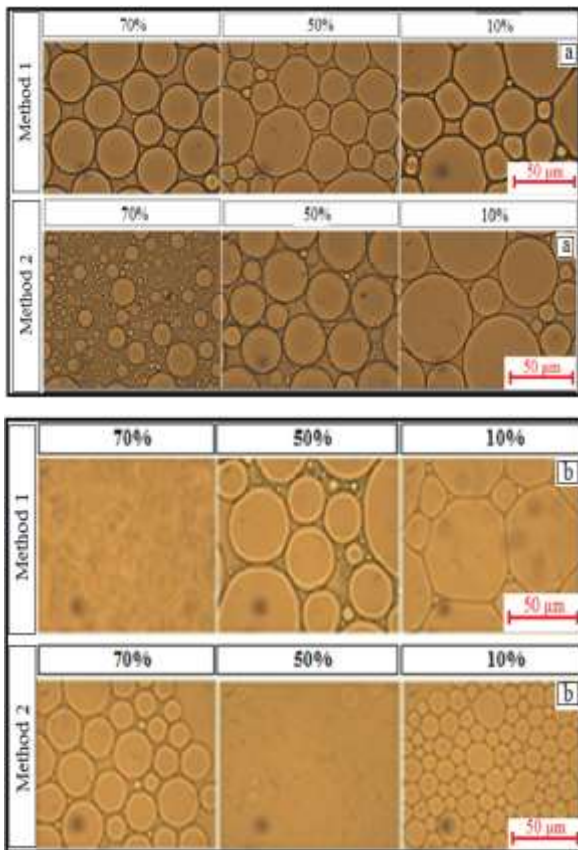
**Figure 6.** Emulsion phase optical microscopic images of (a) graphite/silica (b) activated carbon/silica
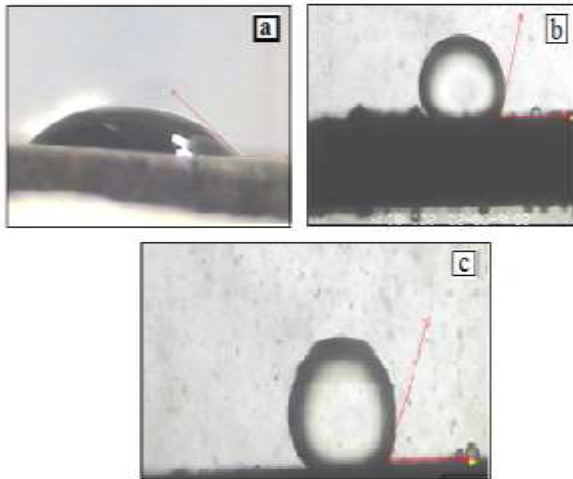
Figure 7. Contact angle between the water droplet and (a) carbonate rock reservoir (b) stone reservoir with a layer of 50% activated carbon/Silica Nanohybrid (c) stone reservoir with a layer of 70% graphite/silica Nanohybrid

The graphite layer structure can presumably be better spread on a stone reservoir compared with spherical activated carbon. Consequently, 70% graphite/silica

nanohybrid (method 2) is more effective in changing the stone reservoir wettability from oil-wet to water-wet.

As indicted by the interfacial tension results (Figure 8), the corresponding amount for injection droplet of (a) water, (b) 50% activated carbon/silica nanohybrid (method 2) and (c) 70% graphite/silica nanohybrid (method 2) are 53.90, 31.21, and 29.95 mN.m^{-1}, respectively.

The maximum amount corresponds to the injection of water, and the minimum amount is associated with the injection of nanofluid of 70% graphite/silica nanohybrid (method 2). Thus, 70% graphite/silica nanohybrid (method 2) Pickering emulsion shows the best properties in comparison with other nanohybrids investigated in this work, and therefore, it can used in C-EOR.
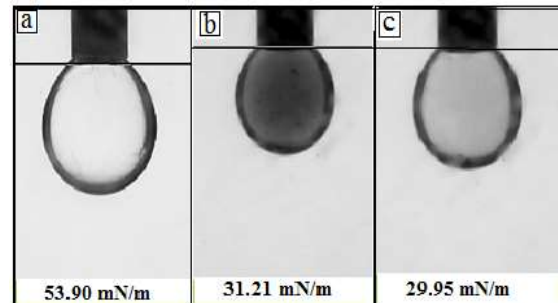
Figure 8. Interfacial Tension of (a) water, (b) 50% activated carbon/silica nanohybrid, (c) 70% graphite/silica nanohybrid

4. CONCLUSION

In this work, graphite and activated carbon nanohybrids with silica nanoparticles synthesized with different weight percentages via the sol-gel method. The corresponding nanohybrid Pickering emulsions were prepared using n-octane as the model oil, a suitable anionic surfactant (such as SDBS) and 2-propanol as an alcoholic co-surfactant at pH=7, and room temperature using distilled water. Further, the nanohybrids were prepared via two different approaches including the addition of carbon compound before the beginning of silica nanoparticle synthesis (Method 1) and addition of carbon compound during the step of synthesizing silica nanoparticle (Method 2). Optical microscopic images have used to investigate emulsion phase morphology. The best samples were 70% graphite/silica and 50% activated/silica nanohybrids prepared by method 2, as indicated by comparison of the results. According to contact angle and interfacial tension measurement results, the 70% graphite/silica nanohybrid (method 2) was more effective on the improvement of the stone reservoir wettability alteration from oil-wet to water-

wet. The results show that 70% graphite/silica nanohybrid (method 2) Pickering emulsion was better than activated carbon/silica nanohybrids which can be applied in C-EOR.

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REFERENCES

1. Pickering, S. U., "CXCVI.—emulsions", *Journal of the Chemical Society, Transactions*, Vol. 91, (1907), 2001-2021.

2. Ramsden, W., "Separation of solids in the surface-layers of solutions and 'suspensions'(observations on surface-membranes, bubbles, emulsions, and mechanical coagulation).—Preliminary account.", *Proceedings of the Royal Society of London*, Vol. 72, No. 477-486, (1904), 156-164.

3. Tang, M., Wu, T., Xu, X., Zhang, L. Wu, F., "Factors that affect the stability, type and morphology of Pickering emulsion stabilized by silver nanoparticles/graphene oxide nanocomposites", *Materials Research Bulletin*, Vol. 60, (2014), 118-129.

4. Shen, M., Resasco, D. E., "Emulsions stabilized by carbon nanotube-silica nanohybrids", *Langmuir*, Vol. 25, No. 18, (2009), 10843-10851.

5. Delhaes, P., "Graphite and Precursors", CRC Press, (2014).

6. Lipson, H., Stokes, A. R., "A New Structure of Carbon", *Nature*, Vol. 149, No. 3777, (1942), 328-328.

7. He, H., Klinowski, J., Forster, M., Lerf, A., "A new structural model for graphite oxide", *Chemical Physics Letters*, Vol. 287, No. 1-2, (1998), 53-56.

8. Hummers Jr, W. S., Offeman, R. E., "Preparation of Graphitic Oxide", *Journal of the American Chemical Society*, Vol. 80, NO. 6, (1958), 1339-1339.

9. Dillon Jr, E. C., Wilton, J. H., Barlow, J. C., Watson, W. A., "Large surface area activated charcoal and the inhibition of aspirin absorption", *Annals of Emergency Medicine*, Vol. 18, No. 5, (1989), 547-552.

10. Khosravani, S., Alaei, M., Rashidi, A. M., Ramazani, A., Ershadi, M., "O/W emulsions stabilized with γ-Alumina nanostructures for chemical enhanced oil recovery", *Materials Research Bulletin*, Vol. 48, No. 6, (2013), 2186-2190.

11. Ershadi, M., Alaei, M., Rashidi, A., Ramazani, A., Khosravani, S., "Carbonate and sandstone reservoirs wettability improvement without using surfactants for Chemical Enhanced Oil Recovery (C-EOR)", *Fuel*, Vol.153, (2015), 408-415.

12. Khosravani, S., Ershadi, M., Alaei, M., Bornaee, A. H., Rashidi, A., Ramazani, A., Manteghian, M., "Compositions and methods employing multi-walled carbon nanotube-based nanohybrids and applications thereof in oil recovery", U.S.Patent Application 14/622,908.

13. AfzaliTabar, M., Alaei, M., Khojasteh, R. R., Motiee, F., Rashidi, A. M., "Preference of multi-walled carbon nanotube (MWCNT) to single-walled carbon nanotube (SWCNT) and activated carbon for preparing silica nanohybrid pickering emulsion for chemical enhanced oil recovery (C-EOR)", *Journal of Solid State Chemistry*, Vol. 245, (2017),164-173.

14. AfzaliTabar, M., Alaei, M., Bazmi, M., Khojasteh R. R., Koolivand-Salooki, M., Motiee, F., Rashidi, A. M., "Facile and economical preparation method of nanoporous graphene/silica nanohybrid and evaluation of its Pickering emulsion properties for Chemical Enhanced oil Recovery (C-EOR)", *Fuel*, Vol. 206, (2017), 453-466.

15. AfzaliTabar, M., Alaei, M., Ranjineh Khojasteh, R., Motiee, F., Rashidi, A. M., " Preference of nanoporous graphene to single-walled carbon nanotube (SWCNT) for preparing silica nanohybrid Pickering emulsion for potential Chemical Enhanced Oil Recovery (C-EOR), *Scientia Iranica*, Vol. 24, No. 6, (2017), 3491-3499.

16. Musić, S., Filipović-Vinceković, N., Sekovanić, L., "Precipitation of amorphous SiO$_2$ particles and their properties", *Brazilian Journal of Chemical Engineering*, Vol. 28, No. 1, (2011), 89-94.

17. Zhang, T., Davidson, D., Bryant, S. L., Huh, C., "Nanoparticle-stabilized emulsions for applications in enhanced oil recovery", In *SPE, Improved Oil Recovery Symposium*, Society of Petroleum Engineers, Tulsa, Oklahoma, USA, 24-28 April (2010).

18. Whitby C. P., Wanless, E. J., "Controlling Pickering emulsion destabilisation: a route to fabricating new materials by phase inversion", *Materials*, Vol. 9, No. 8, (2016), 626.

19. Yang, Y., Fang, Z., Chen, X., Zhang, W., Xie, Y., Chen, Y., Liu, Z., Yuan, W., "An overview of Pickering emulsions: solid-particle materials, classification, morphology, and applications", *Frontiers in Pharmacology*, Vol. 8, (2017), 287.