Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 1, January - March 2019, p. 1 - 5

INTERFACIAL TENSION AND CONTACT ANGLE ALTERATION OF NANOFLUIDS BY USING LANTHANUM SUBSTITUTED MANGANESE-ZINC FERRITE NANOPARTICLES

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This work reports on employment of Lanthanum (La) substituted Manganese-Zinc (Mn-Zn) ferrite ($MnZnLa_xFe_2$-xO_4) nanoparticles (NPs) for enhance oil recovery (EOR) applications. $MnZnLaxFe_2$-xO_4 NPs with different La concentration were synthesized by using sol-gel auto-combustion method. The best magnetization parameters can be achieved at La composition, x = 0.08 with the highest value of saturation magnetization, remanence and coercivity which are 23.6 emu/g, 7.42 emu/g and 197.7 Oe, respectively. The sample with best magnetization parameters was used in nanofluid under different concentrations. Interfacial tension (IFT) and contact angle measurement for nanofluids were then performed. Increased Mn-Zn ferrite concentration in nanofluid reduced the oil-water IFT and contact angle indicating the increase in oil wettability.

(Received August 24, 2018; Accepted January 2, 2019)

Keywords: Ferrite, Nanoparticles, Nanofluid, IFT, Contact Angle

1. Introduction

Oil and Gas industry still dominates the energy industry across the globe especially the developing countries. Due to its high demand and depletion of oil wells, nanotechnology might be the way to overcome this issue. Nanotechnology has been used in oil and gas fields such as exploration, drilling, enhanced oil recovery and in the refining and petrochemical stage [1-3]. By introducing NPs during the water injection into oil wells, one can expect the improvement of oil production such as reduction in oil viscosity, decreased oil-water IFT, and wettability alteration [4-7]. The intent of using ferrofluid as a smart-nanofluid was first introduced by Kothari et al. [8]. However, the research was only restricted to focusing the rheological properties of the ferrofluid and did not study the utilization of this fluid in EOR processes specifically. Surfactant was introduced to coat the ferromagnetic nanoparticles in order to avoid agglomeration and significantly decrease the interfacial tension [8]. On the other hand, Huh et al. utilized super paramagnetic, hydrophobic magnetic, and paramagnetic NPs combined in the fluid as quick crude oil tracers [9]. These particles have a formula of XY_2O_4, where X and Y are metal atoms, or X and Y can both are Fe. Although the use of magnetic nanofluids in EOR has been reported to improve oil recovery, the influence of magnetic properties on reduction in IFT and wettability of the reservoir rock between crude oil and brine phases was not widely reported. Therefore it is essential to investigate the super-exchange interaction and spin alignment in magnetic materials and their effect on wettability and oil-water IFT. In this work, we report the synthesis and characterizations of La substituted Mn-Zn ferrite namely $MnZnLa_xFe_{2-x}O_4$ (x= 0.06, 0.08, 0.10) and how the magnetic properties influence the IFT and wettability when used as nanofluids.

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2. Experimental

All chemicals used are reagent grade-purity ≥ 99%. Metal salts $Mn(NO_3)_2$ $.4H_2O$, $Zn(NO_3)_2$ $.6H_2O$, $Fe(NO_3)_2$ $.9H_2O$, and $La(NO_3)_3$ $.6H_2O$ were weighed in a require amount, dissolved in deionized water and then stirred together at room temperature. The mixed solution will then be heated at 80°C until gelation occurs. The resulting gel was heated at 300°C for auto-combustion. All samples were calcined at 1000°C for 6 hours. The $MnZnLa_xFe_{2-x}O_4$ powder was characterized by X-ray diffractometer to investigate its crystallinity. The morphology was studied by using FESEM. Vibrating Sample Magnetometer (VSM) was used to investigate he magnetic properties. The $MnZnLa_xFe_{2-x}O_4$ nanofluids were prepared at three different weight percent (wt of 0.01 %, 0.03 % and 0.05 %. The stabilizer used in this experiment is Sodium Dodecyl-benzene Sulfonate (SDBS). The appropriate amount of SDBS were dispersed in brine as the base fluid and magnetically stirred until it forms homogenous solution. The NPs suspensions were further agitated in an ultrasonic bath for 30 minutes to reduce agglomeration and ensure longer dispersion in an aqueous solution. A Rame-Hart Model 500 Standard goniometer was used for real-time IFT measurements. The inverted pendant drop method was adapted to determine the contact angle of the suspended droplet.

3. Results and discussion

The XRD spectra for $MnZnLa_xFe_{2-x}O_4$ NPs at different La concentrations are depicted in Fig. 1. The diffraction patterns for all three samples matches well to that of spinel manganese ferrite (JCPDS 38-0430) with accompanying secondary phases, $LaMnO_3$ and Fe_2O_3. The intensity of $LaMnO_3$ has increased when La^{3+} ion concentration increased. It is found that the formation of cubic spinel structure with the presence of lanthanum ortho ferrite, $LaFeO_3$ dominated as a secondary phase. As La^{3+} ions are greater than Fe^{3+} ions, some of them do not move into spinel matrix and form aggregates on the grain boundary [10]. The crystallite sizes calculated from Scherer's equation are from 10.6 nm, 9.8 nm, and 15.3 nm, respectively. The variation of crystallite values attributed to the presence of lanthanum in B-sub lattice [11-12] and corresponds to the strain in the lattice and compression by the secondary phase [10] which affects the grain formation.

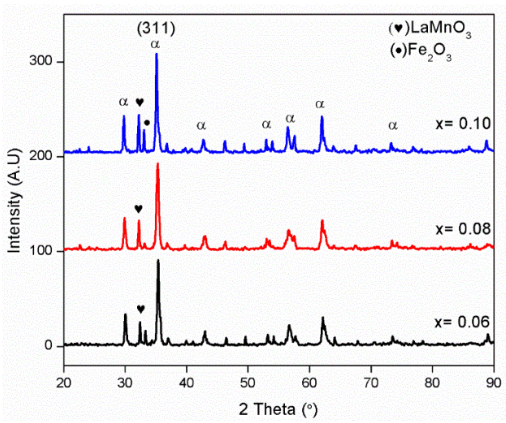


Fig. 1. XRD spectra for $MnZnLa_xFe_{2-x}O_4$ (x=0.06, 0.08, 0.10).

The FESEM image of $MnZnLaxFe_2xO_4$ (x= 0.08) is shown in Fig. 2. Microstructure exhibits polyhedral shape. As the concentration of La^+ ion increased, the grain size of the nanoparticles increases for x = 0.06, 0.08 and 0.10 which is 16.2 nm, 18.1 nm, and 19 nm, respectively. The annealing temperature of 1000 °C is ideal to produce a homogenous microstructure and uniform size distribution with an average grain size about 19 nm. We also observed the presence of grain boundary pores resulting from discontinuous grain growth.

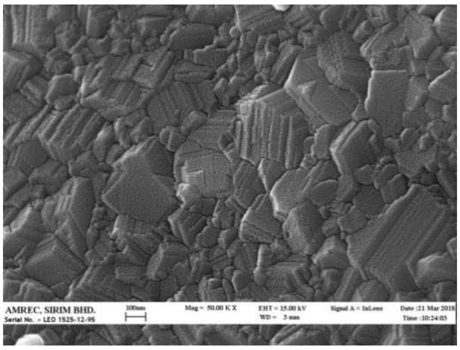


Fig. 2. FESEM image of MnZnLaxFe2xO4 (x= 0.08).

The magnetic hysteresis loop is shown in Fig. 3. The value for magnetic parameters; magnetic saturation, coercivity and remanence were tabulated in Table 2. Based on the results, it can be observed that sample with x= 0.08 has the highest saturated magnetization, M_s of 23.6 emu/g (Table 2). Higher saturation magnetization is probably due to the increase in particle and grain size as mentioned at section above. However, the coercivity of the nanoparticles decreased when the La content increased. Smaller value of coercivity is attributed to the increase in grain size. Sample with x= 0.08 was chosen as a nanofluid candidate to test the IFT and wettability due to larger grain size and higher magnetic saturation.

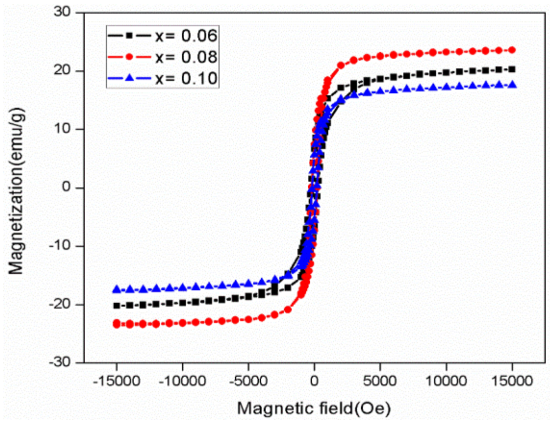


Fig. 3. Hysteresis loop of $MnZnLa_xFe_{2-x}O_4$ (x=0.06, 0.08, 0.10).

Table 2. Variation of saturation magnetization (M_s), coercivity (H_c) and remanence (M_r).

	X= 0.06	X=0.08	X= 0.10
M_s (emu/g)	20.30	23.60	17.70
H_c (Oe)	252.56	197.70	185.33
M_r (emu/g)	6.64	7.42	5.58

Fig. 4 displays the reduction of IFT with increased nanofluid concentration. 0.05 wt% has the lowest IFT compared to 0.03 wt% and 0.01 wt%. IFT reduced from 12.43 mN/m to 9.80 mN/m when nanofluid concentration increased from 0.01 to 0.05 wt%. This result indicates that nanofluids have a potential to improved oil recovery by reducing IFT. The NP is attached to the surface and due to adsorption process it decreases surface tension indicating NP is a potential option for EOR application. Reduction of IFT will ease the mobility of the oil since the friction force between water-phase and oil-phase will also decrease [13].

Fig. 4 shows the contact angle between oil and nanofluids with different concentration. The findings indicate by increasing nanofluid concentration, the contact angle will decrease which makes the substrate more water-wet. This trend exhibits the increase of water wetness is due to the increase of hydrophilic magnetic nanofluid concentration. The massive amount of nanoparticle will be attributed to higher electrostatic repulsion force between the particles. Thus, aqueous force driven by bulk liquid, nanofluid will spread alongside the solid surface and decrease contact angle [14].

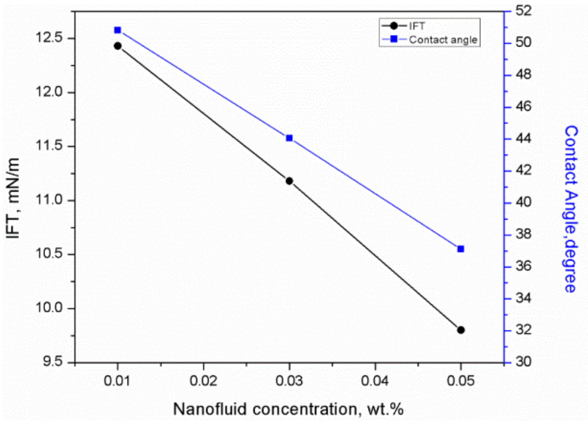
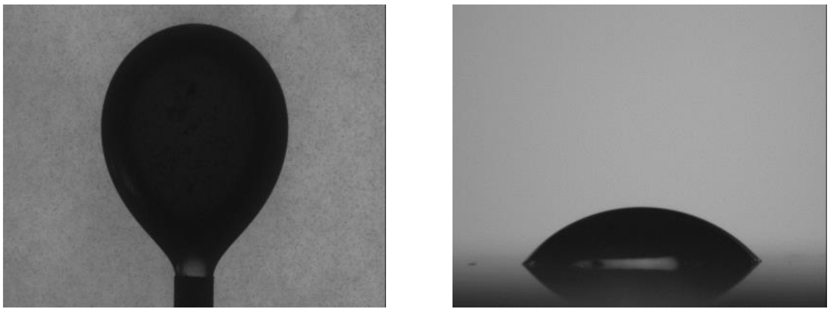


Fig. 4. Interfacial tension and contact angle measurement for crude oil against brine with different nanofluid concentrations at room conditions.



a) *b)*

Fig. 5. a) Crude oil drop shape from goniometer, 0.05 wt.% and crude oil, b) Contact angle creation on soda lime glass between crude oil and brine/nanofluids.

4. Conclusions

In conclusion, La substituted MnZn ferrite has been successfully synthesized via sol-gel method. Significant reduction of interfacial tension has been observed by introducing nanoparticles into brine.

The higher concentration of nanofluids will give the lower IFT. This IFT reduction due to introduction of La substituted MnZn ferrite NPs in nanofluids can be applied for EOR. La-MnZn ferrite nanofluid with suitable concentration also altered the wettability of the oil. Nanofluid with 0.05 wt% is the best candidate in terms IFT reduction and wettability alteration.

Acknowledgment

This work was supported by Universiti Teknologi Petronas (UTP) through the YUTP grant with cost-center number 0153AA-E18.

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