Journal of Thermal Analysis and Calorimetry (2019) 135:1323–1334
https://doi.org/10.1007/s10973-018-7662-4

Stability and magnetization of Fe_3O_4/water nanofluid preparation characteristics using Taguchi method

Abazar Abadeh[1] · **Mohammad Passandideh-Fard**[1] · **Mohammad Javad Maghrebi**[1] · **Majid Mohammadi**[1]

Received: 12 May 2018 / Accepted: 13 August 2018 / Published online: 8 September 2018

Abstract

In this paper, the effect of different parameters on Fe_3O_4/water nanofluid preparation characteristics is investigated experimentally. Two criteria, stability and magnetism, are employed to characterize prepared ferrofluids. Dynamic light scattering methods (DLS) distribution and transmission electron microscopy (TEM) images are applied in nanoparticle size investigation. Two-step preparation method is used to prepare the ferrofluid samples. Zeta potential and vibrating sample magnetometer (VSM) methods are used to study the stability and magnetism characteristics of prepared ferrofluid samples, respectively. The effect of six parameters (surfactant material, surfactant mass, heater stirring speed, heater stirring time, pH, initial sonication time and final sonication time) with three levels and one parameter (surfactant material) with six levels on the stability and magnetization is considered. The Taguchi method is applied in design of experiments, and 18 samples are prepared. The results show that the effective parameters on the stability of the prepared ferrofluid as their importance are: surfactant material, pH number, initial sonication time, surfactant mass, final sonication time, heater stirring speed and heater stirring time, respectively. According to magnetization viewpoint, the order of importance for effective parameters is: surfactant material, surfactant mass, pH number, final sonication time, heater stirring time, initial sonication time and heater stirring speed, respectively.

Keywords Taguchi Method · Ferrofluid stability · Ferrofluid magnetization · Zeta potential · VSM measurement

Introduction

The famous phrase of “There’s plenty of room at the bottom” by Richard Feynman (winner of the Nobel Prize in 1959) was used to introduce nanoscience and nanotechnology [1]. Nanotechnology was initially introduced by Nario Taniguchi at the University of Tokyo in 1974 [2]. The mixture of nanoparticles with usually higher thermal conductivity suspended in the base fluids is nanofluid [3]. In 1995, Choi successfully prepared a nanofluid in Argonne Laboratory-USA. Afterward, the researchers attention was drawn to nanofluids and its thermal properties as the next generation heat transfer fluids. High thermal conductivities, considerable stability and little penalty due to an increase in pressure drop are the advantages of well-prepared nanofluids [3, 4].

Using different nanofluids as a coolant has been very common since last decade and economic and environmental surveys show a bright future for these new fluids. Using energy and exergy analysis shows that the size of existing heat transfer systems could be decreased by significant amount [5, 6].

Ferrofluids have unusual optical, electronic and magnetic properties that can be altered by applying a magnetic field. These properties draw others attention to use these kinds of nanofluids. The main characteristic of a ferrofluid, i.e., reaction in the presence of an external magnetic field, has led to an increasing interest during recent years [7].

✉ Mohammad Javad Maghrebi
mjmaghrebi@um.ac.ir

Abazar Abadeh
abazar.abadeh@mail.um.ac.ir

Mohammad Passandideh-Fard
mpfard@um.ac.ir

Majid Mohammadi
mohammadi.ma@mail.um.ac.ir

[1] Mechanical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, P.O.Box 9177948944, Mashhad, Iran

Magnetic field is used as a stimulating factor in ferrofluid flows that leads to enhanced heat transfer characteristics. Abadeh et al. experimentally investigated the effect of constant magnetic field on heat transfer characteristics of ferrofluid flow through a helically coil. They reported that applying constant magnetic field of 600 G will improve heat transfer up to 7% [8].

Cooling, power generation, defense, nuclear technology, aerospace, microelectronics, nonlinear optics, magnetic electro-catalysis and bioengineering are some of the important applications of magnetic nanofluids. Therefore, it has been widely investigated, both numerically and experimentally, in research laboratories. Heat transfer enhancement is widely applicable in various industries, specifically in heat exchangers. Enhancing heat transfer with lower increase in pumping energy will result in higher total efficiency in those systems [9].

Magnetic drug delivery in biomedical applications is based on supplying drugs by magnetic fluids in the site of interest. It has been acknowledged that these fluids can be promising solutions for cancer therapy [7, 10].

Hosseinzadeh et al. experimentally investigated ferrofluid flow and heat transfer in straight tube under constant magnetic field. Based on their study, the Nusselt number and friction factor increase by using ferrofluid instead of water, while the performance index shows higher values. Furthermore, increasing the magnetic field strength enhances the heat transfer coefficient [11].

Magnetic field effects on convective heat transfer of magnetic nanofluid flow in a circular tube in presence of constant heat flux condition are experimentally investigated by Asfer et al. They indicated that several factors can be effective on the convective heat transfer coefficient. Some of these effective factors are: ratio of magnetic force to inertia force, interaction of ferrofluid flow with the aggregate of nanoparticles formed at the wall of the tube, and enhancement in local thermal conductivity of ferrofluid flow [12].

Yarahmadi et al. experimentally study the effects of using ferrofluids and magnetic field on heat transfer characteristics with constant heat flux boundary condition in laminar flow regime. The effects of strength, frequency and arrangement of magnetic field, and also its oscillatory mode were studied. They reported that using the ferrofluid and oscillatory magnetic field has positive effects on convective heat transfer, while the constant magnetic field showed adverse effects. The maximum enhancement of 19.8% was obtained in their work. [13].

Magnetite (Fe_3O_4), iron (Fe), nickel (Ni) and cobalt (Co) nanoparticles dispersed in a base fluid are some of magnetic nanofluids which provide extraordinary large thermal conductivities. However, due to broad potential and practical applications of Fe_3O_4 nanoparticles, they are generally used to obtain ferrofluid [14].

Preparation of nanofluids is the first step in all relevant experimental studies. There are several methods to prepare nanofluids: single-step preparation, two-step preparation and specific methods for particular types of nanoparticles.

In a single-step process, synthesis of nanoparticle and production of nanofluid simultaneously occur. The nanoparticle agglomeration minimization is the greatest advantage of one-step synthesis method, and its drawbacks are that it is expensive and only fluids with low vapor pressure are compatible with this process [1, 15, 16].

In a two-step process, commercially available nanopowders are initially obtained from different mechanical, physical and chemical approaches such as milling, grinding, sol–gel and vapor phase methods. Secondly, a two-step preparation process is accomplished through mixing base fluids with the obtained nanoparticles. Ultrasonic vibration, stirring, adding surfactants and high shear mixing are the methods used in order to disperse the nanoparticles in the base fluid and reduce particles agglomeration [1, 17]. This method is the most economical process for nanofluids production, but its biggest challenging issue in nanofluid production is stability. Van der Waals force within the nanoparticles makes them prone to be easily agglomerated [1].

There are several other methods to prepare nanofluids for particular types of nanoparticle: aqueous organic phase transfer method for preparation of gold, silver, platinum nanoparticles by Feng et al. [18], phase transfer method to prepare kerosene based Fe_3O_4 nanofluids by Yu et al. [19], synthesis of water-soluble Fe-decorated multi-walled carbon nanotubes by Shanbedi et al. [20], and using a continuous flow microfluidic microreactor to synthesize copper nanofluids by Wei and Wang [21].

The most common method to prepare magnetic nanoparticles is chemical co-precipitation. In this method, a mixture of salts suspended in an aqueous alkaline medium is prepared. Subsequently, different procedures such as decantation, magnetic separation, centrifugation and dilution are applied to the suspension [22].

Preparation of ferrofluid through co-precipitation technique is very popular. The process includes the mixture of ferrous ($FeCl_3$ $6H_2O$) and ferric ($FeCl_2$ $4H_2O$) salts in the molar ratio of 1:2. Furthermore, vigorous stirring is commonly utilized, while NaOH solution makes the alkaline environment. Black dark color of suspension is the sign of magnetite [19, 22]. Subsequently, different procedures such as decantation, magnetic separation, centrifugation and dilution are applied to the suspension. Magnetic separation method and washing with distilled water and absolute ethanol for several times is the deposit procedure [22]. The reaction of co-precipitation is carried out by motor stirring under N2 and argon atmosphere and surfactant is also used [14, 23].

Long-term stability of nanofluids is a major concern for the engineering applications. Nanoparticles naturally tend to aggregate and sediment in the base fluid. As a result, stable suspension with large volume concentration is not easy to obtain [24]. To avoid the agglomeration, nanoparticles are usually covered with a shell of an appropriate material called surfactant. These additives usually come with water-loving chains [25, 26].

Preparing stabilized water-based magnetic nanofluids at higher mass fraction values, particularly over 0.5, has been proved to be a difficult task that involves combinations of surfactants in various chain lengths [27]. Surfactant coating of magnetite nanoparticles by adding lauric acid, myristic acid or oleic acid, shortly after the co-precipitation reaction at a fixed temperature is done to prevent agglomerations by Cheraghipour et al. [25]. In order to prepare stabilized suspension, sodium dodecyl-benzenesulfonate (SDBS) as the surfactant is selected for covering the nanoparticles [28]. Vekas et al. [27] used dodecyl-benzenesulphonic acid, lauric acid, myristic acid and oleic acid for coating magnetite nanoparticles in order to be dispersed in a transformer oil.

Creating turbulence by placing the reaction flask in an ultrasonic bath (100 W) and controlling the homogenization by a stirrer during the reaction are very helpful. Citric acid is added to the suspension as a surfactant in an incubating process [25, 29]. Sodium oleic and sodium dodecyl-benzenesulfonate are applied as inner and outer surfactants, by Bica et al., respectively. Moreover, centrifugal process is used to examine whether a well-dispersion is obtained [28]. Other steps of ferrofluid preparation are: separation of phases, decantation, washing by distilled water, elimination of residual salts, *p*H correction and purification. The result is water-based magnetic fluid with approximately 12 kA/m saturation magnetization [29, 30].

It is important to be able to fully characterize the ferrofluids under inspection for heat transfer enhancement and magnetic applications. The steps of inspection are quantifying the composition and size of nanoparticles, and the stability and magnetization of ferrofluids [28, 31, 32]. There are various methods for nanofluid and ferrofluid characterization and qualification, such as: zeta potential analysis [1, 24, 28, 33], sedimentation method (visual method) [1, 14, 24, 33], centrifugation method [1], spectral analysis method [1, 24, 33], omega method [1, 33], electron microscopy(SEM) and dynamic light scattering methods(DLS) [1, 14, 31, 33], vibrating sample magnetometer(VSM) [14, 32, 34, 35], neutron activation analysis (NAA) [31], X-ray powder diffraction (XRD) measurements [14] and infrared spectrum (FT-IR) measurements [14].

As it is clear from the aforementioned part, there are several effective parameters in nanofluid preparation, which show a wide range of variations. As a result, no specific method to prepare magnetic nanofluid with high-quality features has been clearly addressed in the literature. The objective of the present paper is to experimentally study the effect of each parameter on the main characteristic of ferrofluid. Two ferrofluid quality features considered in this study are stability and magnetization. The tools utilized to characterize and qualify ferrofluids include transmission electron microscopy imaging (TEM), dynamic light scattering (DLS), zeta potential criteria, vibrating sample magnetometer (VSM) and visual inspection.

Materials and methods

Design of experiments

Design of experiment (DOE) methods are approaches to reduce the costs of experiments. Some of the most common DOE types are: one-factor designs, factorial designs (including general full factorial designs, two level full factorial designs, two level fractional factorial designs, Plackett–Burman designs, Taguchi's orthogonal arrays), response surface method designs and reliability DOE [36]. The one employed in this paper is the Taguchi method. This method was developed by Taguchi to improve the process or product quality by statistical concepts. The Taguchi method has been used extensively in engineering analyses due to its wide range of applications. It has been proved that the method can be very effective provided that the proper considerations are taken [37].

Taguchi is an experimental optimization method that uses the standard orthogonal arrays that form the matrix of experiments. It helps to get maximum value of information from minimum number of experiments and, subsequently, to find the best level of each parameter [38]. This method is an optimal parametric design of experimental tool, which first chooses several effective parameters of relative characteristics and puts them into an appropriate plan table with several levels for each parameter [39].

In this method, the number of parameters and levels are identified based on the existing system. According to the number of control parameters and levels, the appropriate orthogonal array (OA) is first selected. Next, the optimum number of experiments is determined. The minimum number of experiments needed in the Taguchi optimization technique can be determined by the following formula:

$$N_{\text{Taguchi}} = 1 + \text{NV}(J - 1)$$

where N_{Taguchi}, J and NV are the number of experiments, the level and given number of the control parameters, respectively [40].

Signal-to-noise ratios (SNR) are used to calculate the responses in data analyzing. Three types of performance characteristics are applied in analyzing: the-larger-the-better and the-smaller-the-better and the-nominal-the-better [40, 41]. Signal-to-noise analysis by two performances of the-larger-the-better and the-smaller-the-better is defined as follows:

$$SN = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_{\mathrm{i}}^{2}}\right)$$

$$SN = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}y_{\mathrm{i}}^{2}\right)$$

where y_{i} is a quality measurement and n is the total number of the experiments.

After performing the experiments, by using SNR, the results are analyzed. To find out the percentage contribution of individual parameter in the experiment, ANOVA (analysis of variance) is applicable.

Nanofluid preparation

All chemicals were of analytical grade (chemical grade) and used as received without further treatment. All suspensions were prepared with twice-distilled water. Citric acid (CA), arabic gum, SDS (sodium dodecyl sulfonate), SDBS (sodium dodecyl benzene sulfonate), Ctab (cetyltrimethylammonium bromide) and Tween 80 were purchased from Merck (Germany). Fe_3O_4 nanoparticles were prepared from US research nanomaterials, Inc., USA. The purity of these nanoparticles was 98%, and their size was almost 20–30 nm. Figures 1 and 2 show the TEM images (Transmission Electron Microscope, LEO 912AB, Zeiss, Germany, Specified line resolution of 0.2 nm, Acceleration Voltage: 120 kV, Gun type: tungsten) and DLS distribution (Dynamic Light Scattering, Vasco-3, Cordouan Technologies, France, measuring domain 1–6000 nm) of prepared nanoparticle, respectively. DLS report of nanoparticle is presented in Table 1.

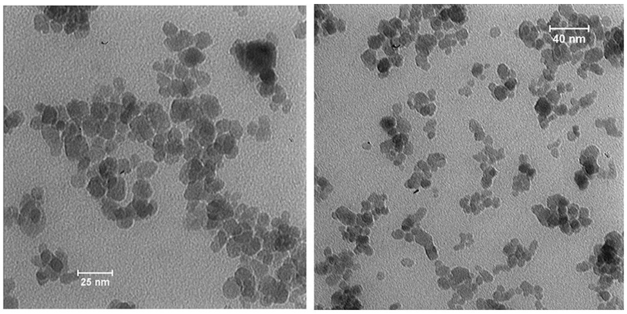


Fig. 1 Nanoparticle TEM images in this study

Two-step method is used to prepare ferrofluid. Initially, Fe_3O_4 nanoparticles are grinded by a mortar to prevent or reduce agglomeration. Then, Fe_3O_4 nanoparticles are added to the distilled water by 1% mass fraction and the suspension is stirred manually for at least 5-min.

The prepared suspension is placed in the ultrasonic bath (Elma, Elmasonic, S60H, Germany) under sonication with a frequency of 37 kHz, a power of 400 watts, under 100% amplitude and a temperature of 50 °C for a specified time (T_1). Using a certain amount of 1 molar Ammoniac solution, the acidity of the suspension is fixed and the pH number is set. Subsequently, the selected surfactant with a certain mass is added to the suspension and stirred manually (M).

The prepared suspension is incubated in a hot plate heater stirrer (Corning PC-420D, USA), while the temperature rises up to 80 °C for a specified speed (N) and time (T_2). Then, the nanoparticle is washed several times with distilled water and iridium magnets to remove extra surfactant. Finally, the suspension is put under sonication in the ultrasonic bath for a second period of time (T_3) and the temperature is set to 50 °C to increase the stability of final suspension. In all experiments, the mass fraction of nanoparticle in the base fluid is 1%.

Figure 3 shows preparation steps of Fe_3O_4/water nanofluid samples in this paper.

Experimental

Different parameters that affect ferrofluid characteristics have been introduced in the literature. Some of these parameters for Fe_3O_4/water nanofluid are: base fluid type, surfactant material, surfactant mass, ultrasonic exposed time, ultrasonic exposed temperature, heater stirring time, heater stirring temperature, stirring speed, pH, nanoparticle mass fraction in ferrofluid and shape/size of the nanoparticle. [33].

In this paper, after conducting several primary experiments to prepare Fe_3O_4/water nanofluid, the following are selected as the most effective parameters on the ferrofluid stability and magnetization: initial sonication time (T_1), pH, surfactant material, surfactant mass (M), heater stirring time (T_2), stirring speed and final sonication time (T_3). Parameters and selected values, along with the materials, are listed in Table 2:

In this paper, the design of experiments is accomplished by the Taguchi method. As mentioned in Table 2 there are six parameters with 3 levels (initial sonication time, pH, surfactant mass, heater stirring time, heater stirring speed and final sonication time) and one parameter with 6 levels

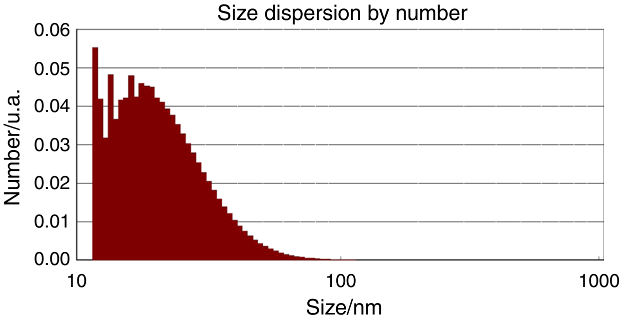


Fig. 2 Nanoparticle DLS distribution in this study

Table 1 Nanoparticle DLS specification

Characteristics	Dmean number	Dmean volume	Dmean intensity
Size/nm	21.22	46.44	90.98

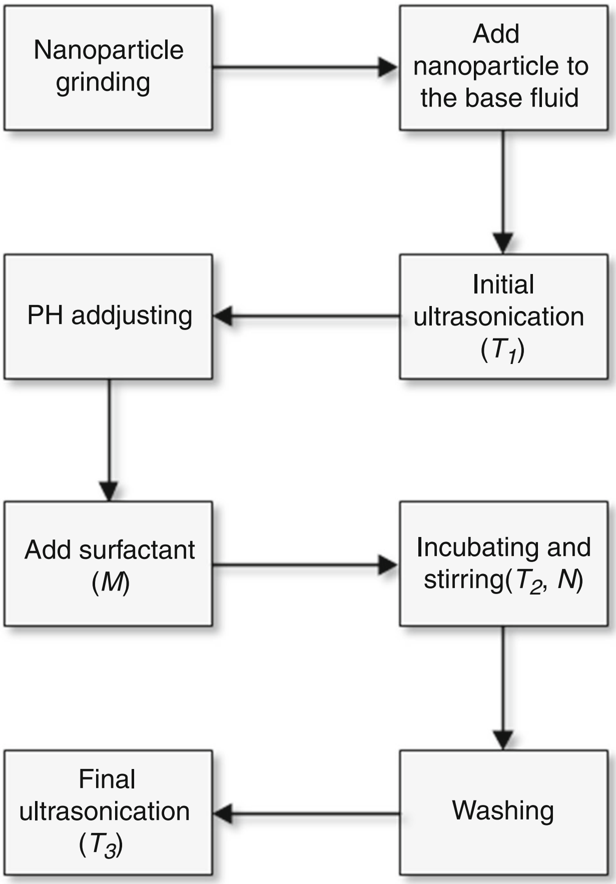


Fig. 3 Fe_3O_4/water nanofluid samples preparation steps

which is surfactant material. Using the Minitab software and choosing the Taguchi method, along with selecting six parameters with 3 levels and one parameter with 6 levels, 18 experiments are designed as shown in Table 3. Figure 4 shows the prepared Samples 1–6 related to Table 3.

Results and discussion

Using the two-step method for preparing the ferrofluid and the steps shown in Fig. 3, two approaches are employed to examine the suspension characteristics from two viewpoints: stability analysis and magnetism characteristic.

Stability analysis viewpoint

Zeta potential measurement is a reliable method to study the stability analysis of prepared suspension. Zeta potential is electric potential in the interfacial double layer, and it shows the potential difference between the stationary layer of fluid attached to the dispersed particle and the dispersion medium. The significance of zeta potential can be related to the stability of colloidal dispersions and this potential can be used as a criteria of ferrofluid stability. So, colloids with high absolute zeta potential are electrically stabilized, while colloids with low zeta potentials tend to agglomerate. Generally, 20 or 25 mV (positive or negative) can be taken as the criterion value that separates low-charged surfaces from highly charged surfaces and absolute value of zeta potential from 40 to 60 mV is believed to be good stable and that with more than 60 mV has excellent stability [1, 24, 42, 44–46].

In the present study, the zeta potential criterion (Zetameter Compact, USA) is used for each prepared suspension sample. Having selected three samples for each prepared suspension, every measurement is repeated three times and the average result of 9 values is reported. Figure 5 shows the variation of the zeta potential criterion for Sample 1. As presented in Fig. 5, the absolute average of the zeta potential is more than 40, indicating that this sample is well stable. The measurements and the corresponding results for the zeta potentials are presented in Table 4 for the entire samples (18 samples). Subsequently, based on the SNR ratios obtained through the experiments, the main effects of each control factor can be calculated and the corresponding response graph can be plotted. The results are shown in Fig. 6.

As shown in Fig. 6a, the most zeta potential value is obtained for citric acid. Next, the Arabic gum is recommended as another suitable surfactant. Tween 80 is considered as the weakest surfactant for the stability of the product suspension. It seems that the lighter surfactant molecules (except for acetic acid) are more suitable for ferrofluid stability due to their lower weight. Furthermore the hydrophilic acid surfactants are more suitable, while hydrophobic acid surfactants are not ideal choices for

Table 2 Parameters and selected values

Parameter	Value/material					
Surfactant material	Citric acid [25]	SDBS [42]	Arabic Gum [3]	SDS [14]	CTAB [29]	Tween 80 [29]
Surfactant mass (M) [35]	1M		2M		4M	
Heater stirring speed (N) [25, 35]	400		600		800	
Heater stirring time (T_2) [25, 35]	30		60		90	
pH [41]	7		10		11	
Initial sonication time (T_1) [29, 43]	20		40		60	
Final sonication time (T_3) [29, 43]	0		20		40	

Table 3 18 Taguchi-designed experiments

Exp	Surfactant material	Surfactant mass	Heater stirring speed	Heater stirring time	pH number	Initial sonication time	Final sonication time
1	1	1	1	1	1	1	1
2	1	2	2	2	2	2	2
3	1	3	3	3	3	3	3
4	2	2	1	3	2	3	1
5	2	3	2	1	3	1	2
6	2	1	3	2	1	2	3
7	3	1	1	2	3	3	2
8	3	2	2	3	1	1	3
9	3	3	3	1	2	2	1
10	4	3	1	2	2	1	3
11	4	1	2	3	3	2	1
12	4	2	3	1	1	3	2
13	5	3	1	3	1	2	2
14	5	1	2	1	2	3	3
15	5	2	3	2	3	1	1
16	6	2	1	1	3	2	3
17	6	3	2	2	1	3	1
18	6	1	3	3	2	1	2

stability. As shown in Fig. 6b, increasing the surfactants mass (M) from 1M to 2M enhances the ferrofluid stability. However, increasing the mass further from 2M does not lead to a significant effect. Therefore, an amount of 2M is introduced in this paper. The saturation of the nanoparticles by surrounding surfactants can be considered as a reason for the lack of surfactants greater effect on stability. However, the extra surfactant will be removed in washing step.

Figure 6c shows the effect of the heater stirring speed (N) on the stability of the ferrofluid. The increase in the

Fig. 4 1–6 Prepared samples

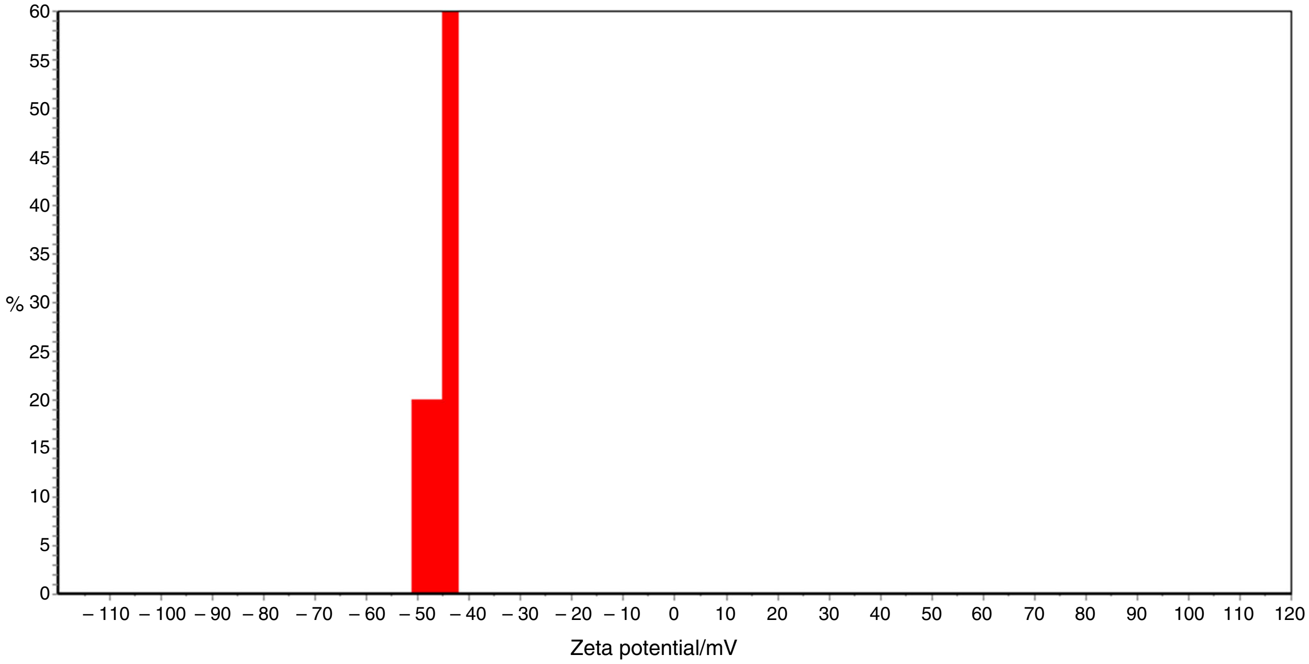


Fig. 5 Sample 1 zeta potential variation

Table 4 18 samples zeta potentials results

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Zeta potential	41.7	57.6	66.6	23.5	21.5	14.6	43.6	40.7	45.2	24.1	25.5	23.5	12.9	16.0	21.6	6.7	9.4	7.3

speed of the stirring from 400 to 600 rpm improves the ferrofluid stability. Increasing the speed higher than 600 rpm, however, does not have a positive effect on the stability (see Fig. 6c). The effect of the ferrofluid recess time in the heater stirring (T_2) on the stability is presented in Fig. 6d. As shown in the figure, keeping the product on the device for 60-min gives the optimum results. The probable reason of the unfavorable effect of increasing the heater stirrer time and speed, beyond their optimum values, can be separation of surfactant from nanoparticles.

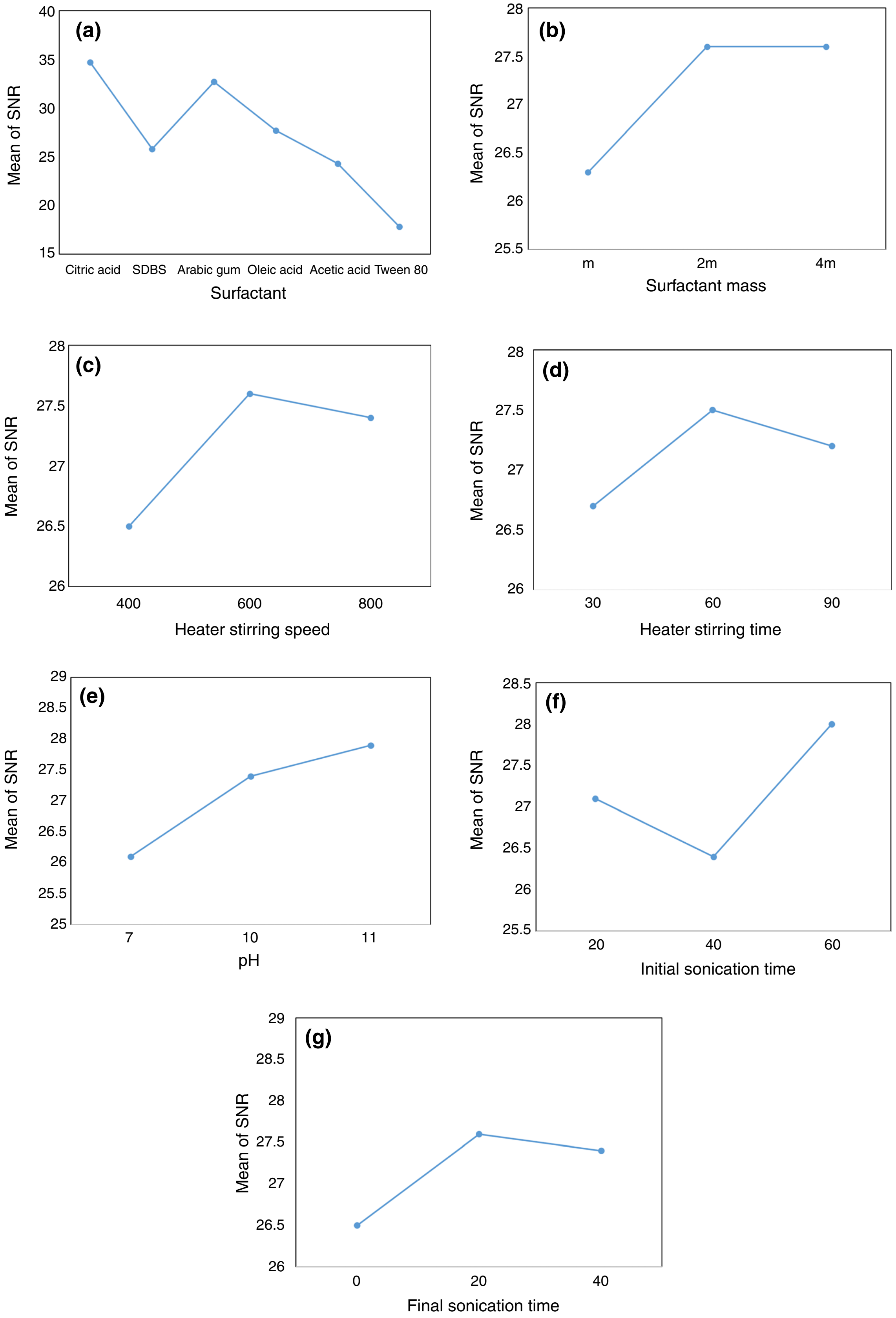
The effect of increasing pH number on the ferrofluid stability is shown in Fig. 6e. It is clear that the environment alkalization at the pH adjustment phase improves the stability. Positive effect of pH increasing on ferrofluid stability is predictable. However, it is important to protect nanoparticles change from acidic and alkaline environment. The effect of ferrofluid initial placing time (T_1) in the ultrasonic bath on the stability is presented in Fig. 6f. It is observed that raising the bathing time from 20 to 40 min reduces the stability. On the other hand, increasing the bathing time from 40 to 60 min improves the stability. Therefore, the 60-min bathing time is selected in this paper.

The positive effect of using the final ultrasonic period (T_3) is evident in Fig. 6g. The stability improvement of ferrofluid is determined by a 20-min ultrasonic bath. Increasing the suspension bathing time from 20 to 40 min slightly reduces the stability. The reason of the adverse effect of increasing final sonication time after 20-min is likely separation of surfactant from nanoparticles.

As it is shown in Fig. 6, stability enhancement of 5% and 7% by adding surfactant from 1*M* to 2*M* and increasing pH from 7 to 11, respectively. Furthermore, it can be concluded that these two parameters collective effects on stability are positive. However, the superposition principle is not applicable to this case due to nonlinearity of the phenomena.

As shown in the response graphs (Fig. 6a–g), the surfactant material has a strong influence on the stability of the prepared suspension. The other effective parameters are, respectively: pH number, initial sonication time, surfactant mass, final sonication time, heater stirring speed and heater stirring time.

Based on the above-mentioned results, the best conditions for preparing a magnetic ferrofluid by a stability analysis can be presented as: employing citric acid as


(a)
Mean of SNR
40
35
30
25
20
15
Citric acid
SDBS
Arabic gum
Oleic acid
Acetic acid
Tween 80
Surfactant
(b)
Mean of SNR
28
27.5
27
26.5
26
25.5
m
2m
4m
Surfactant mass
(c)
Mean of SNR
28
27.5
27
26.5
26
400
600
800
Heater stirring speed
(d)
Mean of SNR
28
27.5
27
26.5
26
30
60
90
Heater stirring time
(e)
Mean of SNR
29
28.5
28
27.5
27
26.5
26
25.5
25
7
10
11
pH
(f)
Mean of SNR
28.5
28
27.5
27
26.5
26
25.5
20
40
60
Initial sonication time
(g)
Mean of SNR
29
28.5
28
27.5
27
26.5
26
0
20
40
Final sonication time

◀ **Fig. 6** SNR report of zeta potential for: **a** surfactant material, **b** surfactant mass, **c** heater stirring speed, **d** heater stirring time, **e** pH, **f** initial sonication time and **g** final sonication time

surfactant, 600 rpm heater stirring speed, final sonication time of 20-min, use of 2*M* surfactant mass, adjusting pH on 11, 60-min heater stirring time and initial sonication time of 60-min.

Magnetism characteristic viewpoint

Another approach to examine the suspension characteristics is based on the magnetism characteristic viewpoint [47]. In order to determine the magnetic properties of prepared ferrofluids, a vibrating sample magnetometer (VSM) is used at room temperature [35]. In this method, a magnetic field is applied to the sample, and thus, the environment magnetism increases immediately. The magnetic field is increased exponentially until a saturated value of M_s. Decreasing the magnetic field will result in a change in the sample magnetism. However, the change is not proportional to the increasing in the magnetic field. This disproportionality is due to the magnetic anisotropy of the environment that leads to energy storage in the sample. However, when the magnetic field is reduced to zero, the sample magnetism will not be zero. The remaining magnetism of the sample is called magnetism residue (M_r) [48]. The magnetization power is the maximum value of curves that shows saturated magnetization. Figure 7 shows the magnetic behavior of Sample 15 under the VSM magnetic field. As shown in the figure, Fe_3O_4 nanoparticles in the sample are magnetized proportionally to the magnitude of magnetic field. As the magnetic field is reduced to zero, the magnetism of the sample becomes zero, as well (i.e., no magnetism residue). This indicates that by implementing the magnetic field, Fe_3O_4 never remains a magnet. Therefore, the Fe_3O_4 nanoparticles do not agglomerate and, consequently, the ferrofluid remains stable.

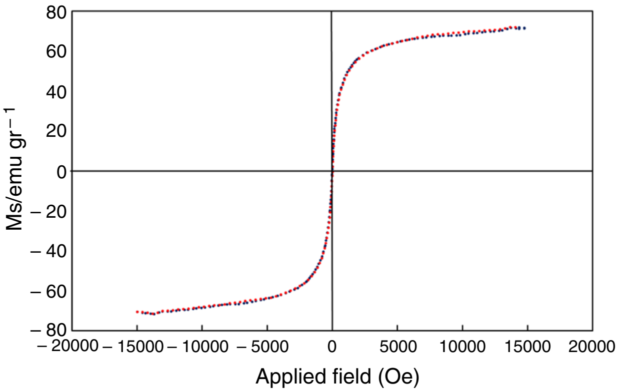


Fig. 7 Sample 15 magnetic behavior under VSM measurement

Another important factor in determining the ferrofluid characteristics is magnetism power of prepared suspension. The results of these measurements for 18 samples are shown in Table 5. Samples 1, 4, 6, 11, 13, 14 and 15 show a superparamagnetic behavior.

Using the VSM data from Table 5 and Taguchi method, the results are displayed in Fig. 8. The effect of the surfactant material on the magnetization of the ferrofluid is presented in Fig. 8a. As shown in this figure, acetic acid provides the best magnetization result, while the SDBS and oleic acid present moderate results. The lowest magnetization values are seen by Arabic gum and tween 80. The reason for various effects of different surfactants on magnetization could be justified by their different chemical behavior.

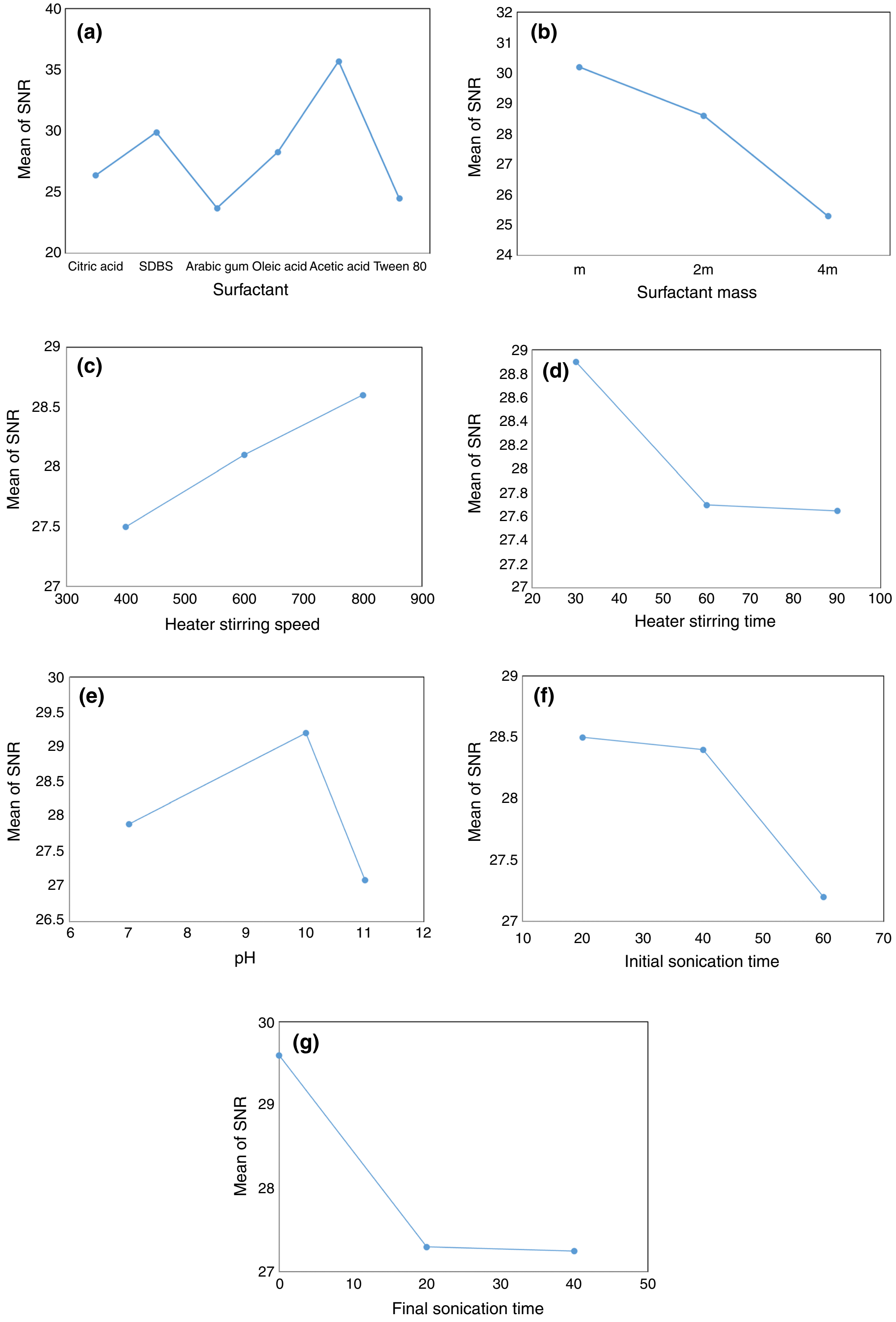
Figure 8b presents the effect of surfactant mass on magnetization. As expected, the magnetization reduces by increasing the surfactant mass. It is clear that when the amount of the surfactant increases, the magnetization of the particles is reduced. The reason can be described in terms of surrounded nanoparticles by surfactant molecules. Surfactant mass shows dual behavior on stability and magnetism of the prepared ferrofluids.

Figure 8c shows the effect of the heater stirring speed on the magnetization of the ferrofluid. The positive effect of the heater stirring speed on magnetization is clearly observed in this figure. The variation of heater stirring speed against the SNR is nearly linear. Separation of surfactant from the nanoparticles that causes less nanoparticles covered by surfactant molecules could be explained as the main reason for the magnetization enhancement by increasing the heater stirrer speed.

Figure 8d reports the effect of the placing time in the heater stirring on magnetization. As shown in the figure, placing the product on the device for 30 min gives the best result. When the heater stirrer time is increased, the mixing of the solution and covering nanoparticle by surfactant are enhanced, as a result the magnetization of ferrofluid is

Table 5 18 samples VSM results

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
VSM	33.6	23.4	11.4	36.6	21.6	37.8	13.2	15	18.6	18.6	35.4	26.4	37.2	81	73.8	15.6	12.6	24


(a)
Mean of SNR
40
35
30
25
20
Citric acid
SDBS
Arabic gum
Oleic acid
Acetic acid
Tween 80
Surfactant
(b)
Mean of SNR
32
31
30
29
28
27
26
25
24
m
2m
4m
Surfactant mass
(c)
Mean of SNR
29
28.5
28
27.5
27
300
400
500
600
700
800
900
Heater stirring speed
(d)
Mean of SNR
29
28.8
28.6
28.4
28.2
28
27.8
27.6
27.4
27.2
27
20
30
40
50
60
70
80
90
100
Heater stirring time
(e)
Mean of SNR
30
29.5
29
28.5
28
27.5
27
26.5
6
7
8
9
10
11
12
pH
(f)
Mean of SNR
29
28.5
28
27.5
27
10
20
30
40
50
60
70
Initial sonication time
(g)
Mean of SNR
30
29
28
27
0
10
20
30
40
50
Final sonication time

◀ **Fig. 8** SNR results of magnetization for: **a** surfactant material, **b** surfactant mass, **c** heater stirring speed, **d** heater stirring time, **e** pH, **f** initial sonication time and **g** final sonication time

reduced. Magnetization enhancement of prepared ferrofluid is obtained by adjusting the pH number at a value of 10. Chemical reaction in the nanoparticles and reduction of the ferrofluid magnetic behavior by increasing pH to 11 may be the reasons for the sharp decrease in the magnetization.

The effect of initial ferrofluid placing time in the ultrasonic bath on the magnetization is presented in Fig. 8f. 20 or 40-min initial sonication time indicates better results compared to those of 60 min. By increasing initial sonication time, the solution mixing and surfactant covering are improved, and as previously stated, magnetization is reduced.

The negative effect of using the final ultrasonic period can be observed in Fig. 8g. The figure shows that the magnetization of the prepared samples is reduced during the final sonication period at 20 and 40-min. Same reasons for initial sonication time can be considered to justify the current observation.

As shown in the response graphs (Fig. 8a–g), the surfactant material has the maximum influence on the magnetization, followed by surfactant mass, pH number, final sonication time, heater stirring time, initial sonication time and heater stirring speed in sequence.

As a result, the best conditions for the production of a magnetic nanofluid by magnetization viewpoint are: using acetic acid as surfactant, 800 rpm heater stirring speed, no final sonication, using a surfactant mass of 1*M*, adjusting pH at a value of 10-, 30-min heater stirring time and 20- or 40-min initial sonication time.

Conclusions

The effect of different parameters on the stability and magnetization of Fe_3O_4/water nanofluid is investigated experimentally. The DLS distribution and TEM images are applied to study the nanoparticle size. The two-step preparation method is used for preparation of ferrofluid samples. The two criteria of stability and magnetism are employed to characterize the prepared ferrofluids. zeta potential and VSM method are used to study stability and magnetism characteristics of prepared ferrofluid samples, respectively. The effect of six parameters (surfactant material, surfactant mass, heater stirring speed, heater stirring time, pH, initial sonication time and final sonication time) with three levels and one parameter (surfactant material) with six levels was considered. Taguchi method is used as a DOE tool. The results of stability criteria show that the effective parameters on the stability of the prepared ferrofluid as their corresponding importance are: surfactant material, pH number, initial sonication time, surfactant mass, final sonication time, heater stirring speed and heater stirring time. From the magnetization viewpoint, however, the effective parameters as their importance are: the surfactant material, surfactant mass, pH number, final sonication time, heater stirring time, initial sonication time and heater stirring speed.

Acknowledgements The authors would like to express their appreciation to the Mrs. Narges Eider for her helpful support. The support of Khorasan Razavi Gas Company is also gratefully acknowledged.

References

1. Sayantan M, Somjit P. Preparation and stability of nanofluids-a review. IOSR J Mech Civ Eng (IOSR-JMCE). 2013;9(2):63–9.
2. Taniguchi N. On the basic concept of ‘nano-technology‘. In: Proceedings of international conference production engineering. Tokyo. Part II. Japan Society of Precision Engineering. 1974.
3. Ding Y, Alias H, Wen D, Williams RA. Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids). Int J Heat Mass Transf. 2006;49:240–50.
4. Choi SUS, Eastman JA. Enhancing thermal conductivity of fluid with nanoparticles. In: ASME International mechanical engineering congress and exposition, San Francisco, CA. 1995.
5. Abadeh A, Rejeb O, Sardarabadi M, Menezo C, Passandideh-Fard M, Jemni A. Economic and environmental analysis of using metal-oxides/water nanofluid in photovoltaic thermal systems (PVTs). Energy. 2018;159:1234–43.
6. Salehi H, Zeinali Heris S, Sharifi F, Razbani MA. Effects of a nanofluid and magnetic field on the thermal efficiency of a two-phase closed thermosyphon. Heat Transf Asian Res. 2013;42–7:630–50.
7. Dandamudi S, Campbell R. The drug loading, cytotoxicity and tumor vascular targeting characteristics of magnetite in magnetic drug targeting. Biomaterials. 2007;31:4673–83.
8. Abadeh A, Mohammadi M, Passandideh-Fard M. Experimental investigation on heat transfer enhancement for a ferrofluid in a helically coiled pipe under constant magnetic field. J Therm Anal Calorim. 2018. https://doi.org/10.1007/s10973-018-7478-2.
9. Abadeh A, Passandideh-Fard M, Maghrebi MJ. An experimental energy and exergy analysis of uniform and step heat flux effects on heat transfer over of circular cross-section tube. Modares Mech Eng. 2018;18–4:201–10 **(in Persian)**.
10. Li Z, Kawashita M, Araki N, Mitsumori M, Hiraoka M, Doi M. Magnetite nanoparticles with high heating efficiencies for application in the hyperthermia of cancer. Mater Sci Eng C. 2010;30:990–6.
11. Hosseinzadeh M, Zeinali Heris S, Beheshti A, Shanbedi M. Convective heat transfer and friction factor of aqueous Fe3O4 nanofluid flow under laminar regime an experimental investigation. J Therm Anal Calorim. 2016;124:827–38.
12. Asfer M, Mehta B, Kumar A, Khandekar S, Panigrahi PK. Effect of magnetic field on laminar convective heat transfer characteristics of ferrofluid flowing through a circular stainless steel tube. Int J Heat Fluid Flow. 2016;59:74–86.
13. Yarahmadi M, Moazami Goudarzi H, Shafii MB. Experimental investigation into laminar forced convective heat transfer of ferrofluids under constant and oscillating magnetic field with

different magnetic field arrangements and oscillation modes. Exp Therm Fluid Sci. 2015;68:601–11.

14. Zhao B, Nan Z. Preparation of stable magnetic nanofluids containing Fe_3O_4@PPy nanoparticles by a novel one-pot route. Nanoscale Res Lett. 2011;6:230–7.
15. Zhu H, Lin Y, Yin Y. A novel one-step chemical method for preparation of copper nanofluids. Colloid Interface Sci. 2004;277:100–3.
16. Eastman J, Choi SUS, Li S, Thompson LJ, Lee S. Enhanced thermal conductivity through the development of nanofluids. Symp V Nanophase Nanocompos Mater II. 1996;457:3–11.
17. Eastman J, Choi SUS, Li S, Yu W, Thompson LJ. Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles. Appl Phys Lett. 2001;78–6:718–20.
18. Feng X, Ma H, Huang S, Pan W, Zhang X, Tian F, Gao C, Cheng Y, Luo J. Aqueous-organic phase-transfer of highly stable gold, silver, and platinum nanoparticles and new route for fabrication of gold nanofilms at the oil/water interface and on solid supports. J Phys Chem B. 2006;110–25:12311–7.
19. Yu W, Xie H, Chen L, Li Y. Enhancement of thermal conductivity of kerosene-based Fe_3O_4 nanofluids prepared via phase-transfer method. Colloids Surf A. 2010;355:109–13.
20. Shanbedi M, ZeinaliHeris S, Amiri A, Eshghi H. Synthesis of water-soluble Fe-decorated multi-walled carbon nanotubes: a study on thermo-hysical properties of ferromagnetic nanofluid. J Taiwan Inst Chem Eng. 2016;60:547–54.
21. Wei X, Wang L. Synthesis and thermal conductivity of microfluidic copper nanofluids. Particuology. 2010;8–3:262–71.
22. Lopez JA, Gonzalez F, Bonilla FA, Zambrano G, Gomez ME. Synthesis and characterization of Fe_3O_4 magnetic nanofluid. Revista Latinoamericana de Metalurgia y Materiales. 2010;30–1:60–6.
23. Nigam S, Barick K, Bahadur D. Development of citrate-stabilized Fe_3O_4 nanoparticles: conjugation and release of doxorubicin for therapeutic applications. J Magn Magn Mater. 2011;323:237–43.
24. Yu W, Xie H. A Review on nanofluids: preparation, stability mechanisms, and applications. J Nanomater. 2012;2012:1–17.
25. Cheraghipour E, Tamaddon A, Javadpour S, Bruce I. PEG conjugated citrate-capped magnetite nanoparticles for biomedical applications. J Magn Magn Mater. 2013;328:91–5.
26. Kazeminezhad I, Mosivand S. Effect of surfactant concentration on size and morphology of electrooxidated Fe_3O_4 nanoparticles. In: Proceedings of the 3rd conference on nanostructures, Kish Island, I.R. Iran, 10–12 March. 2010.
27. Vekas L, Bika D, Marinica O. Magnetic nanofluids stabilized with various chain length surfactants. Romanian Rep Phys. 2006;58–3:257–67.
28. Wang X, Zhang C, Wang X, Gu H. The study on magnetite particles coated with bilayer surfactants. Appl Surf Sci. 2007;253:7516–21.
29. Jama M, Singh T, Gamaleldin SM, Koc M, Samara A, Isaifan RJ, Atieh MA. Critical review on nanofluids: preparation, characterization, and applications. J Nanomater. 2016. https://doi.org/10.1155/2016/6717624.
30. Bica D, Vekas L, Avdeev M, Marinica O, Socoliuc V, Balasoiu M, Garamus VM. Sterically stabilized water based magnetic fluids- synthesis, structure and properties. J Magn Magn Mater. 2007;311:17–21.
31. Williams W, Bang I, Forrest E, Hu LW, Buongiorno J. Preparation and characterization of various nanofluids. NSTI Nanotech. 2006;2:408–11.
32. Bica D, Vekas L, Rasa M. Preparation and magnetic properties of concentrated magnetic fluids on alcohol and water carrier liquids. J Magn Magn Mater. 2002;252:10–2.
33. Ghadimi A, Saidur R, Metselaar HSC. A review of nanofluid stability properties and characterization in stationary conditions. Int J Heat Mass Transf. 2011;54:4051–68.
34. Li Q, Xuan Y, Wang J. Experimental investigations on transport properties of magnetic fluids. Exp Therm Fluid Sci. 2005;30:109–16.
35. Cheraghipour E, Javadpour S, Mehdizadeh AR. Citrate capped superparamagnetic iron oxide nanoparticles used for hyperthermia therapy. J Biomed Sci Eng. 2012;5:715–9.
36. Montgomery DC. Design and analysis of experiments. 8th ed. New York: Wiley; 2012.
37. Kotcioglu I, Cansiz A, Nasiri Khalaji M. Experimental investigation for optimization of design parameters in a rectangular duct with plate-fins heat exchanger by Taguchi method. Appl Therm Eng. 2013;50:604–13.
38. Sivasakthivel T, Murugesan K, Thomas H. Optimization of operating parameters of ground source heat pump system for space heating and cooling by Taguchi method and utility concept. Appl Energy. 2014;116:76–85.
39. Lu S, Li Y, Tang J. Optimum design of natural-circulation solar-water-heater by the Taguchi method. Energy. 2003;28:741–50.
40. Verma V, Murugesan K. Optimization of solar assisted ground source heat pump system for space heating application by Taguchi method and utility concept. Energy Build. 2014;82:296–309.
41. Lin W, Ma Z, Cooper P, Sohel MI, Yang L. Thermal performance investigation and optimization of buildings with integrated phase change materials and solar photovoltaic thermal collectors. Energy Build. 2016;116:562–73.
42. Zhu D, Li X, Wang N, Wang X, Gao J, Li H. Dispersion behavior and thermal conductivity characteristics of Al2O3–H2O nanofluids. Curr Appl Phys. 2009;9:131–9.
43. Garg P, Alvarado JL, Marsh C, Carlson TA, Kessler DA, Annamalai K. An experimental study on the effect of ultrasonication on viscosity and heat transfer performance of multi-wall carbon nanotube-based aqueous nanofluids. Int J Heat Mass Transf. 2009;52:5090–101.
44. Qiang AH, Zhao LM, Xu CJ, Zhou M. Effect of dispersant on the colloidal stability of nano-sized CuO suspension. J Dispers Sci Technol. 2007;28:1004–7.
45. Pastoriza-Gallego MJ, Casanova C, Legido JL, Pineiro MM. CuO in water nanofluid: influence of particle size and polydispersity on volumetric behaviour and viscosity. Fluid Phase Equilib. 2011;300:188–96.
46. Hwang Y, Lee JK, Lee JK, Jeong YM, Cheong S, Ahn YC, Kim SH. Production and dispersion stability of nanoparticles in nanofluids. Powder Technol. 2008;186:145–53.
47. Odenbach S. Ferrofluids: magnetically controllable fluids and their applications. Bremen: Springer; 2002.
48. Vekas L, Bica D, Avdeev MV. Magnetic nanoparticles and concentrated magnetic nanofluids: synthesis, properties and some applications. China Particuol. 2007;5:43–4.