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Experimental Study on Synergistic Demulsification of Microwave-Magnetic Nanoparticles

Nana Sun, Huayi Jiang,* Ruiyu Su, Lanxin Zhang, Lisha Shen, and Huina Sun

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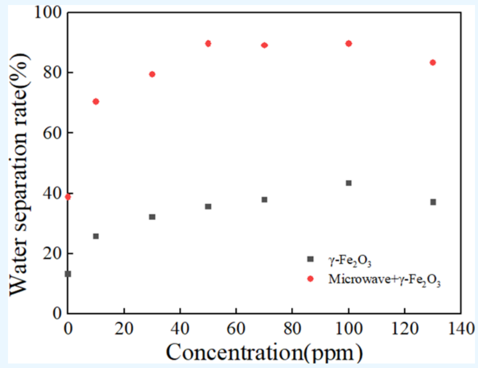

ABSTRACT: Owing to the difficulty in the demulsification of heavy oil-in-water (O/W) emulsions, the demulsification rules of magnetic nanoparticles, microwave radiation, and magnetic-nanoparticle-assisted microwaves were investigated in this study. The surface potential and droplet size of the emulsion under different demulsification conditions were investigated by using a ζ potentiometer and polarizing microscopy to reveal the mechanism of demulsification. The results showed that γ-Fe_2O_3 exhibited the best demulsification performance among the six magnetic nanoparticles used for demulsification. With an increase in the concentration of γ-Fe_2O_3, the water separation of the heavy O/W emulsion first increased and then decreased, and with a decrease in pH, the demulsification performance gradually increased. The experimental results showed that microwave demulsification had an optimal power. The demulsification efficiency was significantly improved at the synergistic action between magnetic nanoparticles and the microwave, proving that magnetic nanoparticles had a promoting effect on microwave demulsification. In addition, the recycling experiment results showed that the magnetic nanoparticles exhibited good recyclability and reusability. Finally, a temperature field model of the emulsion under the synergistic effect of microwaves and magnetic nanoparticles was established and evaluated. Both before and after the addition of the magnetic nanoparticles, the theoretical temperature of the heavy O/W emulsion was consistent with the experimental temperature at different microwave powers and radiation times.

1. INTRODUCTION

The primary solutions for addressing the difficulty in the demulsification of heavy oil-in-water (O/W) emulsions currently include several physical and chemical demulsification methods. The physical methods include heating, gravity sedimentation, centrifugal demulsification, and microwave demulsification methods. Compared with other demulsification methods, the microwave demulsification method has the advantages of high efficiency, no pollution, and automated control. Numerous studies have been conducted on microwave demulsification. Becher[1] found that microwave radiation can reduce the ζ potential on the surface of oil droplets, thereby damaging the stability of the double layer of emulsion, weakening the electrostatic repulsion between the oil droplets, and promoting the coalescence of the oil droplets. Chang et al.[2] studied the effects of pH on microwave demulsification. The results showed that the demulsification efficiency increased with decreasing pH value. Martínez-Palou et al.[3] observed that compared with the traditionally heated oil droplets, those under microwave irradiation have a larger particle size and more uneven distribution. Yang[4] studied the effects of the demulsifier concentration, microwave power, and water content of emulsions on microwave demulsification. The results showed that at a constant microwave power, an increase in the demulsifier concentration first increased and then decreased the water separation rate of the emulsion. When the demulsifier concentration was 100 mg/L, the demulsifiction efficiency was the maximum. When the temperature was constant and the power was 480 W, the water separation rate of the emulsion reached the maximum value. When the water content of the emulsion was 5−40%, the water separation rate of the emulsion gradually increased with increasing water content.

For a heavy oil emulsion with a high emulsification degree, achieving the dehydration standard by employing only microwave demulsification is difficult, and it usually needs to be used in combination with chemical methods. As the conventional chemical demulsifiers have limitations such as large dosage requirement, aggravated corrosion and scaling of pipeline equipment, and production of flocculates after demulsification that are difficult to separate in both water

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and oil phases, a new type of high-efficiency demulsifier must be developed to address the aforementioned problems.

In recent years, magnetic nanoparticles have attracted considerable attention as new demulsifiers with no pollution, easy recovery, and repeated usability. Magnetic nanoparticles are superior to other chemical demulsifiers because of their excellent magnetism and large surface area.[5] Moreover, they affect the emulsion interface properties, droplet morphology, particle size, and surface potential, thereby affecting the stability of the emulsion.

In the demulsification process, the concentration of magnetic nanoparticles has a positive impact on the demulsification effect.[6−8] With an increase in the magnetic nanoparticle concentration, the demulsification efficiency increases. Huang et al.[9] described the apparent morphology and motion-state response behavior of oil droplets wrapped with magnetic nanoparticles under the action of an external magnetic field and comprehensively analyzed the influence of the characteristic properties of magnetic nanoparticles and the interface behavior on emulsion stability. Fang et al.[10] conducted oil−water interface comparison experiments and found that a smaller size of magnetic nanoparticles led to a better dispersion performance, stronger adsorption capacity at the interface, and more evident flocculation effect. Lü et al.[11,12] studied the demulsification performance of magnetic nanoparticles under different pH conditions and found that under alkaline conditions, the magnetic nanoparticles were adsorbed on the surface of oil droplets through hydrophobic interactions, and the magnetic separation and demulsification relied on the external magnetic field. Under acidic and neutral conditions, electrostatic attraction was mainly used to flocculate oil droplets and achieve demulsification.

Peng et al.[13] synthesized and used functionalised magnetic nanoparticles to treat waste-metal-processing emulsions and discussed their demulsification mechanism. The particles exhibited excellent demulsification performance, confirming that the electrostatic interaction between the functionalised magnetic nanoparticles and surfactants was the driving force behind demulsification. Zhao et al.[14] evaluated the demulsification effect of magnetic nanoparticles in surfactant-stabilized O/W emulsions, and the results showed that the demulsification rate increased with an increase in the particle concentration but decreased with an increase in the pH and surfactant concentration.

Because of the domestic and foreign research status, the demulsification performance of magnetic nanoparticles is often studied in isolation. Few reports have been published on the synergistic demulsification of microwave electromagnetic fields and magnetic nanoparticles.

In this study, the water separation rate is considered as the evaluation index and the synergistic demulsification of magnetic nanoparticles, microwave demulsification, and microwave-magnetic nanoparticles was examined using a ζ potential analyzer and polarizing microscopy (PLM). The effects of the impact law and mechanism of magnetic nanoparticles on microwave demulsification are analyzed and discussed.

2. EXPERIMENT SECTION

2.1. Experimental Materials and Drugs. The main experimental materials were heavy oil obtained from the Xinjiang Oilfield, distilled water, petroleum ether, and anhydrous ethanol. In addition, several drugs, nonionic surfactant octyl phenyl polyoxyethylene ether (TX-100), and organic base triethanolamine (TEOA) were used. The magnetic nanoparticles used in the experiment are listed in Table 1.

Table 1. Magnetic Nanoparticles Used in the Experiment

commodity name	chemical name	commodity name	chemical name
$ZnFe_2O_4$	nano zinc ferrite	γ-Fe_2O_3	nano gamma type iron oxide
$NiFe_2O_4$	nano nickel ferrite	Co_3O_4	nano cobalt oxide
Fe_3O_4	nano ferric oxide	Ni	nano nickel powder

2.2. Laboratory Apparatus. The laboratory apparatus consisted of a BS224S electronic balance (precision: 1/10 000 g, Sedolis, Germany), HH-2 digital-display constant-temperature water bath (Jintan Huafeng Instrument Co., Ltd.), digital-display electric stirrer (Jiangsu Changzhou Putian Instrument Manufacturing Co., Ltd.), constant-temperature magnetic stirrer (Jintan Medical Instrument Factory), MAS-II atmospheric-pressure microwave synthesis/extraction reaction workstation (Shanghai Xinyi Microwave Chemical Technology Co., Ltd.), CX40P reflective-lighting polarizing microscope (Shangguang (Suzhou) Instrument Co., Ltd.), nano ZS90 ζ potential analyzer (British Marvin Company), and several colorimetric tubes, beakers, and measuring cylinders (Chengdu Kelong Chemical Reagent Factory).

2.3. Experimental Methods. (1) First, a binary active water system containing 1.25% TX-100 and 0.25% TEOA was prepared. The heavy oil from the Xinjiang Oilfield was mixed with the binary active water in a ratio of 7:3. The mixed sample was placed in a constant-temperature water bath at 25 °C for 30 min. The mixture was stirred at a constant speed using a mechanical stirrer. The stirring speed was set to 1000 r·min^{-1}, and the mixture was stirred for 3 min to prepare an heavy O/W emulsion.

(2) The prepared emulsion was poured into a 50 mL graduated tube, and the suspension of magnetic nanoparticles was added to it. The sample was shaken evenly 200 times manually. It was then poured into a double-hole round-bottom flask and placed in a microwave device for reactions based on the present radiation parameters. The temperature of the emulsion was recorded using an infrared temperature measuring device.

(3) The irradiated emulsion was poured into a colorimetric tube, which was placed in a constant-temperature water bath at 25 °C for 1 h. The water separation height was measured every 2 min for the first 10 min and every 10 min for the last 50 min. The sample was placed for 24 h, and its total height was measured after the emulsion was completely defoamed. The water separation rate was determined by employing the bottle test method. The calculation formula is as follows

$$f = \left(\frac{V_1}{V_2}\right) \times 100\% = \left(\frac{h_1}{h_2 \times 30\%}\right) \times 100\% \tag{1}$$

where, f—water separation rate (%); V_1—volume of precipitated water (mL); V_2—total water volume (mL); h_1—height of precipitated water (cm); h_2—total emulsion height (cm).

(4) A fixed external magnetic field was used to adsorb and recover the magnetic nanoparticles after demulsification. The

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magnetic nanoparticles were extracted several times by using petroleum ether and anhydrous ethanol. After being thoroughly cleaned, the magnetic nanoparticles were dried in a vacuum drying box and recovered.

(5) Nano γ-Fe_2O_3 having a concentration of 50 mg/L was selected for addition in the emulsion microelement. The heat balance equation of the emulsion microelement before and after this addition was analyzed. Based on the electromagnetic field theory, the relationship between the electric/magnetic field intensity and microwave power in the microwave cavity was established, and the electric/magnetic field intensities of the continuous and dispersed phases of the emulsion were determined. The dielectric parameters of the continuous and dispersed phases of the emulsion and the convective heat transfer coefficient of the emulsion were determined experimentally and were considered as functions of the temperature and radiation time. The relevant parameters were then substituted into the emulsion temperature field model, and the fourth-order Runge−Kutta method was applied to program and solve the model by using MATLAB. Thus, the temperature distribution of the emulsion before and after the addition of magnetic nanoparticles under different microwave parameters was obtained.

3. RESULTS AND DISCUSSION

3.1. Effect of Magnetic Nanoparticle Type on Stability of O/W Emulsion of the Heavy Oil. For the O/W emulsion of the heavy oil from the Xinjiang Oilfield, the static stability was first tested without any demulsifier, and then, the stability of the six magnetic nanoparticles with a concentration of 50 mg/L was tested within 1 h. The results are shown in Figure 1.

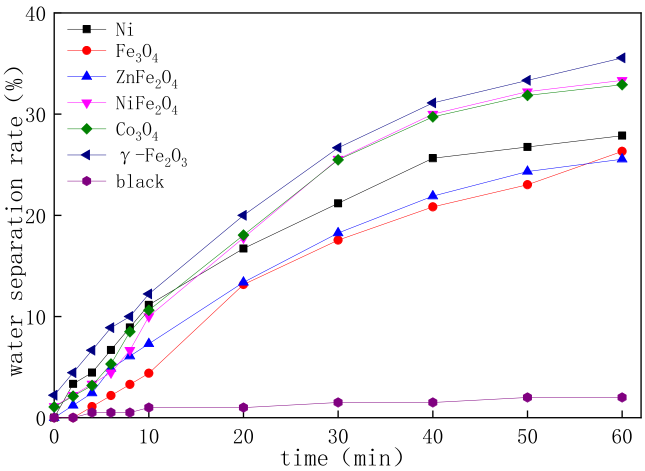

Figure 1. Effect of six different types of magnetic nanoparticles on the stability of emulsion.

As shown in Figure 1, the water separation rate of the heavy O/W emulsion is low in the absence of any demulsifier and only 6% at 1 h, indicating that the emulsion exhibits strong stability. After the addition of 50 ppm of magnetic nanoparticles, the water separation rate of the emulsion improves significantly. The order of the effects of the different types of magnetic nanoparticles on the stability of the heavy O/W emulsion was nano γ-Fe_2O_3 > nano Co_3O_4 > nano $NiFe_2O_4$ > nano Fe_3O_4 > nano Ni > nano $ZnFe_2O_4$.

The reasons for the aforementioned phenomena are as follows: (1) magnetic nanoparticles have a large specific surface area and high surface energy and exhibit good dispersibility and adsorption owing to their nanoparticle size. They are adsorbed at the oil−water interface to replace the surfactant molecules, forming a mixed membrane structure, wherein the surfactants and magnetic nanoparticles coexist. The mixed membrane structure weakens the strength of the original interfacial membrane,[15,16] thereby reducing the interfacial stability. In the process of contact and collision between droplets, adjacent droplets accumulate owing to the bridging action to form droplets with the larger-sized particles, reducing the stability of the emulsion. (2) The surface of magnetic nanoparticles accumulates a large amount of charge. Under acidic or neutral conditions, the surface of some magnetic nanoparticles is positively charged[17] and adsorbs to the surface of negatively charged oil droplets under an electrostatic action, reducing the electrostatic repulsion of the electric double layer on the surface of the oil droplets and promoting their coalescence. (3) When magnetic nanoparticles are dispersed in an emulsion, a certain magnetic field intensity exists near the particles, and it attracts the surrounding particles and small droplets to form large particles with the magnetic nanoparticles as the core, thereby exhibiting magnetic flocculation.[18]

3.2. Effect of Magnetic Nanoparticles Concentration on the Stability of Heavy O/W Emulsion. For γ-Fe_2O_3, which had the best demulsification effect as determined in the previous section, a full concentration experiment at 10−130 mg/L was conducted to further determine the effect of the magnetic nanoparticle concentration on the stability of the heavy O/W emulsion. The experimental results are as follows.

As shown in Figure 2, as the concentration of the magnetic nanoparticles increases, the water separation rate of the heavy O/W emulsion initially increases and then decreases.

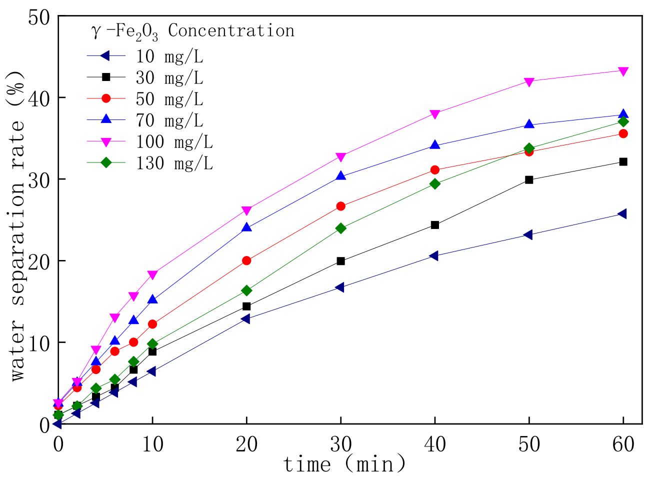

Figure 2. Results of total concentration experiments of γ-Fe_2O_3.

This is because when the concentration of magnetic nanoparticles was low, the added magnetic nanoparticles formed a mixed film structure at the oil−water interface, gradually reducing the strength of the interface film and promoting droplet coalescence.[18] However, with a further increase in the concentration of the magnetic nanoparticles, the surface of the dispersed phase droplets formed a magnetic nanoparticle film structure,[19] thereby enhancing the stability of

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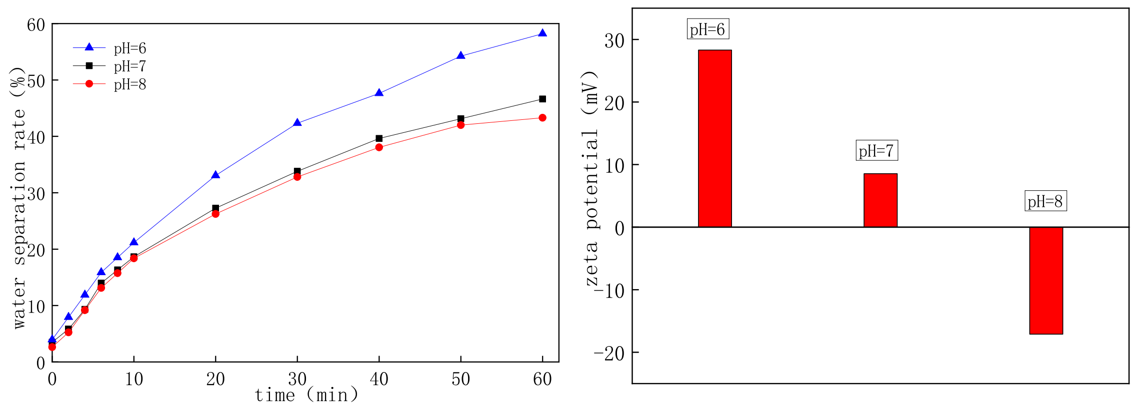
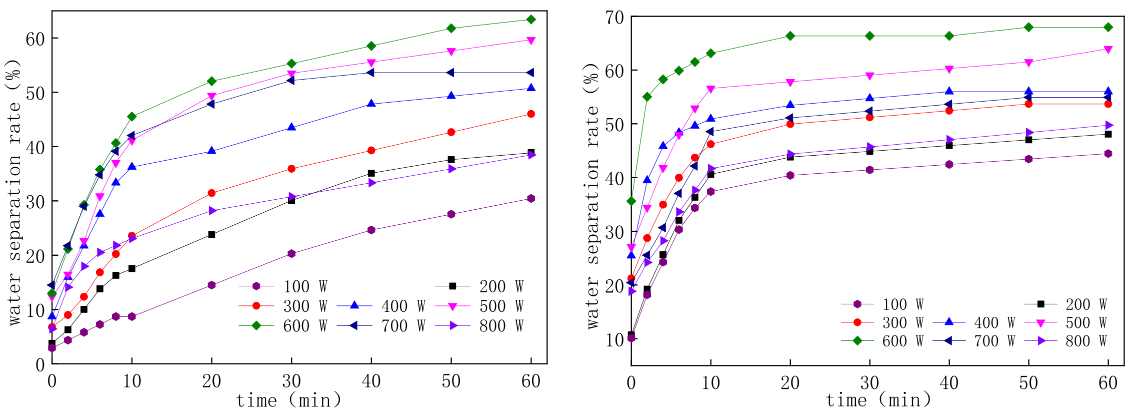


(a) Water separation rate (b) Electric quantity

Figure 3. Demulsification experiments of magnetic nanoparticles at different pH values.



(a) Full-power experiment in 20 s (b) Full-power experiment in 30 s

Figure 4. Results of demulsification experiments under different radiation parameters.

the droplet interface film and reducing the probability of coalescence between the droplets due to collision and extrusion. In addition, when the concentration of the magnetic nanoparticles was high, the magnetic nanoparticles, particles and droplets, and droplets and droplets all cross-linked with each other, forming a three-dimensional network structure in the continuous phase of the emulsion,[9] resulting in a spatial steric hindrance and increasing the energy barrier to be overcome by droplet contact. Macroscopically, the viscosity of the emulsion system increased,[20] resulting in the stability of the emulsion structure. This is the reason behind the decrease in the water separation rate of the emulsion when the concentration of the magnetic nanoparticles was high.

3.3. Effect of the pH Value on Demulsification of Magnetic Nanoparticles. With a change in the pH value of the system, the charge of the magnetic nanoparticles changed, altering the binding ability of the magnetic nanoparticles on the surface of the oil droplets, and thereby affecting their demulsification performance. Based on these experimental results, 100 mg/L of γ-Fe_2O_3 was selected. The demulsification effect was investigated at pH values of 6, 7, and 8, and the corresponding experimental results are shown in Figure 3.

The experimental results (Figure 3a) reveal that the water separation rate of the emulsion gradually increases with decreasing pH value. The reason for this phenomenon is that at a low pH value, H^+ is adsorbed on the surface of the nanoparticles, and the net charge is positive, as shown in Figure 3b, thereby enhancing the electrostatic attraction between the nanoparticles and negatively charged oil droplets, reducing the thickness of the electric double layer around the oil droplets, weakening the electrostatic repulsion between the oil droplets, and promoting droplet coalescence. With an increase in the pH value, the ζ potential of the oil droplet surface gradually decreased, the impact on the electric double layer gradually weakened, and the corresponding water separation rate gradually decreased. Moreover, some researchers have reported that at a high pH, the dispersion of oil droplets in the emulsion increases, thereby increasing the stability of the emulsion system.[21]

3.4. Effect of Different Radiation Powers on Microwave Demulsification. To clarify the demulsification effect and mechanism of microwave power on the heavy oil emulsion and compare with the microwave-magnetic nanoparticles synergistic experiment in the next stage, demulsification experiments with different microwave powers at irradiation times of 20 and 30 s were conducted. The experimental results are shown in Figure 4.

Figure 4 depicts that at microwave irradiation times of 20 and 30 s, with an increase in the power, the water separation rate of the emulsion first increases and then decreases. The reason for this experimental phenomenon is that with increasing microwave power, the temperature of the emulsion

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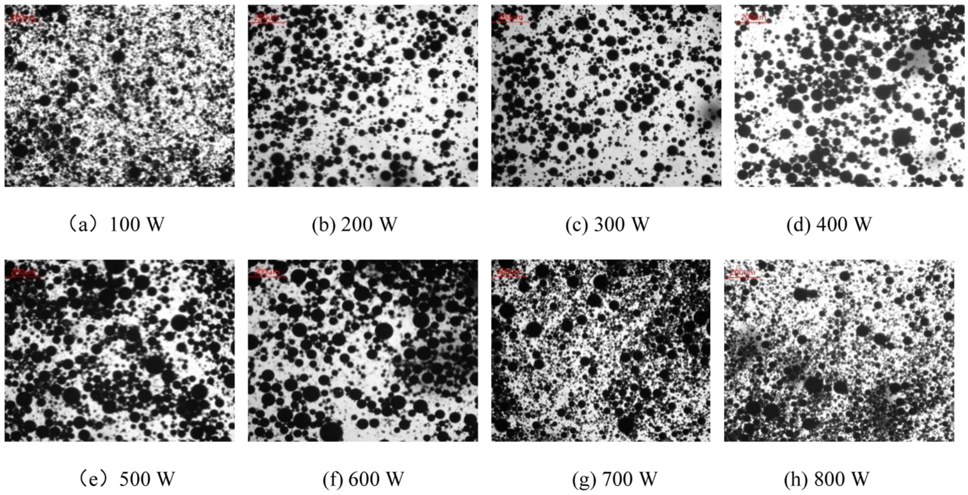

Figure 5. PLM images of emulsion droplets at 30 s with different radiation powers.

increases, intensifying the collisions between the droplets and promoting the coalescence and flocculation of the droplets. However, with an increase in the temperature, the adsorption capacity of the naturally active substances and surfactants on the oil−water interface decreases,[22] increasing the oil−water interfacial tension of the emulsion and reducing the stability of the emulsion. In addition, the microwave radiation can deteriorate the hydrogen bond between the interfacial active component and water molecules, and this deterioration ability increases with increasing microwave power, thereby weakening the thickness of the hydration layer near the interfacial film and coalescence resistance between the droplets.[23,24] The droplet size of the emulsion increases with increasing power, and the water separation rate reaches the maximum at 600 W, as shown in Figure 5a−f. When the radiation power further increases, the emulsion temperature rises rapidly, prompting the droplets to coalesce and separate owing to violent collisions with each other. Finally, with a further increase in the power, the water separation rate decreases, as shown in Figure 5g−h. Thus, an optimal radiation power for microwave demulsification exists, and a rapid destruction of the emulsion can be achieved at this optimal power.

3.5. Microwave-Magnetic Nanoparticle Synergistic Demulsification. The experimental results of the simple microwave demulsification indicated that microwave demulsification had rapidity, but the demulsification effect was unsatisfactory and meeting the field requirements was difficult. Owing to the unique physical and chemical properties of the magnetic nanoparticles, a combination of magnetic nanoparticles and microwaves was considered. B 50 mg/L of γ-Fe_2O_3 and a 200 W microwave were selected for synergistic demulsification for 30 s. The corresponding experimental results are shown in Figure 6.

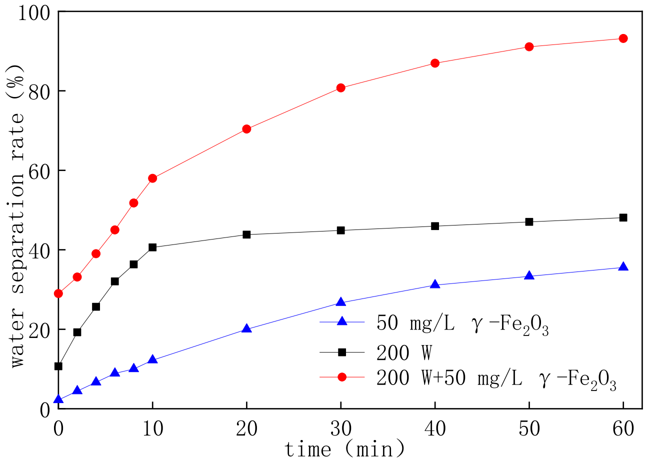

Figure 6. Demulsification efficiency under different conditions.

Figure 6 shows that the synergistic demulsification effect of the microwave and magnetic nanoparticle is better than that of the simple microwave demulsification and magnetic nanoparticle demulsification effects. Under the synergistic effect of the 200 W microwave power and 50 mg/L γ-Fe_2O_3, the water separation rate of the emulsion reaches 93% within 60 min.

The reasons for these phenomena are as follows: (1) as high-loss dielectric materials, magnetic nanoparticles have strong microwave absorption ability.[25,26] Thus, the microwave absorption ability of the emulsion is substantially enhanced with their addition. Further, more heat is generated in the emulsion system, resulting in the rapid heating of the emulsion, thereby promoting the "thermal effect" of the microwaves. (2) Magnetic nanoparticles exhibit significant magnetic responsiveness. When they are adsorbed and wrapped on the surface of suspended droplets, the droplets are magnetic. In a high-frequency microwave electromagnetic field, the magnetic nanoparticles that are subjected to the magnetic field force quickly move in the direction of the magnetic field. They also pull the droplets to migrate with them, resulting in the contact and collisions between the dispersed droplets and prompting the membrane structure to crash and break. The small droplets quickly coalesce into larger droplets, eventually aggravating the demulsification, as shown in Figure 7. (3) Under the action of a microwave electromagnetic field, the magnetic nanoparticles may fall off the surface of the droplet, resulting in the collapse of the membrane structure and causing the dispersed oil phase to gradually flow out and accumulate to form a continuous phase.[4]

3.6. Recycling Experiment. Compared with other traditional chemical demulsifiers, magnetic nanoparticles can both significantly improve the microwave demulsification efficiency and be recycled after demulsification. Therefore, a recycling experiment was conducted under the synergistic

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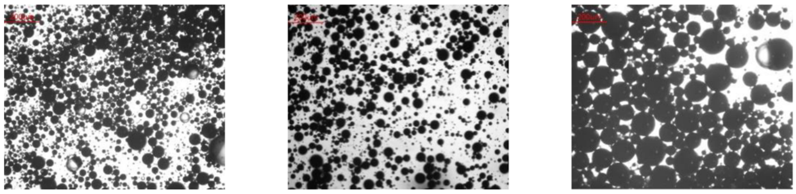
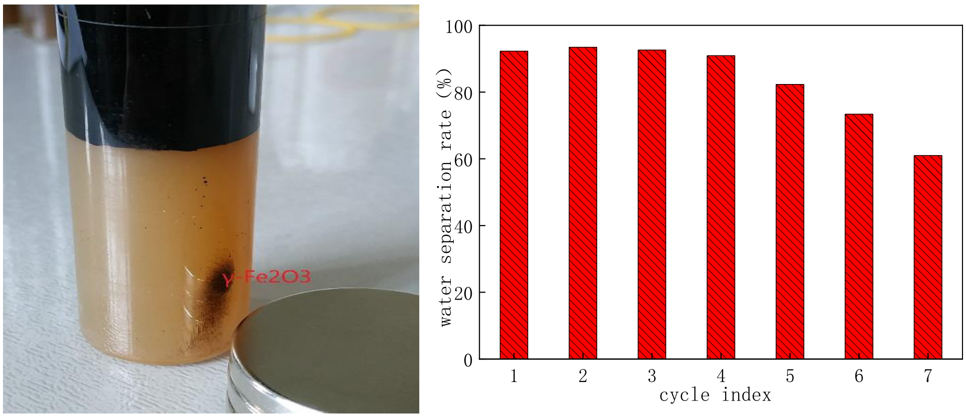


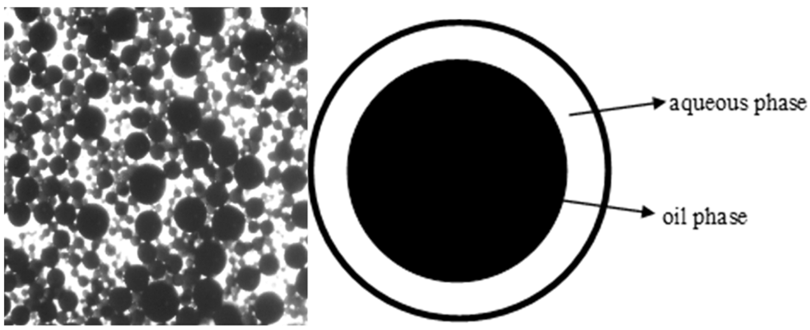
(a) 50 ppmγ-Fe_2O_3 (b) 200 W Microwave (c) 200 W Microwave and 50 mg/L γ-Fe_2O_3 synergy

Figure 7. PLM images of emulsion droplets under different demulsification conditions.



(a) Magnetic nanoparticles adsorbed under external magnetic field (b) Demulsification efficiency of magnetic nanoparticles under multiple cycles

Figure 8. Experimental results of magnetic nanoparticles recovery.



(a) Microscopic image (b) Simplified infinitesimal model

Figure 9. Microscopic image of the heavy O/W emulsion and a simplified microelement model.

effect of 50 mg/L γ-Fe_2O_3 and 200 W microwave irradiation to verify the recycling performance of the magnetic nanoparticles.

The recycled magnetic nanoparticles were used for demulsification again, such that seven cycles of recycling experiments were performed. Figure 8 shows that the magnetic nanoparticles continue to exhibit good demulsification ability after four recycling cycles, and the water separation rate of the emulsion decreases after the fifth cycle, indicating that the magnetic nanoparticles can be recycled many times. The characteristics of easy recovery and multiple recyclability are helpful in reducing the cost of demulsification. In addition, the recovery of magnetic nanoparticles from complex multiphase systems can effectively prevent the damage caused by traditional demulsifiers to the environment or subsequent pipeline equipment.

3.7. Temperature Field Model of Emulsion under Microwave-Magnetic Nanoparticle Interaction. A microscopic image of the heavy O/W emulsion is shown in Figure 9a. The physical model of the emulsion microelement is established with a single dispersed-phase oil droplet and the water phase on its outer surface as the microelement. The model is displayed in Figure 9b.

To further simplify the model, the following assumptions were made: (1) each microelement was a sphere of equal size, and the dispersed-phase oil droplets were uniformly wrapped in the continuous water phase. The dispersed-phase oil droplets were spherical having a diameter d, and the oil-water volume ratio in the microelement was 7:3. (2) The temperature of the continuous phase in the microunit was uniform, i.e., t_1, and the temperature of the dispersed phase in the microelement was also uniform, i.e., t_2. (3) The convective

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heat transfer coefficient of the emulsion was h. (4) The magnetic nanoparticles in the microelement were spherical particles of equal size and were distributed throughout the continuous phase and interface film.

For the continuous phase part of the microelement, according to the law of conservation of energy, the following heat balance equation was applicable within any microwave radiation time interval: the total heat transmitted into the continuous phase + the heat generated by microwave action in the continuous phase = the total heat transmitted outward from the continuous phase + the increment of internal energy of the continuous phase. Owing to the addition of the magnetic nanoparticles, the total heat generated by the continuous phase from microwave irradiation mainly included the following two parts: the heat generated by the continuous phase due to dielectric loss and that generated by the magnetic nanoparticles in the continuous phase due to the magnetocaloric effect.

Therefore, for initial temperature t_0, the temperature field model of the heavy O/W emulsion based on the synergistic effect of microwave magnetic nanoparticles is

$$\begin{cases} \dfrac{dt_1}{d\tau} = \dfrac{P_1'}{\rho_1 c_1} + \dfrac{P_1''}{\rho_1 c_1} - \dfrac{hA(t_1 - t_2)}{\rho_1 c_1 V_1} \\ \dfrac{dt_2}{d\tau} = \dfrac{P_2'}{\rho_2 c_2} + \dfrac{hA(t_1 - t_2)}{\rho_2 c_2 V_2} \\ t_1(0) = t_2(0) = t_0 \end{cases} \tag{2}$$

The temperature field model of the heavy O/W emulsion under microwave irradiation alone is

$$\begin{cases} \dfrac{dt_1}{d\tau} = \dfrac{P_1'}{\rho_1 c_1} - \dfrac{hA(t_1 - t_2)}{\rho_1 c_1 V_1} \\ \dfrac{dt_2}{d\tau} = \dfrac{P_2'}{\rho_2 c_2} + \dfrac{hA(t_1 - t_2)}{\rho_2 c_2 V_2} \\ t_1(0) = t_2(0) = t_0 \end{cases} \tag{3}$$

In the above formulas, P'_1—dissipation power of a continuous phase in a high-frequency microwave electric field; P''_1—heat generated by the magnetocaloric effect of magnetic nanoparticles in a continuous phase at unit time and unit volume; P'_2—dissipation power of a dispersed phase in a high-frequency microwave electric field; ρ_1—density of an emulsion continuous phase, kg/m^3; ρ_2—density of a dispersed phase of emulsion, kg/m^3; c_1—specific heat capacity of active water, J/(kg·°C); c_2—specific heat capacity of heavy oil, J/(kg·°C); V_1—volume of a continuous phase in a microelement, m^3; V_2—volume of a dispersed phase in a microelement, m^3; A—oil−water interface area, m^2; h—convective heat transfer coefficient of emulsion, W/m$_2$ · K; t_0—initial temperature of emulsion, °C; t_1—continuous phase temperature, °C; t_2—temperature of dispersed phase, °C;τ—time, s.

Based on the recursive format of the fourth-order Runge−Kutta, the model was programmed by using the MATLAB software, and the corresponding water-phase temperature, t_1, and oil-phase temperature, t_2, at different microwave powers and radiation times were obtained. The weighted average of the oil−water two-phase temperatures and numerical solution of the emulsion temperature with two controllable parameters (microwave power and radiation time) before and after the addition of magnetic nanoparticles were obtained according to the volume composition of the emulsion. The corresponding solution results are presented in Figures 10 and 11.

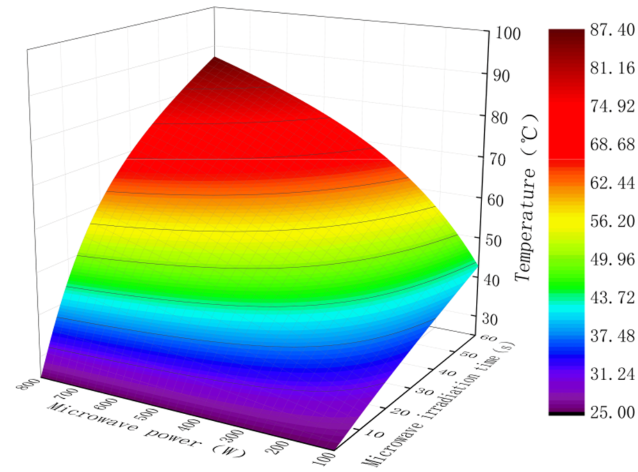

Figure 10. Temperature distribution of emulsion without magnetic nanoparticles.

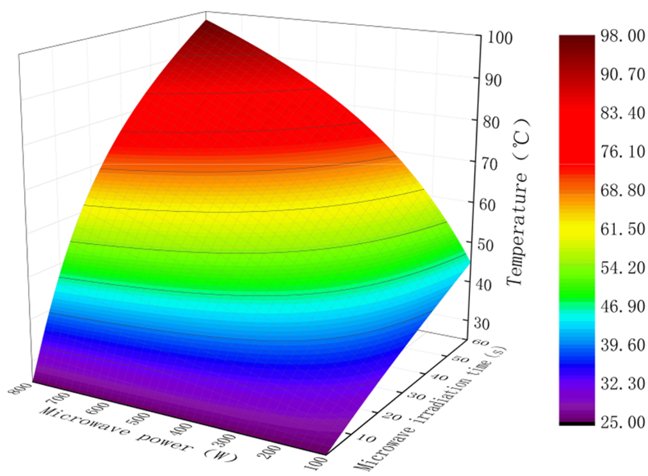

Figure 11. Temperature distribution of emulsion.

As depicted in Figures 10 and 11, when the microwave power is constant, the increase in the emulsion temperature gradually decreases with increasing radiation time. Similarly, when the radiation time is constant, the increase in the emulsion temperature gradually decreases with increasing microwave power.

The squares of the electric and magnetic field strengths in the microwave cavity were positively correlated with the microwave power. Therefore, for the same microwave irradiation time, with increasing microwave power, the electric and magnetic field strengths in the continuous and dispersed phases of the emulsion increased, the heat energy converted by the polar medium increased, and the heat generated by the magnetic nanoparticles increased, thereby gradually increasing the temperature of the emulsion. However, with a further increase in the emulsion temperature, the loss factors of the continuous and dispersed phases in the emulsion gradually decreased, thereby reducing the power density of microwave dissipation. Thus, the temperature of the emulsion increased gradually with increasing power.

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Table 2. Comparison of Theoretical and Experimental Temperatures of Emulsion with/without Magnetic Nanoparticles under Different Microwave Powers (30 s)

microwave power/W		100	200	300	400	500	600	700	800
microwave	theoretical value/°C	34.5	42.4	49.0	54.5	59.2	63.2	66.7	69.7
	experimental value/°C	37.3	45.5	51.1	55.2	61.5	64.6	68.4	72.0
	absolute relative error/%	7.51	6.81	4.11	1.27	3.74	2.17	2.49	3.19
γ-Fe_2O_3 + microwave	theoretical value/°C	35.6	44.4	51.9	58.3	63.9	68.7	72.9	76.6
	experimental value/°C	38.0	47.2	54.5	58.5	64.3	68.4	72.6	75.8
	absolute relative error/%	6.32	5.93	4.77	0.34	0.62	0.44	0.41	1.06

Table 3. Comparison of Theoretical and Experimental Temperatures of Emulsion at Different Radiation Times with/without Magnetic Nanoparticles (500 W)

microwave radiation time/s		10	20	30	40	50	60
microwave	theoretical value /°c	38.9	50.6	59.2	65.8	71.2	75.9
	experimental value/°C	37.3	52.2	61.5	69.4	74.1	80.2
	absolute relative error/%	4.29	3.07	3.74	5.19	3.91	5.36
γ-Fe_2O_3 + microwave	theoretical value/°C	40.5	53.8	63.9	71.8	78.4	84.2
	experimental value/°C	43.1	56.5	64.3	73.1	77.0	82.1
	absolute relative error/%	6.03	4.78	0.62	1.78	1.95	2.55

When the power was constant, an increase in the radiation time increased the total heat energy converted from the microwave electromagnetic energy by the polar molecules and magnetic nanoparticles in the emulsion, thereby increasing the temperature of the emulsion. Meanwhile, the increase in radiation time gradually decreased the temperature difference between the oil and water phases, in turn, gradually weakening the convective heat transfer between the two phases of the emulsion. However, the loss factor of the medium in the emulsion decreased with increasing temperature. The combined effect of these two aspects causes the emulsion temperature to gradually decrease with increasing radiation time.

Considering the calculation error of the convective heat transfer coefficient of the emulsion, a verification experiment was conducted to analyze the applicability of the temperature prediction model of the heavy-oil emulsion at different powers and durations under microwave irradiation.

The emulsion temperature was measured at a radiation time of 30 s with the radiation power varying between 100 and 800 W and a radiation power of 600 W with the radiation time varying between 10 and 60 s. The calculated and measured emulsion temperatures after microwave irradiation with or without magnetic nanoparticles were compared to verify the accuracy of the model. The comparison results are presented in Tables 2 and 3.

As listed in Table 2, the average relative errors of the theoretical and experimental temperatures of the heavy O/W emulsion are 3.91 and 2.49%, respectively, and their maximum relative errors are 7.51 and 6.32%, respectively, before and after the addition of magnetic nanoparticles under different microwave powers for 30 s.

Table 3 shows that the average relative errors of the theoretical and experimental temperatures of the heavy O/W emulsion are 4.26 and 2.95%, respectively, and their maximum relative errors are 5.36 and 6.03%, respectively, before and after the addition of magnetic nanoparticles at a microwave power of 500 W for varying radiation times.

Thus, the theoretical temperature of the O/W emulsion is in good agreement with the experimental temperature at different microwave powers and radiation times before and after the addition of magnetic nanoparticles. Therefore, the model can be used to predict the temperature of heavy oil emulsions at different microwave powers and irradiation times.

4. CONCLUSIONS

In this study, the demulsification mechanisms of magnetic nanoparticles, microwave radiation, and magnetic nanoparticles-assisted microwaves were studied for heavy O/W emulsions. The demulsification mechanism was further studied by using a ζ potential instrument and PLM. The main conclusions are as follows:

(1) The demulsification effects of different magnetic nanoparticles were different, with that of γ-Fe_2O_3 being the best. With an increase in the concentration of γ-Fe_2O_3, the water content first increased and then decreased, indicating the existence of an optimal demulsification concentration. With the decrease in the pH value, the ζ potential of the magnetic nanoparticles increased and their ability to bind oil droplets enhanced, promoting the gradual enhancement of the demulsification performance.

(2) The results of the microwave demulsification experiments showed that with increasing microwave power, the water content of the emulsion first increased and then decreased, and the demulsification effect peaked at 600 W. The PLM images of the emulsion microdroplets at different microwave powers showed the droplet size to be the maximum at 600 W and the distribution to be random.

(3) Under the synergistic effect of 50 mg/L γ-Fe_2O_3 and 200 W microwave irradiation, the water separation rate of the emulsion reached 93% within 60 min. The experimental results showed that magnetic nanoparticles had a promoting effect on microwave demulsification. Under the synergistic effect of the low magnetic nanoparticle concentration and microwave power, the demulsification effect improved significantly. In addition, the recycling experiments showed that magnetic nanoparticles exhibit good recyclability and reusability.

(4) The results of the model confirmed that the emulsion temperature under microwave action was higher after the addition of magnetic nanoparticles. Therefore, compared with the pristine microwave demulsification, the cooperative demulsification can be performed at lower temperatures. A

comparison of the theoretical and measured values of the emulsion temperature before and after the addition of the magnetic nanoparticles at different radiation powers and times verified that the model exhibits high accuracy.

AUTHOR INFORMATION

Corresponding Author

Huayi Jiang − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*; Email: hyjiang@xsyu.edu.cn

Authors

Nana Sun − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*

Ruiyu Su − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*; orcid.org/0000-0003-1042-0597

Lanxin Zhang − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*

Lisha Shen − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*

Huina Sun − *College of Petroleum Engineering, Xi'an Shiyou University, Xi'an City 710312 Shaanxi Province, P. R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02226

Notes

The authors declare no competing financial interest.

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