AZƏRBAYCAN RESPUBLİKASI ELM VƏ TƏHSİL NAZİRLİYİ

AZƏRBAYCAN DÖVLƏT NEFT VƏ SƏNAYE UNİVERSİTETİ

MINISTRY OF SCIENCE AND EDUCATION

REPUBLIC OF AZERBAIJAN

AZERBAIJAN STATE UNIVERSITY OF OIL AND INDUSTRY

“NEFTİN, QAZIN GEOTEXNOLOJİ PROBLEMLƏRİ VƏ KİMYA” ELMİ-TƏDQİQAT İNSTİTUTUNUN

ELMİ ƏSƏRLƏRİ

SCIENTIFIC PROCEEDINGS

SCIENTIFIC RESEARCH INSTITUTE

“GEOTECHNOLOGICAL PROBLEMS OF OIL, GAS AND CHEMISTRY”

Sci. Proc. SRI GPOGC. Volume 24, Number 1, 2024

BAKU-2024

Application of nanoparticles for water-oil emulsions de-emulsification process

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Abstract.

The main objective of the study is to evaluate the effect of nanoparticles on the demulsification process of water-oil emulsions. Specifically, the influence of Fe_2O_3 nanoparticles on the separation of oil and water phases was examined under laboratory conditions at varying concentrations and temperature settings.

During the experiments, the use of nanoparticles significantly enhanced the separation rate of the emulsion and improved the quality of the recovered oil. The high surface energy of the nanoparticles disrupted the stable emulsion layer, allowing for more efficient separation of oil and water. Furthermore, the study determined that application of Fe_2O_3 nanoparticles is an effective demulsification method.

These findings broaden the prospects of applying nanotechnology in the oil industry, offering both ecologic and economic advantages in oil production processes.

Keywords: water-oil emulsion, demulsification, nanoparticles, demulsifiers, nanotechnology, oil and gas extraction.

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1. Introduction:

As we know, during the extraction of oil through wells, the raw material obtained is not merely oil but is often produced in the form of oil emulsions. An oil emulsion is formed when two or more liquids (e.g. oil and water) mix through physical and chemical processes, resulting in a stable structure. The most commonly encountered emulsions in the oil industry are oil-in-water (O/W) and water-in-oil (W/O) emulsions.

The formation of oil emulsions is one of the most frequently observed processes during oil production, transportation, and processing. Below are the main causes of oil emulsion formation:

Physical Impacts.

During oil production through wells, water migrates from water layers to oil layers. Due to the reservoir pressure being higher than the bottom-hole pressure, these liquids mix and move from the reservoir to the bottom of the well and then to the wellhead, creating turbulent flow due to the joint movement of oil and water. Electrostatic repulsive forces between water droplets make their coalescence difficult. In this process, the mechanical interaction of liquids causes emulsion formation. Additionally, the mixing of gas with oil under high pressure in the reservoir accelerates the emulsification process.

Chemical Factors

Surface-active agents (SAAs) in oil, such as resins, asphaltenes, and paraffins, enhance the stability of emulsions. SAAs adsorb onto the interface, preventing the coalescence of water and oil droplets. By forming a spatial layer between water and oil, SAA molecules hinder the merging of water droplets, leading to a stable emulsion. High SAA concentrations increase the stability duration of emulsions [1].

Temperature Variations

A decrease in temperature increases oil viscosity and restricts water droplet movement, resulting in the long-term stability of the emulsion.

4. Inorganic Impurities:

Clay, sand, salt, and other solid components in oil enhance the mechanical stability of emulsions.

Types of Emulsions

Oil-in-water (O/W) emulsion: Formed when oil droplets are dispersed in water. These emulsions are commonly observed during oil production through wells.

Water-in-oil (W/O) emulsion: Formed when water droplets are dispersed in oil. This is the most frequently encountered type of emulsion and occurs mainly in light and medium-viscosity oils.

Complex emulsions Examples include water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) structures. These complex emulsions are rare.

Considering the above, the importance of emulsion separation processes should be discussed. Stable emulsions create significant challenges both during oil and gas extraction through wells and during processing. Therefore, carrying out the demulsification process is a primary task of critical importance. The purpose of this process is to separate oil from water, remove salts and other impurities, and prepare the oil for processing and transportation [2].

The Importance of the Demulsification Process:

Improving Oil Quality: Separating water and salts from oil significantly enhances its quality and facilitates processing.

Equipment Protection: Salts in emulsions accelerate corrosion in equipment, causing leaks and rapid wear in operational pipelines.

Reducing Ecological Impact: Properly treating separated water prevents ecological contamination [3].

Stages of the Demulsification Process:

1. Addition of Chemical Agents

Demulsifiers (emulsion breakers) are used to destabilize emulsions and accelerate the separation of oil and water. Demulsifiers are primarily nonionic, anionic, or cationic surface-active agents. Below are some examples of different types of demulsifiers:

Polymer-based demulsifiers:

Polyethylene glycol (PEG): Water-soluble and used for water-in-oil (W/O) emulsions.

Polypropylene glycol (PPG): Oil-soluble and effective for breaking stable emulsions.

Alkylphenol-formaldehyde: Highly effective for high-viscosity oils, dissolving in oil and disrupting the stability of water droplets.

Epoxy-based demulsifiers: Used for heavy oil treatment by reducing the impact of surface-active agents.

Amide-based demulsifiers: Effective for emulsions rich in asphaltenes and resins.

Silicone-based demulsifiers: For efficient oil-water separation using substances like polydimethylsiloxanes (PDMS) [4].

Alkanolamines: Compounds like diethanolamine and triethanolamine assist in water droplet coalescence.

Nonionic surfactants: Modified glycerin or alcohols weaken stable emulsions.

Metal complexes: Complexes based on Fe_2O_3 or magnesium aid separation by adsorbing surface-active agents.

Hybrid systems: Modern industry often employs mixed demulsifiers combining polymers and silicone-based compounds or polymer and alkanolamine blends.

The choice of demulsifier depends on the characteristics of the emulsion, oil composition, and conditions (temperature, pressure). Laboratory analyses and field data are essential for selecting the correct demulsifier [5].

2. Increasing Temperature

Raising the temperature reduces the viscosity of oil and water, facilitating their separation.

Challenges in the Demulsification Process:

Heavy Oils: Demulsification is more challenging in heavy oils with high viscosity.

Stable Emulsions: Breaking emulsions with high concentrations of surface-active agents is difficult.

Contaminated Equipment: Deposits in separators and pipelines can slow the process.

The use of toluene to enhance the efficiency of demulsifiers is a widespread practice in oilfield operations.

Recently, as in other fields, nanotechnology has been increasingly applied in the oil and gas industry. By using nanotechnology products, both oil recovery factors and the demulsification of oil-water emulsions can be improved, altering the rheophysical properties of the solution. This process has been extensively studied through scientific research and field experiments [6].

The aim of the work is to study the influence of Fe_2O_3 nanoparticles on the destruction of emulsions in the oil-water system.

Methodology

The surface activity of nanoparticles plays a crucial role in their impact on the rheophysical properties of water-oil emulsions. Specifically, Fe_2O_3 nanoparticles, with their high surface energy and magnetic properties, are effective in regulating the stability and rheological characteristics of emulsions. Due to their surface activity, nanoparticles create a kind of barrier on the surface of water droplets in the emulsion, preventing their coalescence and the process of droplet merging. To better understand this effect, a series of experiments were conducted to study the influence of Fe_2O_3 nanoparticle concentration, size, and surface activity on droplet stabilization.

Surface Activity of Nanoparticles and Its Mechanism

Nanoparticles, possessing high surface energy, accumulate at the emulsion interface and form a boundary between water and oil droplets. This boundary prevents droplet coalescence, thereby enhancing emulsion stability. Surface-active nanoparticles reduce surface tension at the water-oil interface and slow down droplet merging. These properties enable nanoparticles to act as a "physical barrier" on the droplet surface [7].

Experiments were conducted to understand the accumulation of Fe_2O_3 nanoparticles in the water-oil phase. For instance, the experiments investigated how nanoparticles positioned themselves at the water-oil interface and their effect on long-term emulsion stability. Results indicated that the positioning of nanoparticles on the surface is directly linked to their surface activity.

Effect of Fe_2O_3 Nanoparticle Concentration on Stability

In a series of experiments, varying concentrations of Fe_2O_3 nanoparticles were added to water-oil emulsions to measure their impact on stability. At low concentrations, droplets merged more quickly due to insufficient barrier formation on the surface. At higher concentrations, nanoparticles completely covered the droplet surfaces, preventing their merging and ensuring prolonged emulsion stability.

Data from these experiments showed that an optimal nanoparticle concentration is necessary to form an adequate barrier at the water-oil interface and maintain stability. However, excessively high concentrations can increase emulsion viscosity, which may pose challenges in certain studies.

Effect of Nanoparticle Size on Stability

To enhance surface activity, it is essential for nanoparticles to be small in size. Smaller Fe_2O_3 nanoparticles, due to their larger surface area, cover more droplet surfaces in emulsions and more effectively prevent droplet merging. Experiments using 10-20 nm-sized Fe_2O_3 nanoparticles tested the stability of water-oil emulsions. Results demonstrated that smaller particles exhibit stronger surface activity and ensure greater stability.

Larger particles, however, distribute unevenly on the droplet surface, accelerating the merging process. These experimental findings underscore the importance of optimizing the size of Fe_2O_3 nanoparticles to enhance surface activity and stability.

Based on the above findings, a scientific research process was carried out to observe the effects of nanoparticles on the separation of water-oil emulsions. Due to its specific surface energy, Fe_2O_3 nano-powder was used as the nanoparticle [8].

The laboratory conditions were specifically tailored for the study. The emulsion used was a water-oil emulsion obtained from well #1491 of the Lokbatan field. Specific reagents were added to the emulsion to conduct the experiments.

Two 150 mL measuring cylinders were used for the experiment. The empty cylinders were weighed using an electronic laboratory scale and numbered as 1 and 2 for observation purposes. 150 mL of water-oil emulsion from well no. 1491 was poured into each cylinder. Then, reagents were added to the test cylinders according to the following table. The solutions were mixed intensively for 5 minutes to ensure uniform distribution of the reagents throughout the emulsion.

Afterward, both test cylinders were placed on a heating device, and the temperature was maintained using a thermocouple. The separation of the water-oil emulsion was measured every 5 minutes with a ruler and recorded in the following table. The experiment was repeated several times under varying temperatures and reagent ratios according to the specified conditions. These experiments were conducted based on the ratios described below (Table 1).

Table 1. The reagents added according to experiments

Experiment #	Test #1	Test #2
1	0.5 toluol	0.5 toluol and 0.5toluol+ Fe_2O_3 nanoparticles
2	0.25 toluol	0.25 toluol and 0.25toluol+ Fe_2O_3 nanoparticle
3	0.1 toluol	0.1 toluol and 0.1 toluol nanoparticle
4	0.75 toluol	0.75 toluol and 0.75toluol+ Fe_2O_3 nanoparticle

During the experiment, the room temperature was 22ºC. Experiments were conducted at 2 temperatures (60ºC and 65ºC).

During the study, it was observed that the deemulsification process in the 2nd test bottle (with nanoparticle added) was faster than in the 1st test bottle. At the same time, it was determined as a result of the research that the amount of water released from the emulsion with nanoparticle added is more than the amount of water released from the emulsion without nanoparticle added. According to general experiments, the fastest deemulsification occurred in the emulsion with the addition of 0.75 g of toluene and 0.75 g of toluene+Fe_2O_3 nanoparticle mixture, and the latest separation occurred in the emulsion with the addition of 0.1 g of toluene (figure 2). It was determined that it is more than the amount of water separated from emulsions (figure 1).

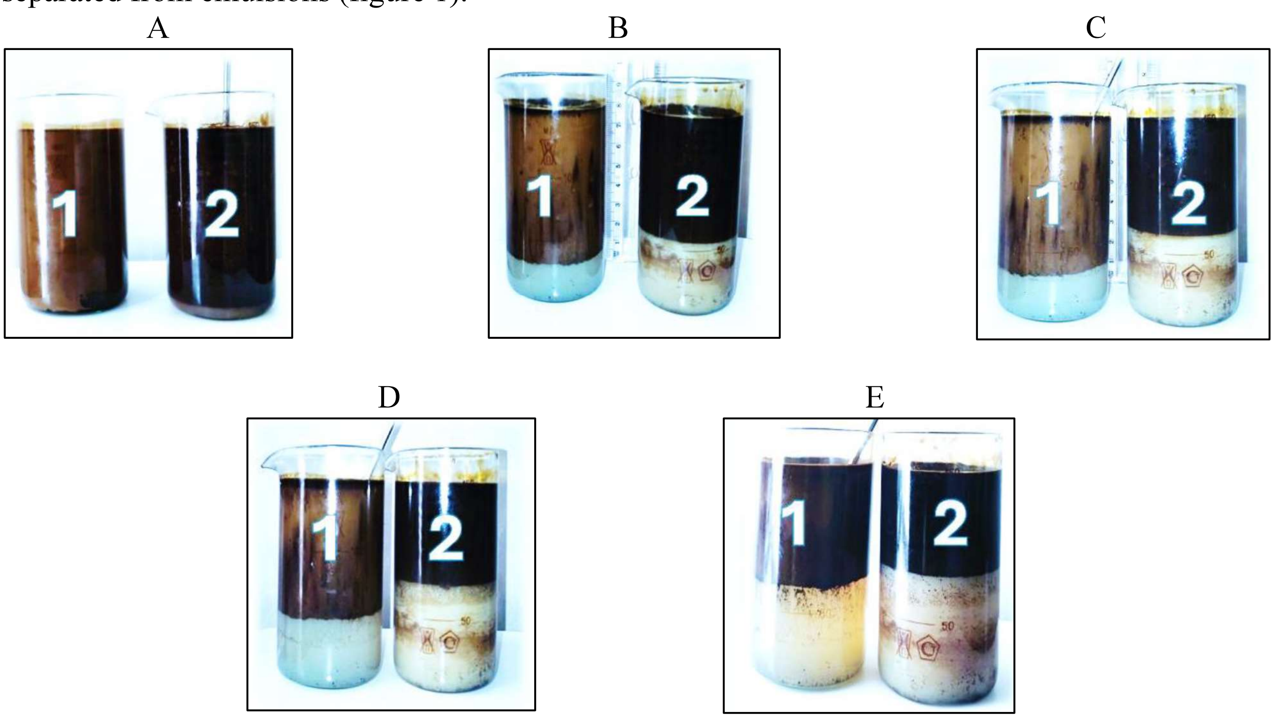

Figure 1. Time-dependent liquid separation from emulsions with N1 0.75 toluol, N2 0.75 toluol and 0.75toluol+ Fe_2O_3 nanoparticle mixture added at 60C (A-5 min, B-20 min, C-30 min, D-45 min, E-180 min)

The table of the change in the rate of liquid separation from the water-oil emulsion as a function of time, depending on the amount of reagents at 60°C, and the graph showing the change in the amount of separated liquid over time are shown below (table 2) (figure 2).

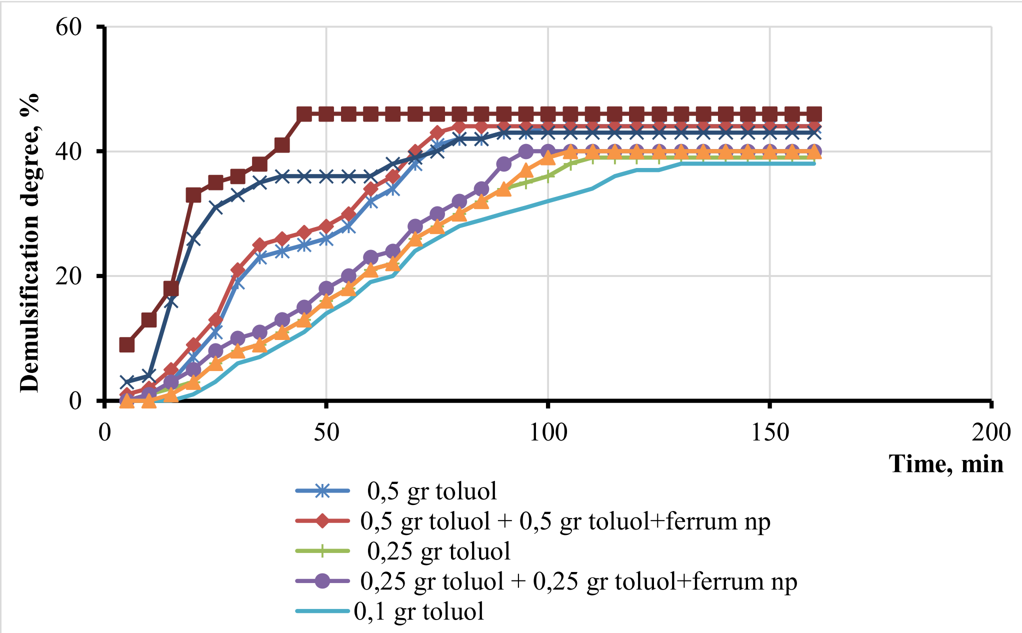

Figure 2. Change of demulsification volume (60°C).

Table 2. Change in the demulsification degree (60°C)

Temperature 60ºC	Time, min															
Demulsification degree/%	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**
0,5 gr toluol	0	1	3	7	11	19	23	24	25	26	28	32	34	38	41	42
0,5 gr toluol + 0,5 gr toluol + Fe_2O_3	1	2	5	9	13	21	25	26	27	28	30	34	36	40	43	44
0,25 gr toluol	0	1	2	3	6	8	9	11	13	16	18	21	22	26	28	30
0,25 gr toluol + 0,25 gr toluol + Fe_2O_3	0	1	3	5	8	10	11	13	15	18	20	23	24	28	30	32
0,1 gr toluol	0	0	0	1	3	6	7	9	11	14	16	19	20	24	26	28
0,1 gr toluol + 0,1 gr toluol + Fe_2O_3	0	0	1	3	6	8	9	11	13	16	18	21	22	26	28	30
0,75 gr toluol	3	4	16	26	31	33	35	36	36	36	36	36	38	39	40	42
0,75 gr toluol + 0,75 gr toluol + Fe_2O_3	9	13	18	33	35	36	38	41	46	46	46	46	46	46	46	46
Temperature 60ºC	**Time, min**															
Demulsification degree/%	**85**	**90**	**95**	**100**	**105**	**110**	**115**	**120**	**125**	**130**	**135**	**140**	**145**	**150**	**155**	**160**
0,5 gr toluol	42	43	43	44	44	44	44	44	44	44	44	44	44	44	44	44
0,5 gr toluol + 0,5 gr toluol + Fe_2O_3	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44
0,25 gr toluol	32	34	35	36	38	39	39	39	39	39	39	39	39	39	39	39
0,25 gr toluol + 0,25 gr toluol + Fe_2O_3	34	38	40	40	40	40	40	40	40	40	40	40	40	40	40	40
0,1 gr toluol	29	30	31	32	33	34	36	37	37	38	38	38	38	38	38	38
0,1 gr toluol + 0,1 gr toluol + Fe_2O_3	32	34	37	39	40	40	40	40	40	40	40	40	40	40	40	40
0,75 gr toluol	42	43	43	43	43	43	43	43	43	43	43	43	43	43	43	43
0,75 gr toluol + 0,75 gr toluol + Fe_2O_3	46	46	46	46	46	46	46	46	46	46	46	46	46	46	46	46

The experiments conducted above were repeated at 65°C. The table showing the change in the rate of liquid separation from the water-oil emulsion as a function of time, depending on the amount of reagents, and the graph showing the change in the amount of separated liquid over time are shown below (Table 3) (figure 3).

Table 3. Change in the demulsification degree (65°C)

Temperature 65ºC	**Time, min**															
Demulsification degree/%	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**65**	**70**	**75**	**80**
0,5 gr toluol	2	3	5	9	13	21	25	26	27	28	30	34	36	40	43	44
0,5 gr toluol + 0,5 gr toluol + Fe_2O_3	3	4	7	11	15	23	27	28	29	30	32	36	38	42	45	46
0,25 gr toluol	2	3	4	5	8	10	11	13	15	18	20	23	24	28	30	32
0,25 gr toluol + 0,25 gr toluol + Fe_2O_3	2	3	5	7	10	12	13	15	17	20	22	25	26	30	32	34
0,1 gr toluol	2	2	2	3	5	8	9	11	13	16	18	21	22	26	28	30
0,1 gr toluol + 0,1 gr toluol + Fe_2O_3	2	2	3	5	8	10	11	13	15	18	20	23	24	28	30	32
0,75 gr toluol	5	6	18	28	33	35	37	38	38	38	38	38	40	41	42	44
0,75 gr toluol + 0,75 gr toluol + Fe_2O_3	11	15	20	35	37	38	40	43	48	48	48	48	48	48	48	48

Temperature 65ºC	**Time, min**															
Demulsification degree/%	**85**	**90**	**95**	**100**	**105**	**110**	**115**	**120**	**125**	**130**	**135**	**140**	**145**	**150**	**155**	**160**
0,5 gr toluol	44	45	45	46	46	46	46	46	46	46	46	46	46	46	46	46
0,5 gr toluol + 0,5 gr toluol + Fe_2O_3	46	46	46	46	46	46	46	46	46	46	46	46	46	46	46	46
0,25 gr toluol	34	36	37	38	40	41	41	41	41	41	41	41	41	41	41	41
0,25 gr toluol + 0,25 gr toluol + Fe_2O_3	36	40	42	42	42	42	42	42	42	42	42	42	42	42	42	42
0,1 gr toluol	31	32	33	34	35	36	38	39	39	40	40	40	40	40	40	40
0,1 gr toluol + 0,1 gr toluol + Fe_2O_3	34	36	39	41	42	42	42	42	42	42	42	42	42	42	42	42
0,75 gr toluol	44	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
0,75 gr toluol + 0,75 gr toluol + Fe_2O_3	48	48	48	48	48	48	48	48	48	48	48	48	48	48	48	48

The experiments conducted above were repeated at 65°C. Due to the increase in temperature, a decrease in viscosity was observed, and it was determined that the separation process of the water-oil emulsion occurred faster compared to the experiments conducted at 60°C.Based on the above-mentioned graphs and tables from the scientific research, it can be concluded that iron nanoparticles intensify the progress of the de-emulsification process.

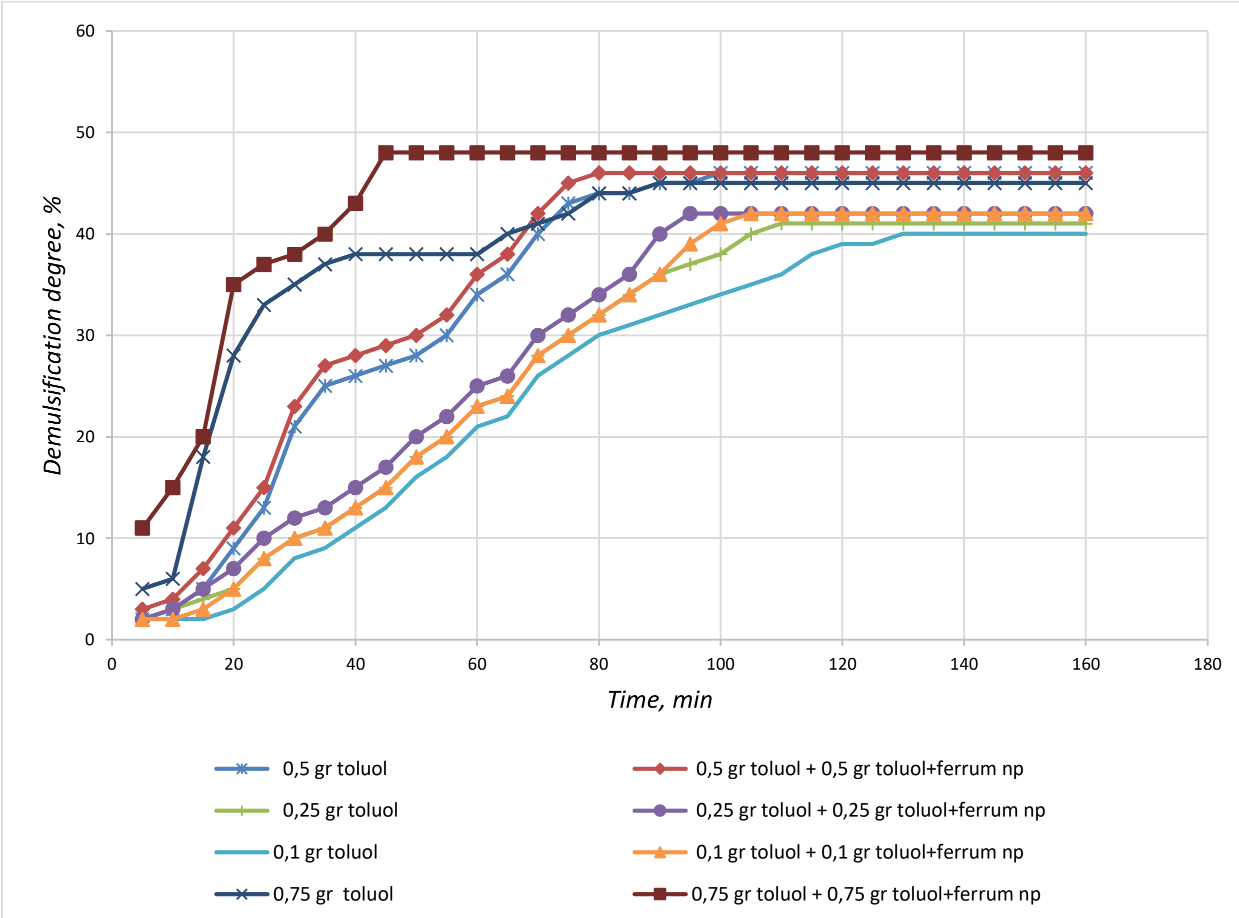

Figure 3. Change of the demulsification volume (65°C).

Results and discussions:

The research focused on evaluating the de-emulsification process of water-oil emulsions using Fe_2O_3 nanoparticles and the synergistic effect of temperature and nanoparticle concentration. The results obtained provide significant insights into the role of Fe_2O_3 nanoparticles in accelerating the de-emulsification process and improving separation efficiency.

The addition of nanoparticles significantly enhanced the rate of de-emulsification in the water-oil emulsions. Fe_2O_3 nanoparticles, due to their high surface energy and magnetic properties, interact with the interface between water and oil droplets. This interaction disrupts the emulsification, promoting the coalescence of water droplets and leading to faster separation of the two phases. The experiments showed that Fe_2O_3 nanoparticles were highly effective in breaking down the emulsion, with a noticeable improvement in the rate of phase separation compared to the control sample without nanoparticles.

The concentration of Fe_2O_3 nanoparticles played a crucial role in the efficiency of the de-emulsification process. Increasing the concentration of nanoparticles led to a higher rate of separation, with a significant reduction in the amount of water remaining in the oil phase. However, very high nanoparticle concentrations resulted in a slight increase in viscosity, which could potentially hinder the separation process due to the higher resistance to flow. The optimal concentration was found to be around 0.5 wt%, where the de-emulsification process was most effective without causing significant viscosity changes.

Temperature was found to have a profound impact on the de-emulsification process. Increasing the temperature from 60°C to 65°C resulted in a noticeable decrease in the viscosity of the emulsion, which accelerated the separation process. The reduced viscosity allowed for easier coalescence of water droplets, thus speeding up the overall de-emulsification. This suggests that temperature plays a synergistic role in enhancing the efficiency of Fe_2O_3 nanoparticles in breaking emulsions.

The presence of toluene further improved the efficiency of the de-emulsification process when combined with Fe_2O_3 nanoparticles. Toluene, a non-polar solvent, reduced the surface tension between the water and oil phases, facilitating the separation of the two phases. This combination of Fe_2O_3 nanoparticles and toluene resulted in a more effective and faster phase separation compared to the use only Fe_2O_3 nanoparticles. This interaction between the solvent and nanoparticles contributes to the enhanced de-emulsification observed.

The incorporation of Fe_2O_3 nanoparticles into the de-emulsification process offers several environmental and economic advantages. By improving the separation efficiency, this method reduces the amount of water and other contaminants in the oil, which can improve the quality of the extracted oil and reduce the need for further treatments. Additionally, the use of nanoparticles can potentially reduce the chemical additives required in the de-emulsification process, leading to lower environmental impact and cost savings in the long term.

Nanoparticles should be used effectively not only in the de-emulsification process but also in enhancing the oil recovery factor in the oil and gas industry. Previously, a study was conducted using Al_2O_3 nanoparticles to increase the oil recovery factor, achieving high effectiveness [13]. It is proposed to conduct research on the use of Fe_2O_3 nanoparticles in improving the oil recovery factor.

4. Conclusion:

Based on the conducted experiments and the data provided, it can be concluded that the use of Fe_2O_3 nanoparticles significantly enhances the demulsification process of water-oil emulsions. The nanoparticles, due to their high surface energy and magnetic properties, create a barrier at the oil-water interface, preventing the coalescence of water droplets and promoting faster separation of the two phases. The results clearly show that the addition of Fe_2O_3 nanoparticles improves the separation rate and increases the volume of water separated from the emulsion, particularly when combined with toluene as a demulsifier.

The study also indicates that the optimal concentration of nanoparticles is crucial for achieving effective separation. In experiments with varying nanoparticle concentrations, it was observed that higher concentrations of nanoparticles led to better emulsion stability and quicker demulsification, though excessively high concentrations may lead to increased viscosity and potential challenges. Additionally, the temperature of the system plays a significant role in the demulsification process. The increase in temperature from 60°C to 65°C resulted in faster separation due to the reduction in viscosity, confirming the synergistic effect of both temperature and nanoparticles on the efficiency of the separation process.

Moreover, the combination of Fe_2O_3 nanoparticles with toluene proved to be an effective method for enhancing the demulsification of water-oil emulsions. The study not only demonstrates the practical application of nanotechnology in oil and gas industries but also highlights the ecological and economic advantages it offers, such as reducing the environmental impact of oil production and improving the overall quality of the recovered oil.

In conclusion, the findings from this research open new avenues for the application of nanotechnology in the oil industry, suggesting a promising method for efficient demulsification with potential for both enhanced oil recovery and better environmental management.

Conflict of Interest
The authors declare that they have no conflict of interest in relation to this research.

This work was supported by the Azerbaijan Science Foundation-
Grant № AEF-MCG-2023-1(43)-13/07/2-M-07

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