



Comprehensive Review of Demulsifiers based on Magnetic Nanoparticles for Oil-water and Water-oil Separation

Y. Rozhkova^a, A. Lekomtsev^{*b}, V. Lisin^b, V. Poilov^a, E. Safiullina^c, D. Efremenko^c, A. Dengaev^d, W. Kang^e, Z. Li^e, H. Yang^e

^a Faculty of Chemical Technology, Perm National Research Polytechnic University, Perm, Russia

^b Mining and Oil Faculty, Perm National Research Polytechnic University, Perm, Russia

^c Oil and Gas Faculty, Saint Petersburg Mining University, St. Petersburg, Russia

^d Department of Petroleum Engineering, Gubkin National University of Oil and Gas, Moscow, Russia

^e School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong, China

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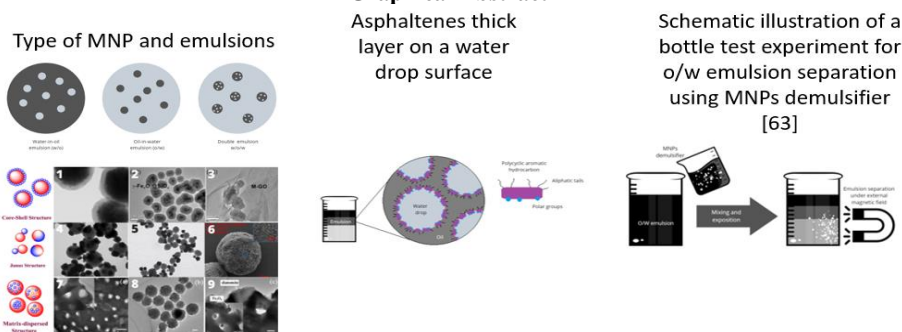
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ABSTRACT

Oil-water emulsion causes a wide range of problems, one of which is the emergence of significant decreases in pressure in flow lines resulting in higher pumping and transportation costs. The most widely developed trend among oil/water separation technologies is using demulsifiers based on magnetic nanoparticles (MNPs). MNPs have specific chemical and mechanical properties, providing unique opportunities to solve oil production issues. The key features of such magnetic nanoparticles for their sustainable application are their reusability and stability; the opportunity of remote manipulation using external magnetic fields gives them a singular benefit in transport operations. The main objective of the study is the systematization of MNPs researches for effective oil and water emulsion separation. This review provides MNP demulsifier characteristics, Oil-water emulsions (OWE) separation mechanism, and factors influencing oil-water emulsions efficiency disruption by MNP demulsifier. The relevance of this study is that oil-water emulsions are often encountered in practice during field development. To solve this problem, the use of demulsifiers based on magnetic nanoparticles is proposed. The novelty of the work lies in the fact that the work collects several factors affecting demulsification at once and describes the impact of each factor. Among these factors, the most influential are: emulsion characteristics, water salinity, pH, reservoir temperature, addition of chemical surfactants, time and magnetic field. The mechanism of formation of oil-water emulsions of various types is also described, and negative consequences of emulsion formation are discussed. The results showed that the magnetic nanoparticles need a protective layer and the demulsifier should have good wettability by the continuous phase of the emulsion.

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Graphical Abstract



*Corresponding Author Email: lav@pstu.ru (A. Lekomtsev)

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NOMENCLATURE

H	Strength of the applied magnetic field	χ_a	Linear component of the susceptibility
M_0	Saturation magnetization of superparamagnetic nanoparticles	V	Volume of magnetic nanoparticle
$L(x) = coth - 1/x$	Langevin function	M	Magnetization of magnetic nanoparticle
x	Langevin parameter	∇H	Gradient of magnetic field
μ_p	Average magnetic moment of each superparamagnetic nanoparticle	μ_0	Magnetic permeability in vacuum
T	Temperature		

1. INTRODUCTION

The oil industry faces the continuing challenge of improving operating well efficiency. This acquires particular relevance in the development of anomalous oil deposits, where well operation is complicated by high oil viscosity, asphalt-resin-paraffin deposits, and stable oil-water emulsions (OWE) in the form of intermediate emulsion layers during crude oil production and preparation. The large deposits of the Volga-Ural region are represented by the anomalous oils in the Devonian and Carboniferous deposits that are currently the region's main development targets. The operating features of such deposits include low reservoir and wellhead temperatures, high water cut, and high viscosity in the phase inversion sites typical for most of the fields located in the Perm Territory. Such problems are especially relevant during the well production of crude oil with water cut in the 60-70% range (1). The instability of the in-line demulsification process and oil treatment at on-site facilities leads to the production of poor-quality products and ultimately to a decrease in the latter's consumer cost. Maintaining the required oil conditions and processing off-grade oily fluids using affordable and economically-justified thermal, physical, and chemical methods at all stages of collection, transportation, and preparation are among the most important tasks of full-production-cycle oil companies. Oilfield experience shows that complex emulsion separation methods are considered more effective at the current stage of the development of cross-functional and end-to-end technologies. Among them, the application of magnetic nanoparticle (MNP) demulsifier is the most perspective technology for the intensification of in-line OWE demulsification due to its unique properties, particularly quick response, easy separation from the oil-water system under a magnetic field, and reusability even in complex field conditions. This systematic review presents an analysis of MNP research cases for the separation of crude material which is presented by oil – water (o/w and w/o) emulsion starting 2015, and provides information about the types, methods of particle synthesis, and demulsification test results. The authors hope that this article will help the novice researcher quickly grasp the main aspects of the MNP application.

2. MATERIALS AND METHODS

There are several approaches to preparing a review research (2). One most commonly used model is the PICO(S) model, which is mostly used for medical reviews (3, 4). The researcher must consider several questions when performing a literature review: problem, intervention, comparison, and outcomes. We decided to apply this approach for the article. As such, this article is divided into sections in accordance with the questions suggested by the PICO(S) model. The first section of the article declares the problem and formation mechanism of crude OWE. The second section presents a short review of modern approaches to OWE separation. The following sections are devoted to MNP demulsifiers, their characteristics, mechanisms and factors influencing OWE demulsification efficiency. At the end of the article, the outcomes impacting the effectiveness and prospective of magnetic demulsifiers application are represented.

The comprehensiveness of the literature research is provided by the quality of research data. All references to articles were taken from Science Direct, ACS Publications, and One Petro databases.

Analysis of search results for the request “magnetic crude oil demulsifier” on Science Direct gave 279 results, and 161 research articles were published from 1988 to 2022. Figure 1 shows a well-established trend of an increase in the number of articles, which is evident of a constant increase of researchers' interest in the study and development of magnetic demulsifiers. In this review, we

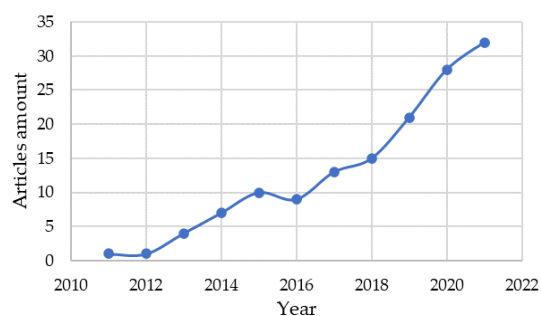


Figure 1. The growth in the number of articles since 2010 on the topic of magnetic demulsifiers for crude oil

will mainly consider research articles published since 2015.

3. OWE DAMAGE AND FORMATION MECHANISMS

OWE formation is a very undesirable and inevitable process in the petroleum industry. OWE can cause problems such as the appearance of high pressure drops in flow lines and higher pumping and transportation costs; an escalated corrosion rate; a lower oil API gravity (5). Hydrocarbon field development over 1-3 years inevitably leads to emulsion formation in the reservoir before its appearance on the surface onsite facilities. The emulsion is broken into two phases before transportation and treatment, the specific water and salt residual standard must be met, and the water content must be less than 1% (6). Several reviews describe crude oil/brine formation mechanisms (7, 8). In this section of the article, we will shortly consider several types of oil and water emulsions; mechanisms, and reasons for their formation.

Emulsion is a two-phase system consisting of several immiscible liquids one of which (the dispersed phase) is constantly dispersed in the form of balls in the second phase (solid phase) under the action of emulsifiers (9, 10). It is known three types of emulsion: water in oil (W/O), oil in water (O/W), and multiple (complex or double) emulsions (see Figure 2) (11, 12). Crude oil and reservoir water contain components contributing to emulsion formation and stabilization, that is, natural emulsifiers. These emulsions can be highly sustained due to the appearance of interfacially active compounds such as naphthenic acids, resins, asphaltenes, or solids (13, 14). For better understanding, the MNP demulsification mechanism, in this section, we will consider basic crude oil emulsifier-components, their structure, and their impact on emulsion formation.

3. 1. Asphaltenes Asphaltenes are represented by a non-homogeneous fraction consisting of polyfunctional molecules of crude oil that are insoluble in n-alkanes (typically heptane and etc.) and soluble in toluene (15). This fraction has the lowest H/C ratio among all crude oil components (16). It concentrates the majority of heteroatoms like oxygen, sulfur, and nitrogen (see Figure 3) and metallic elements like vanadium and nickel (15, 16). Asphaltenes contain both acid (e.g. phenolic functions) and basic (e.g. derivatives of pyridines) functionalities. Different models describe the asphaltene structure. One is the archipelago model, which views asphaltenes as small polyaromatic parts linked together by aliphatic or naphthenic moieties. The other is the continental model, which considers asphaltenes as single polyaromatic rings (polycyclic aromatic hydrocarbon) with connected aliphatic or naphthenic chains (15). A recently research has demonstrated that asphaltenes are small molecules mainly containing a polycyclic aromatic

group made of about 7 rings with linear attached hydrocarbon chains. The molecule has a molecular weight of 750 Da (16). The main properties of asphaltenes are self-association in solution and the ability to adsorb at interfaces (both the solid/liquid and liquid/liquid) (15-17). These properties allow asphaltenes to stabilize water/oil emulsions by leading to the difficulty of water droplets coalescence through organizing a thick layer on its surface (Figure 4) (15, 17). Asphaltenes adsorb at the liquid/liquid (water/oil) interface as shown by interfacial tension measurements. It has been discovered that asphaltenes form a rigid film at the interface of both phases - water and oil.

3. 2. Resins Resins have structural similarity with typical surfactant molecules: One part of chain is hydrophilic with polar functional groups; the other part of chain is hydrophobic and consists of alkyl chains. The stability of the emulsion maintained by asphaltenes is due to the highly viscoelastic films surrounding the water droplets, while resins enhance stability by replacing asphaltenes when the bond of asphaltenes decreases for a certain period (6).

3. 3. Naphthenic Acids The group of aliphatic organic carboxylic acids that contain one or more rings, such as monocyclic and polycyclic carboxylic acids and small amounts of acyclic and aromatic acids, includes naphthenic acids (18). The chemical formula of naphthenic acid is $C_nH_{2n}+ZO_2$, where n denotes the number of carbon atoms and Z is zero or a negative (in the event of a lack of hydrogen due to ring formation or double bonds) (19, 20). Naphthenic acids can be described mainly as C10–C50 compounds with 0–6 rings (21). The possible structures of naphthenic acids are represented in Figure 5. Naphthenic acid concentration in crude oil can reach as high as 4 wt.% (19). The naphthenic acids properties depend on the ionization degree, i.e., the pH of the produced water. They can react with cations (such as Ca^{2+} and Na^+) forming active surfactants (15, 21, 22). Together with asphaltenes, naphthenic acids take part in the stabilization of water/oil emulsion. The stabilization mechanism of emulsion may differ depending on the acid structure. In particular, unsaturated monocarboxylic acids co-adsorb at the water/oil interface together with asphaltenes; dicarboxylic acids form naphthenic salts and then create

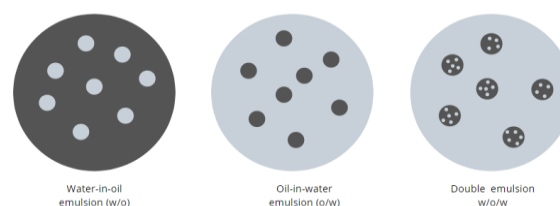


Figure 2. Types of emulsion

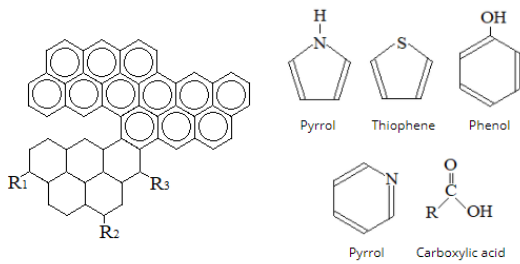


Figure 3. Typical asphaltene molecules

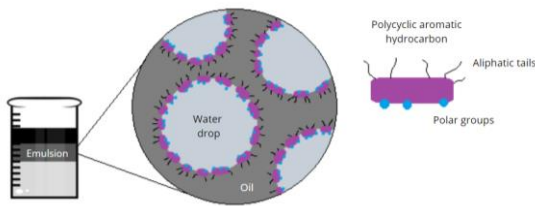


Figure 4. Asphaltenes thick layer on a water drop surface

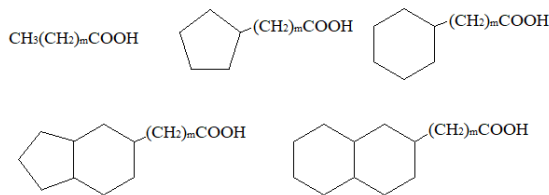


Figure 5. Structures of naphthenic acids

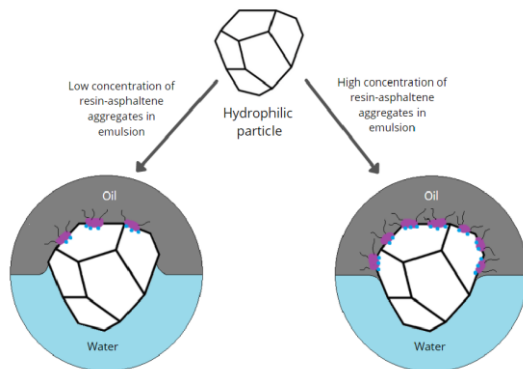


Figure 6. Resin and asphaltene aggregates adsorption onto a hydrophilic particle surface

the first layer on the water drop, which favors asphaltene adsorption (23).

3. 4. Inorganic Particles (Clay, Sand, Minerals)

Emulsions stabilized by solid particles are called Pickering emulsions. The type of emulsion depends on the wettability of solid particles at the interface of oil and

water: the liquid with better wetting properties to solid particles becomes the continuous phase, while the other (with worse wetting properties) becomes the dispersed one (24). Particles with a contact angle of $\theta < 90^\circ$ (water-wet particles) are effective in stabilizing oil-in-water (O/W) emulsions, while those with a contact angle of $\theta > 90^\circ$ (oil-wet particles) are effective in stabilizing water-in-oil (O/W) emulsions. If the particles are too hydrophobic (high θ) or too hydrophilic (low θ), they will be dispersed in the aqueous or oil phase, leading to emulsion separation (25).

The hydrophobicity of inorganic particles present in reservoirs can be caused by long-term contact with the oil. These results show a change in particle wettability due to the accumulation of particles at interfaces caused by the adsorption of asphaltenes and resins from crude oil. (see Figure 6) (26). By increasing particle concentration raises emulsion stability (26-28).

3. 5. Tertiary EOR Methods Contribution to Oil and Water Emulsification

Basic tertiary EOR methods contributing to OWE formation are alkaline, surfactant, polymer flooding and their combinations (for example, alkaline-surfactant-polymer flooding) (29-31). Several mechanisms have been identified that facilitate oil recovery in the alkaline process: interfacial tension lowering; oil emulsification; and changes of the rock formation wettability. In the case of alkaline flooding, emulsion formation becomes the oil recovery enhancement mechanism. The higher the acid number of oil, the more reactive it will be and the more readily it will form surfactants (27). Surfactant formation is the reason for OWE stabilization.

In addition, divalent cations existing in clays and water interact with alkali and precipitates (scale problems) and the large amounts of alkali lead to the stable emulsion formation. Therefore, the alkali is mostly combined with the polymer and surfactant for a higher oil recovery factor (28). However, Li et al. (29) explored the effect of partially hydrolyzed polyacrylamide (HPAM) on the formation of oil/water emulsion. The research establishes that HPAM may be adsorbed at the interface and increase the strength of the interfacial film and the absolute value of Zeta potential (29).

Li et al. (30) described a field case of alkaline-surfactant-polymer flooding using sodium hydroxide as the alkali component to enhance oil recovery on on-shore oil fields at Daqing in China. The alkali injected into the reservoir formed a stable W/O emulsion, although the crude oil was represented predominantly by a paraffinic fraction. They explained emulsion creation through interfacially-active soap molecule formation from carboxylic acids of the Daqing crude oil. These formed interfacially-active molecules are responsible for providing stability to the W/O emulsion (30).

4. MODERN APPROACHES TO CRUDE OIL-WATER EMULSION SEPARATION

Emulsion stability is ensured by the absence of a disperse-phase droplet coalescence (21, 26). This process occurs in the following steps: aggregation (the distance between dispersed liquid droplets is reduced; of the droplets drops are deformed, a thin film forms between them); and coalescence (the film breaks and the droplets coalesce) (9, 31). There are several mechanisms that resist coalescence: the Marangoni-Gibbs effect; steric repulsion; electrostatic repulsion, which retards film drainage; and thin film stabilization (26). Demulsification can be achieved using four main approaches: mechanical (filtration, membrane separation), electrical (voltage application), thermal, chemical (pH adjustment, treatment by demulsifier) and their combinations (6, 22). Several reviews exist that cover the physical and chemical approach for oil/water emulsion separation, particularly mechanical, thermal, electric, microwave, and other approaches (32-34). However, chemical demulsification is still the most widespread method because the application of the chemical is a cost-effective solution that saves energy and time (9, 35). Raya et al. (2), Grenoble and Trabelsi (31) gathered most of the above approaches to chemical demulsifier composition formulation. There are different types of surfactants functioning as demulsifiers like block co-polymeric of polypropylene and polyethylene oxide (pluronic surfactants) (36, 37) and its amine derivatives (like poloxamines), alkylamines, quaternized ammonium based cationic surfactants, zwitterionic demulsifiers (betaine-type), polysiloxane-polyether copolymer, unconventional surfactants like ionic liquid derivatives. A comparative test of such compounds as amie demulsifiers, polyhydric alcohol (PEGs, ethylene and propylene glycols), acid (sulphonate group), and polymeric demulsifiers (oilyethelen oxides and other) were conducted (38). The test results showed that reagents containing amino groups are more effective compared to demulsifiers containing hydroxyl and carboxyl functional groups (38). It was demonstrated that ionic liquids and polymers are more effective than traditional nonionic and anionic surfactants. Adewunmi and Kamal (39) presented studies of demulsifiers based on phosphonium-type ionic liquids with anionic components (including chloride, decanoate, and dicyanamide ions). In addition, imidazole-based ionic liquids (40), quaternary ammonium compound salts (N-alkyltriethylammonium bromide), and others can be used as demulsifiers (41). Among biodemulsifiers, such substances as ethyl cellulose, ethoxylated cocoamine, and α -amylase are considered (33). Detailed studies of α -amylase are presented by Jiang et al. (42). It has been shown that α -amylase is an effective biodemulsifier for W/O emulsion even at room temperature. However,

chemical demulsifiers must meet the following requirements: full removal of water and salts in small consumption per ton of oil; accessibility; low cost; must be environmentally friendly and meet the requirements of environmental standards and regulations (9, 43). One more highly developed trend in oil/water separation is demulsifiers based on magnetic nanoparticles (MNPs). MNPs have specific chemical and mechanical properties, and therefore offer unique opportunities for solving well production issues in new ways. The key features of such magnetic nanoparticles for their sustainable application are their reusability and stability (44); the possibility of remote manipulation by external magnetic fields which give them a special benefit in transport operation (45, 46). The main objective of this study is a systematization of MNPs research cases for effective oil and water emulsion separation.

5. MNP DEMULSIFIERS AND THEIR MAIN CHARACTERISTICS

MNP demulsifiers are chemical structures made by combining MNPs with other substances that perform a protective function, surface hydrophobization, or hydrophilization, and other functions.

The core exhibits superparamagnetic or ferromagnetic properties, which facilitates directional migration and magnetic induction heating under various magnetic fields. The reactive groups of the species degraded from the shell can be conjugated to specific molecules and thus functionalized. Therefore, functionalized MNPs possess the characteristics of magnetic particles and shell materials, which helps to improve the demulsification effect (45-48).

MNP magnetic cores can be made from iron oxides $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$, pure metals Fe and Co, and spinel-type ferromagnetics MgFe_2O_4 , MnFe_2O_4 , or CoFe_2O_4 (45, 47, 48). A number of materials, such as propyleneoxide-ethyleneoxide, block polyether, oleic acid, chitosan, N-isopropylacrylamide, sodium methacrylate, graphene oxide, tetraethyl orthosilicate, and other substances have been used for MNP surface modification (see Table 1). The quality of MNPs coated by modification material is estimated using the zeta potential. For example, the zeta potential of Fe_3O_4 nanoparticles in mmol/L KCl aqueous solutions was positively charged with a mean 22.07 mV. After its surface modification by SiO_2 , the MNPs became negatively charged with a mean zeta potential of -53.13 mV. This result also confirmed a full surface coverage of silica films on the MNPs (49).

Magnetite (Fe_3O_4) is an ideal magnetic material because of its low cytotoxicity and good biocompatibility (46). The synthesized Fe_3O_4 MNPs exhibited good demulsification performance. However, they are oxidized in the atmosphere and corroded in acidic

TABLE 1. Systematization of available cases of developed MNP-demulsifiers since 2015

Substance code	Method of synthesis and MNP's type	MNPs size, nm	The saturation magnetization, emu/g	Type of emulsion	Concentration	Effectiveness, %	Test temperature, C	Period of demulsification	pH	Recycle test (cycles)	Source
Fe ₃ O ₄ @OA	Chemical co-precipitation, Fe ₃ O ₄ with oleic acid (OA). OA molecules formed a single layer coating on the Fe ₃ O ₄ surface	12–14	No data	O/W	30 g/L	80	25	3 h	6.3–9.5	6	(46)
Fe ₃ O ₄ @OA	Chemical co-precipitation, Fe ₃ O ₄ with oleic acid. Spherical shape	12–14	24.07	O/W	100 g/L	97	25	12 h	4.0–7.5	5	(50)
PEMN	Solvothermal reaction, propyleneoxide-ethyleneoxide block polyether was endowed with the magnetism by reacting with iron (III) acetylacetonate. Core shell structure	11,41	9.08	W/O	0,625 g/L	100	70	30 min	No data	3	(51)
M-DMEA	Fe ₃ O ₄ @SiO ₂ nanoparticles covered by (3-glycidoxypropyl) trimethoxysilane, block copolymer of ethylene oxide (EO) and propylene oxide (PO) prepared by using N,N-dimethylethanolamine and 4-dimethylaminopyridine. Irregular shape with a core-shell structure	251	55.20	O/W	2,5 g/L	92,3	65	No data	No data	3	(49)
M-GO	Amino-functional Fe ₂ O ₃ @SiO ₂ (coded like c-Fe ₂ O ₃ @SiO ₂ -NH ₂) were anchored on the surface of GO matrix dispersed structure. Nearspherical core-shell nanoparticles where grinded on the GO particles	GO particles 100-1500 nm; amino-functional Fe ₂ O ₃ @SiO ₂ 100 nm	8.70	O/W	0,04-0,25 wt%	98,3-99,98	No data	5 min	2.0-4.0	6–7	(52)
Fe ₃ O ₄ @APFS-G-CS	Fe ₃ O ₄ MNPs were synthesized by using a solvothermal method with further coating of aminopropyl-functionalized silica (APFS) to form a surface for further grafting of chitosan molecular chains. Coreshell structure	350	30.5	O/W	0,4 g/L	90	25	30 min	pH 4.0 and 7.0	7	(53)
Fe ₃ O ₄ @AEAPFS MNPs	Fe ₃ O ₄ MNPs were synthesized by using a solvothermal method, AEAPFS layer was formed through a sol-gel process involving the hydrolysis and condensation of TEOS and N-(aminoethyl)-aminopropyl triethoxy silane (AEAPTES, 96%). Nearly spherical in shape, coreshell structure	360	51.9	O/W	650-800 mg/L depending on pH	99,9	no data	No data	various pH levels	5	(54)

Samples codes varies from S2 to S6	Fe ₃ O ₄ @SiO ₂ -MPS modified by N-isopropylacrylamide (NIPAM) and sodium methacrylate (SMA). Globular shape, core-shell structure	200	42.90-33.60	O/W	for S2 - 200 mg/L	99.9% at pH 6.0	30	No data	different	5	(55)
EP@APTE S-Fe ₃ O ₄	The expanded perlite (EP) was firstly modified by 3-aminopropyl triethoxysilane (APTES) to form the EP@APTES, and then magnetic Fe ₃ O ₄ nanoparticles (NPs) were further grafted onto the surface of EP@APTES. Globular shape, core-shell structure	200–300	46.30-34.10	O/W	500 mg/L	89-93% (pH ≤6)	No data	60 sec	pH 4.0-6.0	4	(56)
M-MWCNTs	Fe ₃ O ₄ @SiO ₂ -APTES particles are grafted onto the multi-walled carbon nanotubes amphiphilic surfactant. The type of structure is not clear, look like Janus particles	200–300	12.80	O/W	400 mg/L	93.3-94.2,	No data	No data	pH 2.0-6.0	5	(57)
P(MMA-AA-DVB)/Fe ₃ O ₄	Micro scale Poly(methylmethacrylate-acrylic acid-divinylbenzene) iron oxide Janus magnetic submicronic particles were prepared through soap free emulsion polymerization with methylmethacrylate and acrylic acid as a monomer, divinylbenzene as a cross-linker and potassium peroxy sulphate as initiator. Janus magnetic submicronic particles, raspberry like surface morphology	250	25.0	W/O	500 ppm	98%	60	1 h	pH 7.0-13.0	5	(58-60)
MAG-CMC-EC or M-CMC-EC	Fe ₃ O ₄ subsequently coated with carboxymethyl cellulose (CMC) (electrostatic force and hydrogen bonding), ethyl cellulose (EC) (esterification reaction). Core-shell structure	100	71.0	W/O		92%	25	3 h with magnetic field	No data	3	(44, 61)
M-Janus	Fe ₃ O ₄ subsequently coated with carboxymethyl cellulose (CMC) (electrostatic force and hydrogen bonding), ethyl cellulose (EC) (esterification reaction) and again CMC Janus magnetic particles	145	69.7	W/O, O/W		95% for W/O, 90% for O/W	No data	2 h without magnet, 30 min after setting strong magnet	No data	5	(44)
Fe ₃ O ₄ @PD A-PDMAPS (FPPM)	MNPs coated by Poly{3-[dimethyl(2-methacryloyloxyethyl) ammonio]propanesulfonate}. Core-shell magnetic microspheres	216	No data	W/O	0,85%-1%	no data	23	3 h without a magnet, then 68 hours on magnet	No data	No data	(62)
M-DM	Deatomite coated by (3-aminopropyl)-triethoxysilane, MNPs of Fe ₃ O ₄ , and polyethylenimine. Matrix dispersed structure	200–300	36.6	O/W	450 mg/L	95.3	25	60 sec	broad pH levels	5	(53)
MJ NPs	Fe ₃ O ₄ subsequently coated with carboxymethyl cellulose (CMC), ethyl cellulose (EC) and wax and again CMC. Core-shell structure	no data	No data	W/O	0,50%	78	25	15 min	No data	6	(63)

PEDHA- Fe ₃ O ₄	Synthesized through the covalent functionalization of magnetite (Fe ₃ O ₄) nanoparticles with Polyester bis-MPA dendron, 2-hydroxyl, 1-azide dendrimer. Core-shell structure	63.913 and 39.559 emu/g depending on the funct. layer thickness	W/O	15 mg/L	~78	60	50 h	No data	2	(64)	
Fe ₃ O ₄ @SiO ₂ @C	Fe ₃ O ₄ particles were first coated by dense silica through hydrolysis of tetraethyl orthosilicate (TEOS) at room temperature. Hydrophobic carbon could adsorb the air within their surroundings to form air film. Near-spherical, core-shell structure	464.4±19.85	no data	W/O	1%	100	25	5 days	No data	6	(65)
Fe ₃ O ₄ -SiO ₂	Preparation of Fe ₃ O ₄ -SiO ₂ by modified Stober process at room temperature. Sphere-shaped particles with clear-core shell structure	28.0 ± 3	42.3 ± 0.3	O/W	10 mg/L	93%-94.9%	25	10 min under the external magnetic fields	94-98	9	(66)
A-MNPs	Co-precipitation (co-ppt) method was used to synthesize MNPs, the MNPs surface has been consistently coated by 3-amino propyltriethoxysilane (3-APTES), sphere-shaped particles	21 to 255 nm	90	O/W	0.875 g/L	99.9 %	25	0.2 to 20 h, depending on the particle size	No data	No data	(67)

conditions. To protect it from corrosion, the surface of Fe₃O₄ MNPs is modified. Usually, the MNPs are first coated with a silica shell to prepare Fe₃O₄@SiO₂ MNPs, and then some functional macromolecular chains are imposed (54). MNPs prepared on the basis of Fe₃O₄ can generally be classified into four types according to their structures: Fe₃O₄@SiO₂@compounds particles, Fe₃O₄@compounds particles, compounds of cross-linked polymers and Fe₃O₄, and magnetic amphiphilic composites (51).

Adewunmi et al. (68), Wunet al. (69) presented MNP synthesis methods like: co-precipitation synthesis, solvothermal synthesis, sol-gel synthesis, redox synthesis, microemulsion, hydrothermal, sonochemical, and chemical vapor deposition. Zhu et al. (70), considered the advantages and disadvantages of MNP synthesis methods. For example, they considered the co-precipitation method to be a simple and efficient technique; however, unlike other methods, co-precipitation does not allow to control particle size distribution. The microemulsion method allowed controlling particle size, but the synthesis takes a lot of time and large amounts of solvent (70).

MNP-demulsifier type and size depending on the synthesis method. There are three basic types of MNP-demulsifier structures: core-shell, matrix-dispersed, and Janus structure (45). We selected photographs (mostly made by transmission electron microscopy, TEM) of different types of magnetic nanoparticles from different sources (see Figure 7).

All the cases that we analyzed show a wide range of examples of MNPs with a core shell structure, a few examples with a Janus structure, and only one with a matrix-dispersed structure. There is an opinion that the magnetic properties of nanoparticles can be affected by the type of MNP (14, 47).

MNPs with core-shell structures are considered less efficient demulsifiers due to the possibility of their desorption from the interface under an external magnetic force (11). Janus MNPs have a unique surfactant-like structure and, consequently, an asymmetric surface

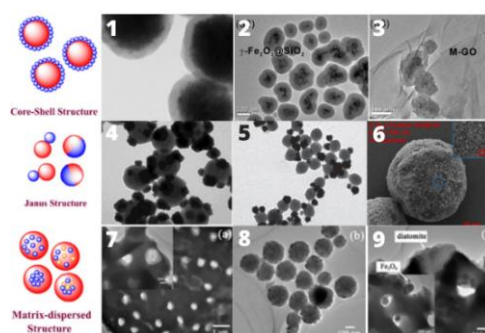


Figure 7. Typical structures of MNPs. The basic visual structures of MNPs were taken from (left column). 1-9 pictures were taken as real MNP examples from the following sources: 1 - Fe₃O₄@PDA-PDMAPS (FPPM); 2 - γ -Fe₂O₃@SiO₂; 3 - M-GO; 4 - P(MMA-AA-DVB)/Fe₃O₄, raspberry like structure (version of Janus like MNPs); 5-6 - M-Janus MNPs; 7-9 - M-DM MNPs

wettability. These types of MNPs can perform higher interfacial tension than conventional core-shell MNPs and demonstrate a stronger deposition on a water or oil droplet surface, as they require higher energy to desorb from the interface (22). However, Janus MNPs are better applied to O/W emulsions due to their high hydrophilicity (22-25). In fact, it is quite difficult to establish any correlation between MNP structure and demulsification efficiency: according to the data in Table 1, a high demulsification efficiency is typical of all three types of particles.

In Table 1, we collected data on available cases of MNP-demulsifiers that were developed basically since 2015. MNP-demulsifier size may vary from 12-14 nm (46, 50) to 465 nm (46). MNP-demulsifiers are made using magnetite nanoparticles of size about 200-300 nm.

The physical properties of magnetic nanoparticles and their magnetometric property are considered in detail in the reviews (45, 48). MNP-demulsifiers considered in this article (Table 1) have supermagnetic properties. This means that in the presence of an external magnetic field, a single domain of superparamagnetic MNPs aligns with the applied magnetic field. In the absence of an external field, superparamagnetic MNPs will exhibit no magnetization. Superparamagnetic MNP magnetization describes by the modified Langevin function (Equation 1) (48, 51).

$$M = M_0 L\left(\frac{\mu_p H}{k_B T}\right) + \chi_a H \quad (1)$$

One more important characteristic is the magnetic force (F) acting on the MNPs (Equation 2):

$$F = \mu_0 VM \nabla H \quad (2)$$

According to this equation, the ability of MNPs to move under an external magnetic field depends on particle magnetization: the greater the particle magnetization value, the easier the movement in the magnetic field. Practical research data for MNPs made on the basis of Fe_3O_4 represented in Table 1 shows that the larger the MNP diameter (i.e., the thicker the modified layer), the less the magnetization. It is important for magnetic materials to retain their superparamagnetic properties for them to be effectively separated from a complex multiphase system (49).

Further, in the article we will analyze the mechanism of O/W and W/O emulsion separation by MNP demulsifiers.

6. MECHANISM OF DEMULSIFICATION BY MNPs

Crude oil is usually produced in the form of a water-in-oil (W/O) or oil-in-water (O/W) emulsion (50). The emulsified water, crude oil, and bitumen are highly undesirable, as they may lead to problems of oil

transportation and catalyst deactivation in refinery operations (48).

For both types of emulsions (W/O and O/W), researchers connect the MNP demulsification activity with two basic factors: 1) ability of increasing the oil and water interfacial tension and 2) ability to interact with resins, naphthenic acids, asphaltenes and at the interface between oil and water (56, 57). The main reason for the stability of W/O emulsions is the "skin-like" asphaltene protective layer surrounding the water droplet phase. The broken asphaltene layer significantly increases the probability of water droplet coalescence and promotes demulsification (62). MNPs may exhibit demulsifying activity both independently and under a magnetic field. The demulsification process is shortened under a magnetic field (61, 63, 66). This is due to their easy separation from multiphase systems in the presence of external magnetic field. MNPs accumulate at oil-water interfaces of dispersed droplets, impart the magnetic properties to them, and then magnetically tagged droplets can rapidly coalesce and be isolated from the continuous phase (53, 55, 61, 67, 71-73).

The ability of MNPs to increase the interfacial tension is because of their amphiphilic structure. The structures of the hydrophobic and hydrophilic parts of MNPs are responsible for particle wettability. MNP wettability is the main difference between W/O and O/W demulsifiers. MNPs have to be wettable by the continuous phase of emulsion for better dispersion: a low contact angle for O/W emulsions and a high contact angle for W/O emulsion (26). The wettability of synthesized MNPs ($Fe_3O_4@AEAPFS$) was studied by Lü et al. (54). They studied the distribution behavior of MNPs between oil phase and water phase. The gravity effect makes $Fe_3O_4@AEAPFS$ -MNP pass through the oil-water interface and enter the aqueous phase. This is because the MNPs are surrounded by water and cannot fully come into contact with the diesel fuel. These MNPs have a large hydrophilic part (Fe_3O_4) and a small hydrophobic part ($EP@APTES$), so the particles are easily dispersed in the aqueous phase and reach the oil-water interface (56).

There are some examples of how researchers explain the mechanism of O/W demulsification by the developed MNPs (see Table 1). The demulsification of wastewater produced from flooding is considered in the article (49). The process was investigated under an optical microscope.

These M-DMEA particles accumulated at the O/W interface, enhancing the coalescence of oil droplets. After M-DMEA treatment, a clean aqueous phase without visible oil droplets was finally obtained. This work attributed the phenomenon to the interaction between N,N-dimethylethanolamine of MNPs and the surfactants of the emulsion such as asphaltenes, resins, and polymer residues (49).

Xu et al. (57) considered the demulsification mechanism of M-MWCNTs MNPs ($\text{Fe}_3\text{O}_4@SiO_2$ -APTES modified multi-walled carbon nanotubes), which have a similar structure to amphiphilic surfactants: hydrophobic carbon skeleton and hydrophilic MNPs. Partial $\text{Fe}_3\text{O}_4@SiO_2$ -APTES. MNPs show excellent interfacial activity and ability to adsorb asphaltenes. MNP surface functional groups ($-\text{NH}_2$, $-\text{OH}$ and $-\text{COOH}$) can serve as electron donors to form π - π bonds with aromatic molecules. Xu et al. (53), Lü et al. (71) also developed P(MMA-AA-DVB)/ Fe_3O_4 MNPs demulsification efficiency with the presence of carboxyl groups on the MNPs surface, which makes them interfacially active (53, 71). Vega et al. (72) used graphene oxide (GO) for MNPs surface modification (M-GO). Non-covalent interaction analysis attributed the strong affinity between M-GO and asphaltenes/resins to the π - π interactions.

Ko et al. (67) developed A-MNPs with a positive surface charge (amine group, $-\text{NH}_2$). The experiment results show that oil droplets are successfully separated negatively-charged oil droplets using cationic surfactant-coated MNPs (Figure 8). Xu et al. (53) described M-DM MNPs with a matrix dispersed structure based on diatomite (DM) coated by (3-aminopropyl)-triethoxysilane (APTES), MNPs of Fe_3O_4 , and polyethylenimine (PEI). The M-DM surface has a large number of amino groups. The asphaltene molecules are composed of aromatic rings and polar functional groups, such as hydroxyl, carboxyl, and epoxy. They considered that amino groups from the M-DM surface can form the hydrogen bonds with the hydroxyl groups derived from asphaltenes (53).

The MNP demulsifiers for W/O emulsions have to be wetted by oil fraction. For example, $\text{Fe}_3\text{O}_4@SiO_2@C$ MNPs are easily wetted by toluene, so they can easily transfer to the interface of the W/O emulsion and decrease the surface tension of water and ultimately lead to the coalescence of water droplets and separation of two phases (65, 74). Another example is PEMN MNPs received by solvothermal reaction propyleneoxide-ethyleneoxide block polyether with iron (III) acetylacetonate. A confocal microscope was used to observe the water droplets in W/O emulsions. After PEMN was added, the water droplets started to coalesce with each other and become bigger, making the emulsions more unstable. They supposed that PEMN MNPs could adsorb on the O/W interface by replacing some natural surfactants (51).

Lü et al. (71) explained that MNPs were synthesized: $\text{Fe}_3\text{O}_4@APFS$ (magnetite coated by aminopropyl-functionalised silica (APFS)) and $\text{Fe}_3\text{O}_4@APFS$ -G-CS (previous one MNPs coated by chitosan molecular chains). The zeta potential of these two types of MNPs was analyzed for the prediction of demulsification

efficiency. These nanoparticles have slightly different zeta potential: under pH 7.0, the potential of $\text{Fe}_3\text{O}_4@APFS$ was 18.2 mv, and of $\text{Fe}_3\text{O}_4@APFS$ -G-CS was 17.6 mv. This means that the positive charge intensity of the second type of MNPs was less than the first. Based on this fact, the authors assumed that for $\text{Fe}_3\text{O}_4@APFS$ MNPs, the electrostatic attraction of asphaltenes, resins, and naphthenic acids and demulsification efficiency could be higher. However, $\text{Fe}_3\text{O}_4@APFS$ -G-CS attracted negatively-charged oil droplets more effectively: the formation of aggregates of oil droplets and magnetic flocs was very fast and its size could reach 100 μm . They authors consider that the efficiency of demulsification by the $\text{Fe}_3\text{O}_4@APFS$ -G-CS is the consequence of hydrophobic interaction between grafted CS and oil droplets.

The demulsification mechanism for both W/O and O/W emulsions is practically the same: MNP demulsifiers disperse in a continuous medium of emulsion, interact with asphaltenes and other compounds of droplets' surface of dispersion medium, the shell is destroyed, and the droplets merge. MNP interaction with asphaltenes can be achieved mainly through Van der Waals interactions and Coulomb interactions. Many studies have been conducted on the zeta potential of asphaltenes under different conditions. Their main conclusion is that the surface of asphaltenes can be both positively and negatively charged (72, 73). Parra-Barrazaa et al. (73) reported that the anionic and the cationic surfactants adsorbing on the asphaltenes through the electrostatic interactions are able to reverse the zeta potential sign. In the research cases that we studied in this article, this conclusion is also true for MNP demulsifiers. The observed removal efficiency can be connected to the effect of MNP demulsifiers on the zeta potential of dispersed phase droplets in the continuous phase that leads to a decrease in electrostatic repulsion between droplets and enhancement of the removal efficiency (66).

This property of MNP-demulsifiers makes them an ideal reusable instrument for solving the problem of oil and water emulsion formation. In the following section, we collected factors affecting MNP demulsification efficiency.

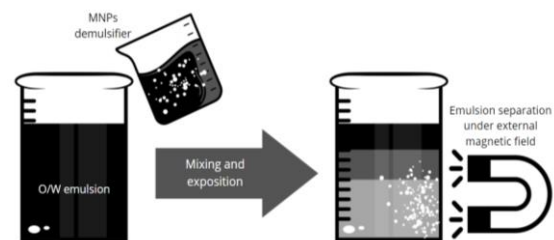


Figure 8. Schematic illustration of a bottle test experiment for O/W emulsion separation using MNPs demulsifier [63]

7. FACTORS AFFECTING MNP DEMULSIFICATION EFFICIENCY

Functional effectiveness of MNPs depends on three key environmental parameters: pH value, temperature, and ionic strength of water (55). However, the literature review hereunder showed that the demulsification efficiency of MNPs also depends on the characteristics of the emulsion and the MNP demulsifier itself. The aim of this section is to collect practical examples of factors that, according to the researcher's opinion, potentially influence the functional effect of modified MNPs.

7. 1. Emulsion Characteristics In preparing this review, we studied many examples of MNP demulsifiers that were developed for both O/W and W/O emulsions. We have collected some cases where authors discuss the properties of emulsion that have an influence on MNP demulsification effectiveness.

One characteristic of water and oil emulsion is viscosity. Liang et al. (50) revealed that emulsion viscosity is not the factor that significantly influences the demulsification capability of MNPs. Developed $\text{Fe}_3\text{O}_4@OA$ MNPs (Fe_3O_4 modified by oleic acid) were tested on two O/W emulsions with similar viscosities 1.68 and 1.43 mPa.s. In the experiment on the demulsification of MNPs at a concentration of 30 g/L, the separation effectiveness differed twice (36% and 80%, respectively). Microscopic analysis of the emulsion showed that droplet size was three times different (262 nm and 76 nm) (50). They concluded that the smaller the droplet size of O/W emulsion, the more difficult the demulsification process (50).

Another example of unexpected results of MNP testing on emulsions (W/O) with different API densities has been described by Ali et al. (58). $\text{P(MMA-AA-DVB)/Fe}_3\text{O}_4$ MNPs (polymethylmethacrylate-acrylic acid-divinylbenzene) showed high coalescence efficiency at a concentration of 600 ppm, at 60° C for 1 hour and effective separation of water from a stable emulsion with viscosity 35.95 API (7 wt.% asphaltenes) and 16.66 API having a higher asphaltens content (15 wt.% asphaltenes). Despite the significant difference in viscosity, the demulsification efficiency was high in both cases: 99 and 95%, respectively (58). They attributed this phenomenon to the high asphaltene content contributing to the adsorption of the MNP demulsifier on the interface between the water and oil.

One more important emulsion characteristic that can influence MNP demulsification efficiency is the emulsion phase volume ratio.

According to literature (52, 58-60, 64, 75-82) the water content in W/O emulsion is one of the primary factors that affects demulsification efficiency or emulsion stability. Stable emulsions require water content in addition to asphaltenes, resin, and paraffin

content. In their experiments, the researchers demonstrated that demulsification efficiency increases with an increase in water content from 30% to 50% using 500 ppm $\text{P(MMA-AA-DVB)/Fe}_3\text{O}_4$ MNP as demulsifiers; additionally, MNPs exhibit excellent efficiency and separation time optimization at half the water content.

7. 2. Water Mineralization

Lü et al. (54) discovered a remarkable increase in the efficiency of separating O/W emulsion after adding NaCl or CaCl_2 within the concentration range of 0-0.15 mol/L. During their study on $\text{Fe}_3\text{O}_4@APFS$ MNPs at pH 7.0, they observed that MNPs exhibited attractive electrostatic interaction with oil droplets. The addition of salt weakened this electrostatic attraction due to electrostatic screening. However, as the ionic strength increased, the hydrophobicity of $\text{Fe}_3\text{O}_4@APFS$ MNPs improved, promoting their sorption at the surface of oil droplets. Consequently, the separation efficiency of oil was significantly enhanced (54).

The demulsification efficiency of MNPs described by Lü et al. (55) ($\text{Fe}_3\text{O}_4@SiO_2$ -MPS modified by N-isopropylacrylamide (NIPAM) and sodium methacrylate (SMA)) was significantly enhanced by increasing water ionic strength. They explained this phenomenon by the fact that cations partly shielded the MNPs surface negative charge that concentrated on sodium methacrylate monomers and the charge repulsion was therefore reduced; salt addition also enhanced the MNP hydrophobicity. Increasing ionic strength in this case was also favorable for MNP accumulation on the oil droplet surface.

7. 3. Influence of pH

The pH value is an important factor to consider during demulsification by MNPs. Depending on the compounds used for MNP modification, the magnetic particles are able to change their performance at different pH levels. For example, MNPs modified by the co-polymer of sodium methacrylate (SMA) and N-isopropylacrylamide (NIPAM) became pH-sensitive due to the acid comonomer (55). MNP separation efficiency decreased with an increase in pH; the influence of pH on its separation efficiency became more significant with an increasing amount of SMA in coverage of MNPs. The authors explain these phenomena as due to the ionization of SMA under higher pH levels leading to an increase in MNPs hydrophilic properties. As a result, the repulsive forces between nanoparticles and oil droplets increased (55).

Another example of pH sensitive MNPs is M-GO sample (amino-functional $\text{Fe}_2\text{O}_3@SiO_2$ anchored on the surface of GO) (52). It was found that the M-GO maintained a good demulsification performance in an acidic condition. They attributed this phenomenon to the

ionization of the alcohol and carboxyl functional groups on the M-GO MNPs under the acid condition, which makes them less hydrophilic (52).

Successful examples of magnetic nanoparticles (MNPs) have been adapted to a wide range of pH values, as described Lü et al. (54) where Fe_3O_4 MNPs were modified by TEOS and N-(aminoethyl)-aminopropyl triethoxy silane (AEAPTES). The demulsification efficiency of these MNPs is achieved through different mechanisms under different pH values. At pH 4.0 and 7.0, the positively charged Fe_3O_4 @AEAPTES MNPs utilize both electrostatic attraction and interfacial activity to promote the sorption of MNPs onto the surface of oil droplets. However, at pH 10.0, the negatively charged Fe_3O_4 @AEAPTES MNPs repel the oil droplets through electrostatic interactions. Nevertheless, hydrophobic forces can still overcome the electrostatic repulsion, allowing the MNPs to successfully attach to the emulsified oil droplets. The synthesized Fe_3O_4 @AEAPTES MNPs demonstrate satisfactory separation performance at various pH levels, although their efficiency slightly declines with an increase in pH.

The pH value has a significant impact not only on functional groups of MNP demulsifiers, but also on the functional groups of asphaltenes. Under high or low pH, asphaltenes become charged, which increases their surface activity and hydrophilic behavior. In this condition, charged asphaltenes move to the oil-water interface and accumulate more easily. At acidic conditions, this property of asphaltenes is more pronounced due to the large number of carbocyclic groups in the structure. The stability W/O emulsion increases at pH below 7.0, as water drops do not merge well (60, 64, 74-86). In this case, the cationic type MNP demulsifier is preferable.

7. 4. Influence of Temperature Temperature also plays a crucial role in demulsification. Several examples discussed by Xu et al. (53) and Lü et al. (55) illustrated the influence of temperature on MNP demulsification efficiency. Xu et al. (53) have found that an increase in temperature from 15 to 60°C resulted in an increase in demulsification efficiency. This is mainly due to enhanced thermodynamic movement of interface molecules and decreased interfacial viscosity at higher temperatures, leading to emulsion instability. Meanwhile, Lü et al. (55) showed that the efficiency of an MNP demulsifier significantly decreased once the temperature was above the lower critical solution temperature (LCST) due to a hydrophobicity transition (55).

Ali et al. (58, 59) presented an example of W/O emulsion separation under 60°C covered different periods of time from 20 to 60 min. It was described that P(MMA-AA-DVB)/ Fe_3O_4 MNPs showed effective

demulsification efficiency for very stable W/O in 60 min at 60° C.

7. 5. Addition of Chemical Surfactants

Elmobarak and Almomani (66) organized MNP testing in combination with ordinary surfactants. Tests were carried out under three different surfactant concentrations of 0.05, 0.1 and 0.5 g/L at a constant concentration 10 mg/L of Fe_3O_4 - SiO_2 MNPs. It was found that demulsification efficiency slightly decreased by increasing the surfactant concentration in O/W emulsions. It was reported earlier that MNPs can attach to oil droplets in O/W emulsion as a result of the attractive force. The authors consider that surfactant added to emulsion increases the hydrophobicity of the oil droplets; the electrostatic repulsion between oil droplets becomes less pronounced and the interaction between oil droplets and the MNPs becomes worse. In addition, the anionic surfactants can interfere with acidic components in the oil and generate new compounds that can increase the density of the negative charge on the surface of oil droplets and enhance their stability (66). Nevertheless, we consider the influence of this factor as poorly understood. The right combination of surfactants will perhaps improve the demulsification efficiency.

7. 6. Time Ko et al. (67) described the results of experiments for studying the influence of mixing time on demulsification efficiency. They conclude that as the mixing time increases, the probability of collision between free MNPs and between free MNPs and MNP-oils increases. As a result, the particles might get more aggregated, and magnetic separation time gets shorter.

7. 7. Presence of Magnetic Field During MNP demulsifier application, a magnetic field can be applied with two aims: for MNP collection and for intensification of its activity. A magnetic field promotes quick and high demulsification efficiency and can compensate long time required for ordinary settling. For example, the experiments described by Elmobarak and Almomani (66) required 2 h settling time with a dose of 163 mg/L to achieve 94.9% demulsification, while this efficiency can be achieved in 8 min at a 10 mg/L concentration under a magnetic field.

The magnetic field influenced not only the MNP demulsifier, but also the OWE itself. The research findings conducted by Romanova et al. (75) showed that a magnetic field, constant and alternating electromagnetic fields applied to emulsion samples (W/O) of different composition lead to the destruction of the emulsion with 99 wt.% demulsification efficiency. However, the mechanism of that phenomena remains unclear. Khajeh et al. (76) have found that a magnetic field decreases the interfacial tension in the system of

water-toluene-asphaltenes and the number of hydrogen bonding between water and asphaltene molecules (76).

8. CONCLUSIONS

Interest in MNP demulsification technology is constantly growing. This review summarizes the research cases of MNP modification and testing for the demulsification of both types of OWEs (O/W and W/O). The range of bottle tests that were studied confirmed that MNP demulsifiers demonstrate excellent demulsification efficiency.

During the development of MNP demulsifiers, it is important to take it into account the following factors:

1. MNPs need a protective layer to avoid oxidation and corrosion.
2. The functional modification of MNPs have to be made in accordance with the type of emulsion and emulsifier characteristics (basically asphaltene). MNP demulsifier must have good wettability by continuous phase of emulsion.
3. It is also necessary to analyze the target OWE emulsifier characteristics (basically zeta potential of asphaltene). The functional groups of the MNP demulsifier must provide the necessary zeta-potential for electrostatic interaction with asphaltene.

This research experience proves MNPs as prospective substances for field application. The undoubted advantages of MNPs over conventional demulsifiers are their safety for the environment and reusability.

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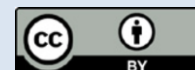
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**Persian Abstract****چکیده**

امولسیون نفت-آب طیف وسیعی از مشکلات را ایجاد می کند که یکی از آنها کاهش قابل توجه فشار در خطوط جریان است که منجر به افزایش هزینه های پمپاژ و حمل و نقل می شود. گسترده ترین روند توسعه یافته در میان فناوری های جداسازی نفت/آب، استفاده از دمولسیفایرهای مبتنی بر نانوذرات مغناطیسی (MNPs) است. MNP ها خواص شیمیایی و مکانیکی خاصی دارند و فرصت های منحصر به فردی را برای حل مسائل تولید نفت فراهم می کنند. ویژگی های کلیدی چنین نانوذرات مغناطیسی برای کاربرد پایدار آنها قابلیت استفاده مجدد و پایداری آنهاست. فرصت دستکاری از راه دور با استفاده از میدان های مغناطیسی خارجی به آنها یک مزیت منحصر به فرد در عملیات حمل و نقل می دهد. هدف اصلی این مطالعه، نظام بندی تحقیقات MNPs برای جداسازی موثر امولسیون روغن و آب است. این بررسی ویژگی های امولسیفایر MNP، مکانیسم جداسازی امولسیون های روغن-آب (OWE) و عوامل مؤثر بر اختلال در کارایی امولسیون های روغن-آب توسط دمولسیفایر MNP را ارائه می کند. ارتباط این مطالعه این است که امولسیون های نفت-آب اغلب در عمل در طول توسعه میدان با آن مواجه می شوند. برای حل این مشکل، استفاده از دمولسیفایرهای مبتنی بر نانوذرات مغناطیسی پیشنهاد شده است. تازگی کار در این واقعیت نهفته است که کار چندین عامل موثر بر دامولسیفکاسیون را به طور همزمان جمع آوری می کند و تأثیر هر عامل را توصیف می کند. از میان این عوامل، مهمترین آنها عبارتند از: ویژگی های امولسیون، شوری آب، PH، دمای مخزن، افزودن سورفکتانت های شیمیایی، زمان و میدان مغناطیسی. مکانیسم تشکیل امولسیون های روغن-آب در انواع مختلف نیز توضیح داده شده است و پیامدهای منفی تشکیل امولسیون مورد بحث قرار می گیرد. نتایج نشان داد که نانوذرات مغناطیسی نیاز به لایه محافظ دارند و دمولسیفایر باید ترشوندگی خوبی در فاز پیوسته امولسیون داشته باشد.