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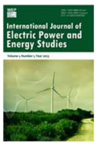

Comparative Study on the Treatment Performance of Different Reverse Demulsifiers for High-Iron Produced Water from Middle Eastern Oilfields

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ABSTRACT

Historically, due to variations in reservoir geological conditions, production technologies, and the duration of extraction across different oil and gas fields, the produced water exhibits a highly complex composition, significant quality fluctuations, and severe emulsification. Furthermore, as the water cut in mature oilfields worldwide continues to rise, the rate of produced water reinjection has failed to keep pace. Consequently, the volume of oily produced water requiring discharge from these mature fields is increasing steadily. In this context, ensuring that the treated effluent meets regulatory discharge standards has emerged as a critical challenge for wastewater treatment projects in such oilfields. Currently, the application of high-efficiency reverse demulsifiers represents a highly effective approach to address the challenge of destabilizing these difficult-to-treat produced water emulsions.

KEYWORDS

Wastewater Treatment; High Iron Content Produced Water; Reverse Demulsifier.

1. OILY PRODUCED WATER

Oilfield produced water is a multicomponent complex system comprising oil, solid impurities (such as clay particles), dissolved gases (e.g., H_2S, CO_2), and soluble salts (e.g., Fe^{2+}, Ca^{2+}). It is characterized by high emulsification, high oil content, high salinity, high hardness, high suspended solid content, high iron content and low pH. Due to the presence of Fe^{2+} and sulfides, it also exhibits water quality instability and strong corrosiveness. Oilfield produced water forms a highly stable emulsion and is associated with other issues such as corrosion and scaling[1-3].

2. REVERSE DEMULSIFIER

2.1. Analysis of the Action Mechanism of Reverse Demulsifiers

The demulsification process of a reverse demulsifier can be divided into three steps: droplet aggregation, interfacial film rupture, and droplet coalescence[4].

Droplet aggregation refers to the ability of the reverse demulsifier to reduce the electrostatic repulsion between water droplets and neutralize the surface charge on the droplets. Targeting this negative electronegativity, substances with opposite charges are added to neutralize the charge, thereby compressing and disrupting the electric double layer. This weakens the strength of the interfacial film, promoting contact and aggregation among water droplets. It also creates a bridging and flocculation effect, which compromises the stability of the emulsion. The emulsified droplets collide and aggregate with each other, achieving the goal of demulsification and oil-water separation[5].

Interfacial film rupture occurs because the surfactants present in the reverse demulsifier can displace natural emulsifiers. They adsorb onto the oil-water interfacial film, forming a new interfacial membrane that reduces the strength and stability of the original film. The reverse action of the demulsifier can cause the emulsion to transition between Water-in-Oil (W/O) and Oil-in-Water (O/W) types. During this phase inversion process, the interfacial film becomes prone to rupture, thereby accelerating demulsification[6] [7].

Droplet coalescence is the process where aggregated droplets merge into larger droplets with an increased diameter. This leads to a reduction in the number of droplets, which gradually separate out from the oil phase, ultimately resulting in the breakdown of the emulsion[8].

2.2. Types of Reverse Demulsifiers

Most demulsifiers for produced water are surfactants; therefore, their classification is similar to that of surfactants. Generally, there are four classification methods [10] [11]:

(1) Classification by ion type[9]:

Anionic

Cationic

Nonionic:

Ether type: Polyoxyethylene alkyl alcohol ethers and polyoxyethylene alkylphenol ethers

Ester type: Polyoxyethylene alkylphenol ethers

Amine type: Polyoxyethylene alkyl amines

Amide type: Polyoxyethylene alkyl amides

Amphoteric demulsifiers: e.g., Sodium polyoxyethylene alkyl alcohol ether sulfates.

(2) Classification by molecular weight:

Low molecular weight demulsifiers: Molecular weight typically less than 1,000 Daltons.

High molecular weight demulsifiers: Molecular weight between 1,000 and 10,000 Daltons.

Ultra-high molecular weight demulsifiers: Molecular weight ranging from 50,000 to 5 million Daltons.

(3) Classification by number of polymer blocks:

Two-block polymer demulsifiers: In the synthesis of nonionic demulsifiers, an initiator is first reacted with a specific proportion of PO (propylene oxide) to form a "lipophilic head" (this is the first block). Then, a certain amount of EO (ethylene oxide) is attached (this is the second block). The resulting demulsifier is called a two-block polymer.

Three-block polymer demulsifiers: A three-block polymer is obtained by adding another segment of PO to a two-block polymer base, and so on.

(4) Classification by initiator type:

The initiator, which can also be called a catalyst, uses substances containing active hydrogen to start the reaction with PO or EO. The demulsifier is formed after one or two blocks of polymerization. Substances containing active hydrogen include:

Phenols (e.g., octylphenol, nonylphenol, isobutylphenol)

Alcohols (e.g., ethylene glycol, propylene glycol, octanol)

Fatty alcohols

Currently, initiators based on ethylene amines are widely used, such as in AE and AP types.

2.3. Determination of the Technical Route

A series of poly(amidoamine) dendrimers with a nonylphenol (NP) core were synthesized utilizing the Mannich reaction and Michael addition reaction. These compounds were subsequently neutralized with organic acids to yield organic ammonium salt-type reverse demulsifiers. The structure and properties of these demulsifiers were characterized. Furthermore, various types of reverse demulsifiers were synthesized for subsequent demulsification performance studies[12].

2.4. Formulations of Reverse Demulsifiers

(1) Quaternary Ammonium Salt-Modified Multi-Branched Block Polyether Reverse Demulsifier

When bisphenol A (BPA) is used as the initiator for the block polyether, the hydrogen atoms adjacent to its phenolic hydroxyl groups can undergo an aminomethylation reaction with formaldehyde and ethyleneamine. This results in a multi-branched demulsifier structure with BPA as the core, ethyleneamine as the branches, and block polyether as the terminal groups. Specifically, BPA phenolic amine resin is subjected to ring-opening polymerization with ethylene oxide (EO) at varying ratios. The terminal groups are then modified with quaternary ammonium salts to achieve different degrees of cationization. The demulsification performance of these compounds on oily wastewater is subsequently evaluated.

Multi-branched block polyethers possess more complex and diverse structures, endowing them with unique properties such as enhanced hydrophilicity, wetting capability, and permeability. These characteristics allow them to rapidly migrate to the oil-water interface. Moreover, due to their branched architecture, they occupy a larger interfacial area than linear molecules, displacing a greater number of emulsifier molecules and thereby achieving higher oil-removal efficiency. Since the fine oil droplets in oily wastewater are generally negatively charged, demulsification can also be facilitated through charge neutralization[13].

(2) Organic Ammonium Salt-Type Polyamidoamine Reverse Demulsifier

This category primarily comprises dendritic and hyperbranched polyamidoamine (PAMAM)-based demulsifiers. These are polymeric nanomaterials characterized by a high degree of branching and specific topological structures. They are synthesized by modifying the active amine nitrogen atoms within the branched framework. For instance, a hyperbranched PAMAM reverse demulsifier can be prepared using nonylphenol (NP) as the core: first, active hydroxyl groups are grafted via the Mannich reaction, followed by reaction with ethylenediamine, and finally Michael addition with methyl acrylate[14].

(3) Organic/Inorganic Hybrid Cationic Reverse Demulsifier

Reverse demulsifiers in this group are based primarily on nonionic block polyethers, grafted using N,N-dimethylethanolamine as the "head" group. Diallyldimethylammonium chloride (DADMAC), a common water-soluble cationic monomer, is used in conjunction with nano-SiO_2 (which exhibits improved dispersibility after modification) to prepare the DRD series of reverse demulsifiers via controlled/living radical copolymerization. The DAD series, on the other hand, is prepared by direct copolymerization of hydrophilic monomers. The demulsification performance of both series is investigated in combination with other demulsifiers[15].

3. REVERSE DEMULSIFICATION TREATMENT PROCESS FOR PRODUCED WATER AND LABORATORY SCREENING TESTS

3.1. Screening of Reverse Demulsifiers for Produced Water

To evaluate the efficacy of different reverse demulsifier formulations in treating produced water from Middle Eastern oilfields, four reverse demulsifiers with distinct structures were selected for demulsification tests. The initial oil content in the produced water was 119.5 mg/L, the dosage of demulsifier was set at 30 mg/L, and the operating temperature was maintained at 70°C. The dewatering results are presented in Table 1.

Table 1. Treatment Performance Data of Various Reverse Demulsifier Formulations for High-Iron Oilfield Produced Water

No.	Reverse Demulsifier	Initial oil content /mg/L	Treated Water oil content /mg/L	Treated water quality
1	**DRD-5117**	119.5	**15.8**	**I**
2	DCP-1	119.5	20.29	I
3	DWL-21	119.5	21.48	I
4	DAP-13	119.5	25.87	II

4. CONCLUSION

A targeted research program was undertaken to develop effective reverse demulsifiers for treating produced water with high iron content. This involved a methodological approach of selecting diverse raw materials and employing distinct synthesis techniques. Through iterative experimentation and systematic screening, an optimal formulation was successfully identified. This tailored demulsifier significantly enhances the treatment efficiency of oily produced water, enabling the stable and compliant treatment of high-salinity effluent, even in the presence of elevated iron concentrations.

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