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Microbubbles improve removal of oil-in-water emulsions stabilized by humic acids

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ABSTRACT

This study examined the stability of fine oil-in-water (O/W) emulsions containing natural organic matter (500 mg·L^{-1} soybean oil and 25 mg·L^{-1} humic acid), named O/W-HA emulsions, formed by high-speed mixing. The calculated stability values from a 300-min stability test indicated that O/W-HA emulsions were more stable than O/W emulsions. Size distribution and Sauter mean diameter (D_{32}) of oil droplets were calculated to evaluate the use of microbubbles (MB) in treating fine O/W-HA emulsions at different airflow rates, pH levels, and sodium chloride concentrations. At a practical pressure (0.45 MPa), the designed column flotation system, featuring an F.BT-50 nozzle, produced a variety of gas bubbles to enhance separation. The application of MB in treating O/W-HA emulsion droplets (<15 μm, mean: 4.91 μm) and/or the addition of NaCl (30 mg·L^{-1}) after 30 min of treatment increased the removal efficiency (from 60% to 82%) at pH 4.0. The results are meaningful for scale-up at treatment plants that produce oily wastewater because they indicate a high potential for the reduction and reuse of oil-floated products to improve treatment efficiency.

Keywords: Emulsions; Flotation; Humic acid; Microbubbles; Oil-in-water; Wastewater treatment

1. Introduction

Oil has been a part of the environment for millions of years. In daily human activities, numerous industries discharge wastewater with oil content ranging from several parts per million to a few percent (1%–10% or even higher) by volume [1–3], even though the content generally ranges between 100 and 1,000 mg·L^{-1} [3,4]. Without treatment, oily wastewater may have serious effects on the living environment of aquatic life, produce odor and color pollution, and reduce the purity of natural water. The oil-in-water phase can occur in several forms based on droplet size: free oil (>150 μm), dispersed oil (20–150 μm), emulsified oil [oil-in-water (O/W) emulsions, <20 μm], and dissolved oil (fine emulsions, <5 μm) [4].

O/W emulsions are formed by turbulent mixing and shearing actions of oily wastewater in transfer pumps, the addition of certain organic chemicals (e.g., soaps and detergents), or heat [1,2]. O/W emulsions are colloidal systems in which fine oil droplets are dispersed and stabilized in the water phase by a combination of complex physical and chemical mechanisms [1,5]. An emulsifier is a complex molecule that often has a hydrophilic and a lipophilic group. In the water phase, the emulsifier has an affinity for both

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water and oil and promotes their coalescence. O/W emulsions usually have negative surface charges, which provide stability to emulsion systems. Static electric charges accumulated by friction between the oil and water phases can enhance the stability of O/W emulsions. Additionally, fine solid particles may stabilize an emulsion by adsorbing at the oil/water interface to prevent coalescence of the dispersed droplets. Practically, the treatment of fine oil droplets (2–30 μm) in water is very challenging [2,6], and it is a significant point of focus for improving downstream water quality, water reuse, and oil recovery.

As a main component of natural organic matter (NOM), humic acids (HA) naturally occur in soil particles, ground water, and surface water. The presence of HA in water has received much attention because it leads to color pollution and traps other toxic pollutants (e.g., heavy metals and polycyclic aromatic hydrocarbons) [7], which are the main foulants in water treatment [8]. Harmful by-products can be formed by the interaction of NOM with chlorination processes [9]. Both O/W emulsions and HA are common pollutants found worldwide in oily wastewater effluents, particularly palm oil mill effluent (POME) or soybean oil refining effluent from plant oil refining processes. Nevertheless, the stability of fine O/W emulsions containing NOM, such as HA has not been widely investigated.

Various methods have been suggested to treat O/W emulsion, such as adsorption [10], coagulation [11], membrane filtration [12], hydrocyclone [5], electrocoagulation [13], electroflotation [4], and flotation. The application of microbubbles (MBs) (with and without coagulants or surfactants) in flotation has attracted much attention [3,14–18]. Some reviews of the O/W emulsion treatment are listed in Table 1. MB technologies are efficient for the separation of O/W emulsions, owing to their high treatment efficiency, ability to handle high-shock loads and enhance oil recovery, and low capital investment and operational costs [4,16]. The size of MB is a key factor affecting the efficiency of collisions and attachment between particles and MB, which have diameters of less than several hundred micrometers [19]. MB formation, growth, and collapse in a solution can be termed cavitation. Hydrodynamic, acoustic, and optic cavitation techniques have been developed for MB generation [20]. Hydrodynamic cavitation is widely used in water treatment systems. Here, MB generators involve mechanical parts (i.e., a pump and a nozzle) that produce strong shear forces to impact the liquid. MBs can be created by decompression in the nozzle or injection devices [19,20]. MBs have various useful characteristics, including high solubility in liquid, a large gas–liquid interfacial area, high inner pressure, and long residence time [20]. Consequently, the MB technique has been applied in many fields [21].

To date, few studies have investigated the effect of MB on O/W-HA separation in emulsified wastewater. The main objectives of this study were (1) to compare the stability of O/W and O/W-HA emulsions and (2) to investigate the effectiveness of using MBs in flotation treatment of fine O/W-HA emulsions. The ready applicability of the findings of this study can quickly increase the removal efficiency of oily pollutants and promote the reuse of floated products to improve green wastewater treatment.

2. Material and methods

2.1. HA solution and O/W emulsion samples

Pure HA (Fujifilm Wako Pure Chemical U.S.A. Corporation: 082–04625, blackish brown color) was mixed with O/W samples; the resultant mixtures were named O/W-HA emulsions. At room temperature (25°C ± 0.2°C), 1.0 g of HA was dissolved in up to 1.0 L of 0.01 M NaOH (Merck) and used as a stock solution. O/W emulsions (oil: 500 mg·L^{-1}) and O/W-HA emulsions (oil: 500 mg·L^{-1} and HA: 25 mg·L^{-1}) were prepared from soybean oil (ChemSrc, CAS number: 8001-22-7, density: 0.917 g mL^{-1} at 25°C, purity: 98.0%), HA stock solution, and warm tap water (39°C ± 1.0°C) using a high-speed blender [Toshiba (1.5 L) BL-60PHNMY, 25,000 rpm, working volume: 1.0 L] within 4 min of mixing time; the emulsions were investigated for stability at pH 7.0. Samples of O/W-HA emulsions were used to observe the effect of MB treatment at typical pressure (0.45 MPa) and different airflow rates (1.0–5.0 L·min^{-1}), pH levels (4.0 and 7.0), and NaCl concentrations (10–50 mg·L^{-1}) (Fujifilm Wako Pure Chemical U.S.A. Corporation: 191-01665, purity > 99.5%).

2.2. Analysis of droplet size and stability of O/W and O/W-HA emulsions

Under high-speed mixing for sufficient mixing time, all components of warm water, oil, and organic compounds formed emulsions. After 4 min of mixing and pH adjustment, the droplet sizes of O/W and O/W-HA emulsions were observed using a laser light scattering particle size distribution analyzer (Horiba LA-920, Japan) and a light microscope (Olympus DP10 digital camera and Thoma hemocytometer 0.1 mm depth, 0.0025 mm^2, Japan). Ultraviolet–visible (UV-Vis) spectrophotometry scanning (Genesys 10S UV-VIS, USA) was used to measure the absorbance of the HA and O/W-HA emulsion samples.

Because of a wide distribution of oil droplet size, the Sauter mean diameter (volume to surface, D_{32}) was used to calculate the diameters of O/W and O/W-HA emulsion droplets according to Eq. (1). where d_i is the diameter of a droplet and n_i is the number of oil droplets.

$$D_{32} = \frac{\sum_{i}^{n} n_i d_i^{3}}{\sum_{i}^{n} n_i d_i^{2}} \tag{1}$$

The stability of O/W and O/W-HA emulsions was determined by pouring 1,000 mL of each emulsion into an extractor funnel (1,000 mL), and the liquor temperature was continuously monitored under laboratory conditions (approximately 25°C). Aliquots (10 mL) were withdrawn via the valve at the funnel bottom after 300 min of testing. The concentrations of O/W and O/W-HA emulsions were measured by chemical oxygen demand (COD) method (5220D, APHA) [22]. The emulsion stability constant (K_{st}) was calculated using a first-order model [23], given in Eq. (2), where C and C_o are O/W concentrations (according to

Table 1
Some reviews on the O/W emulsion treatment methods

Method	Application	O/W emulsions		Operating conditions	Oil concentration		References
		Method	Size, µm		Influent, mg·L^{-1}	Removal, %	
Adsorption	Stabilized petroleum O/W emulsion	Sampling oily wastewater	–	Bentonite: 1.0 g; or Powdered activated carbon (PAC): 1.0 g O/W emulsion: 0.2 L Stirring time: 4 h	1,012 836	98.3 93.5	[10]
Coagulation	POME	Sampling POME	–	Chitosan dose: 0.5 g·L^{-1}; contact time: 15 min; mixing rate: 100 rpm; sedimentation time: 20 min; pH: 4	2,000	95	[11]
Membrane filtration: - composite polymer - polymer - inorganic composite - composite metal - gel and biomass	O/W emulsion	–	–	Number of cycles: 5–20 3–30 3–10 10–30 5–80 (the weak antifouling property of membrane)	–	 95–99 85–100 82–100 99–100 86–100	[12]
Electrocoagulation	10 mL benzene and Tween 80 (0.5 g·L^{-1})	Stirring 1,500 rpm, 12 h	–	NaCl: 0.8 g·L^{-1} Al plate-SS mesh (304) pH = 7.0; 25 V Treatment time: 60 min	28,000–32,000 (COD)	90.9	[13]
Electroflotation	Crude oil	Stirring, 24 h	–	pH: 4.72 5.0 V and 0.4 A current Treatment time: 30 min Salinity: 4 mg·L^{-1}	50	94	[4]
Coagulation and dissolved air flotation (DAF)	Surfactant Span 20: 0.3%, oil and deionized water	Mixing	–	pH: 8; Aluminium sulfate 100 mg·L^{-1} pH: 7; Ferric sulfate 120 mg·L^{-1} Treatment time: 20 min	1,630	>90	[14]
Coagulation and modified induced air flotation	Palm O/W emulsion, tap water and anionic surfactant	Mixing	–	Gas flow rate: 5 mL·s^{-1} Treatment time: 30 min Without alum Alum: 0.8–1.4 g·L^{-1}	 10,000	 80 94–97	[15]
Coagulation and column flotation	Palm O/W emulsion, warm tap water	Mixing	<20	MB-PAC Treatment time: 2.5 min, PAC: 50 mg·L^{-1} pH: 3–7 MB-Cetyltrimethylammonium chloride (CTAC) Treatment time: 2.5 min, CTAC: 0.5 mg·L^{-1} pH: 5–7	1,000 1,000	90 82	[16]
DAF with micro and nanobubbles	Emulsified crude oil in saline water 30 g-NaCl·L^{-1}	Mixing 24,000 rpm 10 min	–	MBs, D_{32} = 30–40 µm NBs, D_{32} = 150–350 nm pH: 7 Saturation time: 30 min Flotation time: 5 min Without Dismulgan V3377 Dismulgan: 5 mg·L^{-1}	 334–450	 <65 99	[18]

COD, mg·L^{-1}) at the withdrawal time (t, min) and beginning time (t = 0, min), respectively.

$$Ln\frac{C}{C_o} = K_{st} \times t \quad (2)$$

2.3. Experimental setup

The main components of the designed flotation system were a long acrylic tank (approximately 12 L working volume, diameter of 10.8 cm, and height of 130.8 cm), a small air pump, a controlled airflow meter, and a pressurized MB generator system that featured a pressure pump, dissolution tank, and pressure meter with an F.BT-50 nozzle (Fig. 1). Air enters via the F.BT-50 nozzle and air tube and forms a variety of gas bubbles based on depressurized water. The airflow rate was adjusted from 1.0 to 5.0 L·min^{-1} to generate MB at 1 L·min^{-1} and to form MB with coarse bubbles (diameter = 0.5–5 mm at higher airflow rates) in the treatment system.

Initially, the pressurized generator was operated at a pressure of 0.45 MPa, water flow rate of approximately 180 mL·s^{-1}, and airflow rate of 1.0 L·min^{-1} (named MB_1.0) to produce a large number of MBs. The sizes of MBs in tap water at different pH levels (4, 7, and 9), temperatures (from 39°C ± 1°C to 59°C ± 1°C), and sodium chloride concentrations (10–50 mg·L^{-1}) were rapidly analyzed using a laser light scattering particle size distribution analyzer. Airflow rates of 2.0 and 5.0 L·min^{-1} in the flotation system were labeled as MB_2.5 and MB_5.0, respectively.

In each batch mode operation, 20 L of the samples (O/W-HA emulsions with or without NaCl) was prepared by high-speed mixing (oil: 500 mg·L^{-1}, HA: 25 mg·L^{-1}, mixing time: 4 min, temperature: 38°C–40°C), of which 8.0 L was used to restart the system twice. Solutions of 1.0 M NaOH and 2.5 M H_2SO_4 were used to adjust the pH of the samples. During treatment, a 100 mL aliquot of treated water was collected from the bottom of the flotation tank for measuring dissolved oxygen (DO), temperature (°C), COD, and droplet size.

3. Results and discussion

3.1. Relationship between COD values and emulsified oil concentrations

The mixtures had a uniform milk-white color for O/W emulsions and a uniform milk-light brown color for O/W-HA emulsions. To fully investigate the relationship between COD and O/W emulsions, O/W emulsions were observed at concentrations between 0 and 1,000 mg oil L^{-1} with and without the addition of 25 mg·L^{-1} HA.

A very clear relationship between COD and O/W emulsions was evident, with a COD value of 2.7377 × oil concentration ($R^2 > 0.99$) (Fig. 2A); therefore, COD measurements were used to evaluate O/W emulsion treatment efficiency [15,16]. At the emulsion stage, 1.0 mg soybean oil was equivalent to approximately 2.74 mg COD. Adding 25 mg HA to 1.0 L O/W emulsion samples (from 0 to 1,000 mg oil L^{-1}) led to an increase in the COD value (approximately 35 mg·L^{-1}) for each concentration. Therefore, 1.0 mg HA was equivalent to 1.40 mg COD. The obtained UV-vis spectrophotometry results (from 190 to 1,100 nm) for samples of the 25 mg·L^{-1} HA solution and O/W-HA emulsion (oil: 500 mg·L^{-1} and HA: 25 mg·L^{-1}) showed evident changes in absorbances below 690 nm. The O/W-HA emulsion had the highest absorbance (approximately 3.8) at UV wavelengths of 215 ± 5 nm (Fig. 2B), and the absorbance gradually decreased at the visible wavelengths. The solution of 25 mg HA L^{-1} showed a blackish brown color, with the highest absorbance (approximately 3.28) at UV wavelengths of 197 ± 2 nm.

3.2. Droplet sizes and stability of emulsified oils

The fine O/W emulsion was very stable because of its colloidal state [1,2]. In warm water (approximately 40°C) at pH 7.0, after 4 min of mixing, 100% of O/W (oil: 500 mg·L^{-1}) and O/W-HA (oil: 500 mg·L^{-1} and HA: 25 mg·L^{-1}) emulsions were transferred to emulsified oil (diameter < 15 μm). More than 80% of O/W and 91% of O/W-HA emulsions had fine droplet sizes (diameter < 5 μm). Remarkably, the presence of HA as NOM in O/W-HA emulsions led to an increase in the number of fine emulsified droplets after high-speed mixing: 43% of droplets were smaller than 2.0 μm, in contrast to 13.7% of droplets in O/W emulsion. The Sauter mean diameters of O/W and O/W-HA emulsions were 6.30 and 4.91 μm, respectively (Fig. 3A). Additionally, light microscopy showed that most of the O/W-HA emulsion droplets displayed Brownian motion (Fig. 3C). Painmanakul et al. [15] also reported Brownian motion with O/W emulsion droplets smaller than 5 μm.

During the O/W emulsion stability test (300 min) at laboratory temperature (25°C), the temperature of the samples gradually decreased from 40°C to 25°C in the first 90 min, then remained constant at 25°C ± 0.2°C. The straight lines obtained for the O/W and O/W-HA emulsions during this interval showed low K_{st} values of 0.0011 (R^2 = 0.95) and 0.0004 (R^2 = 0.91) min^{-1}, respectively. Consequently, with decreasing temperature, the O/W-HA emulsions were 2.75 times more stable than the O/W emulsions because of their smaller droplet size. However, the COD values of the samples were not reduced after 90 min (Fig. 3D).

Recently, Erica et al. [7] used HA as a natural surfactant to promote emulsification and indicated that HA increased the stability of toluene-in-water emulsions in the presence of bitumen. The major components of soybean oil are long-chain fatty acids, such as palmitic acid, oleic acid, linoleic acid, stearic acid, and unsaturated fatty acids [24]. Moreover, HA is a complex macromolecule with several of –OH and –COOH groups present in aromatic rings. In the water phase, O/W emulsions have a negative charge and an affinity for both water and oil, which promotes their coalescence [1]. Compared to low-energy mixing, with high-energy mixing, fine O/W-HA emulsions can be more stabilized by the electric charge and can more effectively dissolve HA adsorbed at the oil/water interface to prevent coalescence.

In breaking processes of O/W emulsions, pH is a key influencer owing to its impact on the surface charge of oil droplets [11], and strong acidic solutions (e.g., H_2SO_4 and HCl) can be applied to adjust the pH to suitable levels before de-emulsification [1,6]. In this study, the size distribution of O/W-HA emulsion (oil: 500 mg·L^{-1} and HA:

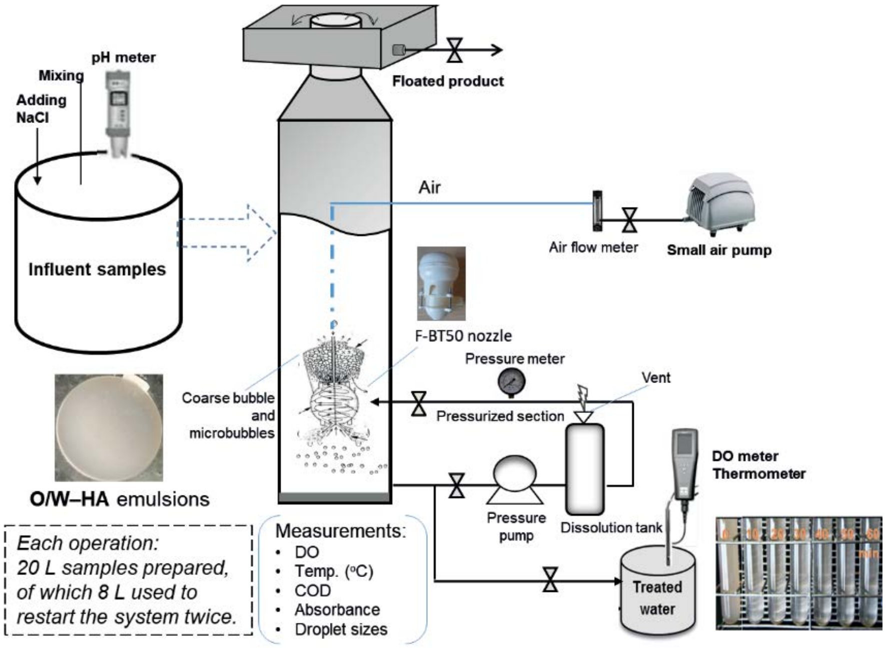

Fig. 1. Experimental setup. COD, chemical oxygen demand; DO, dissolved oxygen; O/W-HA, oil-in-water emulsion with humic acid.

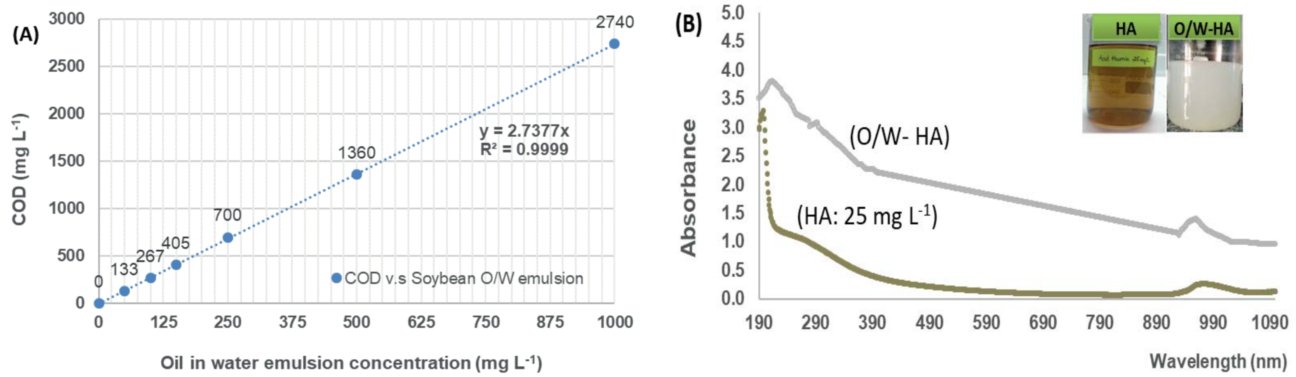

Fig. 2. (A) Chemical oxygen demand (COD) values and concentrations of oil-in-water (O/W) emulsions (from 0 to 1,000 mg oil L^{-1}) at 40°C ± 1.0°C, pH: 7.0, and mixing time: 4 min. (B) Absorbance values of the 25 $mg\cdot L^{-1}$ humic acid (HA) solution and O/W-HA emulsion (oil: 500 $mg\cdot L^{-1}$ and HA: 25 $mg\cdot L^{-1}$).

25 $mg\cdot L^{-1}$) droplets at different pH values (4.0, 7.0, and 9.0) was analyzed after adjusting the pH from over approximately 10 min, as shown in Fig. 3B. The O/W-HA emulsion droplets were more agglomerated at low pH than under alkaline conditions. Decreasing the pH values to 9.0, 7.0, and 4.0 resulted in increases in the Sauter mean diameter of O/W-HA emulsions to 4.29, 4.91, and 6.99 μm, respectively. This phenomenon could be explained by the protonation of carboxylate ions under acidic conditions to produce carboxylic acid [1] and reduce the negative zeta potential of the O/W-HA emulsion droplets [14], thereby allowing the fine oil droplets to agglomerate to larger sizes.

3.3. MB size in warm water

MB size is a key factor affecting the efficiency of flotation [18]. Smaller MBs in water increase the performance of the flotation, as demonstrated by white water collector modeling [19]. The application of a pressure MB generator leads to an increase in temperature in batch mode flotation, which changes the size of MBs during treatment and affects the treatment efficiency. With respect to practical pressure (0.4–0.6 MPa) in dissolved air flotation, in this study, the pressure across the F.BT-50 nozzle was controlled at 0.45 MPa. The airflow rate was easily adjusted using the nozzle to create MBs and “coarse bubbles” of a stable size range without affecting the inlet water pressure.

The size distribution of MBs in warm water (pressure: 0.45 MPa, water flow rate: 180 $mL\cdot s^{-1}$) was rapidly analyzed at an airflow rate of 1.0 $L\cdot min^{-1}$ (MB_1.0) and MB generation time of 10 min at different pH values (4.0, 7.0, and 9.0) and temperatures (from 39°C ± 1°C to 59°C ± 1°C). The results of size distribution analyses of MBs indicated that 100% of the droplets were smaller than 35 μm at 39°C ± 1°C,

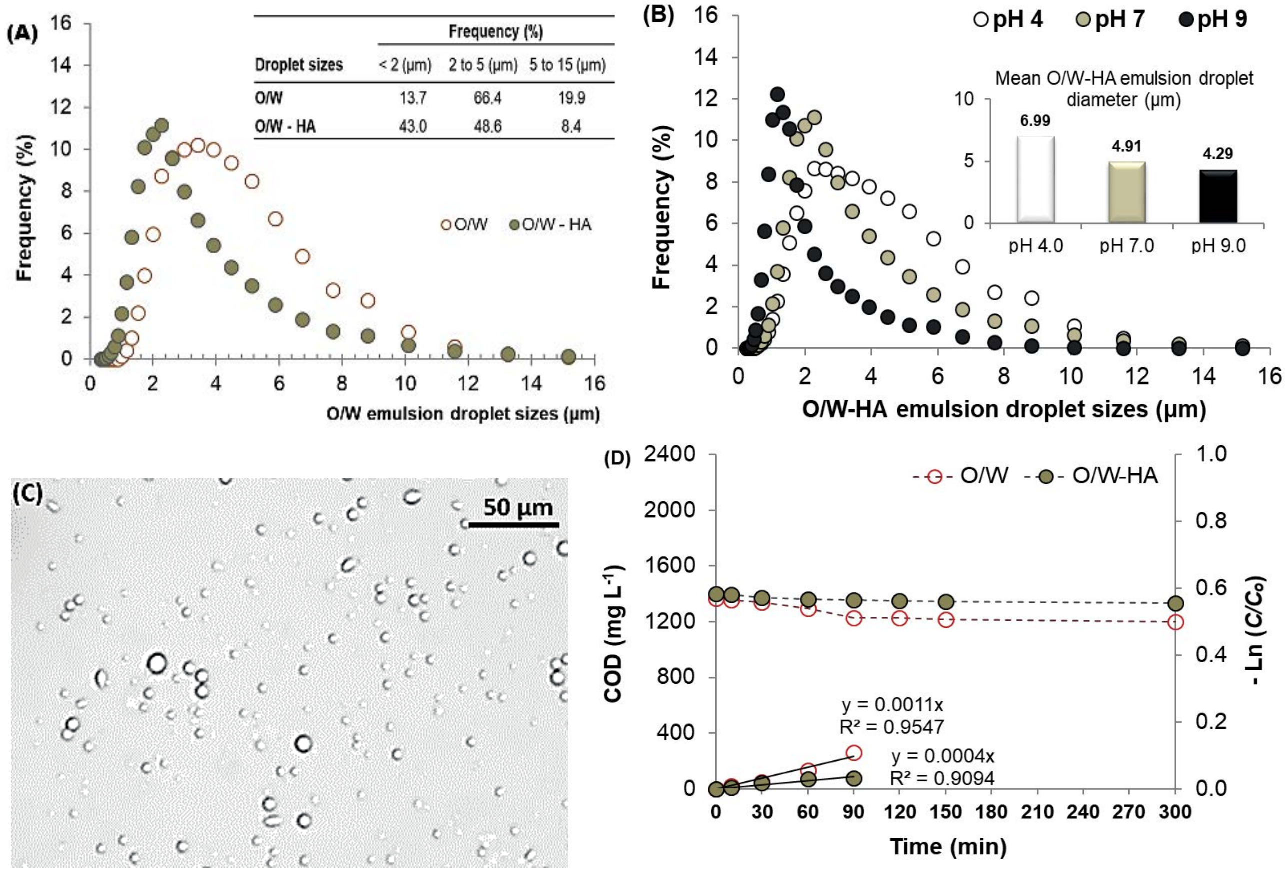

Fig. 3. (A) Size distribution and frequency (%) of oil-in-water (O/W) emulsion (oil: 500 mg·L^{-1}) and O/W-HA emulsion (oil: 500 mg·L^{-1} and HA: 25 mg·L^{-1}) droplets at pH 7.0. (B) O/W-HA emulsion droplet sizes at different pH values. (C) Microscopic image of O/W-HA emulsion at pH 7.0. (D) Stability of O/W and O/W-HA emulsions at pH 7.0 ± 0.1.

with a Sauter mean MB diameter of 8.2 ± 0.7 μm at pH 7.0 (Fig. 4A), which was nearly twice the diameter of O/W-HA emulsion droplets (4.91 μm, pH: 7.0). Adjusting the pH to either acidic or alkaline conditions had a significant effect on the size of MBs. The average bubble size (95.7 ± 21.9 μm) under alkaline condition (pH 9.0) was outside the typical MB size range (10–60 μm) [20] and was more than 20 times larger than the average target size of O/W-HA emulsion droplets. Without the addition of coagulants, the separation of the O/W emulsion was weak at pH > 7.0 [16]. A decreasing frequency (%) of MBs smaller than 35 μm and an increasing frequency (%) of MBs of 35–200 μm were observed at high temperatures (44°C–59°C) (Fig. 4B).

3.4. Effect of MB treatment with different airflow rates and pH on fine O/W-HA emulsions

The performance of MB treatment upon changing airflow rates (1.0–5.0 L·min^{-1}) and pH (4.0 and 7.0) (pressure: 0.45 MPa) using the F.BT-50 nozzle was investigated at oil and HA concentrations of 502 ± 2 and 25 mg·L^{-1}, respectively, and at 38.5°C ± 0.5°C temperature (Fig. 5A). At pH 7.0 ± 0.1, the mean size of O/W-HA emulsion droplets (4.9 μm; Fig. 3A and B) was 1.7 times smaller than that of MBs (8.2 μm, Fig. 4A). At pH 4.0 ± 0.1, the mean MB size increased to 26.8 μm, which was 3.8 times higher than that of the O/W-HA emulsion droplets and produced agglomerations of up to 6.99 μm.

MB flotation showed weak treatment efficiency for fine O/W-HA emulsion droplets (4.9 μm) at neutral condition (oil removal efficiency < 15%, pH: 7.0) after 30 min of treatment, and changing the airflow rates (1.0–5.0 L·min^{-1}) did not affect the separation. Therefore, both MB and fine O/W-HA emulsions had very fine droplet sizes that carried negative charges and contained a high percentage of emulsified oil and bubbles that displayed Brownian motion in water (diameter < 5 μm).

Nevertheless, fine O/W-HA emulsions under acidic conditions (pH 4.0) were separated well within a short time using MBs (5 min, oil removal approximately 40%), and the rate gradually increased with time. Herein, adjusting the airflow rate to 2 L·min^{-1} (MB_2.0) exhibited improved efficiency (approximately 70%) in separating fine O/W-HA emulsions after 30 min of MB treatment compared with the yields of approximately 52% and 50% for MB_1.0 and MB_5.0. Acidic conditions enhanced de-emulsification of fine O/W-HA droplets and improved the efficiency of bubble/oil aggregate formation (Fig. 5B), resulting in an improved efficiency of separation. A significant change in the size of bubble/oil aggregate droplets was observed between 5 and 60 min of flotation; the Sauter oil-MB diameter increased rapidly from 5 min (11.0 μm) to 10 min (19.3 μm), and then decreased gradually until 60 min (9.7 μm). These significant results could be explained by the presence of small, high density MBs (Fig. 4A). Although the mean MB size is substantially larger than the mean O/W-HA emulsion droplet size (6.99 μm), acidification should modify the surface charge of the fine O/W-HA emulsion and lead to the formation of larger MB aggregates. In this flotation, adjusting airflow rates via the F.BT-50 nozzle was found to be beneficial for removal of bubble/oil aggregates owing to the increase in bubble volume [25]. The aggregates increased more rapidly in the long (height: 130.8 cm) and narrow (diameter: 10.8 cm) flotation reactor. Additionally, the use of MBs and coarse bubbles of optimum sizes promoted the formation of larger aggregates [6]. Bubble/oil aggregates in water can reduce the viscosity [26] and increase the differential density [25]. However, the energy of air turbulence energy could reduce the yield of bubble/oil aggregates at an airflow rate of 5.0 L·min^{-1}, consequently decreasing the separation efficiency [6,15].

Oily wastewater generally contains both O/W emulsions and NOM. Moreover, oily wastewater from plant oil processing (e.g., soybean oil refining effluent or POME) is warm to hot after processing and can remain stably warm (30°C–40°C) in a series of receiving ponds or tanks, specifically in tropical climates in Asian countries, such as Malaysia and Thailand. Over time, wastewater with lower pH (e.g., POME, which has a pH of 4.0) would be formed owing to biological degradation of oil and organic compounds, which is conducive to the use of MBs in flotation treatment of POME. The promising results of this study indicate the high potential of a relatively rapid

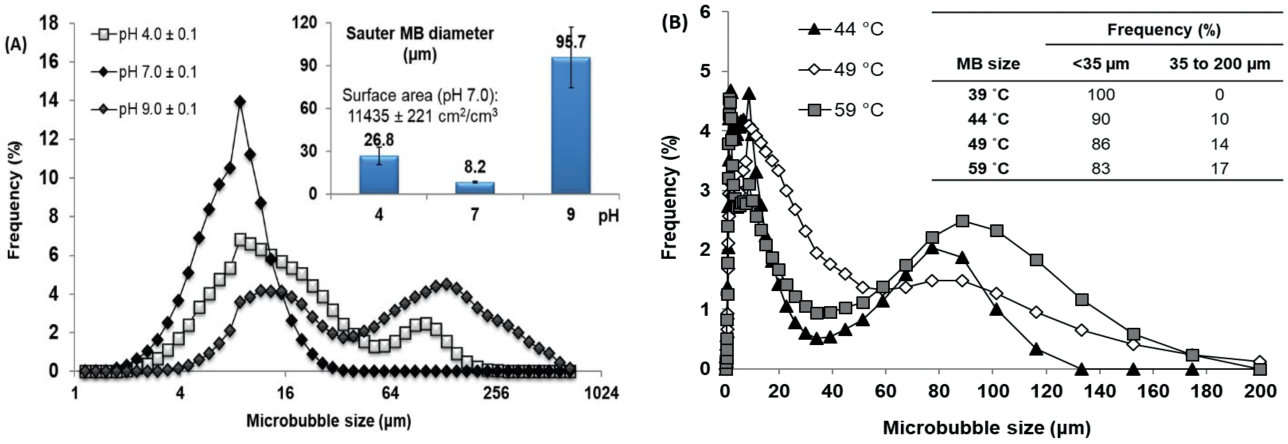

Fig. 4. (A) Microbubble size (MB) distribution at different pH levels in warm water (39°C ± 1°C); airflow rate 1.0 L·min^{-1}, MB generator time: 10 min, and pressure: 0.45 MPa. (B) MB size at different temperatures; pH: 7.0, airflow rate 1.0 L·min^{-1}, and pressure: 0.45 MPa.

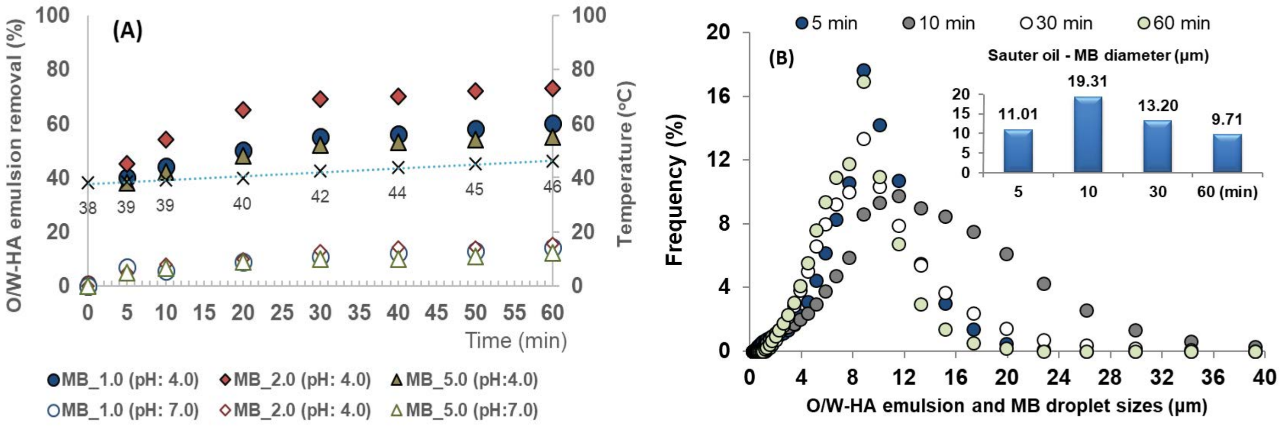

Fig. 5. (A) Effect of airflow rates (1.0–5.0 L·min^{-1}) on fine oil-in-water emulsions with humic acid (O/W-HA) at pH 7.0 ± 0.1 and 4.0 ± 0.1 and pressure 0.45 MPa during treatment. Oil: 502 ± 2 mg·L^{-1} (mean ± SD, n = 18) and HA: 25 mg·L^{-1} (according to COD: 1,410 ± 22 mg·L^{-1}), temperature: 39.0°C ± 1.0°C. (B) Distribution of O/W-HA emulsion and microbubble (MB) droplet sizes in the withdrawn water during treatment, pH 4.0 ± 0.1.

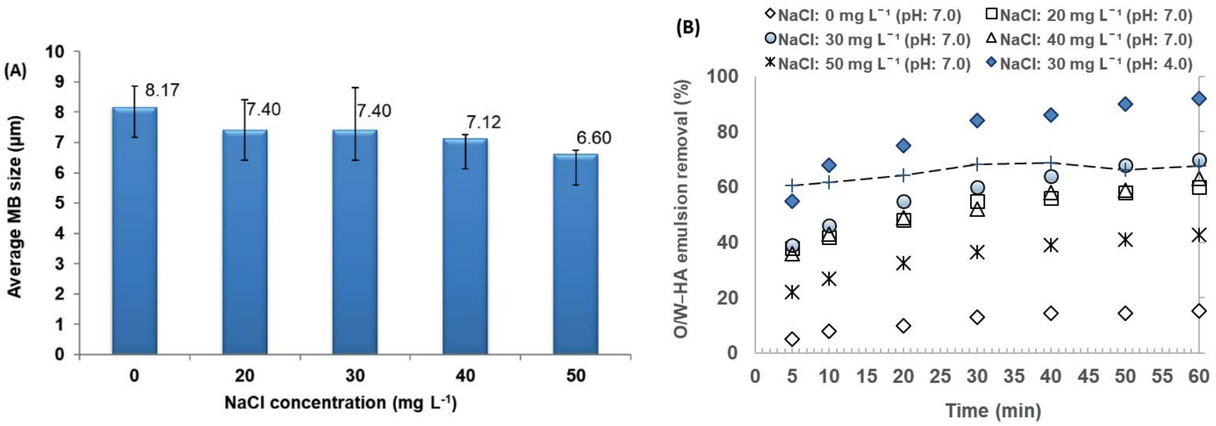

Fig. 6. (A) Effect of NaCl concentrations (0–50 mg·L⁻¹) on microbubbles (MBs) at pH 7.0, airflow rate: 1.0 L·min⁻¹, MB generator time: 10 min, and pressure: 0.45 MPa in warm water (40°C ± 1°C). (B) Effect of NaCl concentration on removal efficiency in oil-in-water emulsions stabilized by humic acid. Oil: 503 ± 2 mg·L⁻¹; temperature: 38.0°C ± 0.5°C; and airflow rate: 2.0 L·min⁻¹.

(<30 min) MB treatment of acidic oily wastewater containing NOM, which may improve the land use efficiency for oil companies.

3.5. Effect of sodium chloride on MB size and O/W-HA emulsion treatment

Sodium chloride is a very popular chemical compound and mineral supplement in animal and human food. In practice, sodium salts are commonly found in oily wastewater effluents (e.g., petroleum waste) [23], crude oil in saline water [18], soybean oil refining processes [24], and brackish seafood processing wastewater. In this study, the addition of NaCl (0–50 mg·L⁻¹) significantly increased the efficiency of O/W-HA emulsion treatment at pH 7.0 and 4.0. The fine O/W-HA emulsion was successfully separated by >90% within 60 min of treatment at pH 4.0 with 30 mg·L⁻¹ NaCl and >60% after 30 min at pH 7.0 (Fig. 6B). Theoretically, salt addition improves the effectiveness of MB treatment by modifying the surface charge of MBs and oil [25] and improving the ionic interaction between bubble–bubble and bubble–particle [19]. In this study, at a typical flotation pressure (0.45 MPa), adding a low concentration of NaCl resulted in a decrease in MB size and increase in bubble density in warm water (Fig. 6A). Consequently, the addition of sodium chloride influenced treatment efficiency. However, the addition of higher concentrations of salt (e.g., 50 mg·L⁻¹ NaCl) reduced flotation efficiency. This phenomenon, which occurs because of the collapsed double layers around the MBs and oil droplets, has also been reported in previous studies [4].

In all flotation experiments, the DO concentration was at a higher saturation (>9.0 mg·L⁻¹). Moreover, MBs have a long retention time in water. Therefore, the oil or bubble flocculants could be continuously floated, and the remaining DO could be suitable for subsequent biological treatment (e.g., using an oxidation pond). Therefore, with a high number of very small droplets, MBs could be considered to cause a "white water blanket filtration" effect [19]. MBs can handle high-shock loading of many contaminants in a suspension without fouling or replacement of costly filter materials. The remaining dissolved oil (50–100 mg oil L⁻¹ in the effluent analyzed in this study, treatment efficiency of 80%–90%) would be easier to separate by a practical combination of methods (e.g., with membrane technology, biological treatment, or advanced oxidation processes) to ensure that the maximum oil concentration in the final effluent (5–40 mg·L⁻¹) does not exceed the standards set by most countries [8]. Nevertheless, operating the flotation system at a practical pressure (0.45 MPa) is a limitation of this study, which hinders effective treatment of the remaining dissolved oil and NOM. To enhance the efficiency of MB treatment without increasing the pressure, among the aforementioned suggested potential combinations, the addition of oxidizing agents, such as ozone gas or H_2O_2, to purify the remaining dissolved oil and NOM can be considered. This may continuously increase treatment efficiency without modifying the flotation system.

4. Conclusions

At 4 min of high-speed mixing, soybean oil (500 mg·L⁻¹) and HA (25 mg·L⁻¹) formed an O/W-HA emulsion with fine emulsion droplets (mean diameter, 4.91 µm) and was found to be 2.75 times more stable than O/W emulsions (mean droplet diameter, 6.30 µm) during a 90-min stability testing. Careful analyses of the sizes of MB, O/W-HA emulsion droplets, and emulsified oil-and-MB aggregate droplets, and the distribution of droplet sizes revealed that MB size, pH, temperature, and salt concentrations affected the treatment efficiency of fine O/W-HA emulsions. Oil removal efficiency of 60% to 82% within 30 min and more than 90% after 60 min could be theoretically achieved by applying practical pressure (0.45 MPa, using an F.BT-50 nozzle), adjusting the pH of fine O/W-HA emulsions to a reasonable value (pH ~4.0), adjusting the airflow rate (1.0–2.0 L·min⁻¹), and/or adding a small amount of sodium chloride (20–30 mg·L⁻¹) in a typical oil-in-water concentration (500 mg oil L⁻¹). These results indicate good potential for scale-up application in oil field wastewater treatment (e.g., soybean oil refining effluent or POME or petroleum wastewater). Moreover, because of the absence of harmful de-emulsion chemicals, floated products could be reduced and reused for various purposes.

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CRediT authorship contribution statement

T.V. Le: Conceptualization, methodology, investigation, formal analysis, writing—original draft, project administration, writing—review and editing. L.T.T. Dang: conceptualization, methodology, investigation, resources, formal analysis, writing—review and editing. H. Yasui: methodology, writing—review and editing. T. Imai: conceptualization, methodology, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

Authors have declared that no competing interests exist.

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