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Application of Nanobubbles in Floating Kinetics Models for Efficient Oil Removal from Produced Water

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Abstract. The primary objective of this study was to gain insight into the kinetics mechanism involved in the removal of oil from produced water using nanobubbles. A small-scale device called Solari - N MBG 0.35, manufactured by Solari Energy Limited, was employed to generate nanobubbles. Batch experiments were conducted to evaluate the impact of varying nanobubble concentrations on oil removal. The results revealed that at initial of contact time led to enhanced oil removal. This improvement was attributed to factors such as increased interfacial energy, improved mixing, and enhanced contact between the nanobubbles and oil droplets. However, after a 30-minute duration, the efficiency of oil removal reached a plateau due to the presence of smaller and more stable residual oil droplets. To analyze the nanobubble flotation process, the study employed five distinct models using experimental data. These models included the first-order model, first-order model with a rectangular distribution, fully mixed factor model, improved gas/solid adsorption model, and second-order model. Statistical analyses were performed, considering parameters such as coefficient of determination (R^2), root mean squared error (RMSE), mean absolute percentage error (MAPE), and mean absolute deviation (MAD). The fully mixed factor model, improved gas/solid adsorption model, and second-order model demonstrated excellent fitting performance at different contact times. These findings deepen our understanding of the oil removal efficiency of nanobubbles, emphasizing the significance of factors like concentration, contact time, and the selection of appropriate kinetic models. The study provides valuable insights into the application of nanobubbles in flotation processes and underscores the importance of selecting suitable models based on specific conditions and particle sizes.

1. Introduction

Nanobubbles have been investigated as a potential method for the removal of oil from produced water. Produced water is a byproduct of oil and gas production that contains significant amounts of oil and other contaminants, making it difficult to dispose of safely. Nanobubbles are extremely small bubbles, typically less than 100 nm in size, which have unique properties compared to larger bubbles [1]. These properties, such as increased stability and longer lifetime, make them potentially useful in oil removal applications. Studies have shown that nanobubbles can effectively remove oil from water, with removal efficiencies up to 99% [2-4]. From the previous study [3], the researchers found that the charged nanobubbles significantly increased the removal of hydrocarbons compared to traditional remediation methods, such as chemical treatment or mechanical stirring. [4] mentioned that the use of micro- and nanobubbles significantly improved the flotation efficiency and oil recovery compared to conventional methods. However, further research is needed to fully understand the kinetics mechanisms by which nanobubbles interact with oil and other contaminants in produced water.

Kinetics models are mathematical expressions that describe the rate at which a reaction occurs. These models are essential in predicting the behaviour of chemical systems, such as the progress of a reaction over time or the effect of changing the reaction conditions. The six kinetics models have been used to simulate the experimental data of conventional and carrier flotation of −74 μm coal fines to show that second-order model with rectangular distribution model was the most effective in predicting flotation behavior with a high degree of accuracy. In addition, the authors noted that the carrier flotation process exhibited different kinetic behavior, adhering to a first-order kinetic model, while conventional flotation followed a second-order model with rectangular distribution model [5]. The performance of different coal size fractions with nanobubbles was studied by [6] revealed that the classical first-order model was the most appropriate for describing the single size fraction, except for −0.045 mm, due to the relatively low correlation coefficients observed for other models.

Many researchers have been comparing floating kinetic model compatibility frequently employs statistical evaluation utilizing the three different statistical criteria i.e. coefficient of determination, R2, and root mean square error, RMSE [7-9]. Despite its wide usage, this technique has limitations in deriving definitive conclusions and assessing overall competency. Thus, this study proposes that incorporating supplementary statistical assessments can enhance the precision of performance evaluation for kinetic models, specifically in the context of nanobubbles application in removing oil from produced water. In order to address the issues outlined above, the present study aims to accomplish the following objectives: (i) assess the efficacy and reliability of different percentage of nanobubbles as a means of capturing oil from produced water in aquatic environments for the facilitating further observation; and (ii) to evaluate the utility of five kinetic models in describing the behavior of removal oil from produced water by using nanobubbles.

2. Materials and Methods

2.1. Nanobubbles Generation

Micron nanobubbles (MNBs) were produced through the utilization of a small-scale Solari - N MBG 0.35 device, manufactured by Solari Energy Limited. The dimensions of the device were measured at H 300 v W280 x D140. The generation process involved a water flowrate of 3 m^3/hr and an air rate of 0.5 m^3/hr. The gas utilized for the generator was sourced from an air inlet. Following a minute of operation, a gas-liquid mixture with a visually opaque appearance, reminiscent of a "milky" composition, was successfully generated.

2.2. Produced Water Sampling and Analytical Analysis

A sample of produced water effluent was collected from the effluent outlet point of one crude oil terminal produced water treatment system located in east Malaysia. The water sample was collected via grab sample method at the existing water sampling point that represented the overall water quality or served as a critical control point. All sampling equipment was prepared byensuring cleanliness and freedom from contaminants, which involved rinsing or using appropriate cleaning agents. An adequate volume of water was collected to meet analysis requirements and ensure reliable results. The sample was handled carefully to maintain its integrity, avoiding agitation that could alter water properties.

Preservation techniques were applied during transport and storage by adding sulphuric acid.

In the determination of oil in water in lab, the analysis was first conducted according to APHA 5520 B followed by using fluorescent technique [10]. APHA 5520 B analysis involves multiple steps. Initially, a solvent (n-hexane) is used to extract the oil and grease from the water, through a specialized apparatus. Once the extraction is complete, the solvent is evaporated, leaving a concentrated residue. This residue is then weighed to determine the mass of oil in the sample. Gravimetric analysis is recommended by the APHA 5520 B method, where the weight of the residue is measured and reported as milligrams per liter (mg/L) or parts per million (ppm) of oil in the original sample. The fluorescent technique was utilized to measure oil concentration in water using the TD500D instrument by Turner Designs. This technique relies on the principle that oil compounds emit fluorescence when exposed to specific wavelengths of light. The TD500 instrument emits ultraviolet light onto the water sample, causing any oil present to fluoresce. The instrument then measures the intensity of the fluorescence, which is directly proportional to the oil concentration in the water. By calibrating the instrument with known oil concentrations, accurate measurements can be obtained. The fluorescent technique offers a rapid and reliable method for quantifying oil in water, making it suitable for various applications such as environmental monitoring and industrial wastewater treatment.

2.3. Batch Experiment of Flotation Kinetics

In the batch experiment, a total of 27 samples were meticulously prepared for analysis. The concentration of the nanobubbles enriched water in the oily produced water was systematically varied across the ranges of 5%, 10%, 15%, and 20%. Each sample consisted of an initial quantity of 200 ml of oily water. The experimental apparatus employed for this purpose entailed the arrangement of a transparent 500 ml separatory funnel, firmly secured on a ring stand. The separatory funnel served as the container for the oily water sample. Precise quantities of the nanobubbles enriched water were collected and introduced into the system using a pipette. A glass beaker was employed to collect the post-treatment sample, which would subsequently undergo rigorous analysis. This analytical approach allowed for meticulous examination and assessment of the effects of varying nanobubbles concentration on the oily produced water. By manipulating the experimental conditions and employing meticulous apparatus, it was possible to derive valuable insights into the impact of nanobubbles enrichment on the treated samples, thus enabling informed analysis and subsequent conclusions.

2.4. Flotation Kinetics Models

Adsorption In flotation kinetics, the magnitude of the K-value of the flotation rate constant represents the recovery of the concentrate product over a given time. However, the modified flotation rate constant (Km = R ∗ K) has been utilized in several studies as an alternative approach for evaluating the overall flotation process under varying conditions [5,11-13]. The flotation rate constant (K) and maximum theoretical recovery (R_{max}) indicators provide effective means for evaluating flotation performance. This section presents a comparison of five different flotation rate models (see Table 1) applied to datasets of oil removal by nanobubbles obtained from batch experiments. Nonlinear regression analysis with Excel Solver was utilized to evaluate the unknown kinetic parameters (R_{max} and K).

Table 1. Flotation Kinetic Equation

Model	Equation
First-Order	$R = R_{max}\ (1 - e^{-k_1 t})$
First-order with a rectangular distribution	$R = R_{max}\left[1 - \frac{1 - e^{-k_2 t}}{k_2 t}\right]$
Fully mixed factor model	$R = R_{max}\left[1 - \frac{1}{(1 + \frac{t}{k_3})}\right]$
Improved gas/solid adsorption model	$R = \frac{R_{max} k_4 t}{1 + k_4 t}$
Second-order	$R = \frac{{R_{max}}^2 k_5 t}{1 + R_{max} k_5 t}$

2.5. Statistical Analysis

There was a wide range of statistical analyses used to evaluate the performance of all models, including R^2 coefficient, root mean squared error (RMSE), percentage of error in maximum estimated value (Emax), percentage of error in minimum estimated value (Emin), percentage of error in mean absolute percentage error (MAPE), and mean absolute deviation (MAD) as listed in Table 2. Based on the smallest arithmetic mean rank, the best model was selected. All kinetic models have significance tests for statistical analysis. Accordingly, the most often used and easily understood central tendency measure, the arithmetic mean, is used to pick a possible model and to compare different models as a function of the model's word count. Finally, the minimal average ranking value (ARV) was used to identify the optimum model order.

Table 2. Statistical Analysis Equation

Model	Equation
Coefficient of determination	$R^2 = \frac{1-\sqrt{\sum(X_{0,i}-X_{m,i})^2}}{\sum(X_{0,i}-X_0^-}$
RMSE	$RMSE = \frac{\sqrt{\sum_{i=1}^{n}(X_{0,I}-X_{M,I})^2}}{n}$
Emax	$E_{max} = \frac{X_{maxm}-X_{maxmo}}{X_{maxmo}} * 100$
Emin	$E_{min} = \frac{X_{minm}-X_{mino}}{X_{mino}} * 100$
MAPE	MAPE = $(\frac{1}{n}\sum\frac{X_{0.i}-X_{m,i}}{X_{o,i}}) * 100$
MAD	MAD = $\frac{1}{n}\sum(X_{o,i}-X_{m,i})$

3. Results and discussions

3.1. Efficiency of nanobubble in oil removal

In Figure 2, the recovery patterns obtained from batch experiments involving varying concentrations of nanobubbles are depicted. The graphs indicate that it took approximately 3 minutes for half of the oil to be recovered for concentrations of 5%, 10%, 15%, and 20% of nanobubbles. The figure also shows that when the concentration of nanobubbles was increased from 5% to 20%, the removal of oil by nanobubbles increased from 67% to 72%, after a contact time of 5 minutes. Earlier studies have shown that the high surface area-to-volume ratio of nanobubbles generated in a water-oil mixture produces a strong interfacial energy, which creates a strong attractive force between the nanobubbles and oil droplets, causing the oil droplets to adsorb onto the nanobubbles quickly [14]. The small size of nanobubbles results in Brownian motion, which boosts the mixing and contact between the nanobubbles and oil droplets, leading to a faster rate of oil removal in the initial stage of the process [15]. As the contact time increased from 10 to 25 minutes, the removal of oil increased gradually for all nanobubble concentrations. However, after 30 minutes of contact time, the removal efficiency levelled off due to the smaller and more stable remaining oil droplets, which made it more difficult for nanobubbles to adsorb them, resulting in a decreasing rate of oil removal [16-18].

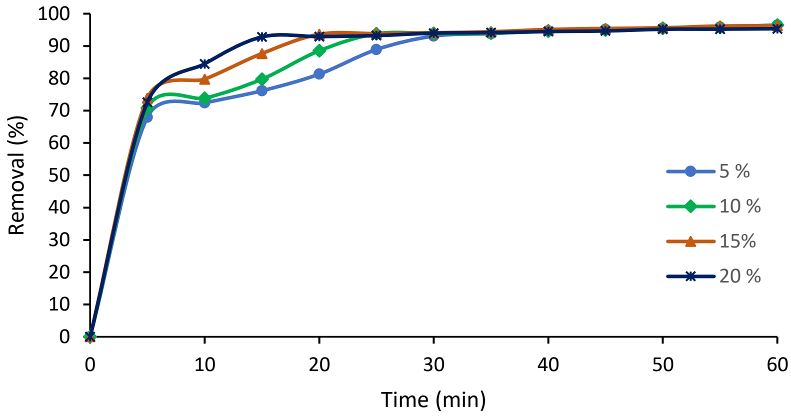

Figure. 1. Removal of oil as a function of flotation time in different percentages of nanobubbles.

3.2. Floating Kinetics Analysis

In this study, five adsorption kinetic models were used: first-order, first-order with a rectangular distribution, fully mixed factor model, improved gas/solid adsorption model and second-order. The calculated parameters of the model are tabulated in Table 3. It is noted that the models, including the fully mixed factor model, the improved gas/solid adsorption model and the second-order model share the same fitting performance for each time-recovery profile.

Table 3. Parameter equation values for the oil flotation kinetic models

Kinetics Models	Parameter	Value
Pseudo-first order	R∞	92.3
	k_1	0.1881
First-order with a rectangular distribution	R∞	97.9
	K_2	0.4721
Fully mixed factor model	R∞	100
	K_3	3.2403
Improved gas/solid adsorption model	R∞	100
	K_4	0.3086
Second-order	R∞	100
	K_5	0.0031

Figure 2 shows the experimental data and model curve fitting. Graphical evaluation and analysis have identified that all of kinetics models fit well at contact time less than 5 minutes and between 30 minute and 60 minutes. At contact time between 10 to 25 minutes, the varies of modelling curves were shown as figure 5. Fully mixed factor, improved gas/solid adsorption and second-order models satisfactorily predicts the experimental data between 10 to 25 minutes of contact time. On the contrary, the first-order and first-order with a rectangular distribution does models are not fit well for contact time between 10 to 25 minutes.

Table 4 and 5 were listed the values of every statistical analysis method for the removal of oil by nanobubbles. A very good agreement between the model equation and experimental curves is obtained, which is verified by the lowest value of ARV in Table 4. The ARV range was used to rank the well-fit testing of kinetics models to experimental data as follows ARV ≤ 1.8; 1.9 ≤ ARV ≤2.6; 2.7 ≤ ARV ≤

3.4; and 3.5 ≤ ARV ≤ 4.2; and ARV≥ 4.2 represent very good, good, satisfactory, poor, and very poor kinetics flotation performance of nanobubbles, respectively (see Table 5).

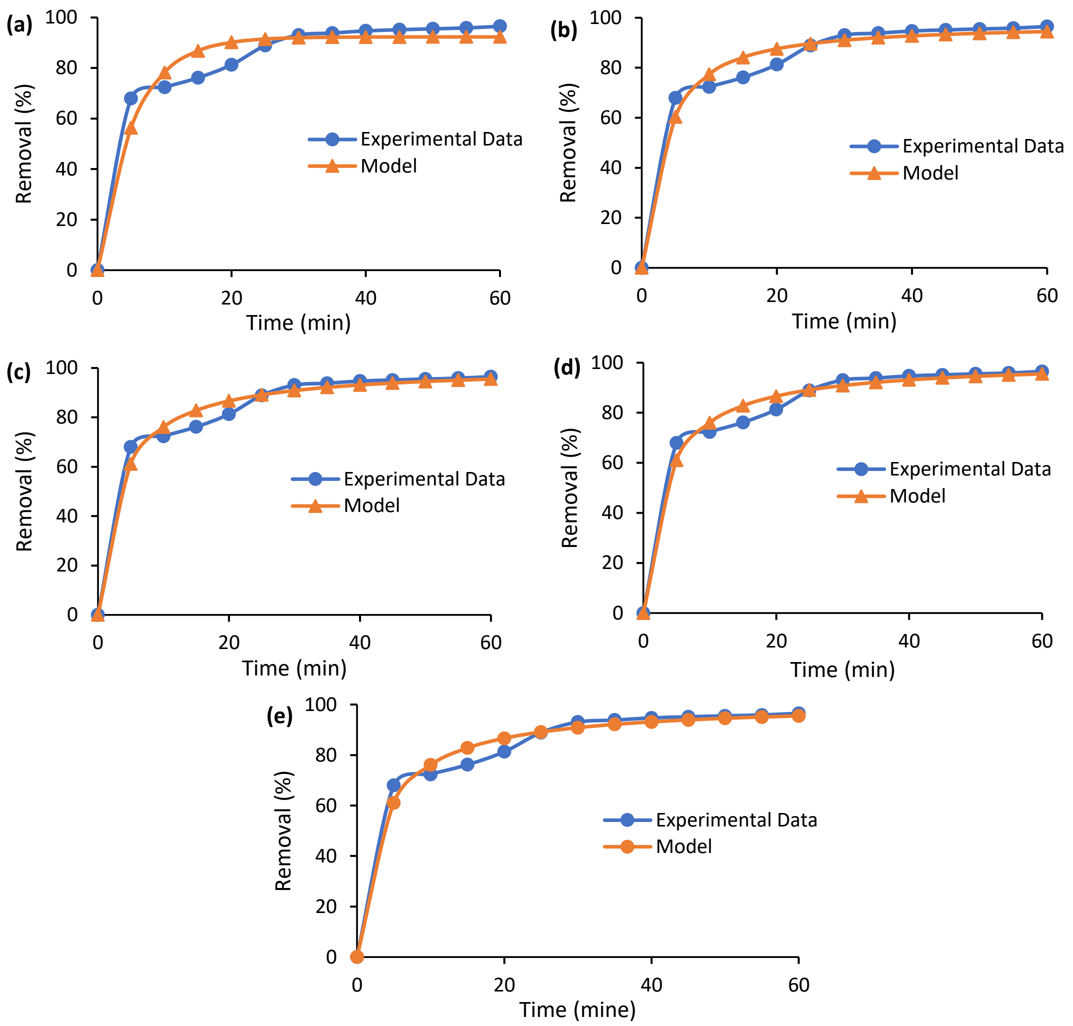

Figure. 2. Comparison of (a) 1st order; (b) 1st order with rectangular distribution; (c) fully mixed factor; (d) gas adsorption; and (e) 2nd order kinetic models fitted to the experimental data

Table 4. Values of the statistical analysis for the flotation kinetic models

Statistical Model	1st Order	1st Order with Rectangular Distribution	Fully Mixed Factor Model	Gas Adsorption Model	2nd Order
R^2	0.6770	0.8320	0.8760	0.8760	0.8760
MAD	4.8950	3.3910	2.6897	2.6897	2.6895
RMSE	5.9830	4.1960	3.5127	3.5127	3.5127
MAPE (%)	6.0940	6.0942	3.4004	3.4002	3.4002
Emin	4.3590	2.0965	1.0380	1.0380	1.0374
Emax	17.2310	11.1980	10.1516	10.1515	10.1555

Table 5. Average ranking values of the statistical analysis for the flotation kinetic models

Statistical Model	1st Order	1st Order with Rectangular Distribution	Fully mixed factor model	Gas Adsorption Model	2nd Order
R^2	5	4	1	1	1
MAD	5	4	2	2	1
RMSE	5	4	1	1	1
MAPE (%)	4	5	1	1	1
Emin	5	4	2	2	1
Emax	5	4	2	1	3
ARV	4.8	4.2	1.5	1.3	1.3

Table 5 listed the result of ARV being obtained from each analysis of the statistical method for removal of oil from produced water by using concentration of 5% nanobubble. The results have been verified with the lower value of AVR in statistical analysis showed that gas adsorption, 2nd order and fully mixed factor models giving a very good level of fit to experimental data with ARV value of 1.3, 1.3 and 1.5, respectively. ARV values of 4.2 for 1st order with rectangular distribution models were verified indicating that a poor fit to the experimental data. The model data from the 1st order model can be considered very poor because of the ARV value more than 4.2. Etchepare et al. [19] reported that the first-order flotation kinetics model provided a better fit for the experimental data compared to the García-Zuñiga kinetic model of flotation for the separation of emulsified crude oil in saline water using microbubbles and nanobubbles. Conversely, Xiangning et al. [5] reported that the second-order model with a rectangular distribution was the optimal fit for the experimental data of conventional flotation and carrier flotation of -74 µm coal fines. Hence, it is plausible that the choice of the appropriate model for describing flotation kinetics may be influenced by the particle size and flotation technology used.

4. Conclusion

A total of six statistical analysis methods were employed to assess the suitability of five kinetics models for describing the removal of oil using nanobubbles. The findings demonstrate that the flotation kinetics of oil by nanobubbles exhibit a stronger alignment with gas adsorption models and 2nd order kinetics. This conclusion underscores the pivotal role of particle-bubble collisions and attachments in governing the flotation process. According to this mechanism, the rate of particle removal is directly proportional to the square of the particle concentration, indicating that the probability of two particles colliding is directly proportional to their concentration. The verification of the five kinetics models using experimental data establishes their validity and reliability, thereby contributing significantly to the understanding of oil flotation kinetics studies involving nanobubbles.

5. References

[1] Jin N, Zhang F, Cui Y, Sun L, Gao H, Pu Z and Yang W 2022 Environment-friendly surface cleaning using micro-nano bubbles. *Particuology* **66** 1-9

[2] Liu C, and Tang Y 2019 Application research of micro and nano bubbles in water pollution control *E3S Web of Conferences*

[3] Oliveira H A, Azevedo A C, Etchepare R and Rubio J 2017 Separation of emulsified crude oil in saline water by flotation with micro-and nanobubbles generated by a multiphase pump *Water Sci. Technol.* **76** 2710-2718

[4] Bui T T, Nguyen C D, Shim N, and Han M 2022 Total petroleum hydrocarbon removal from oil-sand by injecting charged nanobubbles *Environ. Nanotechnol. Monit. Manag.* **17** 100653

[5] Bu X, Wang X, Zhou S, Li B, Zhan H and Xie G 2020 Discrimination of six flotation kinetic models used in the conventional flotation and carrier flotation of− 74 µm coal fines *ACS Omega*, **5** 13813-13821
[6] Han H, Liu A, Wang C, Yang R, Li S and Wang H 2022 Flotation kinetics performance of different coal size fractions with nanobubbles *Int. J. Miner. Metall. Mater.* **29** 1502-1510
[7] Fulazzaky M A, Salim N A A, Khamidun M H, Puteh M H, Yusoff A R M, Abdullah N H and Zaini M A A 2021 The mechanisms and kinetics of phosphate adsorption onto iron-coated waste mussel shell observed from hydrodynamic column *Int. J. Environ. Sci. Technol.* **19** 1-14
[8] Salim N A A, Fulazzaky M A, Puteh M H, Khamidun M H, Yusoff A R M, Abdullah N H and Zaini M A A 2022 Mass Transfer Kinetics and Mechanisms of Phosphate Adsorbed on Waste Mussel Shell *Water, Air, Soil Pollut.* **233** 223
[9] Guo Y, Hong Nhung N T, Dai X, He C, Wang Y, Wei Y and Fujita T 2022 Strontium ion removal from artificial seawater using a combination of adsorption with biochar and precipitation by blowing CO_2 nanobubble with neutralization *Front. Bioeng. Biotechnol.* **10** 106
[10] American Public Health Association (APHA) 2017 *Standard Methods for the Examination of Water and Wastewater* 23rd edition (Washington DC, USA: American Public Health Association,)
[11] Polat M and Polat H 2023 A phenomenological kinetic flotation model: Distinct Time-Variant floatability distributions for the pulp and froth materials. *Miner. Eng.* **201** 108217
[12] Palazuelos L P.Á, Guerrero M U F, Labra M P, Domínguez I A R, García R E, Cardona F P, ... and Pérez M R 2023 Silver (I) Recovery by Ion Flotation Process from Aqueous Solutions in Cells with Spargers *Miner.* **13** 572
[13] Ab Aziz, N A H, Ali U F M, Ahmad A A, Dzahir M I H M, Khamidun M H, and Abdullah M F 2023 Non-functionalized oil palm waste-derived reduced graphene oxide for methylene blue removal: Isotherm, kinetics, thermodynamics, and mass transfer mechanism *Arab. J. Chem.* **16** 104387
[14] Zhou Y, Albijanic B, Tadesse B, Wang Y, Yang J, Li G and Zhu X 2019 Surface hydrophobicity of sub-bituminous and meta-bituminous coal and their flotation kinetics *Fuel* **242** 416-424
[15] Wu J, Zhang K, Cen C, Wu X, Mao R and Zheng Y 2021 Role of bulk nanobubbles in removing organic pollutants in wastewater treatment *AMB Express* **11** 1-13
[16] Eklund F, Alheshibri M, and Swenson J 2021 Differentiating bulk nanobubbles from nanodroplets and nanoparticles *Curr. Opin. Colloid Interface Sci.* **53** 101427
[17] Ma X, Li M, Pfeiffer P, Eisener J, Ohl C D and Sun C 2022 Ion adsorption stabilizes bulk nanobubbles *J. Colloid Interface Sci.* **606** 1380-1394
[18] Shen W, Mukherjee D, Koirala N, Hu G, Lee K, Zhao M and Li J 2022 Microbubble and nanobubble-based gas flotation for oily wastewater treatment: a review. *Environ. Rev.* **30** 359-379
[19] Etchepare R, Oliveira H, Azevedo A and Rubio J 2017 Separation of emulsified crude oil in saline water by dissolved air flotation with micro and nanobubbles *Sep. Purif. Technol.* **186** 326-332

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