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# Application of Ultra Fine Bubbles for Deoxygenation of Produced Water and Tap Water via Nitrogen Purging Scheme

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**Abstract:** In this study, we present our findings from examining a gas lift tower for produced and tap water de-oxygenation, applying the nitrogen purging at an ultra-fine bubble scale (18 µm average size). The experiments were conducted for produced water samples grafted with polyacrylamide concentration 300 ppm with a measured bulk viscosity of 5 mPa.s. Upon applying a series of experimental sets, 0 ppm DO was attained in all examined operational schemes (semi batch and once through) within various time limits, depending on the water level in the column. Considering the zero DO level as an objective function, the results showed an improvement of 5.7–14 folds in reaching the 0 ppm DO upon experimenting with the ultra-fine bubble purging in different schemes, compared with of the results obtained from the ordinary bubble size (mm scale). The results show that DO reached <10 ppb within 23 minutes with nitrogen flowrate 3 L/min while DO reaching <10 ppb within 28 minutes with nitrogen flowrate 5 L/min. Furthermore, implementing the ultra-fine bubble nitrogen purging was successful in running the de-oxygenation tower in a full continuous mode at a balanced inlet/outlet water flow rate. This has been done after reaching stability in the column operation (lasting around 1 hour for 422 L of examined water sample). The stable fine bubbles cloud in the column was quite efficient in treating water influent stream to be exited directly at 0 ppm DO within the same effluent flow rate. The treatment efficiency has shown an increase with increasing water level in the column, resulting in a denser layer/cloud of fine bubbles. This result suggests a unique approach/solution for the complete removal of DO from produced water, which is accounted effective to be adopted industrially

**Key words:** Produced water treatment, dissolved oxygen, $N_2$ purging, ultra-fine bubbles.

## Introduction

Application of bubbles functions significantly in chemical, petrochemical, food and other industries, in terms of reaction and separation paths. The mixing, heat and mass transfer processes occurring in a multiphase medium are highly dependent on the movement of the bubbles, leading to vital changes in yield/efficiency (Rajeev and Subrata, 1981). Attaining higher efficiency transfer processes in a multiphase system is dependent on the availability of higher interfacial area, which could be introduced through seeding fine bubbles (micro scale and less) in the medium (Lopez et al., 2013). Subject to the application category, fine bubbles are classified

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as micro and nano. Microbubbles are known to be less than 40 microns in diameter while nano-bubbles are ranged below 200 nm (Sakr et al., 2022; Tsuge, 2014). These fine bubbles provide a high surface area per unit volume compared with conventional bubbles; hence, it leads to significant improvement in diffusion and transport processes (Wang et al., 2020). Moreover, fine bubbles are featured with their shrinking characteristics, resulting in higher diffusion of gas in the liquid surrounding (Bredwell, 1998). As a consequence, bubble size becomes smaller, the rising velocity becomes slower, the surface area becomes larger, and accordingly, the chances of adhesion to suspended particles become higher (Sillanapa and Shestakova, 2017). In other words, as long as the bubble becomes smaller, the interior gas pressure increases because it is inversely proportional to the size of the bubble. Higher internal pressure leads to a faster diffusion of entrapped gases. Thus, the bubbles shrink further and ultimately collapse. As a consequence, higher mass transfer efficiency is expected in very small bubbles (Li et al., 2013, 2014). Another important feature of the fine bubbles is the the adhesion to suspended particles. This is attributed to the high zeta potential for the fine bubbles in addition to other factors such as large specific surface area and longer contact time between the bubble and suspended matter, which suggests the use of fine bubbles for separation processes (e.g., micro flotation) (Liu and Tang, 2019).

Studies demonstrated that microbubble dispersions in aqueous solutions can be long-lived. For instance, 20-micron size bubbles take on the order of a day to rise one meter whilst coarse bubbles (millimeter scale) rise 3 orders of magnitude faster than fine bubbles (micro to nano scale), taking tens of meters of liquid column height to achieve similar thermal, mass, and chemical equilibrium (Kim et al., 2019). This fact protrudes the need for investigating the application of fine bubbles in any gas/liquid contact process to evaluate the improvement gained in efficiency. In our previous study (Al-Dawery et al., 2022), we investigated the de-oxygenation of tap water produced water (PW) via a nitrogen purging scheme in a gas lift tower, applying coarse bubbles (≈ 3 mm as an average diameter). Our results demonstrated success in removing the dissolved oxygen (DO), within a few minutes of nitrogen purging, from the saturation level (≈ 6 ppm) up to a certain limit, however, less than 0.5 ppm could not be removed even when applying various contact schemes and extending the purging time up to 300 minutes. The obtained results raise the necessity to investigate the produced water de-oxygenation through an ultra-fine bubble nitrogen purging scheme and evaluate the efficiency towards proposing a unique approach to be adopted on an industrial scale.

Large quantities of wastewater are produced with oil production reaching 80-95% (Azetsu-Scott et al., 2007; Kaur et al., 2009; Ebenzer et al., 2014). Around 300 million barrels of produced water were produced per day from oilfields (Larson, 2019) from which 40% is discharged into the environment (Ebenzer et al., 2014; Fakhru'l et al., 2009; Larson, 2019). PW is considered as highly salty formation water (TDS = 5000 to 250,000 mg/L); low TSS concentration and not heavily emulsified oil in water. In commensuration with global efforts towards preserving water resources, there is a big demand to re-use the produced water, especially for oilfields located in water-scarce regions. However, the major challenge to the reuse of PW is the high content of dissolved oxygen (DO). DO is considered a corrosive agent that converts $H_2S$ or FeS into S compounds (Skovhus et al., 2017); in addition, DO promotes microbiological growth in the reservoirs which is undesirable for effective oil recovery processes. Both chemicals as oxygen scavenging agents (e.g. sodium sulphite and ammonium sulphite) and physical treatments were applied for the removal of DO (Ian et al., 1994; Mohammad et al., 2019; Snaveely, 1971). Nonetheless, these methods come with shortcomings such as water contamination, high capital and operating costs, low production rate, and may be low efficiency. Therefore, the physical method was used, which indicated that $N_2$ purging is the most effective and practical technique for the de-oxygenation of deionised water (Liu and Tang, 2019).

## Materials and Methods

The schematic diagram of the system is illustrated in Figure 1, which is based on the gas lift tower used in our previous work (Al-Dawery et al., 2022). However, the work in the current study was dedicated to examine the ultra-fine bubbles gasification tower rig (pilot scale), illustrated in Figure 2.

The rig shown in Figure 2 is custom designed/manufactured to examine different experimental approaches (i.e., semi-batch and once-through counter-current gas/liquid flows). The degassing tower, made of food-grade stainless steel, is of 1.08 $m^3$ liquid capacity (0.6 m × 0.6 m × 3.0 m) provided with 2 rectangular sight glasses (made of polycarbonate) at two levels of the column. Those are intended to monitor the bubble cloud generated in the column, and hence, control the

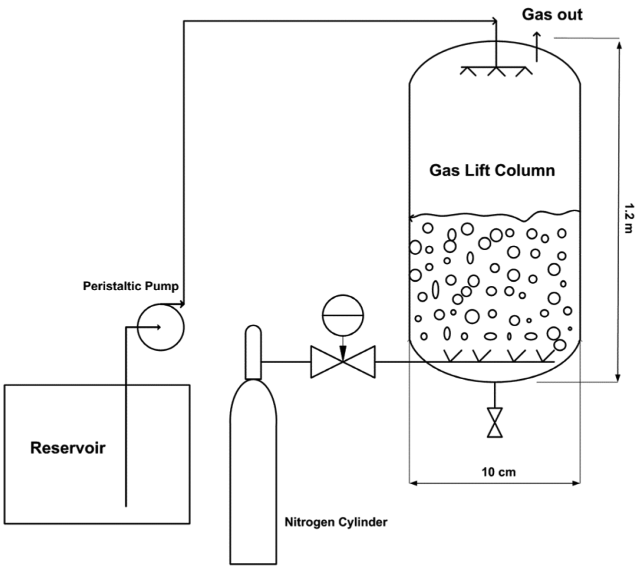


**Figure 1: Schematic diagram for the cylindrical gas lift column.**

**Figure 2: Pilot scale (1.08 $m^3$ liquid volume) gasification tower equipped with an ultra-fine bubble's pump.**

bubble size, respectively. The tower is equipped with an ultra-fine bubble pump which can produce a minimum of 850 nm, an average of 18 μm bubble size at a density of 1600000 bubbles/1 $cm^3$. The bubble size can be adjusted manually by changing the valve opening on the suction and discharge lines, respectively. Several online sensors were provided to monitor the dissolved oxygen, pH, conductivity, and temperature throughout the experimentation period. The rig operation is controlled through an electrical board in which all switches for the running items as well as the digital screens of the sensors are affixed.

## Results and Discussion

The experiments were conducted at first, examining tap water to set the operational parameter of the de-oxygenation tower. The tower was fed with different quantities of water, approaching various water levels. The nitrogen gas was injected into the bubble generation pump at several flow rates and hence entered the system at a fine bubble scale. Two types of tests were conducted to evaluate the system performance (semi-batch and once-through) compared with schemes previously adopted (Al-Dawery et al., 2022). It's worth mentioning that all operational scenarios investigated in the current study were successful in reaching 0 ppm dissolved oxygen, subject to the nitrogen purging duration and the capacity of the examined produced water (PW) sample. Hence, the time spent to reach 0 ppm DO level is adopted as an objective function to compare the results of different approaches.

### Semi Batch Approach

In the semi-batch approach, the tower was fed with 105 L of tap water and nitrogen purging at 3 L/min was implemented at a fine bubble scale. Figure 3 illustrates the time required to reach 0 ppm level upon applying fresh tap water and re-used tap water (re-saturated with oxygen). The oxygen content in both before nitrogen purging was measured to be around 6

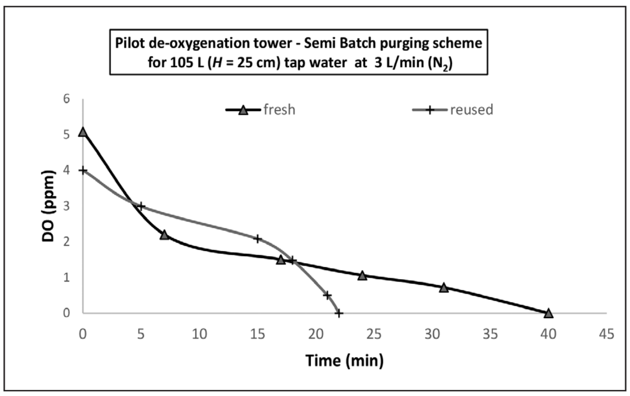


**Figure 3: Comparison between de-oxygenation of fresh and re-used tap water.**

ppm. However, the re-used tap water was faster towards reaching 0 ppm compared with that of fresh water. This could be attributed to a partial oxygen saturation level accomplished, by applying the oxygen stream fed from the generator.

In order to compare the results of the pilot scale de-oxygenation tower examined in this study with the ordinary degassing tower previously used (Al-Dawery et al., 2022), the ratio (time to reach 0 ppm DO per volume of water in the column) (*t*/*v*) was adopted, as presented in Figure 4. It is noteworthy that the size of the bubbles used in our previous study was 3 mm.

The results of various semi-batch schemes indicate that the application of ultra-fine bubbles nitrogen purging has enhanced the efficiency by 9 folds and 6 folds compared with small bubbles, via an ordinary de-oxygenation tower, of no packing and 20 cm packing layer, respectively. The improved performance of the ultra-fine bubble – semi-batch scheme is attributed to the enhanced diffusion rate of the dissolved oxygen which depends on the mass transfer area of gas–liquid phases, accounted higher for fine bubbles, and accordingly can cause the gas dissolution rate in water to reach the supersaturated state (Zhang et al., 2020). This has been confirmed by calculating the number of transfer units (NTU) achieved upon applying intermediate bubbles (< 3 mm) and small (fine) bubbles models, respectively.

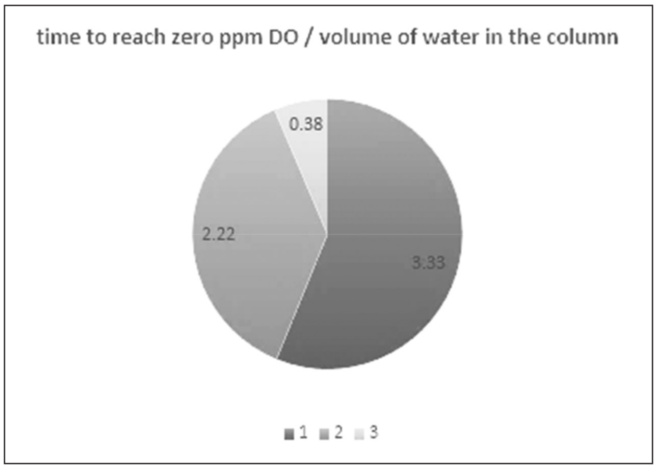


**Figure 4: Comparison between *t/v* ratio measured for various semi batch contact schemes at 3 L/min nitrogen purge rate: 1. (dark gray = 3.33) ordinary column with no packing (9 min/2.7 L), applying small bubbles (Al-Dawery et al., 2022) 2. (pale gray = 2.22) ordinary column with 20 cm packing layer (6 min/2.7 L), applying small bubbles (Al-Dawery et al., 2022) 3. (whitish gray = 0.38) pilot scale column (40 min/105 L), applying ultra-fine bubbles (current study)**

The comparison is shown in Figures 5 and 6, which illustrates the huge difference between the attained NTU between the two cases. It's worth mentioning that the number of transfer units (NTU) required is a measure of the difficulty of the separation. A single transfer unit gives the change of composition of one of the phases equal to the average driving force producing the change (Wauguier, 2000). The NTU is similar to the number of theoretical trays required for the tray column (i.e., a larger number of transfer units will be required for a very high-purity product). Hence, higher NTU achieved

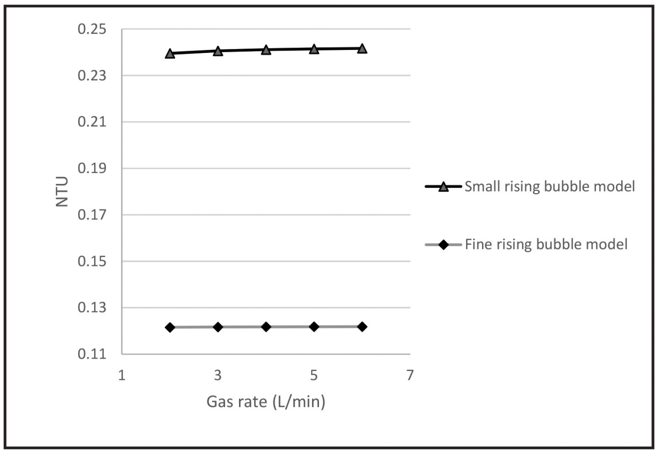


**Figure 5: NTU calculated upon applying different gas throughputs (constant liquid rate) in a semi batch mode using rise velocity in the distorted-inertial regime for small rising bubble (Mendelson model) and terminal velocity of slowly moving spherical bubble for fine rising bubble (Hadamard and Rybczynski model).**

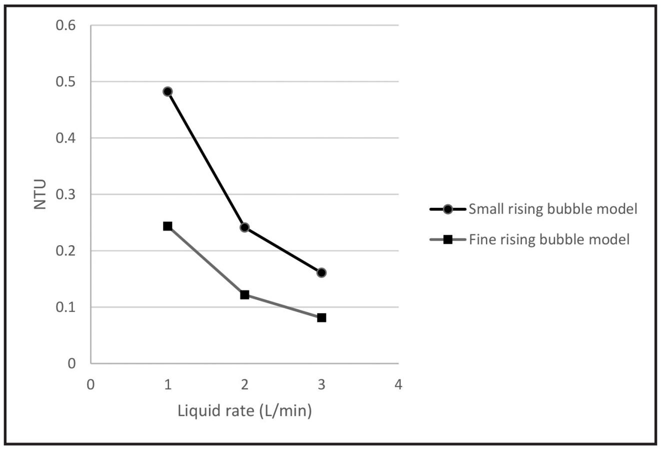


**Figure 6: NTU calculated upon applying different liquid throughputs (constant gas rate) in a once through counter current mode using rise velocity in the distorted-inertial regime for small rising bubble (Mendelson model) and terminal velocity of slowly moving spherical bubble for fine rising bubble (Hadamard and Rybczynski model).**

when using a small bubble size (Al-Dawery et al., 2022) indicates a more complicated oxygen removal process. On the contrary, the use of ultra-fine bubbles (current study) results in a higher transfer coefficient ($k_L = D_{AB}/\sigma$) as a result of depleting the resistance promoted by the liquid layer thickness (σ) due to fine bubble cloud presence in the water bulk, illustrated in Figure 7. This suggests that the ultra-fine bubbles cloud play the role of the resistance scavenger in the gas-liquid interface, leading to a simplified diffusion mechanism compared with the application of small bubble for purging.

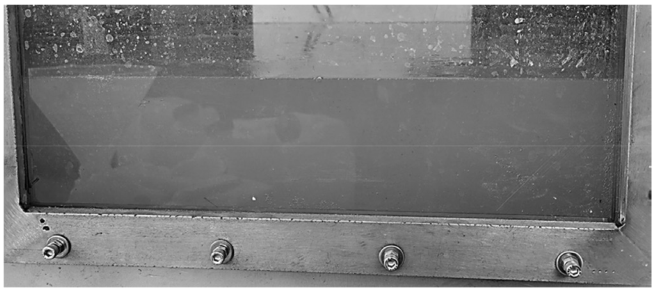

**Figure 7: Ultra-fine bubble cloud formed in the pilot scale de-oxygenation tower.**

The number transfer units (NTU) was calculated according to equation 1 (Dumont, 2019).

$$\mathrm{NTU} = \frac{K_L a}{U_G}\left(\frac{\mu^2}{\rho^2 g}\right)^{1/3} \quad (1)$$

where $K_L$: gas mass transfer coefficient; $a$: interfacial area; $U_G$: bubble rising velocity; μ: gas viscosity; ρ: gas density; $g$: gravitational acceleration

It's worth mentioning that the rising velocity for the small bubble regime described by the Mendelson model (Maneri et al., 2003) has induced the surface tension as a dominant parameter affecting the movement of the gas in the interfacial liquid phase. Nevertheless, the rising velocity for fine bubbles described by the Hadamard and Rybczynski model (Clift et al., 2005) has taken no account of the surface tension role in the interphase region. This suggests that as bubbles become smaller, the interface resistance becomes lower leading to a higher mass transfer coefficient approaching infinity, and ultimately higher mass transfer rate of the dissolved gas away from the liquid bubble.

**Semi Batch Approach – Application of Various Water Levels**

The results adopting various water levels are shown in Figure 8, in which a significant effect was observed for increasing the water level on reducing the time to reach

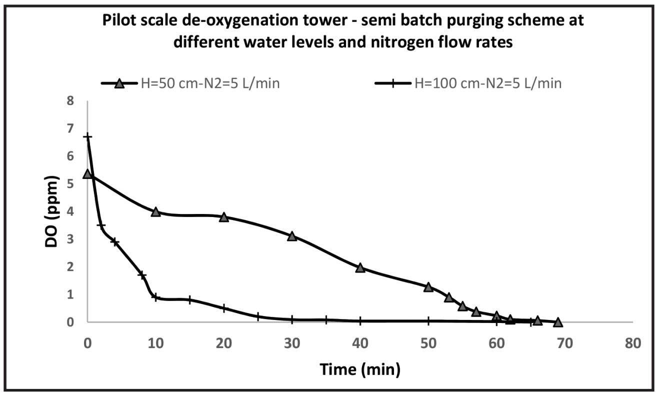


**Figure 8: Operation of the de-oxygenation tower at different water levels.**

zero ppm DO. Figure 8 illustrates the enhancement in reaching 0 ppm DO level with respect to doubling the water level in the tower. In this sense, applying 5 L/min nitrogen purging in the pilot scale tower for 22 L (height of level = 50 cm) litres and 422 L of tap water (height of level = 100 cm) has resulted in (*t/v* ratio) of 0.31 and 0.154, respectively; meaning that increasing the water level in the column was reflected in a positive way on approaching the 0 ppm DO limit. This is attributed to a denser fine bubbles cloud formed in the column with a higher water level, which has induced an integrated effect, resulting in speeding up the stability ultimate level. In terms of comparison with the semi-batch in the ordinary column (small bubble) (Al-Dawery et al., 2022), the enhancement attained via the ultra-fine bubbles purging was 7 folds and 14 folds for 221 and 422 L of water, respectively. The above findings suggest the feasibility of adopting the ultra-fine bubble purging at an industrial scale.

**Once Through Counter Current Approach**

In this test, the tap water was purged by nitrogen by applying the once-through scheme in which water was fed to the column at the beginning up to such a level to be a base point. After getting stability, water was entrained to the column/streamed out of the column at a specific rate, while getting purged by the nitrogen. The results of this test are shown in Figure 9, in which 6 folds enhancement in efficiency was attained using ultra fine bubbles compared with the results of the ordinary column with small bubbles application, reported in our previous study (Al-Dawery et al., 2022).

**Once Through Counter Current Approach – Effect of Applying Disturbance**

The de-oxygenation industrial scale tower was fed with 400 L of tap water and purged with nitrogen (at

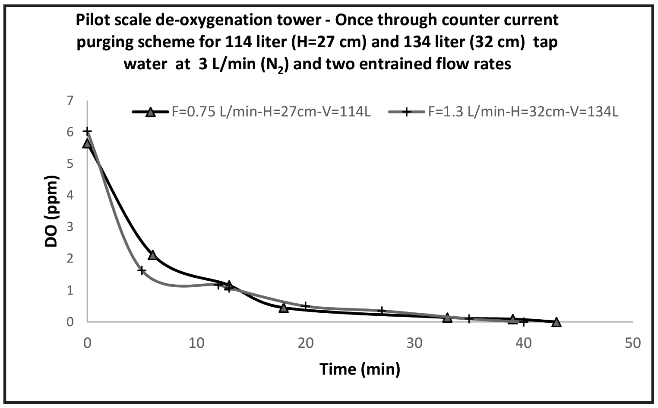


**Figure 9: Attainment of 0 ppm DO level when applying once through counter current scheme.**

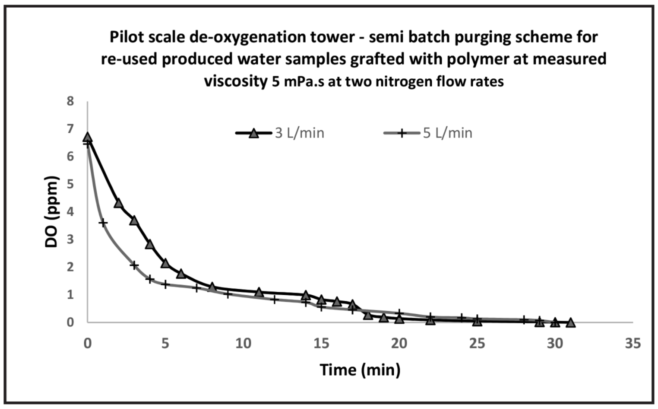


**Figure 10: DO reduction towards 0 ppm upon applying PWP grafted with polymer.**

7 L/min and 50 psi) forming ultra-fine bubbles cloud. The nitrogen purging was continued for 65 minutes to reduce the DO level from 6.0 to 0.0 ppm. After getting stability and continuing nitrogen purging at the same rate, a water stream was entrained to the side of the column (using a peristaltic pump) and streamed out of the column (by gravity) at the same rate (0.336 L/min). The implemented disturbance resulted in a DO level increase of up to 0.18 ppm within 1 minute of applying the disturbance; however, the DO level returned to zero ppm within 20 minutes. This indicates that whatever disturbance occurs, the system will be back to stability within duration dependent on the applied operational parameters (e.g. nitrogen purging rate). This suggests an operational approach to be adopted for scaling up requirements, in which the operated de-oxygenation tower should be loaded with a design top limit water volume and the system is purged in a semi-batch scale forming the fine bubbles cloud until reaching the zero ppm DO level. After getting stability, the system can be loaded with a continuous water stream to be streamed out at the same rate. Hence, considering these conditions, the pilot scale tower can be operated in a continuous mode which is quite important and demandable.

### Application of Produced Water Grafted with Polymer (PWP) Using Ultra-Fine Bubbles De-oxygenation Tower via Semi batch Approach

The last test adopted in this study was dedicated to examining produced water grafted with polymer with different concentrations of polyelectrolyte (300 ppm) with a measured bulk viscosity of 5 mPa.s. Two nitrogen flow rates were used and the profile for reaching 0 ppm DO is presented in Figure 10. The results show that DO reached <10 ppb within 23 minutes with nitrogen flowrate 3 L/min while DO reaching <10 ppb within 28 minutes with nitrogen flowrate 5 L/min.

Comparing the DO reduction profile for the PWP case with the tap water examined in both semi-batch and once-through schemes indicates that chemicals in the investigated produced water proved useful in lowering the purging duration to 30 minutes when 152 L of PWP was applied. As previously denoted, the reason could be attributed to a reduction of the surface tension due to the chemical's existence in the liquid. Comparing the enhancement in the duration to reach 0 ppm DO, the application of the semi-batch scheme for PWP in the pilot scale ultra-fine bubbles tower has attained a *t/v* ratio equal to 0.22 and improved the efficiency 5.6 folds compared with the ordinary small bubble column (*t/v* ratio = 1.11) (Al-Dawery et al., 2022).

## Conclusions

Examining the customised design pilot scale ultra-fine bubbles de-oxygenation tower for tap water and PWP resulted in a significant enhancement in the nitrogen purging treatment approached 14 folds compared with the samples examined with the ordinary de-oxygenation tower investigated in the previous study (Al-Dawery et al., 2022). The important findings from the study are listed below:

1. Increasing the water level in the column induced a positive impact on approaching the 0 ppm DO limit.
2. Increasing the nitrogen flow rate from 3 to 5 L/min causes a slight enlarging in the bubble size and leads to a longer time to reach DO less than 10 ppb.
3. The implemented disturbance resulted in a slight DO level increase within 1 minute of applying the disturbance; however, the DO level retrieved to 0 ppm within 20 minutes.

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## Conflict of Interest

The authors declare that there is no conflict of interest.

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