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Produced Water Deoxygenation: Investigation of Nitrogen Purging Scheme– Parametric Study – Part1

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HIGHLIGHTS

- De-oxygenating samples of PW collected from Omani oil fields were attempted via a gas lift column
- Co-current and counter-current purging schemes applied via un-packed and packed column
- A considerable reduction in the DO from saturation to less than 1 ppm was detected in 3 minutes
- Examining purging durations up to 300 minutes slightly improved DO removal
- Residues of DO (approaching 0.5 ppm) were left unremoved.

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ABSTRACT

Produced water (PW) is water that comes out of the well with the crude oil during crude oil production. A well-known obstacle hindering the reuse of the produced water in different sectors is the high dissolved oxygen (DO) content as it can cause corrosion and polymer degradation. This study reports the experimental investigations for de-oxygenating samples of PW collected from Omani oil fields via a gas lift unpacked and packed column. Two types of packing (polyethylene rushing rings and spherical glass balls) were used. Upon treating the PW samples grafted with different concentrations of polyacrylamide; 100-500 ppm, through different purging techniques at various N_2 throughputs, a considerable reduction in the content of the dissolved oxygen (from saturation level to less than 1 ppm) was detected in the first duration (3 minutes). Upon examining purging durations up to 300 minutes, the DO removal efficiency was slightly improved; however, residues of DO (approaching 0.5 ppm) were left unremoved, indicating the necessity for elaborating another approach for treating the shallow DO levels.

1. Introduction

Petroleum production has been shown globally as the most important industrial activity in the twenty-first century. Though widespread research endeavors paid towards finding alternative energy resources, it is estimated that world daily petroleum consumption will continuously increase, approaching 106.6 million barrels by 2030 [1]. Petroleum production is associated with large quantities of wastewater of approximately 80% [2] and approaching 95% in aging oilfields [3]. Statistics in 2014 showed that around 300 million barrels of water were produced daily from oil and gas fields [16,17], and more than 40% of this production is discharged into the environment [4, 16]. As reported in the literature, the oil/water volume ratio is commonly set in the range of 1:3 [5]. However, higher water demands are required in some regions depending on the oil reserves and conditions. In Oman, around 900,000 m^3/day of water is produced as an associated co-product of its oil output of 135,000 m^3/day, making the ratio of 9 barrels of water to one barrel of oil [23]. This indicates a huge amount of wasted water that should be treated appropriately for recovery, reuse, and disposal. Produced water (PW) is formed water, always found together with petroleum in reservoirs. It is slightly acidic and sits below the hydrocarbons in porous reservoir media [4]. Constituents accompanying the produced water (PW) could be a kind of organic and/or inorganic; including but not limited to: dissolved oxygen (DO), other dissolved gases, heavy metals, dispersed and dissolved oils, grease,

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waxes, chemical agents (e.g., corrosion inhibitors, scale inhibitors, de-emulsifiers, methanol, glycol, polyelectrolyte), salts, solids, scale products, microorganisms, and possibly radioactive materials [6-8]. The Water Environment Federation [16] classified the PW quality according to the oil/gas production scheme, in which conventional and unconventional schemes exist. Conventional PW is commonly streamlined from traditional oil and gas wells and is known to be highly salty formation water (TDS = 5000 to 250,000 mg/L), low TSS concentration (mostly formed at the surface), and oil in water (not heavily emulsified) is commonly dominating the wastewater.

On the other hand, unconventional produced water [i.e., flow back and produced water from hydraulic fracturing] is highly salty water that contains lots of suspended solids mixed with oily material. Also, the produced water to the surface can be with back-produced polymer traces due to enhanced oil recovery processes in some oil fields. In line with diverse global efforts to preserve water resources and comply with the recent stringent environmental regulations, there is a big demand for reusing the produced water, especially for oil and gas production wells located in water-scarce regions or with limited freshwater resources. This is in conjunction with the high treatment cost for PW discharge, making it beneficial to reuse PW. Treatment-wise, the high content of dissolved oxygen (DO) in the produced water (with or without the presence of polymer along with other contaminants) is accounted as one of the major challenges to the vast reuse of PW. Furthermore, it is worth noting that DO promotes microbiological growth in the reservoirs and impacts material integrity, which is undesirable for effective oil recovery processes. In this respect, certain bacteria produce polysaccharides, resulting in the bacteria adhering to each other and forming lumps, leading to the plugging of the injection wells. In addition, microbial flora can increase the production of CO2, H2S, and organic acids, which further promotes corrosion [14].

Moreover, DO is the most common corrosive agent, converts H_2S or FeS into S compounds, and it is accounted several times more corrosive than carbon dioxide (CO_2) and other corrosive agents [13]. On that basis, either in the oil/gas industry or other applications, oxygen must be removed from the PW (i.e., water must be de-aerated) before sending it through miles of pipelines. This reduces the risk of corrosion and other consequences in those pipelines and other downstream equipment [12]. DO can be removed from the solution by both chemical and physical means. Chemical methods can be extremely effective, in which the addition of titanium (III) citrate was proved useful when experimented with the synthesis of framboidal pyrite [15]. Another chemical method is applied by adding an oxygen scavenging agent (e.g., sodium sulfite and ammonium sulfite) [18]. Nonetheless, most of the mentioned methods have shortcomings, such as low efficiency, water contamination; high capital and operating cost; low production rate; and production volume limitations.

However, in experiments where the addition of a redox poise is undesirable, a physical method must be employed to remove oxygen. These could be done through several techniques: purging with nitrogen, argon, or a similar inert gas; boiling at atmospheric pressure; sonication under vacuum, and boiling under vacuum. All those physical methods were experimented with within a comparative study [19]. The results indicated that the N_2 purging is the most effective and quick technique for de-oxygenation of saturated deionized water. It's also reported that the kinetics of the degassing process depends upon the gas/liquid interface area, indicating that the removal of DO is proved faster when nitrogen is introduced as small bubbles. To the authors' best knowledge, not enough information is reported in the literature for a case of DO removal from PW by applying a degassing mechanism. One limitation known for the physical methods is that complete elimination of oxygen from the solution is not possible by any known physical techniques. Not all oxygen could be removed, and traces are commonly left in the examined bulk. This could be considered a drawback and must be investigated thoroughly before depicting a treatment path. This is so essential for a case of treating PW as it may contain different constituents. Hence, this part of the research examines N_2 purging in a lab-scale rig. This is to measure the performance and elucidate the suitability of the purging technique to the investigated PW.

2. Materials and Methods

A working principle in this part of the research is based on the information extracted from references [15,19], which indicated a unique performance for DO removal from deionized water by applying N_2 purging. Accordingly, it hypothesized that a DO in the liquid bulk of produced water would be removed in the same sequence and should be purged efficiently with N_2. An atmospheric cylindrical lab-scale gas lift column consisting of a glass tube (3 mm thickness, 1.2 m height, 10 cm diameter, fitted with a gas diffuser of 8 cm diameter at an average hole size of around 10 mm) was designed and fabricated in the labs of the University of Nizwa, Figure 1, to examine the above hypothesis. Hence, the dispensed gas bubble size was estimated to be in the coarse-scale range (larger than 3 mm). In terms of process kinetics and process modeling, the purging applied in both semi-batch and counter-current schemes operational mode.

Nitrogen gas, purchased from "Muscat gas co." was supplied through gas cylinders. The gas flow rate was controlled through a gas rotameter (Tucsen/China). Various amounts of produced water supplied from PDO were loaded to the column and purged through nitrogen according to a configured experimental plan, using semi-batch and counter-current operational schemes. In the first instance, an average sample of PW was analyzed using the standard chemical methods, and the oil content was found to be around 20 ppm. Also, several mineral salts were detected in the PW content, such as Sodium, Calcium, Magnesium, Chlorides, Sulphates, and Bicarbonates leading to PW salinity of 188.5 kg/m^3 and total dissolved solids of 189.3 kg/m^3.

For the consistent experiment with semi-batch protocol, all experimental sets were conducted by applying a fixed level of water in the column at room temperature (30 cm height, equivalent to 2400 mL) and purging nitrogen at different flow rates. The experimental sets were designated to test tap water (TW), produced water (PW), and artificial samples prepared from produced water grafted with a polymer (hydrolyzed polyacrylamide) in a range (100-500 ppm); will be referred to as (PWP) throughout this paper. This elucidates the effect of different constituents in the PW examined samples on the DO removal efficiency. For the case of counter-current tests, PWP sample was pumped from liquid reservoir to the top of column using peristaltic pump applying different liquid flow rates.

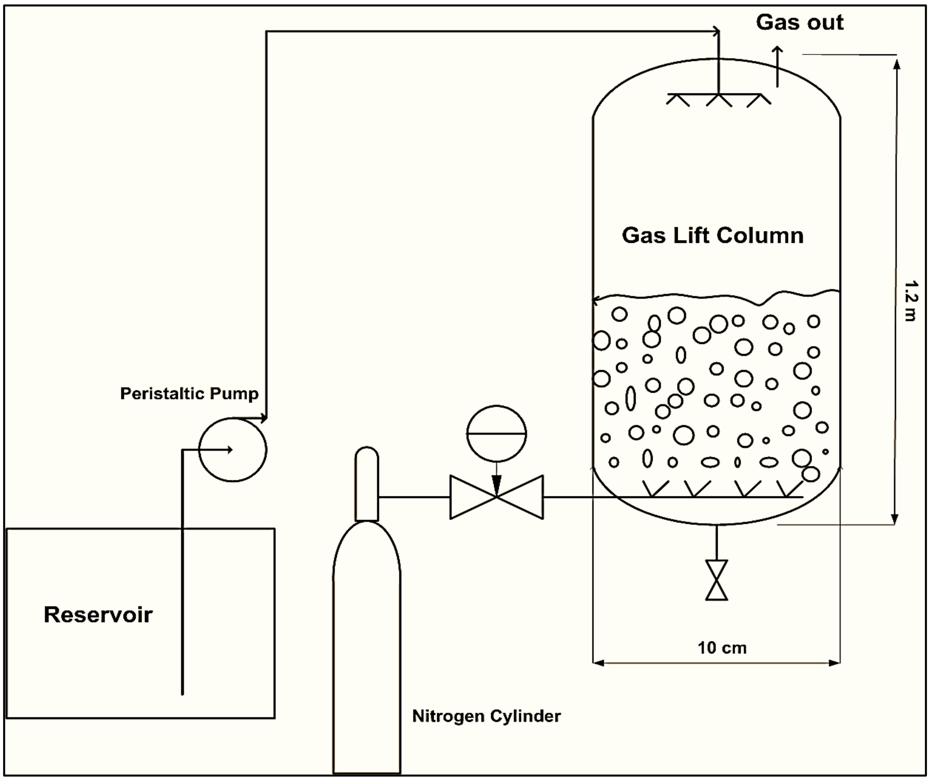


Figure 1: A schematic diagram for the cylindrical gas lift column

The PWP samples were generated by dissolving the polymer powder (hydrolyzed polyacrylamide, received from PDO) in the produced water, applying appropriate agitation (via a magnetic stirrer running at 700 rpm) for 5 hours. After completing dissolution, the prepared PWP samples were left stagnant for more than 12 hours to ensure no separation occurred for the dissolved polyelectrolyte.

The first trials were implemented through an unpacked column, whereas a packed column with 2 types of packing (polyethylene rushing rings, OD = 10 mm, L = 10.7 mm, thickness = 2.3 mm) and spherical glass balls (D = 13.5 mm), distributed randomly in the allocated packed layer) were investigated in the next trials. This is to contemplate the effect of the packing geometry on the removal efficiency. The implemented experiments were designed according to a 2nd-order central composite rotatable design plan [20]. Four variables (nitrogen flow rate, L/min; polymer concentration, ppm; packed layer height, cm; and the nitrogen purging time, min) were depicted in the experimental sets, targeting the measured dissolved oxygen (DO, ppm) as the objective parameter. A polynomial experimental model with considerable accuracy was produced for each examined set for system analysis integrity. During the experiment time, several measurements were taken for the targeted parameter (DO), using both the Winkler chemical method [21] and DO tester (Hanna DO Model OX-2P). According to the standard test procedures, other parameters (pH, conductivity, BOD_5, COD) were also measured/estimated (according to the standard test procedures) at the start and end of every experimental set. To avoid varied DO levels at the start point, all experimental sets in this study were implanted using water samples that reached the DO saturation point. This has been done by subjecting the examined water sample to a compressed air purging (overnight), reaching oxygen saturation level (≈ 6 ppm).

3. Results and Discussion

3.1 DO Measurements

The experimental sets were dedicated to measuring the efficiency of the applied N_2 purging method for reducing DO content in the examined samples. Hence, other parameters which would affect the process were fixed in the current research part for all sets. Throughout the experiment duration, DO was measured using two methods (DO measuring device and Winkler chemical method). However, we observed a considerable difference between the results from the two methods (the DO measure through the device was around 30% higher than the value estimated in the chemical method). In contrast, the working principle of the DO measuring device is based on the oxygen permeated in such a selective membrane and detected due to conductivity increase in a gaseous bulk between two electrodes (cathode and anode). On the other hand, the Winkler chemical method is a multi-stage titration procedure using various chemicals, leading to deviations from the measured values through the DO device. This observation became certain when samples of PW and PWP were experimented with, and the chemical method failed to detect any DO content in the PWP samples. This could be attributed to interactions resulting from the chemical contents of PWP and the chemicals used in the **Winkler** chemical method. Thus, the measured DO values through the chemical method are shown here just to document the conducted procedures in this study. At the same time, the

DO measurements through the device are adopted in all experiments conducted in the current study. Table 1 illustrates a comparison between the DO measured in the abovementioned procedures.

Table 1: Measured DO in the experimented water samples

Purging time, minutes	**Tap water (TW)**		**Produced water (PW)**		**Produced water grafted with polymer (PWP)**				
	DO (ppm)		**DO (ppm)**		**DO (ppm) [Measured through the device]**				
	Device	**Titration**	**Device**	**Titration**	**100ppm**	**200ppm**	**300ppm**	**400ppm**	**500ppm**
0	5.4	5.0	4.87	5.0	4.84	4.04	5.08	4.41	5.01
30	1.1	1.1	N.A.	N.A.	N.A.	2.38	1.38	0.98	1.3
60	1.07	N.A.	0.57	0.6	0.45	1.85	1.06	0.7	1.02
90	1.03	1.1	N.A.	N.A.	N.A.	1.39	0.97	0.8	0.82
120	1.02	0.5	0.43	0.0	0.41	1.11	0.71	0.26	0.72
150	0.85	0.6	N.A.	N.A.	N.A.	0.74	0.61	0.2	0.61
180	N.A.	N.A.	0.41	0.45	0.35	N.A.	N.A.	N.A.	N.A.
210	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
240	N.A.	N.A.	0.38	0.0	0.32	N.A.	N.A.	N.A.	N.A.
270	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
300	N.A.	N.A.	0.31	0.3	0.29	N.A.	N.A.	N.A.	N.A.

3.2 Other Parameters Measurements

Other parameters, pH, conductivity, COD, and BOD_5, were also measured/assessed for the processed water samples by applying the standard chemical procedures (ASTM D1252-95, 00(B) for COD and 5210B for BOD_5). Table 2 illustrates the average values for measurements evaluated at the beginning and end of the experiments conducted for purging various samples for 1 hour. The data presented in Table 2 shows that pH was increased due to adding the polyelectrolyte to the PW while the conductivity remained almost the same. In addition, COD was increased in samples of PWP compared to that of PW. This is attributed to the organic contents of the added polymer. Furthermore, BOD_5 results indicated negligible bacterial contents in the PW.

Table 2: Measured pH, conductivity, COD, and BOD_5 in the experimented samples

Source of water	**pH**	**Conductivity, mS**	**COD, ppm**	**BOD_5, ppm**
Tap water	7.72	0.30	NIL	NIL
PW	8.2	10.15	750	0.31
PWP, grafted with 100 ppm of polyelectrolyte	9.68	10.09	1064	NIL
PWP, grafted with 200 ppm of polyelectrolyte	9.54	10.10	953	NIL
PWP, grafted with 300 ppm of polyelectrolyte	9.29	10.27	841	NIL
PWP, grafted with 400 ppm of polyelectrolyte	9.24	10.07	1183	NIL
PWP, grafted with 500 ppm of polyelectrolyte	9.24	10.4	1163	NIL

3.3 Experimentation of The Gas Lift Column – With No Packing

Both co-current and counter-current operational schemes were applied for the PW purging with N_2.

3.3.1 Semi-Batch Purging Scheme of Un-Packed Column

An experimental plan was followed in the semi-batch purging scheme with no-packing considering three variables (N_2 flow rate, L/min; polyelectrolyte concentration, ppm; and the purging time, min) measuring the DO, ppm, as the objective parameter. The plan was designed considering the following ranges for the examined parameters:

x1 = Nitrogen flow rate (2 to 6 L/min as real values) equivalent to (-1.682 to 1.682 as coded values)
x2 = Polymer conc. (100 to 500 ppm real values) equivalent to (-1.682 to 1.682 as coded values)
x3 = Purging time (0.5 to 2.5 hrs real values) equivalent to (-1.682 to 1.682 as coded values)
The above values were selected to match the literature in terms of results comparison.
The plan and the measured DO are illustrated in Table 3.

Table 3: The experimental plan for the semi-batch unpacked column scheme

	Variables						
	N2		Poly electrolyte conc.		Purging Time		Dissolved oxyge
Exp. No.	*Code value*	*Real value*	*Code value*	*Real value*	*Code value*	*Real value*	
	x1	*L/min*	*x2*	*ppm*	*x3*	*Hr*	*ppm*
1	-1	3.0	-1	200.0	-1	1.0	1.095
2	1	5.0	-1	200.0	-1	1.0	1.85
3	-1	3.0	1	400.0	-1	1.0	1.46
4	1	5.0	1	400.0	-1	1.0	0.7
5	-1	3.0	-1	200.0	1	2.0	1.045
6	1	5.0	-1	200.0	1	2.0	1.11
7	-1	3.0	1	400.0	1	2.0	1.25
8	1	5.0	1	400.0	1	2.0	0.26
9	-1.682	2.0	0	300.0	0	1.5	1.285
10	1.682	6.0	0	300.0	0	1.5	0.595
11	0	4.0	-1.682	100.0	0	1.5	0.5
12	0	4.0	1.682	500.0	0	1.5	0.645
13	0	4.0	0	300.0	-1.682	0.5	0.525
14	0	4.0	0	300.0	1.682	2.5	0.635
15	0	4.0	0	300.0	0	1.5	0.625
16	0	4.0	0	300.0	0	1.5	0.575
17	0	4.0	0	300.0	0	1.5	0.66
18	0	4.0	0	300.0	0	1.5	0.62
19	0	4.0	0	300.0	0	1.5	0.59
20	0	4.0	0	300.0	0	1.5	0.61

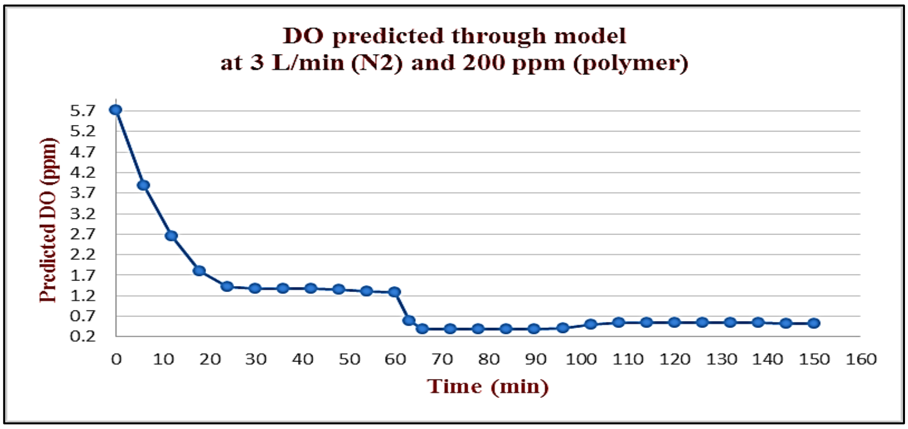


Figure 2: model prediction for a semi-batch purging at 3 L/min (N_2) and PWP at 200 ppm Polyelectrolyte for a purging duration of 150 minutes, noting that the predicted Values between 0 to 30 minutes were estimated through nonlinear extrapolation

Accordingly, a polynomial with 0.148 predictions produces the absolute error, as shown in equation 1. The model prediction for a co-current purging at 3 L/min (N_2) and PWP at 200 ppm polyelectrolyte for 150 minutes is presented in Figure 2.

$$Y = B_0 \,.\, x_0 + B_1 \,.\, x_1 + B_2 \,.\, x_2 + B_3 \,.\, x_3 + B_{11} \,.\, x_1^2 + B_{22} \,.\, x_2^2 + B_{33} \,.\, x_3^2 + B_{12} \,.\, x_1 \,.\, x_2 + B_{13} \,.\, x_1 \,.\, x_3 + B_{23} \,.\, x_2 \,.\, x_3 \qquad (1)$$

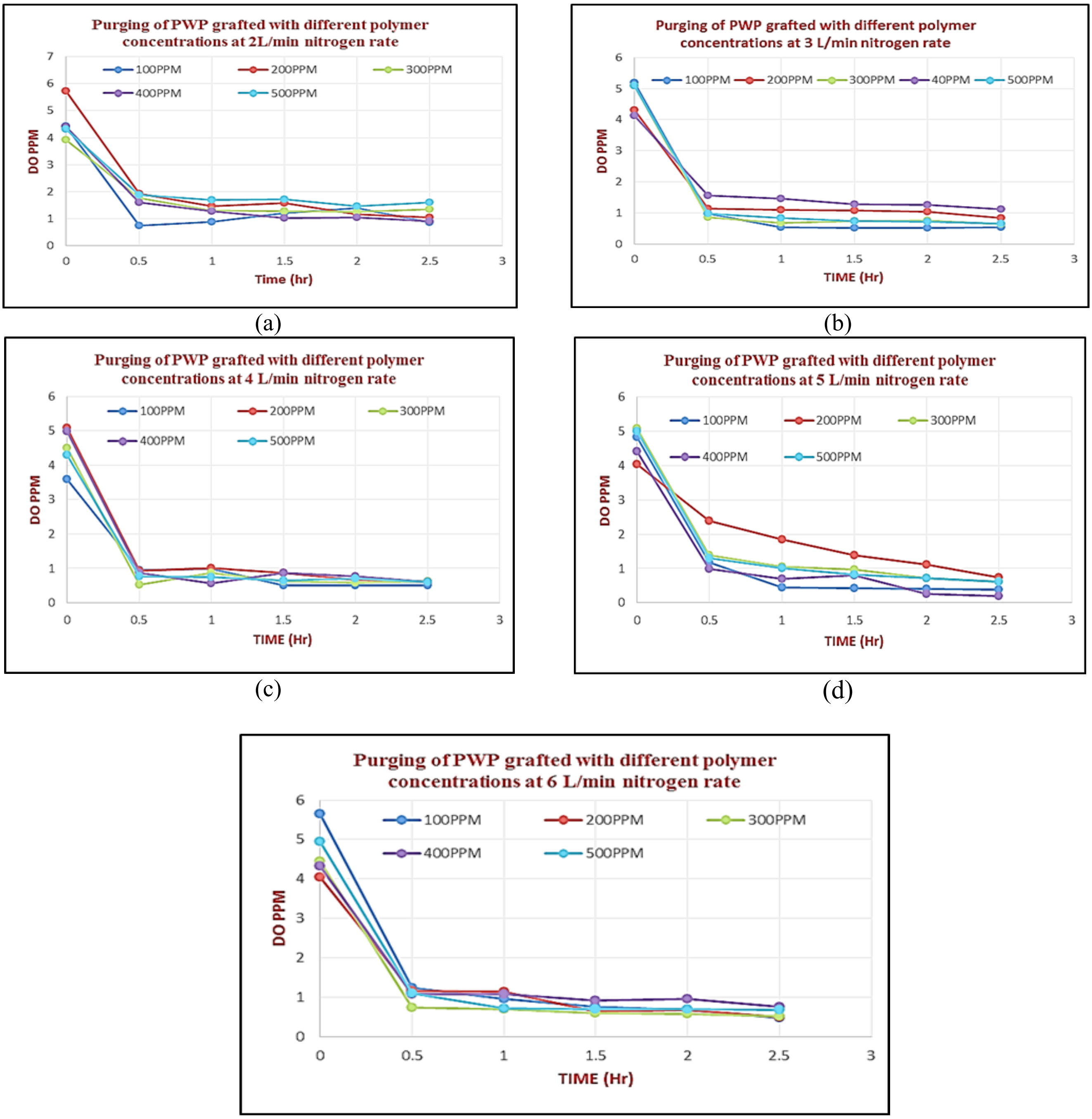
The calculated statistical coefficients B_0 to B_{23} are shown in Table 4, in which B_i represents the coefficients of the linear terms $\delta y/\delta x_i$ whereas B_{ii} and B_{ij} represent the coefficients of the quadratic terms $\delta^2 y/\delta^2_{x_i}$ and the cross-product terms $\delta^2 y/\delta_{x_i}\,\delta_{x_j}$ that refers to the interaction effects, respectively.

Table 4: Statistical coefficients for the generated polynomial (3 variables, semi-batch, un-packed column)

B_0	B_1	B_2	B_3	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
0.6005	-0.1531	-0.0869	-0.0919	0.1986	0.0687	0.0713	-0.3213	-0.1150	0.0175

For experimental data comparison, Figure 3 (a-e) illustrates the DO profile measured for produced water samples grafted with multiple polymer concentrations and purged at various nitrogen flow rates. It's worth noting that the sampling time segments adopted in this part of the study were based on 30 minutes onward, approaching 2.5 hours. However, it is observed that a considerable reduction in the DO content was attained in the first 30 minutes from the experimental runs, while the next purging period resulted in only slight drops in the DO contents. It's also observed that implementing longer duration periods for nitrogen purging has resulted in unexpected ascent in the DO values for some experimented cases, with no clear reason. Therefore, shorter nitrogen purging duration, up to 30 minutes, and sampling time segments of 3 minutes onward were adopted for measuring DO in all experimental sections followed this part. In the actual case, 3 minutes was chosen as it's the least time required by the DO measuring device to process the sample. By screening the results, the impact of increasing the nitrogen flow rate was not found significant in the semi-batch / unpacked column performance.

On the other hand, for solution viscosity less than 9 mPa.s, PWP of higher polymer content has resulted in better DO removal. This observation could be attributed to the effect of various residual contents of the produced water (minerals, hydrocarbons, etc.), which might have resulted in perturbed surface tension and, hence, released the DO particles much easier. Also, it can be observed from Figure 3 that DO is reduced to 0.6 ppm for the solution with 100 ppm at nitrogen purging of 5 L/min.



(a) (b)

(c) (d)

(e)

Figure 3: (a-e) Application of various N_2 purging modes of produced water grafted with different polymer concentrations (PWP)

3.3.2 Semi-Batch Purging Scheme of Un-Packed Column

Several experiments were implemented targeting the highest DO removal performance in the counter-current purging scheme with no-packing. In the first instance, tap water fully saturated with oxygen was purged at different N_2 flow rates; the results are illustrated in Figure 4 and indicate that around 0.7 ppm DO reach by applying a 6 L/min nitrogen flow rate. This scheme was also applied for PWP samples at different concentrations of polyelectrolyte. The results are shown in Figure 5. Observations similar to the experimentation of the semi-batch and no packing scheme were noted. The first 3 minutes of purging duration has significantly reduced the DO content. Also, a PWP of higher polyelectrolyte concentrations resulted in \ higher DO removal efficiency.

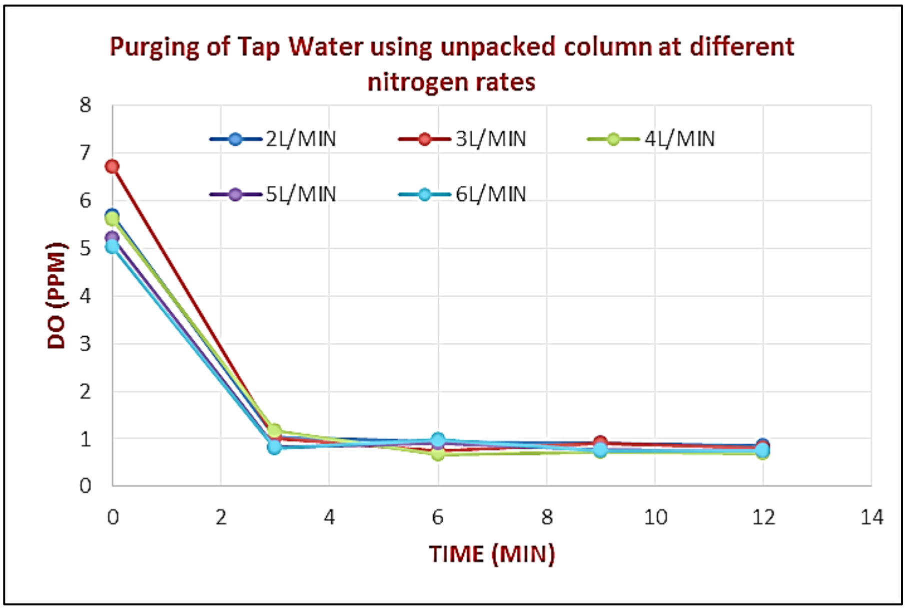


Figure 4: Purging of tap water at different nitrogen throughputs applying the semi-batch scheme with no packing

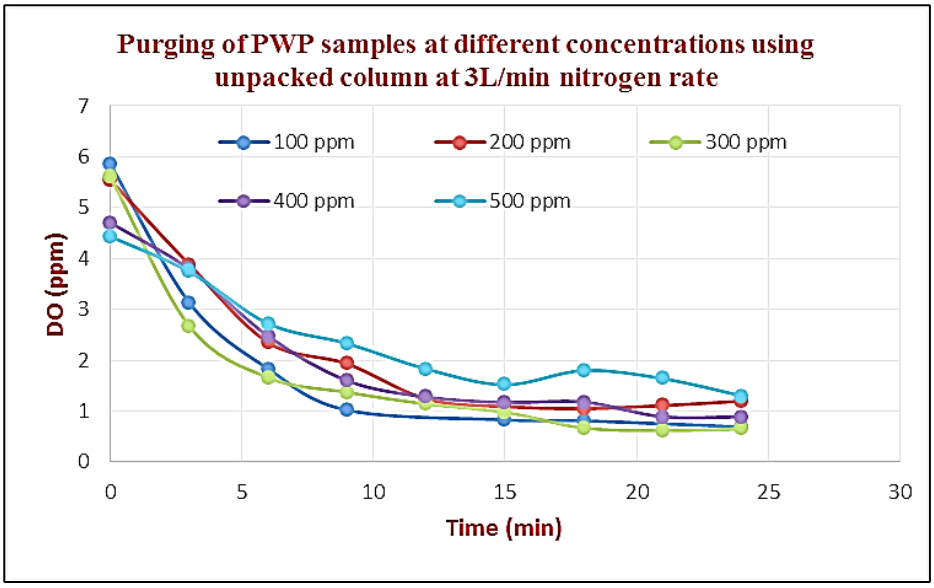


Figure 5: Purging of PWP samples grafted with different concentrations of polyelectrolyte at Different nitrogen throughputs applying the semi-batch scheme with no packing

3.4 Experimentation of The Gas Lift Column – With Packing

In this part, both co-current and counter-current operational schemes were applied for the PWP purging with N_2, using two different types of packing. Figure 6 illustrates the experimented gas lift columns packed with customized polyethylene rushing rings (Figure 6-a) and glass balls (Figure 6-b).

In the first instance, the column with the two types of packing was experimented with separately to depict the implications on the DO removal efficiency, as shown in Figure 6. The results indicated a better removal efficiency when using the spherical balls, which could be attributed to the uniform interfacial area for contact compared with the random one enforced when applying the rushing rings. The uniform interfacial area offered by the distributed spherical glass balls is certainly influenced by attaining a higher mass transfer coefficient and a better diffusion flux. Thus, a packed layer of glass balls was implemented in the next experimental sets applied with the packing modes.

(a) Rushing rings of PE (b) Spherical glass balls

Figure 6: (a-b)Pictures of two types of packing used in the gas lift column

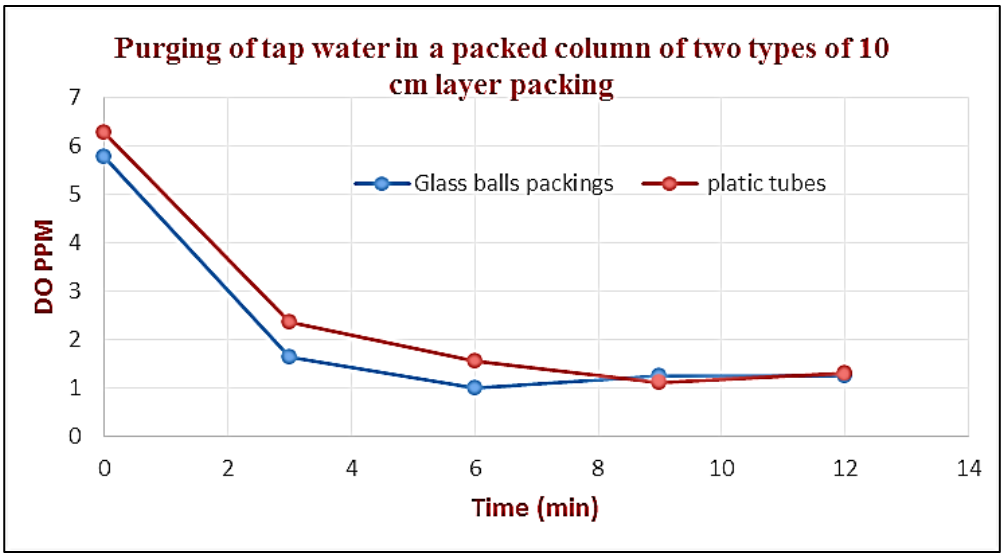


Figure 7: Oxygen saturated tap water was experimented with in a semi-batch purging scheme applying PE rushing rings (orange profile) and spherical glass balls (blue profile)

3.4.1 Semi-Batch Purging Scheme of Packed Column

In the semi-batch purging scheme with spherical glass balls packing, an experimental plan was followed considering four variables (N_2 flow rate, L/min; polymer concentration, ppm; packing layer height, cm, and the purging time, min) and measuring the DO, ppm, as the objective parameter. The plan was designed considering the following ranges for the examined parameters:

x1 = Nitrogen flow rate (2 to 6 L/min as real values) equivalent to (-2 to 2 as coded values)
x2 = Polymer conc. (100 to 500 ppm as real values) equivalent to (-2 to 2 as coded values)
x3 = Packing layer height (10 to 30 cm as real values) equivalent to (-2 to 2 as coded values)
x4 = Purging time (3 to 24 minutes as real values) equivalent to (-2 to 2 as coded values)

The plan and the measured DO are illustrated in Table 5.

Table 5: The experimental plan for semi-batch glass balls packed column scheme

	Variables								
	N2 flow rate		**Poly electrolyte conc.**		**Packing Layer**		**Purging time**		**Dissolved oxygen**
Exp. No.	***Code value***	***Real value***	***Code value***	***Real value***	***Code value***	***Real value***	***Code value***	***Real value***	
	x1	***L/min***	***x2***	***ppm***	***x3***	***cm***	***x4***	***min***	***ppm***
1	-1	3.0	-1	200.0	-1	10.0	-1	6.0	1.33
2	1	5.0	-1	200.0	-1	10.0	-1	6.0	1.17
3	-1	3.0	1	400.0	-1	10.0	-1	6.0	1.31
4	1	5.0	1	400.0	-1	10.0	-1	6.0	1.07
5	-1	3.0	-1	200.0	1	20.0	-1	6.0	1.99
6	1	5.0	-1	200.0	1	20.0	-1	6.0	1.17
7	-1	3.0	1	400.0	1	20.0	-1	6.0	1.31
8	1	5.0	1	400.0	1	20.0	-1	6.0	1.07
9	-1	3.0	-1	200.0	-1	10.0	1	18.0	0.83
10	1	5.0	-1	200.0	-1	10.0	1	18.0	1.22
11	-1	3.0	1	400.0	-1	10.0	1	18.0	0.64
12	1	5.0	1	400.0	-1	10.0	1	18.0	0.78
13	-1	3.0	-1	200.0	1	20.0	1	18.0	1.05
14	1	5.0	-1	200.0	1	20.0	1	18.0	1.22
15	-1	3.0	1	400.0	1	20.0	1	18.0	0.76
16	1	5.0	1	400.0	1	20.0	1	18.0	0.78
17	-2	2.0	0	300.0	0	20.0	0	12.0	1.18
18	2	6.0	0	300.0	0	20.0	0	12.0	1.71
19	0	4.0	-2	100.0	0	20.0	0	12.0	0.77
20	0	4.0	2	500.0	0	20.0	0	12.0	0.92
21	0	4.0	0	300.0	-2	10.0	0	12.0	0.9
22	0	4.0	0	300.0	2	30.0	0	12.0	0.85
23	0	4.0	0	300.0	0	20.0	-2	0.0	5.51
24	0	4.0	0	300.0	0	20.0	2	24.0	1.11
25	0	4.0	0	300.0	0	20.0	0	12.0	0.9
26	0	4.0	0	300.0	0	20.0	0	12.0	0.88
27	0	4.0	0	300.0	0	20.0	0	12.0	0.79
28	0	4.0	0	300.0	0	20.0	0	12.0	0.95
29	0	4.0	0	300.0	0	20.0	0	12.0	0.83
30	0	4.0	0	300.0	0	20.0	0	12.0	0.87
31	0	4.0	0	300.0	0	20.0	0	12.0	0.89

Accordingly, a polynomial with a 0.316 prediction means the absolute error was produced, as shown in equation 2.

$$Y = B_0 . x_0 + B_1 . x_1 + B_2 . x_2 + B_3 . x_3 + B_4 . x_4 + B_{11} . x_1^2 + B_{22} . x_2^2 + B_{33} . x_3^2 + B_{44} . x_3{}^2 + B_{12} . x_1 . x_2 + B_{13} . x_1 . x_3 + B_{14} . x_1 . x_4 + B_{23} . x_2 . x_3 + B_{24} . x_2 . x_4 + B_{34} . x_3 . x_4 \quad (2)$$

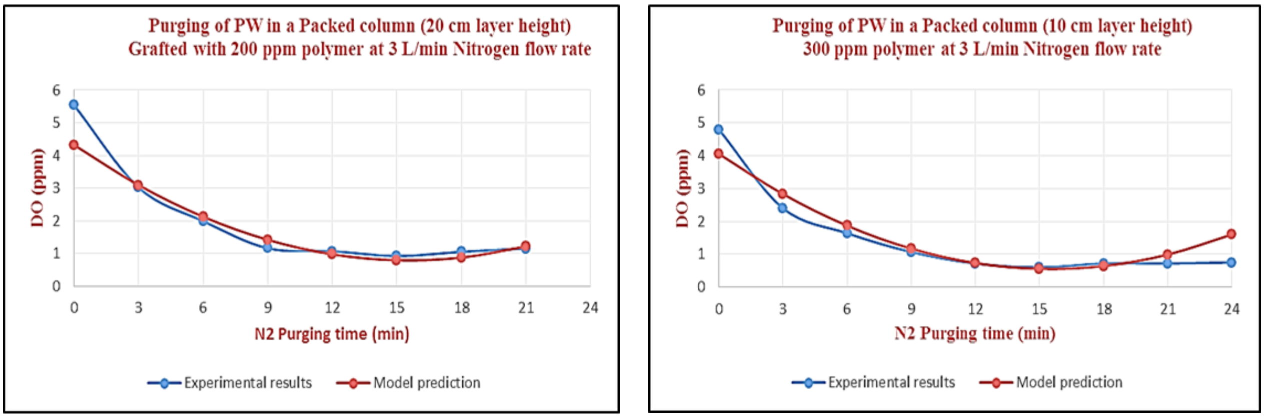
The calculated statistical coefficients B_0 to B_{23} are shown in Table 5, in which B_i represents the coefficients of the linear terms $\delta y/\delta x_i$ whereas B_{ii} and B_{ij} represent the coefficients of the quadratic terms $\delta^2 y/\delta^2_{x_i}$ and the cross-product terms $\delta^2 y/\delta_{x_i}\,\delta_{x_j}$ that refers to the interaction effects, respectively.

Table 6: Statistical coefficients for the generated polynomial (4 variables, co-current, glass balls packed column)

B_0	B_1	B_2	B_3	B_4	B_{11}	B_{22}	B_{33}
0.872887	0.013333	-0.081667	0.037500	-0.497504	0.057600	-0.092400	-0.084900

B_{44}	B_{12}	B_{13}	B_{14}	B_{23}	B_{24}	B_{34}
0.523850	0.006250	-0.062500	0.136250	-0.047500	-0.028750	-0.020000

A comparison between the model prediction and the experimental DO readings for a glass ball-packed column, semi-batch scheme purged at 3 L/min (N_2), and other different parameters are presented in Figure 8 (a & b).



(a) (b)

Figure 8: (a-b) Comparison between the model prediction and the DO experimental measurements For a semi-batch packed column scheme purged at 3 L/min nitrogen and other different Parameters

In terms of experimental data comparison, Figure 9 (a-f) illustrated the DO profiles measured for tap water and produced water samples grafted with multiple concentrations of polyelectrolyte (PWP) and purged at various nitrogen flow rates through glass balls packed layer columns of different heights. The results of all studied cases indicate the enhanced performance upon increasing the packed layer height. This could be attributed to a higher homogeneous interfacial contact between the gas and the liquid, leading to a higher mass transfer coefficient and a higher diffusion flux. However, the improved removal efficiency was hindered when approaching the limits of 1 ppm. Furthermore, only a shallow reduction in the DO (approaching 0.6 ppm in the best case) was shown for all studied cases, even when increasing the purging duration by 12 minutes. These results resemble the findings in the previous sections, which indicates the difficulty of removing DO at shallow levels from all investigated water samples in this study.

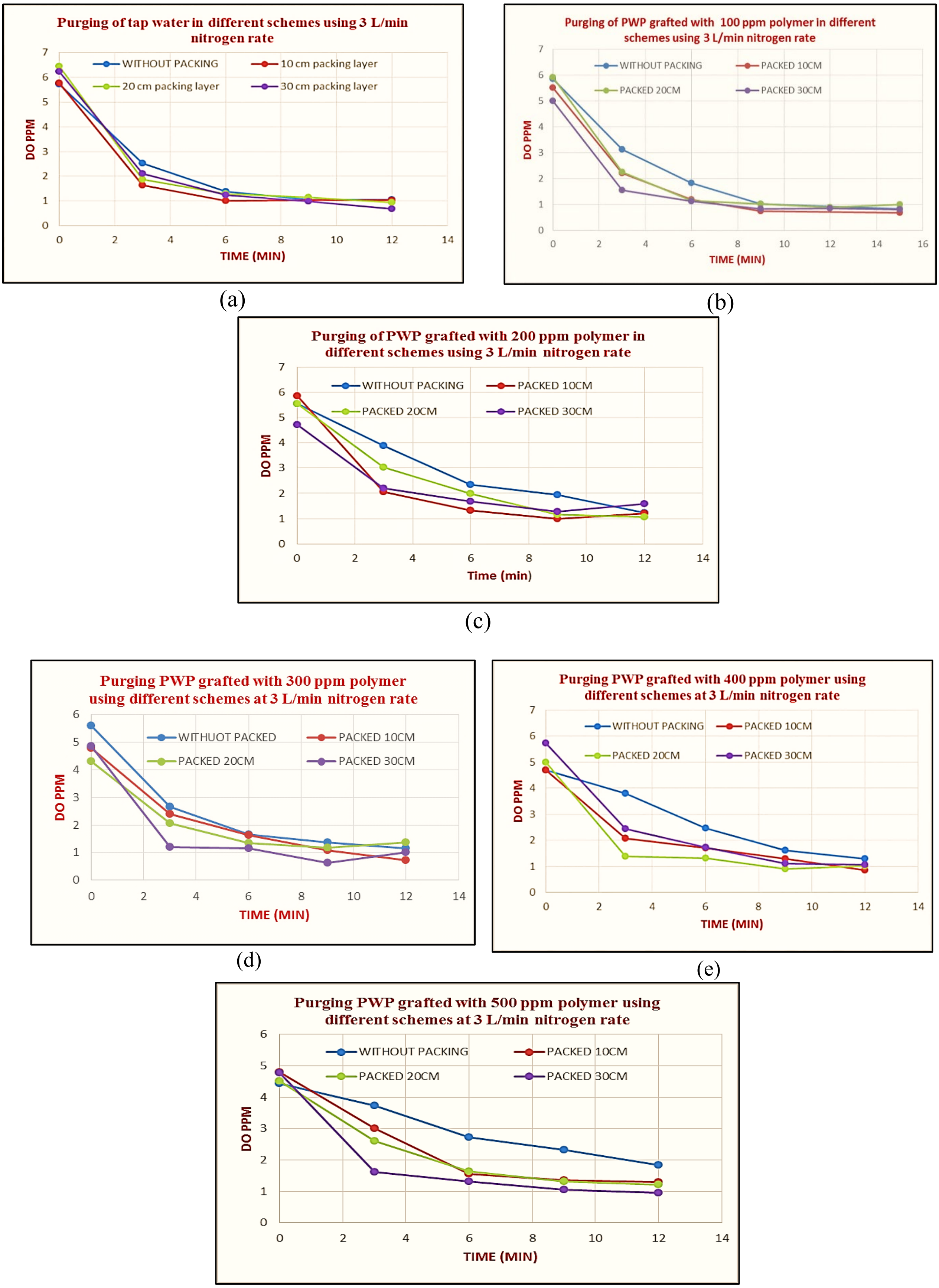
To contemplate the effect of increasing the nitrogen purging rate, the same comparison was made for the semi-batch packed column scheme, fixing the packing layer height and applying different nitrogen flow rates. The results are presented in Figure 10 (a-c).

The above profiles indicate higher DO removal efficiency when the applied scheme increases the nitrogen flow rate. However, limits of 0.5 ppm DO residuals were approached in all investigated cases and could not be overwhelmed in the co-current packed column scheme. This has led us to think about applying the counter-current packed column scheme, as presented in the coming section.

3.4.2 Counter Current Purging Scheme in A Packed Column

The last section of the current investigations discusses the packed column - counter-current mode for N2 purging of different water samples. In the first trials, tap water and produced water samples grafted with different polymer concentrations (PWP) were performed at two liquid flow rates and 3 L/min nitrogen, as shown in Figure 11 (a-e), using a packed layer of 20 cm height. These experiments were implemented to check the scheme's performance upon increasing the purging agent flow rate. The counter-current mode for water containing different hydrocarbons and heavy metals residues is known as sensitive to an aeration scheme and a possible foam formation. The results have shown that applying a 1.8 L/min liquid rate has resulted in lower DO removal efficiency, which conflicts with all previous results due to increased hold-up volume. Moreover, the formation of rising foams was also observed during the run of the counter-current–packed column scheme. Figure 12 illustrates a picture of the rising foams resulting from running the counter-current–packed column scheme.

The formation of rising foams became more significant when applying a higher N_2 purging rate, even when increasing the packing layer height to 55 cm. Operation of this scheme at a 5 L/min nitrogen rate was possible for polymer concentrations up to 300 ppm. However, higher polymer concentrations have resulted in a huge number of foams that hindered the experiment's proceeding. Figure 13 illustrates the DO measurements for the 55 cm packing–counter current mode. Again, limited removal for DO is attained in the shallow region below 1 ppm, leading to the same findings from previous operational schemes.



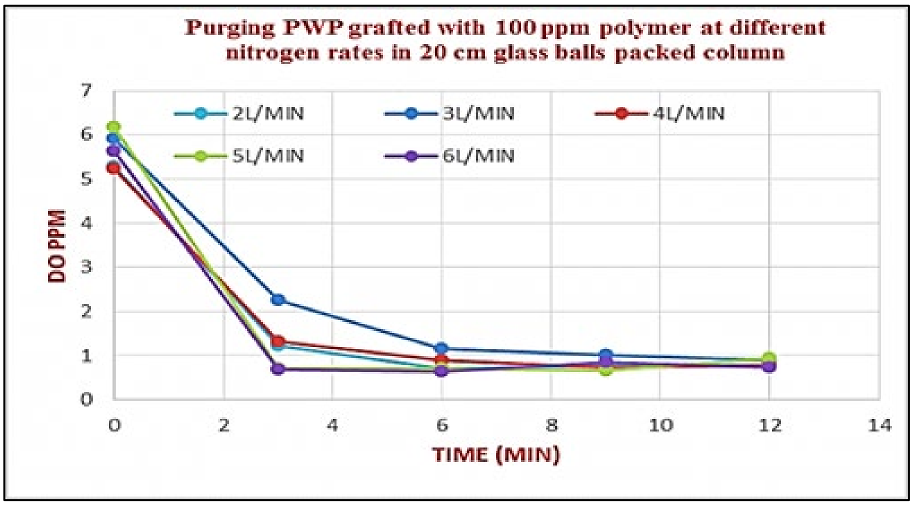
(a) (b)

(c)

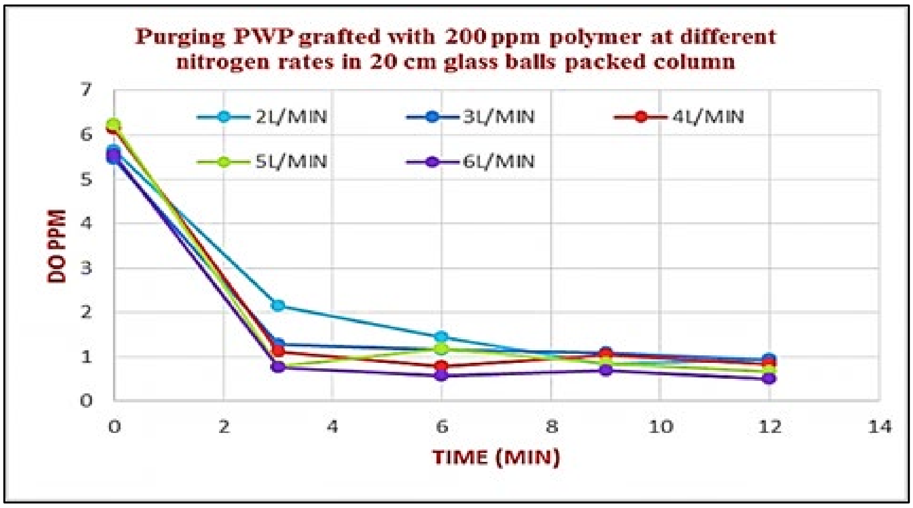
(d) (e)

(f)

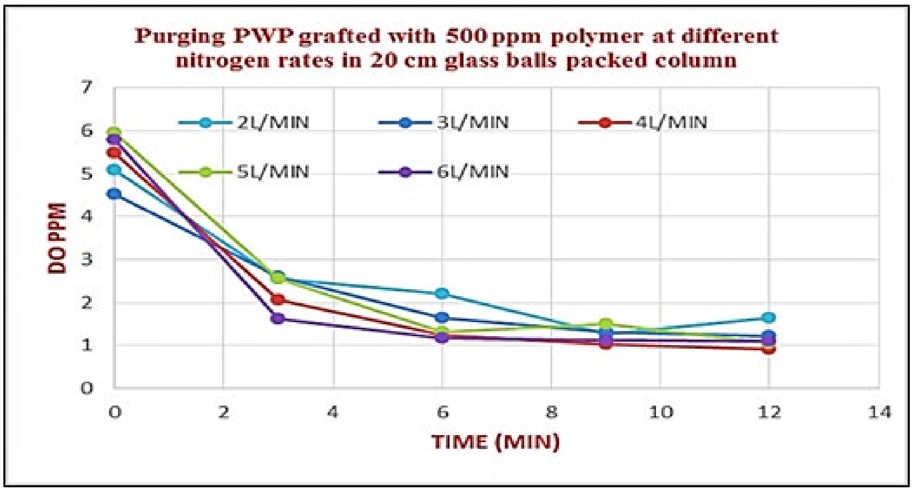
Figure 9: (a-f) Experimental DO measurements for purging tap water (9-a) and PWP grafted of different polyelectrolyte concentrations (9-b to 9-f) at 3 L/min packing nitrogen at various layer height



(a)

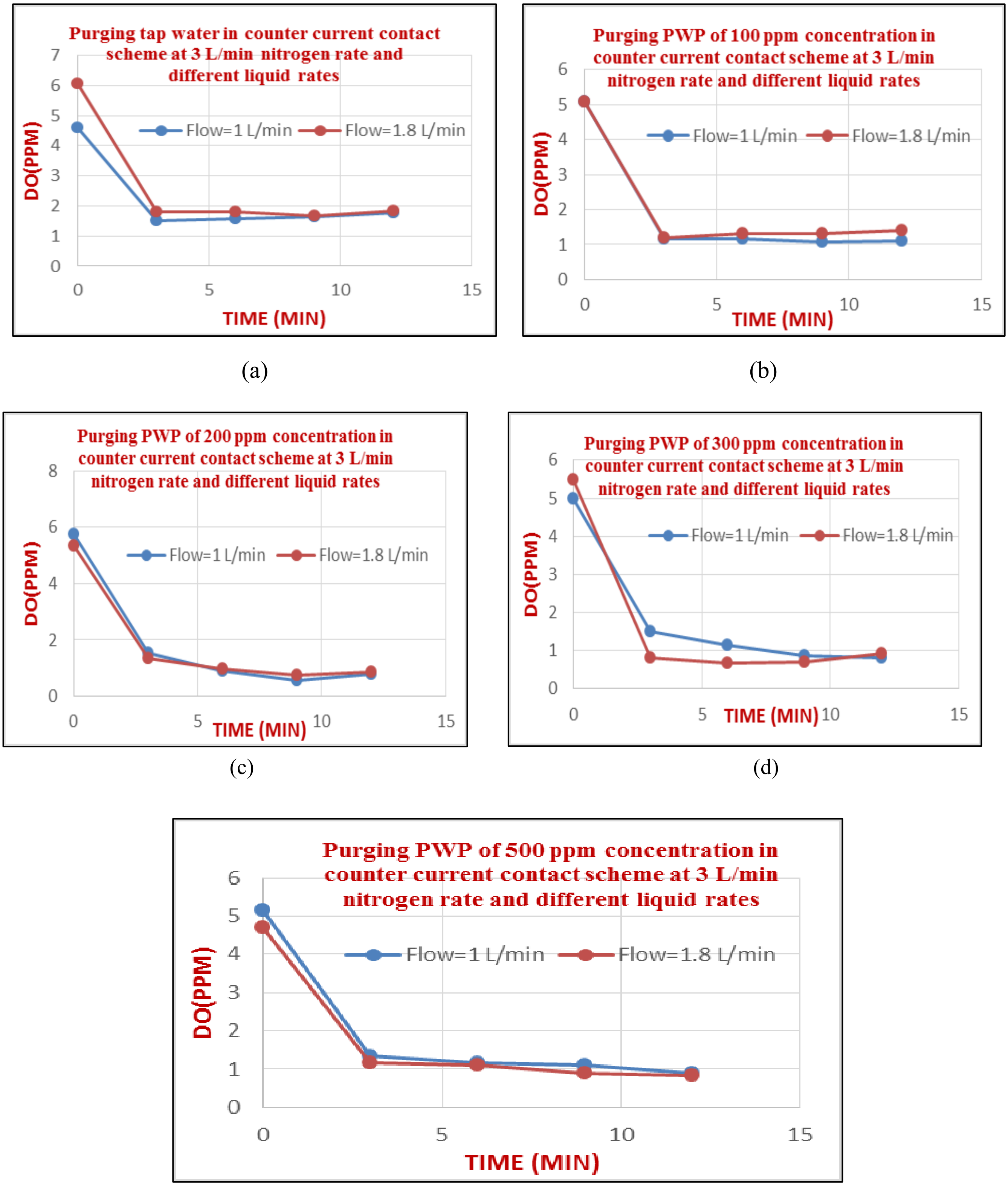


(b)



(c)

Figure 10: (a-c) Comparison between the results of applying different nitrogen purging flow rates while fixing other parameters for a semi-batch packed column scheme



(a)

(b)

(c)

(d)

(e)

Figure 11: (a-e) DO measurements at two nitrogen purging rates for the counter-current–packed column scheme

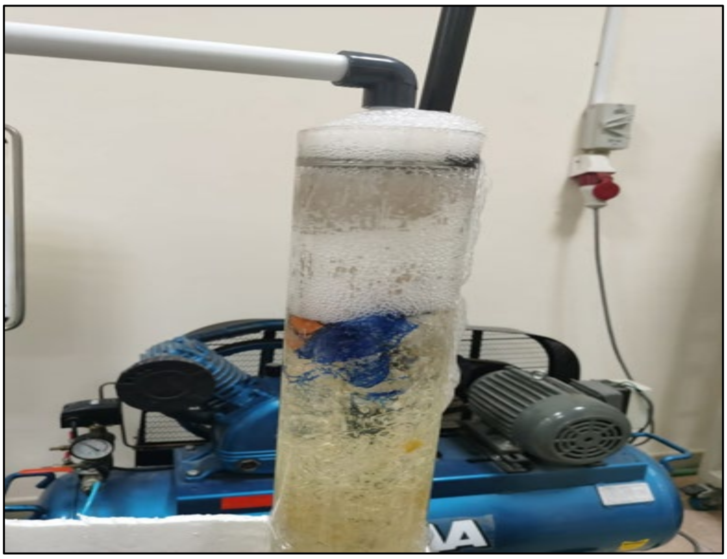


Figure 12: A picture of the rising foams in the counter-current–packed column scheme

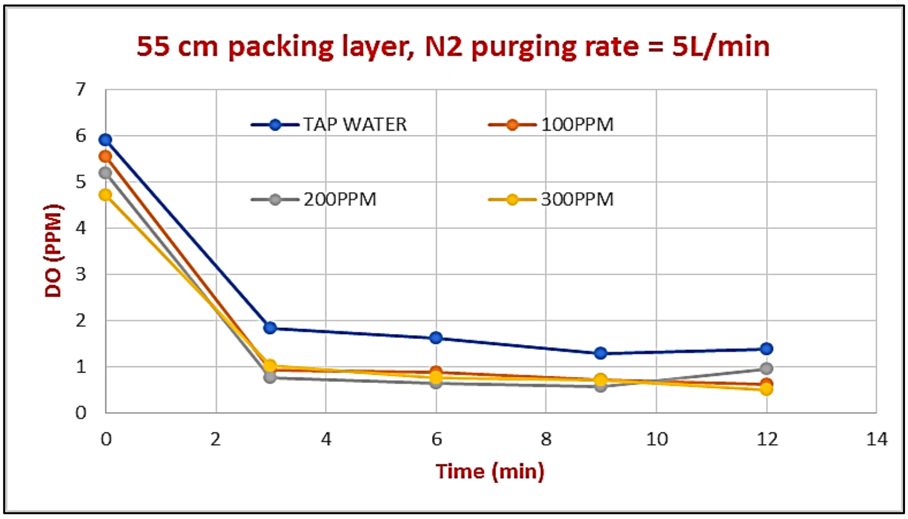


Figure 13: DO measurements for 55 cm packing – counter-current purging mode at 5 L/min, Applying different polymer concentrations

4. Conclusions

Parametric nitrogen purging investigations for produced water grafted with polymer in a gas lift column were performed in this part of the study, applying different operational schemes (co-current and counter-current in both packed and unpacked columns), achieving considerable dissolved oxygen removal efficiencies. Counter-current scheme with glass ball packing is proved more efficient rather than others. However, all applied schemes experimenting with various operational parameters could not remove the dissolved oxygen in the shallow region (≈ 0.5 ppm), which emphasizes the need to find a more efficient purging technique. It's believed that the DO residues in the shallow region will be removed totally should ultra-fine bubbles of stripping gas is used. Hence, the study will be resumed in another part to investigate the mentioned hypothesis toward achieving total DO removal and separation of the accompanied residues in the produced water.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare that there is no conflict of interest.

References

[1] Energy Information Administration. International energy outlook 2009. US Department of Energy, DOE/EIA-0484 (2009). Online, last accessed 10 Feb. 2022.

[2] K. A. Scott, P. Yeats, G . Wohlgeschaffen. Precipitation of heavy metals in produced water: influence on contaminant transport and toxicity, Mar Environ Res., 63 (2007)146–167. https://doi.org/10.1016/j.marenvres.2006.08.001

[3] G. Kaur, AK. Mandal, MC. Nihlani, et al. Control of sulfidogenic bacteria in produced water from the Kathloni oilfield in northeast India, Int. Biodeterior. Biodegrad., 63 (2009) 151–155. https://doi.org/10.1016/j.ibiod.2008.07.008

[4] E. T. Igunnu and G. Z. Chen. Produced water treatment technologies, Int. J. Low Carbon Technol., 9 (2014) 157–177. https://doi.org/10.1093/ijlct/cts049

[5] A. Fakhru'l-Razi, A. Pendashteh, LC. Abdullah, et al. Review of technologies for oil and gas produced water treatment, J Hazard. Mater., 170 (2009) 530–551. https://doi.org/10.1016/j.jhazmat.2009.05.044

[6] T. Hayes, D. Arthur, Overview of emerging produced water treatment technologies, 11th Annual International Petroleum Environmental Conf. 2004.

[7] James P. Ray, Rainer Engelhardt F. Produced water: technological/environmental issues and solutions, Environ Sci Res., 46.1992.

[8] T . Sirivedhin, McCue J, Dallbauman L. Reclaiming produced water for beneficial use: salt removal by electrodialysis, J Membr. Sci., 243 (2004) 335–343. https://doi.org/10.1016/j.memsci.2004.06.038

[9] J. D. Arthur, Langhus BG, Patel C. Technical Summary of Oil & Gas Produced Water Treatment Technologies. NETL, 2005.

[10] M. A. Al-Ghouti, M. A. Al-Kaabi, M. Y. Ashfaq, D. A. Da'na. Produced water characteristics, treatment and reuse: A review, J. Water Process Eng., 28 (2019) 222-239. https://doi.org/10.1016/j.jwpe.2019.02.001

[11] T.Whalen, Challenges in Reusing Produced Water, J Pet Technol., 64 (2021)18–20. https://doi.org/10.2118/1112-0018-JPT

[12] P. Durdevic, C. S. Raju, Z. Yang, Potential for Real-Time Monitoring and Control of Dissolved Oxygen in the Injection Water Treatment Process, IFAC-Papers OnLine., 51 (2018) 170–177. https://doi.org/10.1016/j.ifacol.2018.06.373

[13] T. L. Skovhus, D. Enning, J. S. Lee, Microbiologically Influenced Corrosion in the Upstream Oil and Gas Industry, CRC Press., 2017. https://doi.org/10.1201/9781315157818

[14] L.T. Popoola, A. S. Grema, G. K. Latinwo, B. Gutti, A.S. Balogun, Corrosion problems during oil and gas production and its mitigation, Int. J. Ind. Chem.., 4 (2013) 35.

[15] I. B. Butler, M. A. A. Schoonen, D. T. Rickard, Removal of dissolved oxygen from water: A comparison of four common techniques, Talanta , 41 (1994) 211-215. https://doi.org/10.1016/0039-9140(94)80110-X

[16] A. Larson, Water Environment Federation workshop on produced water, WEF Stormwater Summit 2021 Virtual Event Pre-/Post- Conference Workshops, 2021.

[17] R.R. Horner, Fundamentals of Urban Runoff Management: Technical and Institutional Issues, Terre. Inst., (1994)302.

[18] E. S. Snavelyj, Chemical Removal of Oxygen from Natural Waters, J. Pet. Technol., 23 (1971) 443-446.http://doi.org/10.2118/3262-PA

[19] I. Zeko, M. M. Stack, A note on a design protocol for de-oxygenation of water, Electrochem commun., 103 (2019) 12–16. https://doi.org/10.1016/j.elecom.2019.04.009

[20] G. C. William , M. C. Gertrude, Experimental Designs, 2nd Edition, Wiley classic library(1992) 640.

[21] Z. B. Monica, The Winkler Method - Measuring Dissolved Oxygen. Montana State University. Online, last accessed 10 Feb. 2022 .

[22] Technical Resource Library. Cole Parmer, Online, last accessed Feb. 2022

[23] A. Hirayama et.al. Omani Oil Fields Produced Water: Treatment and Utilization, SPE International Petroleum Conference and Exhibition in Mexico, Villahermosa, Mexico, SPE 74413, Feb. 2002. https://doi.org/10.2118/74413-MS