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Influence of key operating parameters and bio-fouling on simultaneous desalination of seawater & reduction of organic wastes from petroleum industrial wastewater

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ABSTRACT

Bio-cathode microbial desalination cells are emerging technology that utilizes bioelectric potential from organic matter (petroleum refinery effluent) to enhance the desalination process along with the activity of microalgae (*Scenedesmus abundans*). In the present work, the system is assumed to be governed by interdependent key process variables such as salt concentration, anolyte concentration, and external resistance. Three different levels of salt concentration (5, 20 and 35 g L^{-1}), anolyte concentration (250, 500 and 750 mg L^{-1}), and external resistance (100, 560 and 1000 Ω) were analysed and optimized by the statistical and probabilistic tool such as Box Behnken design method and Genetic Algorithm to maximize the desalination performance. The optimized parameters such as salt concentration (35 g L^{-1}), anolyte concentration (500 mg L^{-1}), and external resistance (100 Ω) produced maximum desalination efficiency of 59.6%. The model also distinguished the influence of input parameters on the output responses such as significant responses (Salinity, Total dissolved solids, and Electrical conductivity) and non-significant responses (Chemical oxygen demand removal, power density, and algal growth). The model predicted the desalination efficiency with ±1.25% error. The high impact of bio-fouling was observed in Anion Exchange Membrane on comparison with Cation Exchange Membrane.

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Bio-cathode microbial desalination cell; response surface methodology; genetic algorithm; scenedesmus abundans; bio-fouling

Introduction

Water is the important primary commodity for human existence, development, and preservation of life. However, the threat of potable fresh water availability nearly affects one billion people mainly those living in the least developed countries (Shah 2013). Desalination process is widely used to meet the clean water demand specifically in areas where brackish water is available. Countries with capital expenditure or financial investment and high accessibility to energy are highly accessible to traditional desalination techniques such as reverse osmosis, electrodialysis, etc.

Microbial Desalination Cell (MDC) is considered to be the most appropriate emerging promising technology that integrates wastewater treatment, desalination and bioelectricity production in a single reactor which is evolved from the architecture of microbial fuel cell (MFC) (Cao et al. 2009). The process maintains electroneutrality by simultaneous oxidation of organic matter and electron transfer thus leading to the desalination process. (Sevda et al. 2015) (Lovley 2008) Substantial research over the past decade significantly improved MDC reactor's architecture, performance and its application in various fields. Among different configurations, bio-cathode MDC is gaining importance as it utilizes autotrophic and phototrophic microorganisms (e.g. algal species) in cathode instead of air cathode with an expensive catalyst (e.g. platinum catalyst). Algae conduct

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oxygenic photosynthesis to produce oxygen in the cathode chamber through membrane-bound proteins such as cytochrome b6F complex, PSI and PSII along with plastoquinone (an isoprenoid quinine molecule) and plastocyanin (water-soluble electron carrier) (Taiz and Zeiger 2010). El Nadi reported the direct elimination of 95% of the salt content with the Scenedesmus species (El Nadi, El Sergany, and El Hosseiny 2014). The current study utilizes *Scenedesmus abundans* as catholyte along with petroleum wastewater as anolyte, and it is already studied by our research group with the above species and obtained 55% salt removal efficiency with 35 g L^{-1} salt concentration (Ashwaniy and Perumalsamy 2017).

It is crucial to optimize and control specific parameters such as reactor configurations, mode of operation, operational conditions, initial salt concentration etc to attain higher desalination performance. (Jingyu, Ewusi-Mensah, and Norgbey 2017) (Carmalin Sophia et al. 2016). Ordinary differential equations (ODEs) along with the addition of specific equations on the stereotype models with up gradation are usually applied in MDC to determine the salt removal efficiency on the three-chambered MDC and also the interaction levels of different influential parameters on the desalination efficiency (Luo et al. 2016). The Ping et al. reported the importance of operational parameters such as anolyte supply, salt loading rate, and power generation to obtain optimal desalination efficiency through a mathematical model. The model also utilized the Genetic algorithm (GA) to diminish the relative root-mean-square error between the experimental and predicted data of the estimated parameters (Ping et al. 2014).

This study experimentally demonstrated the importance of optimizing and enriching the key process parameters in specific to improve the adequate performance of the bio-cathode MDC The direct influential key parameters of variable concentrations such as initial salt concentration [5, 20, 35 g L^{-1}], the anolyte concentration of petroleum wastewater [250, 500, 750 mg L^{-1}] and external resistances (ER) [100, 560, 1000 Ω] were considered in batch operation. The probabilistic and statistical tool such as Response Surface Methodology (RSM-Box-Behnken design (BBD)) and GA encourages in analyzing the experimental data and predicts the most optimal solutions. The results perceived by RSM and GA were optimized to identify the best combinations of process parameters that yields higher desalination performance. We also investigated other output responses such as current generation, Chemical oxygen demand (COD) removal rate, and algal growth rate at different combinations provided by the model. Thus the study brings out the importance of process variables through experimental and modeling results in increasing the overall performance of the technology. The bio-fouling images were also reported.

Materials and methods

Bio-cathode MDC reactor set up

The three-chambered rectangular bio-cathode MDC (Figure 1) made of acrylic sheets holds the liquid volume ratio of 1:0.5:1. The chambers separated by two different separators such as Anion exchange membrane (AEM) with exchange capacity of 1.3 meq/g (AMI 7001, Membrane International), i.e. between anode and desalination chamber and Cation exchange membrane (CEM) with exchange capacity of 1.6 meq/g (CMI 7000, Membrane International), i.e. between cathode and desalination chamber respectively. The conductive material such as graphite rods was used as electrode material for anode and cathode. The volume of the anode, middle, and cathode chamber were raised to 300 ml, 150 ml, and 300 ml respectively after the insertion of graphite electrodes. Figure 1 represents the schematic of Bio-cathode microbial desalination cell.

An open circuit MDC is maintained to obtain stability condition. The anolyte was replaced periodically when the voltage of the cell drops to 50 mV. The saline solution and the catholyte solution remained unchanged until the completion of the experimental period. On operating for 23 days in batch mode, the MDC performances were measured periodically in duplicates.

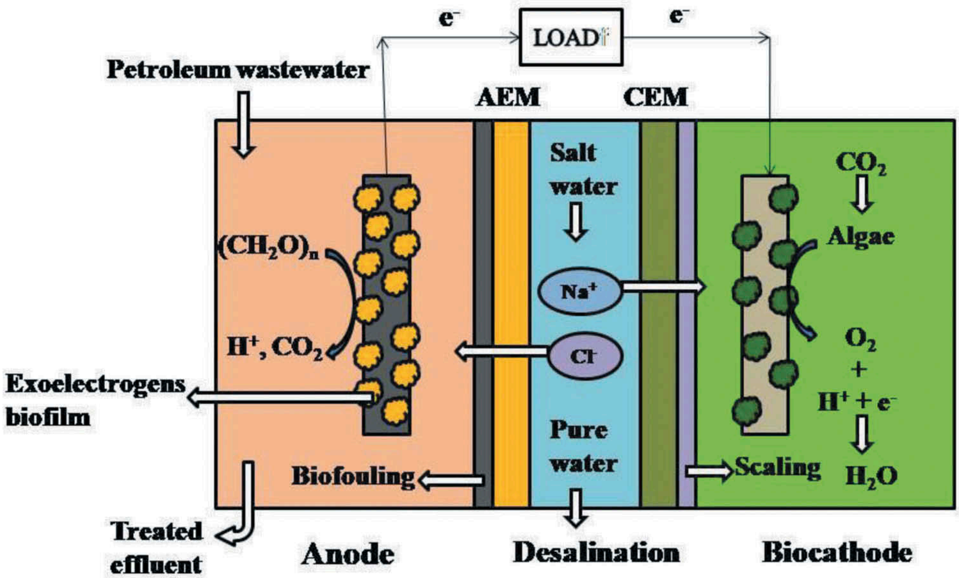

Figure 1. Schematic of the bio-cathode microbial desalination cell.

Operating conditions

Petrochemical raw wastewater obtained from Chennai Petroleum Corporation Limited (CPCL), Chennai, India was used in the anode chamber contains the following composition: mixed bacterial consortia, hydrocarbons, bicarbonates, ammonia, phenol, chlorides, sulfides, and other constituents in minimal concentration. The middle desalination chamber was filled with real-time sea water of NaCl concentration. The microalgae *Scenedesmus abundans* grown in the BG-11 medium was fed in the bio-cathode chamber, contains the following nutrient composition: Ferric ammonium citrate (0.006 g L^{-1}), Sodium nitrate (1.500 g L^{-1}), Citric acid (0.0056 g L^{-1}), Dipotassium hydrogen phosphate (0.0314 g L^{-1}), Magnesium sulphate (0.036 g L^{-1}), Disodium magnesium EDTA (0.001 g L^{-1}), Calcium chloride dihydrate (0.0367 g L^{-1}), and Sodium carbonate (0.020 g L^{-1}). The final pH of the BG 11 media composition was maintained as 7. Respective quantities of Sodium chloride and Vitamin B12 were also added (Allen and Steiner 1968).

Experimental designs strategy

Experimental design for analysis by RSM

A three-level three-factor Box-Behnken Design was employed to conduct 15 experiments. The essential input process parameters such as initial salt concentration (g L^{-1}), anolyte concentration (mg L^{-1}), and ER (Ω) were considered. The RSM analysis by BBD was used to forecast the influence of independent process parameters and their interaction for maximum desalination performance.

The design expert version 10 was used to conduct regression and analysis of variance. ANOVA evaluated the statistical significance of the model equation and also tested the effect of linear, quadratic and interaction terms on the predicted responses. The BBD generated the best fit second order polynomial regression equation with the help of obtained experimental data as given in Equation. (3)

$$Y = \alpha_0 + \alpha_1 A + \alpha_2 B + \alpha_3 C + \alpha_{11} A^2 + \alpha_{22} B^2 + \alpha_{33} C^2 + \alpha_{12} AB + \alpha_{23} BC + \alpha_{13} AC \quad (1)$$

Where Y is the dependent variable (desalination performance, i.e. salinity removal efficiency), α_0, α_1, α_2, α_3 are coefficients of linear terms, α_{11}, α_{22}, α_{33} are quadratic coefficients, α_{12}, α_{23}, α_{13} represents interaction coefficients, A, B, C indicates independent variables such as initial salt concentration (g L^{-1}), anolyte concentration (mg L^{-1}), and ER (Ω). The responses obtained from the interactions of three influential parameters were expressed in three-dimensional surface plots and contors.

Genetic algorithm (GA)

Genetic Algorithm is a probabilistic search procedure that inherits the concept of natural selection and genetics. The algorithm produces a large group of solutions to solve a single problem, i.e. both constrained and unconstrained optimization problems. GA deals the complex optimization problems based on the concept of "survival of the fittest" developed by Charles Darwin (Goldberg and Holland 1988). The solutions are ranked based on the GA fitness level, and the most suitable ones are identified accordingly. The following are the general iterative process:

- Initial population construction
- Evaluation of fitness which reflects the objective value
- Develop a new population for next generation carrying out series of operation such as selection, crossing over, mutation – termination after reaching the maximum number of generation.

In the present study, the empirical quadratic mathematical model to increase the desalination performance obtained from RSM was used as the objective function in the optimization process using the genetic algorithm. MATLAB R2017a toolkit was used as an optimization tool for analyzing results from GA.

The output response is considered as the chromosome, the input parameters such as initial salt concentration (g L^{-1}), anolyte concentration (mg L^{-1}), and ER (Ω) are taken as three genes in the chromosome. An array of the population was initiated and evaluated; the highest achievement of the chromosome was replicated and evaluated. Further, crossing over and mutation on some genes was carried out. The cycles were repeated until the arrival of the best fitness function.

Measurements and analyses

All the experiments were conducted at the ambient temperature approximately equivalent to 30 °C ± 2 ° C. The digital multimeter (VC 97) measures the constant voltage change across the chambers connected by the resistance. The Current (I) was determined from the measured voltage using Ohm's law, $I = V/R_{ext}$. The power density was calculated normalised to the anode reactor volume. Salt concentration in the middle chamber was evaluated by the measurement of Total Dissolved Solids (TDS), NaCl concentration, change in Electrical conductivity along with pH were measured by water analysis kit (Eutech Instruments, Cyber scan series 600). The algal growth rate measurement and the spectra reading in the cathode chamber were carried out by the double beam spectrophotometer (UV 3200, Shimadzu make). The rate of organic compounds reduction in the petroleum wastewater present in the anode chamber was analyzed by the standard APHA methods (APHA 1992). The Scanning electron microscopy (SEM) provided the high-resolution images of changes in surface morphology of the fresh and used AEM and CEM.

Results and discussions

Optimization of desalination performance using RSM

BBD was conducted to optimize the significant factors for maximum desalination performance of bio-cathode MDC. Based on earlier experimentations, the critical, essential parameters were selected, and further optimization was carried out. In the present BBD study, three variables such as initial salt concentration (g L^{-1}), anolyte concentration (mg L^{-1}), and ER (Ω) were studied at three levels. For each of the variable, low, medium and high points were selected, and the construction of full factorial design investigated the effect of each parameter and their interactions. The desalination performance is evaluated based on the salt removal efficiency in MDC, and hence the responses were considered as salinity removal percentage (R1), TDS removal percentage (R2) and percentage of change in electrical conductivity (R3). Table 1 depicts the design, experimental and predicted values for the output responses using RSM.

The desalination performance was calculated based on the decrease in salt concentration in the middle chamber of bio-cathode MDC. The combined effect of the three process parameters on different responses rendered the second order quadratic equation, and the coefficients of the equation were analyzed by multiple regression analysis.

$$\textit{Salinity removal percentage}\ (R1) = +46.11 + 21.41 * A + 3.56 * B - 2.42 * C + 0.41 * AB - 0.83 * AC + 0.052 * BC - 11.48 * A^2 - 2.42 * B^2 - 0.47 * C^2 \quad (2)$$

$$\textit{TDS removal percentage}\ (R2) = +45.40 + 21.33 * A + 3.36 * B - 2.14 * C + 0.66 * AB - 0.68 * AC + 0.044 * BC - 11.60 * A^2 - 2.84 * B^2 - 1.26 * C^2 \quad (3)$$

$$\textit{Change in Electrical conductivity percentage}\ (R3) = +45.69 + 21.41 * A + 3.25 * B - 2.52 * C + 0.41 * AB - 0.58 * AC + 0.31 * BC - 11.56 * A^2 - 2.56 * B^2 - 0.75 * C^2 \quad (4)$$

ANOVA and F test aids in evaluating the adequacy and statistical significance of the model. Li et al. reported that the regression coefficients (R^2) determine the percentage variation in the observed value and also the same differences were determined by the experimental factors and their interactions (Li et al. 2012). The F values for percentages of R1, R2, R3 were observed as 187.56, 145.07, 301.23 and the p-value was used to calculate the robust nature of F-statistics and found to be significant, i.e. <0.0001. The P-values also helps in understanding the pattern of mutual interaction between the independent variables (Garai and Kumar 2013). The adjusted R2 for R1, R2, and R3 were 0.9917, 0.9893, and 0.9948. The above values significantly implied that the model made an ideal prediction for a process with a linear relationship with the variables. The variables were also found to be significant at 95% confidence limit ($p < .05$). The "Lack of Fit F-value" for the three responses was

Table 1. BBD experimental design with the corresponding actual and predicted removal efficiencies.

	A:Salt Conc(gL^{-1})	B:AnolyteConc (mg L^{-1})	C:External Resistance (Ω)	Salinity removal (%) (R1)		TDS removal (%) (R2)		Change in Electrical Conductivity (%)(R3)	
Run	A	B	C	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	5	250	560	9.12	7.60	8.36	6.90	8.45	7.27
2	35	250	560	50.10	49.59	48.50	48.21	49.70	49.24
3	5	750	560	13.40	13.91	12.01	12.30	12.50	12.96
4	35	750	560	56.00	57.52	54.78	56.24	55.40	56.58
5	5	500	100	14.20	14.34	12.25	12.67	13.80	13.90
6	35	500	100	59.66	58.83	57.40	56.68	58.50	57.90
7	5	500	1000	10.30	11.16	9.01	9.76	9.40	10.02
8	35	500	1000	52.50	52.33	51.50	51.05	51.80	51.68
9	20	250	100	40.80	42.14	39.02	40.03	40.90	41.95
10	20	750	100	49.80	49.15	47.54	46.83	48.40	47.85
11	20	250	1000	36.50	37.19	35.10	35.85	35.70	36.29
12	20	750	1000	45.80	44.42	43.52	42.47	44.50	43.41
13	20	500	560	46.30	46.06	45.80	45.35	45.70	45.63
14	20	500	560	46.80	46.06	47.00	45.35	46.30	45.63
15	20	500	560	45.08	46.06	43.25	45.35	44.90	45.63

4.77, 0.82, and 4.70 which implies the Lack of Fit and pure error was not significantly relative. The *p*-value for lack of fit (0.178, 0.5897, and 0.1804) was also not significant. The smaller values of coefficient of variance percentage (CV %) of R1, R2, and R3 such as 4.16, 4.89, 3.34 signify the minimal deviation between the predicted and experimental values. Hence in the present study, the regression equation, values, and *P* value analysis demonstrates that all the three independent factors had a significant influence on desalination performance. Table 2 provides the Analysis of Variance (ANOVA) for the fitted polynomial quadratic model of desalination performance

Effect of process variables on significant responses (salinity, total dissolved solids, and change in conductivity)

The 3D surface plots provide the interactive effects between two input variable and their impact on targeted output, i.e. desalination performance. Figure 2a demonstrates the interaction between salt concentration and anolyte concentration for desalination performance. Increase in salt concentration from 5 g L^{-1} to 35 g L^{-1} shows increases in desalination performance whereas the anolyte concentration at 500 mg L^{-1} showed sufficient desalination when equated with lower anolyte (250 mg L^{-1}) and higher anolyte concentration (750 mg L^{-1}). Figure 2(b and c) indicates the effect of external resistance on anolyte concentration (B) and desalination process (C). Lower External resistance, i.e. 100Ω increased the desalination process when compared with 560 Ω and 1000 Ω. The extensive discussion is explained as follows:

Bio-cathode MDC desalination performance is influenced by factors such as initial salt concentration, anolyte concentration, and ER. The above factors coordinate together and increase the desalination efficiency.

Effect of initial salt concentration on desalination performance. It was found that the initial salt concentration present in the middle chamber plays an influencing role. In the present research study, the influence of three different saline concentrations such as 35 g L^{-1}, 20 g L^{-1}, and 5 g L^{-1} were reported for the increase in desalination rate. Higher salt concentration declined the internal resistance and increased the conductivity of the system. Hence the increase in salt concentration increased the desalination process, algae production, and power generation. Thus in the present study, initial salt concentration 35 g L^{-1} desalinated well and removed 20.88 g of salt at the end of 23 days of operation whereas 9.5 g and 0.7 g of salt were extracted from 20 g L^{-1} and 5 g L^{-1} respectively. Therefore the highest salt removal percentage of 59.6 was obtained when the system utilised process variables of 35 g L^{-1} of initial salt concentration, 500 mg L^{-1} of anolyte concentration and 100 Ω of external resistance. Higher NaCl removal was observed in the first 16 days in bio-cathode MDC and the salinity increased by 20% in the following nine days might be due to the enhancement of internal resistance developed due to the migration of ions across the membranes of the middle chamber.

Effect of variable anolyte concentration on desalination performance. The substrate concentration critically affects the MDC performance to some extent. In the current study, three COD concentrations of 250 mg L^{-1}, 500 mg L^{-1} and 750 mg L^{-1} were examined for the salt removal efficiency. Sevda et al reported the feasibility of utilization of petroleum wastewater for the first time and obtained 19.9% salt removal efficiency and 70.5% Chemical Oxygen Demand (COD) removal (Sevda et al. 2017). Petroleum wastewater has lower conductivity when compared with the conductivity of the saline solution. Hence, Passive ion transfer due to osmotic difference could be another reason for the migration of ions from the desalination chamber to the anode chamber thus promoting the desalination process (Kim and Logan 2011b). Higher saline concentration of 35 g L^{-1} also influenced the activity of the exoelectrogens present in the anode chamber and thus generated maximum current. Yim et al. proposed the same hypothesis concerning the effect of saline concentration on the exoelectrogens activity. Higher substrate concentration of 750 mg L^{-1}has been reported to inhibit the anode performance and thus mild reduction in desalination performance. The inhibitory effects may be due to the decrease in pH of anodic biofilm or poor microbial growth because of high chloride concentration from the desalination chamber

Table 2. Analysis of Variance (ANOVA) for the fitted polynomial quadratic model of desalination performances.

	Sum of Squares			Df			Mean Square			F-value			p-value					
Source	R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
Model	4313.91	4276.96	4308.25	9	9	9	479.32	475.22	478.69	187.56	145.07	301.23	< 0.0001	< 0.0001	< 0.0001	S	S	S
A	3667.63	3637.58	3667.13	1	1	1	3667.63	3637.58	3667.13	1435.12	1110.47	2307.61	< 0.0001	< 0.0001	< 0.0001			
B	101.33	90.25	84.63	1	1	1	101.33	90.25	84.63	39.65	27.55	53.25	0.0015	0.0033	0.0008			
C	46.85	36.47	51.01	1	1	1	46.85	36.47	51.01	18.33	11.13	32.10	0.0079	0.0206	0.0024			
AB	0.66	1.73	0.68	1	1	1	0.66	1.73	0.68	0.26	0.53	0.43	0.6339	0.5001	0.5417			
AC	2.73	1.84	1.36	1	1	1	2.73	1.84	1.36	1.07	0.56	0.86	0.3487	0.4874	0.3973			
BC	0.011	7.909E-003	0.38	1	1	1	0.011	7.909E-003	0.38	4.304E-003	2.414E-003	0.24	0.9502	0.9627	0.6471			
A^2	486.82	496.52	493.45	1	1	1	486.82	496.52	493.45	190.49	151.57	310.51	< 0.0001	< 0.0001	< 0.0001			
B^2	21.67	29.81	24.21	1	1	1	21.67	29.81	24.21	8.48	9.10	15.23	0.0333	0.0295	0.0114			
C^2	0.80	5.87	2.10	1	1	1	0.80	5.87	2.10	0.31	1.79	1.32	0.5994	0.2383	0.3025			
Residual	12.78	16.38	7.95	5	5	5	2.56	3.28	1.59									
Lack of Fit	11.21	9.04	6.96	3	3	3	3.74	3.01	2.32	4.77	0.82	4.70	0.1780	0.5897	0.1804	NS	NS	NS
Pure Error	1.57	7.33	0.99	2	2	2	0.78	3.67	0.49									
Cor Total	4326.69	4293.34	4316.20	14	14	14												
R-Squared	0.9970	0.9962	0.9982															
Adj R-Squared	0.9917	0.9893	0.9948															
Pred R-Squared	0.9577	0.9625	0.9737															
Std. Dev.	1.60	1.81	1.26															
Mean	38.42	37.00	37.73															
C.V. %	4.16	4.89	3.34															

ssA Salt Concentration; B- Anolyte concentration; C- External Resistance; R1- Salinity removal percentage; R2- TDS removal percentage; R3- Change in Electrical Conductivity percentage

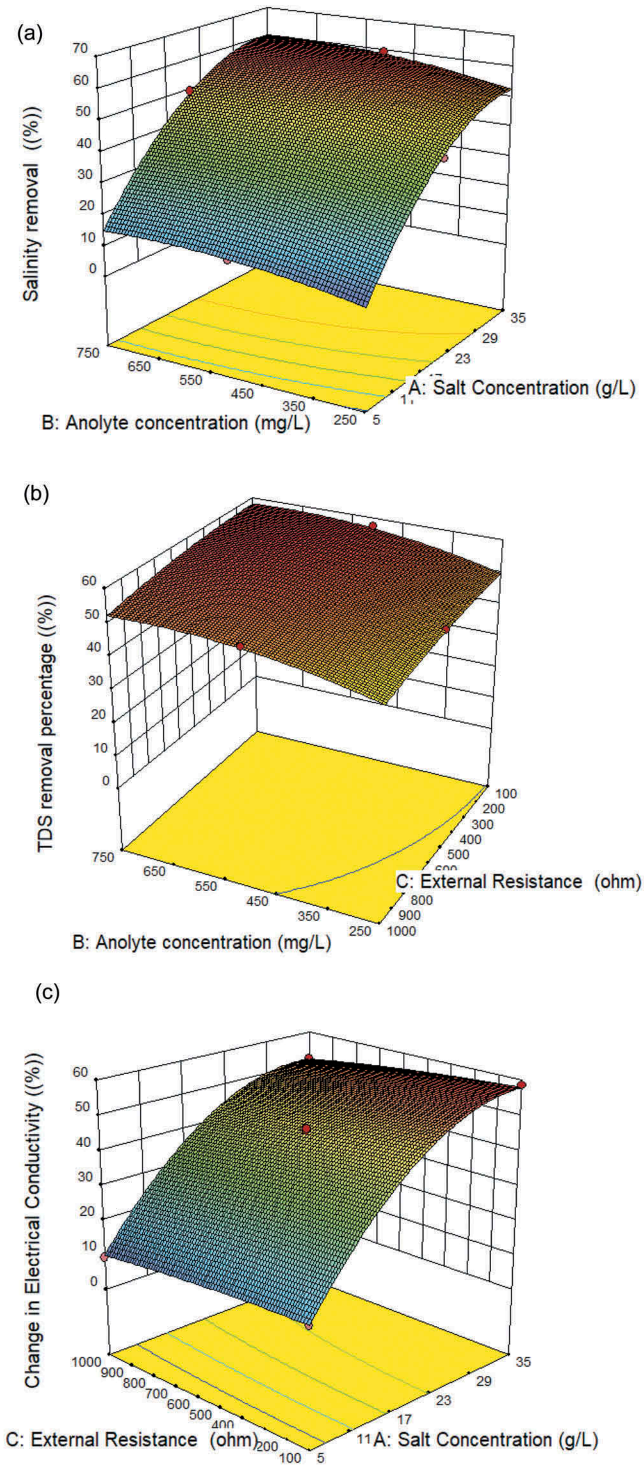

Figure 2. (a-c). The response surface plots for the effect of process variables and their interactions on desalination performance.

(Kim and Logan 2013) (Lee, Torres, and Rittmann 2009). Thus the MDC with substrate concentration of 750 mg L^{-1} displayed minimal reduction in desalination efficiency ie., differential percentage of 3.66 when compared with 500 mg L^{-1}. Substrate limitation was experienced in case of 250 mg L^{-1}in terms of desalination efficiency and COD removal. The highest COD removal of 54% was observed when the system utilised process variables of 35 g L^{-1} of initial salt concentration, 500 mg L^{-1} of anolyte concentration and 100 Ω of external resistance.

Effect of variable external resistances on desalination performance. The other factor such as ER also played a vital role in desalination efficiency. In the present study, three variable ER's of 100 Ω, 500 Ω, and 1000 Ω were investigated for the removal of NaCl ions. The exoelectrogens present in the petroleum wastewater initiated series of electrochemical oxidation reactions in the anaerobic environmental conditions. Then, the conversion of biochemical energy into Adenosine Triphosphate (ATP) prevails with the assistance of microbes by cascading a series of redox reactions, and finally, the electron transmission occurs from organic substances to a solid anode. The electrons produced from the reduction of organic wastes from anode initiates reduction reaction in the bio-cathode through the external resistance. The flow of electrons causes the electrical potential difference between anode and bio-cathode thus leading to the transfer of ions from the middle chamber. Therefore at lower ER, in theory, the desalination rate is proportion to electric current (Sevda et al. 2015). Researchers also demonstrated the increase in current production (680%) and columbic efficiency (275%) when ER reduced from 1000 Ω to 10 Ω (Chen et al. 2013). In the present study, bio-cathode MDCs with 100 Ω produced higher desalination efficiency, maximum current production with respect to three different saline concentrations when compared with MDCs using 560 Ω and 1000 Ω of ER. The maximum power density of 573.78 mW m^{-3} was observed with 35 g L^{-1} of initial salt concentration, 500 mg L^{-1} of anolyte concentration and 100 Ω of ER. Continuous biodegradation of petroleum wastewater (500 mg L^{-1}) led to the increase in transfer of electrons across 100 Ω ER thus enhancing higher removal of ions in 35 g L^{-1} of saline concentration. The study directly demonstrates the proportionality correlation between TDS removal and current generation in the bio-cathode under low ER condition.

Optimization by the genetic algorithm

GA was applied to the regression model obtained from the RSM for optimization of the different process parameter to maximize the desalination performance. The GA optimized parameters were obtained by trial and error method using different combinations of input variables. GA was run in MATLAB, and it generates initial population and generations based on the following constraint dependant initial parameters:

- Initial population – 50
- Scaling function – Rank
- Selection function – Tournament
- Elite count – 0.05 * population size

The program was repeatedly run until the best-optimized solutions have arrived with the regression equation obtained from RSM for salinity, TDS, and conductivity removal percentage. GA tool in the MATLAB is the minimization tool. Therefore the inverse of the objective function was done to maximize the desalination performance,. The upper and the lower boundaries were changed continuously to study the corresponding change in fitness values. The fitness value for E1 was found to increase from G1 to G12 after which it continued to remain constant up to 104 generations. The consistency in generations denotes that no crossing over or mutation occurred among the genes that could affect the desalination performance. The salinity removal percentage for the corresponding fitness value of 0.00686 was identified as 58.8%. The fitness value for E2 and E3 responses changed from G1 to G9 and G1 to G11 after which remained constant for more than 90 generations. The fitness value for E2 and E3 were 0.0067 and 0.00689 and the corresponding TDS and Electrical conductivity removal percentages were 56.7% and 57.9%. Figure 3(a-c) shows the evolution of fitness function for salinity removal percentage (A), TDS removal percentage (B), and Electrical conductivity removal percentage (C) through iteration using GA.

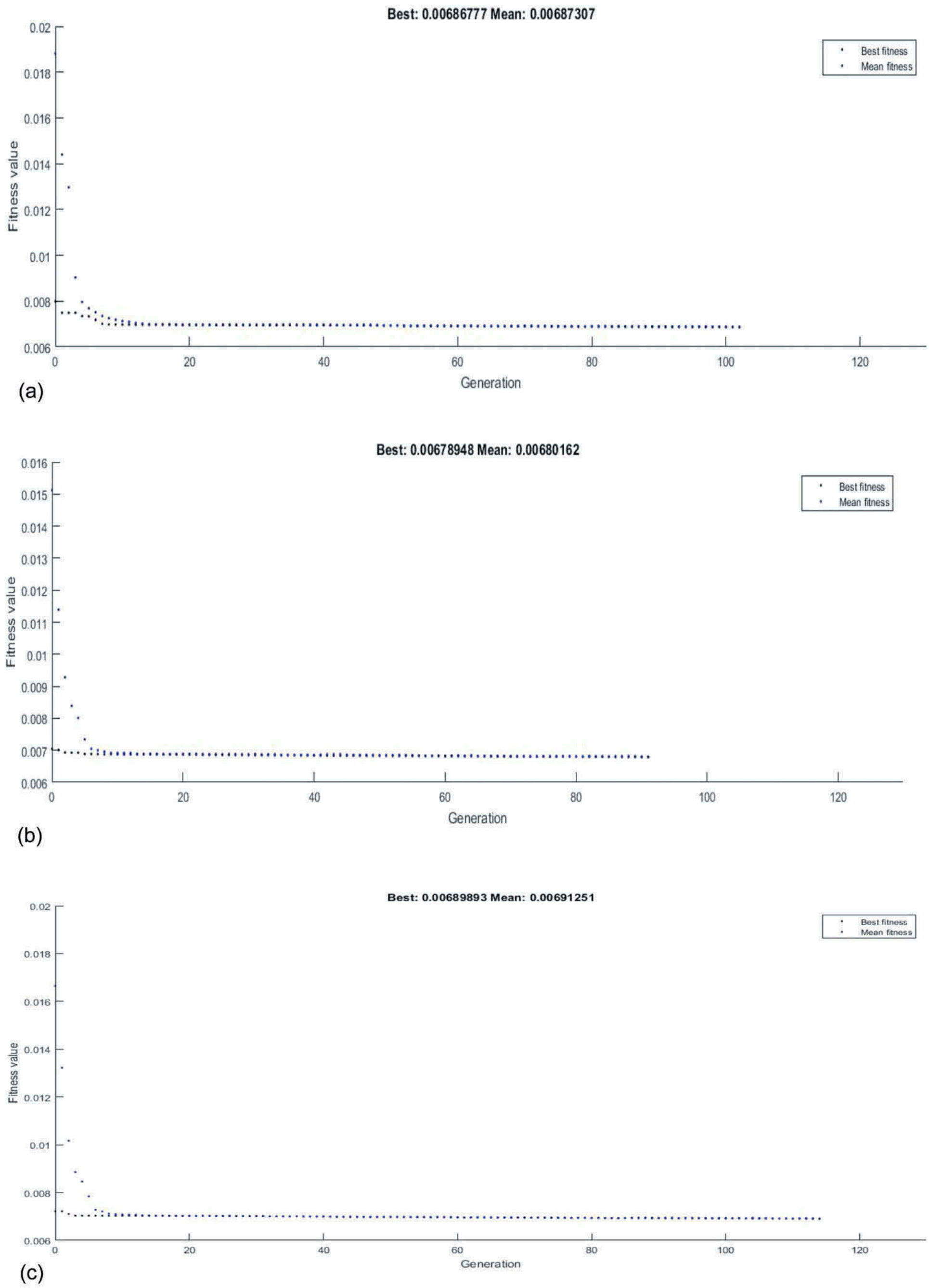

Figure 3. (a-c). Evolution of fitness functions for salinity removal percentage (a), TDS removal percentage (b), and Electrical conductivity removal percentage (c) through iteration using GA.

The maximum desalination performance of 58.9% was obtained with the optimum process parameters such as salt concentration (34.9 g L^{-1}), anolyte concentration (507 mg L^{-1}), and ER (100.5 Ω).

Comparison of optimization by RSM and GA

RSM and GA were employed to predict the optimized process parameters. Table 3 shows the comparison of the results obtained by BBD-RSM and GA. Thus the experimental results correlated with the optimized results of RSM and GA in maximizing the desalination performance with bio-cathode MDC. As per the identical results, obtained, both box-behnken and GA were found suitable for the present study.

Effect of process variables on nonsignificant responses (COD removal and bio-electricity generation)

The desalination performance results were found to be significant and ultimately depend on the mutual interaction of process variables such as salt concentration, anolyte concentration, and ER. The other responses such as COD removal percentage, power density, and algae growth response were considered as nonsignificant responses since the activity most probably depends on bacterial and algal activity; the natural environmental conditions that cannot be justified precisely. But the nonsignificant responses fluctuate accordingly based on the variation of process variables.

The substrate utilization, exoelectrogens activity, the production of metabolite due to redox changes constitutes the determining effect in developing electrochemical gradient which also, in turn, increases the desalination rate in bio-cathode MDC. Substrate utilization was examined by measuring COD. The voltage profiles and the COD removal rates were continuously monitored for the fifteen sets of experiments. The replenishment of fresh petroleum wastewater was done consistently in the anode chamber following the voltage drops. The elevated COD concentration (750 mg L^{-1}) produced higher electricity, and the pattern changed on the continued operation of bio-cathode MDC until reaching the necessary voltage drop. The rapid voltage generation over the initial time was due to the excessive substrate availability for bioelectricity production. Consistent voltage profile was seen in 500 mg L^{-1} when compared with 750 mg L^{-1}. Substrate limitation in 250 mg L^{-1} led to the decrease in bioelectricity generation. The carbon dioxide production by methanogenic bacterial activity in the anode chamber on microalgae photosynthesis could be the reason for voltage fluctuation (Zhou et al. 2012). Maximum of 54% COD removal was experienced using 35g L^{-1} saline concentration, 500 mg L^{-1} of anolyte concentration and 100Ω external resistance. The COD removal percentages with respect to saline concentration of 20 g L^{-1} and 5 g L^{-1} were 48 and 30.1. Further substrate degradation can be enhanced by the optimization of operating conditions such as wastewater pre-treatment and recirculation (Luo et al. 2012).

The increase in migration of chloride ions from higher saline concentration also inhibited the exoelectrogen activity. The chloride ions react with protons generated by microbes and forms hydrochloric acid thus leading to the growth of acidophilic bacteria. The migration of sodium ions to the catholyte solution forms sodium hydroxide also inhibited the algal growth to certain extent. (Cao et al. 2009) (Jacobson, Drew, and He 2011). The significant decrease in pH from 6.54 to 5.89 decreased the electricity production and COD reduction in bio-cathode MDC with 750 mg L^{-1}

Table 3. Comparison of optimised process variables and output responses by BBD-RSM and GA.

	Input Process variables			Output responses		
Model	Salt Conc (gL^{-1})	Anolyte Conc (mg L^{-1})	External Resistance (Ω)	Salinity removal (%) (R1)	TDS removal (%) R2)	Change in Electrical Conductivity (%)(R3)
Box Behken (RSM)	34.33	500.01	100.035	58.836	56.707	57.922
Genetic Algorithm	34.9	507	100.12	58.937	56.797	57.986
Experimental result	35	500	100	59.66	57.4	58.5

petroleum wastewater when compared with 500 mg L^{-1} anolyte concentration (pH decreased from 6.4 to 5.97). Thus to overcome the pH fluctuations, replacement of anolyte was done periodically. The data from the present study indicate that decreasing the anolyte concentration from 750 mg L^{-1} to 500 mg L^{-1} increased the power density. The higher power density of 573.79 mW m^{-3} was obtained using 500 mg L^{-1}anolyte concentration, 35 g L^{-1} of salt concentration and 100 Ω external resistances.

The variable external resistances also influenced bioelectricity production. Decreasing the external resistance increased the transfer of electrons from the anode to cathode chamber produced maximum current and thus enhanced the COD removal. The electricity production declined after a single batch, and the reason was due to the increase in internal resistance because of the conductivity drop during the desalination process and electron acceptor consumption (Cao et al. 2009) (Luo, Jenkins, and Ren 2011) (Kokabian and Gude 2013). Another reason for the decrease in electricity production indicates the presence of vital factors such as scaling and membrane fouling.

Effect of process variable on algae growth

The combined effect of process variables positively affected the growth of algae in the cathode chamber. The shorter lag phase of bio-cathode MDC in the present study showed the impact of in-situ oxygen generation by algae that led to the increase in electron mobility and faster bio-film formation as stated by kokabain et al. The reduction of protons and electrons were found to be higher due to the microbial catalyzed aerobic bio-cathodes (Kokabian and Gude 2013). Sodium is proven to be an essential element for mineral nutrition under neutral conditions (Kol'chugin and Makarova 2005) and also helps in growth of *Scenedesmus abundans*. The transfer of variable concentration of sodium ions played a vital role in the growth of algae. Increase in algal growth occurred in bio-cathode MDC with 35 g L^{-1} saline concentration due to the higher amount of transfer of sodium ions. But over a period, the increase in alkaline pH, i.e. the formation of bases (NaOH) declined the growth of algae and approached the end of the desalination process. The higher base formation was seen with 35 g L^{-1} concentration (pH raise from 7.65 to 9.47) when compared with 20 g L^{-1} (pH – 7.74 to 8.87) and 5 g L^{-1} saline concentration (pH changed from 7.68 to 8.52). The increase in production of electrons due to substrate degradation and the lower external resistances increased the reduction reaction and growth of algae in the cathode chamber. Maximum growth absorbance of 2.508 was observed at the end of 23 days of experimentation on considering the key process variables such as 35 g L^{-1} of initial salt concentration, 500 mg L^{-1} of anolyte concentration and 100 Ω of external resistance. The highest algal growth absorbance of 2.112 and 1.578 was achieved with respect to the important key influential process variable such as salt concentration of 20 g L^{-1} and 5 g L^{-1}. Table 4 depicts the effect of process variables on non-significant responses.

Bio-fouling characterisation by SEM

After 23 days of operation, bio-fouling, i.e. scaling layers because of microbial interactions and movement of ions were more visible on the surfaces of both AEM and CEM in the bio-cathode MDC. The Scanning Electron Microscope (SEM) displayed the characteristic differences between the membrane structures before and after the experimental study and the results were depicted in Figure 4 As previously reported slightly cracked surface was detected in the unused membrane [E] and while bio-fouling layers were found in the used membrane. The mixture of diverse morphological microorganisms such as bacteria and fungi were seen as black spots on the surface of respective membranes facing the seawater side (middle desalination chamber). The light microscope confirmed the different structures of bacteria and fungi on the membranes. The membranes structure inhibits the passage of microorganisms through it. But the bio-fouling on the seawater side might be due to the quality of feeding sea water. On the AEM facing anode, the visual inspection detected brown layer over the membrane. The reason could be mostly

Table 4. Effect of process variables on non-significant responses.

Run	Salt Conc (g L^{-1}) A	Anolyte Conc (mg L^{-1}) B	External Resistance (Ω) C	% COD removal	Voltage generated (mV)	Power density (mWatt m^{-3})	Algae growth
1	5	250	560	23.8	130.4	101.2152	1.325
2	35	250	560	49	177	186.4821	2.247
3	5	750	560	30.1	277	456.7202	1.578
4	35	750	560	51	300.2	536.4288	2.508
5	5	500	100	28.3	106.2	375.948	1.365
6	35	500	100	54	131.2	573.7813	2.487
7	5	500	1000	25	334	371.8533	1.452
8	35	500	1000	50.7	412.3	566.6376	2.331
9	20	250	100	41.5	96.2	308.4813	1.785
10	20	750	100	48	125.3	523.3363	2.105
11	20	250	1000	40.2	354	417.72	1.958
12	20	750	1000	43.7	401.5	537.3408	2.112
13	20	500	560	47.34	254	384.0238	2.046
14	20	500	560	46.3	287.6	492.3438	2.087
15	20	500	560	44.2	266	421.1667	2.016

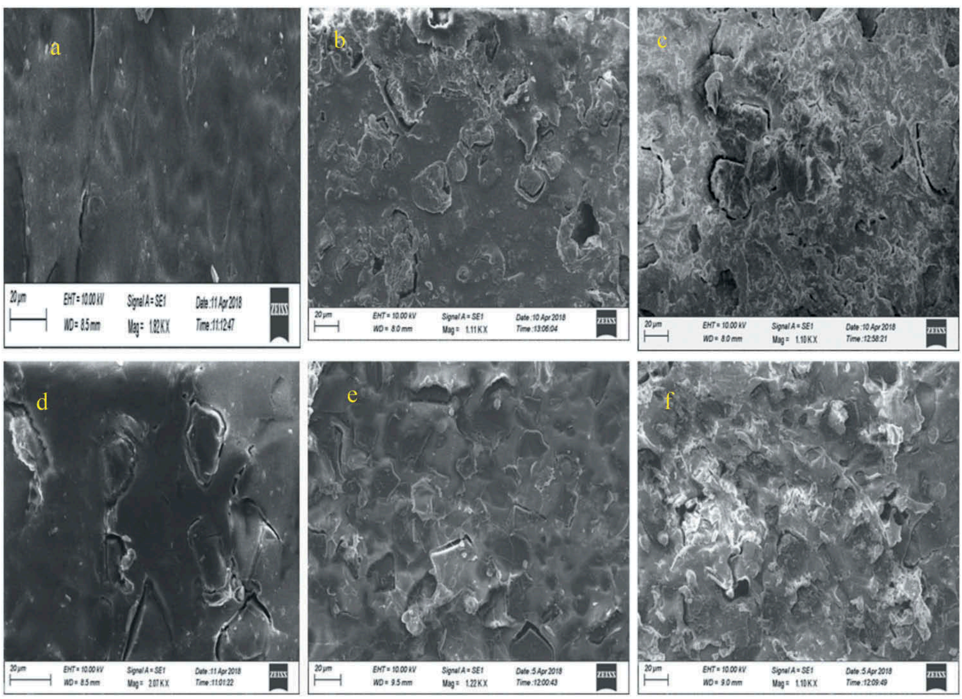

Figure 4. SEM images of membrane fouling in bio-cathode MDCs (unused and after 23 days) – (a) cation exchange membrane (unused); (b) CEM facing saline solution; (c) CEM facing the cathode; (d) Anion exchange membrane (unused); (e) AEM facing the saline solution; (f) AEM facing the anode.

due to the bacterial community and other inorganic components present in the wastewater. The CEM surface the cathode had distinctive appearance of spherical algal cells along with some rod-shaped bacteria and some particle deposits as contaminants. The inorganic ion transport across the AEM and CEM helps in the growth of microorganisms over the surface of the membrane. Ping et al. investigated the long-term performance of AEM and CEM in MDC throughout 8 months indicating biofouling.

Significant bio-fouling was observed in AEM due to the microbial growth across the membrane whereas inorganic scaling occurred in CEM (Ping et al. 2013).

In the present study, the AEM and CEM of the optimized variable's MDC set up showed more cracks and bio-fouling layers over the membrane when compared with the other runs of RSM throughout 23 days. The results indicate that the membranes worked to the greater extent to perform efficient desalination. Increase in cracks and biofouling layers were due to the increase in movement of ions across the membrane, increase in wastewater activity of anode and algal growth in the cathode. Increase in retention time of saline water after 23 days of operation in the current set up could decrease the desalination efficiency, power density thus leading to a decrease in the overall efficiency of the bio-cathode desalination cell. Variable ranges of black spots on AEM and spherical algal cells were seen in other runs of RSM MDC set up. The differences in ranges over AEM and CEM depend on the rate of movement of ions across the membranes. The movement of ions depends on both electric potential and also the water dilution process.

Biofouling of the ion exchange membranes reduces the quality of desalinated water due to the increased microbial growth along the sides of membranes facing the middle chamber. The ionic organic compounds transported through AEM from wastewater also enhanced the growth of microorganisms in the middle chamber. Thus bio-fouling due to chemical or biological interactions adversely affects the bio-cathode MDC concerning desalination performance and bio-electricity generation.

Conclusion

MDC technology came into existence less than a decade and had multiple outcomes from a single reactor. Algae powered MDC is in its embryonic stage of development, and it is now started eventually emerging as a sustainable technology for a greener future. In the present study, MDC with *Scenedesmus abundans* as bio-cathode and petroleum wastewater as the anolyte solution were found to efficiently desalinate the real-time seawater in batch mode. The statistical method of Box-Behnken model followed by response surface methodology was effectively used in prediction and optimization of influential parameters such as initial salt concentration (g L^{-1}), anolyte concentration (mg L^{-1}), and External resistance (Ω). The results obtained were compared with natural selection method of the Genetic Algorithm to reduce the optimization error. The advantage of using computer software not only helps in identification of optimized response but also decreases the number of experiments.

In the present study, the effect of operational parameters on significant (salt removal efficiency) and non-significant (COD removal, algal growth, bioelectricity production) responses was demonstrated. The observed and predicted values were close indicating the success of RSM. The study concluded that deviation in salt concentration and external resistance affected the desalination behaviour of bio-cathode MDC. Changes in anolyte concentration did not bring any remarkable change in desalination performance. The movement of ions across the AEM and CEM and the presence of diverse morphological organisms over the membrane causes bio-fouling and greatly influence the hydraulic retention time of the desalination process. It is necessary to overcome bio-fouling by modifying membrane surface properties such as roughness, and hydrophobicity by surface coating, polymer blending approach, grafting approach and addition of inorganic and antimicrobial additives. It is important to develop a mathematical model by considering other key parameters internal resistance, composition of micro-organism in anolyte solution, membrane salt transfer coefficient, the membrane surface area, membrane thickness, etc. to obtain the effective desalination.

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